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PREFACE

This publication — the Proceedings of the Fourth Conference on Analytical Chemistry in Nuclear Reactor Technology — summarizes much of the recent work on the development or improvement of methods, facilities, and instruments for the analysis of nuclear reactor materials or related substances. The papers which appear herein were contributed by 88 writers in 22 different centers of nuclear energy development throughout the United States and in three foreign countries. With few exceptions, the authors of these papers are actively engaged in the analysis of reactor materials. The scope and diversity of subject matter covered in these papers attest to the ingenuity, resourcefulness, and enterprise which these analytical chemists and their collaborators, the instrument makers, have displayed in providing the analytical services essential to progress in the ever-expanding field of nuclear reactor technology.

Developments in the nuclear reactor field, since the birth of the reactor concept almost two decades ago, have been characterized by a continuing search for and application of new, more promising, reactor materials and by refinements in design and operation based on more precise knowledge of the composition and, especially, changes in composition of reactor materials. In providing this knowledge, the analytical chemist has encountered many challenging problems. These challenges have been met through the development of special methods of analysis, improvements in and increased use of instruments, uniquely designed facilities, the establishment of more reliable standards, and the utilization of computers. These topics comprise, in the main, the subject matter of the papers which appear in these Proceedings. The scope of this compilation is outlined in somewhat greater detail by the categories into which the papers are grouped, namely:

Determination of Fission Products and Low-Level Constituents
Analysis of Reactor Fuels and Related Materials
Separation Techniques in Chemical Analysis
Activation and Radiochemical Methods of Analysis
Advances in Instrumentation and Computer Usage
Facilities for the Analysis of Reactor Materials
Standards for the Chemical Analysis of Nuclear Materials

Of the 47 papers on the conference agenda, 30 are reproduced herein in full. The remainder are to be published elsewhere; in these cases, abstracts only are included in these Proceedings. When known, the place of publication is cited. Since the papers were edited and revised somewhat, when necessary, to ensure some degree of uniformity in publication, the Editor assumes full responsibility for all errors attributable to such changes.

The effectiveness, quality, and merit of a conference such as this is dependent on the united efforts of many persons — particularly the authors, speakers and presiding chairmen. To these individuals, whose names are listed elsewhere in this publication, we give our sincere thanks. We are also much indebted to the Program Committee composed of W. S. Lyon, W. R. Laing, and H. P. House for their manifold efforts in preparation of the agenda and conduct of the conference.

Finally, we are sincerely grateful to the speakers at the two evening sessions for their timely and instructive talks. Albert Simon, Associate Director of the Applied Physics Division at Oak Ridge National Laboratory spoke on "Current Status of Research in Controlled Fusion" and A. J. Wagner, General Manager of the Tennessee Valley Authority, gave an after-dinner talk entitled, "This is TVA". These speakers were presented under the joint sponsorship of this Conference and the First Conference on Nuclear Reactor Chemistry which were held concurrently at the same location.

To provide for the widest possible exchange of information among workers in nuclear reactor development, the Proceedings of this Conference are being published, as were those of the three preceding conferences of this series, viz.

Proceedings	Document Number	Price
First Conference	TID-75555	$3.50
Second Conference		
Part 1 -	TID-7568 (Pt. 1)	3.00
Part 2 -	(Pt. 2)	2.50
Part 3 -	(Pt. 3)	1.00
Third Conference	Talanta 6 (1960)	17.00

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The Fifth Conference on Analytical Chemistry in Nuclear Reactor Technology is tentatively scheduled to be held at Gatlinburg, Tennessee, on October 10-12, 1961. Suggested topics for this forthcoming meeting will be most welcome and are solicited. Any information of this nature will be of real value to the Program Committee in the preparation of an agenda.

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January 24, 1961

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DETERMINATION OF COBALT IN NUCLEAR REACTOR MATERIALS

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ABSTRACT

A photometric method is described for the determination of Co in Be, BeO, and other nuclear materials. To eliminate interferences, Co is separated from other constituents by extraction or ion exchange methods, after which a Co-thiocyanate complex is formed in an acetylacetone medium. Co is then determined photometrically by measuring the absorbancy of the complex at 625 mμ.

The results of interference studies are discussed. In the analysis of Be and BeO, only Cr and Mn, of 68 elements tested, were found to interfere at the 10 mg level. Methods are outlined for eliminating the interference of Cr and Mn as well as the diverse interferences which are encountered when this procedure is applied to the determination of Co in Nb, Ta, U, Th, and Zr.

Experimental data are presented for the determination of Co in Be, BeO, and also in Nb, Ta, U, Th, and Zr.

* * * *

Probably the most widely used method for the determination of cobalt is the extraction of the 2-nitroso 1-naphthol complex and the subsequent photometric determination with nitroso - R salt This method suffers from interference by such elements as copper, nickel, platinum, gold, etc We propose a method whereby most of the elements are separated from cobalt by extraction, and/or ion exchange. followed by the photometric determination of cobalt as the thiocyanate complex in acetylacetone.

Currently, our primary interest is in beryllium and its compounds. Therefore, this method was developed principally for the determination of cobalt in beryllium and the effect of impurities was determined in media suitable for the dissolution of beryllium. No interference was caused by 10 mg amounts of the 68 elements shown in Table I, except for manganese and chromium.

The procedure for the determination of cobalt is essentially as outlined in Figure 1. Beryllium metal is dissolved in hydrochloric acid, and beryllium oxide in sulfuric acid; the media are then adjusted to contain appropriate amounts of both acids. Citric acid is added to prevent the precipitation of those elements which might precipitate without it. Extraction at a pH from 4 to 2 with acetylacetone removes beryllium and most other elements. The extraction of 0.3 g of beryllium with acetylacetone causes a drop in pH from 4 to 2, requiring a readjustment of the pH prior to the final extraction. Sodium thiocyanate is added and the resulting blue cobalt-thiocyanate complex is extracted with acetylacetone. The cobalt is determined photometrically by measuring the absorbance at 625 mμ.

Since chromium and manganese interfere, they should be removed prior to carrying out the extractions. Chromium can be volatilized as chromyl chloride with perchloric acid and hydrochloric acid. Both chromium and manganese can be separated from cobalt by ion exchange. Cobalt is retained on a Dowex 1-X8 resin from a 9 M hydrochloric acid solution while chromium and manganese pass through the column. The cobalt can be eluted from the resin with 0.1 M sulfuric acid.

Since a medium containing sulfuric, hydrochloric, and nitric acid, adjusted to a pH of 4, was used in investigating the effect of impurities, an attempt was made to start with a medium of the same type when determining cobalt in materials other than beryllium. We found that under these conditions relatively large samples of niobium, tantalum, and zirconium could not be kept in solution. Also, uranium is not readily removed from this medium with acetylacetone. Thorium, however, was readily extracted by acetylacetone under these conditions. Therefore, before applying the method to niobium, tantalum, uranium and zirconium, preliminary separations were necessary.

Niobium and tantalum were dissolved in 6 M hydrofluoric acid - 3 M hydrochloric acid solution (Figure 2). Niobium and tantalum are retained on Dowex 1-X8 while cobalt passes through the column. The eluted cobalt solution is evaporated to dryness to remove hydrofluoric acid, the residue is dissolved and appropriate amounts of sulfuric, hydrochloric and citric acids are added.

Uranium was dissolved in nitric acid and separated from cobalt by extraction from 1 M nitric acid with 0.2 M TOPO (tri-n-octylphosphine oxide) in cyclohexane (Figure 3). After evaporation to dryness in the presence of a few ml of sulfuric acid, the residue was dissolved in the starting medium.

Zirconium was dissolved in hydrofluoric acid, and the excess hydrofluoric acid was removed by evaporation with nitric acid. This solution was diluted with water and the pH was adjusted to 1.0 to 1.5 with sodium hydroxide (Figure 4).

TABLE I

AMOUNTS OF VARIOUS NON-INTERFERING ELEMENTS INVESTIGATED

Cobalt Determined = 106 μg

Elements	Amounts Investigated	% Error
Al, Sb(III), Sb(V), As(III), As(V), Ba, Bi, Br, B, Cd, Ca, Ce(IV), Cs Cu(II), Dy, Er, Eu, Gd, Ga, Ge, Au, Hf, Ho, In, I, Ir, Fe(III), La, Pb, Li, Lu, Mg, Hg(II), Mo(VI), Nd, Ni, Nb, Pd(IV), P(as PO_4^{---}), Pt(IV), K, Pr, Re, Rh, Rb, Sm, Sc, Se(IV), Si, Sr, Ta, Te(IV), Tb, Tl(I), Th, Tm, Sn(II), Ti(III), Ti(IV), W(VI), U(VI), V(V), Yb, Y, Zn, or Zr	10 mg	< 3%
F (as HF)	100 mg	< 3%
3 M HNO_3	10 ml	< 3%
2 M $HClO_4$	10 ml	< 3%
2 M Acetic Acid	10 ml	< 3%
Cr(III)	10 mg	6%
Cr(VI)	10 mg	6%
Mn(II)	10 mg	6%
Mn(VII)	10 mg	6%
Mn(II) + Cr(III)	1 g(a)	< 3%

(a) after ion exchange

Fig. 1: Procedure

Medium: 1 g Be, 20 ml 6 M H_2SO_4, 10 ml 6 M HCl, 5 ml 50% citric acid.

Steps:

1. Adjust the pH to 4.0 ± 0.1 with 50% NaOH
2. Extract once with 40 ml and then with 20 ml of acetylacetone until the organic phase is colorless.
3. Readjust the pH to 4.0 ± 0.1 with 50% NaOH.
4. Extract with acetylacetone until the organic phase is colorless.
5. Add 30 ml of 6 M NaCNS in H_2O - acetylacetone (50% v/v).
6. Add 25 ml of acetylacetone and extract.
7. Draw the organic phase into a 25-ml volumetric flask.
8. Dilute, mix and centrifuge.
9. Determine the absorbance at 625 mμ vs acetylacetone.

Fig. 2: Separation of Cobalt From Niobium and Tantalum

Dissolve the sample in HF and evaporate to dryness.

Dissolve the residue in 6 M HF-3 M HCl.

Pass through a Dowex 1-X8 (100 - 200 mesh), 2.5 cm by 25 cm, ion-exchange column.

Wash the resin with 175 ml of 6 M HF-3 M HCl.

Evaporate to dryness and add 20 ml of 6 M H_2SO_4.

Heat to SO_3 fumes; cool; add 10 ml of 6 M HCl and 5 ml of 50% citric acid.

Adjust the pH to 4.0 ± 0.1 with 50% NaOH.

Fig. 3: Separation of Cobalt From Uranium

Dissolve the sample in HNO_3 and evaporate to dryness.

Dissolve the residue in 1 M HNO_3.

Extract with 100 ml of 0.2 M TOPO in cyclohexane.

Wash the organic phase with two 20-ml portions of 1 M HNO_3.

Wash the aqueous phase with two 20-ml portions of 0.2 M TOPO.

Combine the aqueous phases and evaporate to reduce the volume.

Add 20 ml of 6 M H_2SO_4 and heat to SO_3 fumes.

Cool and add 10 ml of 6 M HCl and 5 ml of 50% citric acid.

Adjust the pH to 4.0 ± 0.1 with 50% NaOH.

Fig. 4: Separation of Cobalt From Zirconium

Dissolve the sample in HF and evaporate to dryness.

Evaporate several times with HNO_3 to remove HF.

Dilute with H_2O and adjust the pH to 1 - 1.5.

Extract with 40-ml portions of acetylacetone.

Reduce the volume by heating and add 15 ml of 6 $\underline{M}$ H_2SO_4, 10 ml of 6 $\underline{M}$ HCl and 5 ml of 50% citric acid.

Adjust the pH to 4 with 50% NaOH.

The zirconium was separated from the cobalt by extracting it with acetylacetone. This extraction was carried out at pH 1 to 1.5 because, with large amounts of zirconium, precipitation occurs when the pH is adjusted to 4. After removal of the zirconium, sulfuric, hydrochloric and citric acids were added and the pH was adjusted to provide a medium of the composition desired for starting the determination of cobalt.

Results obtained, using this procedure with niobium, tantalum, thorium, uranium, and zirconium, are shown in Table II. The thorium and zirconium separations were made in the presence of nitrate. Although nitrate probably has no effect on the procedure, this has not been ascertained. Also, it might not be necessary to go through the ion-exchange step to separate niobium and tantalum from cobalt. However, a high concentration of some complexing agent, such as fluoride or oxalate, is necessary to prevent precipitation of the earth acids. Conceivably, this could adversely affect the extraction with acetylacetone of other elements, or the effectiveness of the cobalt determination.

The results of cobalt determinations in beryllium and beryllium oxide by this method are shown in the Tables III and IV.

TABLE II

RECOVERY OF COBALT FROM MATERIALS CONTAINING VARIOUS INTERFERING ELEMENTS

Cobalt "Spike" Added : 100 μg(a)

Element	Separation	Co Recovered, %	
Nb	Ion Exchange	99.2	97.0
Ta	From 6 M HF-3 M HCl	96.6	95.5
Th	Acetylacetone Extraction at pH 4	99.4	98.3
U	0.2 M TOPO Extraction from 1 M HNO_3	98.9	97.0
Zr	Acetylacetone Extraction at pH 1 - 1.5	99.1	98.8

(a) Absorbance of 4 μg of Co/ml of acetylacetone in 5 cm cells = 0.64

TABLE III

ANALYSIS OF NEW BRUNSWICK LABORATORY BERYLLIUM STANDARDS

Medium: H_2SO_4 - 20 ml 6 $\underline{M}$
HCl - 10 ml 6 $\underline{M}$
Citric Acid - 5 ml 50%

NBL Sample No.	Sample Size Grams	Cobalt, ppm	
		Nominal Value	Found
85	1	4	4.0
			4.3
	10		5.2
			5.2
87	1	7	6.9
			6.8
88	1	8	8.4
86	1	22	21.7
			20.9
	5		22.7
			24.7

TABLE IV

ANALYSIS OF NEW BRUNSWICK LABORATORY BERYLLIUM OXIDE STANDARD

Medium: H_2SO_4 - 20 ml 6 M
HCl - 10 ml 6 M
Citric Acid - 5 ml 50%

NBL BeO_2 No	Cobalt, ppm	
	Nominal Value	Found
72-1	7.2	7.3 7.2
-2	3.6	3.6 3.6
-3	1.8	1.8 1.8
-4	0.72	0.76 .65
-5	0.0	0.0 0.0

POLAROGRAPHIC DETERMINATION OF THE LANTHANIDES BY MEANS OF AZO DYESTUFFS

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ABSTRACT

Because of their high neutron cross section and occurrence as fission products, the determination of traces of the lanthanides is of considerable importance in nuclear technology. An investigation into the polarographic behavior of 2,2'-dihydroxy azo dyes led to the development of a new method for the estimation of the lanthanides. The method is based on the effect of lanthanides on the polarographic reduction wave of Eriochrome Violet B (5-sulpho-2-hydroxybenzene-azo-2-naphthol). This dye exhibits well-defined, single polarographic reduction waves in many basic electrolytes. In NH_3, piperidine, and similar buffers, the lanthanides cause a reduction in wave height of the dye, and a second wave appears at a more negative potential. The height of the second wave is proportional to the concentration of lanthanide, and its potential becomes more negative with increasing atomic number of the lanthanide.

The nature of the lanthanide-dye complexes and of their reduction products was investigated extensively by d-c and a-c pen polarography, linear-sweep cathode ray polarography, and controlled-potential coulometry. Spectrophotometry was also used in an attempt to elucidate the structure of the complexes and to determine conditional stability constants.

The analytical method is subject to several interferences, but these can be overcome by pH control, use of masking agents, or quick separations.

INTRODUCTION

The determination of small amounts of lanthanides in diverse materials is of great importance in nuclear technology owing to their occurrence as fission products and since many of these elements also possess large thermal-neutron absorption cross sections.

The published analytical chemistry of the lanthanides is very limited, particularly in the field of trace analysis. Many of the methods lack specificity and the necessary sensitivity. Methods for the determination of the lanthanides include: semi-micro volumetric (EDTA);(1) spectrophotometric;(2,3) controlled-potential coulometric;(4) spectrographic;(5,6) and polarographic.(7)

Polarographic methods for the determination of the lanthanides have not been very successful. The polarography of the lanthanides has been studied in various supporting electrolytes (e.g., ammonium chloride, tetramethylammonium iodide, lithium chloride) and there is some controversy regarding the nature of the polarographic reduction waves.(7) The waves are complicated by the occurrence of hydrogen discharge and irregular capillary response at potentials more negative than -1.7 vs the SCE. Several years ago one of the authors (L.E.S.) failed to obtain analytically suitable waves in lithium chloride, tetramethylammonium iodide, and ethylenediamine base electrolytes. At potentials more negative than -1.7 vs the SCE, irregular capillary response was observed, even when using the Mervyn-Harwell square wave polarograph which has a control to minimize such influences at the voltages applicable. The current-voltage curve also rises steeply beyond -1.7, masking small diffusion currents. It may be said that at the present time, with the exception of Sm, Eu and Yb, there is no reliable polarographic method in common use for the determination of the lanthanides.

The authors considered that a new approach to the determination of the lanthanides was needed. In 1950 Willard and Dean(8) devised a method for the determination of aluminum based on the polarographic reduction of an aluminum-2,2'-dihydroxy-azo complex. The dye, Eriochrome Violet B, [Pontachrome Violet SW, Solochrome Violet RS, or 5-sulpho-2-hydroxybenzene azo-2-naphthol (C.I.169)] exhibits a well-defined reduction wave in an acetate buffer of pH 4.6. In the presence of aluminum a distinct second wave appears, due to the reduction of the aluminum-dye complex. The height of this step is proportional to the aluminum concentration. Further work has resulted in the extension of this method to the determination of aluminum in beryllium,(9) thorium, zirconium,(10) and other metals.(11) A similar dye, Superchrome Garnet Y (C.I. 168), formed the basis for the polarographic determation of Al, Ga and In(12).

The lanthanides form complexes of varying strength with 2,2'-dihydroxy-azo dyes in alkaline medium. We have made an extensive polarographic study with the lanthanides and a number of azo- and anthraquinone-type dyestuffs. In particular, Eriochrome Violet B and its lanthanide complexes have been studied by: cathode ray, ac and dc polarography; controlled-potential coulometry and spectrophotometry, including the determination of stability constants. These studies are reported in detail elsewhere.(13) This paper mainly concerns the use of Eriochrome Violet B (EVB) in a polarographic method for the determination of the lanthanides.

EXPERIMENTAL

Apparatus. Polarograms were obtained using a cathode-ray polarograph(14) or an ac-dc polarograph.(15) Unless otherwise stated, all results were obtained at 25 ± 0.3°C. A scan speed of 0.1 v in 90 seconds was used with the ac-dc polarograph. The voltage sweep rate of the cathode ray polarograph was 0.25 v/sec, with a sweep time of 2 seconds and a delay time of 5 seconds. Polarographic cells utilizing mercury-pool anodes were used for the determinations and half-wave potentials were measured using a H-cell incorporating a saturated calomel electrode. The resistance of this cell was 420 ohms. The dropping mercury electrode used with the cathode ray polarograph had the following characteristics: $m = 1.14 \pm 0.01$ mg/sec; $t = 6.5$ sec; potential, -0.5 v vs pool; buffer concentration, 0.1 M; dye concentration, 2×10^{-5} M. The characteristics of the dropping mercury electrode used with the ac-dc polarograph were: $m = 1.07 \pm 0.01$ mg/sec; $t = 6.93 \pm 0.03$ sec; potential, -0.5 v vs pool; electrolyte, 0.2 M ammonia-ammonium chloride; dye concentration, 2×10^{-4} M. All pH measurements were made with a glass electrode, direct-reading pH meter (Electronic Instruments Ltd., England, Model 23A).

Reagents. All stock and polarographic solutions were prepared from redistilled, demineralized water. Unless otherwise stated, all reagents were of the best analytical grade. Many of the dyes were of commercial purity and master batches of purified dyes were prepared by recrystallization from aqueous ethanol. The purity of EVB was checked by elemental and other analyses. The composition was found to be as follows:

	Theoretical for $NaC_{16}H_{11}N_2O_5\text{-}S\cdot 2H_2O$	Found
	Per Cent	
Na	5.72	5.4
C	47.7	45.9
H	3.73	3.64
N	6.96	6.48
S	7.96	7.4

The purity of EVB was estimated to be 95%.

Stock solutions of the 14 lanthanides were prepared from Johnson and Mathey (England) "Specpure" nitrates. The stock solutions were made 0.01 N in HCl and diluted just prior to use. The principal buffer solutions used were prepared from diethanolamine, triethanolamine, ammonia and piperidine chlorides adjusted to the required pH with sodium hydroxide. The final concentration of the free base was 0.2 M. Other buffer solutions were prepared from the free base and perchloric acid, the final concentration of the free base again being 0.2 M.

FUNDAMENTAL STUDIES

The cathode-ray polarograph was used to investigate the polarographic behavior of a selection of dyes and to test the effect of typical lanthanides on the dye waves. Table I gives results for buffers of six pH values. The buffers and corresponding pH values were: ammonium acetate - $HClO_4$(4,6); diethanolamine - $HClO_4$(8,9.5); and piperidine - $HClO_4$ (11,12). It is seen that double waves formed in three cases. In two cases, there was a large reduction in the height of the dye wave but no second wave.

Figures 1 and 2 show typical polarograms of EVB which appeared to be the most promising dye.

Table II gives values for the peak currents of EVB at different pH values using cathode-ray polarography. Very sharp peaks were obtained at pH 4.3 and 5.8 and well defined peaks at pH 9.3 to 10.3.

Table III gives values for the peak currents of EVB at different pH values in the presence of three typical lanthanides. It is seen that, with solutions of comparable pH, the peak current with a diethanolamine buffer is approximately double that when piperidine is used as a buffer. Piperidine itself is surface active and hence hinders the adsorption of dye anions. Adsorption is high in ammonia and diethanolamine, leading to peak currents 3 to 4 times higher than predicted.(20)

The role of hydrogen ion in the reduction of EVB and the lanthanide complexes is illustrated in Table IV.

Reversibility log plots of EVB reduction waves in various buffers showed that: (a) in piperidine buffers both the dye and the lanthanide complexes are irreversibly reduced; (b) in ammonia buffers the complexes are irreversibly reduced; (c) in ammonia buffers the free dye in the presence of lanthanide complexes is irreversibly reduced; (d) in ammonia buffers the free dye alone appears to add two electrons reversibly. Complete details are reported elsewhere.(13)

Mercury-height dependence studies showed that the reduction is diffusion controlled for both the free dye and its lanthanide complexes.(13) The temperature coefficient for the free dye in ammonia buffer was 1.52%/°C and, for the Gd-dye complex in ammonia buffer, 1.48%/°C.

Diffusion current constants of EVB are given in Table V.

Using an accurate version of the Ilkovic equation,(21) and assuming n to equal 4, diffusion current constants are calculated to be:

I^o (ammonia buffer) = 5.15

I^o (piperidine buffer) = 5.01

I^o (acetate buffer) = 5.05,

while Dean and Bryan,(11) using the uncorrected formula and $m^{2/3}\ t^{1/6} = 3.03$,

TABLE I

REACTION OF THE DYES WITH THE LANTHANIDES

Dye	pH					
	4	6	8	9.5	11	12
Orange II	N.R.	N.R.	N.R.	N.R.	N.R.	N.R.
Eriochrome Black PV	N.R.	N.R.	D.W.(s)	D.W.(s)	-	-
Thoronol	N.R.	N.R.	N.R.	N.R.	N.R.	N.R.
Arsenazo	N.R.	N.R.	D.W.(c)	D.W.(c)	Rn.	N.R.
Alizarin Red S	S.Rn	L.Rn.	L.Rn.	L.Rn.	N.R.	N.R.
Quinalizarin Sulphonate	N.R.	N.R.	S.Rn.	-	-	-
Chrysazin Sulphonate	N.R.	N.R.	N.R.	N.R.	N.R.	N.R.
Chrome Blue K	N.R.	N.R.	L.Rn.	L.Rn.	L.Rn.	Rn.
Chrome Fast Red 2B	N.R.	N.R.	N.R.	N.R.	N.R.	N.R.
Eriochrome Violet B	N.R.	N.R.	D.W.(s)	D.W.(s)	D.W.(s)	D.W.(s)
Chromotrope 2R	N.R.	N.R.	N.R.	N.R.	N.R.	N.R.
Red B	N.R.	N.R.	N.R.	N.R.	N.R.	N.R.

N.R. = no apparent effect on dye wave.

Rn. = reduction in height of the dye wave, but no second wave.

S.Rn. = slight reduction in height of dye wave, but no second wave.

L.Rn. = large reduction in height of dye wave, but no second wave.

D.W.(c) = double wave formed on addition of lanthanide, but not well separated.

D.W.(s) = double wave formed on addition of lanthanide, well separated.

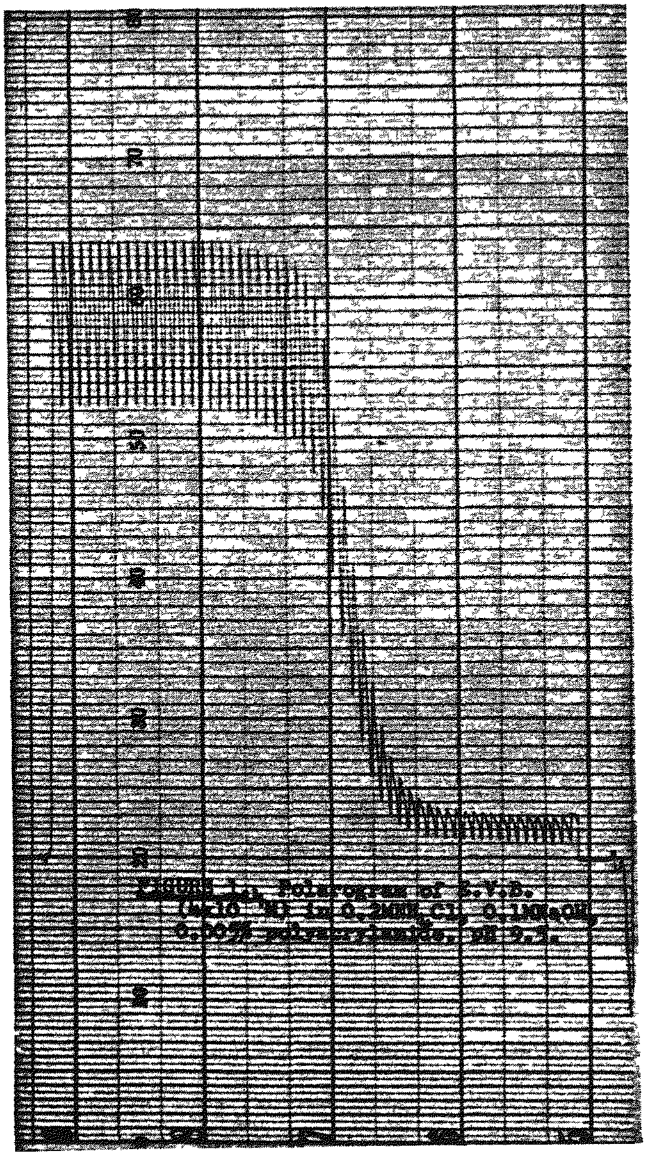

Fig. 1 - Polarogram of Erichrome Violet B (4×10^{-4} M) in 0.2 M NH_4Cl, 0.1 M NaOH, 0.005% Polyacrylamide, pH 9.5

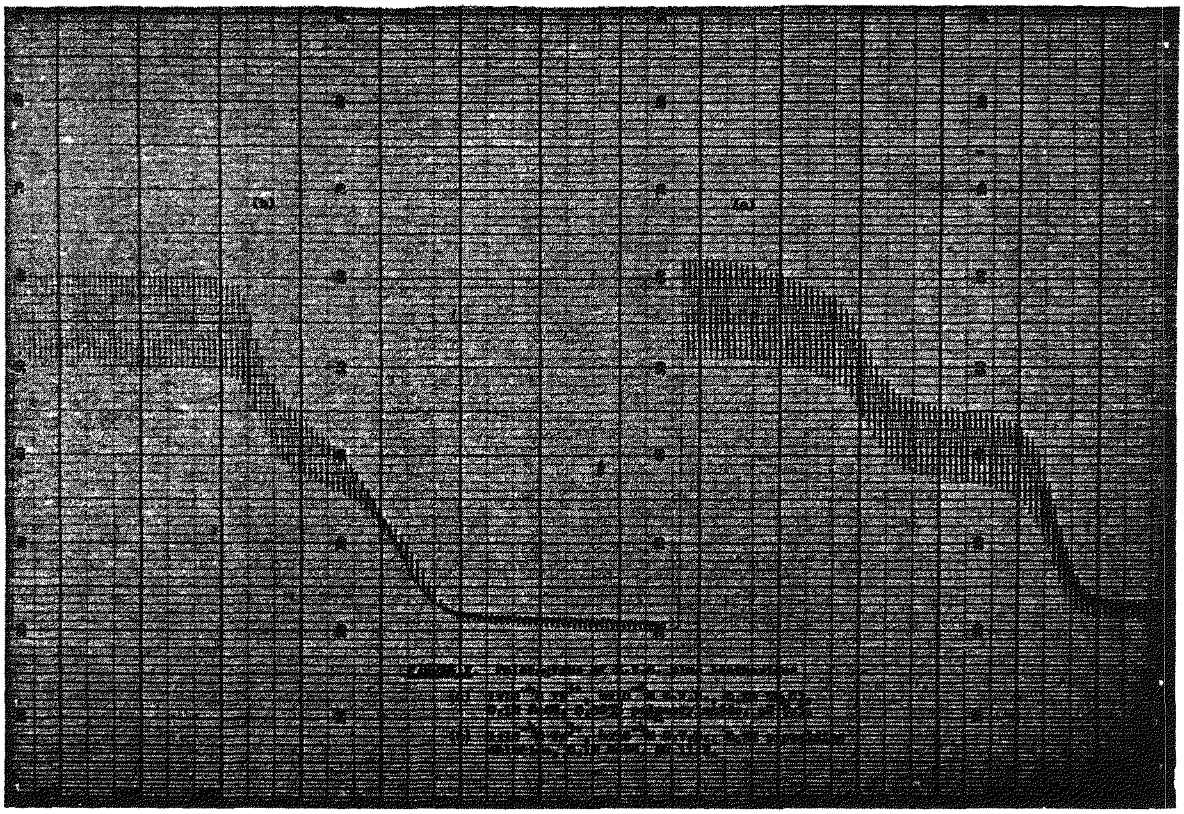

Fig. 2 - Polarograms of Eriochrome Violet B Plus Lanthanides
(a) 1×10^{-4} M Yb^{+++}, 4×10^{-4} M E.V.B., 0.2 M NH_4Cl
0.1 M NaOH, 0.005% Polyacrylamide, pH 9.5
(b) 1×10^{-4} M Pr^{+++}, 4×10^{-4} M E.V.B., 0.2 M piperidine
chloride, 0.1 M NaOH, pH 11.2

TABLE II

THE OSCILLOGRAPHIC POLAROGRAPHY OF ERIOCHROME VIOLET B AT DIFFERENT pH VALUES

Dye concentration - 1.18×10^{-5} M.

Diffusion coefficient of dye - $0.44 \times 10^{-5} cm^2/sec$, ($n = 4$).

$t = 6.5$ sec, $m = 1.14$ mg/sec   Temperature = 25°C

Buffer concentration - 0.1 M.

Buffer System	Peak Current i_p (μa)	Calculated Peak Current (μa)	Wave Shape
Ammonium acetate			
pH 4.3	2.46	0.93	Very sharp
pH 5.8	2.65	0.93	Very sharp
Diethanolamine			
pH 9.30	3.33	0.93	Well defined peak
pH 10.15	3.65	0.93	Well defined peak
Ammonia			
pH 9.30	3.57	0.93	Well defined peak
pH 10.3	3.79	0.93	Well defined peak
Piperidine			
pH 11.3	1.30	0.93	Similar to cadmium wave
pH 11.8	1.02	0.93	Similar to cadmium wave

TABLE III

THE OSCILLOGRAPHIC POLAROGRAPHY OF ERIOCHROME VIOLET B - LANTHANIDE COMPLEXES

Total dye concentration - 1.18×10^{-5} M

Buffer concentration - 0.1 M

Lanthanide concentration - 0.295×10^{-5} M

Solution	Peak Current (μa) Diethanolamine Buffer				Peak Current (μa) Piperidine Buffer			
	pH 9.3		pH 10.2		pH 10.5		pH 11.8	
	1st Wave	2nd Wave	1st Wave	2nd Wave	1st Wave	2nd Wave	1st Wave	2nd Wave
Free Dye	3.35	0.08	3.65	0.05	1.48	0.06	0.99	0.03
Dye + Nd Complex	2.56	0.10	2.52	0.12	0.88	0.63	0.56	0.48
Dye - Gd Complex	2.05	0.46	1.98	0.65	0.84	0.63	0.51	0.49
Dye - Yb Complex	1.57	0.58	1.71	0.48	0.80	0.70	0.62	0.39

TABLE IV

$E^1/2$-pH RELATIONSHIPS FOR ERIOCHROME VIOLET B, AND EVB-LANTHANIDE COMPLEXES

Lanthanide	Buffer	$E^1/2$, v
Nd	Ammonia	-0.355 - 0.033 pH
Nd	Piperidine	-0.502 - 0.031 pH
Gd	Ammonia	-0.434 - 0.032 pH
Gd	Piperidine	-0.521 - 0.030 pH
Yb	Ammonia	-0.463 - 0.032 pH
Yb	Piperidine	-0.506 - 0.031 pH

Notes:

1. EVB in ammonia and diethanolamine buffers (pH 8.5 to 10.5) $E^1/2 = +0.100 - 0.065$ pH

2. In the pH range, 8 to 12, the Dean and Bryan value was: $E^1/2 = -0.035 - 0.060$ pH, for free dye in ammonia and piperidine buffers.

TABLE V

DIFFUSION CURRENT CONSTANTS OF ERIOCHROME VIOLET B

($m^{2/3} t^{1/6} = 1.46$)

Conc of EVB (M)	i_d in NH_3-NH_4Cl Buffer, μa	i_d in Piperidine Buffer, μa	I in NH_3 Buffer	I in Piperidine Buffer
7.40×10^{-4}	6.20	6.05	5.79	5.63
3.70×10^{-4}	3.08	3.01	5.73	5.60
0.740×10^{-4}	0.622	0.603	5.81	5.63
0.185×10^{-4}	0.154	0.149	5.73	5.57
			(Av = 5.77)	(Av = 5.61)

Note: In acetate buffer of pH 4.6, I = 5.65.

found:

I (ammonia) = 5.26

I (piperidine) = 5.07

The dye used by these authors was recrystallized from acetone-ether and assumed to be 100% pure.

If Perkins and Reynolds data(9) is used to calculate I, for pH 4.6, I = 2.65. This value is about one-half that obtained in the present invesigation and in Dean and Bryan's work,(11) and possibly indicates that the dye used was only about 50% pure, since Perkins and Reynolds make no mention of purification of the dye prior to use.

If $I^o = 5.1$ (average)

from $I = 607\ n\ D^{1/2}$

$D = 0.44 \times 10^{-5}$ (when n = 4)

and $D = 1.8 \times 10^{-5}$ (when n = 2)

The value of 0.44×10^{-5} is more likely to be correct, considering the values of 0.33×10^{-5} and 0.41×10^{-5} found for stilbene(16) and azobenzene,(17) respectively. Dean and Bryan(11) found D (free dye) = 1.83×10^{-5}, assuming a 2-electron change, and compared this value with $D = 1.84 \times 10^{-5}$ for stilbene, calculated from diffusion current constant data given by Wawzonek and Fan.(18) However, this data was based on an incorrectly calculated value of $m^{2/3}\ t^{1/6}$ and when the correct value is used, D is found to be much closer to 0.33×10^{-5}. It must be concluded that four electrons are involved in the reduction of the dye. Since the log plot is a straight line with a slope of 32mv in an ammonia buffer, indicating n = 2, the most likely explanation is that the dye is reduced in a potential-determining step, involving two electrons, to the hydrazo compound, followed rapidly by an irreversible disproportionation reaction to give an azo-dye plus amines. This is supported by studies on the controlled-potential coulometric reduction of EVB and its lanthanide complexes which showed n = 4 and amines to be the final reduction product.(13)

ANALYTICAL APPLICATIONS

The difference S between $E^{1/2}$ for the free dye and the dye complex ($\Delta E^{1/2}$) were determined by dc pen polarography for 14 lanthanides in an ammonia buffer of pH 9.5 and are given in Table VI.

Because the height of the second step (and also the first step) was found to be proportional to the lanthanide concentration over a wide range when EVB was used, a suitable analytical procedure could be devised. It was also found that in a triethanolamine buffer of pH 7.6 lanthanides of atomic number greater than 60 may be determined in a two-fold excess of lanthanum or cerium.

TABLE VI

HALF-WAVE POTENTIALS OF LANTHANIDES IN THE PRESENCE OF ERIOCHROME VIOLET B

Total dye concentration = 3.9×10^{-4} $\underline{M}$

Lanthanide concentration = 1×10^{-4} $\underline{M}$

Ammonia buffer, pH = 9.5

Lanthanide	$-\Delta E^{1/2}$ (mv)	log K_c'(13)
La	45	18.4
Ce	66	17.6 (?)
Pr	162	19.2
Nd	146	19.6
Sm	196	19.8
Eu	202	20.0
Gd	210	20.0
Tb	216	20.1
Dy	222	20.4
Ho	230	20.7
Er	227	21.0
Tm	230	21.2
Yb	233	21.6
Lu	234	22.0

Note: K_c' is the conditional stability constant, defined by:

$$K_c' = \frac{[MD_2]}{[M^1][D^2]}, \text{ where}$$

$[MD_2]$ is the concentration of the complex,

$[D]$ is the concentration of the completely ionized form of the dye,

$[M^1]$ is the concentration of metal uncombined with dye.

If total lanthanide determination is required, an ethanolamine, diethylamine or piperidine buffer of pH 10 to 11 is the most suitable.

Very small amounts of the lanthanides can be determined with the cathode ray polarograph, using Alizarin Red S which gives very sharp "adsorption peaks" in acid solutions (see Table I). A four-fold excess of the dye in an acetate buffer of pH 4.5 to 6.5 was found most suitable. Using a dye concentration of 0.55 µg/ml, 0.01 µg of Nd was determined with a precision of ± 10%.

INTERFERENCES

Many elements interfere with the estimation of lanthanides, by producing in alkaline solutions second waves with EVB. Several elements were tested and results are given in Table VII.

The addition of a little KCN prior to the addition of EVB can be used to eliminate the interference of large amounts of elements forming stable cyanides (e.g. Cu, Ni, Cd, etc). Alternatively, a separation of the lanthanides from diverse elements, using well known procedures, can be carried out prior to the polarographic determination.(19,22)

RECOMMENDED METHODS

(a) The Determination of Heavier Lanthanides in the Presence of La and Ce.

Pipette an aliquot of the sample solution into a 10-ml volumetric flask. This aliquot should contain between 0.4 and 1.5 µE (microequivalent) of heavier lanthanides and a total lanthanide content of less than 1.6 µE. Add 2 ml of 1 M triethanolamine chloride, 0.5 ml of 1 M sodium hydroxide, 0.5 ml of 0.1% polyacrylamide and 2 ml of 2×10^{-3} M Eriochrome Violet B. Dilute to volume. Record a polarogram, starting at -0.2 vs SCE. Two waves will be obtained, the first due to free dye, the second to heavier lanthanides. Concentrations may be found from a calibration graph. Precision is 5% at the 1 µE level.

(b) The Determination of Total Lanthanides

The procedure under (a) is followed, using a buffer consisting of 2 ml of 1 M ethanolamine chloride and 1.5 ml of 1 M sodium hydroxide in place of the triethanolamine buffer. The precision is 5% at the 1 µE level.

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TABLE VII

INTERFERENCES USING ERIOCHROME VIOLET B

Element	Effect
Alkaline metals	None
Alkaline earths (Ca, Sr, Ba)	None
Mg	Interferes seriously
Transition elements (Cu, Zn, Ni, Co, Sn, Zr, Fe(II), Fe(III), Cr(IV), etc)	Interferes seriously
Al	Only small amounts may be tolerated
Th	Up to 2-3 times the lanthanide concentration can be tolerated in an ethanolamine buffer of pH 10.3

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THE DETERMINATION OF DISSOLVED GASES IN HIGH-TEMPERATURE, HIGH-PRESSURE WATER SYSTEMS

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ABSTRACT

In pressurized water reactors it is necessary to know the concentration of such dissolved gas as hydrogen and oxygen. Oxygen must be kept to a minimum in the coolant due to its effect on the corrosion rate of steel and hydrogen is usually kept within 10 - 30 cm^3/kg to inhibit corrosion and to remove oxygen under the effect of radiation.

The method of determining H_2, O_2, CO_2, N_2 and He dissolved in water was developed at the Chalk River laboratories of Atomic Energy of Canada Limited and has been used for several years for analysis of samples from in-reactor loops.

Sampling is usually done on a cooled by-pass of the pressurized water system. The sample is collected in an evacuated flask fitted with a 3-way stopcock so that the line between the sampling valve and stopcock can be flushed or evacuated.

The method of analysis consists of separating the gases from the water sample in a vacuum system using a conventional Toepler pump. The volume of the gas is measured in a gas buret and an aliquot is used for the determination of the individual components. Oxygen is removed by catalytically combining it with hydrogen, and excess hydrogen is removed by diffusion through a palladium thimble. Carbon dioxide is frozen out in a liquid nitrogen trap and nitrogen is removed on activated charcoal at the temperature of liquid nitrogen. The gas remaining is helium. The amounts present are calculated from the drop in pressure in the system as each component is removed.

INTRODUCTION

This paper describes a method used at Chalk River for the determination of individual components of gas mixtures containing hydrogen, oxygen, carbon dioxide, nitrogen and helium.

In the NRX and NRU reactors at AECL* several recirculation systems called "loops" are used to test potential fuels under simulated pressurized-water power reactor conditions, i.e. in water at ~500°F and 1000-2000 psi.

The water conditions for these irradiation tests are specified in the test proposals and include the concentration of hydrogen and oxygen dissolved in the coolant. The loop water also contains nitrogen and small amounts of carbon dioxide.

In the early days of loop work at Chalk River (1953) Krenz and Robertson developed a method of analysis for these gases in loop water(1) and later the method was modified slightly.(2)

Dissolved gases are removed from the water sample after which the pressure at constant volume is measured following removal of each component from the mixture.

This method has been in use for several years at AECL for control gas analysis of loop water samples. It has also been used to analyze the gas dissolved in the heavy water in the NRX and NRU reactors.

The method has limitations but it has proved invaluable for the type of analysis required in the loop chemistry program, i.e., following the concentrations of hydrogen and nitrogen which are the major gaseous constituents in the loop water (50-80% H_2; the remainder N_2) and to ascertain that no gross quantities of oxygen or carbon dioxide are present. The coolant in the in-reactor loops contains less than 0.1 ppm of oxygen which is considerably less than 0.5% of the dissolved gas. Concentrations of O_2 in this range are more accurately determined by the Winkler method.

SAMPLING

Samples of loop water for the determination of dissolved gases are normally taken from a cooled by-pass. The high-temperature water can be sampled directly if care is taken to use a low flow rate and to cool the sample bulb.

A photograph of a typical sample flask is shown in Figure 1. The flask has a capacity of 250 ml and is fitted with a three-way vacuum stopcock through a 24/40 standard taper joint. The stopcock has a 12/30 standard taper female joint on the other end for attachment to the loop and vacuum line.

The sample flask is first evacuated in the laboratory to about 10^{-3} mm Hg pressure. The loop sampling line is well flushed with loop water and the sample flask is then attached to the stainless steel 12/30 standard taper

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* Atomic Energy of Canada Limited

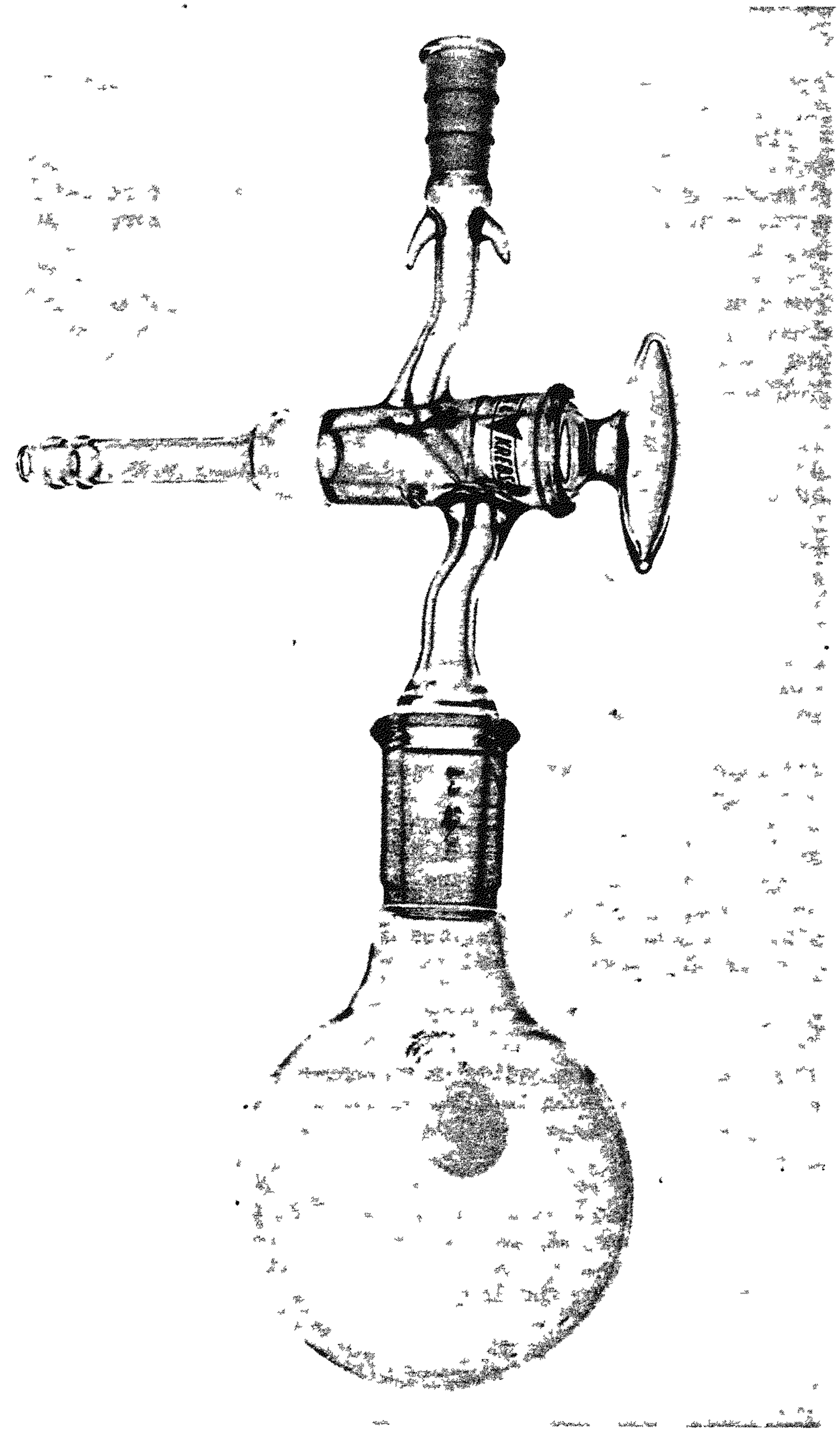

Fig. 1 - Sample Flask

joint at the sample valve. The piping between the stopcock and the sample valve is evacuated through the side outlet on the stopcock. The sample (~100 ml) is then collected. The size of the sample taken is obtained from the weights of the flask before and after sampling. If the water sampled is alkaline or neutral and total CO_2 is desired, some acid salt such as sodium bisulphate must be added to the sample flask before it is evacuated in preparation for sampling.

REMOVAL OF DISSOLVED GAS FROM THE WATER SAMPLE

A diagram of the vacuum system for pumping the gas from the water sample into the gas buret is shown in Figure 2.

The sample flask is connected to the vacuum line below V-2 and the system is evacuated up to the stopcock on the flask to about 10^{-3} mm Hg pressure. The system is then isolated from the vacuum manifold by valve V-3. The stopcock on the sample flask is opened and the Toepler pump is operated to transfer the gas from the water sample to the gas buret A. When the pressure in the system has been reduced again to about 10^{-2} mm Hg the pumping is stopped and the volume of gas in the buret is measured at atmospheric pressure using the mercury leveling bulb B.

A sample of the gas can be transferred directly to the gas analysis system through stopcock V-4 for the determination of the individual components or it can be transferred through V-4 and capillary tube C to a small glass thimble for storage (Figure 3).

GAS ANALYSIS APPARATUS

Reaction Bulb

The gas analysis apparatus is shown in Figure 4. The reaction bulb D is connected at the top to the vacuum manifold through a stopcock and at the bottom to a McLeod-type gauge, MG, through a uniform bore, 1-cm diameter, Pyrex tube E, behind which is a mirror scale ~400 mm in length. The reaction bulb has a capacity of about 250 cm^3 and has four tubes projecting from it. One tube supports a palladium thimble unit for diffusion of hydrogen; a second tube contains a coil of palladium wire for recombination of hydrogen and oxygen; a third tube contains two side-arms, one equipped with a stopcock and containing activated charcoal for nitrogen absorption, the other being used to condense out carbon dioxide at the temperature of liquid nitrogen; the fourth tube is connected through a stopcock to the gas buret on the Toepler system for direct introduction of a gas sample. Each of these components is described in detail below.

Palladium Thimble Unit - This unit is used to diffuse hydrogen from the gas mixture and is shown in Figure 5. The palladium tube is 6 cm long, 4 mm O.D. with a wall thickness of 0.5 - 0.75 mm. It is silver soldered into a stainless steel 12/30 standard taper male joint which fits into the corresponding glass joint on the reaction bulb. Over the end of the palladium tube is fitted a silica tube on which is wound nichrome heating wire (4 ohms per foot). The wire is insulated with asbestos sleeving and is wound along 2.5 cm of the silica tube. An electric current is applied through a Variac.

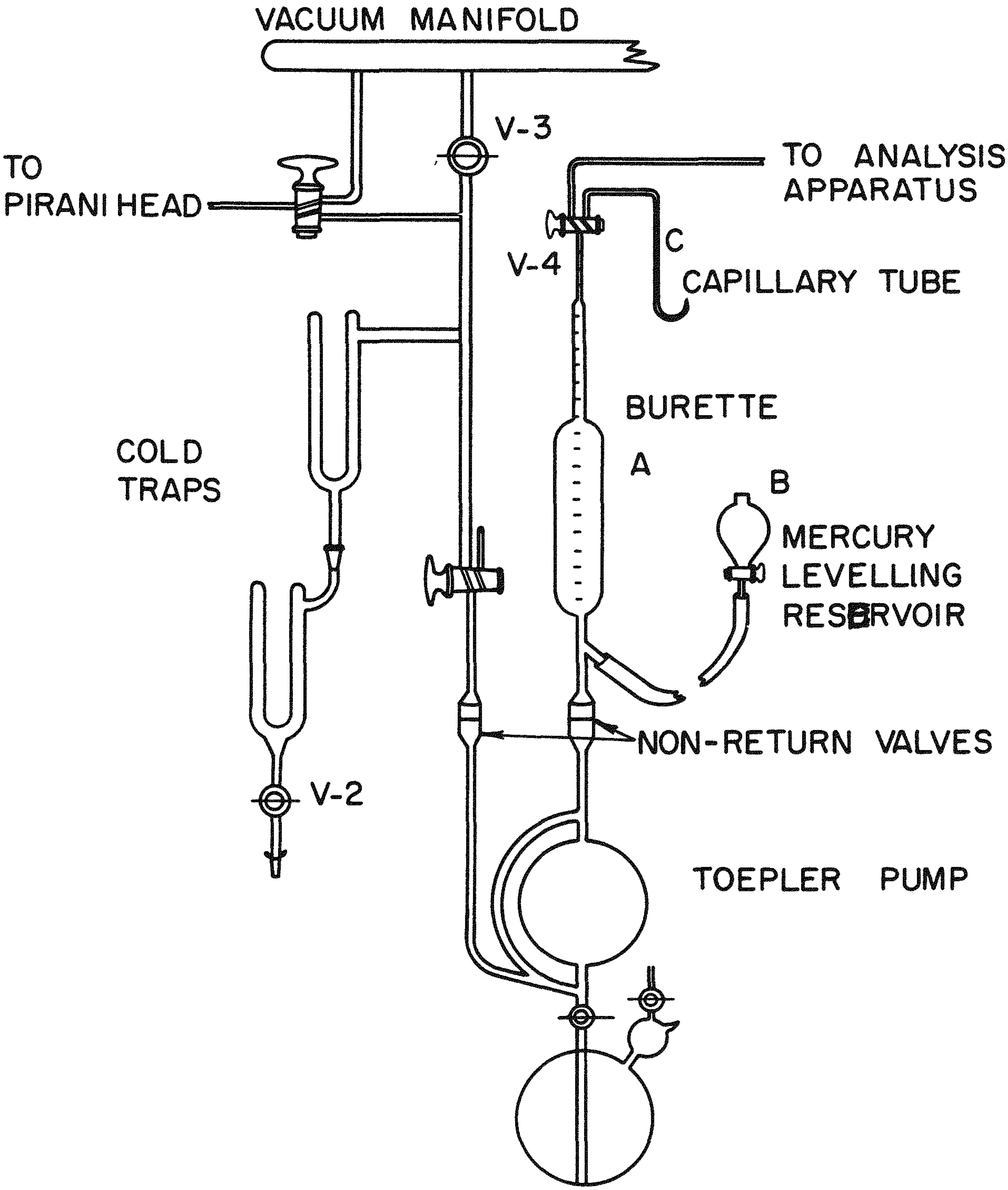

Fig. 2 - Toepler System

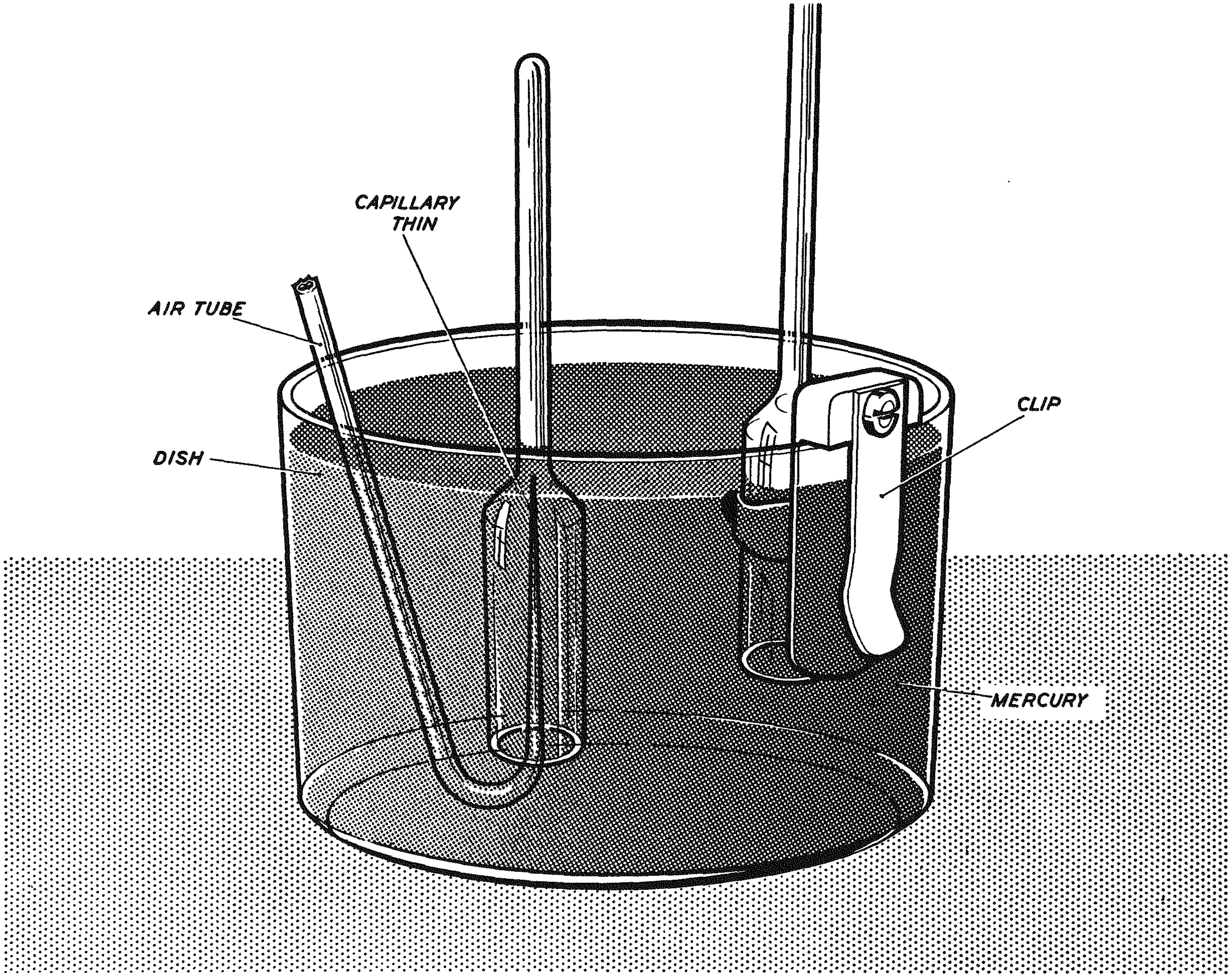

Fig. 3 - Gas Transfer Apparatus

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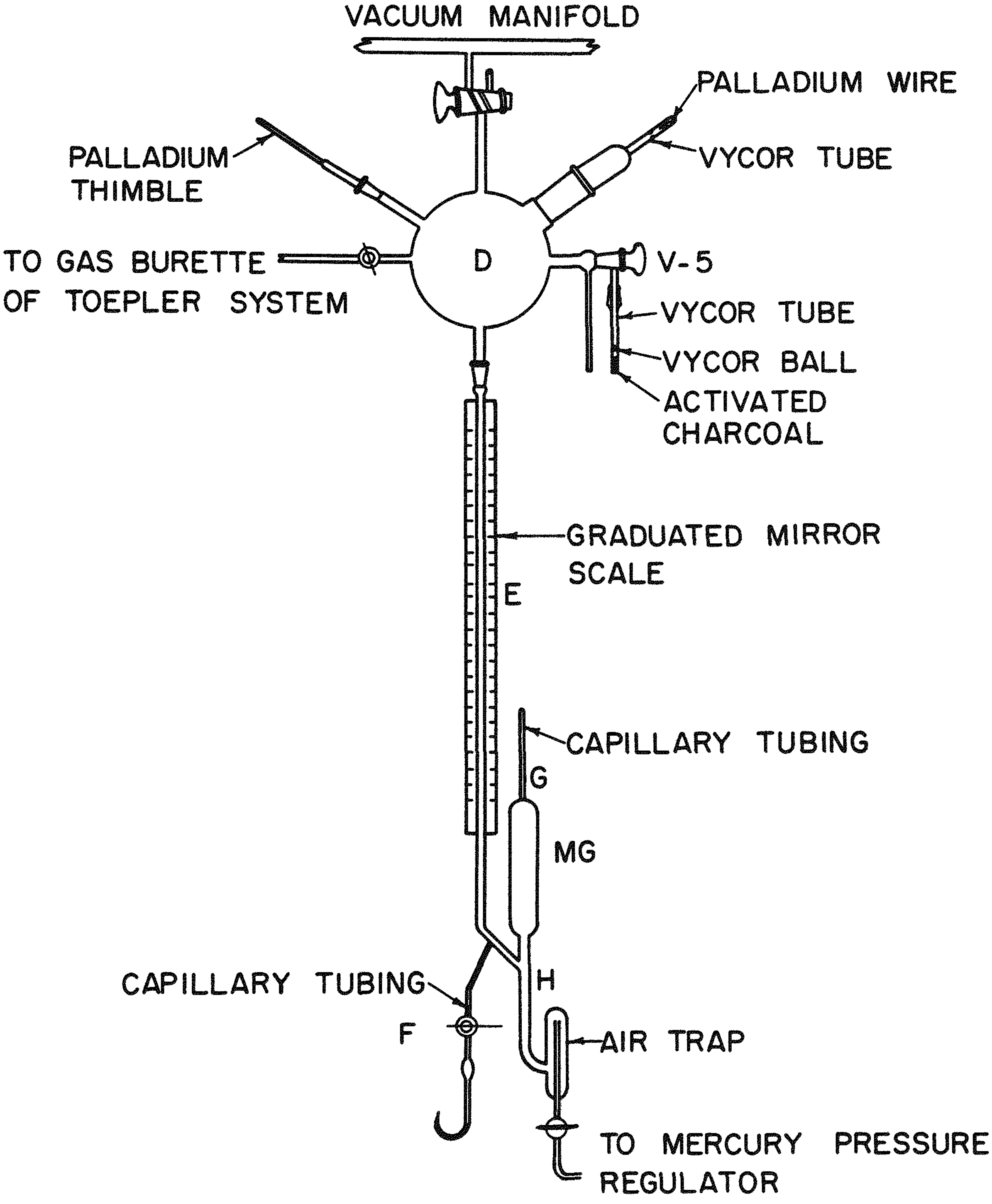

Fig. 4 - Gas Analysis Apparatus

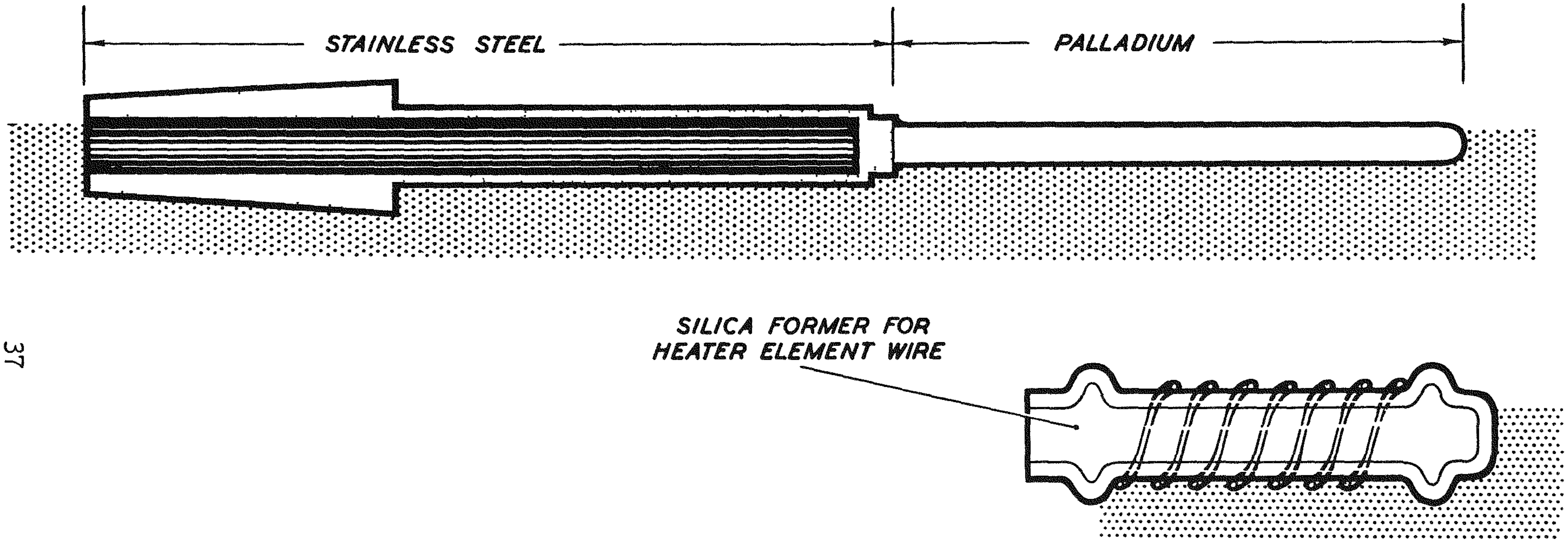

Fig. 5 - The Palladium Thimble

Recombination Unit - The recombination unit consists of a quartz tube attached to the reaction bulb through a 24/40 standard taper glass joint and contains a 4-inch length of palladium wire in a 3-cm coil. The end of the tube is wound with nichrome heating wire similar to that used for heating the palladium thimble. The two heating elements are wired in parallel to a variable resistance and each heater can be operated independently. Sufficient current is applied to cause the heaters to glow red.

CO_2 and N_2 Unit - The two fingers used for the removal of carbon dioxide and nitrogen can be seen clearly in Figure 4. The tube in which the carbon dioxide is condensed is made of Pyrex. The nitrogen absorption tube is made of quartz (Vycor) and can be isolated from the reaction bulb by stopcock V-5. This tube contains activated charcoal which can be degassed by heating strongly in situ while the apparatus is under vacuum. The charcoal is prevented from jumping about in the tube during the degassing operation by the weight of a piece of Vycor on top of it.

Mercury Pressure Regulator

Mercury is raised and lowered in the gas analysis apparatus by means of a "mercury pressure regulator" which is shown in Figure 6. It consists of a steel cylinder in which a piston is moved horizontally by a handle, thereby moving mercury into or out of the apparatus.

Hydrogen Addition

In this analysis scheme, the oxygen is removed by recombination with hydrogen at the palladium wire to form water. To remove all of the oxygen, it is therefore necessary to have more than twice as much hydrogen present as oxygen. This means that for certain samples it might be necessary to add hydrogen to the system before the gas analysis can be completed. This can be done in three ways:

(a) from a glass storage thimble (Figure 3) through the capillary tube F at the bottom of the McLeod-type gauge (Figure 4).

(b) from the gas buret of the Toepler system.

(c) through the palladium thimble by heating the end of the thimble with a hydrogen flame.

Method (c) can only be used if the hydrogen is introduced into the gas analysis apparatus prior to addition of the sample; otherwise, a reaction between the oxygen in the sample and the hydrogen would occur at the hot palladium as the hydrogen was being added.

METHOD OF ANALYSIS

The gas analysis system is first evacuated to 10^{-3} mm or less Hg pressure with the bottom inch of the carbon dioxide and nitrogen absorption tubes immersed in dry ice-trichlorethylene freezing mixture in a Dewar flask and with stopcock V-5 open (Figure 4). The system is then checked for leaks. If tight, stopcock V-5 is closed.

The zero pressure reading on the vertical tube E is taken by raising the mercury with the mercury pressure regulator to a reference mark (G) on the

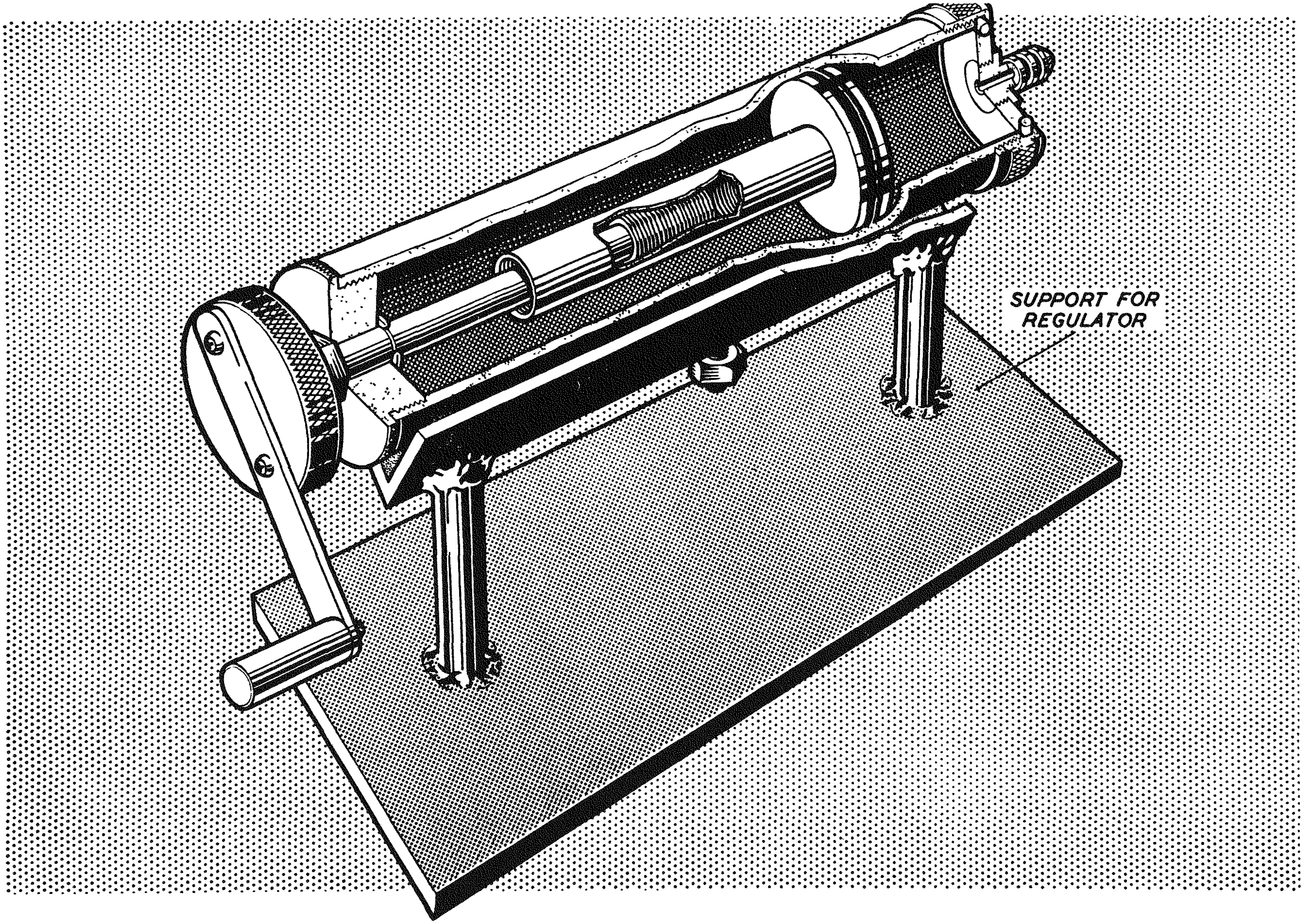

Fig. 6 - Mercury Pressure Regulator

capillary arm of the McLeod-type gauge. The mercury is then lowered to a position H (Figure 4) which is low enough to provide a connecting passage between the arms of the McLeod gauge. Several zero readings should all agree to ± 1 mm.

The sample for analysis is then introduced by one of the methods outlined previously and another pressure reading is taken. The pressure measured is that of the small volume of gas in the capillary of the pressure gauge. The gas sample normally taken is 0.5 cm^3 or less at atmospheric pressure. The constituent gases are then removed in the following order with pressure readings being made after each gas is completely removed. Normally 3 to 5 minutes are required to remove each constituent. Removal is considered complete when three consecutive pressure readings do not vary by more than 1 mm.

Carbon Dioxide

The dry ice-trichlorethylene freezing mixture covering the tips of the carbon dioxide and nitrogen absorption tubes is replaced with a Dewar flask containing liquid nitrogen. This condenses any carbon dioxide present, causing a drop in pressure. Pressure readings are repeated until constant to 1 mm.

Oxygen

The heater on the recombination unit is turned on and the Variac is adjusted until the wire glows red. After 2 to 3 minutes, a pressure reading is taken. Readings are repeated until the pressure is steady. The heater is then turned off. One-third of the drop in pressure is due to oxygen removal and two-thirds due to hydrogen removal.

Hydrogen

The heater on the palladium thimble is turned on and, after 2 to 3 minutes, a pressure reading is taken. Readings are repeated until the pressure stops falling. If there should be no drop in pressure, indicating that no hydrogen is present in excess of that used in the recombination reaction[step (b)], it is necessary to add hydrogen by one of the methods previously outlined and to repeat the steps for removal of oxygen and hydrogen. The heater is finally turned off.

Nitrogen

After all the hydrogen is removed, stopcock V-5 is opened to allow any nitrogen present to be absorbed on the activated charcoal. Since the volume of the system is increased slightly when stopcock V-5 is opened, a correction factor must be applied. This correction is usually only 1 to 2% and can be determined readily with helium alone in the apparatus. Argon, if present, will also be removed by the charcoal.

Helium

The residual pressure in the system is due to helium.

CALCULATION OF RESULTS

The concentration of total gas in the water sample is calculated from the volume of gas pumped from the water and measured in the gas buret and from the weight of water used. The gas volume measured may be corrected to NTP if desired.

The percentages of the various gases in the sample are calculated as follows:

If the zero reading before introducing the sample is P_o mm and the reading after adding the sample is P_t mm, then the sample pressure, P_s mm, is equal to P_t mm - P_o mm.

If, after the removal of the carbon dioxide, the pressure has dropped to P_a, then the drop in pressure equals $P_t - P_a$ and the percentage of carbon dioxide in the gas equals $100(P_t - P_a)/P_s$. The percent of each of the other components is determined similarly. Note that only 1/3 of the pressure drop due to recombination of hydrogen and oxygen is due to oxygen and 2/3 due to hydrogen.

RESULTS

Various mixtures of the gases concerned were prepared with known compositions and were analyzed by the gas analysis method. In preparing the mixtures a gas line was used that had been constructed for the preparation of standards for use in the calibration of a gas chromatograph. The prepared samples were also analyzed by gas chromatography.

The results obtained with the gas analysis method are given in Tables I to V. The accuracies found may be summarized as follows:

Concentration Level	Accuracy
50% or greater	3% or better
15 - 50%	5%; when oxygen is present it may drop to ~10% (Table II and IV)
5 - 10%	10%
1 - 5%	20% to 50%

In Table III larger errors (~15 to 20%) are shown for nitrogen than would be expected. This is due to the error in measurement of the low pressure reading since the nitrogen was the last component to be removed.

Some idea of the precision of the method can be obtained from the results in Table VI which are given for 10 determinations of a sample of helium containing a few percent of the other four gases. It can be seen that, while the average in every instance but one is within 1 per cent of the true value, the spread in the results for an individual component is quite broad with the oxygen results being the poorest.

TABLE I

ANALYSES OF HYDROGEN-NITROGEN MIXTURES

Hydrogen, %			Nitrogen, %		
Present	Found	Error, %	Present	Found	Error, %
50.0	48.6	-2.8	50.0	50.9	+1.8
	49.2	-1.6		50.8	+1.6
	49.0	-2.0		51.0	+2.0
30.0	28.1	-6.3	70.0	71.6	+2.3
	30.0	0		69.7	-0.4
15.0	15.6	+4.0	85.0	84.4	-0.7
	15.1	+0.7		84.8	-0.2
	14.6	-2.7		83.9	-1.3

TABLE II

ANALYSES OF OXYGEN-HYDROGEN-NITROGEN MIXTURES

Oxygen, %			Hydrogen, %			Nitrogen, %		
Present	Found	Error, %	Present	Found	Error, %	Present	Found	Error, %
10.0	9.5	- 5.0	25.0	24.3	-2.8	65.0	66.2	+1.8
	9.8	- 2.0		22.9	-8.4		67.3	+3.5
	9.0	-10.0		24.6	-1.6		66.4	+2.2
*0.85	0.7	-12	9.5	9.2	-3.2	89.6	89.2	-0.4
	1.0	+18		8.8	-7.4		89.3	-0.3
	0.8	- 6.0		9.0	-5.3		89.0	-0.7

*All analyses on this mixture indicated ~1% carbon dioxide present.

TABLE III

ANALYSES OF CARBON DIOXIDE-HYDROGEN-NITROGEN MIXTURES

Carbon Dioxide, %			Hydrogen, %			Nitrogen, %		
Present	Found	Error, %	Present	Found	Error, %	Present	Found	Error, %
10.0	9.9	-1.0	30.0	29.0	-3.3	60.0	61.1	+ 1.8
	9.6	-4.0		28.1	-6.3		62.3	+ 3.8
	9.7	-3.0		28.9	-3.7		61.4	+ 2.3
50.0	49.0	-2.0	40.0	38.8	-3.0	10.0	11.8	+18
	48.6	-2.8		39.2	-2.0		11.9	+19
	49.5	-1.0		39.8	-0.5		11.3	+13

TABLE IV

ANALYSES OF OXYGEN-HYDROGEN MIXTURES

Oxygen, %			Hydrogen, %		
Present	Found	Error, %	Present	Found	Error, %
76.2	74.2	-2.6	23.8	25.8	+8.4
	74.8	-1.8		25.2	+5.9
55.1	52.3	-5.1	44.9	47.7	+7.1
	52.6	-4.5		45.0	+0.2
25.3	23.3	-7.9	74.7	76.7	+2.7
	24.2	-4.4		75.8	+1.5

TABLE V

ANALYSES OF CARBON DIOXIDE-NITROGEN-HELIUM MIXTURES

Carbon Dioxide, %			Nitrogen, %			Helium, %		
Present	Found	Error, %	Present	Found	Error, %	Present	Found	Error, %
28.4	27.0	-4.8	21.2	21.5	+1.4	50.4	51.5	+ 2.2
	28.5	+0.4		21.5	+1.4		50.0	- 0.8
40.0	38.5	-3.8	55.0	56.0	+1.8	5.0	5.5	+10
	40.5	+1.3		55.0	0		4.5	-10
25.0	26.5	+6.0	75.0	73.5	-2.0	0		
	25.2	+0.8		74.8	-0.3			

TABLE VI

PRECISION OF ANALYSIS OF MIXTURE CONTAINING THE FIVE GASES

	Oxygen, %	Hydrogen, %	Carbon Dioxide, %	Nitrogen, %	Helium, %
Present	1.0	2.7	5.0	3.9	87.4
Found	1.0	2.6	5.0	3.9	87.4
	0.6	3.0	4.8	3.9	87.7
	1.0	2.9	4.7	3.8	87.7
	1.1	2.8	5.1	4.7	86.2
	0.9	2.7	5.2	3.6	87.5
	1.2	3.1	4.6	3.5	87.6
	1.1	2.5	5.0	3.4	88.0
	1.0	2.4	5.2	3.7	87.7
	1.0	2.3	5.3	4.2	87.2
	1.0	2.9	5.4	3.4	87.3
Mean	0.99	2.72	5.03	3.81	87.43
Standard Deviation(σ)	0.15	0.25	0.25	0.38	0.47
$\bar{x} \pm 1.1\sigma$ ($P_s = 0.99$, 10 observations)	0.99 ± 0.17	2.72 ± 0.28	5.03 ± 0.28	3.81 ± 0.42	87.43 ± 0.52

EFFECTS WHICH CAUSE ERRORS

Use of Liquid Nitrogen Cold Trap to Remove Carbon Dioxide

In many instances analyses of gas samples have shown small amounts of carbon dioxide (0.3 to 1%) when it was known that none was present. It has been found that with pure nitrogen in the apparatus a small pressure drop (0.5 to 1%) does occur when the dry-ice trap around the carbon dioxide and nitrogen removal tubes is replaced by a Dewar flask containing liquid nitrogen. In order to minimize this effect, it has been specified that only the tips of the tubes be immersed in the liquid nitrogen.

This temperature effect is avoided by filling the Dewar flask to the top with the liquid nitrogen and immersing the tips of the tubes in it. This avoids surrounding the tubes for their entire length with the Dewar flask and the volume cooled is kept to a minimum.

The results in Table II were obtained without using this newer technique. The 1 per cent of carbon dioxide found in every analysis can be explained by the cooling effect.

Recombination Unit

In testing for a temperature effect when the recombination heater was turned on and nitrogen was in the apparatus, a slight rise in pressure (about 3 mm Hg) was noticed. When the heater was turned off and cooled, the pressure remained steady at the higher value. However, when the palladium thimble was heated, the pressure dropped to its original value, indicating that the pressure rise had been due to hydrogen evolved from the palladium wire when the recombination unit was hot.

To substantiate this result, the following experiment was carried out under conditions which would accentuate the effect:

Operation	Pressure Reading (mm Hg)
Pure H_2 added to apparatus	Not measured but 3 to 4 times normal sample size.
Recombination heater on for 5 min; then turned off; cooled. Palladium thimble heater on to remove hydrogen	20 (normal zero reading)
Pure N_2 added	348
Recombination heater on 5 min;	359
Recombination heater off; cooled	359
Palladium thimble heater on to remove hydrogen	348

The first three steps listed were employed to get as much hydrogen as possible into the palladium wire and this was achieved as evidenced by the large (11 mm) rise in pressure when the hydrogen came out of the wire.

Since this effect could possibly hide a pressure rise due to temperature only, an experiment was carried out in which all hydrogen was removed from the palladium wire by heating while the apparatus was open to the vacuum manifold. The heater was then turned off, allowed to cool and the apparatus isolated from the vacuum line. Nitrogen was then added and a pressure reading was taken. The recombination heater was turned on and, after 5 minutes, another pressure reading was made. No rise was observed indicating that, in this particular apparatus and at the temperature used for the heater, there was no effect on the gas pressure due to temperature alone.

It is possible to operate the apparatus in such a way as to avoid trapping hydrogen in the palladium wire and thus prevent odd pressure effects in subsequent analyses. This was demonstrated as follows:

Operation	Pressure Reading (mm Hg)
The recombination unit was heated while the apparatus was being evacuated to strip all H_2 from the palladium wire. The unit was cooled and the apparatus isolated from the vacuum line.	20 (normal zero reading)
Pure H_2 was added	252
Recombination heater on	251
Recombination heater off and cooled	248
Recombination heater on	251
Palladium thimble was heated while recombination heater was still on	20

Therefore, to prevent absorption of hydrogen by the palladium wire and subsequent pressure effects from release of hydrogen, causing analytical errors, the recombination heater should not be turned off when analyzing a sample until after all the hydrogen has been removed through the palladium thimble. At that point in the procedure, both heaters can be turned off or left on until the analysis is completed.

SUMMARY

The gas analysis method described for the determination of hydrogen, oxygen, carbon dioxide, nitrogen and helium has been used satisfactorily for a number of years at Chalk River for the analysis of gas dissolved in loop water where the major components are hydrogen and nitrogen.

Gases which are 50% or more of a mixture can be determined to 3% or better. For constituents at concentrations as low as 15%, good accuracy (5%) is still attainable. However, the method is poor for minor constituents, i.e. those below 5%, where errors of 20 to 50% are found.

If small amounts of hydrogen, oxygen or carbon dioxide are to be determined, errors can be reduced by following the modifications suggested to avoid errors due to temperature effects and to the release of hydrogen from the palladium wire in the recombination unit.

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THE SPECTROGRAPHIC DETERMINATION OF TRACE ELEMENTS IN HUMAN TISSUE

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ABSTRACT

An Atomic Energy Commission program for the determination of trace elements in human tissues has been under way at the University of Tennessee since 1950. This program is now being transferred to the Oak Ridge National Laboratory, where the facilities for tissue preparation and for the trace-element determination are being consolidated in one building. Direct-reading spectrometry, mechanical electrode loading, and other special techniques are being utilized to expedite analysis. The purpose of the program is to determine normal concentration ranges in human tissues, for as many elements as possible, as an aid in establishing maximum permissible concentrations of radioactive isotopes in the human body.

The tissues are frozen for shipping and storage. They are then dissected to remove excess fat, connective tissue, etc., and dried at 110°C. The dried sample is ground and a small portion (1 to 2 g) is ashed at 450°C. Odors from the drying and ashing processes are avoided by combustion of the exhaust gases.

Spectrometric examination of the ash is performed, by d-c arc excitation, on a 1.5-m Industrial Research Quantometer. A Stallwood jet, operated with a mixture of He and O_2, is used to stabilize the arc and to reduce background levels. The resulting arc gives variations in the general exposure of about 7%, and background variations are normally less than 10%. Average deviations of element/Pd intensity ratios range from about 2% for Sr and Ba to 8% for Zr, with most of the other elements near 5%. Detection limits (taken as the concentration in the ash giving a reading of 1.5 times background) range from 0.5 ppm for Be to 300 ppm for Zn.

INTRODUCTION

Since 1950 an Atomic Energy Commission program, requested by the Health Physics Division of the Oak Ridge National Laboratory, for the determination of trace elements in human tissue has been carried out by Dr. I. H. Tipton of the University of Tennessee Department of Physics. The purpose of the program is to establish normal concentration ranges in various organs of the human body for as many elements as possible. These ranges, to include variations with age, sex, geographic location, etc., are used as an aid in establishing maximum permissible concentrations of radioactive isotopes.

Many valuable data have come from this program,(6) but it has become apparent that in order to make a thorough study of the many possible variables, this investigation must be expanded beyond the practical limits of the available equipment at the University. Consequently, this program is now being transferred to the Oak Ridge National Laboratory, where the facilities for tissue ashing and those for the determination of trace elements are being consolidated in one building, and where the techniques herein described are being used to expedite analysis.

TISSUE COLLECTION AND PREPARATION

The samples collected for this program are intended to be representative of the general population, and should not include tissues in which disease or other factors might have disturbed trace element metabolism. To obtain as nearly as possible normal or representative tissues, samples are taken from autopsies of victims of instantaneous accidental death. About 20 different tissues per autopsy are taken by cooperating pathologists throughout the world. Samples from within the United States are placed in plastic bags, packed in dry ice, and shipped to Oak Ridge National Laboratory, where they are stored in freezers. Samples from foreign countries are shipped and are stored in formaldehyde.

Before analysis, tissues are dissected to remove excess fat and connective tissue and then dried in polypropylene evaporating dishes at 110°C for 24 hours

The ashing of tissue samples can be a long, inefficient and somewhat unmanageable process when these samples are large ($\sim$100 g). It, therefore, seemed desirable to use a much smaller portion ($\sim$ 1 g) if this amount of tissue could be properly sampled. For this purpose some method was needed for comminution and mixing the sample without introducing trace metal contamination.

It was first proposed to use an Osterizer blender for the purpose, but samples were found to be contaminated by the stainless steel blades. Samples were next shaken in a tungsten carbide vial which contained a tungsten carbide ball, using a mechanical impact shaker (Spex Mixer/Mill), but contamination resulted from a cobalt binder in the tungsten carbide. Containers made from the more common plastics were tried with the impact shaker, but they were too soft for effective pulverization of dried tissue.

In the pulverization method which now appears to be most satisfactory a double polyethylene container is used on the mechanical shaker. An inner cylinder, which contains the unground sample along with a pure tungsten ball, has end plates of linenized Bakelite, a very hard, tough plastic. The sides of the inner cylinder are perforated with 3/32-in. holes to allow the pulverized material to escape into the outer container, thus hastening pulverization of the material remaining inside. This is a simplified version of a principle used in certain types of commercial crushing equipment.* Samples are effectively pulverized in this device, and none of the parts appear likely to contaminate the sample with trace elements of interest. The Bakelite does contain 0.7% ash, but this ash does not contain major quantities of the trace elements to be determined. Contamination of samples has been looked for, but has not been detected at levels significant for this work.

After grinding, a small (1-2 g) portion of the sample is transferred to a silica crucible and placed in a cold furnace. The furnace is provided with a stainless steel liner. A quartz plate is suspended about 1/16-in. above the crucible tops to reduce the possibility of cross-contamination among the samples, as well as contamination from other sources. The furnace temperature is slowly raised to 450°C overnight and held at this temperature until the ashing is complete (12-24 hr). The ash is then weighed and prepared for spectrometric analysis.

ODOR ELIMINATION

The tissue preparation facility is located in the main research building at ORNL, which necessitates reliable control of the disagreeable odors created by the drying and ashing processes. This problem has been met by completely oxidizing the odorous materials before exhausting them.** The drying oven exhaust (Figure 1) is used as the air intake for an ordinary gas burner. A small intentional air leak into the oven provides a gentle flow of air through the oven. Odorous gases are passed through the flame and are oxidized to odorless forms. The same principle is used with the furnaces (Figure 2), except that electrical heating is substituted for the flame. Approximately 6 liters of air per minute are injected into the side-arm of the quartz tube and, by entrainment, causes a very gentle flow of air through the furnace. By controlling the rate of leakage of air into the muffle, it is possible to prevent any glowing (local combusion) of samples, which might cause localized temperatures to exceed the desired 450°C. The exhaust, together with ample oxygen, is passed through the heated quartz tube ($\approx$ 600°C) where oxidation takes place. Both of these methods have been tested without a hood exhaust and no odor could be detected in the room. These devices are almost completely self-cleaning. A deposit does form in the portion of the tube that lies within the furnace wall but this deposit is easily removed by scraping from inside the furnace.

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* Pitchford Scientific Instrument Corporation, Pittsburgh, Pennsylvania

** The use of combustion to eliminate odors was suggested by R. G. Pickard, Central Scientific Company, Chicago, Illinois (private communication).

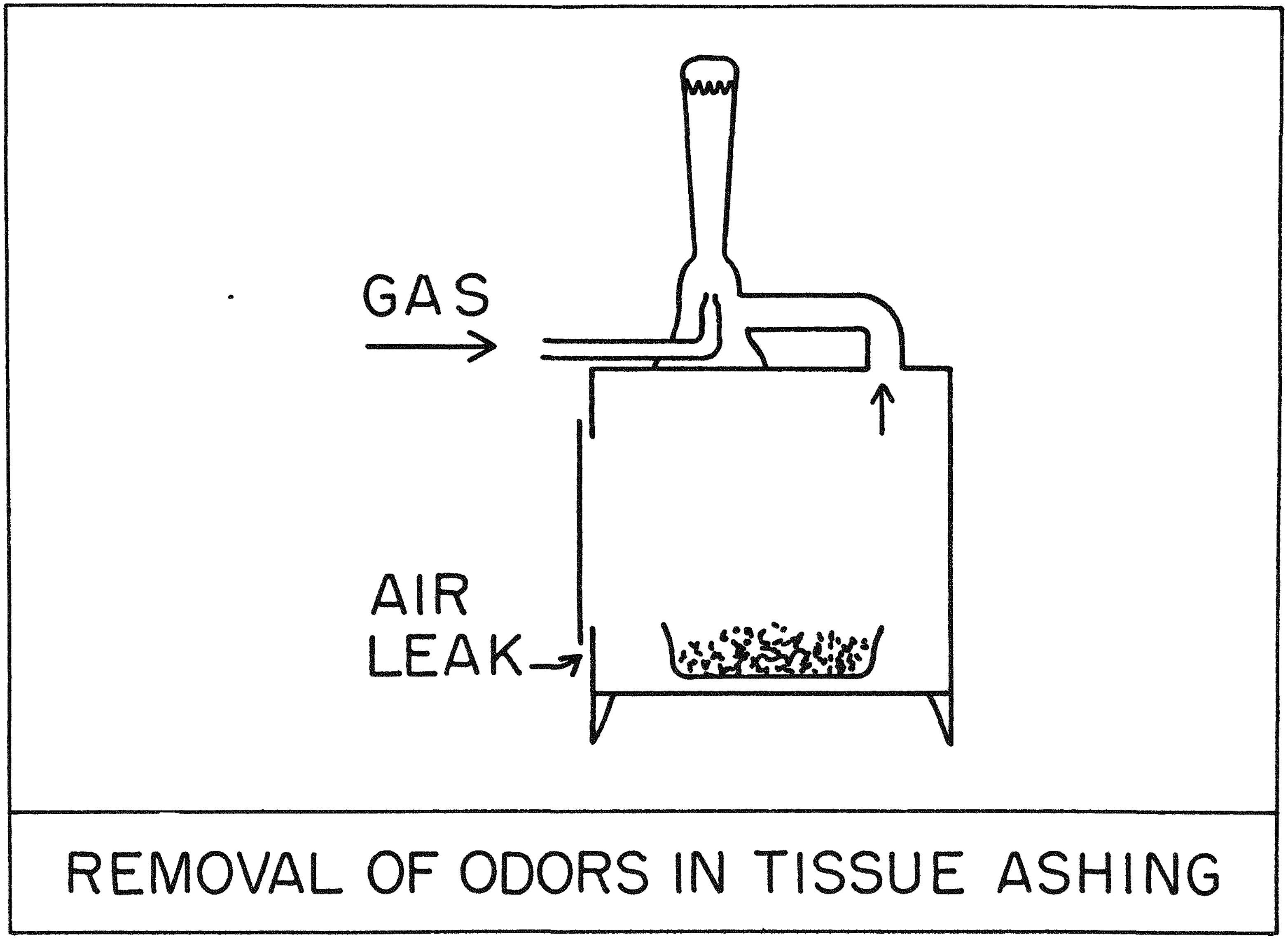

Fig. 1 - Apparatus for Eliminating Odors, Utilizing a Gas Burner

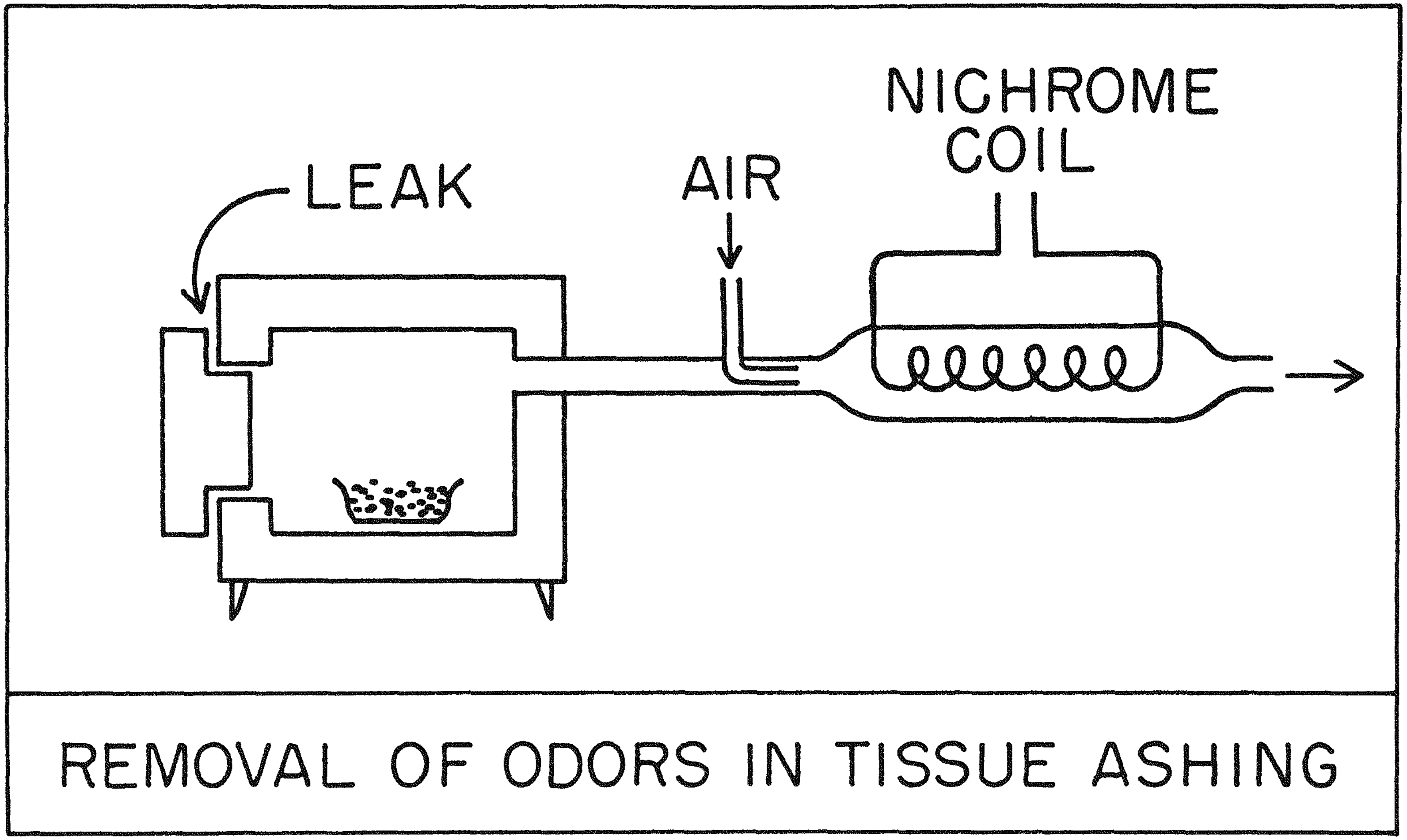

Fig. 2 - Apparatus for Eliminating Odors, Utilizing an Electric Heater

CROSS-CONTAMINATION

Trace element concentrations in various tissues are known to vary widely. Since the same silica dishes are to be used for all samples, the danger of cross-contamination through the dishes must be considered. Routinely, the dishes are washed in a live-steam dish-washer, immersed for two hours in a bath consisting of 1 part concentrated nitric and 5 parts concentrated sulfuric acids, allowed to stand overnight in a solution of Na_2EDTA, and then rinsed thoroughly with deionized water. To test the thoroughness of this cleaning, a sample of liver was ashed and the ash was removed mechanically from the dish in the normal way. The dish was then cleaned by the procedure mentioned. Ten grams of ammonium bisulfate (NH_4HSO_4) were then fused for 1 hour at 330°C in the dish to remove any residual contamination.(1) The excess ammonium bisulfate was evaporated and any sulfate residue which might exist in the dish taken up in 1 ml of dilute sulfuric acid. This solution, along with a reagent blank, was examined by porous cup exposures. No evidence could be found that any trace or major constituent of this liver sample which could be removed by ammonium bisulfate fusion had remained in the dish after the routine washing.

SPECTROMETRIC EXAMINATION OF THE ASH

Instrumentation

The instrument used for this work is a 1.5-meter Applied Research Laboratories Industrial Research Quantometer with 32 fixed and 9 movable receivers. Any 32 of the channels can be used simultaneously. Fixed receivers are set for lines of P, Cd, As, Mg, Pb, Si, Fe, Al, Sn, Cu, Zn, Zr, Ni, Co, Mn, Sr, Cr, Ca, Ba, Na, Bi, Mo, V, Ti, and Ag. In general, the most sensitive arc lines for each element are used. Movable receivers are normally used for Nb, Be, and Pd; the remainder of the movable receivers are used for special problems. The instrument now has a 20 μ primary slit and 150 μ secondary slit on most of the receivers. A few receivers have 75 μ secondary slits. The photomultiplier signal from each channel is integrated in a capacitor. After completion of an exposure the charges on the capacitors are read sequentially and the results recorded on a linear scale by a strip chart recorder. The recorder circuit is provided with a potentiometer which allows the internal standard signal to be set to some predetermined value prior to readout. This raises or lowers the readings from all other channels proportionately and causes the recorder to read intensity ratios directly.

Preparation of Standards

Pure KH_2PO_4, NaCl, MgO, $CaCO_3$, and Fe_2O_3 are required for the preparation of a synthetic soft tissue ash. Reagent-grade KH_2PO_4 and NaCl were found to be sufficiently pure. Ether extraction was used to purify iron used in preparing the Fe_2O_3. Pure MgO was prepared from resublimed magnesium metal. $CaCO_3$ free from Sr and Ba was prepared by precipitating the Ca from alcoholic solution with 8-hydroxyquinoline, as described by Mitchell.(2) The purified $CaCO_3$ contained about 2 ppm Sr and less than 5 ppm Ba, compared with 250 ppm Sr and approximately 50 ppm Ba in the starting material.

The synthetic soft tissue ash consists of 67% KH_2PO_4, 25% NaCl, 3.6% MgO, 3.0% $CaCO_3$, and 1.4% Fe_2O_3. These materials are mixed and heated at 500°C for 24 hours, after which they are thoroughly ground and used as a matrix for the standards.

A trace element mix was prepared, containing Ag, Al, Ba, Be, Bi, Cd, Co, Cr, Cu, Mo, Mn, Nb, Ni, Pb, Sn, Sr, Ti, V, Zn, and Zr (as metals or oxides in most cases) in the approximate proportions in which they are contained in tissue ash. After thorough grinding, appropriate portions of this mix were fused with one gram of $K_2S_2O_7$ to provide greater homogeneity than could be achieved by dry grinding, and to incorporate trace elements into the crystal lattice at high dilutions insofar as possible, rather than leaving them as discrete concentrated particles. Heating was continued in a furnace at 450°C until all of the $K_2S_2O_7$ was converted to K_2SO_4. The fusion cakes (one for each standard concentration) were ground and mixed with sufficient synthetic soft tissue ash to make 10 grams of the standard. Standards were prepared with concentrations in the ratio of 0, 1, 3, 6, 10, 30, 60, and 100. The maximum concentrations of trace elements ranged from 100 ppm for Ag and Be to 6000 ppm for Zn. This large number of standard concentrations was prepared for experimental purposes and only a few of them will be used for routine working curves.

Exposure Conditions

Samples and standards are mixed, using plastic vials and the mechanical shaker, with graphite and NaBr to give an arcing mixture consisting of equal parts of tissue ash, graphite, and sodium bromide. The buffer mixture contains 0.5% PdO to serve as the internal standard. The arcing mixture is loaded into a carbon electrode, using a commercial model of the induced percussion electrode packing machine described by Strasheim.(5) The filled electrodes are heated at 350°C for 1 hour just prior to the exposure to remove any adsorbed moisture from the arcing mixture. Exposures are made using an arc current of 10 amperes d-c with the sample contained in the anode. The initial electrode spacing is 3 mm; the gap is not adjusted during the exposure. Arcing is continued until all of the sample is consumed, which requires about 75 seconds. A Stallwood jet, operated with 8 liters per minute of He and 2 liters per minute of O_2, is employed.

The arcing mixture provides reasonable spectroscopic buffering to reduce errors from matrix variations, and does not reduce the sensitivity excessively through sample dilution. Sodium bromide was chosen as a buffer constituent because of its smooth burning qualities.

Stable and reproducible burning of the arc is always desirable, but it is more important here than in most other investigations. Detection limits and precision at low concentrations of trace elements are adversely affected if background intensities are not reproducible from exposure to exposure. Also, effective internal standardization is hindered by the large number of elements being determined. No internal standard can be expected to give reliable intensity ratios for all elements if the exposures are not reproducible.

The carbon electrode (Figure 3) is undercut immediately below the lip of the crater in order to hasten heating of this area and shorten the initial period of arc wandering. The electrode is filled so that the top of the charge is slightly below the undercut portion. About 12 mg of the arcing mixture is used. The combination of the undercut tip, small electrode diameter and the Stallwood jet, essentially eliminates arc wandering. The shape of the 1/4 inch counter electrode is shown in Figure 4.

The Stallwood jet, which is frequently used to reduce selective volatility in mineralogical analysis (3,4), is utilized here primarily to increase arc stability. The use of helium and oxygen in the jet, rather than air, aids in reducing general background intensities and practically eliminates cyanogen bands.

Instrument Calibration

Exposures are made of several standards which contain the desired trace elements in appropriate concentration ranges. After each exposure, but before the read-out commences, the potentiometer in the recorder circuit is adjusted to give some preselected internal standard (Pd) signal. This potentiometer affects all channels proportionately and thus allows scale deflections to be used directly as intensity ratios. Working curves consist of a linear plot of scale deflection vs concentration in the ash. Figure 5 shows a typical curve. The intercept on the scale deflection axis is caused by spectral background and photomultiplier dark current. A few elements give plots that are curved at higher concentrations due to self-absorption, but for the most part straight lines are obtained.

Precision and Sensitivity

The precision figures given in Table I are calculated from nine exposures of a standard containing 30% of the maximum concentration (top of the working curve) for each trace element.

The detection limits given in Table I are arbitrarily taken as the concentration giving a total signal of 1 1/2 times background. The validity of this figure as a detection limit depends, of course, on the observed variations in background intensity at a given wavelength from one exposure to the next. Such variations have amounted to about ± 4-8% for replicate exposures of a given sample or standard. Larger background variations (± 15-20%) have been observed between different samples. It, therefore, seems reasonable to attribute any signal which is 50% above the normal background for that wavelength to the actual presence of the element in question. More samples will have to be analyzed before a more valid method for deciding on detection limits can be devised.

FUTURE WORK

The 150μ exit slits that are now on the Quantometer are much wider than the line to be received, and allow excessive background radiation to strike the receiver. The spectrometer cabinet of the instrument has recently been insulated with polyurethane foam. As a consequence, the thermal stability has been improved so that narrower slits can now be used. Exit slits 38 μ

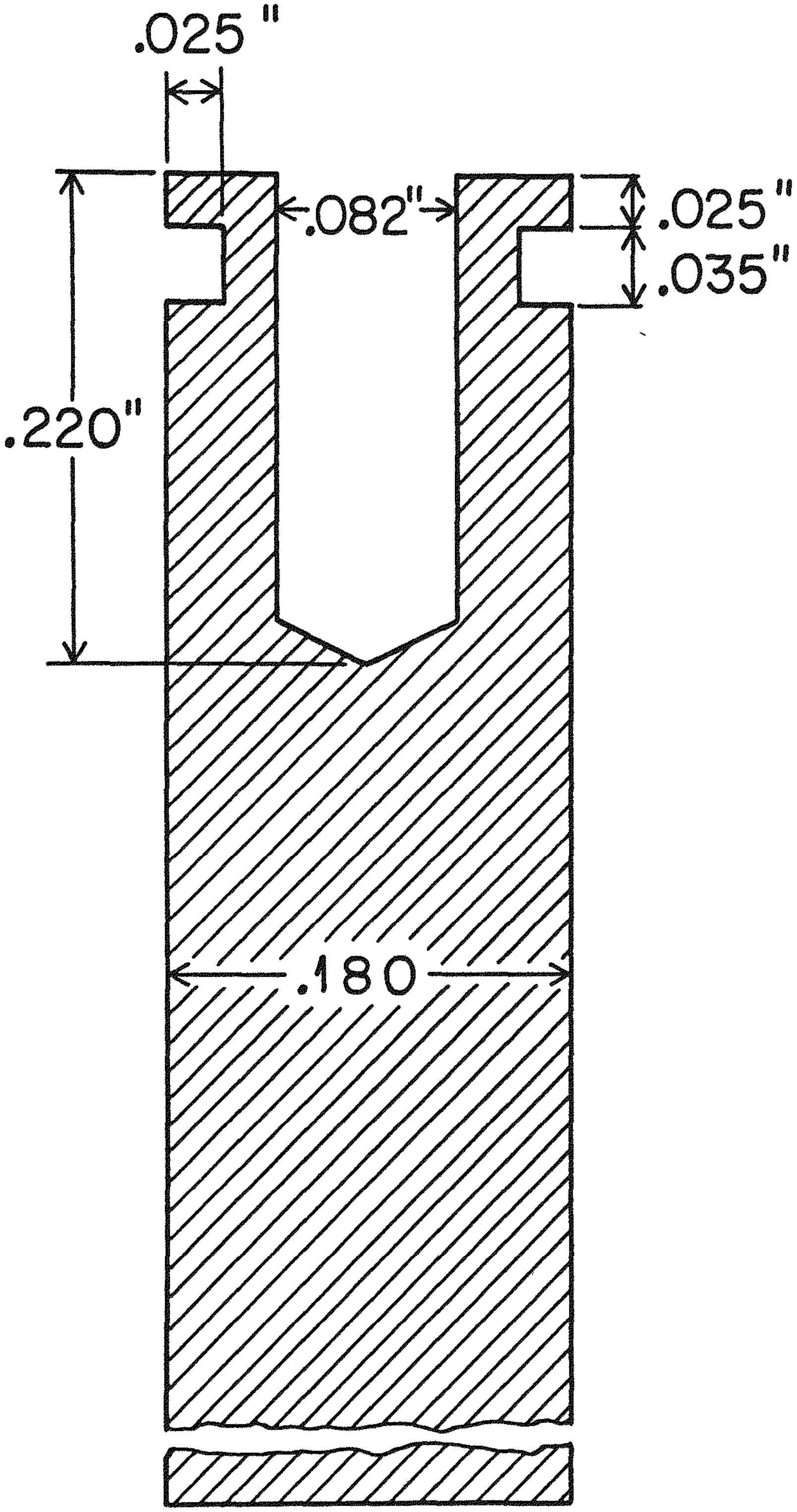

Fig. 3 - Carbon Electrode

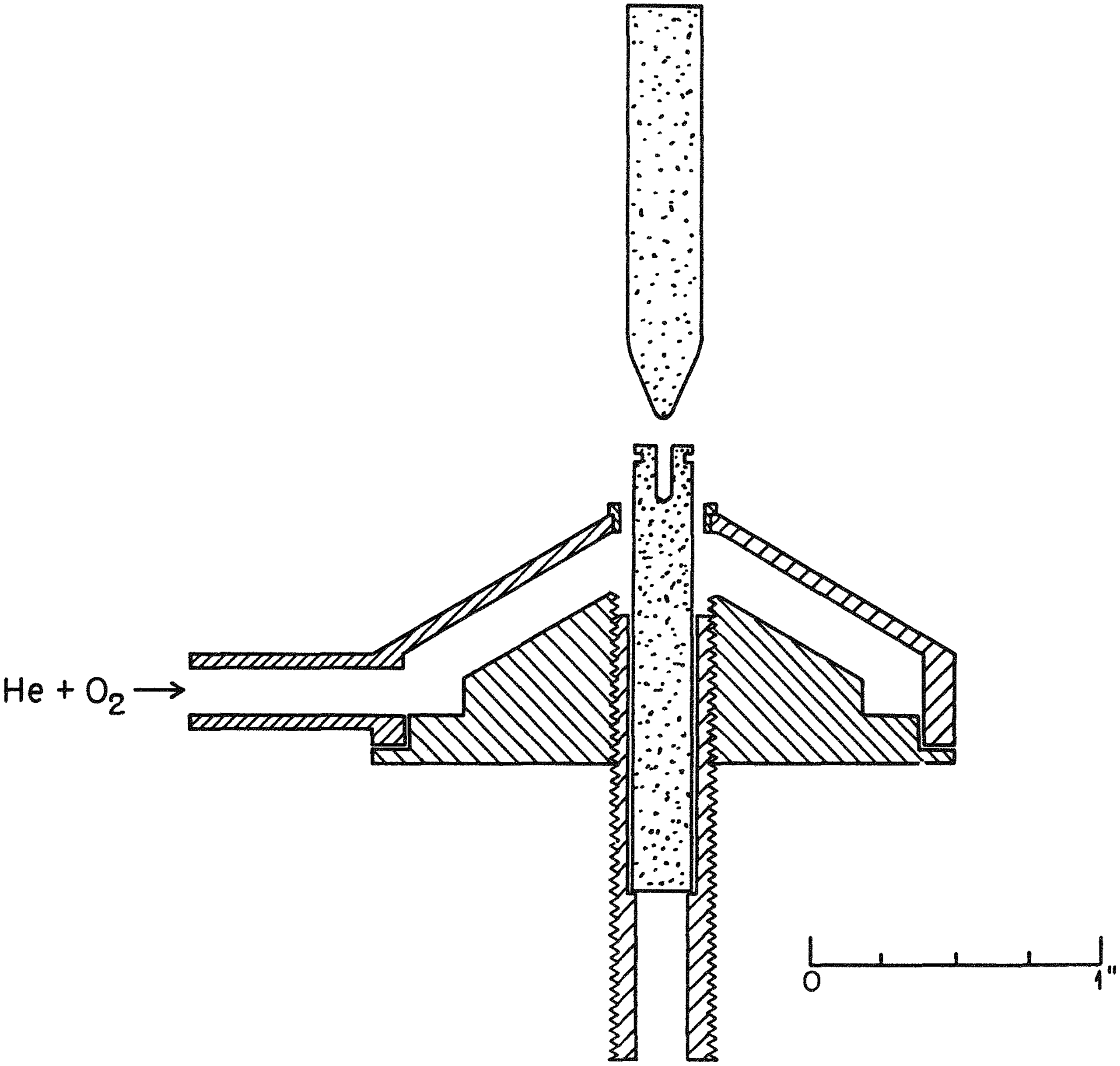

Fig. 4 - Arrangement of the Electrodes in the Stallwood Jet

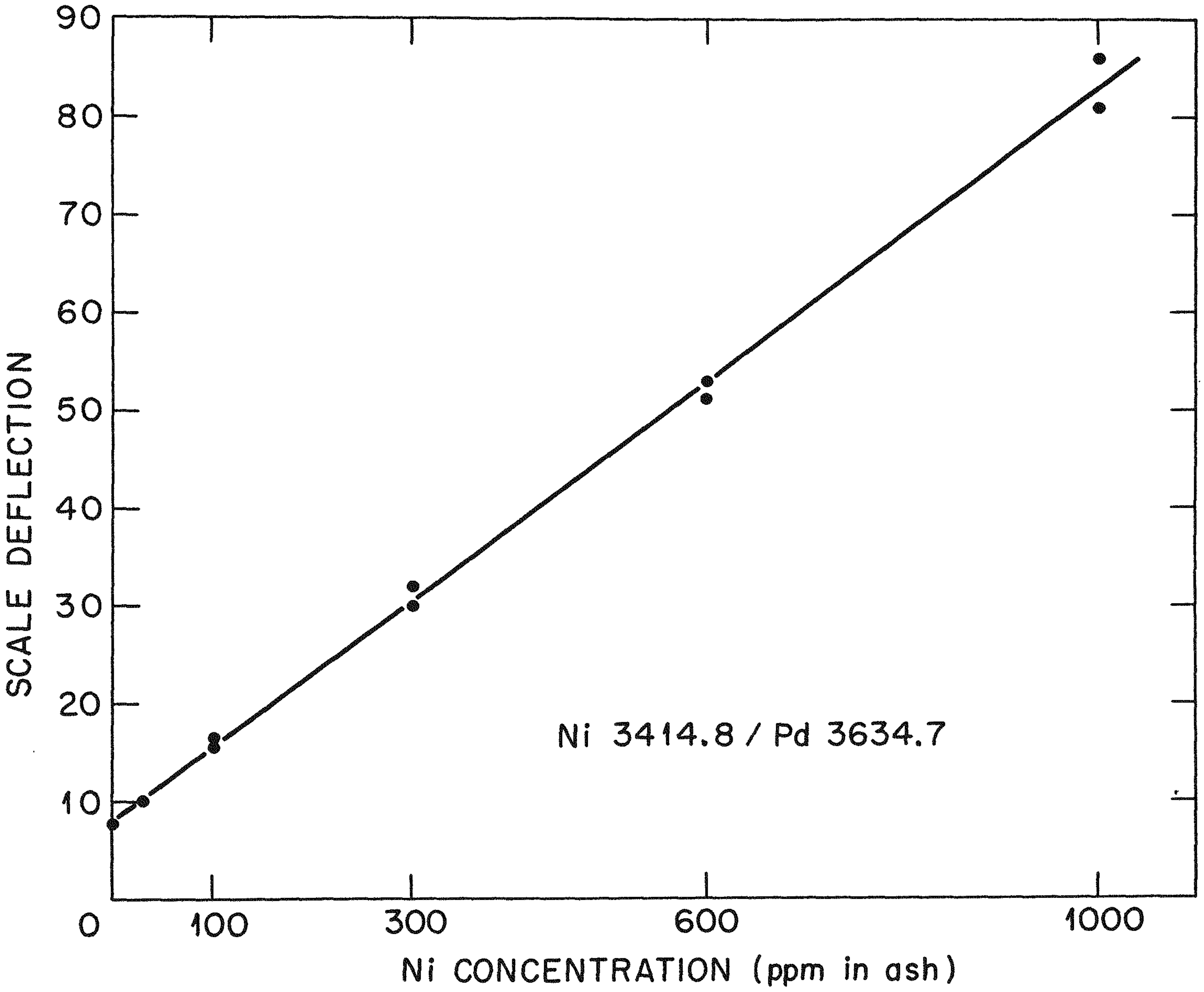

Fig. 5 - Typical Calibration Curve

TABLE I

SENSITIVITY AND PRECISION FOR TRACE ELEMENTS

Element	Line	Detection Limit (1.5 x background)	Photographic Detection Limit	Coefficient of Variation Element/Pd 3634.6
		ppm in ash		
Ag	3382.9	4	0.3	6.0
Al	3082.2	28	5	1.5
Ba	4554.0	11	-	2.1
Be	3130.4	0.6	0.2	7.0
Bi	3067.7	19	5	4.4
Cd	2288.0	25	60	6.4
Co	3453.5	16	2	2.9
Cr	4254.3	14	2	5.3
Cu	3274.0	6	<1	9.4
Mo	3170.3	40	5	4.0
Mn	4030.8	10	2	3.3
Nb	3195.0	120	30	6.3
Ni	3114.8	41	3	4.7
Pb	2833.1	60	3	6.1
Sn	3175.0	70	10	5.3
Sr	4077.7	4	0.2	4.7
Ti	3361.2	15	3	1.8
V	3184.0	30	9	3.4
Zn	3345.0	300	60	6.8
Zr	3392.0	46	5	4.8
			Mean	4.8

wide have been ordered and will be installed in about two months. Experiments with narrow slits on the movable receivers indicate that a reduction in the detection limit by a factor of 2 to 3 can be expected from this change.

Other future plans for the program include completion of the development of a method for the determination of trace elements in bone, development of a method for the determination of the major constituents (Na, K, Ca, Mg, P, Fe) in the samples, and work to determine whether or not some trace elements are lost during ashing.

SUMMARY

The A.E.C. tissue analysis program which is now being transferred to Oak Ridge National Laboratory is being set up for the determination of 20 or more elements in a large number of human tissues. Direct-reading spectrometry and mechanical electrode loading are now being utilized to expedite analysis. Further automation of the processes is planned as the program progresses.

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DETERMINATION OF TRACE QUANTITIES OF FISSION PRODUCTS IN NONIRRADIATED NATURAL AND DEPLETED URANIUM SALTS

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ABSTRACT

The occurrence of a number of fission products in pitchblende and in nonirradiated natural and depleted U salts with 10^{-4} disintegration/sec per gram of U, was recently reported by Kuroda and co-workers. The following nuclides were detected: $Sr^{89, 90, 91, 92}$, Mo^{99}, $I^{131, 132, 133, 134, 135}$, and Ba^{140}.

These fission products are formed predominantly by the spontaneous fission of U^{238}, and it is possible to obtain the general shape of the mass-yield curve for the spontaneous fission of U^{238} from the equilibrium activities of the fission products found in nonirradiated U salts. The spontaneous fission half-life of U^{238} can also be calculated from these data.

Radiochemical procedures have been developed for the determination of each fission product, in which a quantity ranging from 0.1 to 1 disintegration/sec of the fission-product activity is isolated from kilogram quantities of U salts, purified, and then counted.

Where the half-life of the fission product was several months, U minerals, instead of U salts, were used. Removal of the bulk of the U by a liquid extraction method was found to be necessary and/or advantageous in most cases, although it was possible to precipitate certain fission products directly from a concentrated solution of the U salts.

A new procedure is currently under investigation for the isolation and quantitative determination of the isotopes of Ce by a liquid-liquid extraction method. Ce(IV) can be extracted from a 10 $\underline{M}$ HNO_3 solution by a 1 to 4 mixture of TBP and CCl_4 with high extraction efficiency, and further purified by a combination of oxidation-reduction and liquid-liquid extraction procedures.

INTRODUCTION

Nonirradiated uranium salts and minerals contain extremely small, but measurable, quantities of fission products. Relative activities of the fission products in secular equilibrium with U^{238} in natural and depleted uranium salts and in uranium minerals give the general shape of the mass-yield curve for the U^{238} spontaneous fission and it is possible to calculate the spontaneous fission half-life of U^{238} from the radiochemical data.

Contribution from the slow-neutron induced fission of U^{235} appears to be negligibly small in the case of the nonirradiated natural uranium salts. In the case of the uranium minerals, however, the contribution from the induced fission cannot be totally neglected, as it has recently been demonstrated by Kuroda.(1)

Studies along these lines are being continued in this laboratory and the results obtained so far are summarized in this report.

EXPERIMENTAL

Natural Uranium

Commercial uranyl nitrate, uranyl acetate and high-grade pitchblende ores were used in the experiments. The isotopic composition of the natural uranium was assumed to be 99.276% U^{238} and 0.719% U^{235}.

Depleted Uranium

A sample of depleted uranium, of which the isotopic composition was 99.989% U^{238} and 0.011% U^{235}, was made available to us by Dr. H. M. Roth of the Research and Development Division, U. S. Atomic Energy Commission, Oak Ridge, Tennessee.

Counting Equipment

A pancake-type Geiger-Müller counter (Anton 1007TA, 2 mg/cm^2 mica window), which had a background of 1 cpm in anti-coincidence with the surrounding counters, was used for most of the radioactivity measurements.

Analytical Procedures

The most difficult step in the radiochemical procedures for the determination of the fission products in nonirradiated uranium salts and minerals is the initial removal of the bulk of uranium. Attempts have been made to precipitate some of the fission products directly from a large volume of concentrated uranium solution. The method was generally found to be tedious and unsatisfactory, however, except in the case of Mo^{99}. Thus, it appears to be essential to carry out the first separation of the fission products from uranium by liquid-liquid extraction methods.

Table I summarizes the analytical procedures utilized in this laboratory.

The following procedure for cerium, which has recently been developed in this laboratory, depends entirely on the oxidation-reduction and liquid-liquid extraction cycle: Ce(III) carrier is added to a concentrated nitric acid solution of uranium and the bulk of the uranium is repeatedly extracted with 100%

TABLE I

SUMMARY OF ANALYTICAL PROCEDURES

Nuclide	Material[a]	Initial Separation	Major Decontamination	Reference
Sr^{89} and Sr^{90}	P	--	Classical gravimetric procedures, without added carrier	(2)
Ba^{140}	N	Direct precipitation of Ba sulfate	Carbonate fusion and Fe scavenging	(3)
Ba^{140}, Sr^{91}, Sr^{92}	N D	Ether extraction of U	Fuming nitric acid treatment	(4)
$I^{131, 132, 133, etc.}$	N D	Organic solvent extraction of iodine	Liquid-extraction cycle	(5)
Mo^{99}	N D	Direct precipitation of Mo with α-benzoinoxime	Repetition of the precipitation procedure	(6)
Ce^{143}	N	TBP-CCl_4 extraction	Repetition of the oxidation-reduction and liquid-liquid extraction cycle	---

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(a) P, pitchblende; N, natural uranium; D, depleted uranium.

tributyl phosphate (TBP). The aqueous phase is evaporated to a small volume and made 10 M in nitric acid. The solution is then treated with 2 ml of 2 M sodium bromate solution. Twenty five ml of 10 M nitric acid and 1 ml of 2 M sodium bromate solution are added to a separatory flask and shaken with 25 ml of TBP-CCl_4 solution (13.3% TBP by weight; the volume ratio is 1:4). Then the sample solution containing cerium is introduced into the separatory flask and shaken for about 30 seconds. The aqueous phase is separated and again shaken with another 25-ml portion of the TBP-CCl_4 mixture.

The combined organic phase is then shaken with 10 ml of distilled water containing 3 drops of 30% hydrogen peroxide. After repeating the oxidation-reduction and liquid-liquid extraction cycle several times, the cerium carrier is finally precipitated as the oxalate, dried, weighed and counted.

The efficiency of the extraction of Ce(IV) under the conditions described above has been tested and the results are shown in Table II. It was found that the best separations of cerium from lanthanum, neodymium, samarium, yttrium, thorium, and uranium can be accomplished by repeating the oxidation-reduction and liquid-liquid extraction cycle, using the 13.3% TBP-CCl_4 solution. The data shown in Table II indicate that approximately 97 per cent of the cerium carrier should be recovered by repeating the extraction procedure twice with 25-ml portions of the organic solvent. Thus, after three oxidation-reduction and liquid-liquid extraction cycles, the overall recovery of the cerium carrier is expected to be about 91 per cent. This has been confirmed by a series of experiments, in which approximately equal quantities of uranium, thorium and cerium were taken and the cerium was separated from the mixture by the method described above. After three purification cycles, the chemical yield of cerium was found to be 90 per cent and the radioactivity of the final cerium fraction was found to be the same as the background.

It was necessary to repeat the purification cycle at least 10 times to ensure the complete decontamination of cerium from kilogram quantities of nonirradiated natural uranium nitrate, and the overall chemical yield was found to be only 27 per cent. The loss of cerium obviously occurred in the initial step, where the bulk of uranium was removed by extraction with 100% TBP.

Despite the poor chemical yield, however, the final cerium fraction was found to be radiochemically pure, and it was possible to observe the 33-hours decay of Ce^{143}. The equilibrium ratio of Ce^{143}/U^{238} in nonirradiated natural uranium salt was calculated from the counting data to be $(5.5 \pm 1.0) \times 10^{-4}$ disintegrations per second per gram of U^{238}.

RESULTS AND DISCUSSION

Experimental results obtained so far in this laboratory are summarized in Table III. The fission products/U^{238} ratios in natural uranium agreed, within the experimental error, with those in depleted uranium. A theoretical evaluation of the contribution from thermal-neutron induced fission has been made by the application of the principles of the nuclear chain-reaction to the experimental system. The calculated values of the effective multiplication constant indicated a contribution from thermal-neutron induced fission of U^{235} of much less than 1 per cent.

TABLE II

TBP-CCl_4 EXTRACTION OF Ce(IV)

Aqueous phate, 10 M nitric acid,	35 ml
Organic phase,	25 ml
Amount of Ce carrier added,	50 mg

TBP in CCl_4 (Weight %)	Cerium Extracted Into the Organic Phase (%)
100.0	90.0
38.0	87.0
23.4	85.0
13.3	84.0
10.9	81.0
9.25	67.5

TABLE III

EQUILIBRIUM RATIOS OF THE FISSION PRODUCTS/U^{238} IN NONIRRADIATED NATURAL AND DEPLETED URANIUM

Mass Number	Nuclide Measured	Equilibrium Ratio, Disintegrations/sec/g U ($\times 10^{-4}$)
89	Sr	4.1 ± 1.0
90	Sr	4.8 ± 0.4
91	Sr	4 ± 3
92	Sr	8 ± 3
99	Mo	4.4 ± 0.4
131	I	0.3 ± 0.1
132	I	2.5 ± 0.3
133	I	1.0 ± 0.2
134	I	3.6 ± 0.4
135	I	3.5 ± 0.4
140	Ba	6.2 ± 0.7
143	Ce	5.5 ± 1.0

It is possible to make a preliminary calculation of the U^{238} spontaneous fission half-life (T) from the experimental data shown in Table III, by the use of the following relationship:

$$N^{238} \cdot \frac{\ln 2}{T} = \frac{1}{2} \sum N_i \lambda_i \qquad (1),$$

where N^{238} is the number of atoms of U^{238}, and $N_i\lambda_i$ is the cumulative activity of the fission products at mass number i in secular equilibrium with U^{238} in nonirradiated uranium salts.

Kenna and Kuroda(7) have recently estimated the value of $\frac{1}{2} \sum N_i \lambda_i$ to be 72×10^{-4} disintegrations per second per gram of U^{238}. Introducing this value into equation (1), a value of $T = 8 \times 10^{15}$ years is obtained for the spontaneous fission half-life of U^{238}. This value is in excellent agreement with the value of $(8.04 \pm 0.3) \times 10^{15}$ years reported by Segre.(8)

If one accepts Segre's value of the U^{238} spontaneous fission half-life,

$$Y_i = \frac{N_i \lambda_i}{N^{238} \cdot \frac{\ln 2}{T}} \cdot 100 = 1.43\, N_i \lambda_i \qquad (2),$$

where Y_i is the fission yield and $N_i\lambda_i$ is the cumulative activity (expressed in 10^{-4} disintegrations per second) of the fission products at mass number i in secular equilibrium with 1 gram of U^{238}. The values of Y_i are calculated from the data given in Table III and are shown in Table IV.

The U^{238} spontaneous fission yields for a number of additional nuclides have been reported by Russell(9) and his results are also included in Table IV. Mass spectrometric fission yields of krypton and xenon isotopes have been reported by Wetherill(10) and Thode, et al.(11, 12) Wetherill believes that the relative abundances of the stable isotopes of krypton and xenon in euxenite give the relative yields for U^{238} spontaneous fission. The fission yields reported by Wetherill were calibrated, however, by assuming that the yield for Xe^{136} was 6.00 per cent. The mass spectrometric fission yields reported by Wetherill are also included in Table IV. It should be noted that the values for i = 132 and i = 134 given by Wetherill and by Ashizawa and Kuroda(5) are in excellent agreement.

The results obtained in this laboratory are in general agreement with the values reported by Russell,(9) except for the Sr^{89} yield. The Sr^{89} yield was obtained in this laboratory from the Sr^{89}/U^{238} ratio in pitchblende. Kuroda et al.(7, 13) reported the occurrence of Cl^{36} in pitchblende, and they estimated the ratio of the induced fission versus spontaneous fission in Belgian Congo pitchblende and in Great Bear Lake pitchblende to be 0.33 and 0.19, respectively. Thus, contribution from the neutron-induced fission of U^{235} cannot be neglected in the case of the uranium minerals. Measurements of the equilibrium ratios of Sr^{89} and Sr^{90} to U^{238} are now being repeated in this laboratory.

TABLE IV

URANIUM-238 SPONTANEOUS FISSION YIELDS

Mass Number (i)	Nuclide Measured	Yield (Y_i)	Method Used and Investigator(*)
83	Kr	0.036 ± 0.015	MW
84	Kr	0.119 ± 0.040	MW
86	Kr	0.75 ± 0.11	MW
89	Sr	5.9 ± 1.4	RK
	Sr	2.9 ± 0.3	RR
90	Sr	6.8 ± 0.6	RK
91	Sr	5 ± 4	RK
	Sr	6.9 ± 0.5	RR
92	Sr	11 ± 4	RK
99	Mo	6.3 ± 0.6	RK
	Mo	6.0 ± 0.5	RR
109	Pd	less than 0.02	RR
111	Ag	less than 0.05	RR
115	Cd	less than 0.05	RR
129	Xe	less than 0.012	MW
131	Xe	0.455 ± 0.02	MW
	I	0.42 ± 0.14	RK
132	Xe	3.57 ± 0.06	MW
	I	3.47 ± 0.42	RK
	Te	4.5 ± 0.5	RR
133	I	1.4 ± 0.3	RK
134	Xe	4.99 ± 0.07	MW
	I	5.0 ± 0.6	RK
135	I	4.9 ± 0.6	RK
136	Xe	6.00 (assumed)	MW
140	Ba	9.6 ± 1.2	RK
143	Ce	7.9 ± 1.4	RK
	Pr	7.5 ± 0.5	RR
144	Ce	6.5 ± 0.5	RR
147	Nd	4.2 ± 0.4	RR

(*) MW, mass spectrometric data by Wetherill;(10) RR, radiochemical data by Russell;(9) RK, radiochemical data obtained in this laboratory.

ACKNOWLEDGEMENT

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DETERMINATION OF BORON IN NUCLEAR REACTOR MATERIALS, USING PYROHYDROLYTIC TECHNIQUES

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ABSTRACT

In a comprehensive study of the pyrohydrolytic separation of B from various materials, it was found that, at a temperature of 1200°C, a quartz combustion tube and a steam flow rate of 1 to 3 ml/min are satisfactory for complete removal of B from a variety of materials. Micro and macro quantities of B were completely separated by this treatment, after which the B was determined by a quinalizarin or diaminochrysazin colorimetric method, or an NaOH-mannitol titration, depending upon the level of B. In order to simplify the application of the method to a wide variety of materials, the effects of time, temperature, and steam flow rates as well as the movement of macro amounts of B through the pyrohydrolysis tube at a relatively low temperature (600°C) were studied.

The separation procedure not only lends itself readily to the analysis of B in various materials but is also useful as a means of separating B for isotopic assay and of removing B completely to yield B-free matrices.

Procedures were developed for the analysis of trace amounts (< 10 ppm) of B in Zr, Hf, Zircaloy, ZrO_2, uranium oxide, and boron carbide-uranium oxide mixtures. Methods were also devised for the determination of micro amounts of B (10-1000 ppm) in the above metals, alloys, and oxides; B-stainless steels; U-Nb-Zr binary or ternary alloys; and Zircaloy-base fuel alloys.

Procedures for the analysis of macro amounts of B in metals, alloys, compounds, and mixtures have also been developed.

Various tube and boat materials were investigated for their applicability to the separation procedure. Quartz tubes and boats were found to be acceptable for trace, micro, and macro B analysis. Ni boats appear to be superior for use with refractory materials such as B_4C and BN.

Quartz tubes subjected to prolonged use at temperatures of 1300 to 1350°C showed little visible detrimental effect. Quartz tubes may, therefore, be substituted for the more expensive Pt or Pt-lined tubes previously believed necessary for use at this temperature.

EDITOR'S NOTE

This paper is omitted from the Proceedings because it is to be published elsewhere.

SPECTROPHOTOMETRIC DETERMINATION OF TECHNETIUM

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ABSTRACT

A method was developed for the spectrophotometric determination of Tc in the microgram range by reacting it with toluene-3,4-dithiol in an aqueous medium that is 2.5 N in acid. The colored complex is extracted into CCl_4, and the absorbancy of the CCl_4 solution is then measured at 450 mμ. The molar extinction coefficient is of the order of 15,000. Because of the interference of many cations, it is necessary to make a preliminary separation of the Tc. The results of a study of the various factors that influence the formation and extraction of the complex are presented.

EDITOR'S NOTE

This paper is omitted from the Proceedings because it is to be submitted for publication in Analytical Chemistry.

COMPLEXOMETRIC DETERMINATION OF FLUORIDE WITH CERIUM(III)

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ABSTRACT

A volumetric method was developed for the determination of fluoride which is applicable to the analysis of samples containing high concentrations of nitrate. CeF_3 is stoichiometrically precipitated at pH 2.1 to 2.3 by the addition of a measured excess of Ce(III). After centrifugation, the unprecipitated Ce is back-titrated with standard EDTA solution to an arsenazo cresol red end point in a medium buffered with pyridine. The color change from purplish-red to yellow-orange is sharp and is unaffected by the presence of large amounts of nitrate, chloride, and perchlorate. Present methods, in which Th, Al, or Fe(III) is utilized as titrant and various chromogenic agents are used as indicators, are insensitive because the color changes are gradual and often difficult to detect. End-point detection is further impaired by high ionic strength and is pH dependent in many of the existing methods. Unfortunately, like these other methods, the proposed procedure is subject to interference from cations which complex fluoride. Metal ions reactive to EDTA also interfere.

Of the several methods reported for the separation of fluoride from cations, pyrolytic separation developed at Oak Ridge National Laboratory[a] was selected because of its relative simplicity, speed, wide applicability, and minimum sample dilution. Quantitative recovery of fluoride was obtained by raising the pyrolysis temperature to 950°C, starting with a furnace at a temperature of 200°C or less. A WO_3 accelerator was used and moist air was passed through the reactor at a flow rate of 2.5 liters/min. When pyrolyzing samples which contained volatile fluoride compounds such as HF, NH_4HF_2, or HBF_4, a controlled release of fluoride was obtained by complexing the fluoride with $Al(NO_3)_3$.

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[a] R. H. Powell and O. Menis, Anal. Chem. 30, 1546 (1958).

The proposed pyrolysis-complexometric procedure has been used to determine fluoride in a variety of samples. Simulated solutions of reactor fuels containing as much as 3 ml of concentrated HNO_3 and 100 mg each of Zr and Al in the sample aliquot have been analyzed successfully. HBF_4, HF, and NH_4HF_2 samples were analyzed with and without preliminary pyrolysis. With large amounts of H_3BO_3, results were slightly low, due to incomplete precipitation. Be, which prevents precipitation of CeF_3, can be removed by pyrolysis. Large amounts of perchlorate and chloride are without effect, but sulfate and phosphate interfere.

The reliability of the method was evaluated by carrying known amounts of fluoride, in the range of 6 to 36 mg, through the Ce precipitation-EDTA titration procedure. The relative standard deviation based on 18 determinations was 1%. In a subsequent study, 25- and 36-mg portions of fluoride were carried through the complete procedure, including pyrolysis. The computed standard deviation for a single determination, based on six replicate determinations at each of the two levels, was 0.5 mg of fluoride. One complete analysis requires an hour.

EDITOR'S NOTE

This paper is omitted from the *Proceedings* because it is to be submitted for publication in *Analytical Chemistry*.

Analysis of Reactor Fuels and Related Materials

DETERMINATION OF U^{235} IN LOW-ENRICHED, NON-IRRADIATED URANIUM DIOXIDE PELLETS BY GAMMA-RAY SPECTROMETRY

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ABSTRACT

A rapid, nondestructive method was developed for determination of the U^{235} content of UO_2 pellets, through the application of gamma ray spectrometry. The 184-kev gamma ray produced by the U^{235} nuclide is utilized for making a direct measurement of the U^{235} content of pellets. A statistical study was made of this method, in which it was demonstrated that, at the 3% U^{235} level, the relative standard deviation is 0.03%.

As a routine procedure for the isotopic assay of nonirradiated U in the concentration range of 1 to 10% U^{235}, gamma-ray spectrometry is the most economical method known.

INTRODUCTION

The power output and heat distribution in a reactor core depend largely upon the U^{235} content of the reactor fuel; consequently, the isotopic assay of uranium has received much attention in the nuclear field. Contractors and suppliers of reactor fuels are held accountable for the fuel entrusted to them by the U. S. Government. In addition, the cost of nuclear fuel material and the critical concentration of the fuel within a reactor core necessitates developing an analytical method for the determination of U^{235} which is both accurate and economical. The method which consumes a minimum amount of analytical time yet provides an accurate assay of U^{235} content would be most desirable.

The more popular methods for the isotopic assay of uranium are summarized in Table I.

TABLE I

CURRENT METHODS FOR ISOTOPIC ASSAY OF URANIUM

Method	Range$^{(1)}$ % U^{235}	Precision$^{(1)}$ Relative %	Advantages	Disadvantages	Instrument Cost$^{(2)}$
Mass (3) Spectrometry	0 - 100	0.02 - 0.05	All ranges with high precision	Available at Westinghouse APD	\$60,000 to 75,000
Emission (4) Spectroscopy	~1 - 10 80 - 100	2 - 3 2 - 4	Procedure now in use in Westinghouse APD	Cost of analysis	10,000
Neutron (5) Activation	0 - 5	1	Microgram quantities detectable	Interference from impurities	25,000
Neutron (6) Absorption	80 - 100	1	Nondestructive	Interference from impurities	Shielding Cost
Fission (7) Counting	0 - 100		Nondestructive	Zero power reactor necessary	Shielding Cost
Alpha (8) Spectrometry	0 - 100	1	All isotopes and ranges covered	Complex standardization	20,000
Gamma-ray (9) Spectrometry	0 - 100	1	Nondestructive	Limited to non-irradiated fuel	2,600

The table shows a variety of methods now in use which meet the specifications of accuracy in the concentration range of 1 - 10% U^{235}. Initial investment and individual analysis cost vary greatly. Currently, emission spectroscopy is used at Westinghouse APD for the assay of slightly enriched pellets of UO_2. The procedure is well established and is accurate to within 2 - 3% of the U^{235} concentration in the range of 1 - 10% U^{235}. However, the assay is time consuming and the sample is destroyed in the course of the analysis.

The gamma-ray spectrometric method appeared to be a highly feasible means of reducing analytical costs. A relatively inexpensive instrument of this type was available in the Technical Service Laboratories. It was anticipated that the time required for an analysis could be reduced significantly over the standard procedure and the same accuracy could still be maintained. In addition, the gamma-ray method is nondestructive. This paper reports a study conducted on the analysis of U^{235} by gamma spectrometry, and presents the statistical evaluation of the collected data.

Gamma-ray spectrometry, as a technique, translates the energy of emitted gamma-rays to an electrical impulse which can be recorded and identified. In the radioactive decay of natural uranium isotopes, gamma-rays as well as alpha particles of various energies are emitted. U^{235} produces photons with energies of 94, 143, 184, 289 and 386-kev. The 94-and 184-kev gamma-rays produce major photopeaks in the gamma spectrum as illustrated in Figure 1. The 184-kev peak is proportional only to the U^{235} content. The 94-kev peak is a summation peak of a gamma-ray from a Th^{234} daughter product and a U^{235} gamma-ray. Consequently, it was eliminated from consideration.

Morrison and Cosgrove(9), as well as Rider(10), describe procedures for determining the U^{235} concentration by scanning the spectrum of a uranium sample with a multi-channel gamma-ray spectrometer and measuring the area under the photopeaks. This value is then compared to one obtained from a standard uranium sample of known enrichment.

EQUIPMENT

In this study a single channel, sliding window, gamma-ray spectrometer was used to measure all activities. The spectrometer consisted of:

1) A lead-shielded, well type, 2-in. sodium iodide crystal (thallium activated).

2) Dumont phototube 6292.

3) Pulse height analyzer, RIDL Model 115, single channel, sliding window.

4) Count rate meter, RIDL Model 39-2.

5) Brown strip chart recorder; electronik one-second response.

6) Scaler, RIDL Model 200K, high voltage supply incorporated.

7) Sample holder, Lucite cylinder.

Figure 2 shows a block diagram of this assembly.

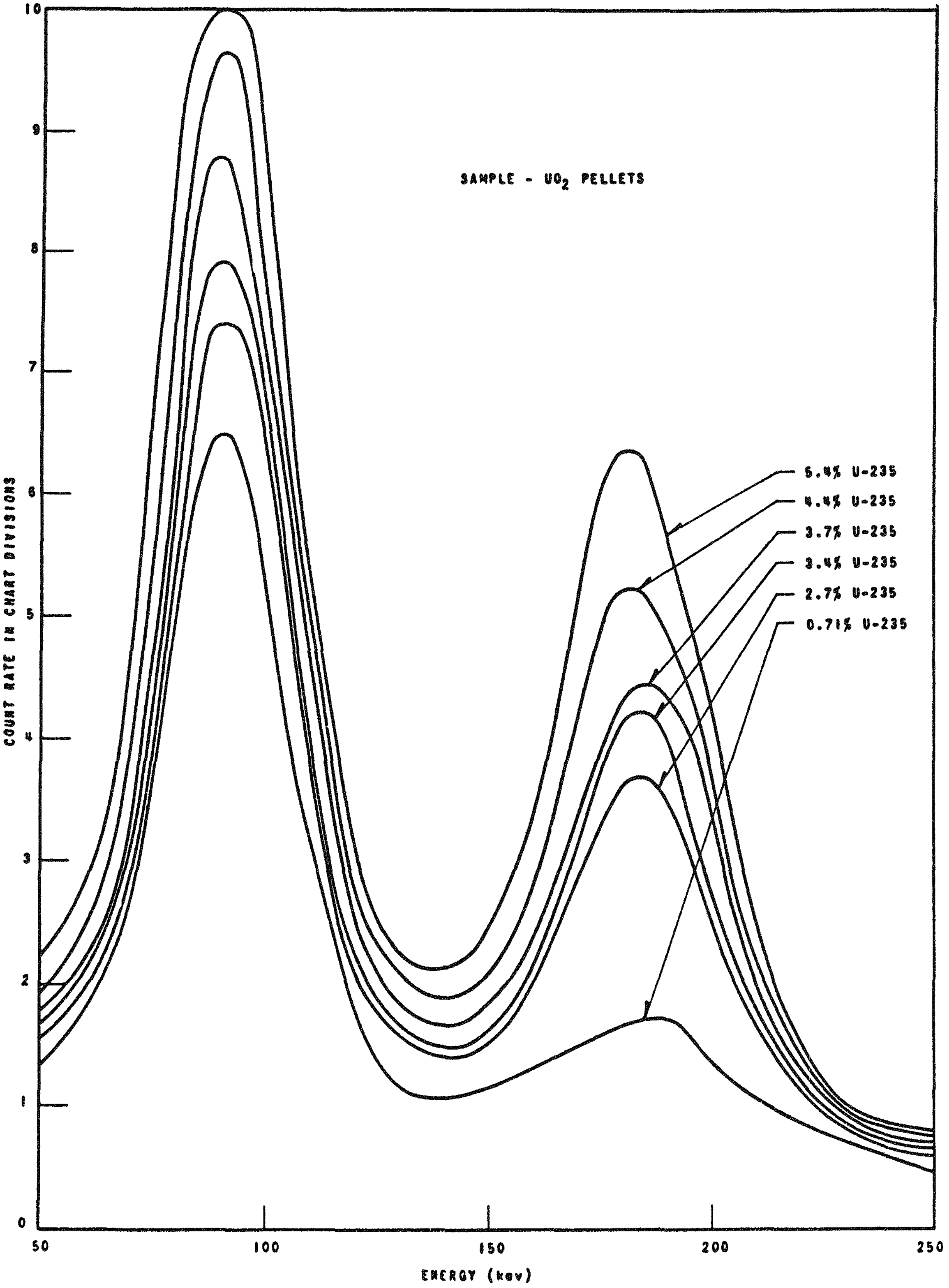

Fig. 1 - Variations of Uranium Gamma-Ray Spectra at Different U-Enrichment in Uranium Dioxide Pellets

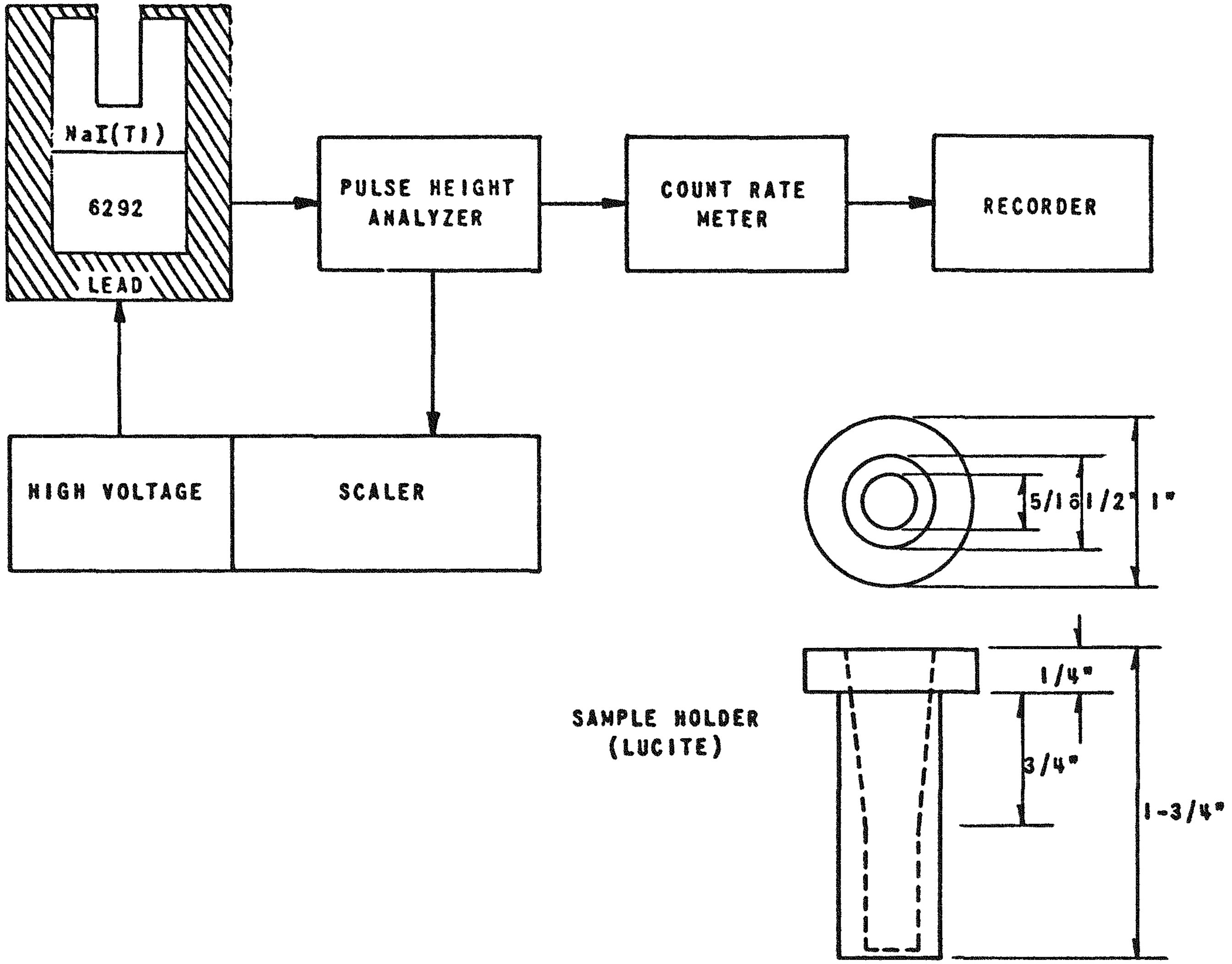

Fig. 2 - Schematic Diagram of Single-Channel, Gamma-Ray Spectrometer

The utilization of this single-channel, sliding-window, gamma-ray spectrometer is a deviation from the standard practice of using a multi-channel spectrometer. Resolution of the U^{235} gamma-rays, however, is practically complete in the single-channel instrument. Preliminary studies were made whereby it was shown that adequate sensitivity for the determination of U^{235} could be attained through integration of the 184-kev photopeak alone. Thus, the less expensive single-channel instrument could provide the same information as the complex multi-channel analyzers.

Integration of the area under the photopeaks of Figure 1 may be calculated by various methods to obtain the U^{235} content of a sample. Peak heights of the 184- and 94-kev photopeaks may be measured and the ratio calculated or the area under the photopeaks may be integrated with a planimeter. In all cases the values obtained are compared to a series of uranium isotopic standards.

A more direct integration of the photopeak area may be accomplished by means of a scaler. Here, the single-channel instrument is set to record the pulses registered in the 155- to 215-kev region; that is, the area under the 184-kev photopeak. This energy interval is isolated by setting the instrument on the photopeak and opening the sliding window to include the complete photopeak area. The output pulses of the spectrometer are then relayed directly to the scaler, which automatically integrates the voltage interval of the 184-kev photopeak. This automatic integration eliminates the human error associated with manual integration.

PROCEDURE

The gamma-ray spectrometer was set by the gain control to give 0-1 Mev full scale. The channel level was set at 185 with a 3-volt window to span the 155- to 215-kev region, and the high voltage was varied to produce a preset count rate with a standard uranium pellet. Sample pellets were identified, weighed on an analytical balance and counted for two minutes. A Lucite sample holder, whose outside diameter matches the crystal well and whose inside diameter is fitted to the pellet diameter, was used to eliminate errors of sample geometry. One hundred pellets were analyzed in this manner by two analysts. The experiment was repeated four times at weekly intervals with each analyst. Ten of the pellets were destroyed by ignition to U_3O_8(11) and submitted for confirmatory analysis by emission spectrography.

STANDARDS

The pellets were fabricated from UO_2 powder converted from UF_6 which had been analyzed for U^{235} by mass spectrometry. The nominal value for the UF_6 was confirmed by emission spectrographic assay of the 10 UO_2 pellets referred to above. Weighed portions of NBS uranium samples of known U^{235} content were used as primary standards. A standard curve is illustrated in Figure 3.

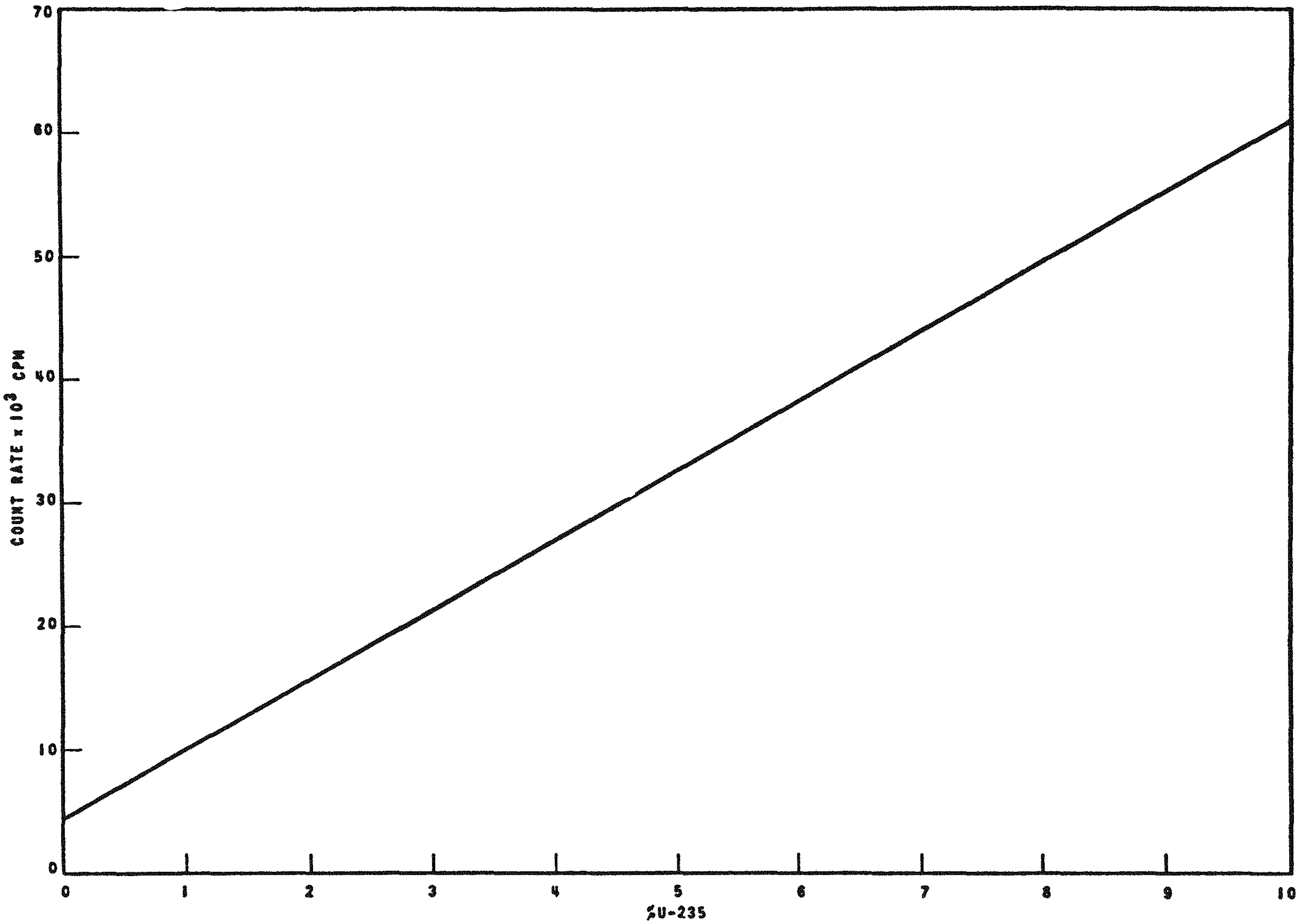

Fig. 3 - Relationship Between Count Rate and Uranium-235 Content of NBS Standards

RESULTS AND DISCUSSION

Since pellet densities are uniform, it was assumed that absorption effects due to density variations are negligible. Variations in pellet weight are due to small changes in dimensions; therefore, the count rate is directly proportional to the weight of the pellet. For each count recorded, a count-per-minute value was calculated, and the background count was subtracted. The corrected count per minute was then divided by the weight of the pellet to give a count per minute per gram of UO_2 (c/m/g) for each sample. The average c/m/g for each run was equal to the mass spectrometric analysis of the original material used to fabricate the pellets. This data is presented in Table II. The average c/m/g varied from run to run and between analysts. This variation results from an inability to duplicate precisely instrumental settings from one analysis to another. In sample analysis, standard pellets of known U^{235} concentration were used to provide a reference count and all samples were compared to the standard.

Decay rates of radioactive materials are not subject to change from any known source; hence nuclear disintegrations are considered random phenomena. Established methods of statistical analysis must, therefore, be applied to all counting data.(12) From the total number of counts collected, and the total time of counting, the precision may be calculated. The statistical estimate of precision, limit of error, is outlined for one sample in the following table.

TABLE III

COUNTING STATISTICS OF A SAMPLE PELLET

	Total Counts	Time Minutes	Rate	Limit of Error		
				Absolute	Relative	
				(3σ)	(2σ)	(3σ)
			c/p/m		Per Cent	
Sample	80,000	2	40,000	400	0.7	0.9
Background	28,000	60	470	7	1.2	1.5
Net	-	-	39,500	400	0.7	0.9

To establish the sources of variability in this analysis, the data of Table II were evaluated by means of an Analysis of Variance technique. In this way, the total variability is separated into two basic factors, designated as (1) known sources of variation and (2) the residual, or random, error of the analysis. The significance of the first type of variation is based on the ratio between that variation and the residual error at some pre-selected probability level. This ratio, designated as the variance- or F-ratio, is compared with values tabulated in standard tables to establish the significance of a particular source of variability.

TABLE II

ANALYTICAL DATA DERIVED FROM UO_2 PRODUCTION PELLETS BY GAMMA-RAY SPECTROMETRY

PERCENT URANIUM-235

Sample Code	Analyst A Run I	Analyst A Run II	Analyst A Run III	Analyst A Run IV	Analyst A Av.	Analyst B Run I	Analyst B Run II	Analyst B Run III	Analyst B Run IV	Analyst B Av.	Sample Av.
A-1	3.407	3.392	3.353	3.373	3.381	3.394	3.393	3.370	3.401	3.390	3.385
A-2	3.413	3.411	3.492	3.392	3.411	3.427	3.419	3.404	3.406	3.414	3.413
A-3	3.403	3.386	3.427	3.377	3.398	3.404	3.383	3.400	3.429	3.404	3.401
A-4	3.397	3.416	3.395	3.395	3.401	3.387	3.403	3.397	3.413	3.400	3.400
A-5	3.387	3.381	3.388	3.345	3.375	3.385	3.382	3.376	3.390	3.383	3.379
A-6	3.410	3.390	3.396	3.382	3.394	3.385	3.414	3.397	3.422	3.404	3.400
A-8	3.381	3.396	3.394	3.340	3.378	3.392	3.370	3.364	3.404	3.382	3.380
A-9	3.419	3.432	3.405	3.353	3.402	3.361	3.405	3.372	3.396	3.384	3.393
Group Av.	3.402	3.400	3.398	3.370	3.393	3.392	3.396	3.385	3.408	3.395	3.394
B-1	3.410	3.410	3.402	3.370	3.398	3.374	3.394	3.378	3.407	3.388	3.393
B-2	3.417	3.393	3.411	3.358	3.395	3.379	3.385	3.382	3.393	3.385	3.390
B-4	3.428	3.422	3.419	3.399	3.417	3.373	3.422	3.393	3.405	3.398	3.408
B-5	3.396	3.406	3.396	3.369	3.392	3.366	3.388	3.382	3.385	3.380	3.386
B-6	3.417	3.403	3.399	3.370	3.397	3.385	3.415	3.406	3.430	3.409	3.403
B-7	3.428	3.388	3.380	3.373	3.392	3.381	3.403	3.402	3.428	3.404	3.398
B-9	3.412	3.401	3.411	3.407	3.408	3.409	3.431	3.388	3.427	3.414	3.411
B-10	3.403	3.403	3.398	3.386	3.398	3.376	3.403	3.403	3.397	3.395	3.396
B-11	3.400	3.386	3.390,	3.381	3.389	3.371	3.401	3.392	3.395	3.390	3.390
Group Av.	3.412	3.401	3.401	3.379	3.398	3.379	3.405	3.392	3.407	3.392	3.397
C-1	3.404	3.375	3.377	3.400	3.389	3.380	3.422	3.399	3.383	3.396	3.392
C-5	3.400	3.397	3.405	3.410	3.403	3.361	3.389	3.396	3.390	3.384	3.394
C-7	3.413	3.369	3.426	3.420	3.407	3.383	3.429	3.401	3.405	3.404	3.406
C-8	3.399	3.392	3.412	3.406	3.402	3.362	3.388	3.384	3.366	3.375	3.389
C-9	3.400	3.396	3.415	3.410	3.405	3.365	3.396	3.395	3.400	3.389	3.397
C-10	3.395	3.371	3.427	3.395	3.397	3.366	3.377	3.396	3.392	3.383	3.390
C-11	3.420	3.422	3.440	3.430	3.428	3.382	3.416	3.420	3.420	3.410	3.419
Group Av.	3.404	3.389	3.414	3.410	3.404	3.371	3.402	3.399	3.394	3.392	3.398

TABLE II (cont'd.)

PERCENT URANIUM-235

	Analyst A					Analyst B					
Sample Code	Run I	Run II	Run III	Run IV	Av.	Run I	Run II	Run III	Run IV	Av.	Sample Av.
D-1	3.424	3.379	3.417	3.387	3.402	3.369	3.392	3.433	3.424	3.404	3.403
D-7	3.427	3.398	3.415	3.414	3.414	3.392	3.414	3.403	3.415	3.406	3.410
D-8	3.412	3.396	3.381	3.392	3.395	3.377	3.408	3.385	3.416	3.396	3.396
D-9	3.408	3.389	3.377	3.409	3.396	3.333	3.410	3.399	3.399	3.385	3.390
D-10	3.417	3.407	3.385	3.375	3.396	3.376	3.429	3.400	3.419	3.406	3.401
D-11	3.397	3.381	3.397	3.365	3.385	3.361	3.416	3.395	3.389	3.390	3.388
Group Av.	3.414	3.392	3.395	3.390	3.398	3.368	3.412	3.402	3.410	3.398	3.398
E-1	3.427	3.405	3.420	3.395	3.412	3.355	3.432	3.445	3.417	3.412	3.412
E-2	3.419	3.406	3.400	3.406	3.408	3.362	3.426	3.407	3.426	3.405	3.406
E-4	3.415	3.419	3.422	3.393	3.412	3.345	3.416	3.400	3.418	3.395	3.404
C-5	3.418	3.422	3.428	3.433	3.425	3.386	3.387	3.388	3.402	3.391	3.408
E-6	3.395	3.416	3.399	3.410	3.405	3.415	3.434	3.415	3.423	3.422	3.413
E-7	3.391	3.405	3.393	3.398	3.397	3.409	3.404	3.397	3.411	3.405	3.401
E-8	3.392	3.423	3.402	3.395	3.403	3.397	3.396	3.426	3.411	3.408	3.405
E-10	3.404	3.427	3.429	3.426	3.422	3.444	3.444	3.394	3.423	3.426	3.424
E-11	3.381	3.430	3.415	3.400	3.406	3.381	3.391	3.365	3.381	3.380	3.393
Group Av.	3.405	3.417	3.412	3.406	3.410	3.388	3.414	3.404	3.412	3.405	3.407
F-1	3.422	3.422	3.418	3.422	3.421	3.431	3.430	3.419	3.428	3.427	3.424
F-2	3.381	3.402	3.399	3.408	3.398	3.372	3.389	3.376	3.415	3.388	3.393
F-3	3.405	3.416	3.433	3.398	3.413	3.417	3.393	3.388	3.402	3.400	3.406
F-4	3.390	3.404	3.398	3.429	3.405	3.391	3.369	3.380	3.404	3.386	3.396
F-5	3.414	3.406	3.412	3.426	3.414	3.414	3.400	3.378	3.408	3.400	3.407
F-6	3.400	3.398	3.416	3.391	3.401	3.393	3.990	3.380	3.393	3.391	3.396
F-7	3.399	3.401	3.425	3.392	3.404	3.402	3.388	3.388	3.416	3.398	3.401
F-8	3.395	3.419	3.397	3.393	3.401	3.466	3.395	3.372	3.397	3.408	3.404
F-9	3.393	3.397	3.407	3.427	3.406	3.495	3.392	3.398	3.387	3.418	3.412
F-10	3.388	3.398	3.405	3.427	3.404	3.461	3.362	3.388	3.373	3.396	3.400
Group Av.	3.399	3.406	3.411	3.411	3.407	3.424	3.392	3.387	3.402	3.401	3.404

Sample Code	Analyst A					Analyst B					Sample Av.
	Run I	Run II	Run III	Run IV	Av.	Run I	Run II	Run III	Run IV	Av.	
G-1	3.411	3.406	3.408	3.412	3.409	3.468	3.389	3.405	3.417	3.420	3.414
G-2	3.413	3.436	3.426	3.441	3.429	3.516	3.410	3.433	3.440	3.450	3.439
G-4	3.402	3.403	3.403	3.436	3.411	3.519	3.403	3.374	3.406	3.426	3.418
G-5	3.404	3.428	3.401	3.443	3.419	3.470	3.429	3.389	3.415	3.426	3.422
G-6	3.389	3.405	3.400	3.415	3.402	3.485	3.414	3.367	3.426	3.423	3.413
G-7	3.383	3.416	3.412	3.409	3.405	3.478	3.403	3.391	3.377	3.412	3.409
G-8	3.404	3.411	3.430	3.429	3.418	3.527	3.401	3.464	3.409	3.450	3.434
G-10	3.403	3.398	3.406	3.426	3.408	3.464	3.400	3.384	3.461	3.427	3.418
G-11	3.408	3.400	3.422	3.442	3.418	3.414	3.403	3.401	3.378	3.399	3.408
Group Av.	3.402	3.411	3.412	3.428	3.413	3.482	3.406	3.401	3.414	3.426	3.419
H-1	3.386	3.395	3.425	3.434	3.410	3.466	3.413	3.376	3.399	3.414	3.412
H-2	3.393	3.400	3.406	3.422	3.405	3.467	3.420	3.417	3.382	3.422	3.413
H-3	3.426	3.400	3.421	3.450	3.424	3.466	3.427	3.406	3.460	3.440	3.432
H-4	3.363	3.426	3.410	3.412	3.403	3.442	3.409	3.392	3.377	3.405	3.404
H-5	3.420	3.414	3.434	3.415	3.421	3.453	3.412	3.399	3.395	3.415	3.418
H-6	3.440	3.410	3.454	3.460	3.441	3.430	3.406	3.421	3.457	3.428	3.435
H-7	3.424	3.418	3.430	3.420	3.423	3.434	3.427	3.396	3.367	3.406	3.414
H-9	3.389	3.398	3.422	3.448	3.414	3.417	3.393	3.390	3.330	3.382	3.398
H-10	3.413	3.396	3.422	3.445	3.419	3.423	3.439	3.417	3.440	3.430	3.424
Group Av.	3.406	3.406	3.425	3.434	3.418	3.444	3.416	3.402	3.401	3.416	3.417
I-1	3.391	3.436	3.385	3.412	3.406	3.415	3.413	3.430	3.387	3.411	3.409
I-2	3.417	3.454	3.400	3.450	3.430	3.420	3.427	3.444	3.446	3.434	3.432
I-4	3.392	3.428	3.386	3.425	3.408	3.400	3.410	3.415	3.325	3.388	3.398
I-5	3.446	3.480	3.400	3.462	3.447	3.430	3.447	3.458	3.473	3.452	3.450
I-6	3.421	3.450	3.391	3.450	3.428	3.420	3.428	3.405	3.404	3.414	3.421
I-7	3.418	3.425	3.402	3.412	3.414	3.390	3.431	3.415	3.387	3.406	3.410
I-8	3.423	3.423	3.392	3.433	3.418	3.405	3.410	3.386	3.414	3.404	3.411
I-9	3.401	3.454	3.383	3.444	3.420	3.387	3.415	3.394	3.382	3.394	3.408
I-10	3.406	3.409	3.400	3.411	3.406	3.392	3.403	3.453	3.373	3.405	3.406
I-11	3.413	3.410	3.425	3.463	3.428	3.414	3.403	3.409	3.379	3.401	3.414
Group Av.	3.413	3.437	3.396	3.436	3.420	3.407	3.419	3.421	3.397	3.411	3.416
Run Av.	3.406	3.406	3.408	3.409	3.4076	3.409	3.407	3.399	3.405	3.4051	3.4064

The Analysis of Variance may be summarized in tabular form with the following headings:

Source of Variation	Degree of Freedom	Sum of Squares	Mean Square	F-Ratio

As its name implies, the sources of variation to be evaluated are listed in the first column. The "Degrees of Freedom" are the number of independent comparisons available for a given source of variation. Thus, when only two levels of an experimental factor are used in an experiment, only one comparison between these levels can be made. When three levels of a factor are used, two degrees of freedom are available. If this were a quantitative factor such as time or temperature, one comparison might be for a linear trend and the other for a quadratic trend. The Analysis of Variance technique partitions the variability in a set of data into the various assignable sources. The "Sum of Squares" is that portion of the variability which is associated with the particular source of variation. The unexplained variation is listed as "Remainder", "Residual", or "Error Sum of Squares."

In order to get the variability on a common per-unit basis, the Sum of Squares is divided by the corresponding Degrees of Freedom to obtain the Mean Square. The ratio of a given Mean Square to its Error Mean Square is called the F-ratio. For certain risks of committing a particular decision error, F-ratios are tabulated for various combinations of Degrees of Freedom. Thus, if the ratio is sufficiently large to conclude that a given effect is statistically significant (at say, the 1-per cent level) one is really saying the following: If the effect were truly not significant, the odds of getting differences as large as those obtained in the data by chance alone are less than 1 to 100. Since these odds are sufficiently small, it can be concluded that the effect is real and the odds of coming to the wrong conclusion are only 1 in 100.

With the previous discussion serving as background for the statistical techniques used, the results of the data are described below.

The simplest partition of the total variation in the data would be into two sources: (1) Among Samples; and (2) Among Runs Within Samples. The corresponding Analysis of Variance tables appear in Table IV-A and IV-B, corresponding to Analysts A and B, respectively. The S in the F-Ratio column denotes that the effect was statistically significant at the 99% level.

The statistical significance of the Among Sample source of variation indicates that the differences among pellets were greater than the average difference among runs on a given pellet. However, this is not surprising. It merely states that although the pellets are said to be homogeneous, the average variation among readings on the same pellet is sufficiently small so that one can discriminate between certain pellets in this range. Note, however, the Within Pellet Mean Square for Analyst B was greater than twice that of Analyst A. For this reason, the data for each analyst will be evaluated separately.

TABLE IV-A

ANALYSIS OF VARIANCE

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio*
Among Samples	76	.054155	.000713	S
Among Runs Within Samples	231	.072376	.000313	
Total	307	.126531	$\frac{713 \times 10^{-6}}{313 \times 10^{-6}} = 2.2 = F$	

TABLE IV-B

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio
Among Samples	76	.091335	.001202	S
Among Runs Within Samples	231	.158994	.000688	
Total	307	.250329	$\frac{1202 \times 10^{-6}}{688 \times 10^{-6}} = 1.74 = F$	

TABLE V-A

ANALYSIS OF VARIANCE

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio
Among Runs	3	.000295	.000098	
Among Samples	76	.054155	.000713	S
Among Groups	8	.031330	.003916	S
Among Samples in Groups	68	.022825	.000336	
Remainder	228	.072081	.000316	
Total	307	.126531		

TABLE V-B

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio
Among Runs	3	.004080	.001360	
Among Samples	76	.091335	.001202	S
Among Groups	8	.034108	.004264	S
Among Samples Within Groups	68	.057227	.000842	
Remainder	228	.154914	.000679	
Total	307	.250329		

*S - Statistically significant at the 99% confidence level.

A more detailed analysis of the variation is presented in Tables V-A and V-B.

The initial partition in Tables V-A and V-B is: (1) Among Runs: (2) Among Samples; and (3) Remainder. One may observe that the Among Samples source of variation in Table V is identical to that in Table IV, as is their total. However, the 231 degrees of freedom in Table IV labeled "Among Runs Within Samples" has been broken down into "Among Runs" and "Remainder" in order to evaluate the overall average differences among runs. If there were a procedural bias associated with runs, it would be reflected by a large Among Runs Mean Square. For example, if this were a weighing experiment and the balances were not zeroed in at each run, this run-to-run bias would be so detected. However, the known procedural error was eliminated by a reference standard. For both Analysts A and B, any additional procedural variation was not statistically significant.

The Among Samples source of variation was divided into two parts: (1) Among Groups; and (2) Among Samples Within Groups. Since the allocation of the pellets into groups was completely at random and the group designation was made merely for convenience in performing the test program, there is no reason to assume that the variation among groups should be any greater than the variation among pellets within the groups. Table V, however, illustrates that a disproportionately high percent of the Among Samples variation is explained by the eight degrees of freedom for comparing groups. However, since the group designation also corresponded to the order in which the tests were performed, the Among Groups variation could reflect instrument drift and other factors associated with the testing procedure.

The Among Groups effect refers to the comparison of the nine groups of pellets, averaged over the four runs. The inconsistency of the magnitudes of the group-to-group differences from run-to-run, which might be called Group by Run Interaction, is contained in the Remainder term of Table V. Although not listed, the Group by Run Interaction is the major portion of the Remainder term. Thus, if the factor or factors causing this phenomenon could be isolated and better controlled, a significant improvement in precision could be attained.

If one were to ascribe the Among Groups variation to "instrument drift," then it would seem worthwhile to sub-divide these eight degrees of freedom into individual trends. Table VI-A and VI-B illustrate that the overall linear trend is the overwhelming one for both analysts. Table II illustrates that the readings tended to increase from the beginning of the run to the end. In the Sample average column, the group average consistently increased. Since a small linear instrument trend can only be detected by a statistical analysis, no compensations were made for it.

The Mean Squares in the Analysis of Variance tables are linear functions of estimates of certain components of variance. The components can be combined to give a measure of random variation appropriate to various experimental situations. For this application, the components referring to the variation among pellets are excluded from the estimate of measurement error but the group-to-group components are assumed to be associated with the procedure rather than the pellets and, hence, are included. Therefore, the overall

TABLE VI-A

ANALYSIS OF VARIANCE

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio*
Among Groups	8	.031330	.003916	
Linear Trend	1	.021674	.021674	S
Residual	7	.009656	.001379	

TABLE VI-B

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-Ratio
Among Groups	8	.034108	.004264	
Linear Trend	1	.021674	.021674	S
Residual	7	.012434	.001776	

*S - Statistically significant at the 99% confidence level.

standard deviation for Analyst A turns out to be 0.020% U^{235} and 0.028% U^{235} for Analyst B. In terms of relative percent, the figures become 0.59% for Analyst A and 0.82% for Analyst B. These deviations compare quite well with the random fluctuations of radioactive disintegration as shown in Table III. Hence, when the error associated with instrumental drift is compensated for, the remaining error is that of random fluctuation.

RECOMMENDED PROCEDURE

The statistical study illustrates that an instrument drift with time is the major assognable source of error. This may be readily compensated for by counting a standard pellet every 30 minutes. The recommended procedure for sample analysis may be outlined as follows:

1. A pellet is identified and weighed on an analytical balance.

2. Two standard pellets are obtained of same size and chemical composition which bracket the sample in $uranium^{235}$ content.

3. Instrument settings are:
   a. Pulse Height Analyzer
      Width range 0-10 V
      Gain 0-1 Mev
      Coincidence and anti-coincidence circuits - off
      Channel level - 185 V
      Channel width - 3 V

   b. Scalers
      Count - Preset time
      Gain - GM
      Scale - 1000
      Discriminator - preset

   c. High Voltage Supply
      The high voltage is varied until a maximum count is obtained with the high standard in the well.

4. A pellet is placed in the sample holder and set into the well crystal.

5. Standard pellets and samples are counted for 2 minutes each and the scaler reading is recorded. One standard pellet is counted every 30 minutes.

6. A one hour background count is obtained with sample holder in well.

ACCURACY

For routine sample analysis, random variations of standards as well as those of the sample must be considered. This is in accordance with the statistical data illustrated in Table VII.

TABLE VII

VARIATIONS IN PRECISION WITH COUNTING TIME

2 σ levels

Method		Precision			Time Required	
Samples	Standard	Net Count c/m	% U^{235} 3.40 Level	% U^{235} Relative %	5 Samples Analysis Hrs.	50 Samples Analysis Hrs.
2-2 min. counts per sample	average of 2 2 min. counts (1 standard) (10 samples)	40,000	± 0.045	1.4	3.5	8
1-2 min. count per sample	average of 2 2 min. counts (1 standard) (10 samples)	40,000	± 0.040	1.2	3.0	5
1-4 min. count per sample	average of 2 2 min. counts (1 standard) (10 samples)	40,000	± 0.030	0.9	3.5	8

It is obvious that longer counting times are statistically better than duplicate countings. When the isotopic level falls significantly below 3.4% U^{235}, the counting time or the sample weight must be increased to maintain the same accuracy. In determining isotopic enrichments greater than 3.4%, the accuracy will improve because the increased concentration of U^{235} will produce higher count rates.

APPLICATIONS

The determination of U^{235} by gamma-ray spectrometry may be extended to other media. Uranium oxide powders or uranium solutions may be assayed for U^{235} content provided that an independent total uranium determination is made. U^{235} may be determined in such mixtures as uranium carbide or uranium-aluminum alloys provided synthetic standards are made to duplicate the sample mixture.

When the isotopic concentration is known, the total uranium content may be determined by gamma-ray spectrometry. If sample size is sufficient, the analysis is rapid and accurate.

SUMMARY

With a single channel, sliding window, gamma-ray spectrometer, a nondestructive procedure was developed successfully to determine the U^{235} content of UO_2 pellets. A program based on repetitive counting of a large sample population by two analysts over a month's time was conducted. Statistical analysis showed that the isotopic content of UO_2 pellets may be determined at approximately 3.4% U^{235} with an accuracy of within ± 1.5% relative at the 2 σ level. Sample pellets in the range of 1-10% U^{235} may be assayed with an equivalent accuracy by varying the counting times.

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ANALYSIS OF URANIUM OXIDE FUEL MATERIALS*

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ABSTRACT

Chemical methods used at Argonne are described for the analysis of uranium oxide containing mixtures that have been used as fuel elements or that have potential applications in reactor technology. The determination of uranium in the ThO_2-UO_2 ceramic fuel that was used for the Borax-IV loading was accomplished by dissolving the ceramic in HNO_3 with a trace of F^-, reducing the uranium, and titrating it with a standard Ce(IV) solution. The EBWR "spike" pellets of ZrO_2-CaO-UO_2 were dissolved in HCl, using the sealed tube technique. Uranium was determined volumetrically; calcium was precipitated with oxalate and determined gravimetrically or volumetrically; zirconium was determined by a gravimetric method. The graphite-urania fuel matrix for TREAT was analyzed by ashing it at 850°C, dissolving the residue, and determining the uranium volumetrically or colorimetrically. The cermet of Al-U_3O_8, used as fuel in the Argonaut reactor, was analyzed for uranium by a volumetric method. A density measurement was utilized by the metallurgists for verifying the composition of each plate prior to loading the reactor.

A ceramic composed of La_2O_3-UO_2, which is now in the research phase as a possible fuel, was analyzed for uranium by a volumetric method. Lanthanum was determined, after an ion-exchange separation, by precipitation with oxalate. Uranium sulfide was analyzed for S^{--} by an evolution-volumetric method, total S by an oxidation-gravimetric procedure, and uranium by a gravimetric method.

Other uranium mixtures of interest include UO_2-polystyrene, UC, UO_2-MgO, UO_2-ZrO_2, UO_2-Al_2O_3, UO_2-Nd_2O_3, UO_2-CaO_3 and UO_2-glass.

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*Based on work performed under contract with the U. S. Atomic Energy Commission.

The interest in uranium oxide-base fuels at Argonne National Laboratory has increased significantly in recent years. A cermet of Al-U_3O_8 is used as the fuel in the Argonne Naught Power Reactor. The fuel assembly, probably one of the most economical to fabricate, is composed of plates of the cermet, clad with aluminum which were produced by a hot extrusion technique. There are many inherent advantages of non-metallic fuels not only for the high-temperature, gas-cooled reactor but also for the water-cooled reactor. The ceramic type element composed of mixed oxides was used in the Boiling Water Experiment (BORAX IV) and the Experimental Boiling Water Reactor (EBWR) "spike." The oxide fuels are not nearly as subject to corrosion by water as metallic elements. Therefore, the consequences of a failure in the protective cladding within the reactor are minimized. The ceramics are also much more stable toward radiation and do not become distorted under intense radiation at high operating temperatures. Although the oxide fuels have rather poor heat transfer characteristics compared to metallic fuels, reactor stability has not been adversely affected. Interest in materials of higher thermal conductivity has been stimulated. At the present time uranium carbide and uranium sulfide are under investigation. A material of recent interest is a solution of uranium oxide in a glass matrix.

The Analytical Group at Argonne, in support of the research programs involved with the use of uranium oxide-base fuels, has analyzed a wide variety of ceramic, cermet, and uranium oxide matrix materials. The analytical methods described herein were used during phase equilibrium studies and investigations of materials over a wide range of composition.

SAMPLE PREPARATION

All ceramic fuel pellets were prepared for analysis by crushing in a diamond mortar.

ANALYSIS OF ThO_2-UO_2, A BORAX IV FUEL (6.35% UO_2; 93% Enriched)

Uranium

A sample of the pulverized ThO_2-UO_2 ceramic containing 100 to 125 mg of uranium is dissolved by heating it with 6 N HNO_3 containing a trace of fluoride (0.01 M to 0.03 M). After the sample is completely dissolved, 10 ml of $HClO_4$ is added and the solution is taken to fumes. The beaker is cooled, the walls washed down with water and the fuming repeated to ensure complete removal of nitrate. After cooling, the perchloric acid solution of the sample is diluted to 50 ml with 3 N HCl and passed through a lead reductor. The column is washed with 150 ml of 0.8 N HCl. Twenty-five ml of 12 N H_2SO_4 and 50λ of ferroin are added to the combined eluates. An excess of standard 0.05 N ceric sulfate is added from a weight buret and the excess is then back titrated with standard 0.025 N ferrous sulfate from a weight buret.

Calculation: $\% U = \frac{(A-BR-b)C}{W} \times 100$

A = Weight of ceric sulfate solution used

B = Weight of ferrous sulfate solution used

R = Weight of ceric sulfate solution equivalent to one gram of ferrous sulfate solution

b = Weight of ceric sulfate solution required for the blank

C = Uranium, in grams, equivalent to one gram of ceric sulfate solution

W = Weight of sample in grams

The relative standard deviation of a single measurement is 0.08%.(1)

If a significant amount of iron is present as determined by colorimetric analysis, using 1-10, phenanthroline,(2) the uranium results must be corrected by multiplying the per cent of iron by the factor 2.13 and subtracting this value from the percent uranium.

ANALYSIS OF ZrO_2-CaO-UO_2, AN EBWR SPIKE (8.93% UO_2; 93% Enriched)

A 1- to 2-gram sample of the pulverized ZrO_2-CaO-UO_2 ceramic is transferred to a well-annealed Pyrex glass tube for dissolution by the sealed-tube technique.(3) The tubes are 15 cm long, 15 mm bore and 2.5 mm wall thickness, with a stem 8 cm long, 4 mm bore and 2 mm wall thickness. Ten to twelve ml of concentrated HCl is added and the open end of the stem is heated with an oxygen-gas flame to produce a gas-tight seal. The sample tube, encased in a gas-tight steel cylinder containing CO_2 to provide a compensating gas pressure, is heated overnight at 300°C. The steel cylinder is then removed from the furnace and allowed to cool to room temperature before opening. The Pyrex tube is chilled in a freezing mixture and opened by making a scratch around the tube just below the stem and applying the molten end of a glass rod to the scratch. The contents of the tube are transferred to a 50-ml volumetric flask and diluted to volume. When a 2-gram sample is dissolved in the sealed tube, a precipitate will often be present after the reaction has been completed. However, the precipitate is readily soluble in water. This ceramic can also be dissolved by treating 1-gram samples with 25 ml of a 1:4 HF-HNO_3 mixture in a platinum beaker and evaporating to near dryness on a steam bath. The sample is treated with an additional 25 ml of the HF-HNO_3 mixture and evaporated to dryness after which 15 ml of concentrated $HClO_4$ is added and the solution is evaporated to fumes on a hot plate. The cover and walls of the beaker are washed with water and the solution is again fumed to ensure removal of the HF. Fifty ml of water is added and the solution is heated to boiling. If any insoluble material remains, it is filtered off, ignited, treated with HF, fumed with $HClO_4$ and added to the filtrate.

Uranium

Uranium is determined in an aliquot of the solution of the sample by the volumetric method.

Calcium

Calcium is determined in an aliquot of the sample solution by precipitation of calcium oxalate.(4) The analysis may be completed either by igniting the calcium oxalate and weighing the calcium oxide or by titrating the calcium oxalate with permanganate.

Zirconium

Zirconium is determined in an aliquot of the sample solution by precipitating the zirconium and uranium with NH_4OH to separate from calcium. The precipitate is dissolved in 10% H_2SO_4 and the zirconium is precipitated with cupferron.(5) The precipitate is filtered off, washed, dried, and finally ignited in platinum to ZrO_2. Zirconium can also be determined in an aliquot of the sample solution by precipitation with p-bromomandelic acid and ignition to ZrO_2.(6)

ANALYSIS OF La_2O_3-UO_2 (25 - 80% Uranium)

Lanthanum

A pulverized sample of La_2O_3-UO_2 ceramic selected to contain about 100 mg of lanthanum is dissolved by heating it with 5 to 10 ml of aqua-regia. After the sample is completely dissolved, 2 ml of HCl is added and the solution is evaporated to dryness on a steam bath. The residue is dissolved with 20 ml of 9 N HCl. An ion-exchange column 16 mm ID and 11 cm in length is filled with 20 cc of Dowex 1-X10, 200 - 400 mesh, resin in the chloride form and equilibrated with 9 N HCl by passing 50 ml of the HCl solution through the column. The sample solution is passed through the column at the rate of 2 to 3 ml per minute. The column is washed with 75 ml of 9 N HCl in 10 to 15 ml portions. The eluate containing the lanthanum is evaporated to dryness on a steam bath. The residue is dissolved with 10 ml of water after which the solution is heated to near boiling and 50 ml of hot 1 N oxalic acid is added slowly with stirring. The mixture is heated to boiling for a few minutes and allowed to stand for at least 2 hours, or preferably over night, at room temperature. The uranium is eluted from the resin by passing 100 ml of 1 N HCl through the column.

Gravimetric Finish - Without unduly disturbing the precipitate of lanthanum oxalate, the supernatant liquid is filtered through a Whatman No. 42 filter paper containing a mat of filter pulp prepared by filtering a water slurry of filter pulp through the paper. After the bulk of the supernatant liquid has been filtered, the precipitate is slurried with a small amount of filter pulp and transferred to the filter by washing with 20 ml of 1 N oxalic acid. The filtrate must be absolutely clear and should be closely observed for the presence of any lanthanum oxalate that may have passed through the filter. The paper plus precipitate is dried, charred and finally ignited to La_2O_3 in platinum at 800° to 850°C.(7)

Volumetric Finish - The precipitate of lanthanum oxalate is filtered onto a fritted-glass crucible of fine porosity and washed very thoroughly with 300 ml of water at room temperature.(7) Methyl orange should be added to the last portions of the filtrate to determine whether all absorbed oxalic acid has been removed. The color produced should match that formed by the addition of methyl orange to the wash water. The lanthanum oxalate is dissolved on the filter with hot, 5:95 H_2SO_4. The precipitate is broken up and stirred while successive portions of the acid solution, totaling 100 ml, is drawn through the filter. The solution is cooled to 30°C and the oxalate is then titrated with standard 0.05 N $KMnO_4$. Approximately 90% of the titrant required is added after which the solution is heated to 60°C and the titration is completed to a faint pink color that persists for 30 seconds.

Uranium

A sample selected to contain 80 to 100 mg of uranium is dissolved with 10 ml of aqua-regia or 5 ml of $HClO_4$. If aqua-regia is used, 5 ml of H_2SO_4 is added and the solution is taken to vigorous fuming twice in order to remove the nitrate. The $HClO_4$ or H_2SO_4 solution is diluted with 50 ml of 3 N HCl and the uranium is then determined volumetrically.

ANALYSIS OF GRAPHITE-UO_2, A TREAT FUEL (0.238% U; 93% Enriched)

The fuel in the TREAT Reactor (Transient Reactor Test) is a dispersion of uranium oxide in graphite. This reactor was designed to produce short intense thermal neutron bursts for the testing of fast-reactor fuels. The fuel matrix is analyzed for ash, impurities, and uranium content.

Ashing

A sample is weighed in a platinum dish and placed in a muffle furnace. The temperature of the furnace is raised to 850°C and maintained at this temperature until ignition is complete. Ashing may require from several hours to overnight, and can be accelerated by introducing a slow flow of air or oxygen through the furnace. If a determination of total ash is required, the platinum dish, which had been previously tared, is cooled and weighed to constant weight.

Metal impurities in the ash are determined spectrographically by the carrier-distillation technique.(8) The most common impurity affecting the volumetric uranium determination is iron. A long series of graphite mixtures for the TREAT Reactor varied in iron content between 0.02 and 0.03% as determined colorimetrically and spectrographically.

Uranium

Uranium is determined by dissolving a weighed amount of the ash with nitric acid. Any residue is separated and fused with pyrosulfate. The melt is dissolved and combined with the nitric acid solution. Five ml of H_2SO_4 are added and the solution is evaporated to strong fumes. The beaker is cooled, the walls washed down with water and the solution is fumed again to insure complete removal of nitrate. The uranium is determined volumetrically. When the sample size is small it may be advantageous to determine the uranium colorimetrically. The thiocyanate method, in which iron does not interfere, has been used successfully.(9)

ANALYSIS OF UO_2-POLYSTRENE

Dispersions of uranium oxide in polystyrene may be analyzed as described for the TREAT fuel except for the ashing procedure. The polystyrene mixture is held at 200° to 300°C, until the volatile material has been removed. The temperature is then increased to 850°C. The ignition at 850°C is generally complete in 30 minutes.

ANALYSIS OF Al-U_3O_8, AN ARGONAUT FUEL (39% U_3O_8; 20% Enriched)

Uranium

Volumetric Method - Sample pieces of Argonaut fuel plates consisting of the cermet, Al-U_3O_8, clad with aluminum are dissolved by treating them with HCl until the reaction is substantially complete and then adding HNO_3 to dissolve the uranium oxide. Sulfuric acid is added to the solution and it is then evaporated to fumes on a hot plate. The cover and walls of the beaker are washed down and the fuming repeated to ensure removal of nitrate after which the uranium is determined by the volumetric method.

Density Method - The plate and cladding were formed at the same time by a hot extrusion method and the thickness of the cladding varied considerably over the area of the plate. Therefore, even though the core was quite uniform in composition, chemical analysis of samples taken from different parts of the plate varied widely and could not be correlated with the uranium content of the whole plate. The Metallurgy Division, however, developed a density method for calculating the uranium content of each plate based on the theoretical density of aluminum and U_3O_8 and the measured density of the plate. The density of a plate was simply calculated from its weight and volume. The volume was obtained from the increase in weight of a container of water when the plate was suspended completely immersed in the water. The validity of the uranium values obtained by the density method was verified by measuring the density of specimens punched from the fuel plates and then dissolving the entire specimen and determining the uranium by chemical analysis.

ANALYSIS OF URANIUM SULFIDE

Sulfide Sulfur

Sulfide sulfur is determined by measuring the amount of hydrogen sulfide evolved when the sample is treated with 3.6 N H_2SO_4.(10) A sample of uranium sulfide weighing between 50 and 100 mg and contained in a small porcelain cup is placed in the round bottom flask, I of Figure 1. The end of the delivery tube is immersed in the solution in flask II which was prepared by adding 10 ml of 0.1 N standard $AgNO_3$, 30 ml of 6 N NH_4OH, and 50 ml of water. Air is slowly bubbled through the system to provide stirring

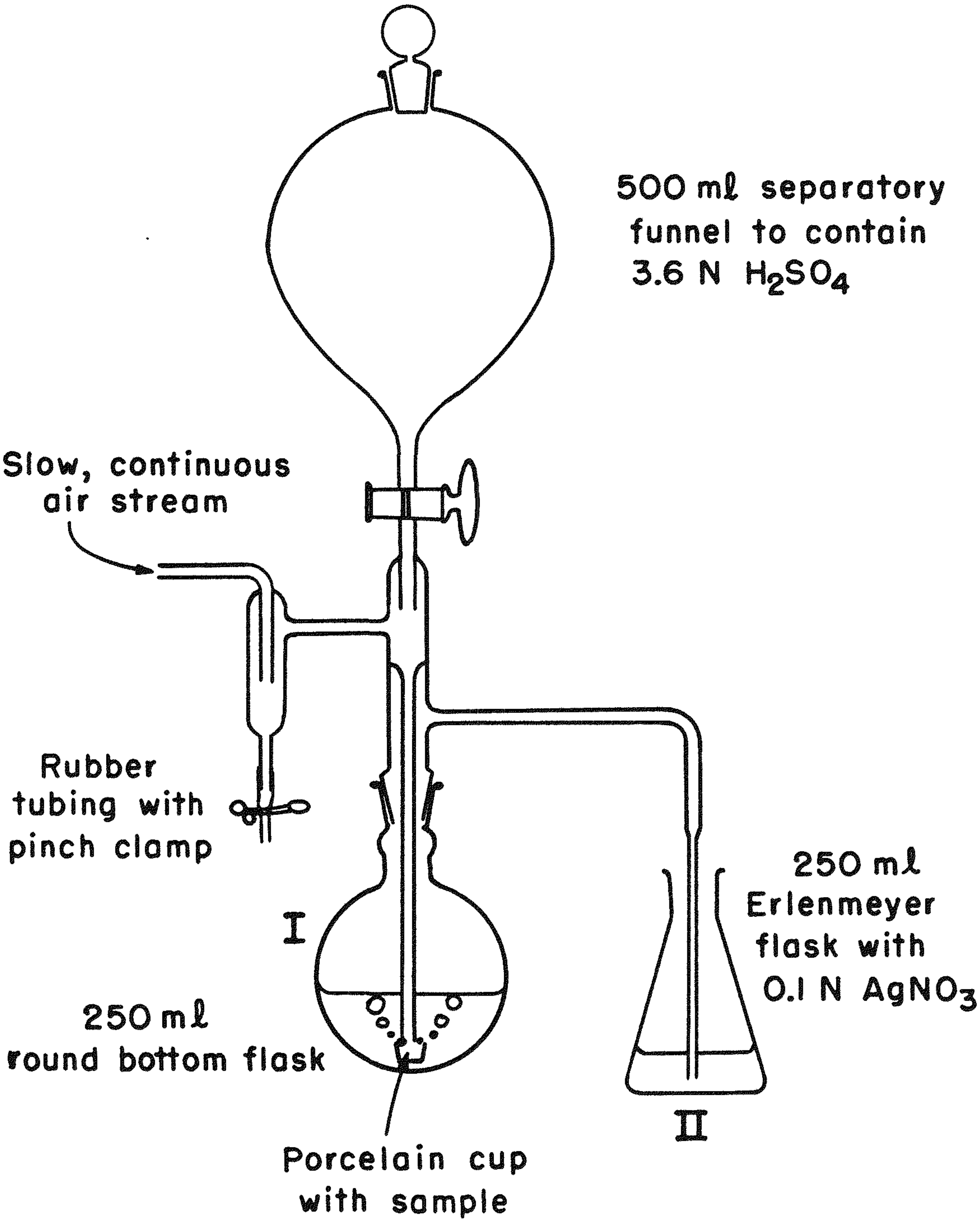

Fig. 1 - Apparatus for Analysis of Uranium Sulfide

and to sweep evolved gases into the receiver flask II. Approximately 100 ml of 10% H_2SO_4 is allowed to flow into flask I. Flask I is heated with a Meker burner and the solution is boiled vigorously to evolve all H_2S. Boiling is continued until the steam passing over into flask II has heated the solution, digesting the precipitated silver sulfide and causing it to coagulate. This should require 15 to 20 minutes.

The receiving flask II is lowered and the steam is allowed to condense a minute or two longer to wash the inside of the delivery tube. The Ag_2S is filtered off through Whatman No. 40 paper and washed with hot water. The filtrate is cooled, acidified with 30 ml of concentrated HNO_3, and 2 ml of 20% ferric alum is added as indicator. The excess $AgNO_3$ is titrated to a faint orange color with standard 0.1 $\underline{N}$ potassium thiocyanate using a 10-ml buret.

Calculation: $$\%S = \frac{(A-BR)N \quad 16.033}{W} \times 100$$

A = ml of titrant (in this case 10 ml of 0.1 $\underline{N}$ $AgNO_3$)

B = ml of KSCN

R = Ratio of standard $AgNO_3$ to KSCN obtained by carrying out the procedure with no sample

N = Normality of $AgNO_3$

16.033 = Equivalent weight of sulfur

W = Weight of sample in mg

If there is a residue in flask I, it is usually indicative of oxygen contamination in the original sulfide. The residue is determined by filtering the solution through a tared, 15-ml, sintered-glass crucible of fine porosity. The residue is washed with water, dried at 110°C, and weighed. Characteristic x-ray diffraction patterns of UO_2, UOS and U alone or in combination have been obtained with the dried residue.

Uranium

Uranium is determined in the filtrate after the removal of the residue by either a gravimetric method or volumetric method, previously described. The preferred gravimetric method involves precipitation with carbonate-free NH_4OH from the hot H_2SO_4 solution. The precipitate is digested in a hot solution for 30 minutes, filtered onto Whatman No. 42 paper, washed with hot ammoniacal 2% NH_4NO_3, and then ignited to constant weight as U_3O_8 at 950°C.

Total Sulfur

Total sulfur is determined by the following method. A Br_2-KBr solution is prepared by dissolving 16 g of KBr in a minimum amount of water, adding 10 g of Br_2 and, after mixing well, diluting the solution to 100 ml with water. A sample weighing 150 to 200 mg is treated with 10 ml of the Br_2-KBr solution and allowed to stand in a cold water bath, with occasional swirling, for 15 minutes. Fifteen ml of concentrated HNO_3 is then added and the solution is allowed to stand for an additional 15 minutes following which the beaker containing the sample is heated gently on a steam bath until the reaction has ceased and the bromine has been volatilized. The solution is then evaporated to dryness. Ten ml of concentrated HCl is added and the solution is again evaporated to dryness to expel the HNO_3. The residue is dissolved with 2 ml of HCl and a little water and then diluted to 200 ml. Sulfur is determined by precipitating it as $BaSO_4$ and weighing the precipitate.(11)

ANALYSIS OF THORIUM SULFIDE

The procedures described for uranium sulfide are satisfactory for the analysis of thorium sulfides. Thorium is determined in the solution in flask I by precipitation as the oxalate and ignition to ThO_2.(12)

ANALYSIS OF URANIUM CARBIDE

Carbon is determined in uranium carbide by combustion in oxygen and absorption of the carbon dioxide in ascarite.(13)

Uranium can be determined in the oxide remaining from the carbon analysis by dissolving the residue and applying the volumetric method. If the carbide is of high purity, the residue may be weighed as U_3O_8. Alternatively, a separate portion of the uranium carbide can be analyzed for uranium by dissolving it in acid and determining the uranium volumetrically.

ANALYSIS OF UO_2-MgO; U_3O_8-MgO

If only uranium is desired, the pulverized sample is dissolved in HNO_3, fumed with H_2SO_4 and the uranium is then determined volumetrically. Uranium and magnesium can be determined by separating the uranium by a double precipitation with NH_4OH in the presence of sufficient NH_4Cl to prevent precipitation of $Mg(OH)_2$. The precipitate is filtered off and either ignited to U_3O_8 or dissolved, following which the uranium is determined volumetrically. Magnesium is determined in the filtrate by precipitation as magnesium ammonium phosphate and ignition to pyrophosphate.(14) Alternatively, the magnesium can be estimated by titration with EDTA.(15)

ANALYSIS OF UO_2-ZrO_2

The pulverized sample is dissolved in HNO_3 plus a few ml of HF. When dissolution is complete, 5 ml of H_2SO_4 is added and the solution is taken to fumes, cooled, the walls of the beaker are washed down and the fuming is repeated to ensure removal of fluoride and nitrate. Uranium is determined by the volumetric method.

A fusion method can also be used for dissolving the UO_2-ZrO_2 ceramic.(16) The sample is fused with 10 times its weight of potassium pyrosulfate, preferably in a Vycor or clear quartz crucible so that the progress of the fusion can be observed. When a clear melt is obtained, the crucible and contents are cooled, dissolved, and the uranium is determined volumetrically.

ANALYSIS OF UO_2-Nd_2O_3; UO_2-Al_2O_3; UO_2-CaO

The UO_2-Nd_2O_3 and UO_2-Al_2O_3 ceramics are dissolved by treating them with HNO_3 and fuming with H_2SO_4. The UO_2-CaO ceramic is dissolved by treating with HNO_3 and fuming with $HClO_4$. The H_2SO_4 or $HClO_4$ solution is diluted with 3 N HCl after which the uranium is determined volumetrically.

ANALYSIS OF UO_2-GLASS

Silica

The sample is pulverized in a diamond mortar and a portion containing 100 to 200 mg of SiO_2 is fused for 30 minutes with 10 g of Na_2CO_3 in a covered platinum crucible using a blast burner. The melt is cooled and disintegrated by 50 ml of water in a beaker. Fifty ml of $HClO_4$ is slowly added and the silica is determined by the perchloric acid dehydration method.(17) The filtrate is reserved for the determination of uranium.

Uranium

The filtrate remaining from the silica determination is fumed until salts begin to precipitate in order to remove excess $HClO_4$. The salts are dissolved with 50 ml of 3 N HCl and the uranium is then determined volumetrically.

Potassium

The pulverized UO_2-glass sample is treated in a platinum beaker with 10 ml of HF and 10 ml of $HClO_4$. The mixture is heated to fumes of $HClO_4$ and boiled almost to dryness, cooled and 25 ml of water is added. If complete dissolution is achieved, 5 ml of $HClO_4$ is added and the solution is again fumed to eliminate traces of fluoride. If the mixture is not completely soluble in water, the treatment with HF is repeated. Excess perchloric acid is fumed off and the potassium is then determined by the perchlorate method.(18)

Calcium

A sample of pulverized UO_2-glass is dissolved by treatment with HF and HNO_3 in a platinum beaker. The solution is evaporated to dryness and the residue is dissolved in water and the solution is transferred to a volumetric flask. An aliquot is evaporated several times with HCl to convert all salts to their chlorides. The residue is taken up with 9 N HCl and the uranium is separated by ion exchange as described under UO_2-La_2O_3. The eluate is evaporated to dryness and taken up with 50 ml of boiling water containing 5 drops of HCl. Calcium is determined by titration with EDTA, using calcein to indicate the endpoint.(19)

Sodium

An aliquot of the nitric acid solution of the UO_2-glass prepared for the calcium determination is evaporated to less than 5 ml and the sodium is precipitated with magnesium uranyl acetate.(20)

The analyses described were carried out by the following members of the analytical group: R. W. Bane, H. B. Evans, I. M. Fox, A. M. Hrobar, K. J. Jensen, J. O. Karttunen, E. Moorhead, P. Peterson, and R. E. Telford.

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THE CHEMICAL DETERMINATION OF BORON IN BORON CARBIDE-ZIRCONIUM

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ABSTRACT

A rapid method is described for the dissolution and chemical determination of B in B_4C-Zr.

The sample is dissolved in a mixture of HF plus HCl contained in a Pt dish which is cooled in a bed of dry ice. Approximately 96 to 99% of the total B remains undissolved. This residue is filtered off, ashed, and fused with Na_2CO_3, and the B is then determined according to the classical mannitol titration method. The acid-soluble B is determined by a modified mannitol titration after separating the Zr and other interfering cations with $BaCO_3$. The acid-insoluble and acid-soluble B are added to give the total B in the sample.

The precision of this method was estimated from the analysis of synthetic mixtures of "standard" B_4C and Zr. At the 2% B_4C level or higher, the precision, on a relative basis, is about 1% for a single measurement, at the 95% confidence level. "Standardization" of the B_4C sample was performed by analyzing for B, C, and impurities. A mass balance of 100.2 ± 0.7% was obtained.

* * * *

In connection with the fabrication of materials containing boron carbide in zirconium, it became necessary to determine the absolute boron level and also the boron homogeneity. Any chemical procedure would also serve as a reference method for calibration of nondestructive instrumental monitors. Furthermore, the total B^{10} plus B^{11} content multiplied by the B^{10} enrichment factor would give the absolute amount of B^{10} loading available.

Previous experience with boron-zirconium alloys indicated that, following a sodium carbonate fusion of finely divided material, the boron can be effectively extracted from the bulk of the zirconium. Various metal-boride powders and powdered boron-zirconium samples were particularly amenable to this treatment. However, coarse millings of boron-zirconium failed to fuse completely and the results for boron were invariably low.

Because boron carbide is lost during the milling of boron carbide-Zircaloy, an alternate method of analysis had to be devised. Fortunately, a procedure had been developed for elemental boron-zirconium alloys whereby the sample was dissolved in dilute HF plus concentrated HCl. The dissolution was carried out in quartz, under reflux conditions, to eliminate possible losses of boron. The zirconium was precipitated with barium carbonate and the boron in the filtrate was titrated potentiometrically by the mannitol method between the empirically determined equivalence points, from pH 6.9 to 7.5. This wet-dissolution method for elemental boron-zirconium was, therefore, adapted to the analysis of boron in boron carbide-zirconium. Accordingly, the acid-insoluble boron carbide was fused with sodium carbonate and analyzed separately; the acid-soluble boron was analyzed after a barium carbonate separation of zirconium.

A particularly objectionable part of this analysis was the lengthy dissolution time. Sometimes one or two weeks were required for dissolving massive samples, usually of the order of 5 g. Consequently, a rapid dissolution method was developed whereby the sample is dissolved in concentrated HF, in a platinum dish cooled on a dry-ice bed to minimize boron losses. The acid insoluble residue is filtered, ashed and fused with sodium carbonate. The melt is dissolved in HCl and adjusted with sodium hydroxide to precipitate any hydrolyzable elements which may interfere with the final boron titration. The boron in the HF filtrate is separated from the zirconium with a barium carbonate precipitation. The acid-insoluble and acid-soluble boron are then determined individually by a potentiometric mannitol titration.

At first, the procedure was used to test the homogeneity of vendor material and of samples prepared at the Knolls Atomic Power Laboratory. The least accurate step in the analysis was believed to be the determination of the acid-soluble boron. However, less than 5 per cent of the total boron was acid-soluble and the procedure was considered adequate. The extreme pressure to turn out large numbers of analyses precluded an intensive study of the accuracy and precision. Experiments indicated that the relative standard deviation of the method was 3 per cent. The accuracy, however, was not known because of the unknown quantity of boron in mocked-up samples of boron carbide plus zirconium. The following experimental procedures, therefore, were used to check the accuracy and precision for calibration of nondestructive instrumental methods.

The final accuracy (not precision) of the test results for total boron in boron carbide-zirconium depends on:

(1) Standards and stoichiometry in the titration of boric acid.

(2) Standardization of the boron carbide.

The boron in a solution may be directly related to the number of gram-milliequivalents of sodium hydroxide required to react stoichiometrically with the boric acid according to the mannitol titration.

The sodium hydroxide solution used for this work was standardized using potassium acid phthalate as a primary standard (National Bureau of Standards - 84C).

The accuracy of the normality determined for the sodium hydroxide titrant and the stoichiometry of the mannitol-boron titration were further checked against prepared "standards"(a) of H_3BO_3 and B_2O_3 containing either isotopically pure B^{10} or B^{11}. Baker and Adams reagent-grade boric acid (natural boron) was also analyzed as a standard. The results of these analyses are shown in Table I.

Table I shows the bias of the titration is only -0.27 relative per cent and can be corrected on the basis of the empirical data.

Approximately 95% of the total boron in boron carbide-Zircaloy is acid-insoluble. A fusion with sodium carbonate (10 parts of Na_2CO_3 to 1 part of boron carbide) is required. The melt is neutralized with HCl, thereby forming a boric acid solution buffered with sodium chloride.

Possible boron losses due to the fusion with sodium carbonate and the buffering effect of NaCl during the titration of the boric acid by the mannitol method were checked as follows. Replicate samples containing 0.1 gram of boron (added as boric acid), with and without spectrographically pure carbon, were fused with 1 gram of sodium carbonate at 950°C for 2 to 4 hours to simulate the fusion conditions for boron carbide. The flux was dissolved and then analyzed for boron according to the conventional procedure. The results, shown in Table II, indicate that at the 0.1-gram boron level, the precision and accuracy are not significantly affected by the fusion or by the buffering effect of sodium chloride.

(a) Prepared by W. O. Haas, Jr., and J. L. Mewherter

TABLE I

ANALYSIS OF H_3BO_3 AND B_2O_3 PREPARED FROM ISOTOPICALLY PURE B^{10} AND B^{11}

Sample	B titrated, mg	Boron Found, % of Theoretical
$H_3B^{10}O_3$	4-5	99.63 ± 0.13
$H_3B^{11}O_3$	4-5	100.0 ± .1
$B_2{}^{10}O_3$	4-5	99.47 ± .07
$B_2{}^{10}O_3$	4-5	99.79 ± .07
$H_3B^{10}O_3$	5	99.88(a)
"	10	99.88
"	10	99.74
"	25	99.32
"	25	99.84
	Av.	= 99.73 ± .22 (95% confidence level)

(a) Baker and Adams H_3BO_3

TABLE II

ANALYSIS OF BORIC ACID WITH AND WITHOUT ADDED GRAPHITE, FOLLOWING FUSION WITH SODIUM CARBONATE

Boric acid, H_3BO_3 - Baker and Adams reagent-grade, containing 0.06% of impurities
Graphite - Spectrographically pure
Sodium Carbonate Added - 1 g

Boron Added	Carbon Added	Boron Found	
Grams		Grams	% of Theoretical
0.1001	0.00	0.1001	100.0
0.0997	0.00	0.0996	99.9
0.1012	0.00	0.1013	100.1
0.0898	0.020	0.0898	99.99
0.0198	0.020	0.0897	99.99
0.0988	0.020	0.0988	100.0

Approximately 5 per cent of the total boron in the boron carbide-Zircaloy was acid soluble. The accuracy of this step in the procedure was checked by analyzing HF solutions containing known amounts of boron (added as H_3BO_3) and zirconium (ZE-4: ASTM zirconium containing about 0.5% Fe, 0.3% Ni, and 0.58% Cr as major impurities) which were prepared to simulate solutions containing 2 to 8% of soluble boron, calculated from the total boron (0.04 to 0.16%) in a 2% boron carbide-Zircaloy sample.

The results from these experiments indicate that the acid-soluble boron may be determined with an error of +0.4 to -1.4% when calculated in terms of total boron. If HCl is added to the HF solution of the boron-zirconium sample, the results for boron are more accurate. It is believed that HCl prevents the coprecipitation of boron when the zirconium is precipitated with barium carbonate as barium fluozirconate.

A sample of boron carbide made by the Norton Company was standardized by determining total boron, carbon, iron, silicon and nitrogen by chemical methods. Oxygen and hydrogen analyses were performed by vacuum fusion. Spectrographic analyses were performed and indicated the relative amounts of other impurities in the sample. In Table III the composition of the sample is listed. The deviation of the mass balance from 100% and the summation of the standard deviations of each element determined were used to evaluate the accuracy of the boron value.

The maximum relative error in the accuracy of the boron values was calculated to be 1.2 per cent for sample KB-331.

On the basis of the acceptable mass balance of KB-331, the boron content of this sample was considered to be absolute within the limits specified above.

Nine loose mixtures of boron carbide (KB-331), zirconium (ZE-4), and soluble boric acid were prepared, dissolved and analyzed for total boron by the method used for the determination of boron in boron carbide-Zircaloy. The test results, shown in Table IV, were treated statistically and the method was shown to be accurate to at least 1.2 relative per cent (95% confidence level). The precision of a single measurement at the 95% confidence level is ± 1.0% relative per cent. The reliability of the data in Table IV is particularly enhanced because the total boron was calculated from the sum of two variables; i.e., the acid-soluble plus the acid-insoluble boron.

In summary, therefore, we have demonstrated that on synthetic mixtures of "standard" boron carbide plus zirconium at the 2-per cent level, the method is accurate to at least 1 relative per cent.

TABLE III

"STANDARDIZATION" OF BORON CARBIDE SAMPLE BY THE MASS-BALANCE METHOD

Sample: KB-331 (~ 270 to 400 mesh)

	Per Cent
Boron	79.73 ± 0.19 (9)
Carbon	19.54 ± 0.08 (9)
Iron	0.15 ± 0.05 (4)
Silicon	0.50 ± 0.18 (8)
Nitrogen	0.20 ± 0.18 (4)
Hydrogen	0.01 ± 0.001 (1)
Oxygen	0.09 ± 0.009 (1)
Mass Balance	100.2 ± 0.7

( ) indicates the number of replicate analyses performed.

TABLE IV

BORON FOUND BY ANALYSIS OF A SYNTHETIC MIXTURE OF BORON CARBIDE, ZIRCONIUM AND BORIC ACID

Mixture:

Zirconium, Zr, g	5
Boron carbide, B_4C, g	0.1
Boric acid, H_3BO_3, g	0.001
Boron in B_4C used, %	79.73

Boron Found, %		
Acid Insoluble	Acid Soluble (a)	Total
74.02	2.45	76.47 (b)
77.40	2.42	79.82
78.78	0.93	79.71
78.06	1.84	79.90
76.87	3.11	79.96
78.25	1.40	79.65
76.20	3.48	79.68
77.09	2.14	79.23
77.00	2.06	79.06
	Av.	79.63 ± .63
		(95% confidence level)

(a) Corrected for 0.001 g of B added as H_3BO_3

(b) Omitted from calculations

THE DETERMINATION OF CARBON IN LITHIUM

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ABSTRACT

Methods are reported for the determination of C in Li by measurement of acetylene which, presumably, is produced when Li contaminated with C is dissolved in water. Unreasonably low results were obtained by measurement of acetylene. Consequently, the assumptions made in the development of this method were examined critically. These assumptions are: that all C present in Li is combined as Li_2C_2 and, therefore, that even trace amounts of C in Li will produce acetylene quantitatively when reacted with water. Considerable doubt is cast on these assumptions by the experiments reported in this paper.

The total C contents of gases evolved during the dissolution of Li samples in CO_2-free water were determined. No measurable amounts of C were evolved from Li samples containing normal levels of C contamination. However, upon acidification of the resultant LiOH solution significant amounts of CO_2 were produced. Acetylene was produced only when Li highly contaminated with C was dissolved.

In view of the uncertainties involved in any analytical approach based on specific products of the reaction of Li with water, microcombustion techniques were examined. A method involving oxidation of all gases released during dissolution and acidification of Li samples. and a method involving direct combustion of Li samples were investigated for the determination of C in Li.

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INTRODUCTION

It has been established that various metals can be significantly carburized when in contact with alkali metals containing added carbon.(6) Since relatively small amounts of carbon exert a disproportionate effect on the mechanical properties of many structural metals, it is important that carbon contamination of these materials be minimized. The low density, high heat capacity, and high boiling point of lithium qualify it for consideration as a high-temperature, heat-transfer agent. In any such application, it would be in close contact with structural metals and, if contaminated with carbon, could contaminate these materials. For this reason, various approaches to the determination of carbon in lithium have been investigated.

A survey of the literature has revealed only one method for the determination of carbon in lithium. Gilbert, Meyer, and White(4) report a method based on the formation of acetylene during reaction of carbon-contaminated lithium with water. Any acetylene formed is absorbed in a concentrated solution of silver perchlorate and determined by the ultraviolet absorption of the resultant silver-acetylene complex. Methods for the determination of carbon in other alkali metals have been reported by Pepkowitz and Porter(8) and by Stoffer and Phillips.(9) Pepkowitz and Porter dissolve sodium samples in water under nitrogen and then convert any carbon to carbon dioxide by a wet oxidation. The final measurement is accomplished by a volumetric, differential freeze-out technique. Stoffer and Phillips determine carbon in sodium-potassium alloy by combustion in oxygen, followed by weighing any carbon dioxide produced.

PRELIMINARY EXPERIMENTS

Subsequent to the work reported by Gilbert, Meyer, and White,(4) this laboratory developed a similar method for the determination of carbon in lithium. This method was based on the use of Ilsovay's cuprous reagent,(5) modified for the determination of acetylene in hydrogen. Application of this method to typical samples of lithium revealed that little or no carbon was present. When lithium was purposely contaminated with various amounts of carbon, very poor recoveries were achieved. These facts occasioned a critical examination of the assumptions involved in analytical methods based on the measurement of acetylene. These assumptions are: that all carbon contained in lithium, even at trace levels, is present as lithium carbide; and that acetylene will be produced quantitatively by the reaction of lithium carbide with water. No support for the first assumption could be found in the literature. It is equally reasonable to suppose that trace amounts of carbon are simply dissolved in lithium. Furthermore, even if all the carbon were present as lithium carbide, the quantitative production of acetylene in the highly reducing environment of a lithium-water interface could be questioned.

In order to determine whether gaseous carbon compounds are produced on reaction of lithium with water, argon was passed through a train consisting of a reaction flask containing water, a tube of heated copper oxide to convert any carbon-containing gases to carbon dioxide, and a conductivity cell filled with dilute sodium hydroxide solution to absorb and measure any carbon dioxide. A number of samples were reacted in this train. Again, practically no carbon was observed in the gases and very poor recoveries were achieved for lithium samples purposely contaminated with carbon. In an effort to detect the possible presence of carbonates, the alkaline solutions of the lithium samples were acidified and the carbon dioxide produced was measured. Surprisingly consistent quantities of carbon dioxide, corresponding to 100 to 500 ppm carbon in typical lithium samples, were observed. One sample was analyzed in duplicate with and without the use of the copper oxide furnace. Results of 119 ppm carbon after oxidation of the gases and of 127 ppm carbon without oxidation indicated that the carbon-containing gas was probably carbon dioxide. Two possible sources of carbonate in the solutions obtained by reaction of lithium with water are: carbonate impurity in the lithium, and carbonate resulting from a reaction of dissolved carbon with the strongly alkaline solution at the lithium-water interface. The possibility of such a reaction was supported by the following experiment. Stoichiometric quantities of lithium and carbon were heated together in an inert atmosphere. An incomplete reaction occurred to form a product which produced little acetylene on reaction with water. The solution contained lithium carbonate, equivalent to about five per cent of the product. The large amount of oxygen required for the formation of this much carbonate could only have come from the water used to dissolve the material. Thus, the experimental evidence obtained in this study indicates the possibility of carbon in lithium reacting with water to produce carbonate as well as acetylene. Further, the evidence suggests the possibility of determining carbon in lithium by measurement of the amount of carbon contained in the gases produced on dissolution of lithium samples in acid solutions. Preliminary work on the development of such a procedure was quite encouraging. Simultaneously, investigation of a direct combustion approach, similar to that of Stoffer and Phillips,(9) was initiated. Because of the rapidity and simplicity of this alternative technique, all further effort was devoted to its refinement.

DETERMINATION OF CARBON IN LITHIUM BY A COMBUSTION METHOD

Combustion Conditions

Samples of lithium, weighing as much as 0.4 gram, can be ignited safely at 900°C in a stream of oxygen. A conventional, resistance-heated tube furnace is suitable. As discussed below, boric oxide is used as a fluxing agent for the lithium oxide formed during the combustion.

Conversion of Gases to Carbon Dioxide

Since the ignition of lithium occurs quite rapidly, there was some concern over the possibility of incomplete combustion of carbon to carbon dioxide. To assure that any carbon monoxide in the combustion products is converted to carbon dioxide, a tube packed with cupric oxide and heated to 600°C is included in the system.

Measurement of Carbon Dioxide

Microgram quantities of carbon dioxide are readily determined by measurement of the loss of conductivity of a dilute sodium hydroxide solution used to absorb the gas.(1, 2, 3) The Laboratory Equipment Company conductometric carbon determinator (Model No. 515) is quite suitable for this purpose.

RESULTS AND DISCUSSION

The general technique indicated above was applied to the determination of carbon in extruded lithium wire. Through an evaluation of the results of this application the general technique was demonstrated to be valid. Furthermore, precautions were suggested that should be observed in applying the method to other types of lithium samples.

It is apparent that lithium carbonate is a likely intermediate in the combustion of carbon to carbon dioxide in the presence of lithium. Therefore, the quantitative decomposition of lithium carbonate under the conditions of the determination had to be demonstrated. At 900°C, in a stream of oxygen, carbon dioxide is quantitatively evolved from lithium carbonate within 10 minutes, as shown by the data of Table I. In the presence of lithium, however, recoveries of small amounts of carbon were low and erratic (Table II). It was postulated that poor recoveries of carbon dioxide in the presence of lithium were due to the large mass of infusible lithium oxide. Examination of the literature indicated that boric oxide might serve as a suitable flux. The system Li_2O-B_2O_3 forms a series of low melting compounds and eutectic mixtures over a wide range of compositions.(7) In addition, the use of an acidic flux, such as boric oxide, would be expected to accelerate the volatilization of carbon dioxide and to decrease attack on refractory combustion boats. The data of Table III demonstrate the effectiveness of boric oxide as a flux during the ignition of lithium samples.

To demonstrate the recovery of carbon dissolved in or reacted with lithium, weighed amounts of carbon black were heated with lithium in the combustion apparatus at 900°C under an inert atmosphere. After 10 minutes of heating, oxygen was passed through the system and any carbon dioxide produced was absorbed in a weighing bulb. The results of these experiments are summarized in Table IV and indicate essentially quantitative recoveries.

The effect of atmospheric contamination of the samples was observed by analyzing pieces of a length of lithium wire after exposure for various periods of time to the air. As shown in Table V, the lithium initially contained 450 ppm of carbon. After exposure for two hours, the carbon content had increased to 850 ppm; and after 18 hours, 1900 ppm was found. This experiment points out the necessity of minimizing the exposure of lithium samples to the atmosphere prior to the determination of its carbon content.

The reliability of the procedure is shown, in a qualitative manner, by the data of Table V. No estimate of precision was made since variations are encountered due to the method, to the particular experimental set up, and to the samples. The lower limit of the method is about 25 ppm of carbon if one-half of the blank value of 20 micrograms is taken as the minimum amount of carbon detectable and 0.4 grams is considered to be the maximum sample weight that can be safely analyzed.

TABLE I

RECOVERY OF CO_2 FROM Li_2CO_3

Conditions: 900°C in Oxygen

Li_2CO_3 Grams	Carbon Dioxide Theoretical Grams	Carbon Dioxide Observed Grams	Recovery Per Cent
0.0598	0.0356	0.0360	101.1
.0536	.0319	.0325	101.9
.0529	.0315	.0311	98.7
.0536	.0319	.0321	100.6
.0485	.0289	.0290	100.3
.0525	.0313	.0310	99.0
.0539	.0321	.0322	100.3

TABLE II

RECOVERY OF CO_2 FROM Li_2CO_3-Li

Carbon Dioxide		
Anticipated	Found	Recovery
Micrograms		Per Cent
410	328	80.0
345	430	124.6
520	494	95.0
660	307	46.5
530	400	75.5
520	270	51.9
505	320	63.4
604	520	81.2

TABLE III

RECOVERY OF CO_2 FROM Li_2CO_3-Li-B_2O_3

Conditions: 900°C in oxygen

Carbon Dioxide Anticipated (Micrograms)	Carbon Dioxide Found (Micrograms)	Recovery Per Cent
518	488	94.2
426	424	99.5
540	505	93.5
1157	1196	103.4

TABLE IV

RECOVERY OF CARBON REACTED WITH LITHIUM

Conditions: 900°C in argon for 10 minutes, then
900°C in oxygen

Carbon		Recovery Per Cent
Added	Found	
Grams		
0.0299	0.0295	98.7
.0482	.0477	99.0
.0490	.0483	98.6
.0266	.0260	97.7

TABLE V

EFFECT OF ATMOSPHERIC CONTAMINATION

Time of Exposure	Carbon, ppm
0	400 490 500
2 hrs.	820 850
18 hrs.	1800 2000

CONCLUSIONS

There is considerable doubt that methods dependent on the production of acetylene provide a quantitative estimate of the carbon content of lithium. The determination of total carbon in lithium by direct combustion has been proven to be safe and quantitative at 900°C in oxygen, using a boric oxide flux. This general technique is recommended because of its rapidity, its simplicity, and its freedom from unverified assumptions.

ACKNOWLEDGEMENT

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ANALYSIS OF TANTALUM AND LUTETIUM IN IRRADIATED HAFNIUM

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ABSTRACT

Interest in the development of methods for the analysis of Ta and Lu in irradiated Hf has grown because of the effect these elements have upon the corrosion resistance of Hf. Formation of Ta, Lu, and W by transmutation adversely affects the corrosion resistance of Hf. The importance of this problem becomes more pronounced when applied to the search for longer-lived reactor cores.

The determination of Ta and Lu begins with a CaF_2-carrier precipitation to separate the rare-earth elements from Ta and Hf. Lu is determined flame photometrically by burning a TTA-hexone extract of a fluoride-free buffered solution in an oxyacetylene flame. Solvent extraction is used to separate Ta from interferences. Ta is then determined colorimetrically as a hydroquinone complex in a concentrated H_2SO_4 solution.

Sensitivity of the Lu procedure is 50 µg for 1-g samples. The limit of detection of the Ta method is 25 µg.

* * * *

Because of the formation of isotopes during irradiation of hafnium, methods for the analysis of two of these elements were made necessary. The two transmutation products of most interest, and for which methods were adapted, are tantalum and lutetium. A third by-product of irradiation is tungsten; however, it is believed that tungsten would behave similarly to tantalum so that conclusions drawn from tantalum results can be extrapolated to include tungsten.

The scheme of the isotopic "burn-in" is shown in Figure 1.

Lu^{175} and Ta^{181} are the two stable isotopes and the ones of greatest abundance and of interest. For the purposes of this study, incremental etches were made from pieces of irradiated hafnium. These etches were made at approximately 5, 15, 20, 25 mil thickness on a single side. These dissolutions represented weights of dissolved hafnium of about 1.5, 5.0, 7.5, 10 grams. The surface of the metal, since it received the highest amount of irradiation, produced the greatest concentration of tantalum and lutetium. Figure 2 shows the concentration of the tantalum and lutetium plotted against mils of hafnium removed in the etching process. The ratio of tantalum to lutetium was about 4:1; and this ratio remained fairly constant in all etch solutions.

The analysis of tantalum and lutetium is based upon solvent extraction in the case of both elements. Tantalum is determined colorimetrically as the hydroquinone complex in concentrated H_2SO_4, while lutetium is estimated flame photometrically by ignition of the organic hexone phase. Stepwise procedures are outlined in the Appendix for the determination of both tantalum and lutetium in hafnium.

In the analysis of lutetium, the separation of lutetium from tantalum and the bulk of the radioactivity in the form of hafnium is made by using a fluoride separation of the rare-earth element with calcium as a carrier. Some calcium is extracted into the hexone but its effect upon lutetium is negligible.

The lutetium fluoride precipitate is easily dissolved in dilute HCl. Aliquots of this solution are taken to dryness several times in order to remove any HF because HF prevents complete extraction of lutetium into the TTA-hexone phase. Lutetium is extracted from a buffered solution into hexone which has been saturated with thenoyltrifluoroacetone, after which the lutetium is determined in the organic phase using an oxyacetylene flame and the conventional Beckman Model B flame photometer.

The efficiency of the separation scheme was checked by spectrographic analysis of the filtrate, after separation of the fluoride precipitate, and by standard addition or "spiking" techniques. Negligible amounts of lutetium were detected spectrographically and recoveries of known concentrations averaged about 99 per cent. Sensitivity of the method is about 50 µg of lutetium. The absolute precision is 0.0018 per cent while the relative precision is about 8 per cent. These values were based upon material which analyzed less than 0.1 per cent Lutetium.

The filtrate from the fluoride precipitation of lutetium contains tantalum and hafnium. Tantalum is separated from the bulk of the hafnium by solvent extraction of tantalum in hexone from an HCl-HF solution. The tantalum is then back-extracted into the aqueous phase, using hydrogen peroxide. The peroxide

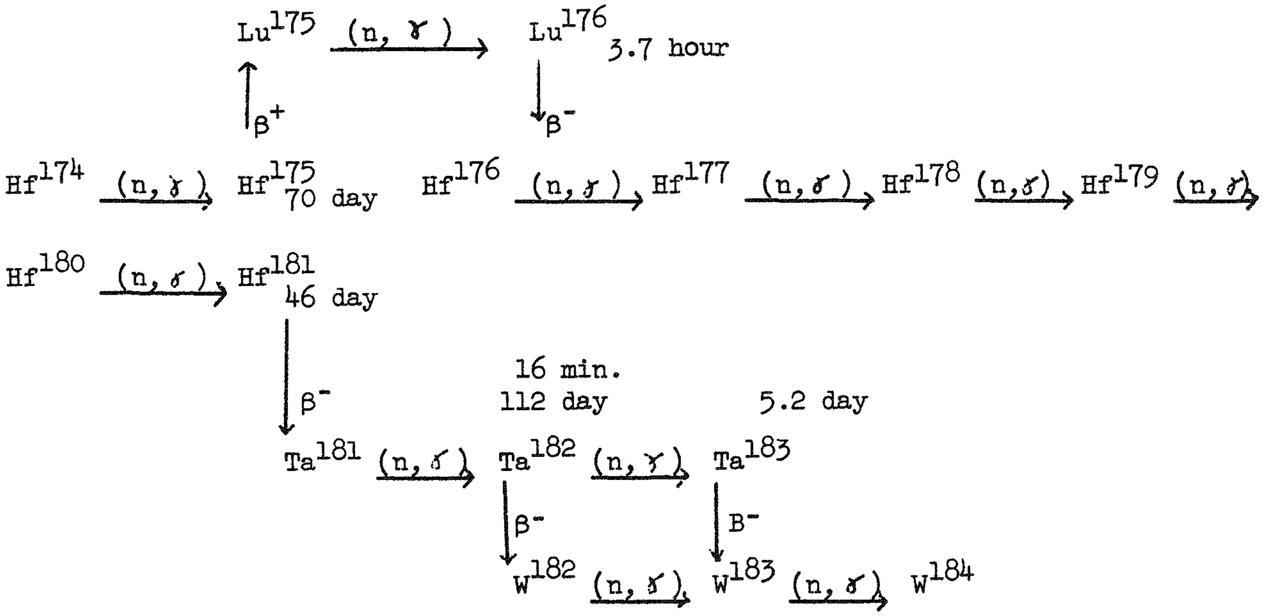

Fig. 1 - Hafnium and Its Irradiation Products

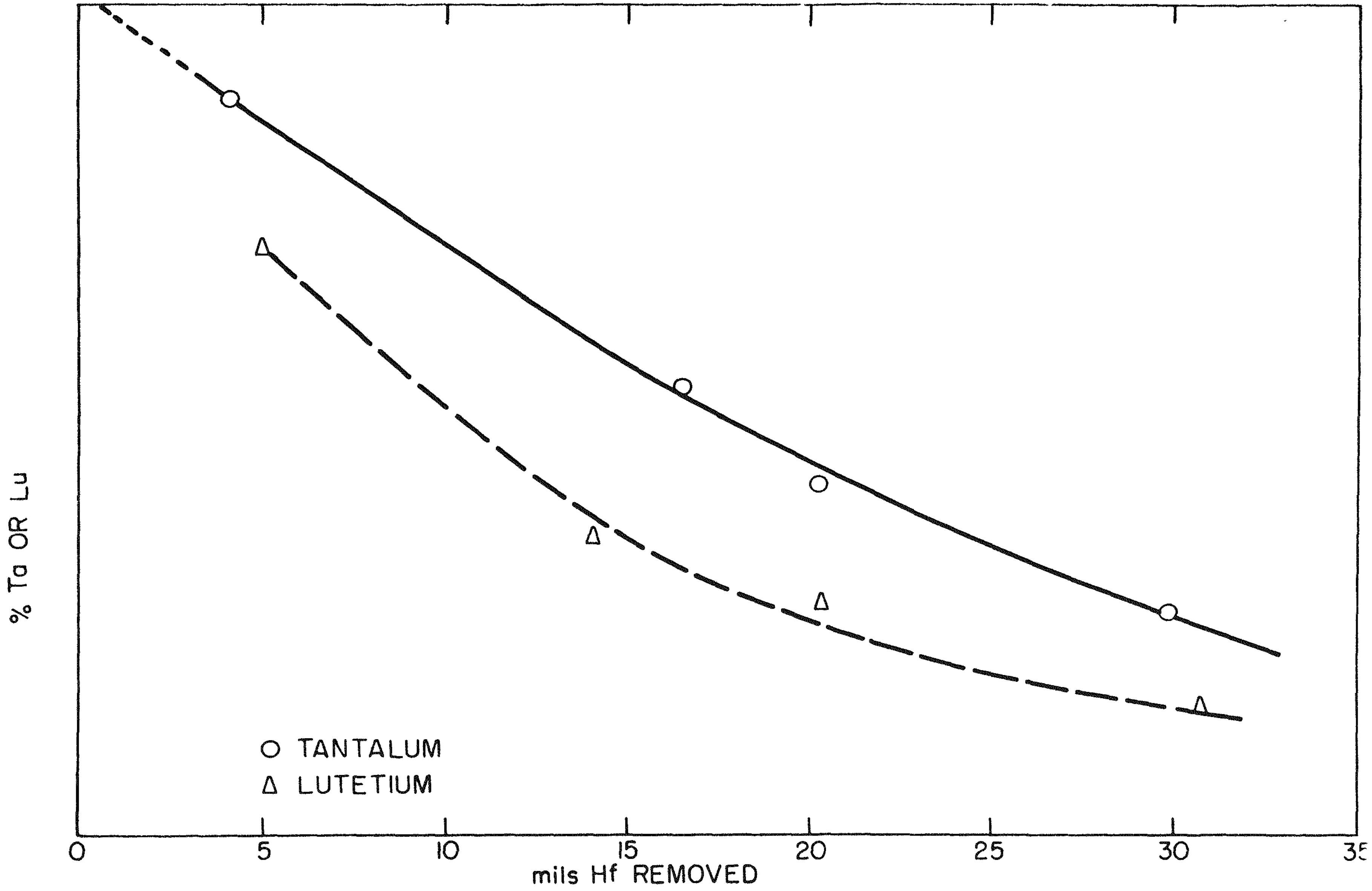

Fig. 2 - Tantalum and Lutetium Concentrations Per Mil of Hafnium Etched

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is then removed by fuming with sulfuric acid. Final color development is made in concentrated H_2SO_4, using hydroquinone to complex tantalum. Absorbance of the tantalum-hydroquinone complex is measured with a Beckman model DU spectrophotometer at 375 mμ in 1-cm cells. A minimum of 25 μg of tantalum may be determined by this method. The precision of the method is 0.004 per cent absolute or about 10 per cent relative.

The efficiency of the method was checked on a step-by-step basis, using Ta^{182} as a tracer. The effectiveness of the method was well within the counting efficiency which was estimated to be about ± 2 per cent.

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APPENDIX

A. DETERMINATION OF TANTALUM IN HAFNIUM

Reagents

1. Hydrofluoric Acid, 48% reagent-grade.

2. Sulfuric Acid, conc. reagent-grade.

3. Perchloric Acid, 70% reagent-grade.

4. Nitric Acid, conc. reagent-grade.

5. Hydrochloric Acid, conc. reagent-grade.

6. Calcium Chloride Solution, ($\sim$100 mg/ml). Dissolve 27.69 g $CaCl_2$ in 75 ml water and adjust the volume to 100 ml.

7. Hexone (4-methyl-2 pentanone), reagent-grade.

8. Hydroquinone Solution. Dissolve 5.5 g of hydroquinone in 100 ml of conc. H_2SO_4.

9. Hydrogen Peroxide, 30% reagent-grade.

10. Standard Tantalum Solution. Dissolve 0.1063 g of tantalum metal (99.9% purity) in 10 ml of HF and 10 ml of HNO_3. Heat the solution until all brown fumes of NO_2 are expelled. Then dilute this solution to a volume of 500 ml. 1 ml $\cong$ 212.6 μg tantalum.

Preparation of Standard Tantalum Curve

1. Pipette 0, 0.25, 0.5, 1, 2, 3 and 5 ml of the standard tantalum solution into a 125-ml separatory funnel.

2. Add 10 ml of H_2O, 1.75 ml of HF, 0.75 ml of HNO_3, 2 ml of HCl and an additional 10 ml of H_2O to make the total volume 24.5 ml.

3. Proceed to step 9 in the scheme of analysis for samples and follow through step 16.

4. Plot the concentration of Ta versus absorbance.

5. Process a blank with each set of unknowns and also, as a control, a 1-ml aliquot of the standard solution.

Procedure

1. Evaporate the solution obtained from the incremental etchings to dryness in a platinum dish.

2. Add 3 ml HF and 10-15 ml H_2O and heat until all salts are in solution.

3. To this solution add 50 mg of Ca as a solution of $CaCl_2$, and evaporate to a syrupy solution. Add 20 ml H_2O and heat.

4. After cooling, filter through a No. 50 Whatman paper and wash the ppt with a 1% HF solution. Save the ppt for the lutetium analysis. The ppt may be washed off the filter paper into a 150-ml beaker.

5. Dilute the filtrate to a volume of 100 ml and then transfer the solution to a clean, dry polyethylene bottle and stopper tightly.

6. Pipet a suitable aliquot (between 100 and 600 μg of Ta) into a platinum dish and evaporate to dryness.

7. To the residue in the platinum dish add 10 ml H_2O, 1.75 ml HF (35 drops), and 0.75 ml HNO_3 (15 drops). Heat gently to assure complete dissolution.

8. Carefully pour this solution into a 25-ml graduated cylinder. Wash the platinum dish several times with water, and add 2 ml of HCl to the solution in the graduate. Keep the volume to about 17-18 ml. Pour this volume into a 125-ml separatory funnel and rinse the graduate with only enough water to make the total volume 24.5 ml.

9. Add 25 ml of hexone and extract for 6 minutes on a Burrell wrist-type shaker. Allow the solution to stand for at least 10 minutes in order to let the water and the organic phase separate well.

10. Draw off the water phase and discard it.

11. Add 24 ml of H_2O_2 solution (3 ml 30% H_2O_2 + 21 ml H_2O).

12. Extract for 6 minutes using an automatic shaker. Let stand for 10 minutes.

13. Draw off the aqueous phase into a 250-ml beaker and add 5 ml of conc. HNO_3, 5 ml of conc. $HClO_4$, and 5 ml of conc. H_2SO_4. Cover the beaker and boil gently until the H_2O_2 is destroyed.

14. Take to fumes of SO_3 seven times, adding 3 ml of conc. H_2SO_4 after every other fuming. The sides of the beaker should be rinsed down with water after each fuming. A minimum of 5 ml of conc. H_2SO_4 should be left in the beaker after the final fuming.

15. To the cooled solution, add 5 ml of hydroquinone solution, (5.5 g hydroquinone/100 ml conc. H_2SO_4). Mix well and transfer to a 25-ml volumetric flask. Rinse the sides of the beaker with conc. H_2SO_4 and add the rinse solution to the 25-ml flask. Adjust to 25 ml, using conc. H_2SO_4. Mix well.

16. Measure the absorbancy on Beckman DU Spectrophotometer at 375 mu and estimate the Ta concentration by comparison with a standard curve. Use 1-cm quartz cells.

B. DETERMINATION OF LUTETIUM IN HAFNIUM

Reagents

Hydrochloric Acid, concentrated

Ammonium Acetate Buffer Solution. Add 385 g of ammonium acetate to 500 ml of water. Adjust the pH to 5.5 with acetic acid; then dilute to one liter.

Hexone - TTA Solution. Dissolve 22 g of thenoyltrifluoroacetone in hexone and dilute to one liter. Keep in a brown bottle, shielded from light as much as possible.

Standard Lutetium Solution. Dissolve 0.25 g of lutetium metal in 10% HCl with gentle heating. Filter off the black insoluble ppt. Transfer the solution to a 250-ml volumetric flask and make to volume with water. 1 ml = 1 mg Lu. This solution may be standardized by taking an aliquot of about 50 ml and precipitating the Lu with NH_4OH. This ppt is then ignited to Lu_2O_3 and the concentration of Lu is then checked against the assumed purity.

Preparation of Standard Lutetium Curve

1. Pipet solutions containing 0, 0.1, 0.25, 0.5, 0.75, and 1 mg of Lu into 125-ml separatory funnels.

2. Add 8 ml of NH_4Ac solution and adjust the volume to 20 ml with water.

3. Add 20 ml of TTA-hexone solution and extract for 6 minutes, using a Burrell shaker.

4. Let the solutions stand for 10 minutes so that the phases separate completely.

5. Draw off the water phase and discard it. Pour the hexone phase out of the top of the separatory into a dry 50-ml volumetric flask.

6. Measure the emissivity on Beckman B flame photometer at 468 mu. Set the photometer at D sensitivity and use oxygen at a pressure of 10 psi, acetylene at 3 psi pressure.

7. Adjust the blank to 15% transmittance and read other solutions.

8. Plot a curve using % Tr versus conc. Lu in mg.

Procedure

1. From step 4 of the tantalum procedure, dissolve the fluoride precipitate in 3 ml of HCl and 10-15 ml of H_2O. Slight heat is necessary to speed the dissolution.

2. After the fluoride ppt has completely dissolved, cool, transfer to a 25-ml volumetric flask and make to volume.

3. Transfer a suitable aliquot (5 or 10 ml) to a 100-ml platinum dish and take to dryness twice under an infrared lamp.

4. To the dry residue in the platinum dish add 0.5 ml of conc. HCl and 10 ml of H_2O. Heat under infrared lamp until all of the ppt is dissolved.

5. Transfer the solution to a 125-ml separatory funnel and wash the platinum dish with 8-ml of NH_4Ac buffer solution. Adjust the total volume to 20 ml.

6. Add a carefully measured 20-ml volume of the TTA-hexone solution. Extract for 6 minutes using a mechanical shaker. Allow the solutions to stand for 10 minutes so that the phases may separate completely.

7. Draw off the water phase and discard it. Pour the hexone phase out of the top of the separatory funnel into a 50-ml volumetric flask and stopper it.

8. Read on a Beckman B flame photometer at 468 mu, D sensitivity, using an oxygen pressure of 10 psi and acetylene pressure of 3 psi.

9. Calculate the lutetium concentration by comparison with a standard curve made with pure lutetium metal.

10. A blank must be carried through the extraction phase and this solution must be adjusted to 15% Tr.

ANALYSIS OF TRACE IMPURITIES IN HELIUM USING GAS CHROMATOGRAPHIC TECHNIQUES*

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ABSTRACT

A gas chromatographic method is described for the quantitative separation and determination of argon, oxygen, nitrogen, carbon monoxide, and methane in helium at the one-volume-per-million level. Standard gas samples, prepared by PVT techniques are used to calibrate the chromatograph. The chromatographic unit includes a Linde 5-A Molecular Sieve as the column adsorbent and thermistor-type thermal conductivity cells as detectors. Data are presented comparing the performance of Molecular Sieve with that of activated charcoal as column materials.

This analytical technique was used to evaluate methods for helium purification. Two systems were investigated: a Linde 5-A Molecular Sieve-hot Titanium system and a cryogenic activated charcoal system. The exit gas was analyzed to correlate purity with flow rates and temperature conditions in the purifiers.

PURPOSE

The need for measuring the impurities in helium used as a blanket or cover gas has long been with those working in reactor engineering and materials development. The impurities of concern are all reactive gases, which include hydrogen, oxygen, nitrogen, water, carbon monoxide and methane. One can spend a short time in a library and find a considerable number of references on various types

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* Work performed at Pratt and Whitney Aircraft - CANEL, Middletown, Connecticut under USAEC contract AT (11-1)-229.

of gettering or gas-purification systems without finding one that includes a satisfactory method for the analysis of the gas being purified.(1,5,11,13,14,16) Techniques for the determination of oxygen(2,10) and water(3,6,9) have been devised for constant monitoring systems; hydrogen,(9,12,15) carbon monoxide(7) and methane(17,18) can be measured only by using bulky and cumbersome methods; nitrogen,(4,8) cannot be determined satisfactorily in low concentrations. Thus, no simple system existed that could adequately meet our needs for the determination of impurities in helium down to one ppm by volume. Based on considerations of diversity, sensitivity and simplicity, gas chromatographic techniques were investigated as the means for performing the required analysis of all the above impurities except water.

INTRODUCTION

In the early 1940's the techniques of liquid chromatography were extended to gas-phase systems. The adsorbent can be any inert solid powder which is capable of resolving the components involved. The solvent or carrier is any non-reactive gas, depending upon the type of detector used. The most commonly used detector is a thermal conductivity cell. Other detectors incorporate ultraviolet transmission, radiation counting tubes or a hot-wire bridge. Basically then, the system consists of a flowing carrier-gas circuit, a flowing process-gas circuit, a sampling device, an adsorbing column and a detector.

A measured volume of the process gas to be analyzed is injected into the carrier-gas just before it enters the column where the gas components are separated by selective adsorption-desorption and eluted individually. The detector senses the change in thermal conductivity corresponding to a change in composition of the gas leaving the column. The change in thermal conductivity is recorded as a deflection on a constant-speed strip chart. Thus, for any set flow of carrier gas, a particular column will yield a deflection on the strip chart at a time peculiar to the component with an amplitude proportional to the quantity of that component present.

APPARATUS

The chromatograph used in this work was a commercially available laboratory unit originally made to be used for organic chemical analysis (see Figure 1). The unit utilizes an in-line sample injection valve which causes only a momentary disruption of carrier-gas flow. The column consists of 16 feet of 1/4-inch stainless steel tubing packed with the adsorbent being evaluated. The detector is a thermal-conductivity cell, with a thermistor housed in each of two separate cavities in a single metal block. The first thermistor, a reference unit, is arranged so that it is continually cooled with helium at a constant pressure and flow. The second thermistor, the analyzing unit, is arranged so that it is continually cooled with the helium coming from the chromatograph column. The two thermistors are arranged in a Wheatstone Bridge circuit powered at a constant current. The output signal is fed to a calibrated attenuator and then to a single-pen 1-mv recorder.

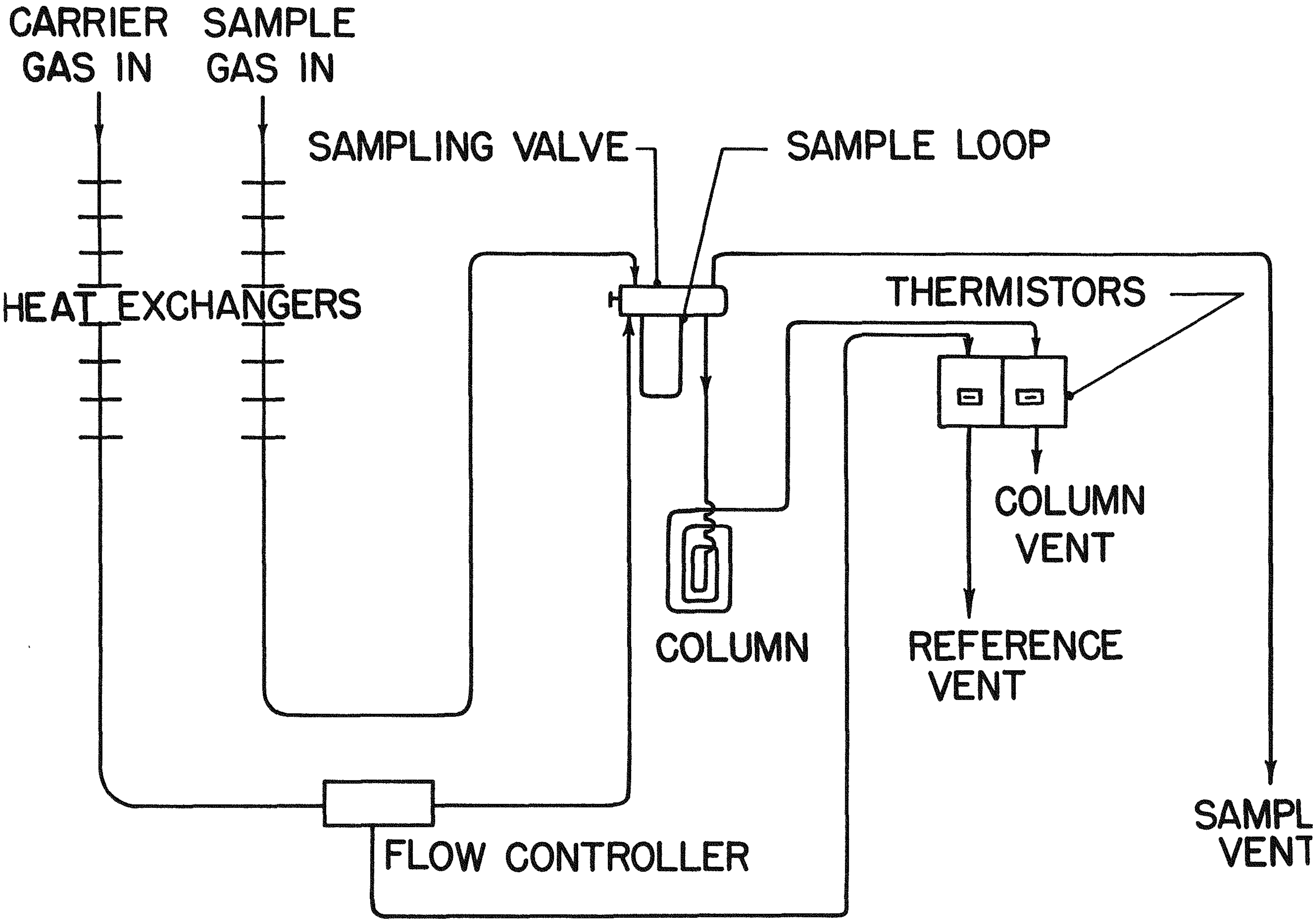

Fig. 1 - Flow Diagram of Gas Chromatograph

PROCEDURE

When the flow rate of the gas over both thermistors is constant, a steady state is established and the recorder traces a line. The recorder is set so that the line, taken as the base line, is recorded at zero on the chart scale. After a sample is injected into the system and the column separates the gases, the eluted component, having a different thermal conductivity than helium, causes a shift in the detector balance and a deflection is recorded on the strip chart. After the gas is washed past the detector, the original equilibrium is re-established. The deflection caused by each constituent is proportional to the quantity of that component present, and is most conveniently expressed in ppm by volume.

Helium was chosen as the carrier-gas in the determination of impurities in helium to take advantage of the large difference in the thermal conductivity between helium and the majority of the impurities under study and to eliminate the problem of separating and concentrating the trace component from the bulk of the sample.

CALIBRATION

The first attempts to calibrate the chromatograph were by means of commercially-available tanks of reportedly analyzed helium. These attempts did not prove satisfactory for the following reasons: (1) the mixed gases could not be obtained in the low concentration required, and (2) complete assurance of the identity of certain peaks was not possible because the amount of impurities could not be controlled. Consequently, a more efficacious technique was required.

A system was, therefore, designed and constructed by which millimicroliter quantities of an impurity gas were successfully introduced directly into the carrier gas line before the gas entered the chromatograph column. This calibration system, diagramed in Figure 2, consists of a vacuum system, a manifold containing several calibrated volumes and a calibrated sample tube. This sample tube is attached through a three-way stopcock whereby it can be filled with a gas of known pressure and then valved so that the carrier-gas sweeps the gas from the sample tube into the chromatograph. A standard tank of the gas being studied was attached to the manifold of the calibration system. The system was evacuated to below one micron to eliminate a blank after which the small calibrated volume was filled from the tank to a pressure measured on the manometer. The manifold was again evacuated and the gas in the small solume was expanded into the rest of the system. The valves were then adjusted so that the impurity gas in the sample tube was swept into the chromatograph. Using this procedure, for each centimeter of original pressure, 65 milli-microliters of the gas being studied were introduced into the chromatograph. This procedure was repeated at various pressures, using each of the gases of interest. Thus, the time of elution and a calibration curve were obtained for hydrogen, oxygen, nitrogen, argon, carbon monoxide and methane. Water could not be determined because it is irreversibly adsorbed on the columns investigated to date.

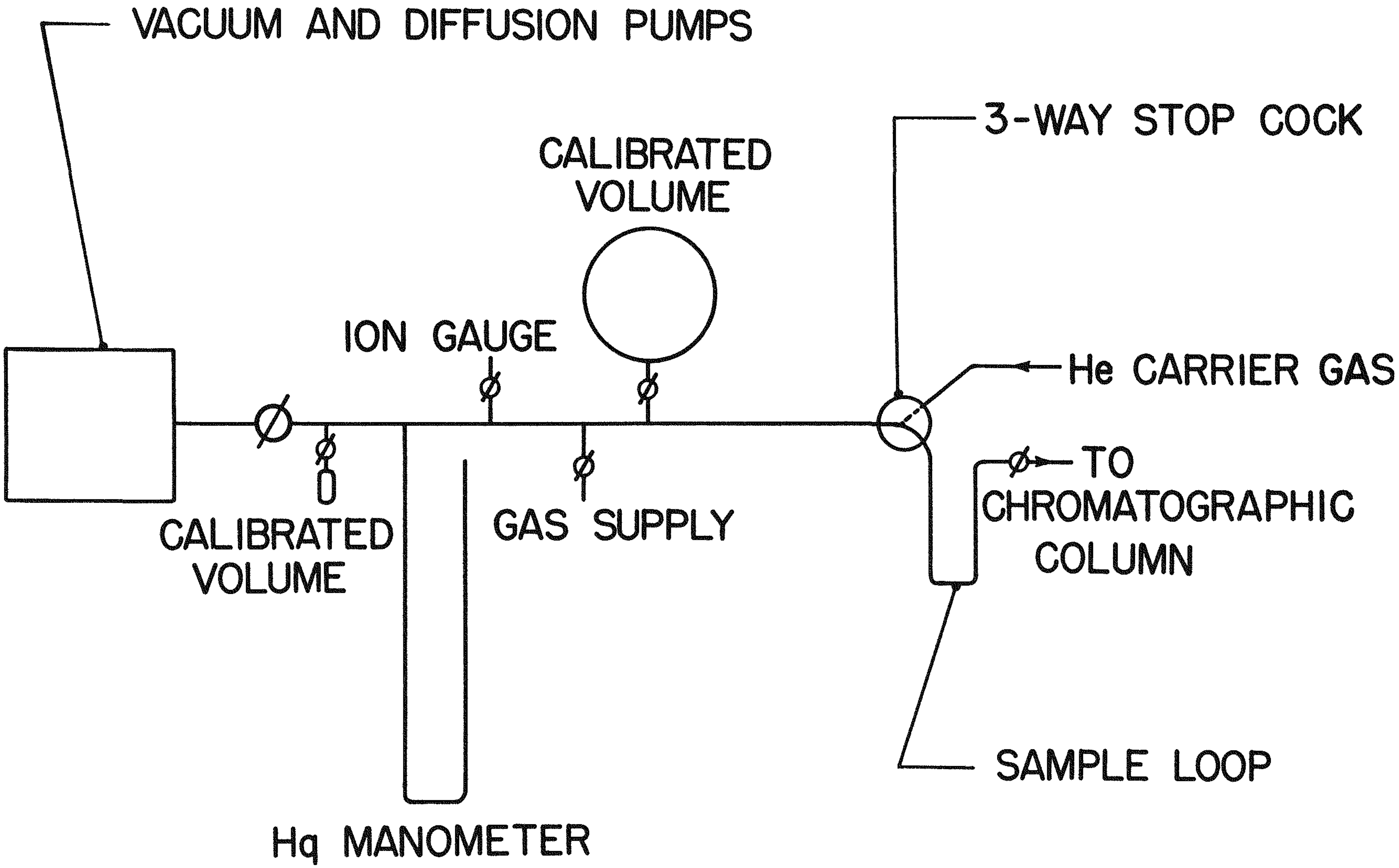

Fig. 2 - Gas Chromatograph Calibration System

SELECTION OF COLUMN MATERIAL

Two column materials, activated charcoal and Molecular Sieve have been investigated. A diagrammatic comparison of the separations obtained from these two columns is presented in Figure 3. In order to use a more convenient reference, the quantities of component detected are expressed as ppm by volume of the sample volume rather than milli-microliters at STP. These peaks represent approximately 950 milli-microliters of each gas in a sample volume of 38 ml. This is equivalent to 25 ppm. The elution peaks are generally sharp and symmetrical; carbon monoxide, an exception, shows some tailing. The time of elution is, of course, of prime importance for identification. Methane could not be analyzed on the charcoal column because it it irreversibly adsorbed in this system. The charcoal column could not completely separate oxygen and nitrogen because their elution times are very similar. Neither column is very sensitive to hydrogen because hydrogen and helium have similar thermal conductivities. On the basis of the complete oxygen-nitrogen separation, Molecular Sieve was chosen as the column material to be used in process gas analysis at CANEL. Argon and oxygen have similar elution times and consequently if argon is present in the helium an analysis for oxygen is not possible, using either Molecular Sieve or charcoal columns. Fortunately, argon is not a natural impurity in helium.

CONTROL OF VARIABLES

Although there is still much to be learned concerning column diameter, length, particle size of adsorbent, and other adsorbent materials as well as sampling techniques, and detector sensitivity, a few observations could be made at this time. The order of elution and peak height versus quantity of component detected are constant for the same adsorbent but the time of elution must be determined for each individual column. The column length must be great enough to effect separation of the components but short enough to avoid a diffuse band. The size of the sample volume is of great importance. By doubling the sample size the sensitivity of the chromatograph is doubled for a constant amount of impurity detected. A limit is reached, however, when the sample size is so large that complete separation does not occur. The flow of helium through both cells of the detector must be kept very constant to eliminate drift in the base line of the recorder. The rate of flow of helium through the reference cell is not critical as long as it is constant, although it appears that optimum stability is attained if the flow rate in the reference cell is about the same as that in the analyzing cell. The flow rate through the analyzing cell, which is the flow rate of the carrier-gas through the column, must be determined for each column and depends upon column length, size of adsorbing particles and packing density. This flow rate must be regulated so that the peaks are sharp and well defined because broad elution peaks do not offer quantitative accuracy.

INTERPRETATION OF CHROMATOGRAMS

The means of interpretation of elution peaks is in considerable controversy in the gas chromatography field. Methods of measuring the peaks include the use of a planimeter or integrator, triangulation, and simply measuring

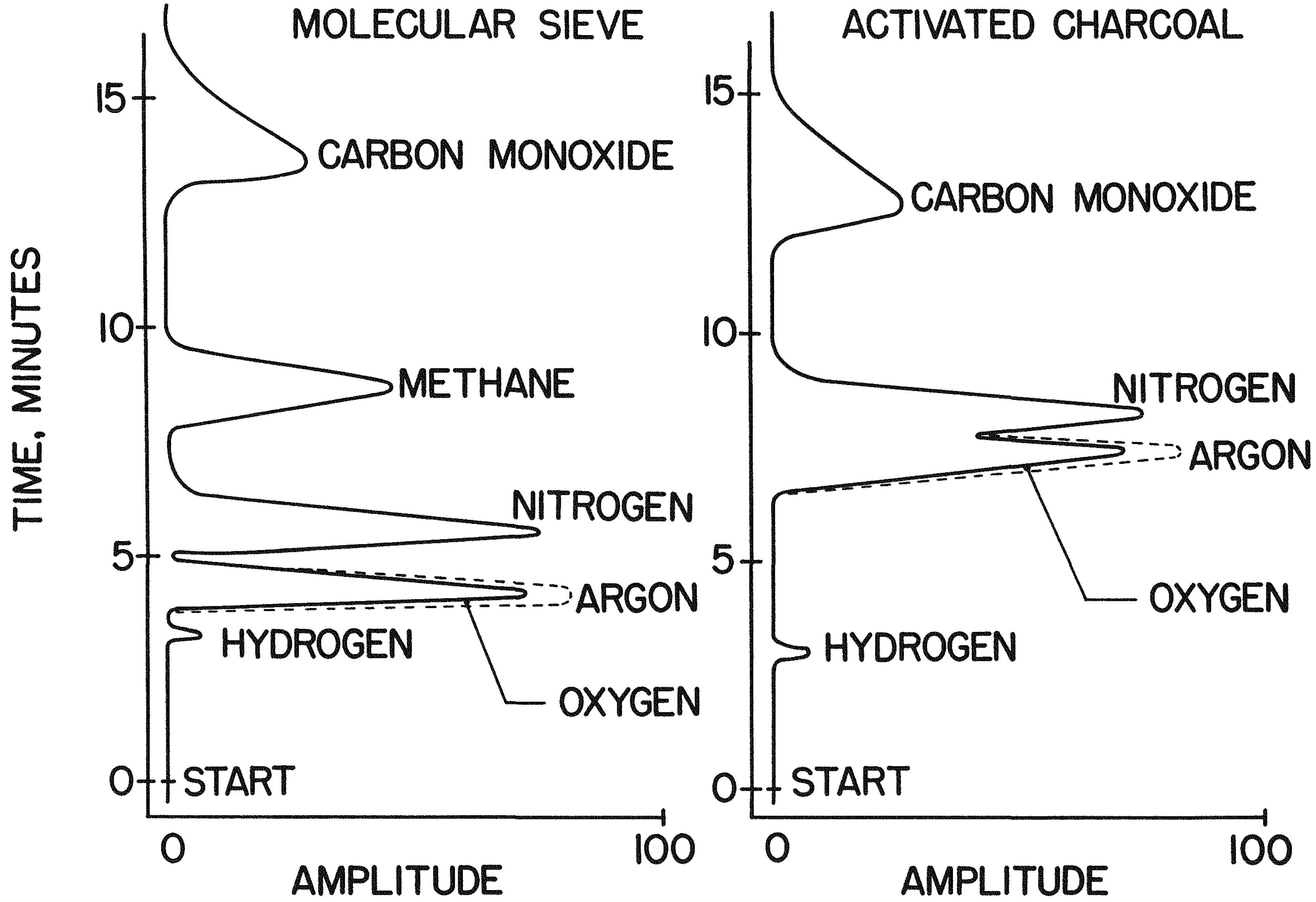

Fig. 3 - Molecular Sieve Versus Activated Charcoal as Column Material

peak height. Using these methods it has been found that, at low concentrations, the concentration of the components is directly proportional to the peak-heights. Figure 4 shows calibration data for a Molecular Sieve column presently being used, in which peak-height is plotted against component concentration and a straight line is obtained which passes through the origin. The sensitivities are such that oxygen, nitrogen, carbon monoxide, methane and argon are being determined to one ppm and hydrogen to five ppm by volume.

Columns can be contaminated by materials which are irreversibly adsorbed. Figure 5 shows two typical chromatograms obtained from the same Molecular Sieve column. In the first case the column had been used for some time and had adsorbed water from the carrier-gas. This apparently limited the number of available adsorption sites to such an extent that complete separation no longer occurred, and base-line drift became a problem. The second chromatogram is from the same column after it had been baked out at 700°F for 24 hours with helium flowing through it. The original separation is obtained, and the instrument regained its stability.

APPLICATIONS

The chromatograph is presently being used to analyze helium in an investigation of helium purification systems. A cryogenic purification system consisting of 110 grams of activated charcoal at liquid air temperatures was used to reduce the impurity levels in helium below the sensitivity of the gas chromatograph. Helium containing as much as 160 ppm total oxygen and nitrogen at flow rates up to 30 cubic feet per hour were easily handled by the purifier. Another purifier being investigated consists of activated zeolite at room temperature and titanium sponge at elevated temperatures. Figure 6 illustrates the "gettering" efficiency of a purifier containing 137 grams of titanium sponge as a function of temperature. The parameters of purifier size and shape and of gas flow are still being investigated.

FUTURE WORK

There is much work to be performed in the development of gas chromatography for trace analysis in noble gases. Experimental work at CANEL is continuing to evaluate columns which can separate oxygen and argon and to apply gas chromatography to the determination of water in noble gases. In addition, the development of a detector for trace analyses in argon is being investigated by the CANEL Instrument Group.

SUMMARY

An analytical method using gas chromatography has been developed for trace impurities in helium. Activated charcoal and Molecular Sieve columns have been evaluated. It has been shown that with a Molecular Sieve column and a thermal conductivity cell detector the determination of hydrogen, oxygen, nitrogen, carbon monoxide and methane can be made to the 1 to 10 ppm level. The method has been applied to the study of systems for the purification of noble gases.

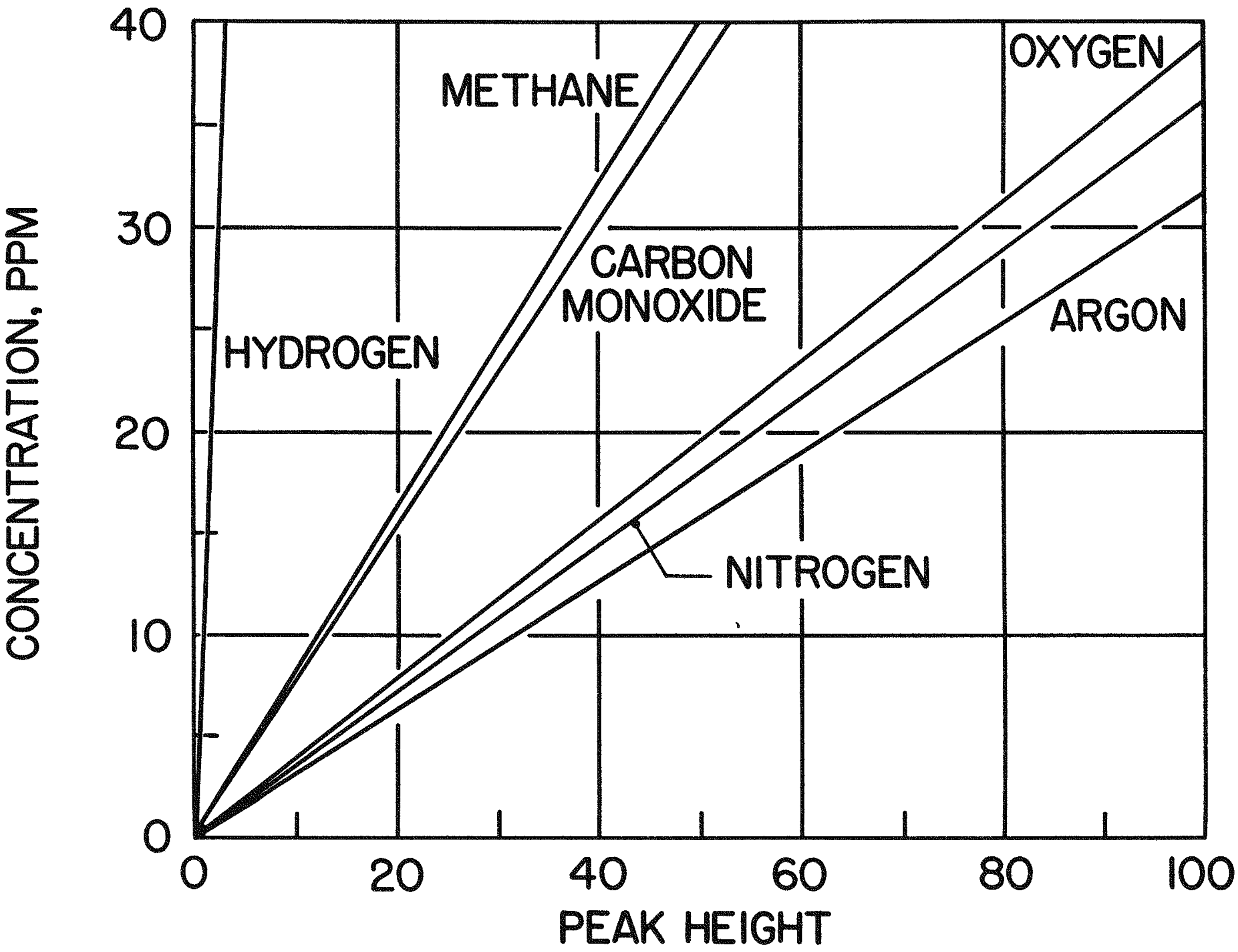

Fig. 4 - Molecular Sieve Calibration Data

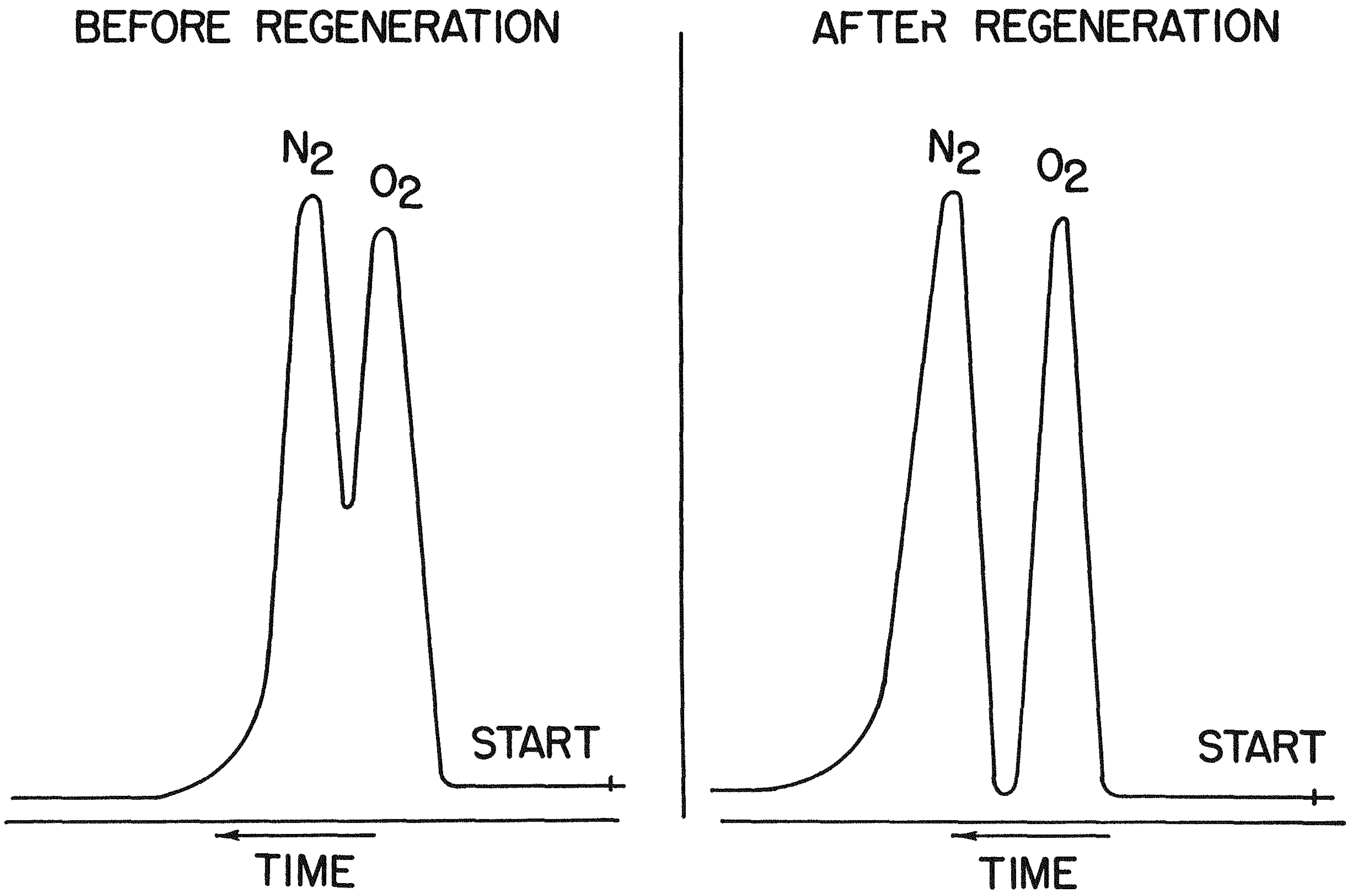

Fig. 5 - Regeneration Effect on Molecular Sieve

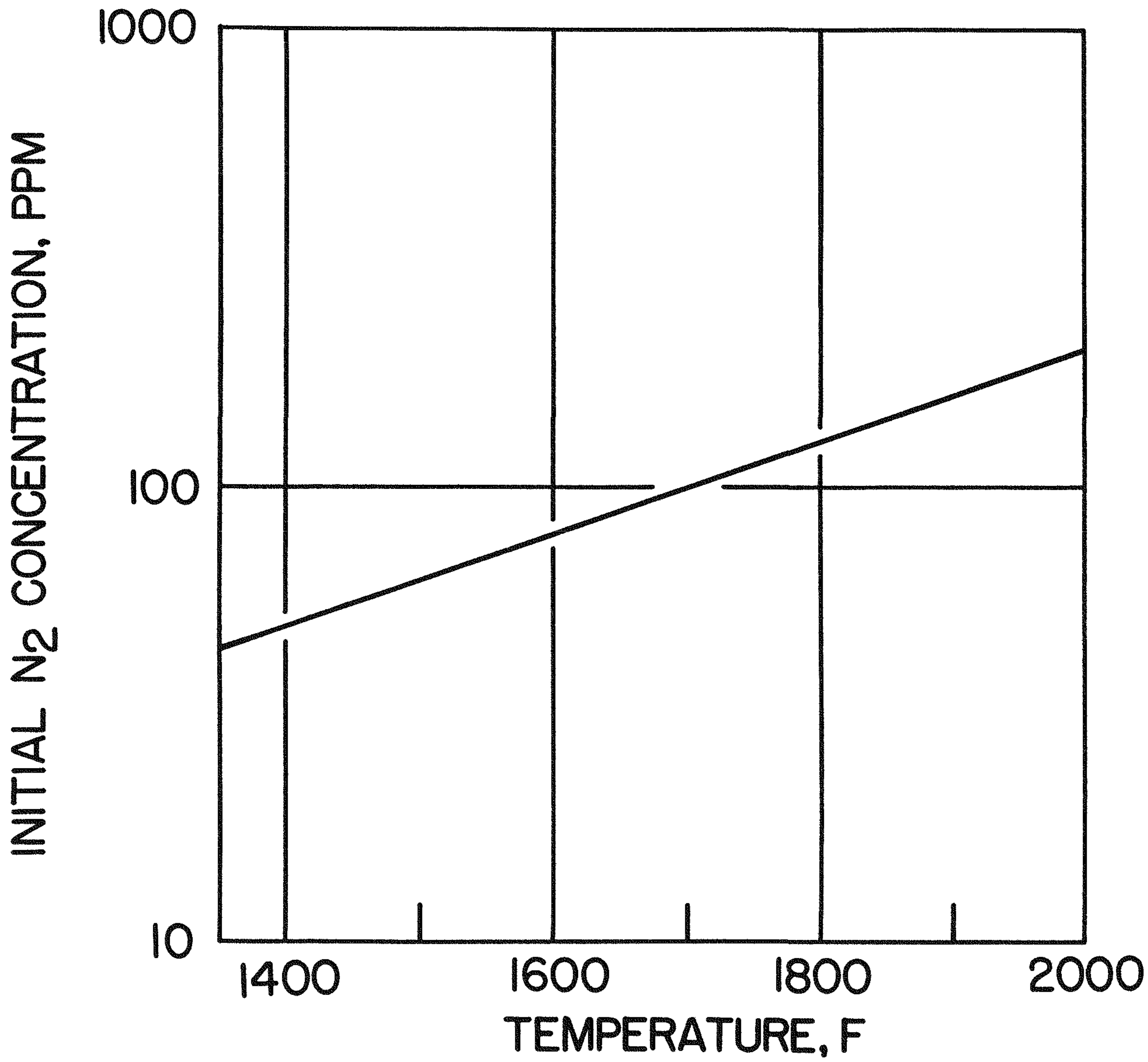

Fig. 6 - Minimum Titanium Temperature for Nitrogen Removal

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THE POLAROGRAPHIC DETERMINATION OF NIOBIUM IN ZIRCONIUM-BASE ALLOYS

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ABSTRACT

A polarographic method is presented for the analysis of Nb in Zr-base alloys containing Sn. The sample is dissolved in a mixture of H_2SO_4, HCl, and HBF_4 and then fumed with H_2SO_4. The resulting H_2SO_4 solution is diluted to volume, and the Nb is determined polarographically by measuring the peak height of its wave at -0.95 v vs SCE, using a cathode-ray polarograph.

INTRODUCTION

The concentration range of niobium usually encountered (1 to 5 per cent) favored the direct polarographic analysis in preference to a gravimetric determination based on separation of the niobium as Nb_2O_5.

Because of the hydrolytic properties of niobium, either a strongly acidic solution or an appropriate complexing medium should be used to keep the niobium in solution. The latter method has been investigated by several authors;(1,2) however, these methods did not appear to be altogether adequate.(3) Numerous papers on the polarography of niobium in acid solution have been published.(4,5,6,7,8) A recent report by Elving and Olson(9) notes that niobium waves are produced in 12 M HCl and in 9 M H_2SO_4. The wave in HCl is better defined because of its longer diffusion current plateau, but tin interferes. In the present procedure, a sulfuric acid medium is utilized as the supporting electrolyte, and a cathode-ray polarograph is used to obtain the polarogram (Figure 1). In this way, a niobium peak is produced which is easily measurable. Furthermore, tin does not interfere. The examination of niobium solutions with various sulfuric acid concentrations revealed that, with decreasing sulfuric acid concentration, the peak potential became more negative and the diffusion current constant became larger. The somewhat arbitrary value of 6 M sulfuric acid was finally decided upon as the polarographic medium.

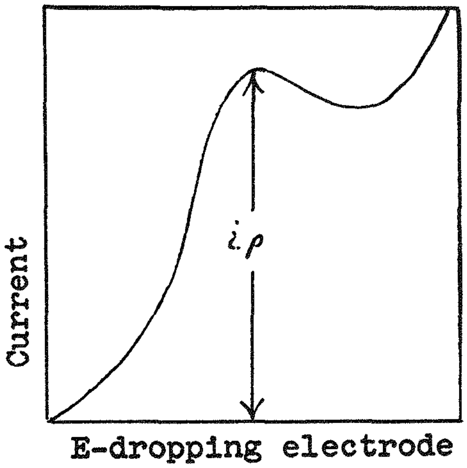

Figure 1. Niobium peak in 6 M H_2SO_4.

EXPERIMENTAL

Apparatus

The polarograph used was the K1000 Polarotrace manufactured by Southern Instruments, Computer Division, of England. A thermostated H-type polarographic cell was used. The saturated calomel reference electrode was isolated by a sintered glass disc and a potassium-chloride agar bridge.

Reagents

Analytical-grade reagents were used throughout. The niobium standard solution was prepared from the pure metal.

Procedure

For alloys containing one to five per cent niobium, weigh out 0.5 gram of sample. Dissolve the sample in a 125-ml Erlenmeyer flask with two ml of sulfuric acid, two ml of hydrochloric acid, two ml of fluoboric acid, and 15 ml of water. The sample may be heated gently during dissolution. At this stage, the solution may take on a brownish color due to the presence of niobium(III).(1) Next, add 14.5 ml of concentrated sulfuric acid and heat to fumes. Cool the resulting sulfuric acid solution and transfer it to a 50-ml volumetric flask. Dilute to the mark with water, being sure the solution is adequately cooled as this is done, and transfer the solution to the polarographic cell. Deaeration of the solution was found to be unnecessary.

Variations of the apparent peak potential were observed from sample to sample. Therefore, to insure that the peak height is measured at the same point in the life of each drop, the niobium peak is first positioned at 0.25 on the x-axis of the grid by means of the start-potential control. Next, the start of the sweep is fixed at zero on both axes, using the x and y shift controls. The sensitivity is adjusted to give a convenient peak height which is measured directly from the grid.

CALIBRATION

The niobium content of the samples is determined by comparison with standard niobium solutions. The standards are prepared by taking appropriate aliquots of a stock solution of niobium in 50-per cent sulfuric acid, adding 0.5 gram of zirconium or Zircaloy, and carrying each through the procedure. The niobium in the samples is then readily determined from the resulting calibration curve.

RESULTS AND DISCUSSION

Typical analytical results for a number of zirconium-base alloys containing various amounts of niobium are found in Table I. The result for each run was obtained on a separately dissolved sample.

TABLE I

NIOBIUM VALUES FOUND POLAROGRAPHICALLY FOR SEVERAL ZIRCONIUM-BASE ALLOYS

Sample	Niobium Found (%)	
	Run 1	Run 2
A	1.10	1.05
B	1.77	1.80
C	1.84	1.87
D	1.99	1.93
E	2.01	1.97
F	2.17	2.17
G	2.23	2.23
H	2.31	2.34
I	2.42	2.48
J	6.61	6.68

Forty samples of an alloy with about 2 per cent niobium and 2.5 per cent tin were analyzed in duplicate as described above. A statistical analysis of the results obtained yielded a standard deviation of ± 0.022 per cent (± 1.0 per cent relative) and 95-per cent confidence limits for a single measurement of ± 0.04 per cent (see Appendix).

The method described is rapid and direct. Twelve samples can readily be analyzed per day. There is no interference from tin; however, if chromium is present, it will interfere since its peak occurs at about the same potential as niobium. In such an event, a separation or an appropriate correction would be necessary. Large amounts of tantalum will also interfere, but its behavior in this medium has thus far been so unpredictable that a correction for it could not be made.

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APPENDIX

The following results were used to compute the standard deviation and 95-per cent confidence limits for the method when applied to zirconium-base alloys with 2 per cent niobium and 2.5 per cent tin.

TABLE II

VALUES OBTAINED FOR NIOBIUM IN ZIRCONIUM-BASE ALLOYS CONTAINING 2 PER CENT NIOBIUM AND 2.5 PER CENT TIN

	Niobium Found	
Sample	Run 1	Run 2
	Per Cent	
1	1.99	1.93
2	1.97	1.97
3	2.16	2.17
4	1.90	1.93
5	2.02	2.02
6	1.99	2.06
7	1.92	1.92
8	2.25	2.21
9	2.17	2.17
10	2.00	2.05
11	1.83	1.89
12	1.92	1.83
13	2.00	1.95
14	1.88	1.81
15	1.70	1.65
16	2.05	2.00
17	2.15	2.15
18	1.97	2.01
19	2.25	2.26
20	2.42	2.48
21	1.80	1.86
22	2.06	1.98
23	2.43	2.49
24	1.90	1.93
25	2.51	2.51
26	2.17	2.20
27	2.13	2.20
28	1.84	1.87
29	2.21	2.19
30	1.82	1.82
31	1.79	1.80
32	1.88	1.91
33	2.26	2.22
34	2.20	2.23
35	2.30	2.32
36	1.84	1.88
37	1.99	2.07
38	2.23	2.23
39	2.31	2.34
40	2.12	2.07

GAS CHROMATOGRAPHIC DETERMINATION OF HELIUM IN NEUTRON-IRRADIATED BERYLLIUM OXIDE

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ABSTRACT

A method has been devised for the separation and determination of micro quantities of helium in beryllium oxide that has been irradiated in nuclear reactors. As little as 3 ppm of helium have been separated and subsequently determined by gas-solid chromatography. From the quantities so far tested, it is indicated that fractional parts per million of helium can be separated and determined. The beryllium oxide samples, approximately 14 g each, which are obtained as cylindrical pellets, are digested for twenty-four hours in a hydrofluoric acid-potassium fluoride mixture at a temperature of 120 to 130°C in an evacuated, silver-plated, copper vessel. At the end of the digestion period the reaction vessel, as well as a trap, is cooled to liquid nitrogen temperature and the non-condensable gases are pumped off through a vacuum manifold into twin sample bulbs. The gas in one bulb is retained for mass spectrometric analysis. The gas in the other bulb is cycled through a hot copper oxide tube and a cold trap in order to convert any tritium and hydrogen to water. This bulb is then transferred to a second vacuum manifold, and the gas is pumped into a 1-cc transfer loop which has been designed for the injection of gas samples into a Perkin-Elmer Model 154 Vapor Fractometer. The helium is then determined gas chromatographically, using nitrogen as the carrier gas, and Linde 5A Molecular Sieve in a column which is 8-feet long and 3/8-inch outside diameter.

Work carried out under contract No. W-7405-eng-26 at Oak Ridge National Laboratory, operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

INTRODUCTION

Beryllium oxide, because of its small capture and high-scattering cross-section for neutrons, and its refractory properties, has distinct advantages for use as a moderator and neutron reflector in nuclear reactors. Under neutron bombardment, however, beryllium is subject to gas formation due to an (n,α) reaction. The product, He^6, with a half-life of less than one second, decays to Li^6 which also is subject to an (n,α) reaction. This formation of helium results in adverse effects nuclearwise on the moderator. Therefore, a measure of the helium content of a sample of beryllium oxide is of great value in evaluating the performance of beryllium oxide as a moderator.

Procedures for the determination of helium in mineral materials have been known for 35 years or more.(1,2,3,4,5) These methods involve solution or fusion of the sample, generally, but not necessarily,(2) in an evacuated system. The procedures used for the determination of helium include isotope dilution,(1) PV measurement,(3) spectroscopy,(4) and mass spectrometry.(5) With the advent of gas chromatography, a new tool has been made available for the separation and determination of the components of gaseous mixtures. Under the proper conditions, helium can be determined gas chromatographically in a complex mixture, by virtue of the fact that the other constituents of the mixture may be retained on the chromatographic column, while the helium essentially is not.(6,7) The procedure which is described below, involves the relatively low-temperature fusion of beryllium oxide pellets with a flux of potassium fluoride and anhydrous hydrogen fluoride, in an evacuated system. The evolved gas is collected and analyzed gas chromatographically, using a Linde 5A Molecular Sieve column and nitrogen as the carrier gas. When a determination of the tritium content is desired, the gas is first cycled through a hot copper oxide tube, and the water is removed in a cold trap.

EXPERIMENTAL

Apparatus

Fusion and extraction apparatus: A photograph (Figure 1) and a schematic diagram (Figure 2) are shown. This apparatus consists of three major segments: the hydrogen fluoride manifold, the reaction vessel, and the vacuum manifold. The hydrogen fluoride manifold consists of an assembly of copper tubing and Dahl diaphragm valves arranged to permit connection of the reactor to a hydrogen fluoride cylinder and to a bourdon pressure-vacuum gauge.

The vacuum manifold consists of the necessary tubing, stopcocks and traps, connected to a diffusion pump, to create and maintain pressures of 1 micron or less. A Hastings thermocouple gauge is used for pressure measurements. A Toepler pump with an automatic controller is used to pump the evolved gas into either the sample bulb or a sample transfer loop. A copper oxide train can be added to the manifold when desired. If the gas is to be pumped directly into the sample transfer loop, evacuation of the loop is effected by means of simple glass tubing connections.

The reaction vessel (Figure 3) is constructed of standard copper fittings which have been silver-soldered together. The whole device is then silver-plated on the inner surfaces. Two Hoke 413 diaphragm valves are used to isolate the reactor from the hydrogen fluoride manifold and from the vacuum manifold. A piece of 3/8-inch copper tubing, sealed at one end, is inserted through the top for use as a thermometer well.

Automatic pump controller: An automatic pump controller (Figure 4), similar to the one described by Goldberg, Meyer and White,(8) is used in order to lift the mercury beyond the upper contact so that the gas may be pumped into a sample bulb or sample transfer loop. The controller has the added feature of a time delay which operates when the mercury is in the "down" position. This allows sufficient time for the gas to expand into the upper portion of the pump, and it becomes increasingly helpful as the pressure decreases.

Vacuum transfer manifold: This manifold (Figure 5) is for the transfer of gases at less than atmospheric pressure from a sample bulb to a special transfer loop. It is essentially the same as the vacuum manifold described above, but all parts are accurately calibrated as to volume. Bulbs of known volumes are used when establishing calibration curves for standard gases. In addition to a Hastings gauge, a McLeod gauge is used for absolute pressure measurements.

Sample bulb: This device (Figure 6) consists of twin bulbs of approximately 5 ml each, separated by a 3-way stopcock. As this sample bulb is generally used, the portion of the gas in the upper bulb is held for mass spectrometric analysis, or gas chromatographic analysis of the whole gas. The portion of the gas in the lower bulb is cycled through the copper oxide train in order to remove hydrogen and tritium, and then the residual gas is analyzed gas chromatographically.

Sample transfer loop: This loop (Figure 10) has been devised for use with the Perkin-Elmer Vapor Fractometer. It is similar in concept to others which have been described, as for example, the one by Russell and Bednas.(9) The loop is connected to the sample valve of the Vapor Fractometer by means of special metal ball joints which fit into the sample loop ports. The sample ports are flushed with the carrier gas by means of the by-pass portion of the transfer loop.

Gas chromatograph: Perkin-Elmer Vapor Fractometer 154C with an 8-foot column of 3/8-inch stainless steel tubing. Linde 5A Molecular Sieve is used as the active solid.

Reagents

Anhydrous hydrogen fluoride.

Potassium fluoride, reagent grade.

The flux is prepared by weighing 225 grams of potassium fluoride into the lower portion of the reaction vessel. The vessel is assembled and evacuated. The vessel is then opened to the hydrogen fluoride manifold, and the latter is evacuated up to the cylinder. When the outgassing is complete, the line to the vacuum manifold is shut off and the hydrogen fluoride cylinder is opened to the reaction vessel. Outgassing of the cylinder is necessary on the first charging operation. The addition reaction is allowed to proceed to equilibrium which may take approximately eight hours. As considerable heat is generated, it is desirable to run some water through the cooling coils. The reaction may be considered complete when the pressure has stabilized at room temperature, at which point the equilibrium pressure is approximately 5 psig and the composition of the charge is approximately 2 $KF \cdot 5HF$. The reactor is then isolated and cooled by a liquid nitrogen bath. The reactor is evacuated, and then heated to about 125°C by means of an ethylene glycol bath. The freezing, evacuating and heating cycle is repeated until all non-condensable gases are removed.

Procedure

A weighed pellet of beryllium oxide (approximately 14 g) is added to the flux in the bottom portion of the reaction vessel; the two parts are assembled and the system is thoroughly evacuated. The fusion is carried out by heating the flux and sample to a temperature of 120°C to 130°C, and maintaining a steady temperature for a period of 24 hours. At the end of this time, the reaction vessel and cold traps are again frozen with liquid nitrogen. The diffusion pump is closed off, and the gas from the reaction vessel is allowed to expand into the vacuum manifold. The sample gas is pumped, by means of the Toepler pump, into the double sample bulb. The portion of the gas in the lower bulb is cycled through the hot copper oxide tube until there is no further reduction in pressure. The residual gas is then pumped back into the lower bulb. As an alternate method, the entire sample may be pumped directly into the sample transfer loop.

The sample bulb is connected to another vacuum manifold that is used for handling samples of gas which are at less than atmospheric pressure. The transfer of gas is accomplished in much the same manner as described above. The gas in the sample bulb is expanded into the evacuated manifold and into a McLeod gauge which has a range of 1 to 1000 microns. The sample is then pumped, by means of the Toepler pump, into the transfer loop. The transfer loop is attached to the sample valve of the Vapor Fractometer, and the sample is injected after first flushing the sample valve with the carrier gas. The chromatographic conditions are as follows:

Instrument:	Perkin-Elmer Vapor Fractometer 154-C.
Column:	Stainless steel tubing 8-feet long, 3/8-inch O.D. Linde 5A Molecular Sieve, 35-50 mesh.
Carrier gas:	Nitrogen, 50 ml/min. P_i, 20 psig P_o, atm.
Temperature:	100°C.

A Leeds and Northrup Speedomax G recorder with a 0-1 mv range and a chart speed of 2 inches per minute was used.

Discussion of Results

A chromatogram of a portion of sample gas is shown in Figure 8. It will be noted that the peaks for helium and hydrogen are quite close together, although at these relative concentrations, the resolution is adequate. The corrected retention volumes, V_R^0,(10) are 85 and 115 ml, respectively. While hydrogen apparently does not interfere with the determination of relatively large quantities of helium, it is obvious that large quantities of hydrogen will interfere with the determination of small amounts of helium. Consequently, it would seem desirable to cycle the sample gas through copper oxide. The third peak shown on the chromatogram is that of argon, which was initially used as the flush gas for the reaction vessel.

A chromatogram of a sample of pure helium gas is shown in Figure 7. It was found that the corrected retention volume increased as the size of the sample increased. For a 340-µl sample, the figure is 80.6 ml. A calibration curve, Figure 9, was prepared for the determination of helium in the range of approximately 5 to 500 µl at STP. The curve is linear, with a precision of 2.5% up to the region of 200 µl. Experience with other gases has indicated that a precision of 2 to 3 per cent can be expected over the entire range.

At present, data pertaining to actual sample analyses are quite incomplete; only two samples have so far been submitted for analysis. The helium content of these samples was determined to be 2.7 and 3.1 ppm.

From the quantities of gas obtained from these samples, indications are that a sensitivity of 0.1 ppm can be attained. Blank determinations have been made on the flux material, and no measurable quantity of helium was found.

In conclusion, a relatively simple procedure has been devised for the extraction and determination of minute quantities of helium in beryllium oxide. The beryllium oxide is fused with a potassium acid fluoride flux at a temperature of about 125°C in an evacuated system. The evolved gas is compressed into a small sample bulb, and the hydrogen and tritium are removed by hot copper oxide. The helium content of the gas is then determined by means of gas chromatography.

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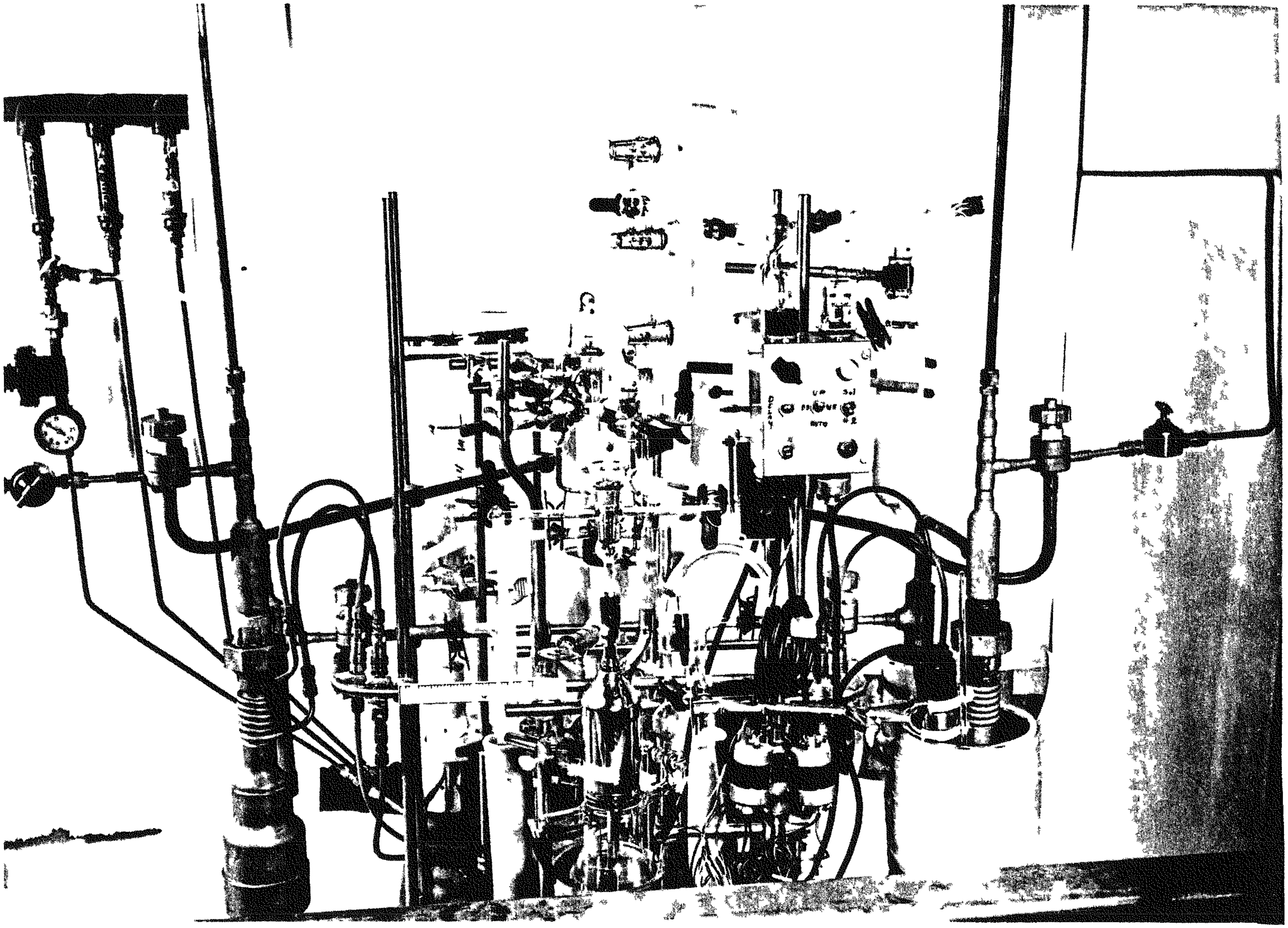


Fig. 1: Apparatus for Extraction of Helium from BeO

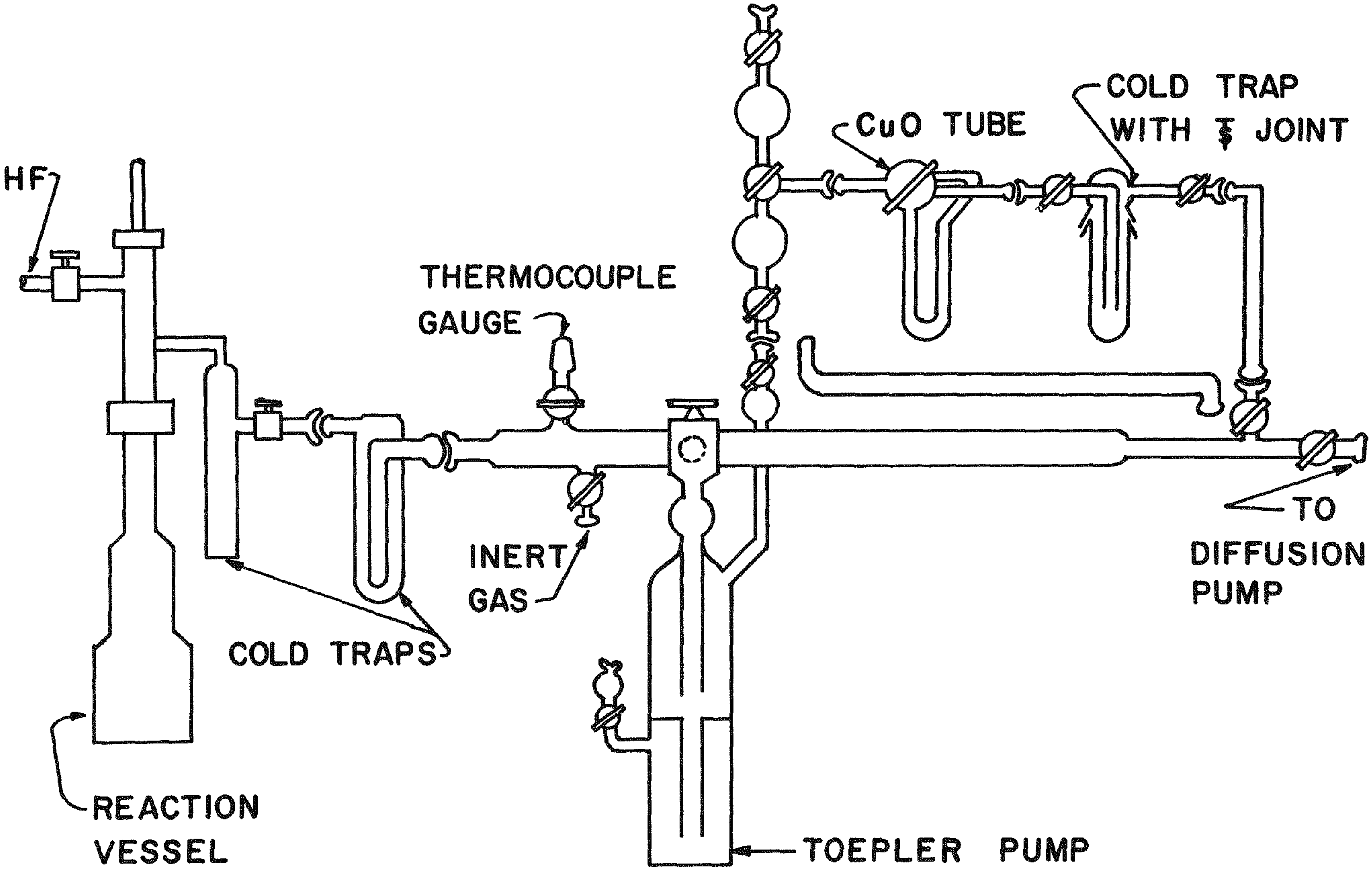


Fig. 2: Schematic Diagram of BeO Apparatus

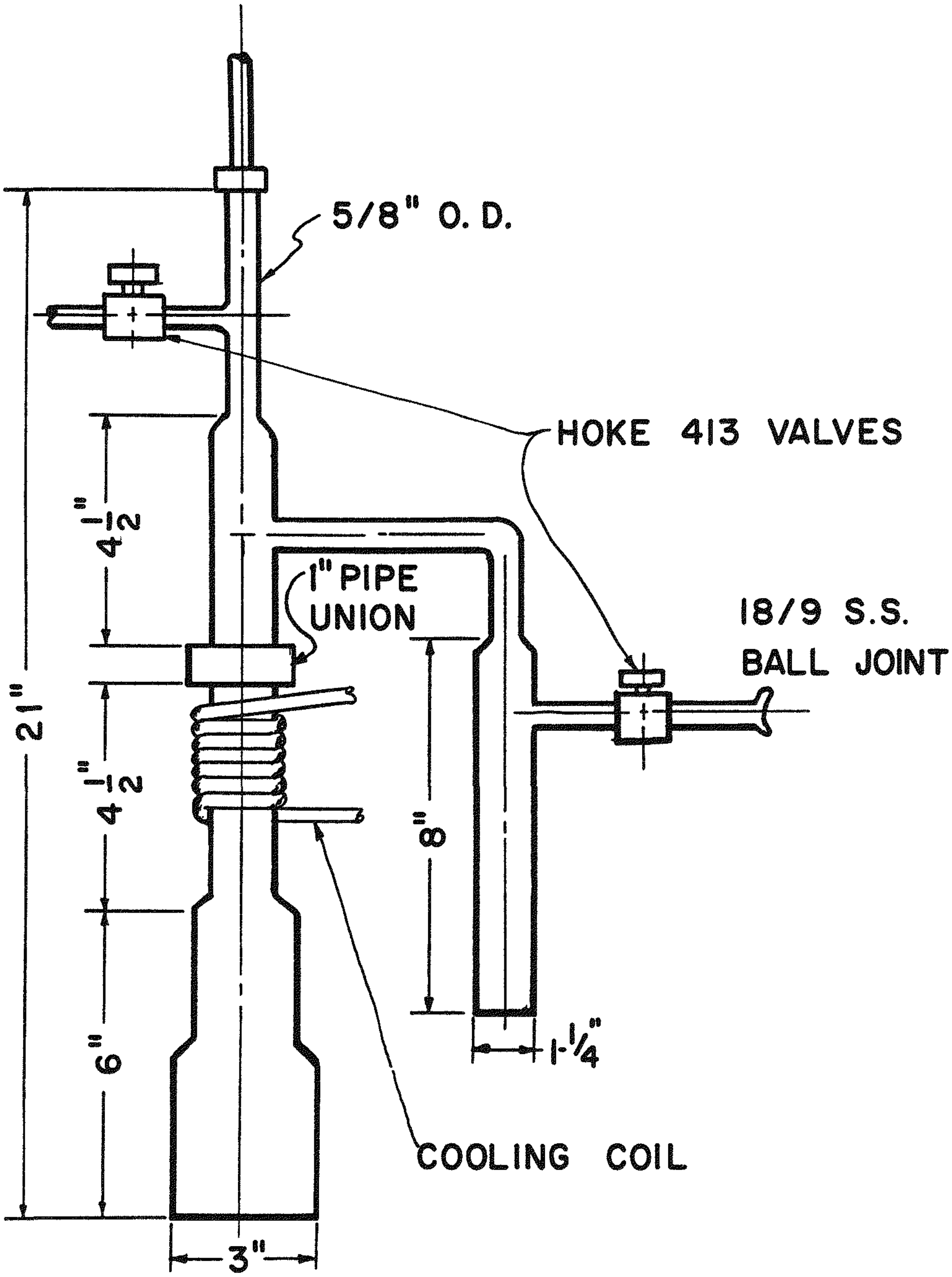
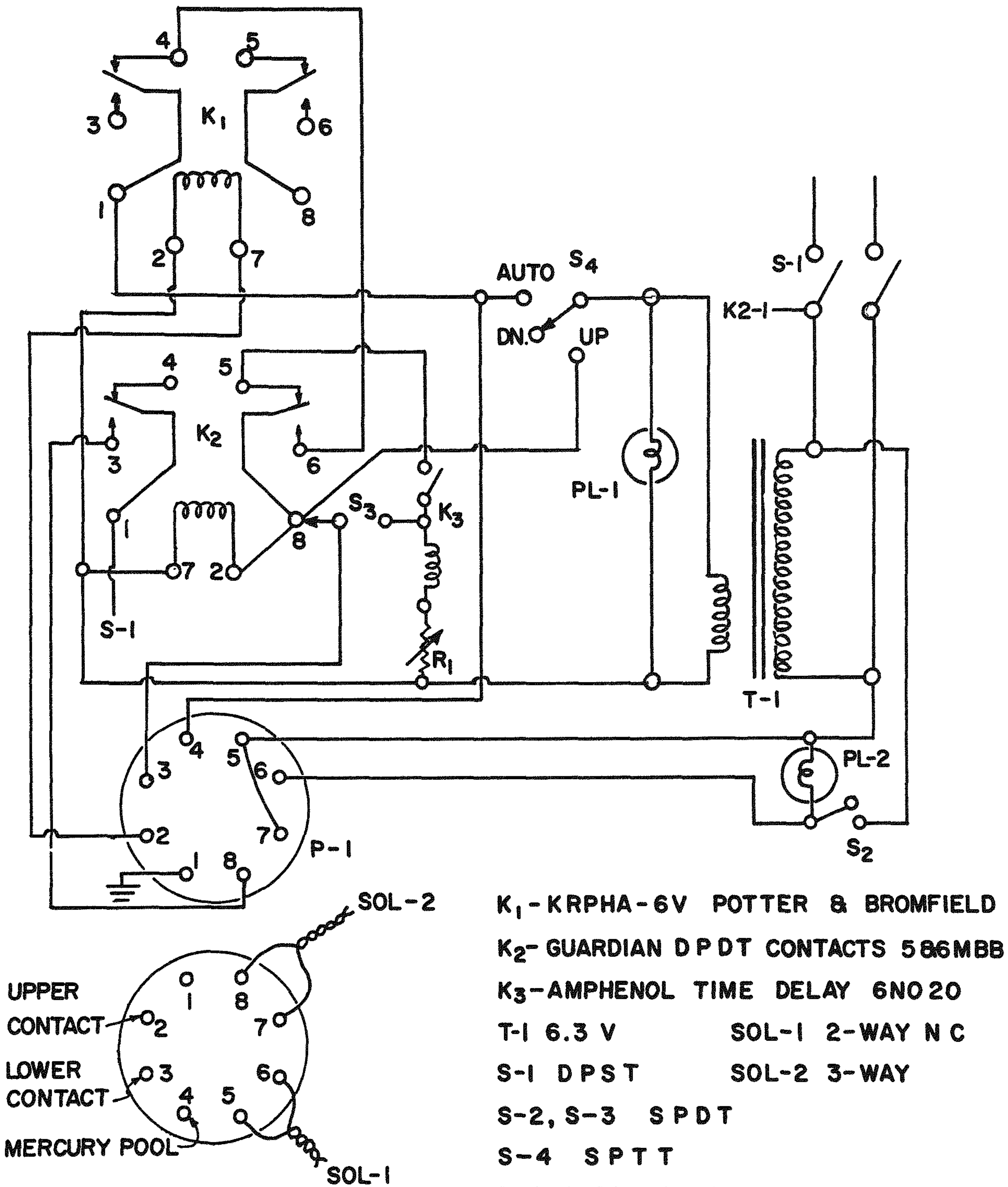


Fig. 3: Reaction Vessel for the Separation of Helium from BeO



K_1 - KRPHA-6V POTTER & BROMFIELD
K_2 - GUARDIAN DPDT CONTACTS 586MBB
K_3 - AMPHENOL TIME DELAY 6NO20
T-1 6.3 V
SOL-1 2-WAY N C
S-1 DPST
SOL-2 3-WAY
S-2, S-3 SPDT
S-4 SPTT
P-1 8-PIN OCTAL.
R-1 25 Ω

Fig. 4: Toepler Pump Control

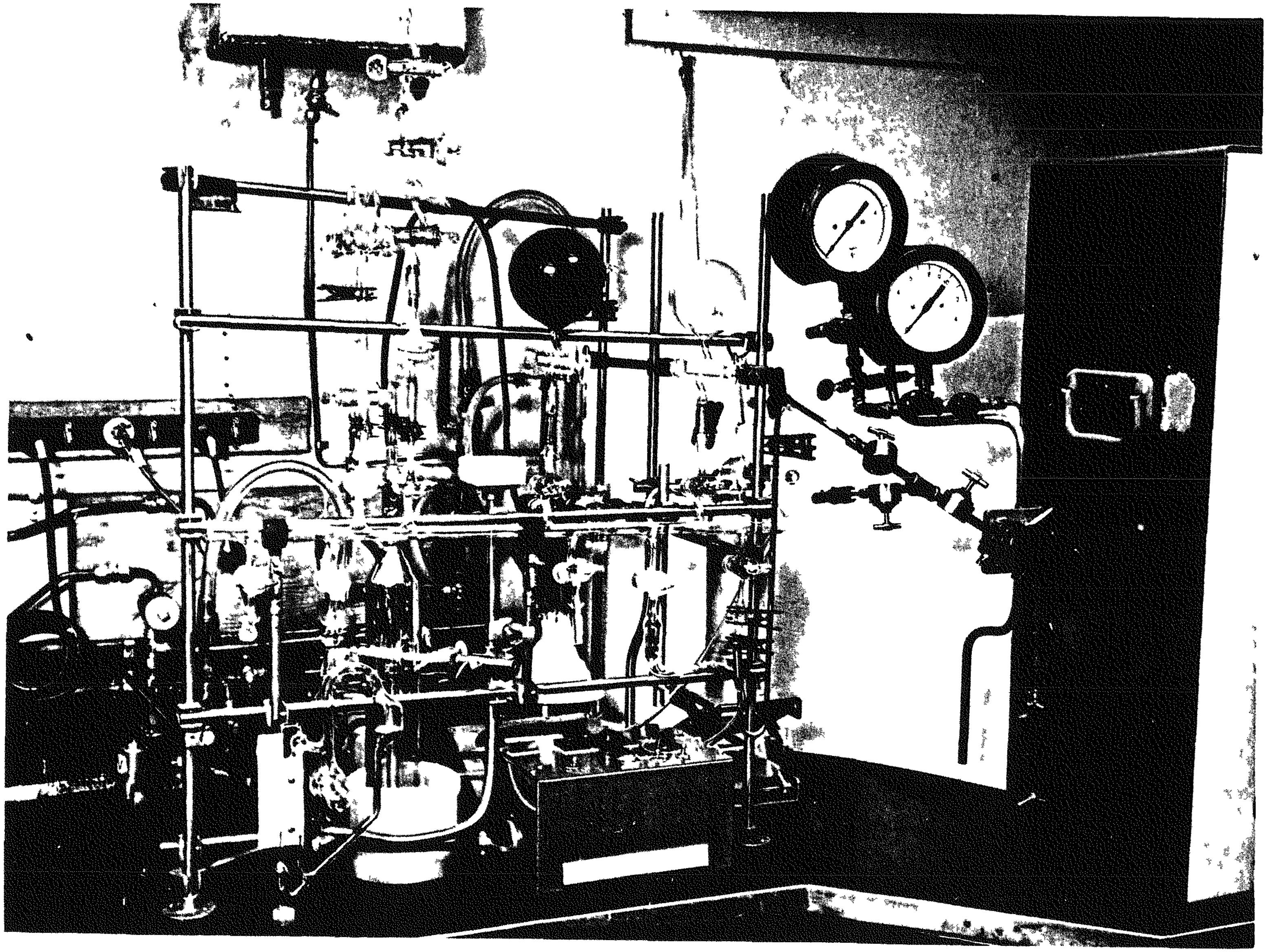


Fig. 5: Vacuum Transfer Manifold

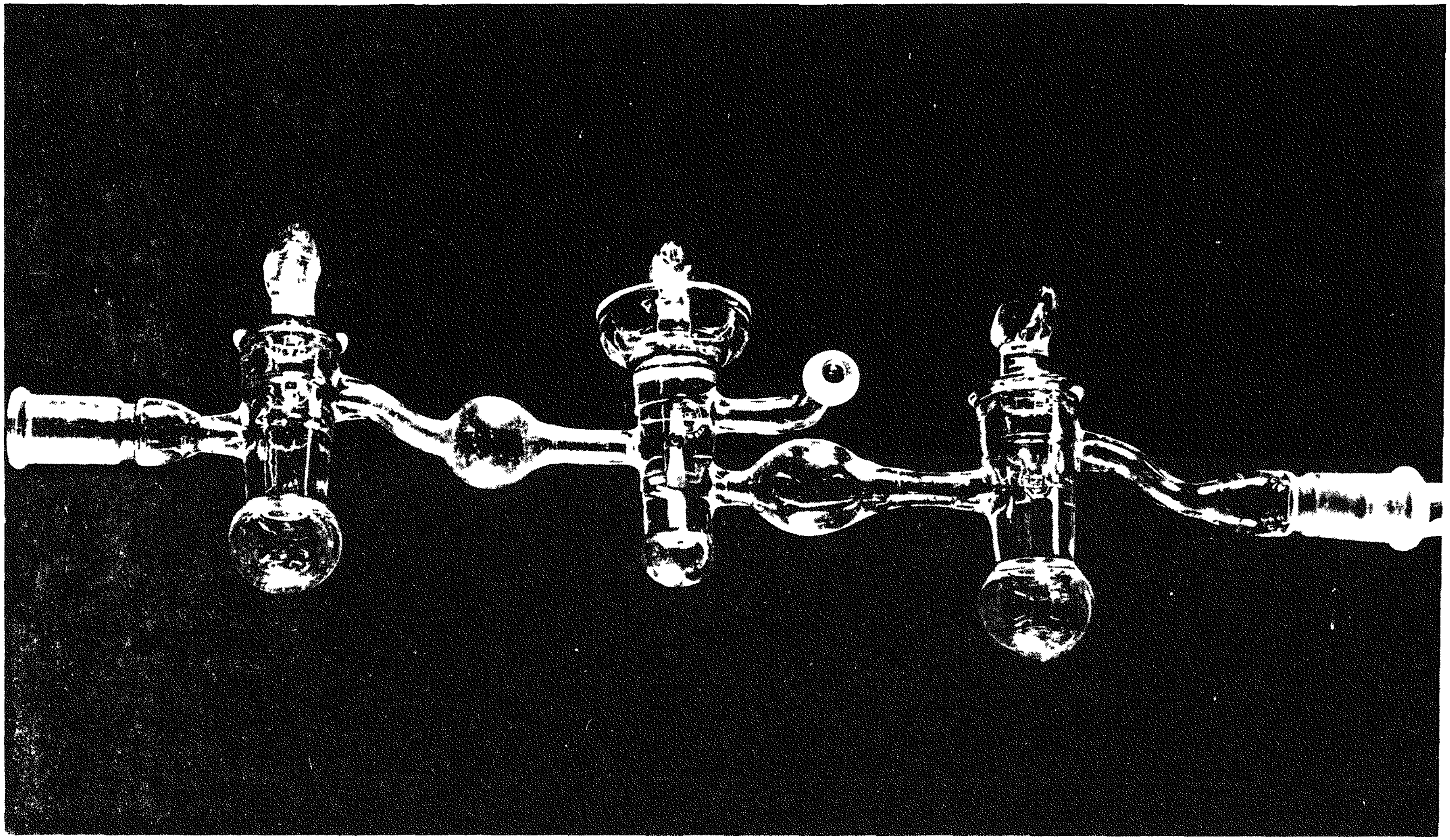


Fig. 6: Double Sample Bulb

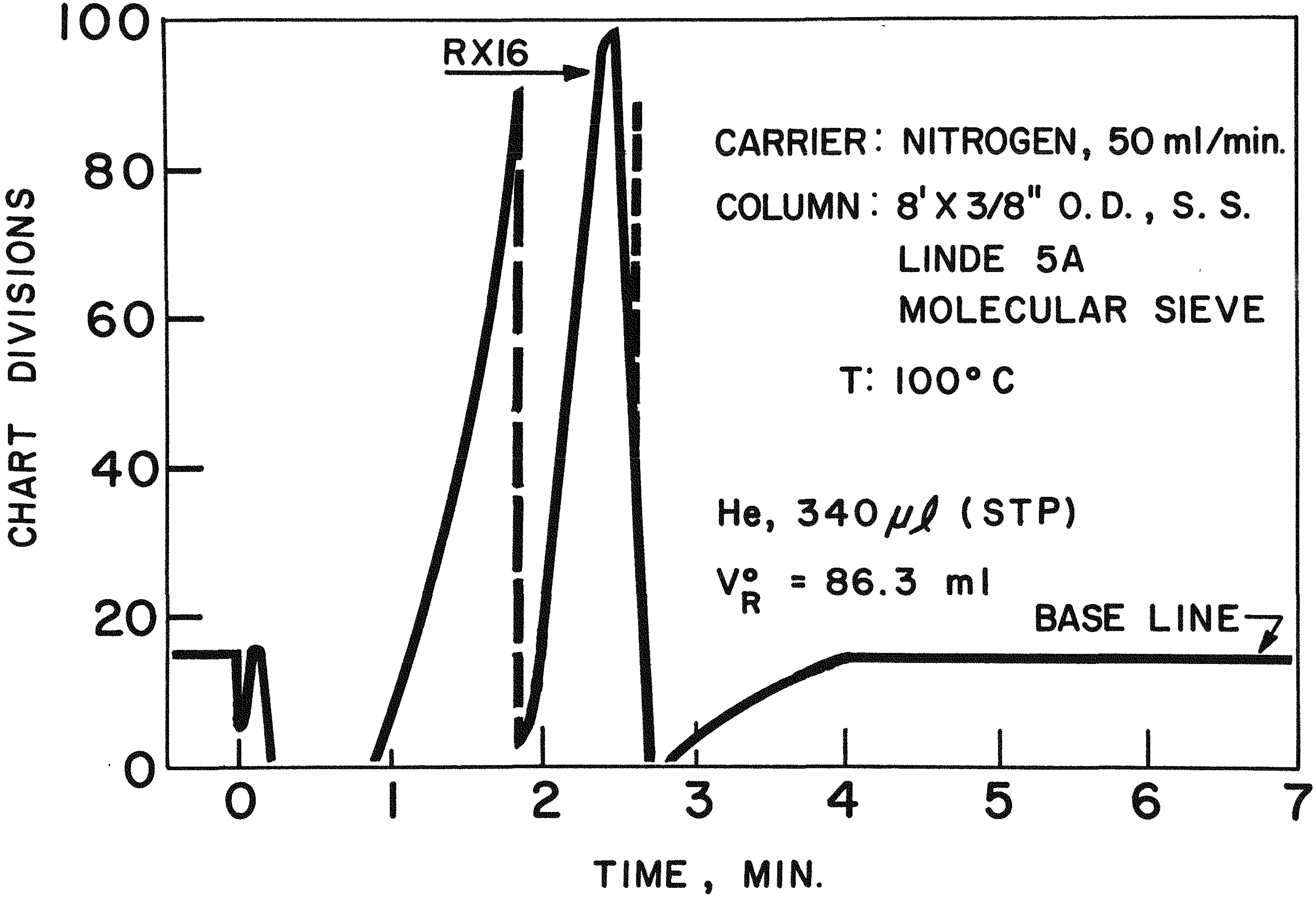


Fig. 7: Chromatogram of Pure Helium

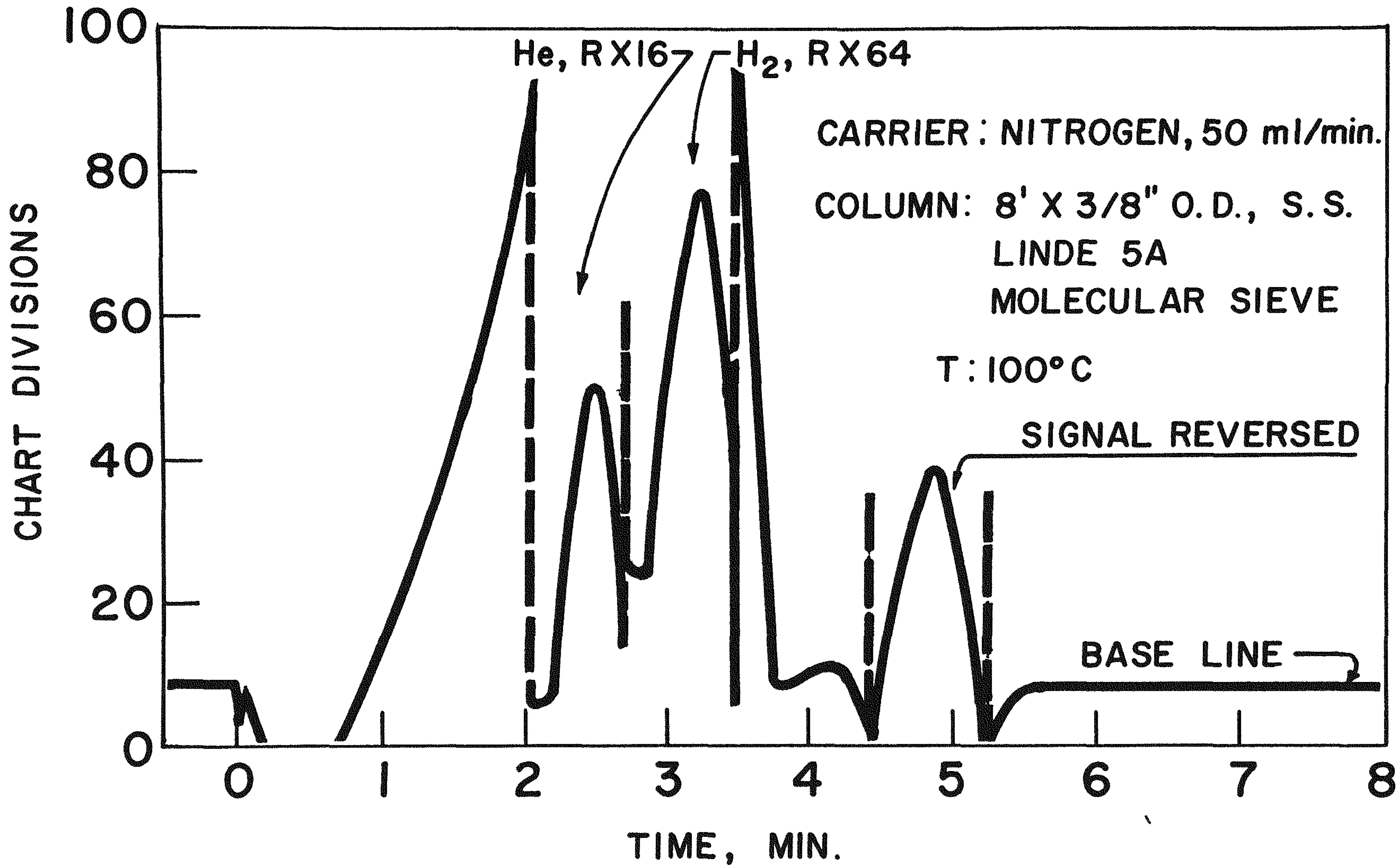


Fig. 8: Chromatogram of BeO Off-Gas

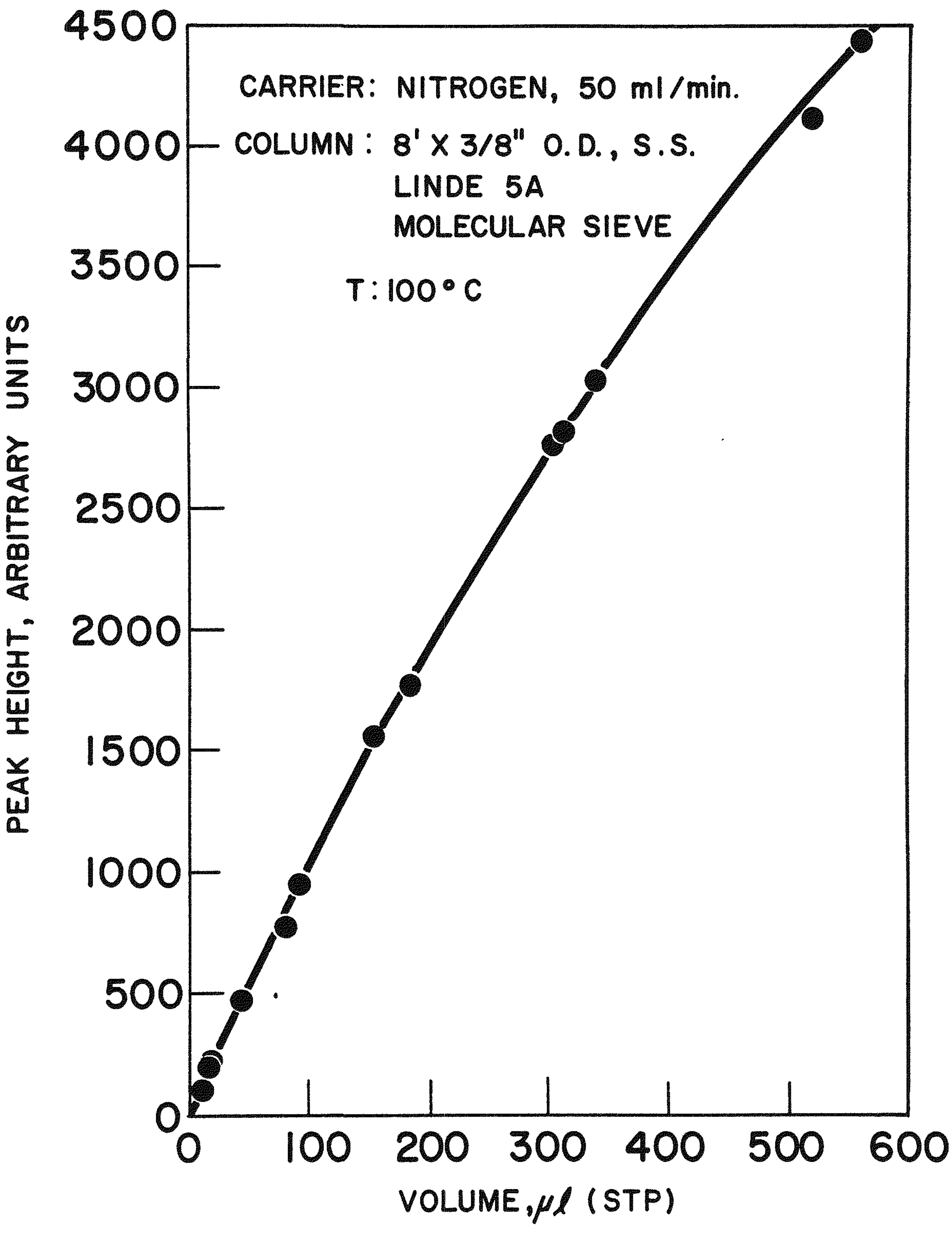


Fig. 9: Calibration Curve for Helium

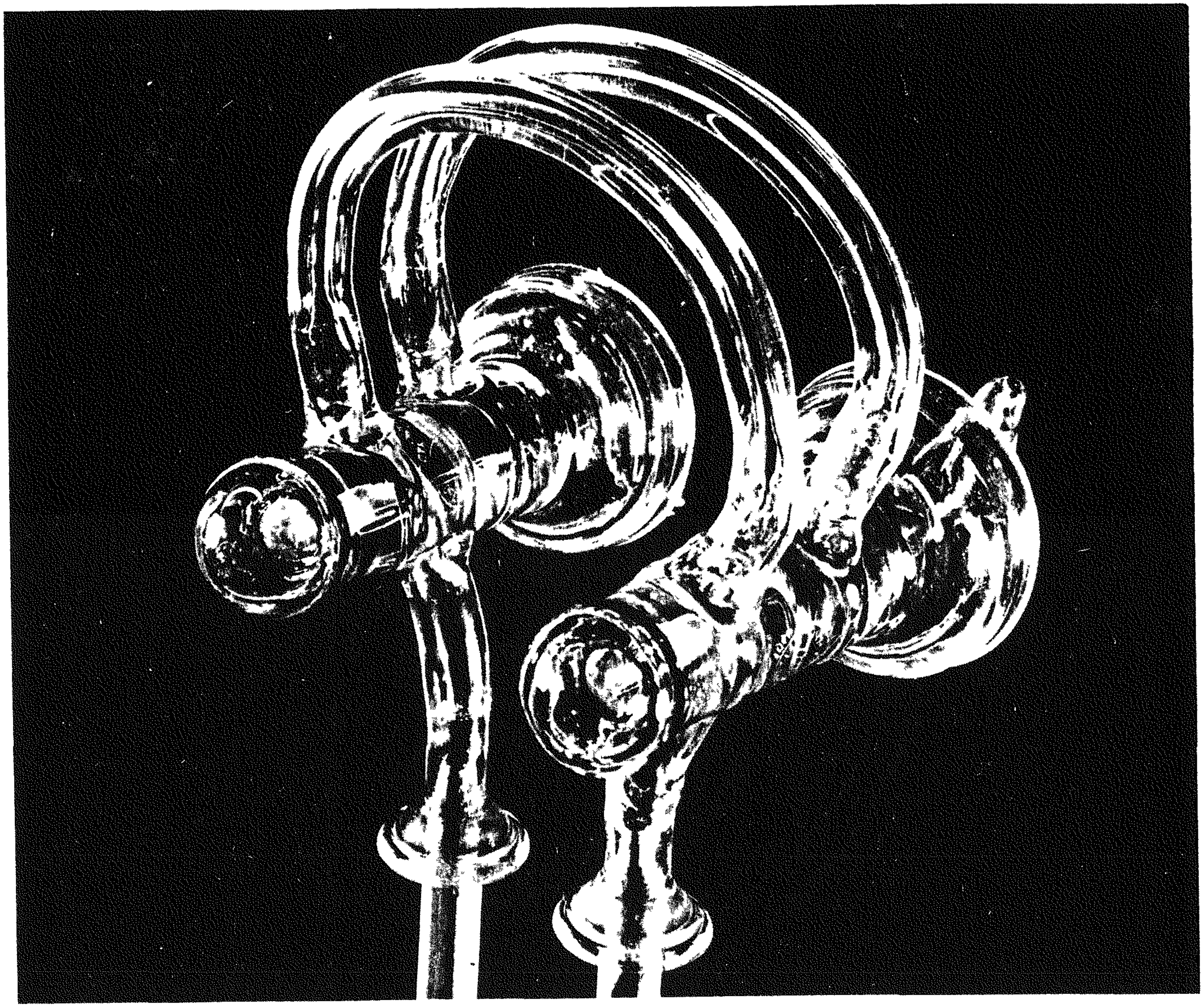


Fig. 10: Sample Transfer Loop

SEPARATION AND COLORIMETRIC DETERMINATION OF TRACE QUANTITIES OF MAGNESIUM IN HIGH-PURITY BERYLLIUM OXIDE

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ABSTRACT

A colorimetric method is described for the determination of trace quantities of Mg in Be and BeO. Be, which is known to interfere with the colorimetric determination of Mg by the available chromogenic reagents, is selectively separated from the Mg by forming Be perfluorobutyrate at pH 3 to 4 and then extracting this Be salt with several portions of diethyl ether. By increasing the number of equilibrations with ether, as much as 1 g of Be can be separated from 10 μg of Mg. The Mg is then measured spectrophotometrically as the highly colored complex with Magon, Na 1-azo-2-hydroxy-3-(2,4-dimethyl-carboxanilido)naphthalene-1-(2-hydroxybenzene-5-sulfonate), which exhibits a peak of maximum absorbance at 510 mμ. Over the range of 0.04 to 0.40 μg of Mg per ml, the absorbance conforms to Beer's law. The method has been applied successfully to the determination of quantities of Mg as low as 10 μg. The coefficient of variation for samples which contain 200 μg of Mg is 2%.

EDITOR'S NOTE

This paper is omitted from the Proceedings because it has been submitted to Talanta for publication.

ANALYSIS OF URANIUM DIOXIDE CERAMIC FUEL MATERIALS FOR THE SHIPPINGPORT PRESSURIZED-WATER REACTOR

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ABSTRACT

In the development and fabrication of UO_2 and UO_2-containing ceramic materials for Shippingport PWR cores 1 and 2, close analytical inspection is required for raw material, "in-process" material, and finished products. In addition to determining the composition of the UO_2, analyses are required for various impurity elements. As a result, a program of analytical method development and modification was initiated.

The determination of the exact composition of the U oxide is accomplished by two methods:

1. Volumetric determination of the total U content by titration with standard $K_2Cr_2O_7$.

2. Polarographic determination of the U(VI) content in an H_3PO_4-H_2SO_4 electrolyte. The U(VI) value is used to determine the O:U ratio and thus the stoichiometry of the oxide. An NH_4HF_2 fusion is used for urania-zirconia ceramics. Polarography of the U(VI) is conducted in an H_2SO_4-H_3BO_3 solution of the melt.

Some of the impurity elements found in U oxide and methods of wet chemical analysis are:

Al (20 to 250 ppm). - U is separated by anion exchange; interferences in the eluate are removed with 8-hydroxyquinaldine followed by colorimetric determination of Al with oxine.

Cd (0.5 to 2 mg). - Cd is extracted at pH 1 with Na-diethyldithiocarbamate in $CHCl_3$ and determined polarographically in 0.1 $\underline{M}$ KCl.

F. - Fluoride is separated by pyrohydrolysis and determined by the Th-thoron lake method.

Fe. - Fe is determined colorimetrically with o-phenanthroline.

Si. - Si is determined colorimetrically as the silicomolybdate blue.

B. - B is separated by pyrohydrolysis and determined colorimetrically with quinalizarin or diaminochrysazin (topic of separate paper).

In the field of UO_2 ceramic materials, wet chemical analysis has been extended to cover:

Zr. - Zr is determined gravimetrically by precipitation with mandelic acid.

Th. - Th is determined gravimetrically by precipitation with NH_3 after a double fluoride separation.

Rare-earth oxides and yttria. - These elements are determined by a method similar to that used for the determination of Th in UO_2.

Ca. - Ca is determined gravimetrically as the oxalate after an NH_3 precipitation of U and Zr or by a complexometric titration with EDTA, following an NH_3 precipitation.

To a large extent, most of the wet chemical analyses of UO_2-base fuel materials carried out at the Bettis Laboratory are an adjunct to, or in direct support of, the spectrographic determination of impurities.

In the spectrographic analysis of UO_2 for impurities, the AgCl-carrier distillation technique was utilized for the determination of B, Cd, Cr, Cu, Fe, Mo, Ni, Pb, Si, and Sn. Only occasional routine production control analyses are necessary because the raw material is of very high purity and, in the fabrication process, the amounts of metallic impurities introduced are too small to warrant close control.

The spectrographic analysis of the UO_2-ZrO_2 ceramic fuel is made in much the same manner. The AgCl carrier is, however, replaced with a mixture of AgCl, BaF_2, and graphite for the analysis of B, Cd, and Si; and, for the analysis of W, the samples are mixed with In_2O_3 and excited in a low-current arc. In addition to the elements mentioned, Cu, Pb, Mg, Sn, Be, Ti, V, Cr, Co, Ca, Mn, Mo, Al, Fe, and Ni are determined in this material. Impurity levels varied from a few ppm for those elements present in the raw materials to a few per cent for those elements introduced during fabrication. Because of the high density of the UO_2-ZrO_2 ceramic material, difficulties were encountered in the preparation of standards and in volatilization of impurities. Specially prepared standards were necessary to overcome these problems. The sintered platelets were extremely hard. Consequently, it was impossible to grind samples for analysis without contamination from the mortar material. Samples were ground in mortars made of Al_2O_3, WC, B_4C, steel, agate, and Zr metal in order to circumvent the pickup of impurities prior to analysis. The most satisfactory mortar from this standpoint was found to be one made of Zr.

A detailed description of the apparatus and conditions utilized is given along with chemical comparison data.

EDITOR'S NOTE

At the request of the authors, this paper was omitted from the *Proceedings*.

AMPEROMETRIC TITRATION OF PLUTONIUM(VI) WITH IRON(II)

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ABSTRACT

A method is described for the amperometric titration of Pu(VI) with Fe(II). Chloride and nitrate solutions are fumed to near dryness with H_2SO_4. The residue is taken up in dilute H_2SO_4, and the Pu is then oxidized to Pu(VI) with AgO. After destruction of the excess AgO by heating, the Pu is titrated with a standard $FeSO_4$ solution, using a rotating Pt-Hg_2SO_4 electrode system. An additional 0.6 v is impressed on the system to maintain the Pt electrode at 1.2 v vs N.H.E. The titrant is delivered from special weight burets fabricated from 1-oz polyethylene bottles.

The coefficient of variation for aliquots containing 10 to 20 mg of Pu is 0.05 per cent. For aliquots containing 100 to 200 µg of Pu, the coefficient of variation is 0.5 per cent. An average value of 99.97 per cent Pu was obtained in the analysis of a sample of metal, the purity of which was reported to be 99.98 per cent.

U and Fe, the two metals most commonly associated with Pu and which interfere in several other methods of analysis, do not interfere in this method. Cr, Mn, and other metals which are oxidized by AgO and reduced by Fe(II) interfere.

EDITOR'S NOTE

This paper is omitted from the Proceedings because it is to be submitted to Analytical Chemistry for publication.

METHODS FOR ANALYSIS OF POLYPHENYL REACTOR COOLANTS

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ABSTRACT

In the study of organic-moderated and-cooled reactors, methods are required for the determination of the coolant components and their pyrolytic-radiolytic decomposition products. Methods developed and used to study the behavior of polyphenyl coolants used in the OMRE are presented. The methods can be used for the quantitative determination of initial coolant components, some individual decomposition products, and gross chemical properties of irradiated coolants as well as separated fractions or groups of decomposition products.

The initial coolant components (biphenyl; o-, m-, and p-terphenyl) are determined by gas chromatography at 300°C, using peak-height measurements with reference to an internal standard (triphenylmethane) after the determination of appropriate calibration factors. A precision of 0.5% absolute is obtained in the analysis of coolants which contain up to 40% of high-boiling components.

Decomposition products are grouped according to boiling points as follows:

Group	Volatility
Low boilers (LB)	> benzene, < biphenyl
Intermediate boilers (IB)	> biphenyl, < p-terphenyl
High boilers (HB)	> p-terphenyl

Low boilers are determined by gas chromatography. Benzene, toluene, and ethylbenzene are determined using o-xylene as an internal standard. The other low boilers, designated OLB, are determined by peak-area measurement with reference to the area of the biphenyl peak. Compounds known to be present in the OLB fraction are p-ethyltoluene, m- and p-xylene, n-propylbenzene, n-butylbenzene, and indane.

Intermediate boilers make up about 3 to 6% of the decomposition products. Compounds known to be present in this fraction are fluorone, phenanthrene, 3-methylbiphenyl, and 9-fluorenone.

Triphenylene (an HB component) is determined in coolant samples by ultraviolet spectroscopy with an accuracy of 5 to 10%, relative to the amount present.

The HB content of the coolant is determined by an analytical distillation which is reproducible to 0.3%. The HB fractions are characterized by C and H content, average molecular weight, Br number, O_3 absorption, and a "group-type" analysis by low-voltage mass spectrometry. These methods are briefly described. The HB fractions are very complex mixtures believed to contain the following types of compounds and their hydrogenation products:

Polyphenyls	Triphenylenes	Phenanthrenes
Polyphenyls	Triphenylene	Phenylphenanthrenes
Alkylpolyphenyls	Phenyltriphenylenes	Alkylphenanthrenes
	Alkyltriphenylenes	

A typical analysis of an irradiated polyphenyl coolant is presented.

THE ANALYSIS OF BERYLLIUM AND BERYLLIUM OXIDE

V THE DETERMINATION OF CADMIUM

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ABSTRACT

A method is described for the determination of cadmium in beryllium or beryllium oxide. Cadmium is precipitated with benzotriazole using nickel as a carrier. A further separation from other elements is made by passing a chloride solution through a column filled with Dowex-1 anion-exchange resin. Cadmium and zinc are retained on the resin column and subsequently eluted with 3 M nitric acid. The cadmium is then selectively extracted from a strongly alkaline solution with a solution of dithizone in chloroform and finally determined spectrophotometrically by measuring the absorbancy of the cadmium-dithizone complex in the organic extract at 518 mμ. The method is accurate to 5% or 0.5 microgram of cadmium, whichever is greater. No interference was caused by the presence of 10 mg amounts of 68 elements.

EDITOR'S NOTE

This paper is omitted from the Proceedings because it has been accepted for publication in Talanta.

Separation Techniques in Chemical Analysis

SOME APPLICATIONS OF ANION EXCHANGE-SPECTROGRAPHIC PROCEDURES IN A NITRIC ACID MEDIUM

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ABSTRACT

The adsorption characteristics of some 60 elements in HNO_3 media were studied with a strong-base ion exchange resin. Both column elution and batchwise procedures were used. Application of optical emission spectrographic techniques in conjunction with chemical and radiochemical analyses resulted in a considerable saving of analytical effort. Spectrographic examination of column effluents was relatively rapid because, with this method of analysis, elements can be added simultaneously to resin columns and the need for many tracer preparations is eliminated.

Most elements were not adsorbed in the range of acid concentrations studied (1 to 14 $\underline{M}$). An adsorption maximum at approximately 8 $\underline{M}$ HNO_3 was noted for Np(IV), Pa(V), Pu(IV), Th(IV), and U(IV), while the adsorption of Au(III), Bi(III), Hg(II), Pd(II), and Re(VII) decreased at acid concentrations greater than 2 $\underline{M}$.

The high anionic adsorption of Th and Np in HNO_3 has been used for the separation of impurities prior to their spectrographic determination. Analyses of microgram quantities of about 50 elements were made after adsorbing a sample on an anion exchange resin. The relatively rapid and simple procedure is applicable to routine trace element analyses.

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*Based on work performed under the auspices of the U. S. Atomic Energy Commission.

INTRODUCTION

During the past several years anion-exchange adsorption from a nitric acid solution has found application in a number of separation processes and analytical procedures. Significant tracer studies have been made by Kraus and Nelson(1) and by Bunney, *et al*(2) of anion adsorption in nitrate media. The adsorption of tetravalent plutonium and neptunium complexes by strong anion-exchange resins has been utilized in processes for the purification of plutonium(3,4) and neptunium.(5) Techniques involving anion-exchange separations have also been incorporated into methods used for the sequential separation of all actinide elements(6,7) and for their isolation from fission products.(8,9) Similar procedures have been used in analytical methods for removal of interferring ions prior to chemical(10,11,12) or radiochemical analysis as well as the isolation and spectrographic determination of trace impurities.(13,14,15)

In order to augment the published information and to obtain data for analytical application, a recent study(16) was made in our laboratory of the anion-exchange adsorption of some 60 metals in a nitrate medium. Spectrographic examination of column effluents was particularly advantageous in this study because the low adsorption of most elements permitted a rapid determination of their elution characteristics and eliminated the need for many tracer preparations or time consuming chemical analyses.

The results of the above investigation, together with other data which had been previously published for anion-exchange adsorption, have facilitated the development of procedures for the separation and spectrographic determination of trace impurities in thorium and neptunium. After adsorption of the matrix material on an anion-exchange resin from a nitric acid solution, the copper spark method was used for estimation of some 50 elements in the effluent.

METHODS OF INVESTIGATION

Spectrographic Procedure

Adsorptions of the elements were studied at room temperature in a range of acid concentration from 1 *M* to 14 *M* using a series of eight columns containing equal weights of Dowex 1-X10 strong-base, anion-exchange resin in the nitrate form. Microgram quantities of the elements were added to equilibrated columns from dilute nitric acid stock solutions and then eluted with nitric acid of the appropriate molarity. Stock solutions contained up to 15 elements at concentrations such that a 25-microliter aliquot gave a spectral line intensity approximately one hundred times that produced by the least amount detectable in an effluent. All solutions were allowed to flow through by gravity, resulting in flow rates of from 2 to 10 ml per hours. Effluents were collected in fractions ranging from 2 ml for 3.5-mm I.D. column containing 0.4 g of resin (dried at 100°C) to 10 ml for a 6-mm I.D. column containing 2 g of resin. A continuous elution procedure was used in which a new stock solution was added to the columns before complete elution of the elements previously added. As a rule, two fractions were collected before introducing a new group of elements.

The effluents were examined spectrographically using the copper spark method.(17) Each fraction was evaporated to dryness, redissolved in distilled hydrochloric acid, and diluted to a known volume. A 0.1-ml aliquot was evaporated on the flat ends of copper (or graphite) electrode pairs and then sparked under standard conditions. The spectra were photographed in appropriate wavelength regions and compared visually with previously prepared standard plates. Individual determinations were estimated to be accurate to within 50% of the amount present.

Elution curves at each concentration of nitric acid were drawn from the estimated percentage of each element in effluent fractions. After correcting for the first column volume of displaced liquid the elution maximum of each curve was used to derive distribution coefficients from the expression, Kd = V/M,(18) where V is the volume in ml that has passed through the column when the elution curve peak is reached and M is the mass of resin in grams. Equilibrium conditions were expected during the column operations because of the low flow rate and low loading with respect to resin capacity.

Additional Procedures

Details of the procedure employed, using chemical and radiochemical methods of analyses, have been presented.(16) Column elution techniques similar to those described above were used for adsorbability measurements of U^{233}, Am^{241}, Cm^{244}, Ce^{144}, Pm^{147}, and Mo^{99}. A batchwise procedure in which a standard amount of an element was equilibrated with a weighed batch of resin and a known volume of the desired molarity of nitric acid was advantageous for those elements having appreciable adsorption. Distribution coefficients were derived from analysis of the aqueous phase using the relationship,

$$Kd = \frac{\text{concentration per gram dry resin}}{\text{concentration per ml solution}} .$$

Radiochemical analyses of the tracers Th^{230}, Pa^{231}, U^{233}, Np^{237}, Pu^{239}, Au^{198}, and Tl^{204} as well as chemical methods for the analysis of palladium and mercury were applied.

RESULTS AND DISCUSSION

Distribution coefficients obtained from the column elution and batchwise determinations are presented in Figure 1 as a function of nitric acid molarity. Tracers found to have a Kd of less than two in all acid concentrations from 1 M to 14 M or elements spectrographically estimated to be quantitatively eluted in the first effluent fraction and not detected in subsequent fractions were placed in the "no adsorption" category. A negligible percentage of an element appearing in a second effluent fraction was indicated by "slight adsorption."

Adsorptions of several elements investigated by the spectrographic procedure were also determined at the tracer level using radiometric methods of analysis or, in macro quantities, employing chemical analyses. Results of some single batchwise equilibration measurements of Th^{230} and U^{233} adsorptions

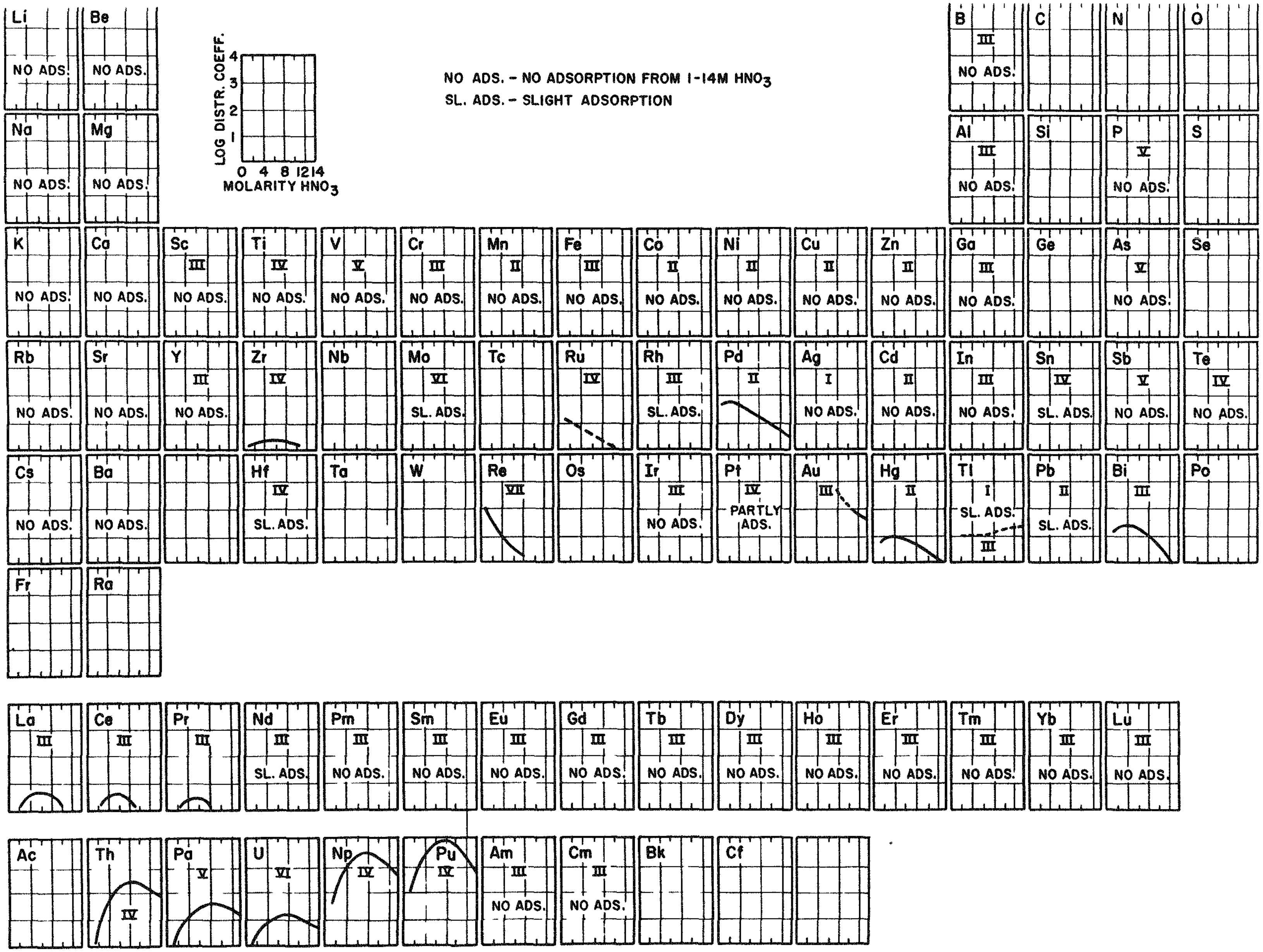

Fig. 1 - Removal of Elements From Solution in 1M to 14M Nitric Acid With Strongly Basic Anion Exchange Resin

and of Pd(II) and Hg(II) adsorptions, utilizing spectrophotometric analysis, are compared with spectrographically determined adsorptions in Table I. Similar agreement was found in column elution experiments with U^{233}, Ce^{144}, and Mo^{99} tracers. It will be noted that the variation of results between the different procedures was less than that obtained from Hg(II) using resin from a different lot.

The majority of the results presented in Figure 1 are in satisfactory agreement with those which have been reported in the literature although many of the comparisons can only be qualitative because of variations in the physical properties and the type of resin used. The spectrographic determinations of Pb(II) and Bi(III) adsorptions were in excellent agreement with those reported by Nelson, *et al.*(19) as was that of Re(VII) with the results of Huffman, *et al.*(20) The adsorption of Zr(IV) compared qualitatively with the published data(2,7) while the batchwise determinations were somewhat higher than those reported for Pa(V)(2) and Pu(IV).(3) The results were also found to agree with those appearing in the literature for Th(IV)(21), U(VI)(1,2), Np(IV)(9), Am(III)(2,6), and Cm(III).(6) The adsorptions given in Figure 1 for Ru(IV) and Tl(III) were considered to be tentative since column elutions suffered from early breakthrough, considerable "tailing", and lack of reproducibility. A substantially larger adsorption function has been reported for Ru(IV)(2) using Dowex-2, anion-exchange resin.

Anion adsorption data in a nitric acid medium have appeared in the literature for several elements not reported in Figure 1. A maximum distribution coefficient of about 12 was found for the adsorption of Np(V)(7) using Dowex-2 resin. Huffman, *et al.*(20) reported distribution coefficients for technetium that decreased from about 300 with 1 *M* acid to about 25 with 4 *M* acid. In ion-exchange studies of polonium, Danon, *et al.*(22) reported distribution coefficients for Po(IV) ranging from approximately 120 with 0.8 *M* acid to approximately 90 with 5 *M* acid. In the presence of an effective reductant the adsorption decreased to give a curve similar to that of Bi(III) in nitric acid. Negligible adsorptions have been reported for Ge(IV),(1) Nb(V)(2) and Pu(III).(6) At acid concentrations below 1 *M* the adsorption of Mo(VI) has been found to increase rapidly.(2)

ANALYTICAL APPLICATION

In the spectrographic analysis of uranium and plutonium, Brody, *et al.*(13) utilized anion-exchange adsorption of U(VI) and Pu(VI) in hydrochloric acid solutions above 6 *M* for the separation of impurities. A sequential elution of additional impurity elements in plutonium was made with 8 *M* nitric acid. From an examination of Figure 1, it is evident that thorium and neptunium can be readily separated from most other elements because, like plutonium, they form strong anionic complexes in nitric acid solutions. The ion exchange-spectrographic procedures developed for the routine analysis of thorium and applied to neptunium are described briefly below.

Analysis of Thorium

A solution of a 1-gram thorium sample in approximately 8 *M* nitric acid was passed through a previously conditioned column containing 15 to 20 grams of

TABLE I

EXPERIMENTAL DISTRIBUTION COEFFICIENTS BY SPECTROGRAPHIC METHOD COMPARED WITH OTHER PROCEDURES AT VARIOUS NITRIC ACID CONCENTRATIONS

			HNO_3 Molarity							
Element	Method	Analysis	1	2	4	6	8	10	12	14
Th^{230}	Batch	R. C.	1.0	6.0	51	216	303	227	130	67
Th	Col.	Spec.	1.0	3.3	47		323		93	51
U^{233}	Batch	R. C.	1.3	3.3	6.7	13	15	9.7	7.2	6.2
U^{233}	Col.	R. C.	3.8	3.8	9.2	17	16	13	12	7.3
U	Col.	Spec.	<2	3.0	7.2	12	12	7.2	5.6	5.4
Pd	Batch	Chem.	45	57	41	29	12	6	14	4.0
Pd	Col.	Spec.	50	52	54	38	18-25	10-18	8.0	4-7
Hg	Batch(a)	Chem.	11	23	20	18.4	5.7	2.5	2.0	<2
Hg	Batch	Chem.		7.8		8.6				
Hg	Col.	Spec.	3.5	8.0	6-9	5.0	3.5	3.0	1.5	<1.5

(a) resin from different lot.

Dowex-1x10, 200-400 mesh, anion-exchange resin. After washing with a minimum of distilled 8 M nitric acid, the collected effluent (total volume 30 to 50 ml) was evaporated to dryness, the residue was dissolved in one ml of distilled hydrochloric acid and impurities were determined by the copper spark method. The limits of detection and elements determined are given in column one of Table II. Visual estimations were made to within 50% of the amount present, an accuracy usually sufficient for the determination of trace elements. Densitometric procedures have been used for the determination of rare-earth elements(14) and could be applied whenever necessary.

The inadvertant introduction of common elements into the sample was kept at a minimum by using analytical-grade resin, deionized water, distilled acids, and columns, containers, etc. made of polyethylene, quartz, or other easily cleaned or inert material. Specific impurities introduced from the materials used were determined by analysis of the effluent from a blank column which had been treated in a manner identical with that used in processing a sample.

When the described procedure together with the carrier distillation method(23) is used for the determination of silicon and some of the more volatile elements, and for attaining better sensitivity in the determination of boron, a means is provided for a rather complete analysis of thorium for metal impurities. Very satisfactory agreement of results for the several elements included in both analytical procedures have been obtained.

Analysis of Neptunium

The strong anionic adsorption of Np(IV) in 8 M nitric acid has been utilized for separation of trace impurities. Analytical procedures were used similar to thosedescribed for thorium. Samples of 25 to 100 mg were reduced to the titravalent state by heating at approximately 90°C for at least an hour in an 8 M nitric acid, 0.2 M hydrazine solution. Although the dark band in the column formed by the adsorbed neptunium complex was larger than expected from the high distribution coefficient, the radioactivity found in the effluent indicated that more than 99% of the neptunium was retained by the resin. For convenience, the limits of detection are given in Table II for a one-gram sample although the maximum weight of neptunium used in the experiments thus far has not exceeded 0.1 gram.

In some instances, particularly for determination of impurities in thorium, adsorption of neptunium from hydrochloric acid was desirable. Satisfactory separations of the non-adsorbed elements(1) were made in 8-10 M acid using a procedure similar to that which has been applied to the analysis of uranium.(13)

DISCUSSION

Adsorption of a matrix material was advantageous because it permitted rapid isolation of the non-adsorbed elements with simple inexpensive equipment. A column could be used indefinitely for similar samples after removing the adsorbed complexes with dilute acid.

The ppm limits of detection in Table II were arbitrarily chosen. Since the spectral limits of detection were absolute, a larger or smaller sample

TABLE II

LIMITS OF DETECTION[(a)] FOR THE ION EXCHANGE - COPPER SPARK METHOD

Element	In Th, Np, (HNO_3)	In U, Np, Pu(HCl)	Add'l. in Pu(HNO_3)
		ppm	
Am	0.5	0.5	
Ag	2		2
Al	0.5[(b)]	0.5[(b)]	
B	0.5	0.5	
Ba	0.1	0.1	
Be	0.002	0.002	
Ca	1[(b)]	1[(b)]	
Cd	0.4		0.4
Ce	0.3	0.3	
Co	0.2		0.2
Cr	0.2	0.2	
Cs	5	5	
Cu	1	1	
Dy	0.2	0.2	
Er	0.1	0.1	
Eu	0.02	0.02	
Fe	1		1
Ga	0.1		0.1
Gd	0.2	0.2	
Hf	0.5	0.5	
Ho	0.2	0.2	
In	0.5	0.5	
Ir	1		1
K	0.5[(b)]	0.5[(b)]	
La	0.02	0.02	
Li	0.001	0.001	
Lu	0.01	0.01	
Mg	0.5[(b)]	0.5[(b)]	
Mn	0.05	0.05	
Mo	0.05		0.05
Na	1[(b)]	1[(b)]	
Nd	0.3	0.3	
Ni	0.2	0.2	
P	20	20	
Pb	0.5	0.5	
Pr	0.3	0.3	
Rb	0.3	0.3	
Re	1		1
Rh	0.2		0.2
Ru	0.5		0.5
Sc	0.01	0.01	
Sm	0.5	0.5	
Sr	0.002	0.002	
Tb	1	1	
Te	5		5
Th		0.5	
Ti	0.05	0.05	
Tl	1		1
Tm	0.2	0.2	
U	2		2
V	0.1	0.1	
Y	0.005	0.005	
Yb	0.01	0.01	
Zn	2		2
Zr	0.1	0.1	

(a) For a 0.1 ml aliquot of effluent from 1 g sample concentrated to 1 ml.
(b) Limited by residual in blank.

weight or aliquot of effluent would result in a corresponding change in the limits of detection.

Although the described procedures have emphasized spectrographic determination of trace elements, the removal of ions from nitric acid solutions by anion exchange could be applied similarly in chemical analyses, tracer separations, and purification processes.

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THE USE OF A GLASS-BEAD COLUMN IMPREGNATED WITH TRI-N-OCTYLPHOSPHINE OXIDE FOR THE ADSORPTION OF URANIUM FROM URINE(a)

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ABSTRACT

A method is presented for the separation of U from urine. U is adsorbed from partially digested urine onto a column of glass beads coated with tri-n-octylphosphine oxide and then stripped from the column with alcohol. The alcoholic solution is then evaporated and ashed, and the alpha activity is determined by counting. The adsorption, stripping, and evaporation sequences are accomplished automatically by an apparatus designed for that purpose. The average recovery of U, which includes extraction efficiency, alpha attenuation, and counter variability, is 73%. The absolute standard deviation is 10%.

INTRODUCTION

A preliminary investigation revealed that uranium could be adsorbed from acidified aqueous solutions onto solid tri-n-octylphosphine oxide (TOPO). This discovery suggested the feasibility of developing a reactive column applicable to our urine program.

COLUMN

The developed column consisted of a 150-mm by 2-mm bed of glass micro beads coated with TOPO. The beads were coated by wetting them with a 0.2 M solution of TOPO in benzene and permitting the benzene to evaporate. The reactive beads were then packed into glass tubes.

(a) Presented by J. H. Rowan, Y-12 Plant, Union Carbide Nuclear Company, Oak Ridge, Tennessee

To test the efficiency of the TOPO column, the following procedure was utilized (Table I).

PROCEDURE

Twenty ml of nitric acid was added to 100 ml of urine; the mixture was boiled 30 minutes and then cooled. The procedure then included, sample elution, removal of residual urine by an acid wash, stripping the reactive TOPO with ethyl alcohol, evaporation of the alcohol, ignition of the residue, and measurement of the residue for alpha activity.

The elution, washing, stripping, and evaporation operations were later performed automatically by a machine subsequently referred to as a "Micturometer."

MICTUROMETER

A view of the Micturometer can be seen in Figure 1. The order and duration of operations are controlled by a sequence timer. Each TOPO column is connected to one leg of a glass "Y" which provides simple column access to the evacuation pump and alcohol delivery systems. During the appropriate operation, sample or acid wash is drawn up the column by a pump. Alcohol is forced down the column by air pressure. Watch glasses shown under the column collect TOPO eluted from the column during the stripping cycle. They are supported by ring-type hot plates which supply heat and provide a means for the continuous evaporation of alcohol. The watch glasses were found to be suitable for use as throw-away counting disks.

The sample beakers now in the load position must be relocated during the procedure. This relocation is effected through a transport mechanism (Figure 2) which retracts the beakers into the shelf, moves the shelf to the right, and elevates the beakers to the elution position. In this position one end of a column extends to a small well in the bottom of each beaker. Later in the procedure, the beakers are returned to the load position. Glass nozzles behind the columns permit delivery of dilute nitric acid during the washing cycle (Figure 3).

COLUMN EFFICIENCY

The column efficiency was evaluated for manual operation by determining the percentage of added uranium found in the extracted residue from "spiked" 100-ml aliquots (Table II). Fluorescence analysis was used in the first two experiments while in the remainder counting techniques were utilized.

In the last three experiments, uranium-233 was used to reduce the error in counting statistics. Also, the alpha activity due to uranium found in the extracted residue was compared to the activity of "masked" standards, which were prepared by pipetting an amount of uranium equivalent to the spike onto the residue of an extracted, unspiked sample.

Comparison of the different per cent efficiency results shows good agreement and constant recovery in the concentration range studied.

TABLE I

PROCEDURE

1. Preparation of Sample
2. Elution of Sample
3. Washing of Column
4. Stripping off TOPO
5. Evaporation of Alcohol
6. Drying of Residue
7. Ignition of Organics
8. Counting

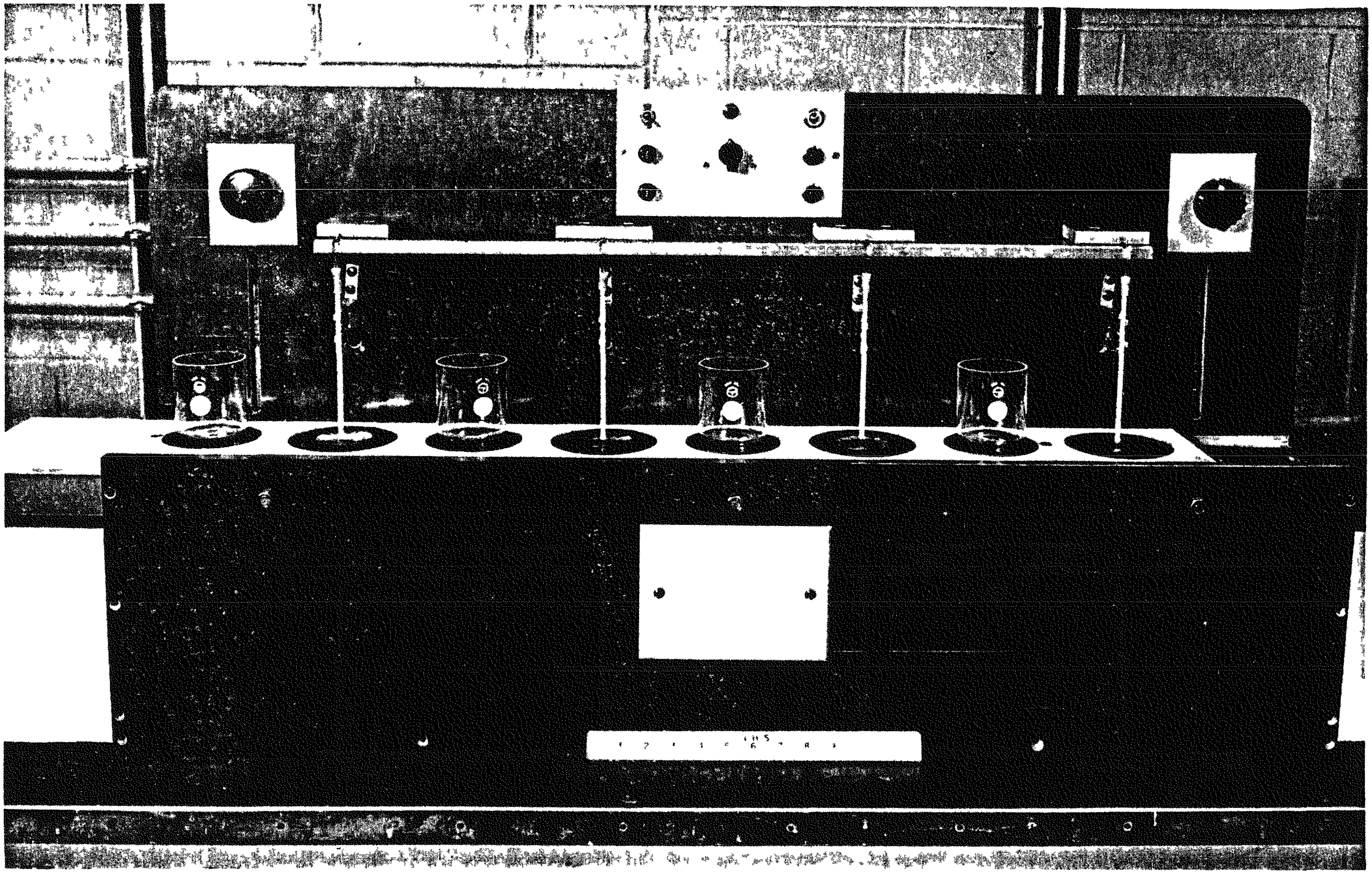

Fig. 1 - Front View of Micturometer

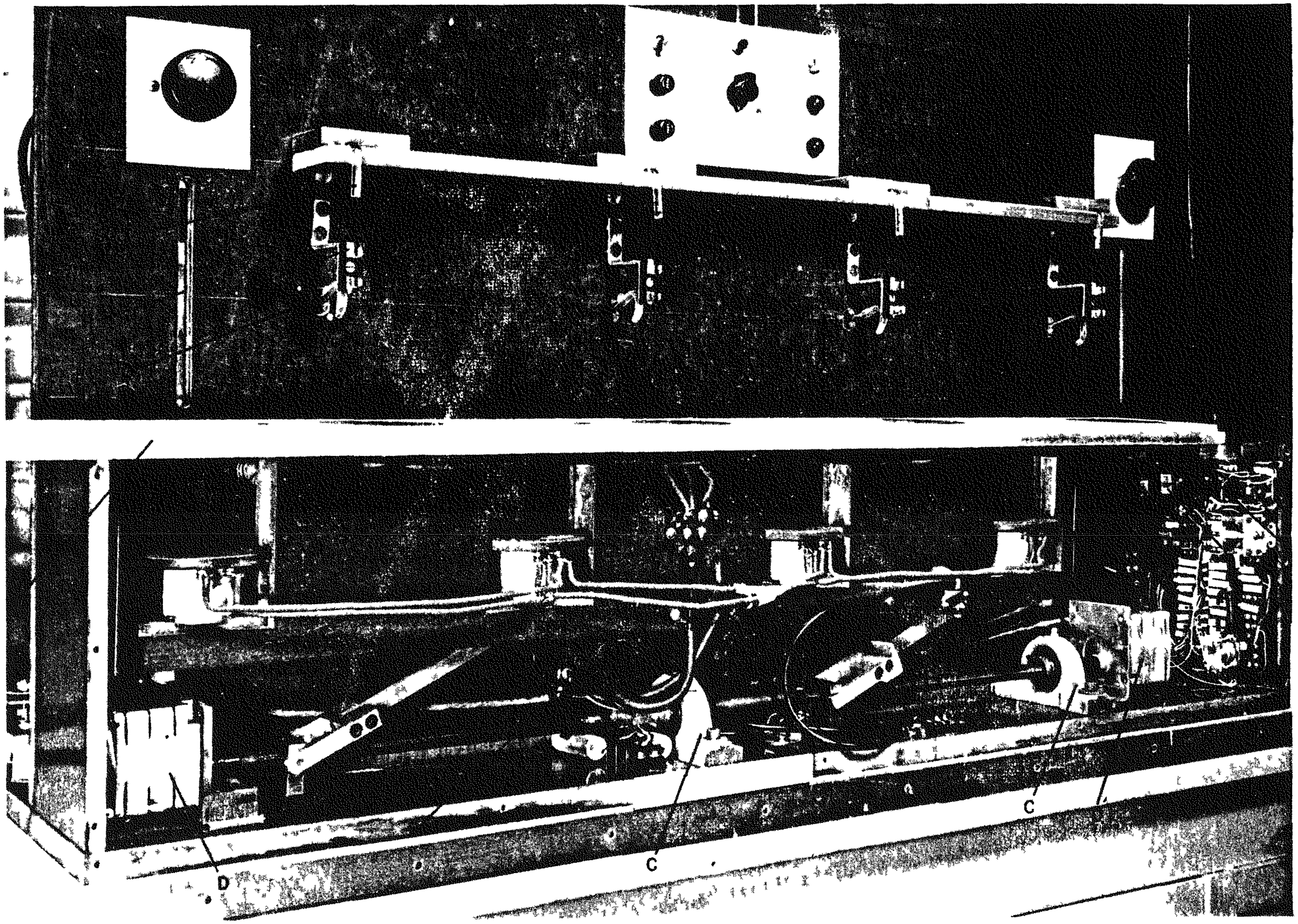

Fig. 2 - Micturometer, Front View With Cover Removed to Show Transport Mechanism

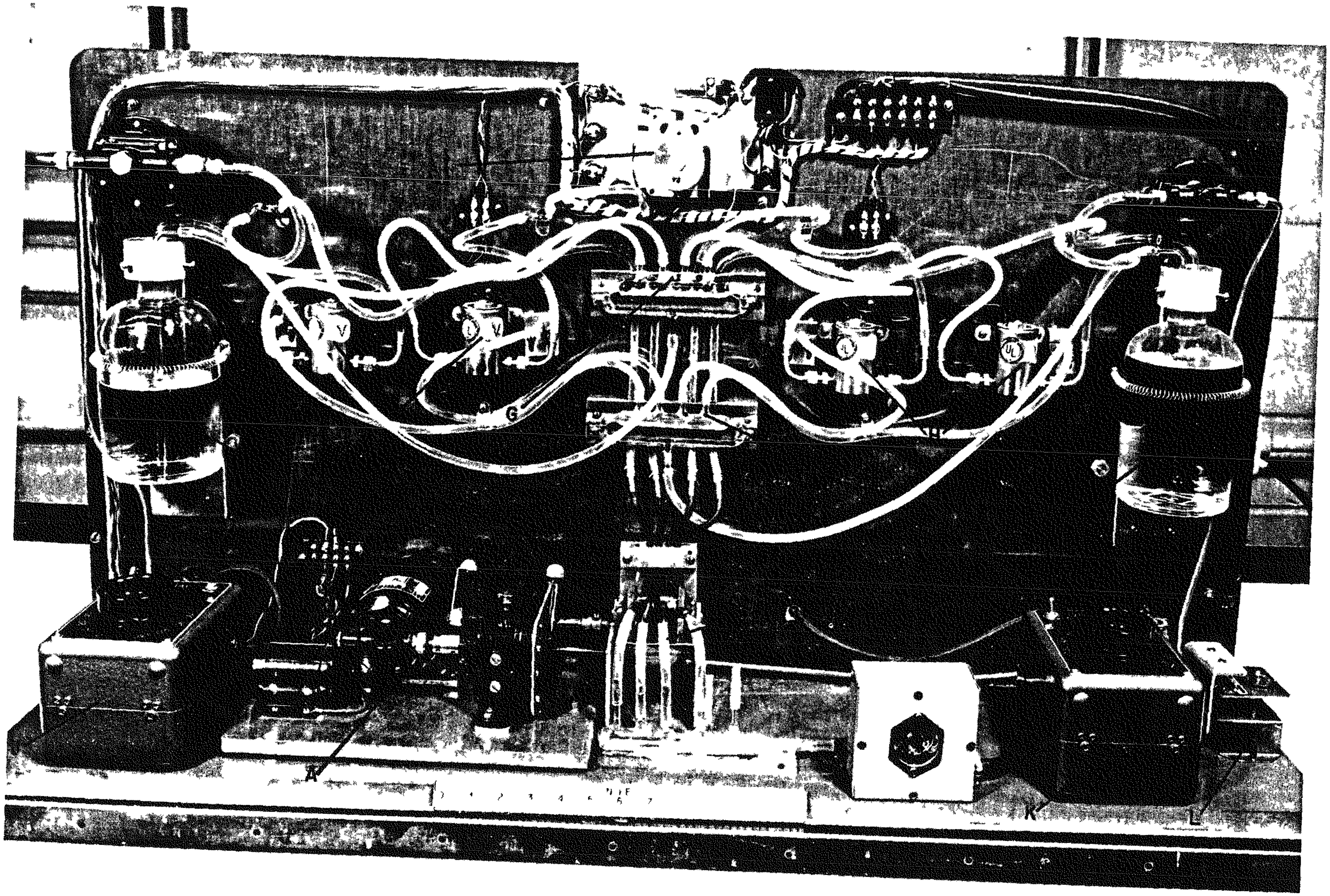

Fig. 3 - Rear View of Micturometer

TABLE II

COLUMN EFFICIENCY IN RECOVERY OF URANIUM FROM "SPIKED" SAMPLES

Uranium Added,μg/l	No. of Analyses		Method	Efficiency ± LE Per Cent
	Extraction	Standards		
1.29	9	-	Fluorescence	85 ± 8
2.00	9	-	Fluorescence	88 ± 15
.005	13	9	Counting	88 ± 30
.50	7	8	Counting	86 ± 9
.50	19	8	Counting	82 ± 5

ROUTINE ANALYSIS

After the column efficiency had been evaluated, sufficient interest was developed to warrant a study of the applicability of this technique to the determination of uranium in routine samples of urine. Twenty-two, 400-ml urine composites were collected. Each composite was divided into two pairs of spiked and unspiked 100-ml aliquots and each spiked sample contained 0.04 µg of added uranium-235. Standards were prepared by adding 0.04 µg of uranium-235 to each of 19 watch glasses. Alpha activity of the standards and extracted residues was determined by a 30-minute measurement in a 2π proportional counter. Results for the standards showed an average count of 77 with a standard error of ± 3.

The per cent recovery of uranium from the spiked samples was computed by the following equation:

$$r = \frac{s - u}{S} \times 100 \qquad (1)$$

where

r = per cent recovery
s = count of spiked residue
u = count of unspiked residue
S = average standard count

Results from this computation are presented in Table III. The average recovery for the 44 spiked samples was 73 per cent with a limit of error for an individual determination of 23%.

Uranium in the unspiked samples was calculated by means of the following equation:

$$y = 100 \frac{u - b}{F} c \qquad (2)$$

where

y = µg of uranium/100 ml of urine
u = count of extracted residue
b = background count
F = average per cent recovery
c = µg of uranium-235/count

The data from these calculations are presented in Table IV. Projection of the estimation of uranium in the routine unspiked samples to millirems per 24 hours resulted in an average of 15 millirems. This value is comparable with results obtained for routine samples, utilizing the present electrodeposition procedure.

TABLE III

RECOVERY OF URANIUM FROM SPIKED SAMPLES

Composite	Per Cent Recovery	Composite	Per Cent Recovery
1	76	12	58
2	79	13	71
3	99	14	54
4	73	15	72
5	79	16	60
6	67	17	67
7	90	18	79
8	88	19	75
9	71	20	74
10	75	21	68
11	64	22	61

mean ± standard error of the mean = 73% ± 5% (95% confidence level)

TABLE IV

TEST RESULTS FOR "METABOLIZED" URANIUM IN SAMPLES

Composite	Uranium µg/100 ml urine	Composite	Uranium µg/100 ml urine
1	0.0100	12	0.0100
2	0.0040	13	0.0092
3	0.0032	14	0.0246
4	0.0050	15	0.0064
5	0.0036	16	0.0075
6	0.0072	17	0.0096
7	0.0378	18	0.0078
8	0.0143	19	0.0125
9	0.0032	20	0.0032
10	0.0196	21	0.0160
11	0.0118	22	0.0082

SUMMARY

A procedure has been presented which provides a simple means of concentrating submicrogram quantities of uranium in urine.

A machine has been described which performs automatically the elution, washing, stripping, and evaporation operations of the procedure.

Data is presented whereby it is shown that the average recovery for spiked routine samples was 73 per cent with the limit of error for an individual determination of about 23 per cent.

Test results were presented for the determination of uranium in routine samples, utilizing this technique.

SEPARATION OF STRONTIUM FROM ALKALINE EARTHS AND FISSION PRODUCTS[a]

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ABSTRACT

A method was established for the separation of gram quantities of Sr from Ca and Ba, and from fission-product contaminants found in an Sr^{90} source solution obtained from the F3P main stream at Oak Ridge National Laboratory. The ion-exchange chromatographic method was modified and extended to give clean-cut separations of Ca and Sr that eliminated the "tailing off" of Sr.

Dowex 50-X12 resin is used for the separation of Sr from Ca, Ba, and a majority of fission products. The remainder of the fission-product contaminants are removed with IR-400 resin.

INTRODUCTION

In conjunction with a program, started at The Martin Company Nuclear Division, to develop a strontium-90 heat source, a procedure was required for separating macro quantities of strontium from gamma-emitting isotopes and stable contaminants, including concentrations of calcium greater or less than the strontium concentration. Calcium had to be separated so that the specific activity of the strontium was not reduced, which would necessitate a larger size heat source. Gamma emitters had to be eliminated to keep the shielding requirements and, therefore, weight of the final generator, low.

This program resulted in the re-evaluation and modification of a method which prior to this time had been used only for separation of micro quantities of strontium, calcium and barium. Various methods for separating and determining strontium in the presence of calcium, as well as fission-product

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(a) This work was done under AEC Contract AT(30-1)2220-Task II.

contaminants have been published, but few quantitative methods have been reported. Among those reported,(1,2,3) the methods of ion-exchange chromatography appeared most feasible for reasonably rapid macro-separations.

The separation method of Lerner and Neiman(1) appeared most adaptable. By adapting this method, macro quantities of strontium, calcium and fission contaminants such as those found in the Oak Ridge strontium-90 source solution obtained from the F3P main stream could be separated.

EXPERIMENTAL

A series of elutions were carried out to determine the best conditions required for separating strontium from, primarily, calcium and then barium. Column lengths and diameters were varied; the pH of the eluant was varied somewhat as was the temperature of the column. Column temperatures reaching as high as 90°C were tested. Temperatures below room temperature were not investigated. Flow rates were varied. The greater part of the data from the various experiments was obtained by means of visual checks of the amount of carbonate formed in each equal aliquot of elutrient. Time did not permit the filtration and weighing of the many samples obtained from each run.

Most of the preliminary experiments were conducted in resin columns 1.7 cm in diameter and 14 to 20 cm in length. These columns were later replaced by columns of 2.5 cm in diameter and approximately 34 cm in length for samples containing approximately one gram each of calcium and strontium. Earlier experiments indicated that barium eluted several column volumes after the strontium had been completely removed from the column; therefore, in most of the experiments, barium was not included in the sample solution. Figures 1 and 2 show the elution curves of strontium and calcium using lactate at pH 7 and 7.3, respectively; the main difference between the two runs was the strontium-to-calcium ratios. Figure 3 shows the results obtained when 1.2 M lactate at pH 4.8 was used. This resulted in a "tailing off" of the strontium being eluted. This undesirable "tailing off" lengthened the time required for separation as well as resulting in more waste solutions being generated--a very objectionable feature when working with radioactive material. This "tailing off" was also noticed when elutions were run with 1.2 M lactate at pH 7, 7.5, 5, 5.3 and 5.7. It became apparent that changing the pH of the eluant would not result in effective elimination of the "tailing off" of the strontium. The next step was to study the effects of varying lactate concentration and especially a step-wise increase in the lactate concentration after elution of the calcium. A 2.4 M lactate solution was made up and the pH adjusted to 5.78. Figure 4 shows the curve obtained. The elution was started with 1.2 M lactate at pH 5.8. As the calcium minimum was approached, the 2.4 M lactate was added. This resulted in a sharp cutoff of the strontium elution curve. The experiment was repeated, using larger concentrations of calcium and strontium, and at the same time, adding barium. The size of the resin column was increased to handle the higher concentration of calcium, strontium and barium. Figure 5 illustrates the elution curve obtained. Lactate of 1.2 M concentration was used for the calcium elution. This was changed to 2.4 M as the calcium minimum was approached. Again, 1.2 M lactate was added as the strontium minimum was approached. Barium began to elute but only in trace quantities and continued to do so over several column volumes. Lactate of 2.4 M concentration was then substituted for the 1.2 M and the

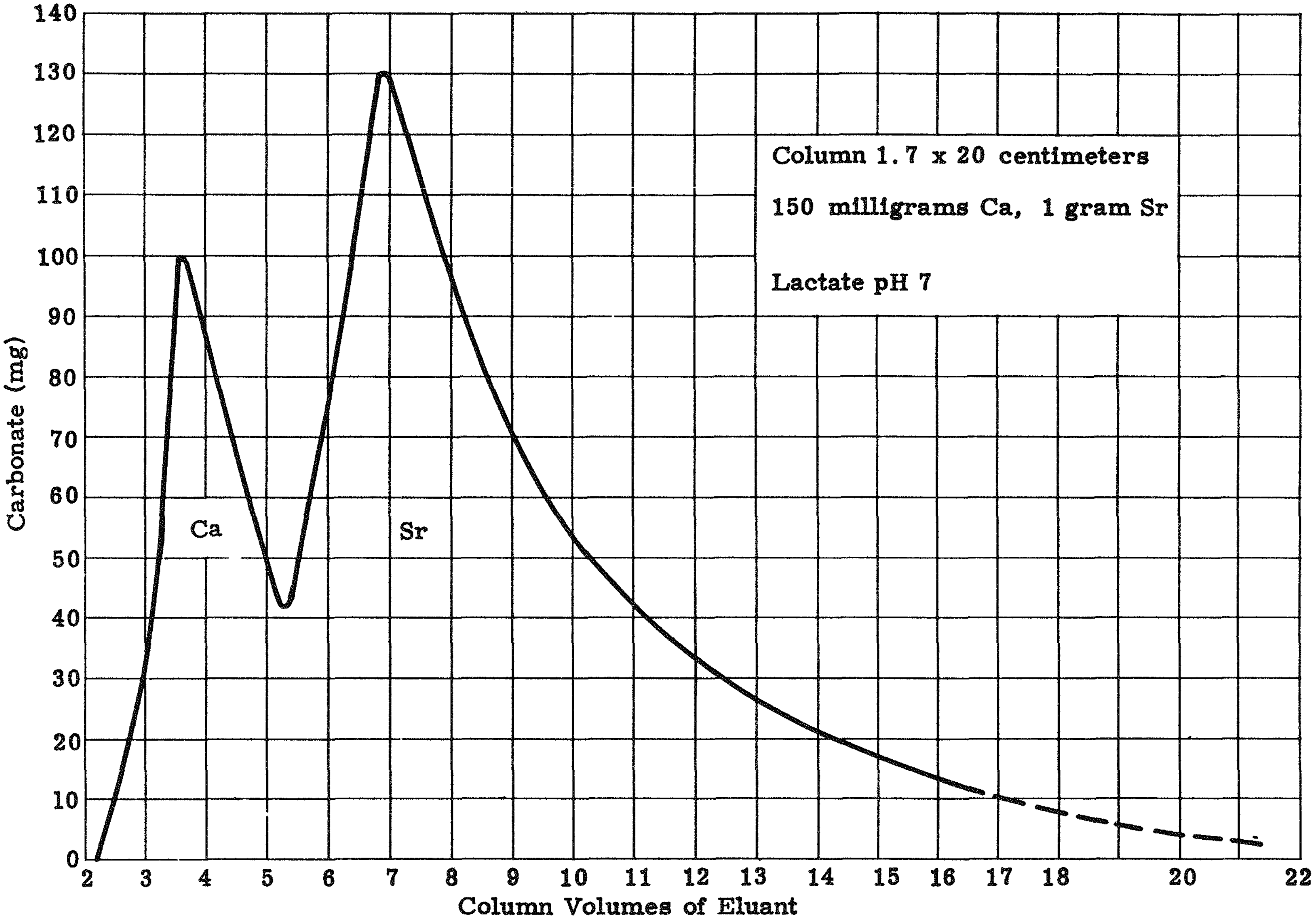

Figure 1. Separation of Strontium from Calcium by Lactate Elution from Dowex 50

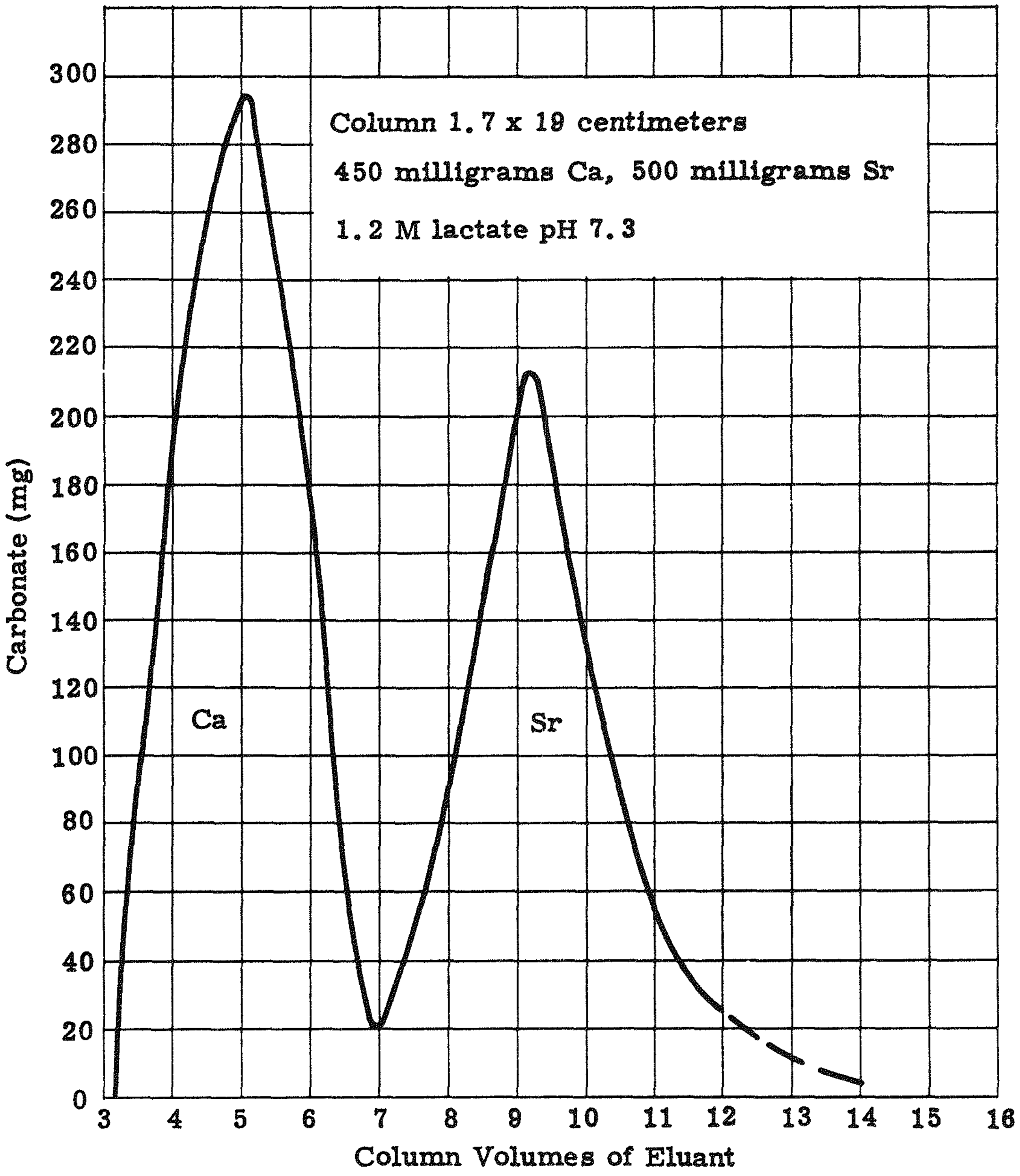

Figure 2. Separation of Strontium from Calcium by Lactate Elution from Dowex 50

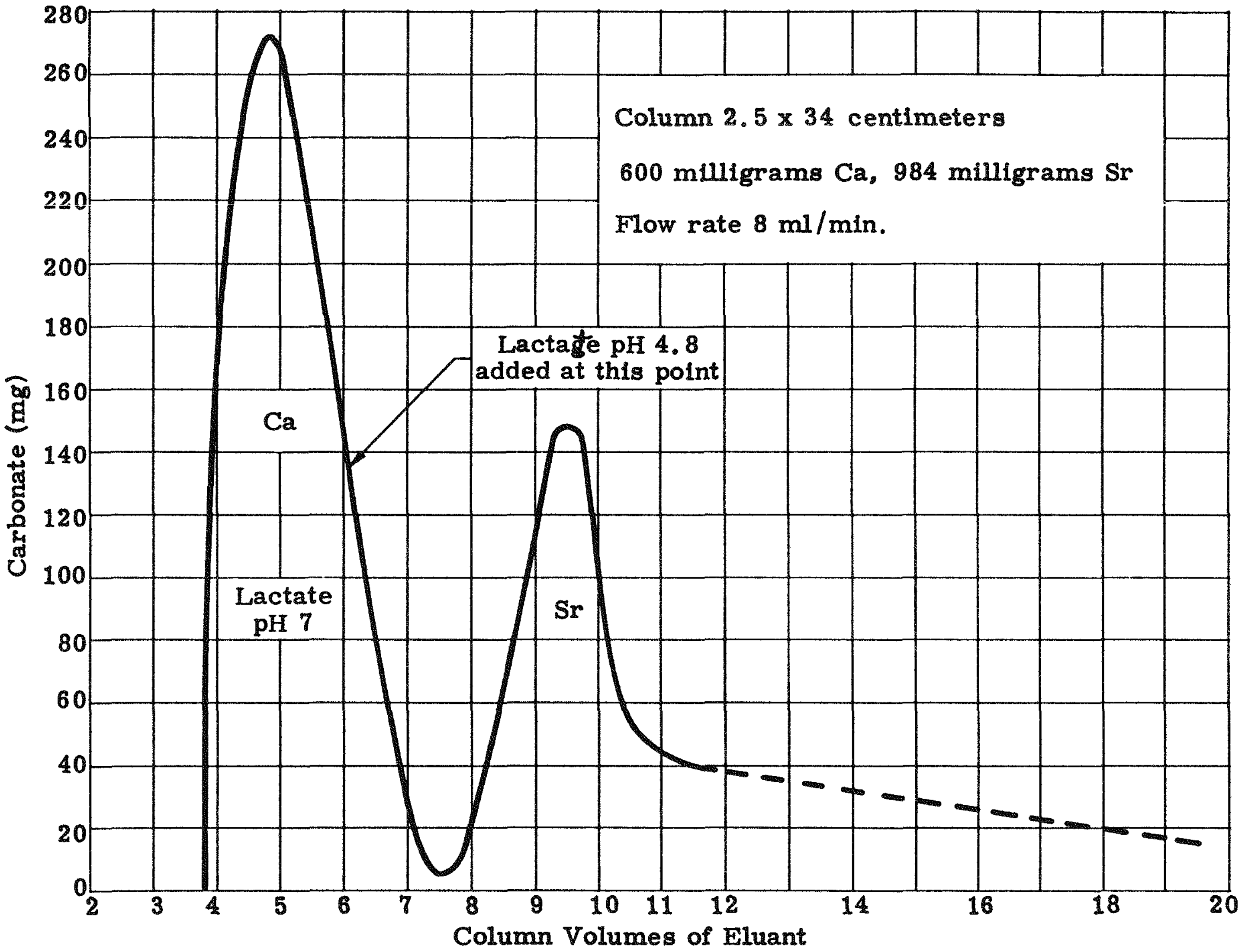

Figure 3. Separation of Strontium from Calcium by Lactate Elution from Dowex 50

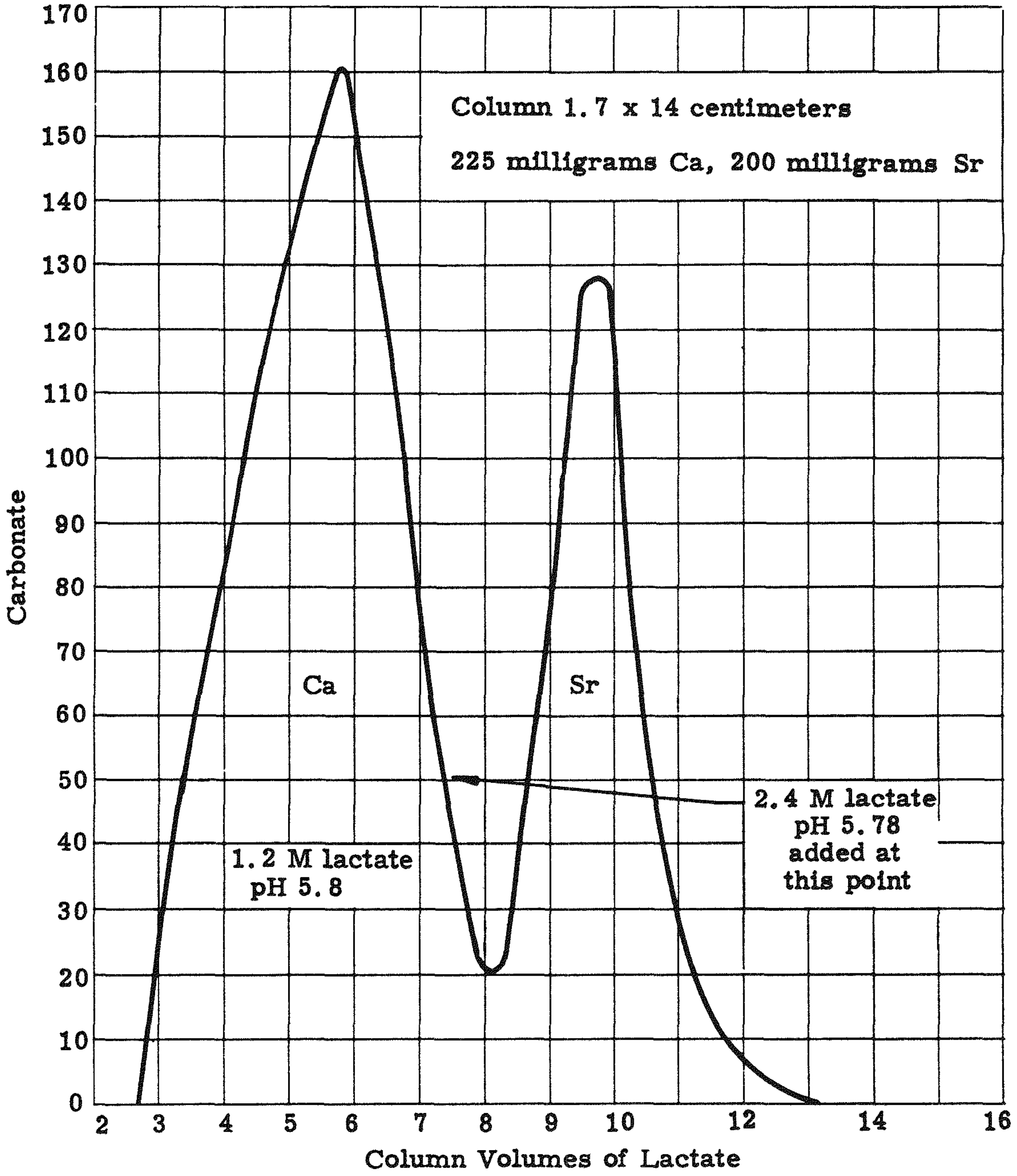

Figure 4. Separation of Strontium from Calcium by Lactate Elution from Dowex 50

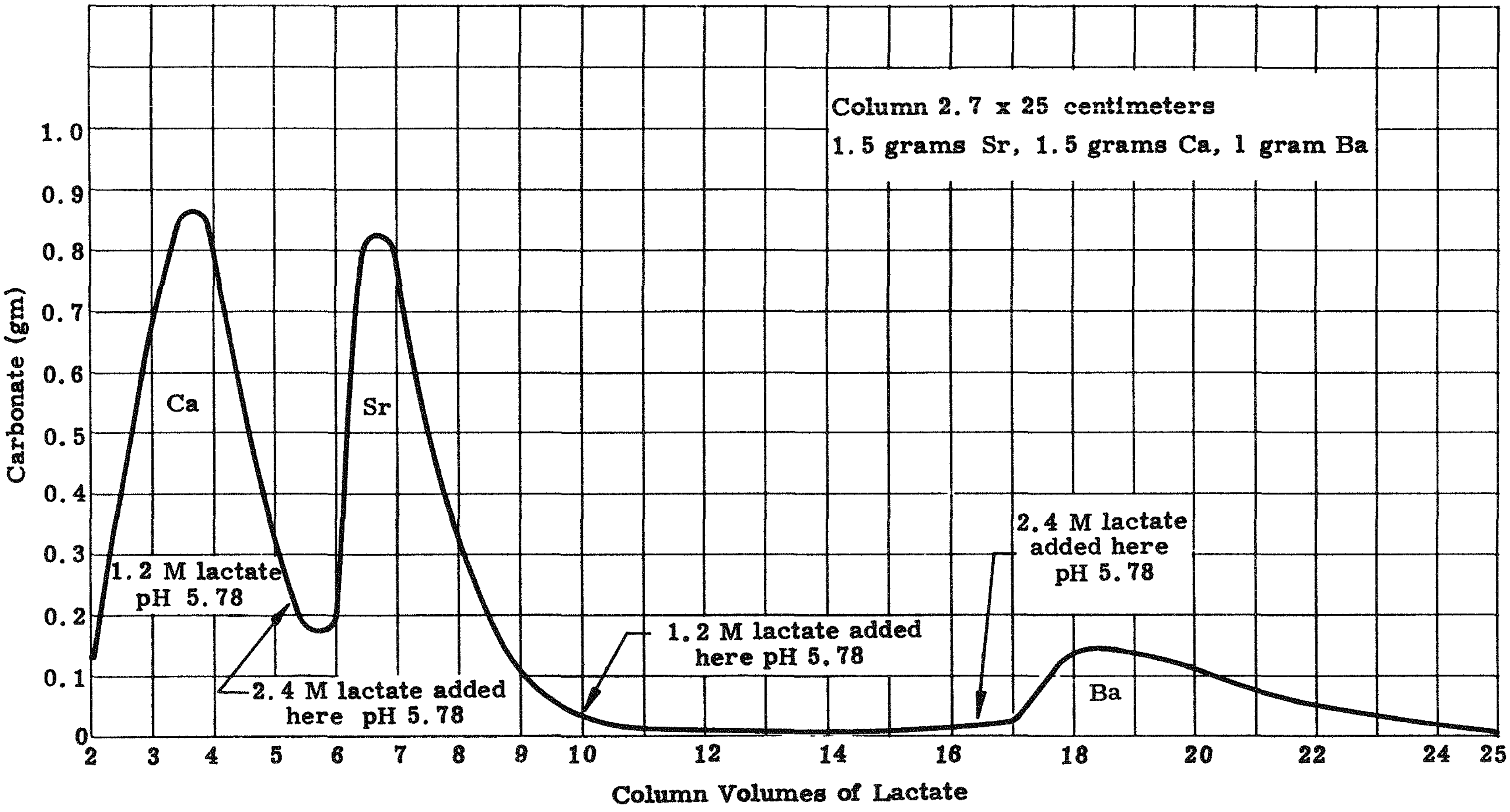

Figure 5. Separation of Strontium from Barium and Calcium by Lactate Elution from Dowex 50

barium began to elute in larger quantities, came to a maximum and then tailed off to nothing. However, from Figures 4 and 5, it is evident that the calcium minimum is not ideal. The ideal separation was approached when the pH of the 2.4 M lactate was adjusted to 7.53 and the experiment repeated. Figure 6 illustrates the results. Several runs were made, each giving very similar results. Calcium begins to elute after approximately 3.5 column volumes of eluants, provided the resin volume is sufficient to handle the charge. If the resin volume is not large enough to handle the charge, calcium will begin to elute sooner. The calcium maximum is reached approximately 1-1/2 column volumes after the initial appearance of the calcium. The calcium minimum is reached 3-1/2 column volumes after the initial appearance of the calcium. One column volume prior to this point, the 2.4 M lactate must be added. Two column volumes after the calcium minimum, the strontium maximum is attained, followed by the strontium minimum five column volumes from the calcium minimum or 8-1/2 column volumes from the initial appearance of calcium. (These results may vary somewhat due to variations in batches of resin.) Again, the concentration of lactate is changed approximately one column volume from the strontium minimum. This will result in, at the most, a trace of barium contamination at the strontium minimum. If the barium is of interest, 2.4 M lactate can then be added one column volume after the strontium minimum and elution continued till the barium is completely eluted. Flame photometric techniques were used for analysis of the aliquots at the minimum points. These data indicated that small quantities of strontium begin to appear as the calcium minimum was approached and small quantities of calcium appeared in the strontium fraction immediately after the calcium minimum. After several successful runs with this modified method on prepared samples containing calcium and strontium, the procedure was applied to a solution containing seven curies of strontium and other fission products obtained from Oak Ridge National Laboratory. This solution from the F3P main stream contained, in addition to fission products, a considerable amount of calcium. One gram of stable strontium was added to the solution and the run was then made through the column prepared as outlined in the section on procedure. After the calcium and many of the fission products coming down with it were eluted, the strontium was collected.

The strontium was precipitated as the carbonate and centrifuged. Following centrifugation, the strontium carbonate was dissolved in the smallest possible volume of 6 N hydrochloric acid. The acid solution of the strontium was then run through a previously prepared ion-exchange column containing IR-400, 50 to 100 mesh.(2) The strontium was eluted with three column volumes of water and reprecipitated as the carbonate. If any cesium was present in the original fission-product solution and had not been completely removed during the separation of calcium from the strontium, it would appear at this point with the strontium. However, the carbonate precipitation here would remove the remaining traces of the cesium. The strontium carbonate was then converted and fabricated into strontium titanate pellets. A small sample of this material, analyzed by gamma pulse-height analysis in a multichannel analyzer, failed to show any trace of gamma-emitting contaminants.

APPARATUS AND REAGENTS

The apparatus used consisted of glass columns at least two cm in diameter. These were equipped with stopcocks and glass wool was used to plug

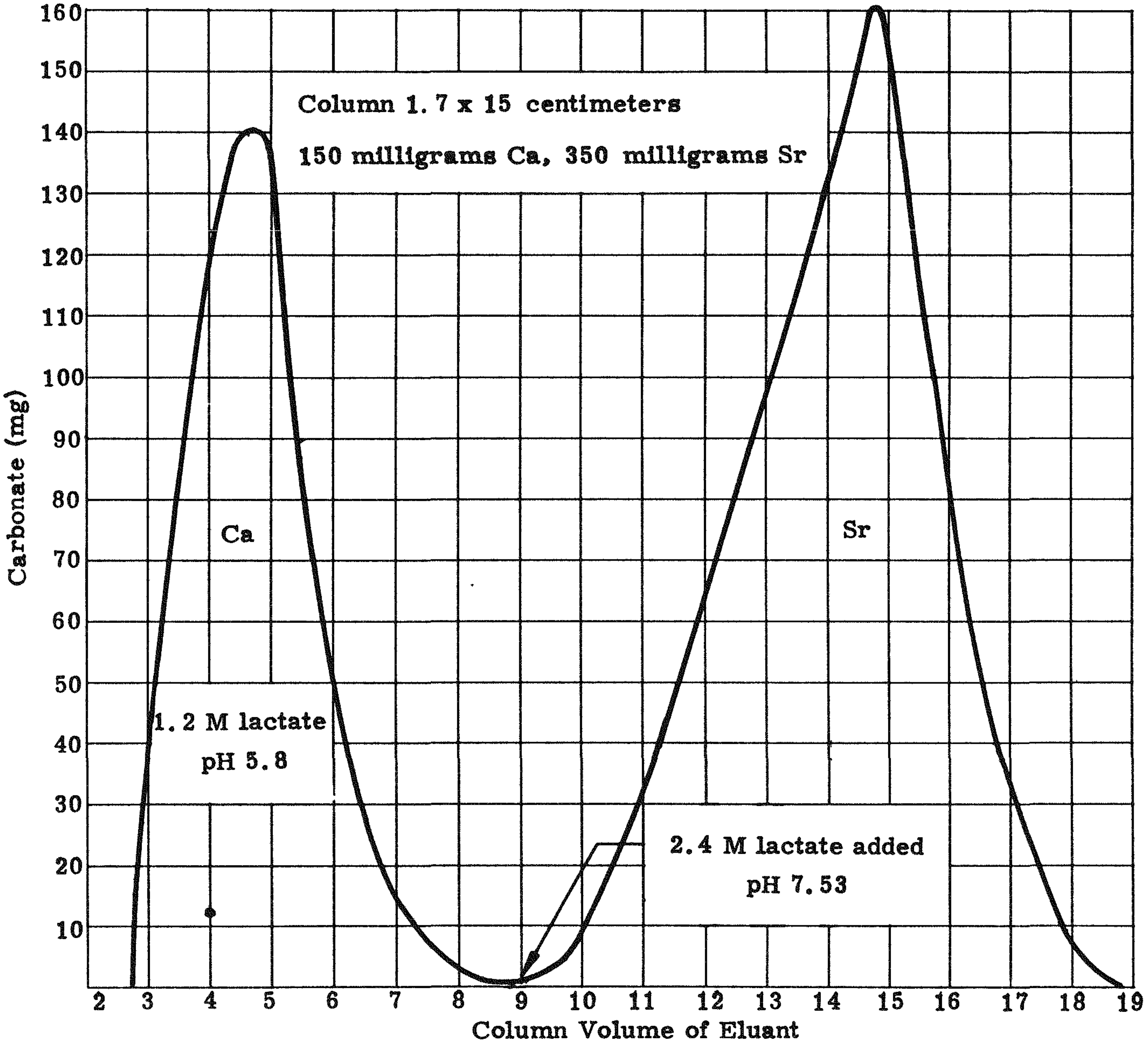

Figure 6. Separation of Strontium from Calcium by Lactate Elution from Dowex 50

the top and bottom of each column. The length of the column depended on the concentration of the material being separated; a 25-cm column was used to separate 1 gram of strontium from 1 gram of calcium.

The reagents used were:

(1) Reagent-grade ammonium lactate, 85%.

(2) Reagent-grade ammonium hydroxide.

(3) Reagent-grade hydrochloric acid.

(4) Potassium carbonate.

Dow Chemical Company Dowex 50-X-12, 50 to 100 mesh, ion-exchange resin and Rohm and Haas IR-400 ion-exchange resin, 50 to 100 mesh, made up the rest of the material needed.

PROCEDURE

Preparation of Columns

Dowex-50. A slurry of the required amount of resin is made with distilled water and poured into the column. The bottom of the column contains a plug of glass wool to keep the resin from running through the stopcock. When the resin has settled, a plug of glass wool is inserted into the top of the column to prevent stirring of the resin when solutions are introduced. The column is washed with water until the elutrient is acid free. The column is then equilibrated with 1.2 M lactic acid of pH 5.7. This reagent is made by diluting 127 grams of 85% lactic acid with distilled water to about 900 ml. This solution is then adjusted to pH 5.7 with NH_4OH and the resulting solution is made up to one liter.

After equilibrating the column, the liquid level is brought below the level of the glass wool plug and the column is ready for the sample.

IR-400. The column is again prepared with glass wool plugs at both ends of the resin bed. The resin is slurried in water and poured into the column. Several column volumes of concentrated NH_4OH are run through the column and then the column is rinsed with several column volumes of water. The column is now ready for use.

Preparation of Sample

The acid concentration of the sample is reduced as much as possible, by neutralizing with NH_4OH, without causing any of the constituents to precipitate out. The final solution should be on the acid side. This solution is poured onto the column and allowed to pass through at about 0.5 ml/min/cm^2 of column area. The liquid level is allowed to drain below the level of the bottom plug. At this point, 1.2 M lactate is added and the elutrient measured. The fraction containing the strontium is made basic with NH_4OH and the strontium precipitated with K_2CO_3. This suspension is centrifuged and the supernate is discarded. The precipitate is dissolved in the smallest amount of 6 N HCl possible and the resulting solution is poured through the IR-400 resin column. The column is rinsed with four or five column volumes of water to make sure all the strontium has passed through. The strontium is again precipitated as the carbonate. This material should be free of fission products at this point.

The procedure for separation of calcium and strontium can be made very close to quantitative by taking small, equal aliquots of the elutrient as the calcium minimum and again as the strontium minimum is approached. These aliquots are precipitated as the respective carbonates. The precipitates are permitted to settle, yielding a visual indication of the calcium and strontium minima and thus locating the respective end points of the fractions of calcium and strontium.

A complete separation can easily be made within an eight-hour day. The time required depends on the quantities of strontium and calcium which must be separated.

ACKNOWLEDGEMENTS

Appreciation is extended to Dr. William W. T. Crane for his efforts in obtaining a gamma spectrometric analysis of the purified strontium sample and, also, to Dr. William McNearney for his valuable assistance in the preparation of this report.

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APPLICATION OF THE DOUBLE WITHDRAWAL COUNTERCURRENT EXTRACTION TECHNIQUE TO ANALYTICAL CHEMISTRY

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ABSTRACT

Application of the double-withdrawal countercurrent extraction technique to chemical analysis has been singularly neglected, probably because of the complexity and tediousness of the associated mathematics. Present-day computer technology proved to be readily applicable to the problem, and information is presented which indicates the possible importance of this separation method to chemical analysis.

The double-withdrawal extraction process is briefly described in order to clarify the terms used. The method used in processing data and computing results is outlined. The advantages of the double-withdrawal extraction procedure in analytical applications and the separations attainable thereby are illustrated graphically.

EDITOR'S NOTE

This paper is omitted from the Proceedings because it has been accepted for publication in Anal. Chim. Acta, (Vol. 20, February, 1961).

Activation and Radiochemical Methods of Analysis

RADIOCHEMICAL ANALYSIS OF KRYPTON-85*

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ABSTRACT

For the radiochemical analysis of Kr^{85} by absolute gamma-ray spectrometry, a knowledge of its gamma branching ratio is required. The 0.513-Mev gamma to beta ratio in Kr^{85} is found to be 0.0036 ± 0.0008.

INTRODUCTION

The amount of fission gas released from irradiated nuclear fuels into the gap between the fuel and cladding can be measured by analysis of the Kr^{85} evacuated from this gap. This measurement plays a part in the calculation of internal pressures developed inside the cladding.

Kr^{85} possesses in low abundance a 0.513-Mev gamma ray which can be conveniently measured even in the presence of active fission-product isotopes of zenon. Such a measurement has been described by Alter(1) wherein the ratio of the 0.513-Mev gamma activity of an unknown sample to that of a standard sample was obtained. This method is valid and has been in use for several years in this laboratory.

Recently an attempt was made to supplant this relative counting procedure with an absolute gamma-counting procedure already successfully applied to Xe^{133}, Xe^{135}, Kr^{85m}, Kr^{87}, and Kr^{88}. It was noted however that the gamma branching ratio of Kr^{85} has been measured only once with a stated uncertainty of 23 per cent.

The purpose of this paper is two fold. The first purpose is to warn that careful absolute gamma spectrometry for Kr^{85} will yield results no more accurate than the gamma branching ratio assumed in the calculation of the results.

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*This work was supported in part by the U. S. Atomic Energy Commission.

The second purpose is to encourage radiochemists to further study the gamma branching ratio in the decay scheme of Kr^{85}. No decay scheme should be considered well known until it has been arrived at independently by two or more experimentalists. Our first measurements of the gamma branching in Kr^{85} were presented in GEAP-3496.(2)

To determine this branching ratio, replicate samples were drawn from each of four rods of a single irradiated fuel assembly. Irradiation was for 73 days and the cooling time exceeded 194 days at the time activity measurements began. Where sample size permitted, aliquots were analyzed mass spectrometrically to obtain the mole per cent of all gaseous isotopes present.

Gamma measurements were made on aliquots at distances of 24 to 100 cm from a 3-in. diameter by 2-in. high NaI(Tl) crystal. The spectra were observed on various magnetic core, multi-channel analyzers in the manner of Heath(3) and Crouthamel.(4) Gamma-disintegration rates were obtained from measurements of photopeak areas. Photopeak efficiencies were determined by counting radioactive standards, including Sr^{85}, in each geometric position used.

After gamma analysis, the same aliquots were introduced into a gas-handling system containing an internal gas counter according to Reynolds.(5) The system was calibrated by use of National Bureau of Standards Kr^{85} standard number 4935.

Averaged results of these analyses are shown in Table I. The 0.513-Mev gamma to beta ratio measurements ranged from 0.0031 to 0.0041. This ratio was reported in 1950 to be 0.0065 ± 0.0015.(6) In this early work the gamma measurements consisted of integral counts from an anthracene crystal and may include a portion of the bremsstrahlung.(7)

EXPERIMENTAL

Table I summarizes beta and gamma measurements made on old fission gas from four fuel elements and the National Bureau of Standards Kr^{85} standard number 4935. The first three samples were sufficiently large to permit a mass spectrometric analysis. The mole per cent of all gaseous isotopes was determined by C. J. Dooley of the Lawrence Radiation Laboratory. The Kr^{85} content ranged from 0.92 to 0.97 mole per cent. The standard volumes of the samples were known, and the numbers of atoms of Kr^{85} were calculated. In turn, the disintegration rates were obtained by multiplying by the decay constant, 1.237×10^{-7} min^{-1}. Additional aliquots of these samples were beta counted in a gas system shown diagrammatically in Figure 1.

This system consisted of an internal gas counter operated in the Geiger region, a krypton carrier bulb, a gamma-counting cell, a manometer and a Toepler pump. A large dump tank was attached for expanding highly radioactive samples to obtain a suitable activity level for counting. A facility was provided for filling the system with Geiger-counting gas consisting of 98 per cent helium and 2 per cent isobutane. The manometer was read with a cathetometer. This system was calibrated with National Bureau of Standards Kr^{85} standard number 4935. The disintegration rate of each of these samples

TABLE I

SUMMARY OF RESULTS[a]

Item	Rod N-5	Rod B-1	Rod A-2	Rod H-1	NBS No. 4935
Mole % Kr^{85} by mass spectrometry	0.92 ± 0.05	0.97 ± 0.05	0.94 ± 0.05	--	--
Std. cc./sample	0.70 ± 0.01	0.40 ± 0.01	0.36 ± 0.01	--	--
Atoms Kr^{85}/sample	$(1.73 \pm 0.09) \times 10^{17}$	$(1.05 \pm 0.05) \times 10^{17}$	$(0.91 \pm 0.05) \times 10^{17}$	--	--
β/min/sample	$(2.15 \pm 0.11) \times 10^{10}$	$(1.30 \pm 0.07) \times 10^{10}$	$(1.13 \pm 0.06) \times 10^{10}$	$(1.53 \pm 0.09) \times 10^{8}$	$(8.2 \pm 0.3) \times 10^{5}$
γ/min/sample	$(8.8 \pm 0.4) \times 10^{7}$	$(5.2 \pm 0.3) \times 10^{7}$	$(4.6 \pm 0.2) \times 10^{7}$	$(5.5 \pm 0.3) \times 10^{5}$	$(2.5 \pm 0.8) \times 10^{3}$
γ/β ratio in Kr^{85}	0.0041 ± 0.0003	0.0040 ± 0.0003	0.0041 ± 0.0003	0.0036 ± 0.0003	0.0031 ± 0.0009

[a] Radioactivity measurements were made between 12-21-59 and 7-21-60 and are normalized to 1-20-60, the date of mass analysis.

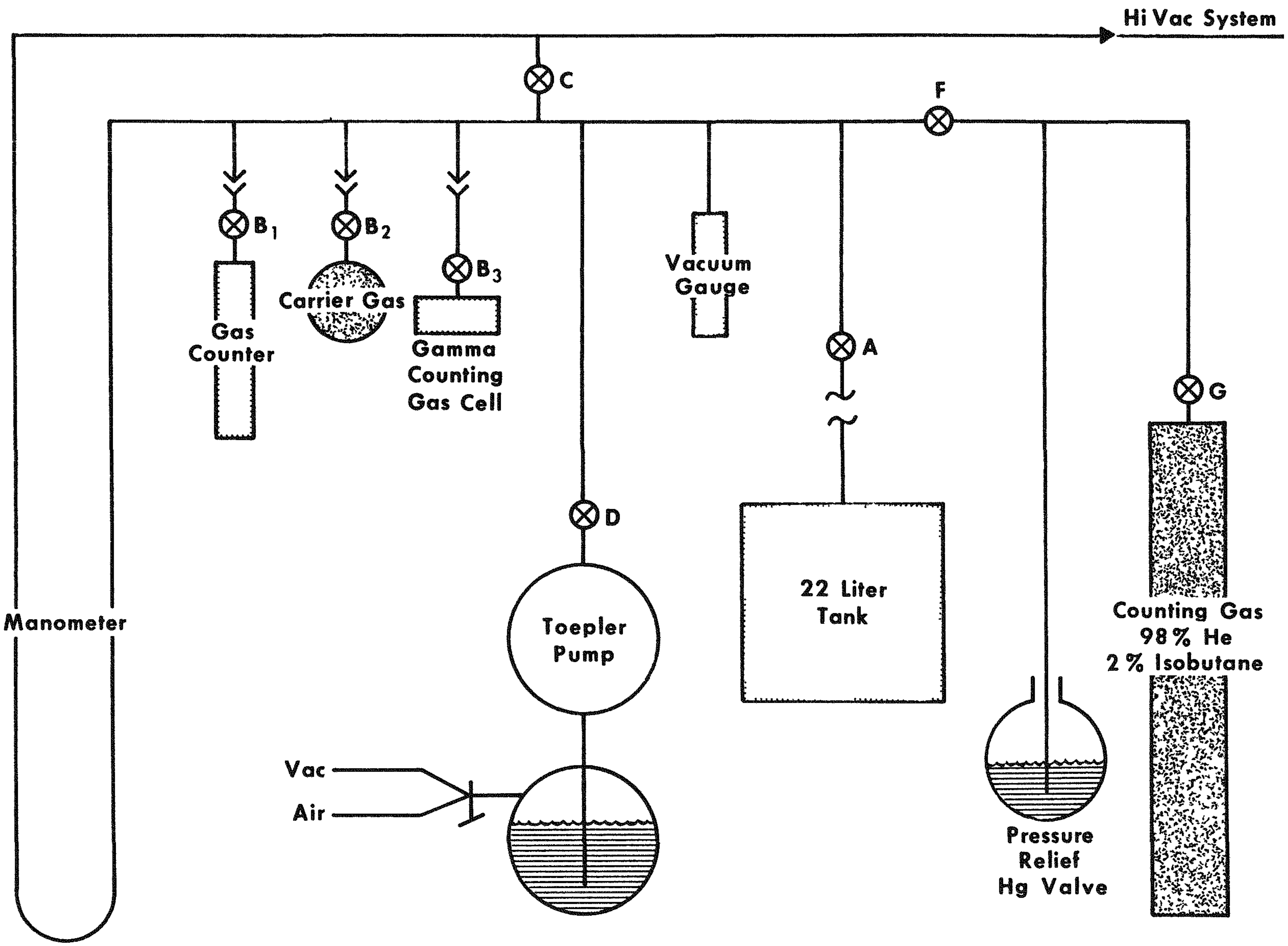

Figure 1. Gas Handling System

agreed with the value obtained by mass spectrometry within 5 per cent which was the standard deviation for an individual analysis.

The gamma-photon emission rates were determined with a NaI(Tl) spectrometer crystal shown in Figure 2. A shelf arrangement consisting of a plywood frame with a movable Lucite shelf 1/8 in. in thickness permits measurements to be made at several fixed low geometries. At distances of 24 to 100 cm, a bulb filled with Kr^{85} can be positioned and counted reproducibly.

The crystal employed is a 3-in. diameter right cylinder 2 in. high with a reasonably good resolution. Figure 3 shows the energy resolution for this crystal which is slightly over 9 per cent for Cs^{137} at 0.66 Mev.

The photopeak efficiency for this crystal was determined for Cs^{137} in each of the eight shelf positions. These data appear in the plot of Figure 4. A Nuclear-Chicago Cs^{137} standard solution, the calibration of which was verified by 4-πcounting, was used to obtain these efficiencies.

The photopeak efficiency for Kr^{85} at 0.513 Mev is greater than that for Cs^{137} at 0.66 Mev. If was found that the photopeak efficiency for 0.513 Mev is 1.24 times as great as that for 0.661 Mev gamma for the crystal used. This value was obtained by comparing at low geometry the photopeak efficiency of a National Bureau of Standards Na^{22} standard sample with the photopeak efficiency of Nuclear-Chicago Cs^{137} standard sample. The upper line in this figure represents the photopeak efficiency for 0.513 Mev gamma after a 5.3 per cent correction has been applied for the loss of gammas by absorption in the glass container walls. The points for the Kr^{85} contained in gamma-counting cells appear at 1.1 cm greater distance from the crystal to allow for the height of the cell. By dividing the number of counts per minute in the photopeak (corrected for background) by the photopeak efficiency for the applicable position, one obtains the absolute gamma-emission rate of the sample.

Figure 5 is a sketch of the Pyrex cell used for counting gas samples for gamma radiation. The center of population of radioactive atoms can be seen to be 1.1 cm above the lower face of the cell. The thickness of the glass is 2.7 mm to prevent collapse under high vacuum.

Figure 6 shows the spectrum obtained from Kr^{85} with this system on a 256-channel analyzer. Superimposed upon the spectrum is the spectrum obtained from Sr^{85} which has a gamma ray with an energy identical to Kr^{85}. The difference between the two spectra results from the presence of bremsstrahlung in the Kr^{85} spectrum from the slowing down and absorption of the many beta particles. The Sr^{85} decays by K electron capture which gives rise to no bremsstrahlung. When only the photopeak area was measured, values for the 0.513 Mev gamma to beta ratio in Kr^{85} ranged from 0.0031 to 0.0041. A median value is 0.0036 ± 0.0008, allowing for reasonable systematic errors. The deviation from the older decay scheme is attributed to the ability of NaI(Tl) crystals to resolve the gamma photopeak from the bremsstrahlung.

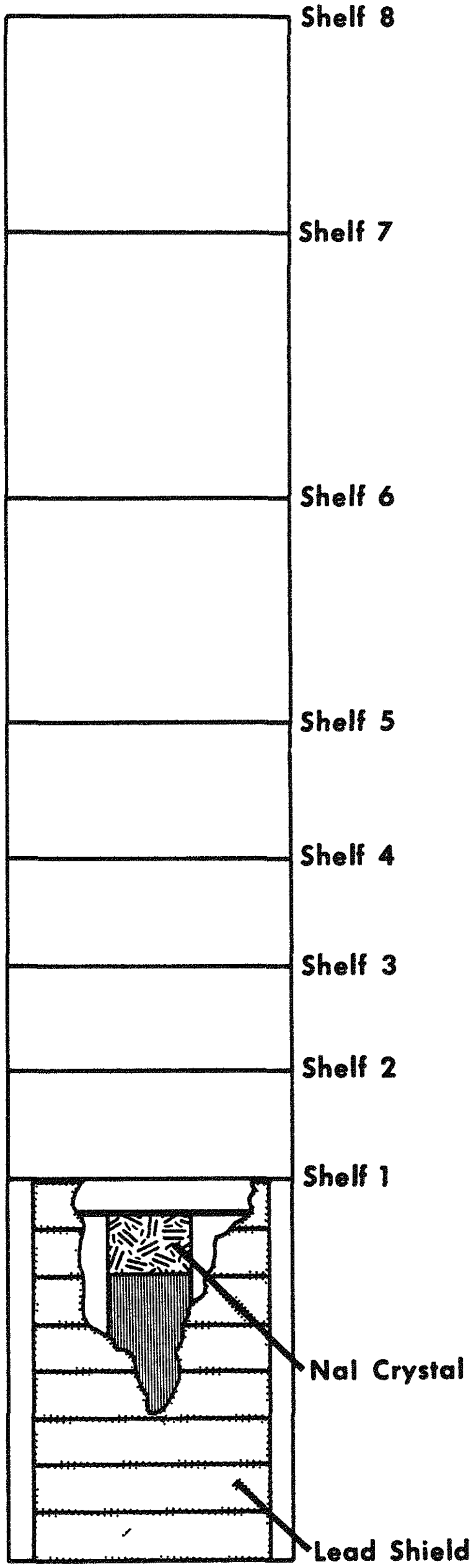

Figure 2. Low-Geometry Arrangement for Gamma Counting

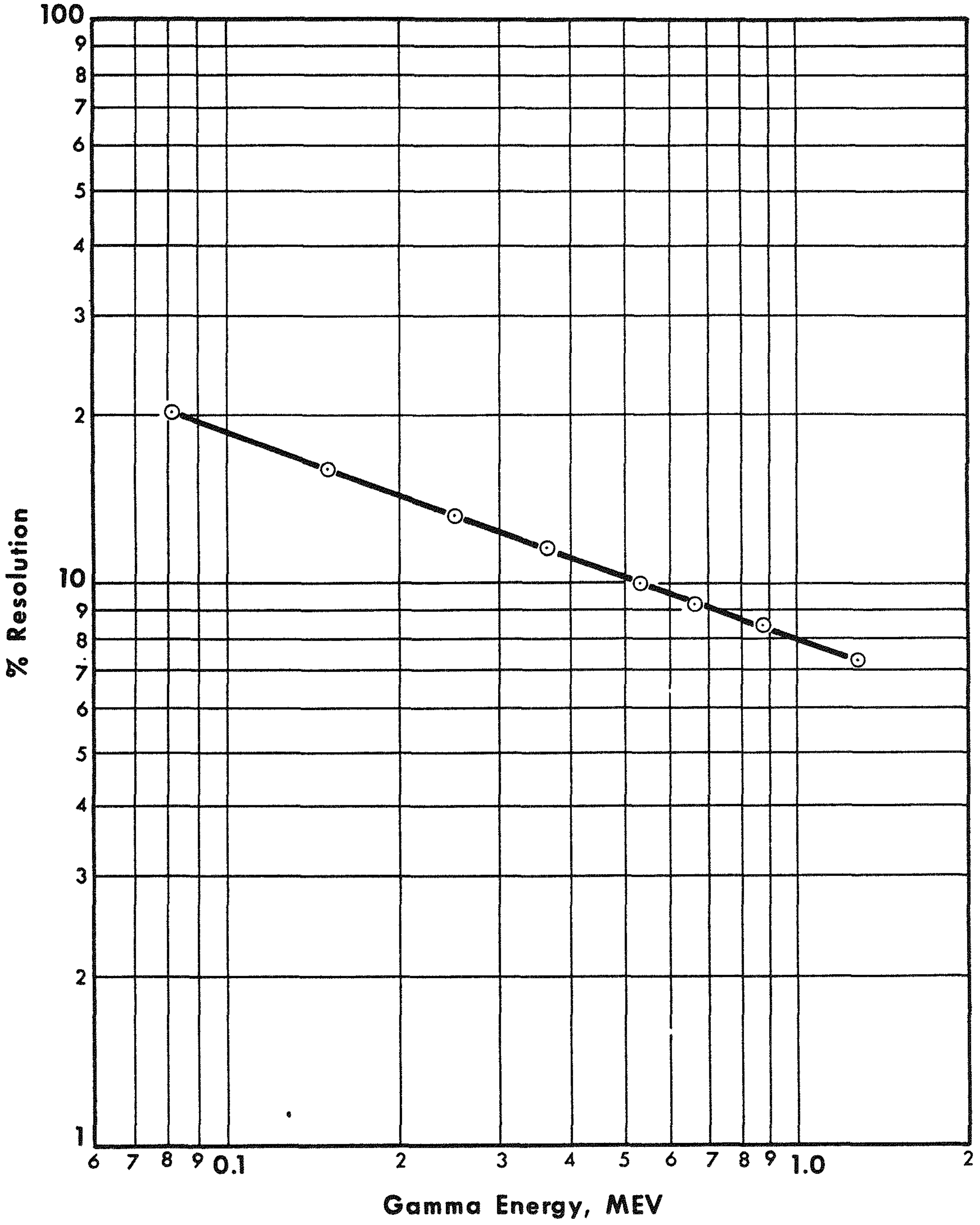

Figure 3. Resolution of Vallecitos Atomic Laboratory 3-In. Diam. by 2-In. High NaI Crystal

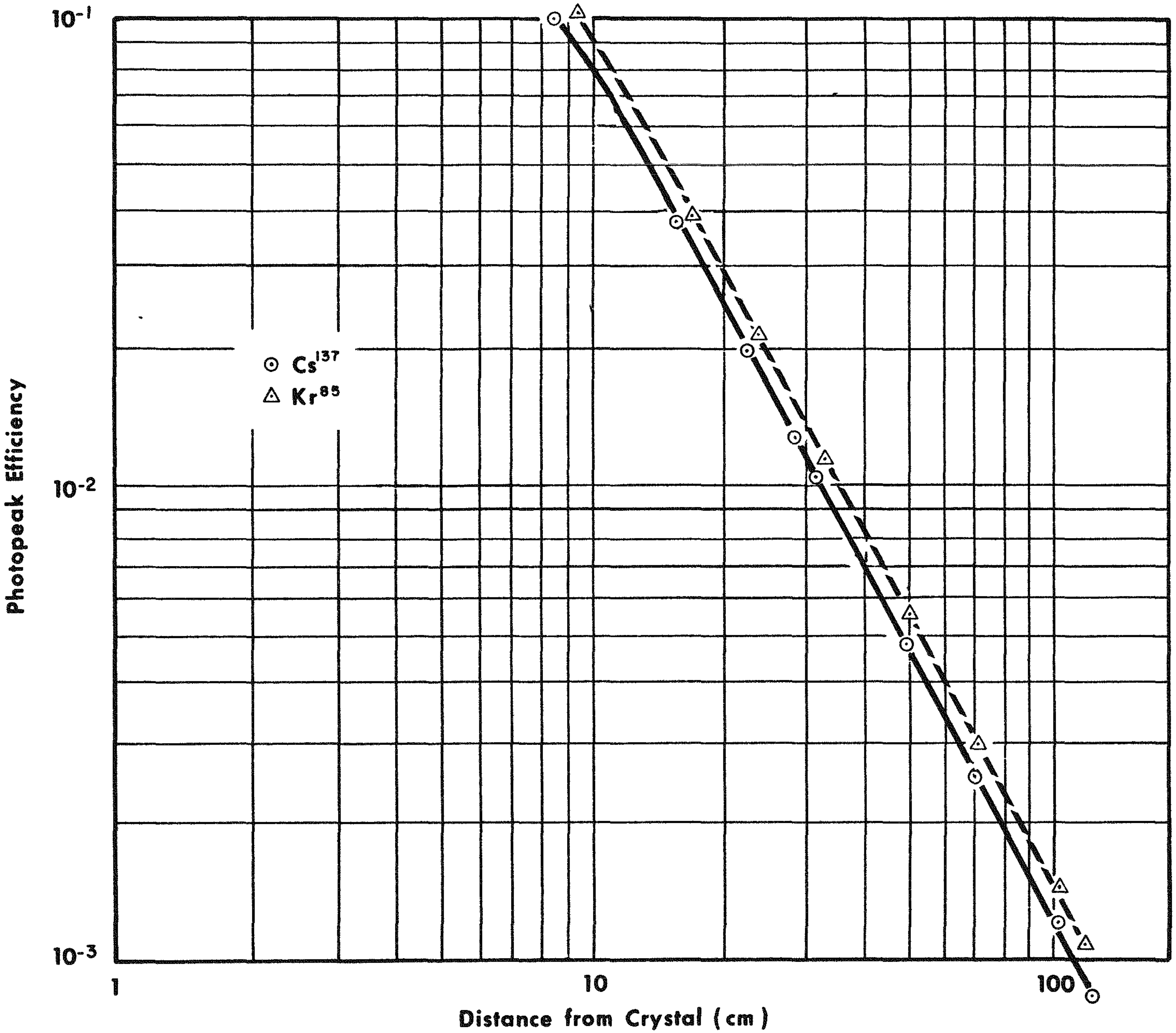

Figure 4. Photopeak Efficiency for 3-Inch Crystal

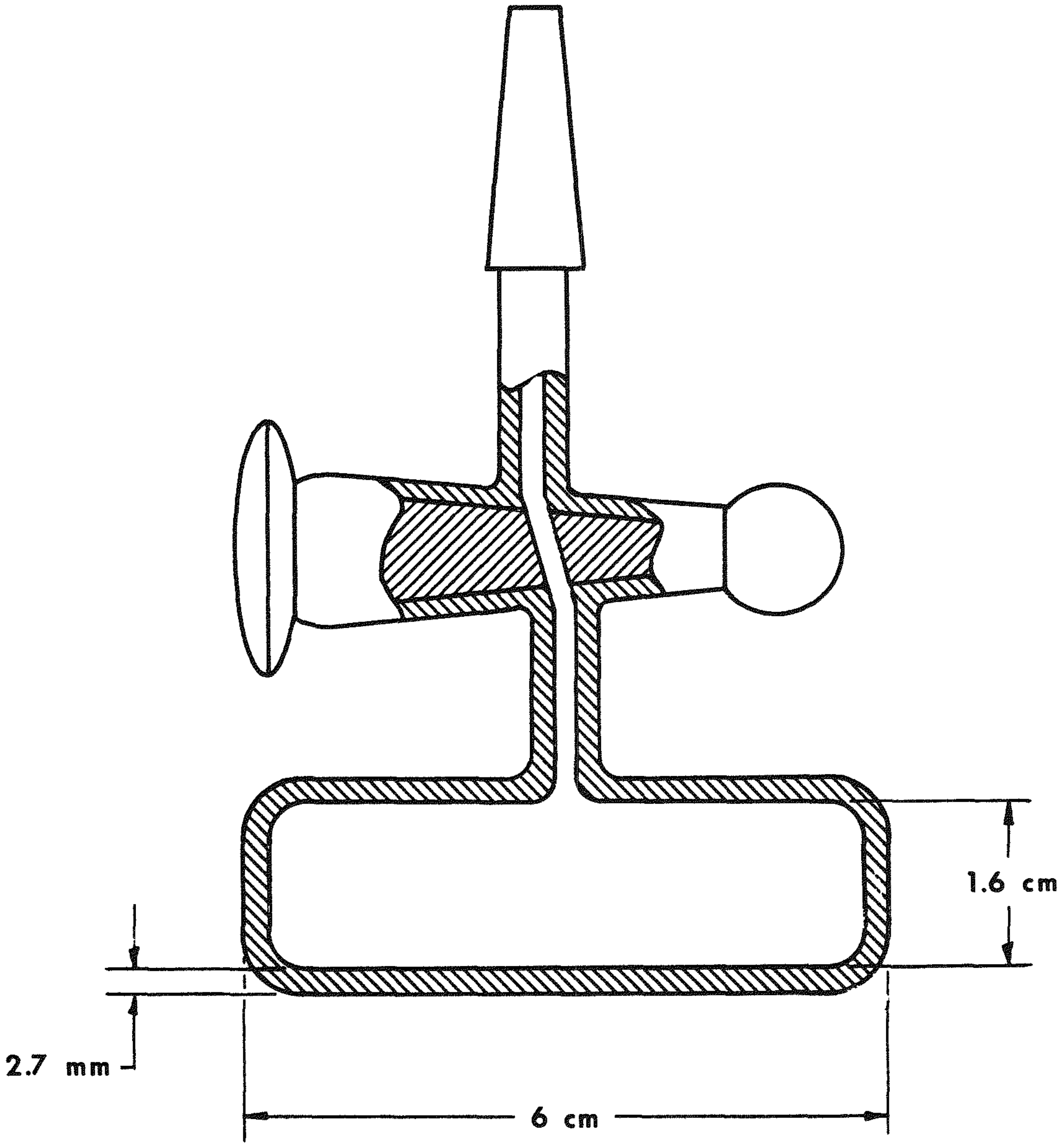

Figure 5. Pyrex Glass Cell for Gamma Counting

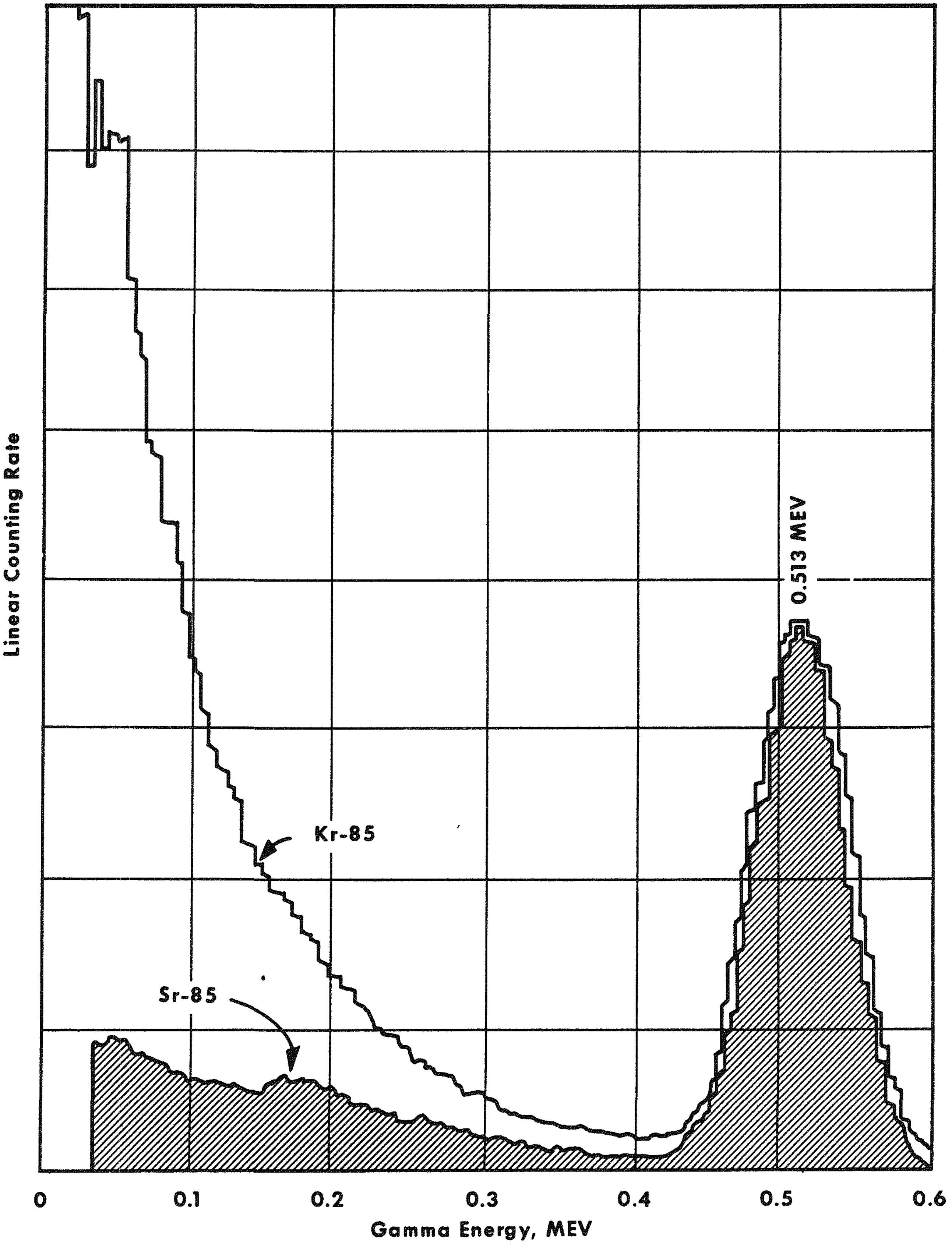

Figure 6. Comparison of Gamma Scintillation Spectra of Krypton-85 and Strontium-85

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APPLICATION OF CONVERSION X-RAY SPECTRA TO ISOTOPIC ANALYSIS. RESOLUTION OF MIXTURES OF Ru^{106}-Rb^{106} and Ru^{103}*

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ABSTRACT

Ru^{103} and Ru^{106}-Rh^{106} activities in a mixture of the isotopes are determined by analyzing both the gamma spectrum and x-ray spectrum of the mixture. The gamma spectrum of Ru^{103} exhibits a photopeak at 500 kev, while Ru^{106}-Rh^{106} shows peaks at 510, 620, 740, and 870 kev. Assay for Ru^{106}-Rh^{106} is obtained from the area under the 620-kev photopeak. Ru^{106}-Rh^{106} exhibits no x-ray, while Ru^{103} shows a 20-kev x-ray resulting from the internal conversion. This is utilized for the assay of Ru^{103}.

INTRODUCTION

There are four known radioisotopes of Ru produced in fission, of which two, Ru^{103} and Ru^{106}, are important because of their relatively high fission yields and long half-lives. The other two, Ru^{105} and Ru^{107}, are not significant because of their short half-lives of 4.5 hours and 4.8 minutes, respectively. The decay chains and fission yields are shown in Figure 1.(1) The more usual technique for analysis of a mixture of isotopes, namely resolution of beta and gamma decay curves, is clearly not feasible due to the long half-lives of the respective isotopes. An additional complication is the great variation in ratio of Ru^{103}/Ru^{106} as a function of irradiation time and decay time. This ratio is determined by the following equation:

$$\frac{Ru^{103}}{Ru^{106}} = \frac{(f.y.)^{103}}{(f.y.)^{106}} \frac{\left(1-e^{\lambda ti}\right)_{103}}{\left(1-e^{\lambda ti}\right)_{106}} \frac{\left(e^{-\lambda td}\right)_{103}}{\left(e^{-\lambda td}\right)_{106}}$$

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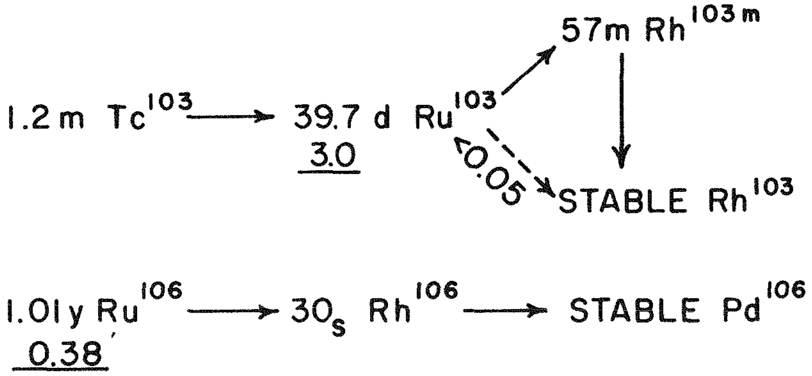
* This work was performed under the auspices of the U. S. Atomic Energy Commission



KATCOFF, SEYMOUR NUCLEONICS, APR 1958, VOL.16, NO.4, PGS 78-85

Figure 1. Decay chains and yields from thermal neutron fissions of U^{235}.

The table in Figure 2 has been prepared for convenience in determining these ratios.

Determinations based on energies of the specific emitted radiations provide other means, which permit a considerably greater degree of latitude with respect to relative abundances and half-lives, for the analysis of radioisotopic mixtures. The development of gamma-ray spectroscopy and multi-channel analyzers has resulted in the current application of this technique for such analyses. There are, however, still many situations where this technique is limited, due to close-lying peaks which are difficult to resolve; such is the case for (Ru^{103}-Rh^{103})-(Ru^{106}-Rh^{106}). Ru^{103} has a predominant gamma peak at 498 kev while the Ru^{106}-Rh^{106} has peaks at 510 kev and 620 kev.

In a mixture of (Ru^{103}-Rh^{103})-(Ru^{106}-Rh^{106}), the Ru^{103} 498-kev peak and the Ru^{106}-Rh^{106} 510-kev peak are additive and result in a single peak at about 500 kev, permitting no distinction between the two isotopes.

The success achieved by Kinsley, Cumming and Finston(2) with Cs^{134}/Cs^{137} analysis, using the x-rays which are emitted after internal conversion of the gamma rays of Cs^{134} and Cs^{137}, indicated that this method could be applied to Ru^{103}/Ru^{106}. Since 100% of the Ru^{103} decay (Figures 3, 4, 5) goes through the 40-kev Rh^{103m} state, the conversion coefficient calculated, using Rose's tabulation(3), is 83.5 and the conversion coefficient calculated for the 510-kev Rh^{106} state is approximately 10^{-2}. Thus the ratio of conversion coefficients for Rh^{103m} and Rh^{106} is 8.35×10^3. It would appear from these calculations that there is a good possibility of detecting small amounts of Ru^{103} in the presence of Ru^{106}. The Ru^{106}-Rh^{106} 620-kev gamma-ray peak is also affected by contribution from a Ru^{103} 613-kev gamma ray. Therefore, the Ru^{103} conversion x-ray peak at 20 kev could be used to correct for contributions of Ru^{103} to the high energy γ spectrum.

EXPERIMENTAL

Gamma Counting Procedure

The high-energy gamma spectra were recorded with a 100-channel pulse-height analyzer: the detectors consisted of a 3 in. by 3 in. NaI(Tl) crystal mounted on a Dumont 6363 photomultiplier tube. An aluminum absorber (984 mg/cm^2) was always interposed between sample and detector to prevent beta particles from reaching the detector. The low-energy spectra ($<$ 100-kev) was detected by a cleaved NaI(Tl) crystal 2-mm thick covered with a 5-mil Be window.

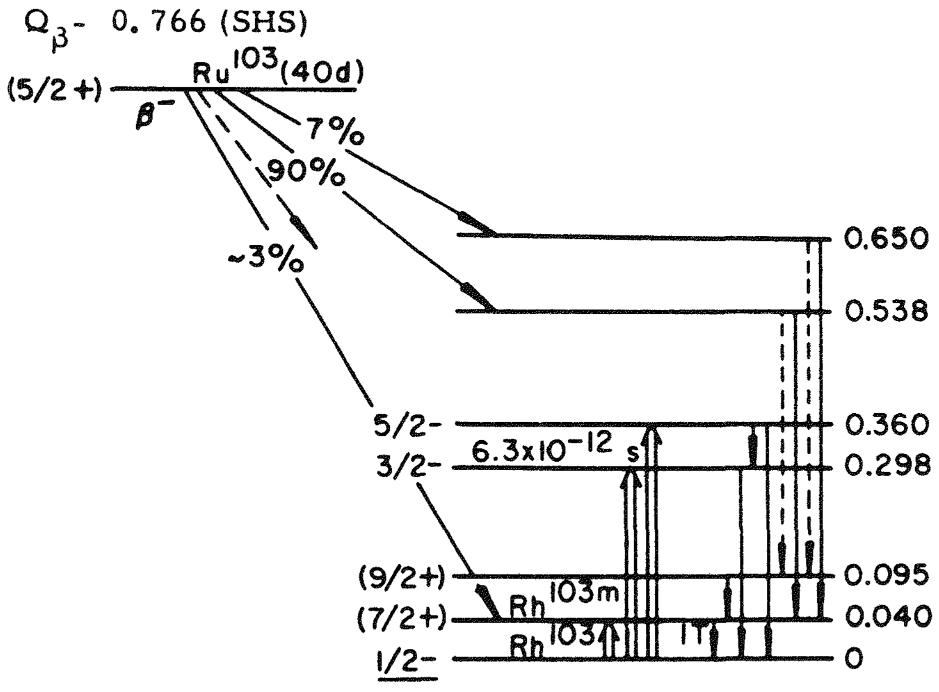
Preparation and Standardization of Samples

The samples were prepared by evaporation of aliquots of the respective solutions on glass planchets 1 in. in diameter (Atomic Accessories Catalog, p. 13). The planchets were subsequently glued onto cardboard counting cards and covered with 1/4-mil Mylar film. The Ru^{103} was prepared by irradiation of $RuCl_3$ for a three-day period at a flux of 7.5×10^{12}. The $RuCl_3$ was enclosed in a quartz tube. Both ends were sealed prior to irradiation. After irradiation, the capsule was opened by cutting through the quartz with a carbide wheel. The two halves were then placed in a beaker containing 0.01 $\underline{N}$ HCl. The quartz pieces were rinsed in the 0.01 $\underline{N}$ HCl and then disposed of. This operation was carried out behind four inches of lead, using overhead manipulators.

RATIO $\frac{Ru^{103}}{Ru^{106}}$

Decay (Days) \ Irradiation (Days) -	1	7	30	60	90	120	150	180
1	69	67	57	47	39	33	29	26
7	64	61	52	43	36	30	26	23
30	45	43	36	30	25	21	19	16
60	28	27	23	19	16	13	12	10
90	18	17	14	12	9.9	8.4	7.3	6.5
120	11.2	10.6	9	7	6.2	5.3	4.6	4.1
150	7	6.7	5.7	4.7	3.9	3.3	2.9	2.6
180	5	4.3	3.6	3.0	2.5	2.1	1.9	1.6
360	2.8	2.7	2.3	1.8	1.5	1.3	1.1	1.0
540	1.8	1.7	1.4	1.2	.98	.8	.7	.6
630	.44	.42	.35	.29	.24	.21	.18	.16
730	.1	.09	.08	.06	.054	.046	.04	.04

Figure 2. Ru^{103}/Ru^{106} ratios as a function of irradiation time and decay time.



(165 S 55a, 52 M 55, SHS)

Figure 3. Decay scheme of Ru^{103}.

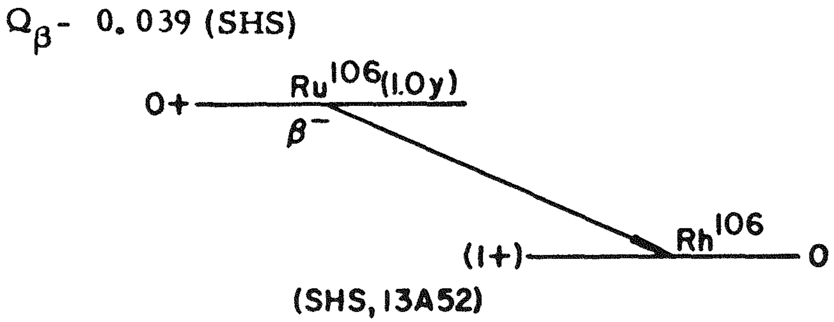
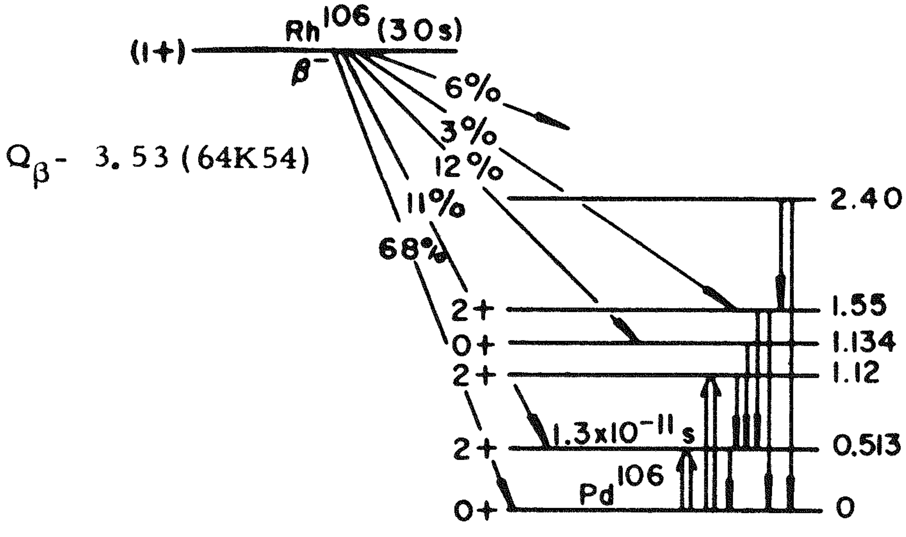


Figure 4. Decay scheme of Ru^{106}.



(13A52, SHS)

Figure 5. Decay scheme of Rh^{106}.

The gamma spectrum of an aliquot of the irradiated $RuCl_3$ solution was determined with a Penco 100-channel analyzer, and indicated the presence of impurities. Purification of the $RuCl_3$ solution was carried out by distilling the ruthenium as ruthenium tetraoxide.(4) The ruthenium tetraoxide distillate was collected in 0.01 N HCl contained in an ice bath. The distilled ruthenium was made up to volume, using 0.01 N HCl. A 4-π count was made of aliquots ranging from 25 λ to 125 λ in increments of 25 λ. The counts were plotted versus the size of the aliquot, giving a straight line. This signified that there was no significant absorption; nor was there any increase in conversion electrons due to solids. An aliquot was evaporated on a glass planchet and counted with the Penco 100-channel analyzer using a 3 in. by 3 in. NaI(Tl) crystal. The high voltage and amplifier gain were set so that each channel corresponds to 12.5 kev. The source was 2.3 cm from the detector with a 984 mg/cm^2 aluminum absorber between source and detector. The area under the 498 kev peak was used to calculate the disintegrations per minute per ml. This was found to be 1.1 x 10^7 d/m/ml, which was in good agreement with the 4-π count.

The Ru^{106}-Rh^{106} sample was prepared from an Oak Ridge National Laboratory standard of Ru^{106}-Rh^{106}. A 1-ml aliquot was made up to 100 ml in 0.01 N HCl. Further aliquots were evaporated on gold-coated VYNS films 10 μg/cm^2 thick. The holder and mounted sample were wrapped in thin aluminum foil (4.63 mg/cm^2) so that only the beta particles from Rh^{106} were counted. The counting was done with a 4-π beta proportional counter. A disintegration rate for Ru^{106}-Rh^{106} of 7.3 x 10^4 d/m/ml was calculated.

Analysis of (Ru^{103}-Rh^{103})-(Ru^{106}-Rh^{106}) Mixtures

Samples were prepared in which the ratio of Ru^{103}-(Ru^{106}-Rh^{106}) was varied while the total disintegration rate was held constant; i.e., d/m Ru^{103} + d/m Ru^{106}-Rh^{106} = constant. The high-energy gamma-ray spectra of these samples were obtained with the 3 in. by 3 in. NaI(Tl) crystal at a source-to-detector distance of 2.3 cm. It may be seen from Figures 8, 9, and 10 that the 510-kev peak of the Ru^{106} adds to the 498-kev peak of the Ru^{103}. The 620-kev peak of the Ru^{106} is somewhat less affected by the presence of Ru^{103} and therefore can be used to analyze for the Ru^{106} after suitable correction.

The counting procedure for all samples, mixtures, and pure isotopes, consisted of collecting approximately the same number of counts in the 500-510 kev peak. The time required to reach this sum of counts was recorded. The low-energy x-ray spectra of the pure Ru^{103}-Rh^{103} and Ru^{106}-Rh^{106} were obtained by counting for 30 minutes; a cleaved NaI (Tl activated) crystal 2 mm in thickness (see Figures 6 and 7) was used.

A sample of pure Ru^{106}-Rh^{106} was then placed in the Penco 100-channel analyzer and counted for a period of time such that the counts under the 510-kev peak were equal to the counts contributed by Ru^{106}-Rh^{106} in the various mixtures. The object of this was to determine the contribution of the Ru^{106}-Rh^{106} in the gamma spectrum of the mixtures. Figures 8, 9, and 10 show the individual contributions of the Ru^{106}-Rh^{106} and Ru^{103}-Rh^{103} to the x-ray and gamma spectra for various ratios. These ratios of (Ru^{103}-Rh^{103})-(Ru^{106}-Rh^{106}) correspond to the following irradiation and decay times:

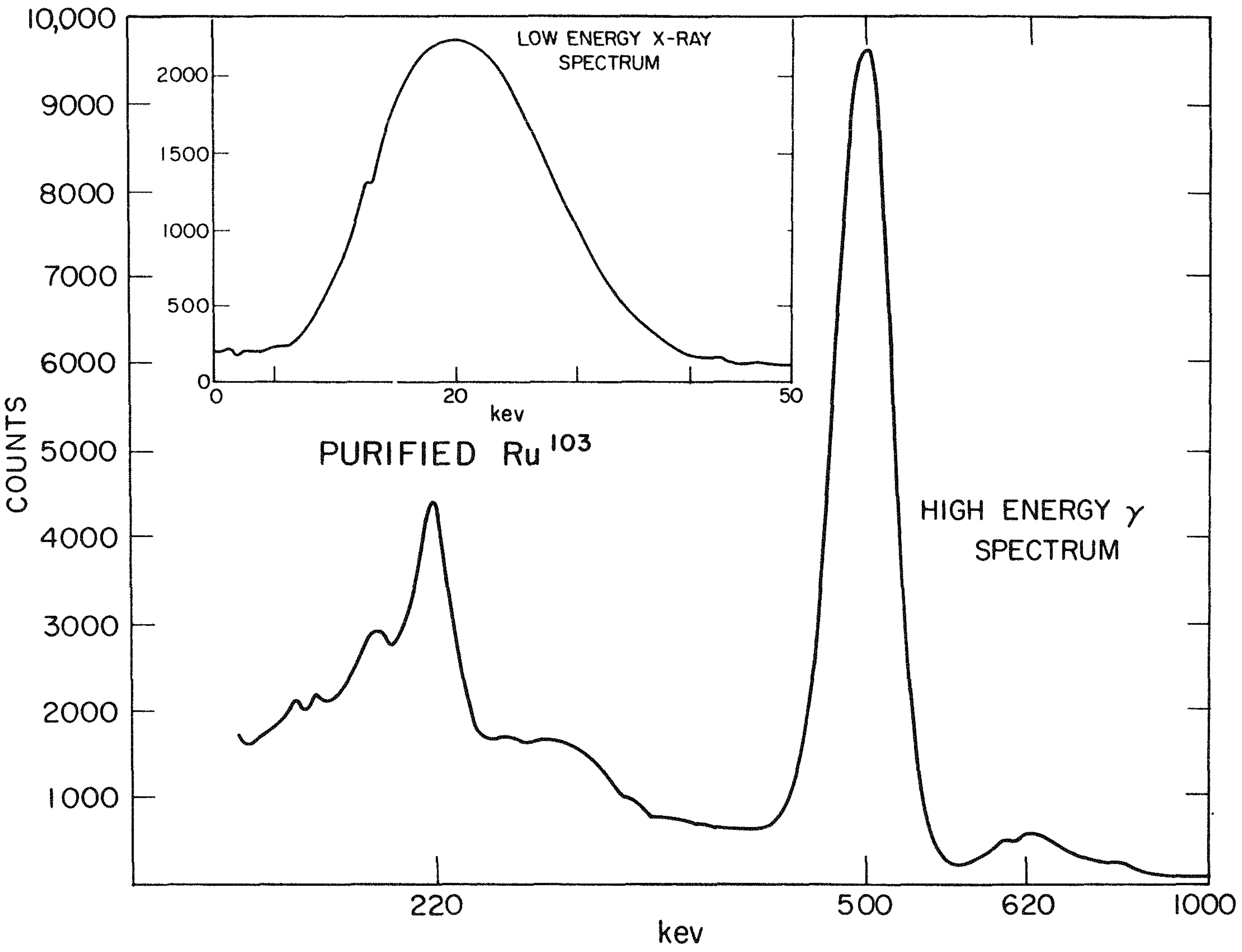


Figure 6. Low-energy x-ray and high-energy gamma spectra of Ru^{103}.

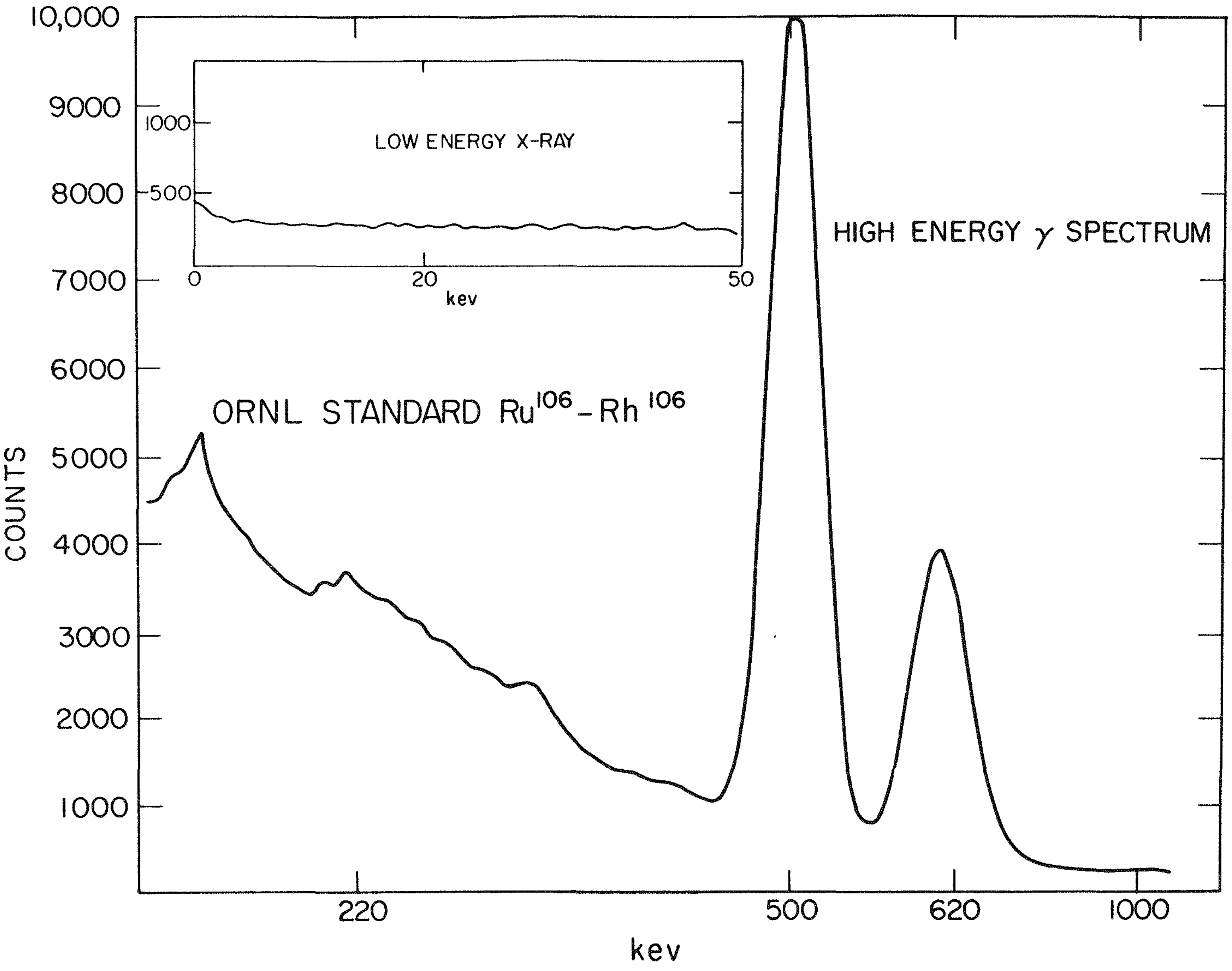


Figure 7. Low-energy x-ray and high-energy gamma spectra of ORNL Standard Ru^{106}-Rh^{106}.

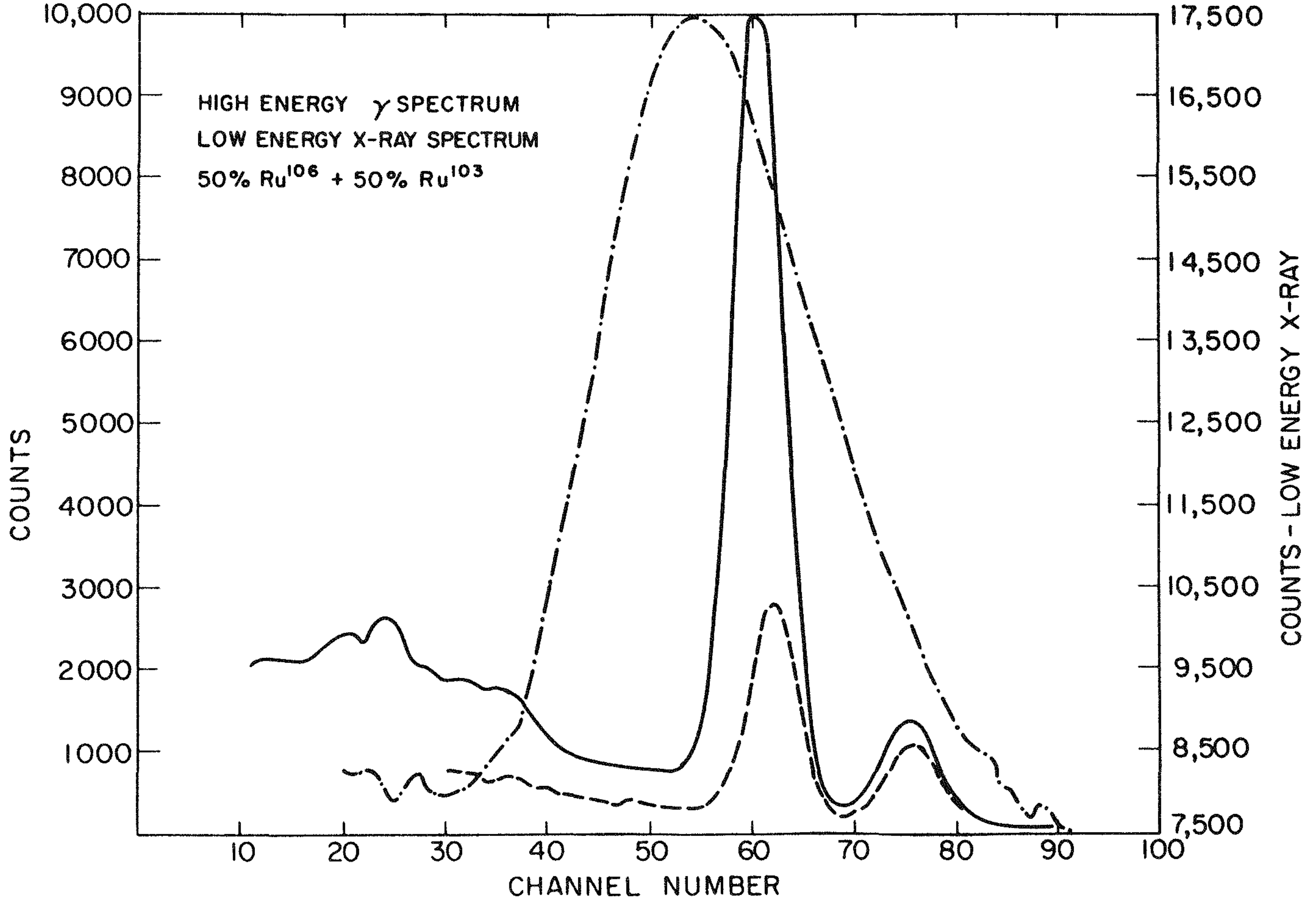


Figure 8. Low-energy x-ray and high-energy gamma spectra of 50% Ru^{106}-50% Ru^{103}.

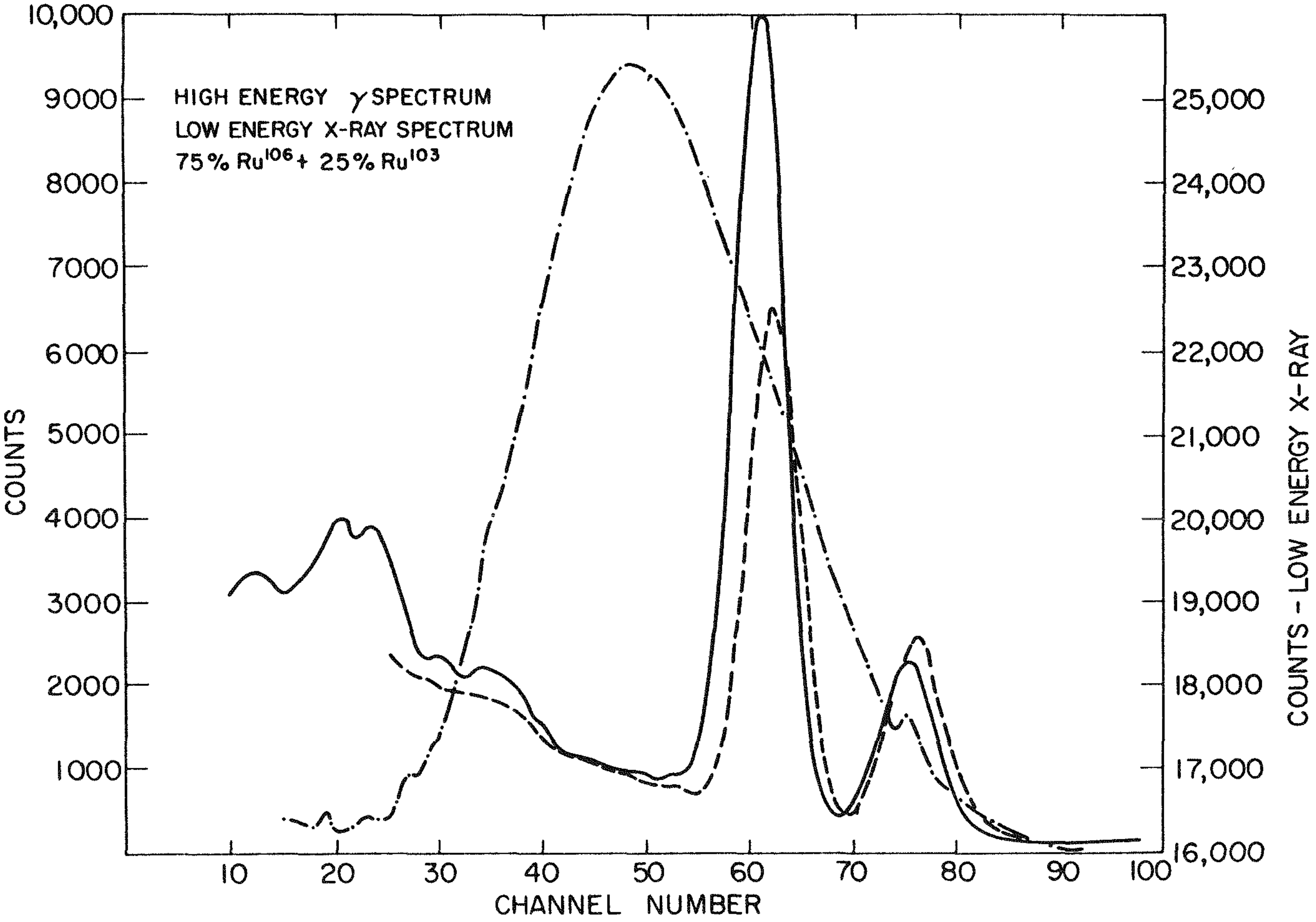


Figure 9. Low-energy x-ray and high-energy gamma spectra of 75% Ru^{106}-25% Ru^{103}.

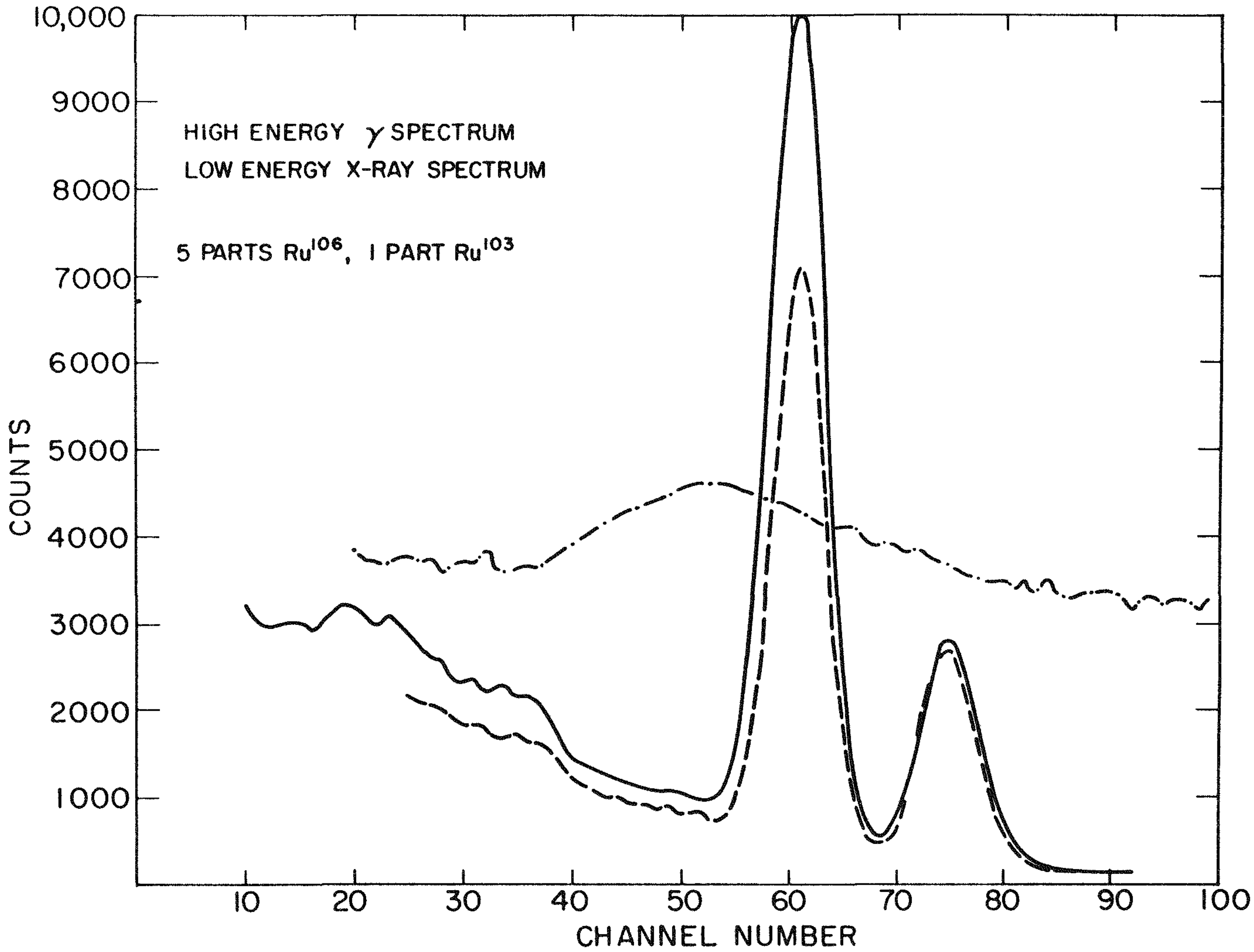


Figure 10. Low-energy x-ray and high-energy gamma spectra of 5-parts Ru^{106}-1-part Ru^{103}.

Ratio	Irradiation Time	Decay Time
5:1	4 months	21 months
3:1	2 months	21 months
1:1	6 months	12 months

CONCLUSIONS

The abundance of Ru^{103}-Rh^{103} activity and Ru^{106}-Rh^{106} activity in a mixture of the isotopes can be detected in ratios up to 9 Ru^{106}-Rh^{106} to 1 Ru^{103}. Such mixtures may be resolved by analyzing both the gamma spectrum and x-ray spectrum of the mixture. It was found that, with the available equipment, the resolution of the low-energy x-ray peak at best was 42%, using a thin crystal. Recent evidence shows that the resolution of these x-ray peaks can be greatly improved by using a proportional counter(5) with a magnetic field to sweep away the interfering beta rays, thereby lowering the background.

It has been anticipated that this technique would constitute a unique and simple method for analyzing such a mixture of isotopes. However, in actual practice, it appears that the well-known(6) method of end-window beta counting through aluminum absorber affords a simpler and more rapid technique for direct analysis of Ru^{106}-Rh^{106}.

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A NEUTRON-ACTIVATION METHOD FOR THE DETERMINATION OF TRACES OF CADMIUM IN ALUMINUM

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ABSTRACT

An activation method is presented for the determination of Cd in Al in amounts as low as 1 part in 10^9. Tablets of Al weighing 300-500 mg together with an aliquot of standard Cd solution were irradiated in the NRX reactor at a thermal flux of about 6×10^{13} n/cm^2-sec. After irradiation, the samples were dissolved, Cd carrier was added, and an anion-exchange separation plus a sulfide precipitation of Cd was made. Irradiated standards were treated in a similar manner.

The purified CdS precipitates were then counted to determine the intensity of the induced radioactivity. A 3-by 3-in. NaI scintillator and 100-channel pulse analyzer were used for gamma counting which gave a gamma spectrum immediately after separation consisting of two photopeaks, that of 53-hr Cd^{115} at 0.523 Mev and that of its radioactive daughter, 4.5-hr In^{115m}, at 0.335 Mev. After one day, the daughter nuclide had grown in to equilibrium and its photopeak appeared in the gamma spectrum with approximately twice the area of that of Cd^{115}. The In^{115m} photopeak area was chosen for the Cd determination. Cd is determined by comparing the sample spectrum with the standard. A comparison of this method with beta counting, using a gas flow proportional counter, gave good agreement.

In order to determine the precision of this method, nine tablets were cut from an Al sample, and each was analyzed separately. From the results, the coefficient of variation was calculated to be 10% at a concentration of 19 ppb. The lowest determinable amount of Cd is estimated to be 10^{-9} g by gamma counting of In^{115m} and 10^{-10} g if the sample is sufficiently pure for beta counting.

ANALYTICAL APPLICATIONS OF DELAYED-NEUTRON COUNTING

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ABSTRACT

Delayed-neutron counting is used as a semiroutine method for the determination of U in a variety of materials. Samples are irradiated in a pneumatic tube of the Oak Ridge Research Reactor. The samples are then transferred from a region near the reactor core to a neutron counting assembly. Submicrogram quantities of U^{235} were determined with a sensitivity greater than 10^{10} counts per gram of U^{235}. Some other fissionable materials are also determined by this method.

EDITOR'S NOTE

This paper is omitted from the *Proceedings* because it is to be submitted to *Analytical Chemistry* for publication.

THE DETERMINATION OF MERCURY IN LITHIUM HYDROXIDE AND LITHIUM CARBONATE BY ACTIVATION ANALYSIS

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ABSTRACT

An investigation was undertaken at the Naval Research Laboratory to determine the magnitude of the Hg contaminant present in LiOH. Hg may be contained in the raw Li minerals, retained in the refining process, and introduced during the process of separating Li isotopes. The potential release of the Hg into a breathing atmosphere, perhaps through some anomalous scrubbing mechanism, and its characteristic toxicity were of considerable concern in this program. As a consequence, interest was provoked to develop sensitive analytical methods for the quantitative detection of minute amounts of Hg in LiOH. Because of the attractive nuclear characteristics of Hg, activation analysis was investigated as a means of determining Hg. A detailed account of a comparator method is described in this report.

Replicate samples of both LiOH and Li_2CO_3 were irradiated in the NRL Reactor for the purpose of determining the amount of Hg present initially in the hydroxide and finally in the carbonate so that information might be gained concerning the fate of the Hg in the scrubbing process. A detailed procedure is described for the irradiation and analysis of the samples, using the radiochemical-carrier technique. Interferences from extraneous induced activity and their subsequent removal are discussed. The principal contaminants are tritium, F^{18}, P^{32}, and Na^{24}. The Hg content is determined by measuring the activity of the Hg^{197m} and Hg^{203} isotopes induced by the (n,γ) reaction. The quantity of Hg in the aforementioned Li compounds was found, by activation analysis, to be of the order of 1 to 2 ppm.

INTRODUCTION

Interest in gas purification utilizing LiOH as a CO_2 absorbent prompted the use of the neutron activation method as a highly sensitive analytical approach to the problem of determining the amount and fate of trace quantities of mercury believed to be present in lithium compounds either naturally or artificially. Favorable cross sections for the reactions Hg^{196} (n,γ) 65h Hg^{197} and Hg^{202} (n,γ) 48d Hg^{203} insured the high sensitivity necessary, about 0.1 μg Hg.(1)

The comparator method was used; that is, a sample of LiOH and Li_2CO_3 containing unknown traces of Hg along with comparators containing known amounts of Hg were irradiated in the Naval Research Laboratory's Swimming Pool Reactor (NRR). Then, after radiochemical separation and purification, the γ-radioactivities of the known and unknown weight of Hg were compared.

IRRADIATION

Samples of LiOH and Li_2CO_3 to be irradiated, ranging from 300 to 400 mg in weight, were sealed in size number 1 gelatin capsules and individually wrapped in 1/4-mil Mylar film. Two comparators of 50 and 100 μg of Hg, as $Hg(NO_3)_2$ in water, were aliquoted onto a Mylar film and dried under a heat lamp. The comparators were also sealed in gelatin capsules and wrapped in Mylar. The Mylar wrapping was necessary as the gelatin becomes very brittle after eight hours or more of irradiation in the reactor.

The above samples were irradiated in the NRR for eight hours at a flux of 10^{12} n/cm^2/sec for a total nvt of 2.9×10^4.

RADIOCHEMICAL SEPARATIONS

The radiochemical purification of the radioactive Hg was a modification of the periodate precipitation method.(2) The samples of LiOH and Li_2CO_3, along with the comparators, were dissolved in water and neutralized dropwise with concentrated HNO_3. An excess of 1-1/2 ml of concentrated nitric acid was added and the solution was diluted to 150 ml with water. Holdbacks of $Cu(NO_3)_2$, $NaNO_3$, H_3PO_4 and H_2SO_4 were added and the solution was heated to the boiling point to facilitate exchange. Two grams of potassium periodate dissolved in 50 ml of water were slowly added to the boiling solution and the precipitate of $Hg_5(IO_6)_2$ was allowed to digest for 1/2 to 1 hours, after which time it was filtered through a medium, sintered-glass crucible and washed with warm water. The precipitate was dissolved off the filter with hot, concentrated HNO_3, diluted with 0.1 $\underline{N}$ HNO_3, and the above radiochemical purification procedure was twice repeated. After the final precipitation and wash with hot water, the $Hg_5(IO_6)_2$ precipitate was dried for an hour at 100°C. The $Hg_5(IO_6)_2$ was weighed in a gelatin capsule and counted gamma wise. A yield of between 40 and 70% was obtained.

Counting was begun on the purified samples 17 hours after removal from the reactor. A well-type scintillation counter with a 2-in. by 2-in. NaI(Tl) crystal was used for gamma counting as well as for determining the γ-spectrum with a single channel analyzer. Purity of the radioactive Hg was verified by the γ-spectrum (Figure 1) and analysis of the γ-decay curves.(3)

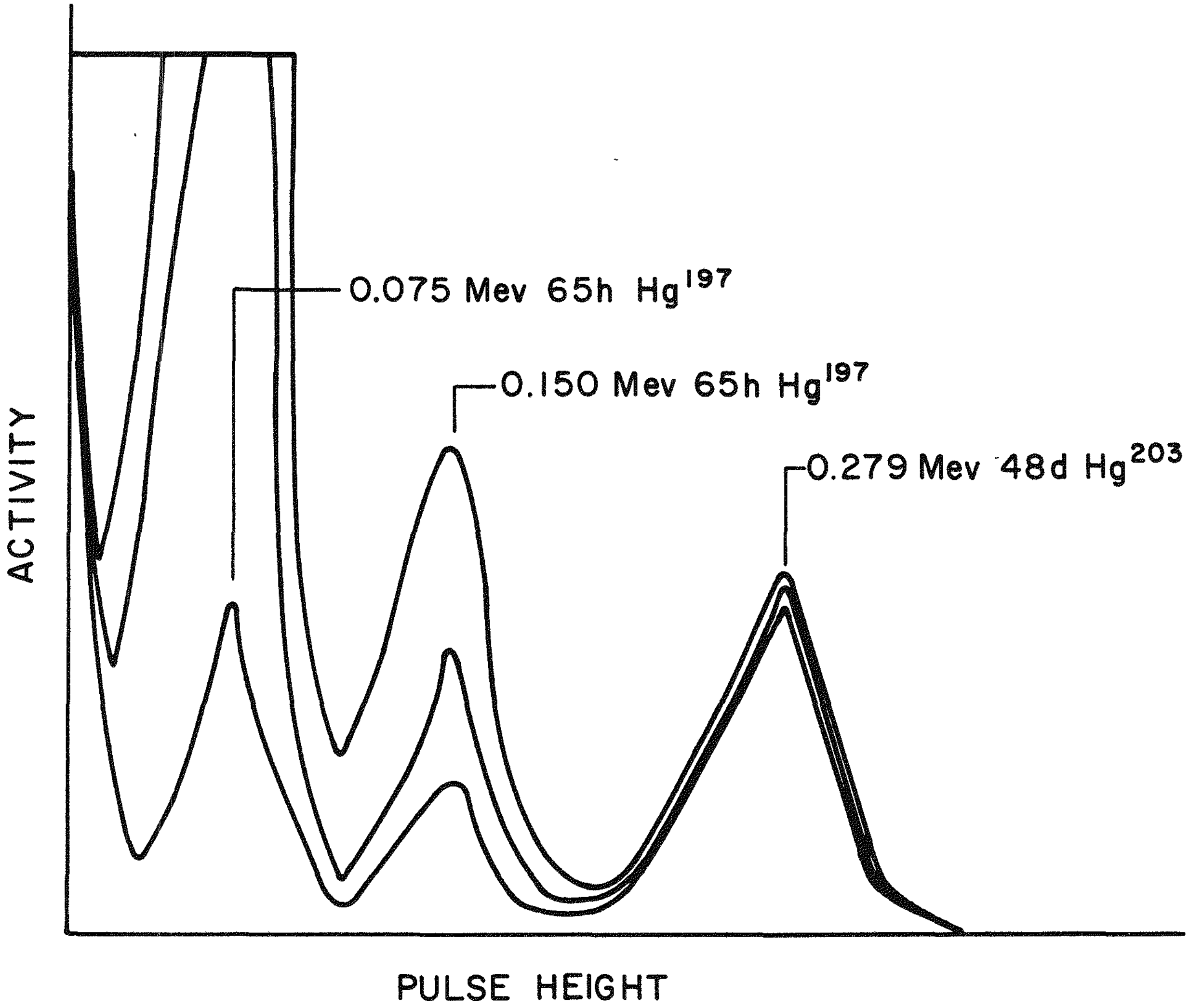

Fig. 1. Gamma-Ray Spectrum for 65-Hour and 48-Day Hg

Extraneous activity found in the LiOH and Li_2CO_3 samples as a result of irradiation include H^3, F^{18}, Na^{24}, Cu^{64}, P^{32} and S^{35}. The radiological health hazard caused by H^3 was minimized by the bulk water added during the first precipitation of $Hg_5(IO_6)_2$. The F^{18} was produced through the interesting reactions $Li^6(n,\alpha)H^3$, and $O^{16}(H^3,n)F^{18}$ and has been used to determine Li^6 and/or O^{16} concentration.(4) The 1.87 hour F^{18} activity did not interfere with the Hg determination due to its short half-life. The long half-life impurities such as Na^{24}, Cu^{64}, P^{32} and S^{35} were removed during purification by holdback carriers. The 15-day P^{32} proved obnoxious by showing up during γ-counting, but could not be identified on the γ-spectrometer. The 15-day P^{32} and also 87-day S^{35} were later identified by Al absorption curves and half-lives with a methane-flow, proportional counter. Subsequent Hg analyses included a P^{32} and S^{35} decontamination sweep. As an added precaution, samples were γ-counted in thick plastic test tubes to reduce bremsstrahlung and β particles from reaching the scintillation crystal.

An analysis of decay curves, even 17 hours out of the reactor, and the γ-spectrum show no signs of 24-hour Hg^{197}. The 65-hour Hg^{197} isotope is dominant for about seven days, at which time 48-day Hg^{203} began to appear. Results calculated from the 65-hour Hg^{197} isotope are given in Table I.

TABLE I

RADIOCHEMICAL ANALYSIS OF LiOH AND Li_2CO_3

Sample	Weight (grams)	Specific Act.* (c/m/µg Hg)	Total 65 hr* Hg^{197} Act.(c/m)	Hg Found (µg)	ppm Hg/ gram of compound
Li_2CO_3	0.4013		6.55×10^3	0.586	1.46
Li_2CO_3	0.3173		5.26×10^3	0.471	1.48
LiOH	0.3678		7.84×10^3	0.702	1.91
LiOH	0.3179		8.24×10^3	0.738	2.32
(Hg) Comparator- 1	5.31×10^{-5}	11.61×10^3	6.17×10^5		
(Hg) Comparator- 2	1.06×10^{-4}	10.72×10^3	1.14×10^6		

* All activities corrected to out-of-pile date. Values given in counts per minute per microgram of Hg (c/m/µg Hg) and counts per minute (c/m).

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APPLICATION OF LOW-LEVEL GAMMA SCINTILLATION SPECTROMETRY

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ABSTRACT

Low-level gamma scintillation spectrometry was investigated as a means of identifying and measuring the gamma radiation emitted by radionuclides in samples of low radioactivity. Determinations of radionuclides in analytical reagents, in environmental samples (water and soils), and in high-purity materials are cited as examples of the applicability of this technique.

The success of this method is attributed to the low environmental background achieved for the detector and the use of large-volume sample containers. Experimental results, showing an integral background count in the range of 0.05 to 4.0 Mev, are presented. Techniques for calibrating the sample containers are described and the complement-subtraction technique of gamma spectral data stripping is explained.

EDITOR'S NOTE

This paper is omitted from the Proceedings because it is to be submitted to Analytical Chemistry for publication.

TECHNIQUE FOR COUNTING LOW-ENERGY BETA EMITTERS

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ABSTRACT

Low-energy beta emitters present an interesting and challenging problem to the radiochemist. The deposit formed by evaporation of liquid samples often introduces uncertainties due to absorption and scattering of beta radiation in the sample itself; in addition, many commonly encountered radioelements form volatile or quite hygroscopic compounds. The methods of 4π beta counting and liquid-scintillation counting have been applied to the assay of a number of these radioelements with considerable success. These two methods are discussed together with the methods for standardization and assay of a number of nuclides, including H^3, S^{35}, C^{14}, Pm^{147}, Tc^{99}, and Ca^{45}.

FAST-NEUTRON ACTIVATION OF SEAPLANE MATERIALS

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ABSTRACT

An experimental study was conducted to determine the fast-neutron activation properties of seaplane hull materials. In the course of this work, a method was devised for measuring the fast-neutron activation cross sections of reactions occurring in metal alloys and a study was made to establish the extent to which activated sea-water materials might adhere to the hull of a nuclear-powered seaplane. Special irradiation and handling equipment was designed for these experiments.

Fast-neutron activation properties were determined for aluminum alloys 2014, 2024, 75ST clad and unclad, and three British aluminum alloys. The major isotope products contributing to the radioactivity of the specimen were identified as Mg^{27} and Na^{24}. The results are presented in the form of curves which are useful for calculating expected dose rates from specimens at any time after irradiation by any combination of fast and thermal neutrons.

A value of 3.5 mb ±20% was obtained for the reaction $Al^{27}(n,p)Mg^{27}$. A previously reported value of this cross section is 2.8 mb.[a] Cross sections were obtained for the $Al^{27}(n,\alpha)Na^{24}$ reactions through analysis of the Na^{24} gamma activity induced in different alloy specimens. The cross section for the $Al^{27}(n,\alpha)Na^{24}$ reaction was found to be 0.58 mb ±17%; this is in close agreement with the previously reported value of 0.60 mb.

The sea-water experiments were performed by irradiating small aluminum specimens in a container filled with sea water. Control specimens were

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[a] D. J. Hughes, Pile Neutron Research, p 100, Addison-Wesley, Cambridge, Mass., 1953.

irradiated in distilled water under otherwise identical conditions. The activity of specimens irradiated by the fast neutrons while in sea water was less than 0.5% higher than the activity of the identical specimens irradiated in distilled water. The quantity of irradiated salt that would correspond to this increase in activity is equal to the amount of salt that normally remains on a specimen, after wetting, without irradiation.

Advances in Instrumentation and Computer Usage

PLASMA-JET EXCITATION OF URANIUM HEXAFLUORIDE*

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ABSTRACT

In the application of emission spectroscopic techniques to the isotopic assay of U at the Goodyear plant, it was initially specified that direct spectral excitation of gaseous UF_6 be utilized. Three approaches to the problem of attaining direct spectral excitation were studied before a satisfactory solution was reached. In the first method, the UF_6 and a carrier gas were introduced directly into an arc gap through a gas-transport electrode. Because of chemical reaction between the UF_6 and the electrode material, it was difficult to use this technique for prolonged excitations. The second method involved the microwave excitation of the UF_6 as it flowed at a low pressure through a glass tube. This technique provided insufficient radiation intensity to be practical with the spectrometers available.

In the third method, which is presently in use, a plasma jet is utilized as a spectroscopic source. In the stabilized version of the plasma jet, as developed at the Goodyear plant, UF_6 is fed into the center of a plasma discharge. The excited spectra are obtained from the radiation of the "flame," 5 mm in height, which forms at the jet orifice. This "flame" has little internal structure. In appearance, the "flame" resembles a radiating tube enclosing a rod radiating at a slightly lesser intensity. The projected image, therefore, is somewhat less intense in the center than at the edges. A slightly better signal-to-noise ratio, however, is available from the central radiation. Optical alignment is simple and noncritical.

Samples are obtained by freezing out UF_6 on the walls of a small trap. The UF_6 is then carried into the jet for excitation by a modest flow of He (10 to 30 ml/min). This flow rate is sufficient to sweep the sample into the jet because of the appreciable vapor pressure of UF_6 at room temperature. Additional

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* This work was performed under Contract AT-(33-2)-1 with the U.S. Atomic Energy Commission.

He is introduced into the sample stream beyond the trap, diluting the sample and speeding it to the excitation zone. Ten to thirty ml of UF_6 is consumed per minute in average excitations. This consumption rate is independent of the size and configuration of the sample trap but is primarily a function of flow rate of the sweep-gas. While direct-current excitations, utilizing currents of from 10 to 30 amp, are practical, experience indicates that a plateau of optimal currents is centered around 20 amp for the units used.

By utilizing a gas-handling system designed for the alternate analysis of two gas samples, standard and unknown samples can be compared. Cross contamination or "memory" is not exhibited.

In tests of the plasma jet source on the ORGDP direct-reading spectrometer, the output was sufficiently constant to permit the recording of a wavelength scan in real time. Such stability makes possible its use with sequential as well as parallel readouts. The device is now available as a radiation source for UF_6 samples in an isotopic direct-reading system. Its performance will be checked with several spectrometers and readout schemes before a complete instrument is specified. Consideration is also being given to the source for continuous monitoring applications.

INTRODUCTION

Plasma-jet spectral excitation of uranium hexafluoride (UF_6) satisfies one of the original specifications proposed for an isotopic analytical system based on a direct-reading, scanning spectrometer.(1) It was proposed that the system accept UF_6 samples as taken from the gaseous diffusion cascade and excite uranium spectra from them without preliminary chemical conversion of the UF_6. In the first approach, UF_6 was introduced into a dc arc gap through a gas transport electrode.(1) This technique, unfortunately, provided a poor signal-to-noise ratio in the uranium spectra and suffered from chemical reaction between UF_6 and the transport electrode.

In the second excitation technique used, 2450-megacycle microwaves were caused to act upon UF_6 gas flowing at reduced pressure in a glass tube.(2) While this technique provided an excellent signal-to-noise ratio, the spectral brightness proved to be impractically low for the spectrograph available.

When a plasma jet was first proposed as a spectroscopic source,(3) it appeared to have characteristics well-suited to the handling of gas samples. Preliminary experiments, using the UF_6 "sweeping" technique of the gas transport electrode approach with a crude plasma jet, suggested that the method was worthy of development. Positional instability of the discharge "flame" from the jet was overcome with the design of an external, yet integral, electrode(4) which served as the cathodic electrical return for the dc power.

JET DESIGN AND OPERATION

The final design of the UF_6 jet, shown operating in Figure 1 and drawn sectioned in Figure 2, provides a discharge "flame" with a useful radiation column, 8 mm high and 3 mm in diameter, between the tungsten electrode A and the orifice electrode B. The UF_6 sample, diluted with helium "sweep-gas," is introduced into the discharge zone through the inlet tube C_2 and the anode electrode C_1.

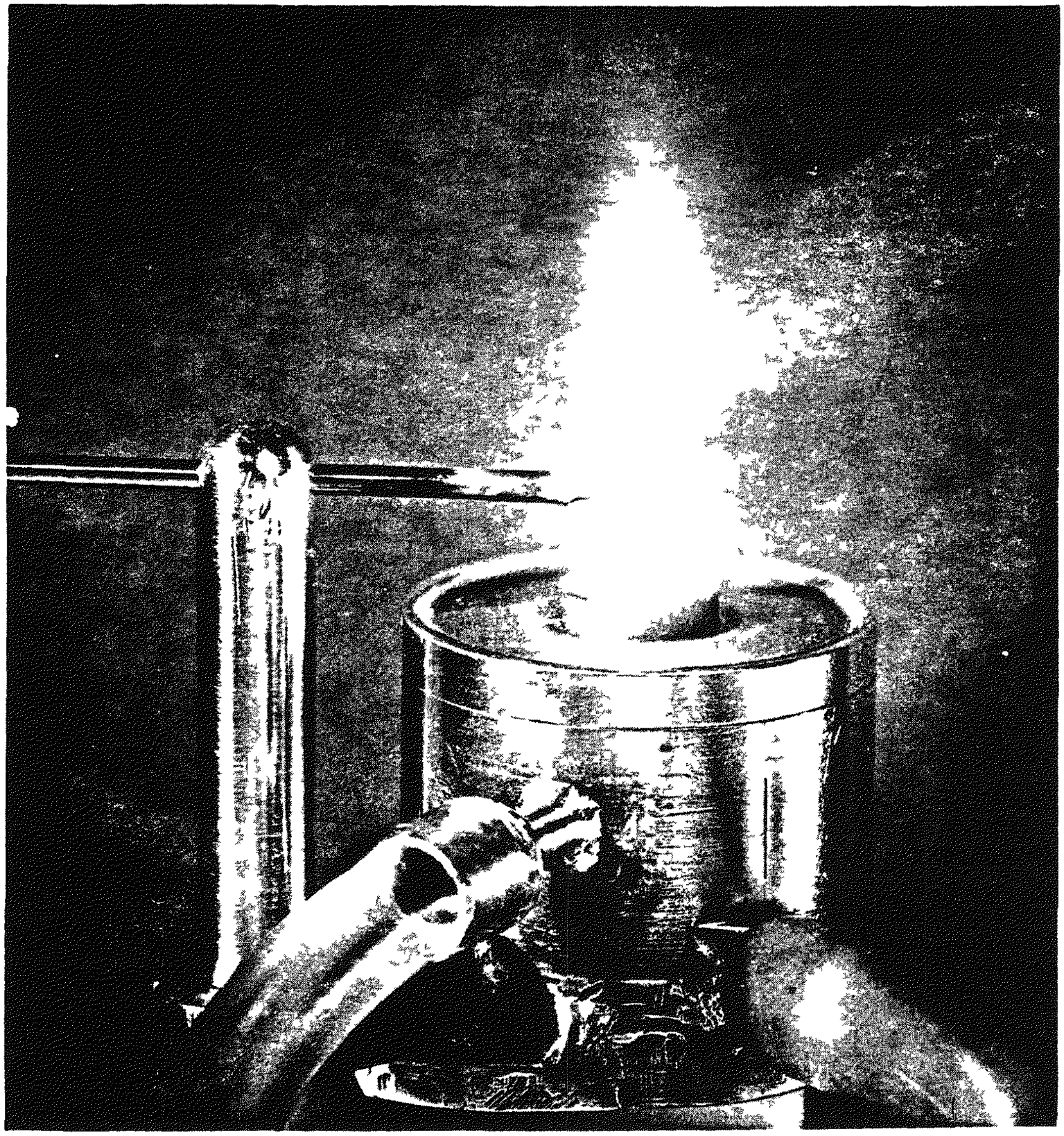

Figure 1. Plasma jet excitation of UF_4.

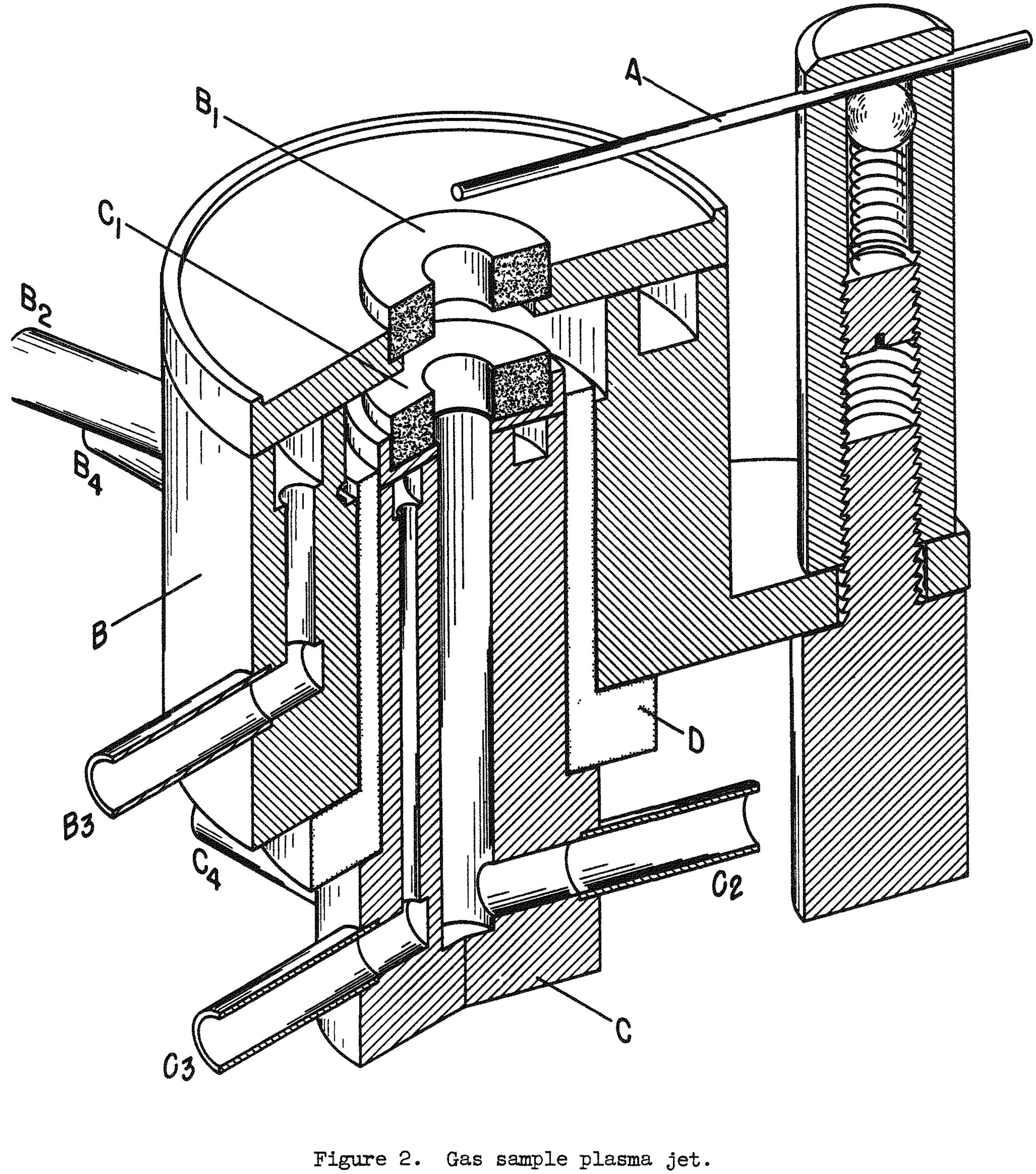

Figure 2. Gas sample plasma jet.

The body of the jet is the cathode assembly B to which the electrode A is electrically connected. The anode assembly C is insulated from B by the Teflon sleeve D. Both B and C are water-cooled through tubes B_3, B_4, C_3, and C_4. The electrical discharge takes place initially between electrodes C_1 and B_1. The cathode return quickly transfers from B_1 to the external tungsten rod A when the discharge, which is blown through B_1 in the form of a "flame," impinges upon A. Emission of radiation above the rod, while providing a flamboyant display to the eye, has no spectroscopic significance since the tungsten does not contribute spectra to the optically useful zone between A and B_1. The tungsten electrode is consumed at such a slow rate that it can be adjusted manually between sample runs. Its position is not critical.

The jet excites the pertinent uranium spectra most efficiently at 20-ampere currents while exhibiting a 95-volt drop across the dc power supply. The principal use of helium is the 20-liters-per-minute introduced through B_2 to swirl the discharge and isolate it from the orifice electrode B_1. Since B_1 is electrically inactive, except at the start of a discharge, it is not subject to erosion.

SAMPLING

Uranium hexafluoride for emission work is obtained from the same traps used to sample the gaseous diffusion cascade for mass spectrometric analysis. The gas stream containing UF_6 flows through the trap, which is immersed in cold water. The UF_6 freezes out on the walls of the tubing, as shown in Figure 3.

For jet use, helium flows through the trap at room temperature at a modest flow rate of 10 to 30 ml/min and acts as a "sweep-gas" to entrain some of the gaseous UF_6 which sublimes from the solid. The solid has a vapor pressure at 20° C of 100 mm Hg. An additional helium flow, labelled "bleed" in Figure 3, of about 1.5 liters/min dilutes the sample and moves it more quickly to the sample inlet C_2.

HANDLING AND CONTROLS

Sample handling and jet operation are made simple and safe by the manifold and controls shown in Figure 4. The sample trap connects directly to two male inlets on the panel face. The flowmeters monitor the flows indicated in the manifold schematic diagram of Figure 5. START, PROGRAMMED OFF, and OFF pushbutton switches control solenoid valves 1 and 2. Solenoid valve 1 is operated at the same time that the R.F.-ignited dc-arc power supply is energized to the jet. Flow of the tangential swirling gas to B_2 and the "bleed" gas to C_2 starts immediately. The sweep gas, however, is initially vented to the atmosphere. At a timed interval after starting, or when desired, solenoid 2 is de-energized and the sweep-gas passes through the sample trap to carry UF_6 to the jet.

For a programmed stop, solenoid 2 is energized to stop the sample pickup and permit the UF_6 to be flushed from the system before the other gas flows and the power are turned off. It is feasible to use a dual sample manifold with the jet since it does not exhibit carry-over contamination, or "memory." Transfer valves placed after the "bleed" and sweep flowmeters are used to select the trap for sampling. The outlets of the two are simply combined as shown in Figure 6. No evidence of cross-contamination was shown in tests using UF_6 with assays differing by a factor of 80.

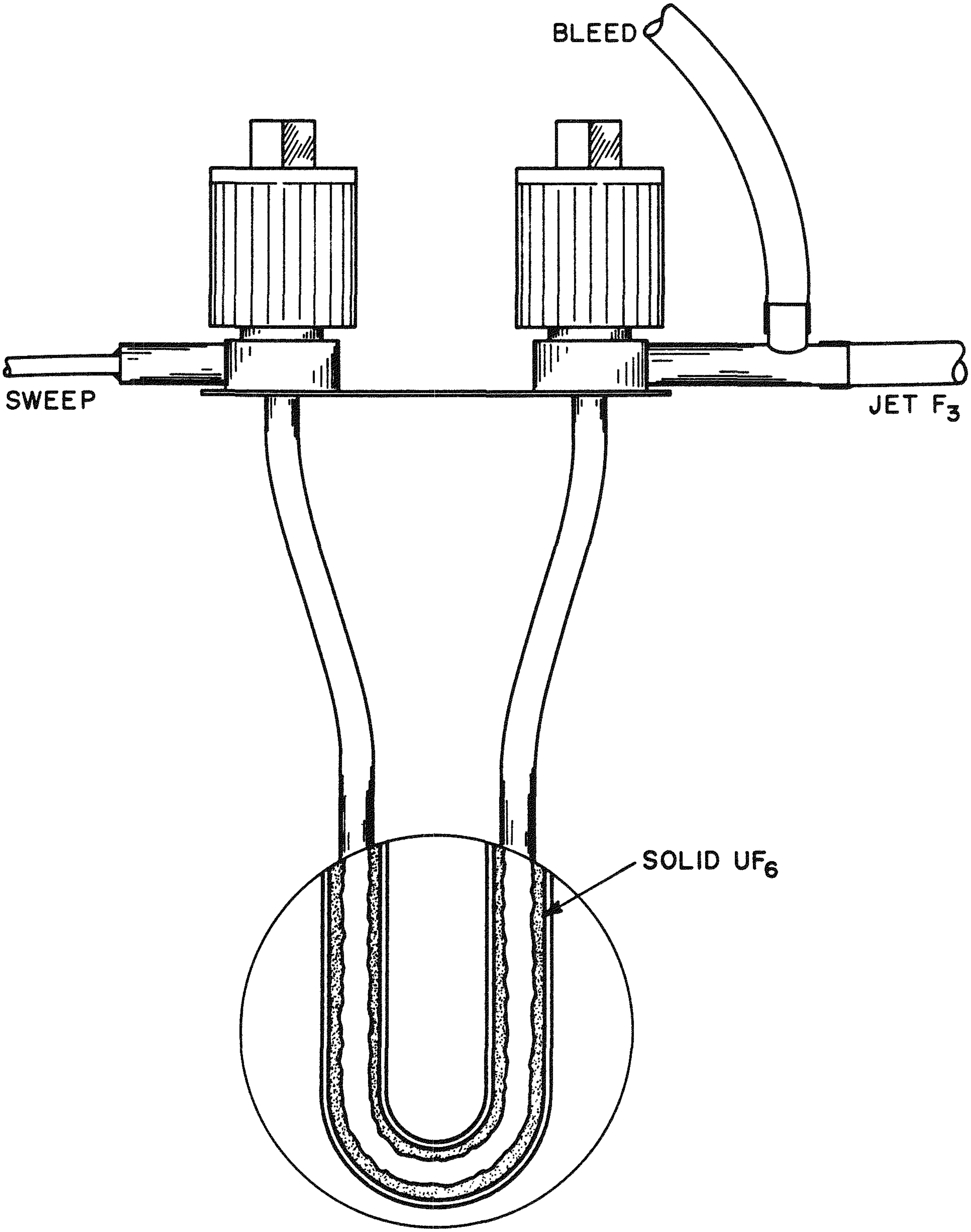

Figure 3. Sample trap for UF_6.

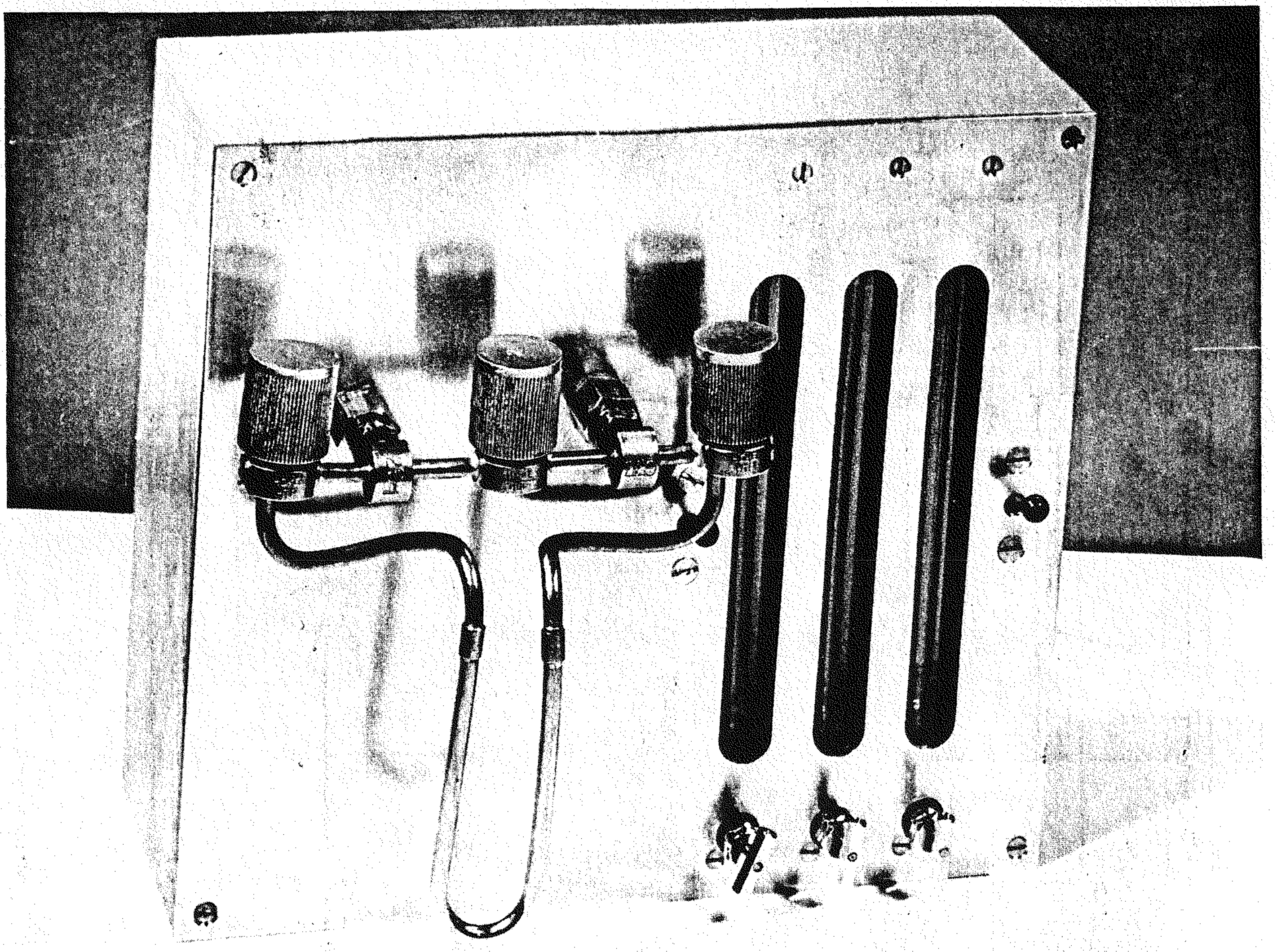

Figure 4. Sample manifold for gas jet.

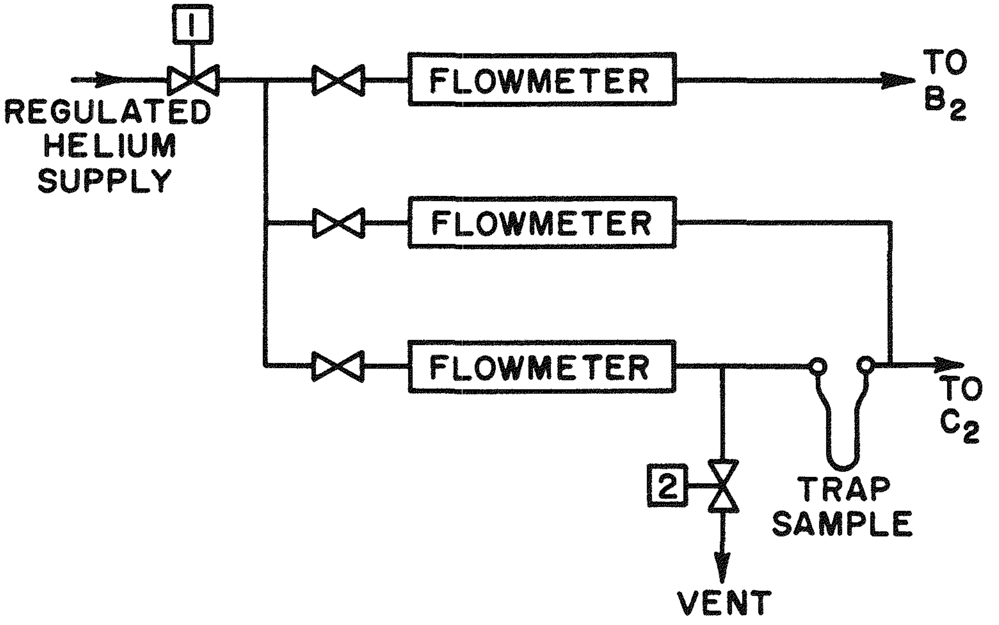

Figure 5. Gas-jet manifold.

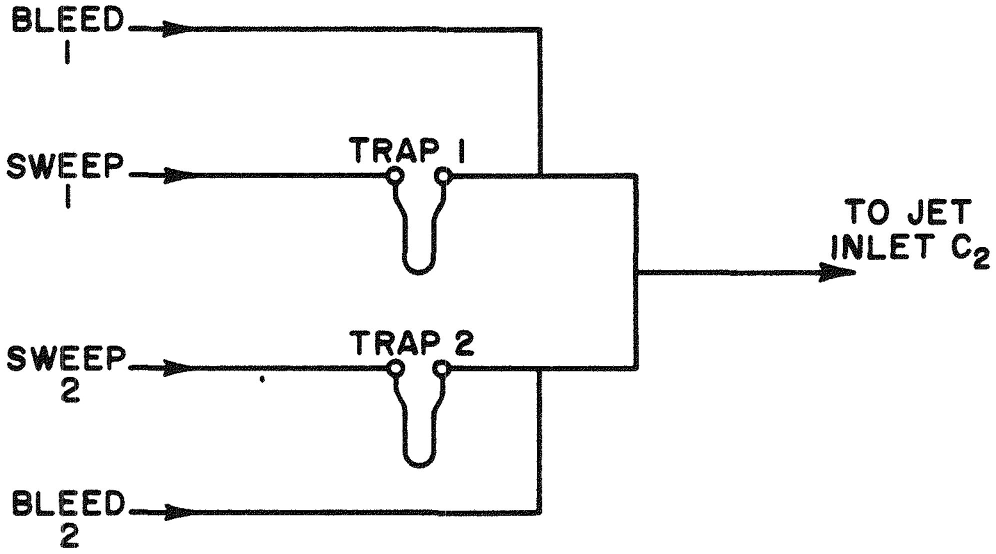

Figure 6. Dual sample connections.

DISCUSSION

The uranium spectra resulting from the excitation of UF_6 in the plasma jet have an excellent signal-to-noise ratio and great intensity. The jet should make possible the assembly of a direct-reading, isotopic-assay spectrometer without the requirement of great optical speed for the monochromator.

This excitation system will be tested with various dispersive instruments and read-out circuits to permit evaluation of the performance of potential analytical systems.

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CHROMATOGRAPHIC ANALYSIS OF RADIOACTIVE GASES*

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ABSTRACT

Failures of the cladding on metallic U fuel elements are signaled by release of radioactive fission products. The noble gases Kr and Xe are among the first of the radioisotopes to enter the coolant, and provide convenient "rupture" signals for suitable monitors.

Significant amounts of radioactive gases are normally produced in the coolant by irradiation of dissolved air. These radioisotopes present a troublesome noise level for conventional activity monitors, and a large increase in noble-gas activity is usually required for reliable rupture detection.

Gas chromatographic rupture monitors can be used to provide high signal-to-noise ratios by separating gases into relatively pure fractions, discarding the irradiated air, and measuring traces of noble-gas fission products with beta-sensitive detectors.

Radioactive gases are stripped from the reactor coolant with He, which is then dried and piped to a monitor. A sequence control actuates three-way solenoid valves to inject samples of the stripped gas into a chromatographic column at preset intervals. This column is a section of aluminum

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*The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

tubing (60 in. long, 0.25-in. OD, 0.035-in. wall), which is packed with 20-50 mesh particles of Linde Molecular Sieve type 5A, and coiled to a 4-in.-diameter spiral. The samples are eluted from the column with fresh He and emerge through discriminator valves to a gas-counting cell. The sequence control can be set to discard N_2 and O_2-Ar fractions by timed operation of the discriminator valves. The instrument will respond to Ar, Kr, and Xe radioisotopes.

A prototype monitor, model 1 GC rupture monitor, gave very good performance during four months of continuous laboratory testing and 11 months of field service. The design of the model 2 GC rupture monitor was based on these tests. With the exception of the automatic chromatograph assembly, which may easily be assembled from standard parts, all components of the model 2 are available commercially.

* * * *

In nuclear reactors with recirculated coolant, high radiation levels can be generated from irradiation of trace contaminants in the coolant. This problem becomes acute when radiation measurements are required for detection of fuel failures, especially when the activated elements are similar to the more abundant fission products with respect to chemical and nuclear decay properties. An instrument was developed to measure small concentrations (1 to 10^4 μc/l) of mixed krypton fission products in the presence of larger and highly variable quantities of activated gases that are produced by irradiation of dissolved air.

Physical separation of nuclear fuel and reactor coolant is required in nearly all reactor designs to avoid gross contamination of the coolant with fissionable material and fission products, and to prolong the life of the fuel itself. The fuel materials are usually fabricated into suitable shapes and clad with thin metallic sheaths. Thin sheaths are required for efficient heat transfer and neutron economy, and occasional cladding failures are to be expected as a result of corrosion attack and high stresses generated at high power density. Failure of a fuel sheath is followed by corrosive deformation of metallic fuels, and rapid destruction of ceramic fuels under some operating conditions. Defective fuel pieces must be located and removed from the reactor promptly to minimize damage to other reactor components and control the contamination of the coolant.

Significant quantities of radioactive gases are released to the coolant when a fuel sheath fails. Analysis of the coolant for the major fission-product gases, krypton and xenon, provides a sensitive measure of fuel integrity. The analyses must be extremely sensitive and selective to measure the minute traces of fission products that are released during the initial stages of cladding failure, especially when larger quantities of other radioactive gases are present. Whenever air is allowed to contact the coolant, as is the case during refueling operations, radioisotopes of nitrogen, oxygen, and argon are produced in profusion. Because the activity of these components fluctuates widely and rapidly during power ascensions and other normal operations, the normal variation in the gross activity of the dissolved gases is frequently greater than the increase experienced during fuel failures.

A reliable monitoring system was achieved by utilizing an automatic gas chromatograph to isolate the fission-product gases for activity measurements. The dissolved gases are stripped from the recirculated coolant and dried prior to analysis. The sample gas is admitted to the chromatograph monitor through sequenced valve action, as indicated in Figure 1. Sample gas enters through valve B and exits through valve C to a waste vent. The connecting pipe between valves B and C serves as an aliquot measure and holds the aliquot for injection when these valves are actuated 10 seconds prior to the preset sampling time. The helium eluent normally flows through valves A and D into the chromatographic column, but is diverted through valves B and C at the required sampling time to inject an aliquot into the column. Valves A and D return to normal 10 seconds before valves B and C, to minimize variations in eluent flow and aliquot size that could be caused by valve "chatter".

The required separation is achieved at room temperature with eluent flows of about 50 cc per minute through a simple chromatographic column. The column is a section of aluminum tubing (60 in. long, 0.25-in. o.d., 0.035-in. wall) which is packed with 20-to 50-mesh particles of Linde Molecular Sieve, Type 5A, and coiled in a spiral 4 inches in diameter. Typical residence times for the gas fractions are: oxygen and argon (not separated under these conditions), 2 minutes; nitrogen, 3-1/4 minutes; krypton, 5 minutes; xenon, 21 minutes. A typical chromatographic scan (Figure 2) shows the response of the instrument to a synthetic mixture of argon, krypton, and xenon radioisotopes. The fractions with highest mobility (oxygen-argon, and nitrogen) are completely removed from the column within four minutes after sample injection. These fractions may be discarded automatically without measurement, if desired, by timed operation of valves E and F.

The automatic chromatograph is assembled on a standard aluminum chassis for mounting in a relay rack, as shown in Figure 3. This is a straightforward assembly of commercial components, with the exception of the chromatographic column, and may be easily adapted to many monitoring requirements. This method of construction provides a sturdy, reliable, and adaptable instrument at very modest cost. Sequenced operation of the six 3-way solenoid valves is controlled by a dial switch on the front panel, clock-driven microswitches, and two delay relays. The dial switch setting determines the mode of operation, and the microswitches and relays provide the required automation for repetitive analyses. Each phase of the operating sequence is indicated by a panel light. Alarm circuits are provided to warn operating personnel of low eluent pressure, high krypton activity, or maloperation of the detector components.

The detector in this monitor is a thin anthracene crystal, optically coupled to a photomultiplier tube, and facing a thin window of a gas counting cell. The details of this construction are shown in Figure 4. A lead

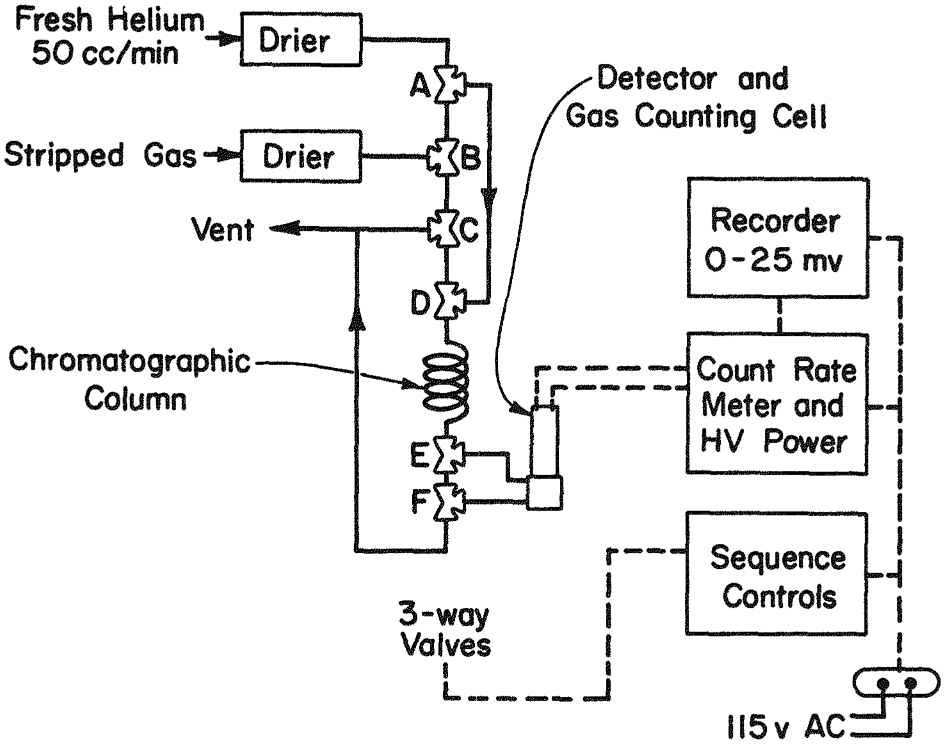

Fig. 1 - Schematic Diagram

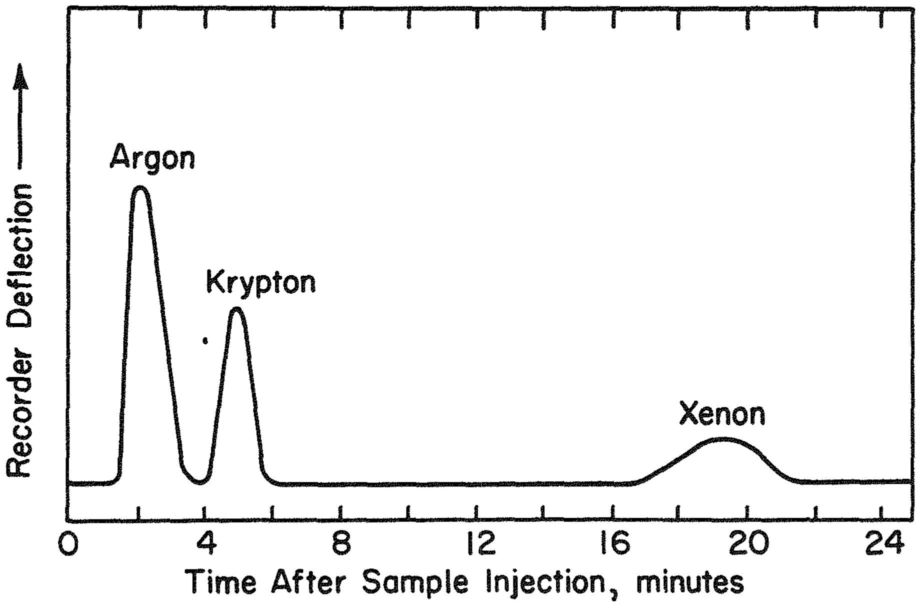

Fig. 2 - Typical Chromatograph Scan

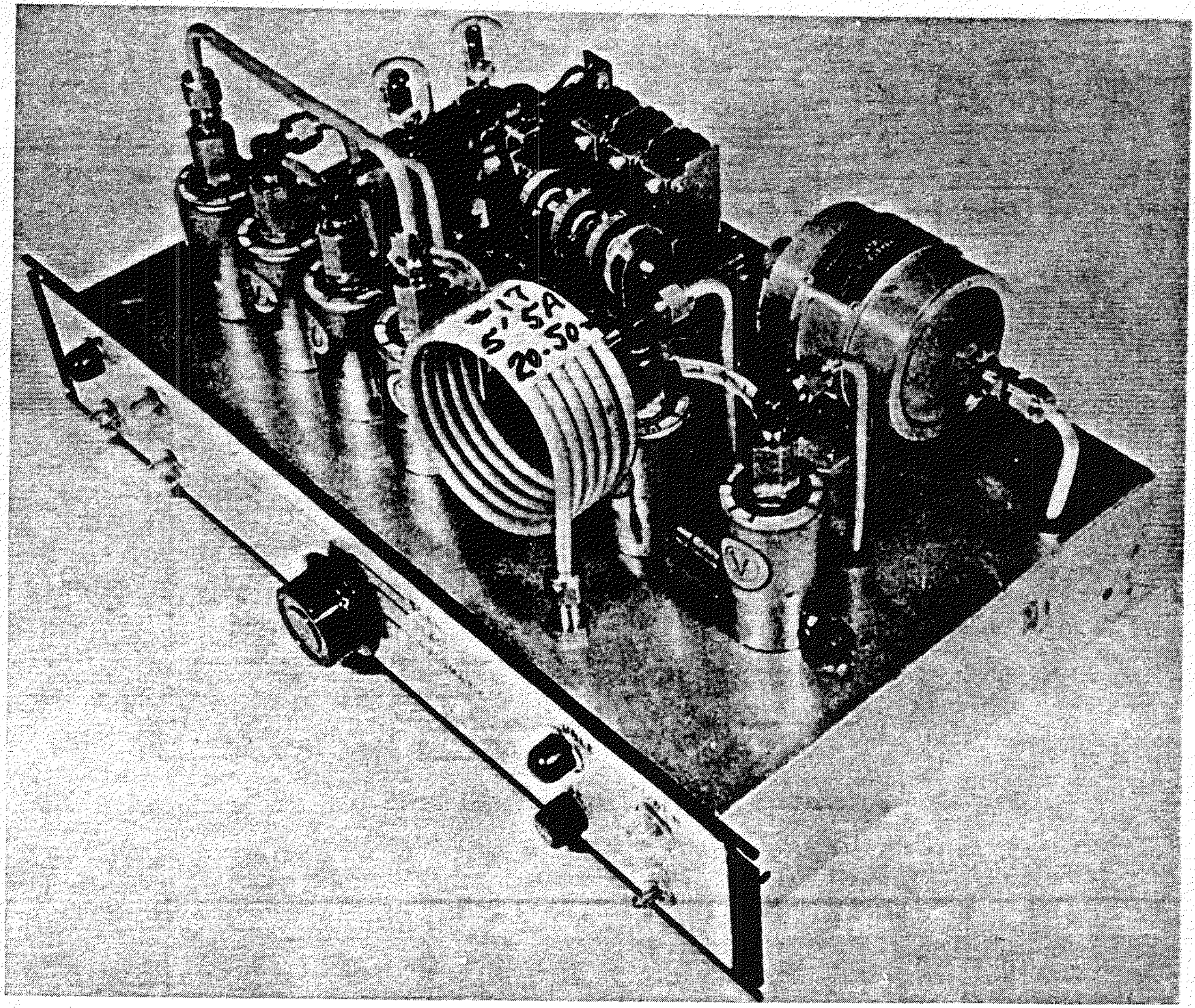

Fig. 3 - Automatic Chromatograph Assembly

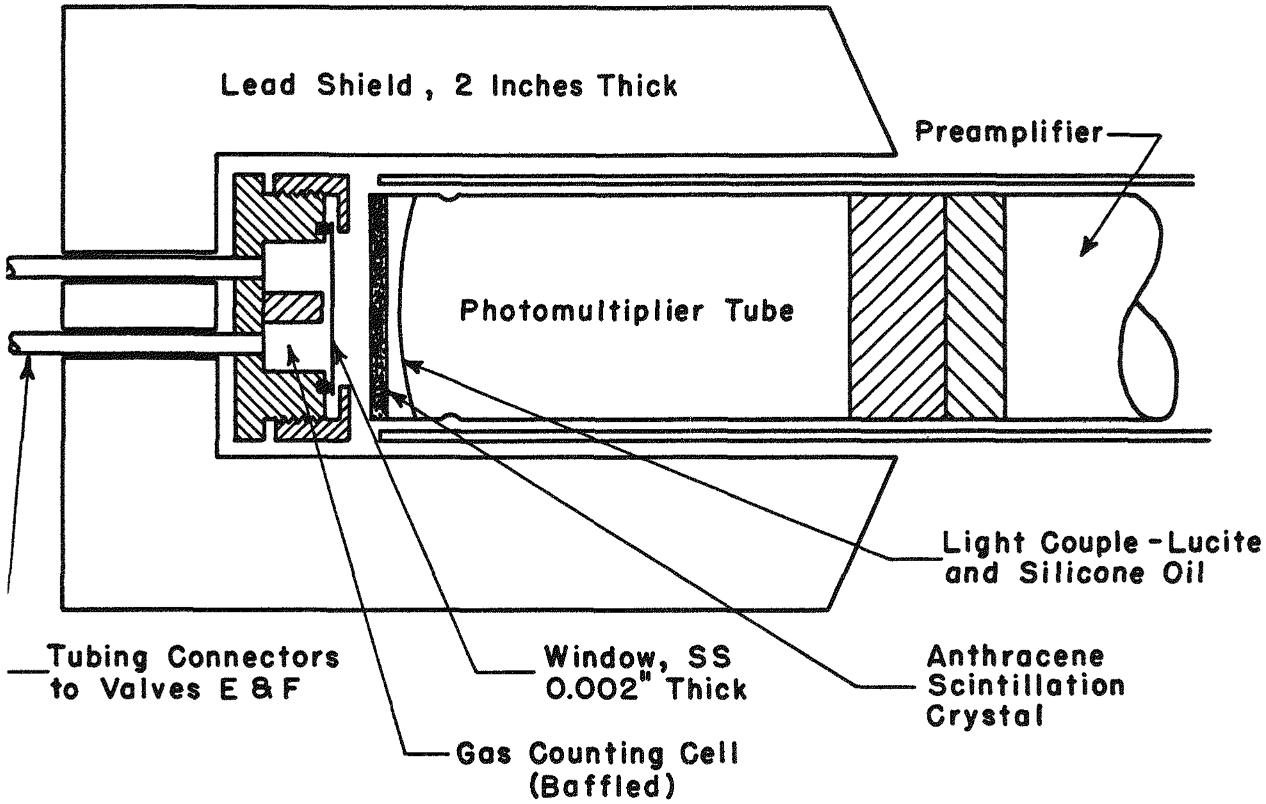

Fig. 4 - Detector Assembly

shield, two inches thick, reduces the background radiation at the detector. Gas fractions from the chromatographic column pass through valve E, the baffled counting cells, and through valve F to a waste vent. The normal residence time in the counting cell is about eight seconds. The beta activity of the gas in the counting chamber is measured through a stainless steel window, 0.002 in. thick, which faces the scintillation crystal. The standard photomultiplier tube - preamplifier assembly, with optical couple and crystal, are housed in a protective steel tube. The scintillation crystal and photomultiplier tube are wrapped with black plastic tape to assure proper alignment and to exclude room light.

All components of this monitor are housed in a standard relay rack, as shown in Figure 5. The components include a Brown recorder with two-speed chart drive, sampling event marker and adjustable alarm contacts; counting ratemeter with high voltage power supply; automatic chromatograph with separate access panel to facilitate column replacement; and the shielded detector assembly (not visible) behind the bottom access panel. Piping and 110-volt power connections are located at the rear of the monitor.

The helium eluent is supplied from a single cylinder, which is sufficient for three months of continuous operation. The eluent flow is controlled by adjusting the cylinder pressure regulator to obtain the desired rate, as measured by an external rotameter.

Two models of this instrument have been evaluated on prototype bases, as in-line monitors in a nuclear reactor. The in-line analyses have permitted immediate diagnosis of several changes in gross activity, thus providing a valuable aid for routine operation. There have been no mechanical failures in the automatic chromatograph assemblies, and only very occasional electronic troubles with detectors and recorders.

Adaptations of this basic instrument should prove valuable for monitoring exhaust gases from nuclear reactors, spent-fuel handling facilities, and spent-fuel processing equipment. The automatic chromatograph design can also be used with proper column packings and detectors, to monitor many nonradioactive processes.

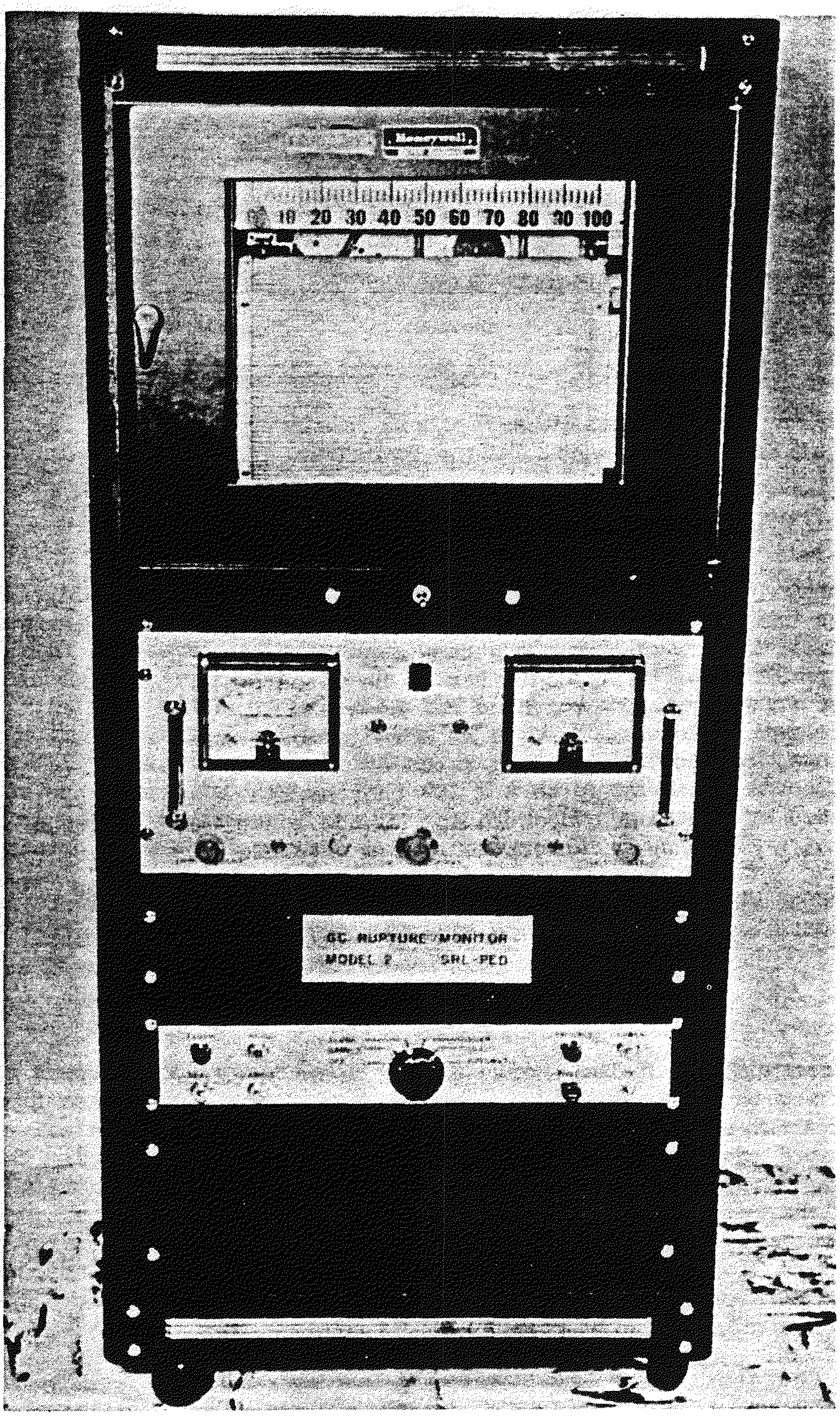

Fig. 5 - Model 2 GC Rupture Monitor

SINGLE-BEAM GAMMA ABSORPTIOMETER

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ABSTRACT

A single-beam gamma absorptiometer was developed at Oak Ridge National Laboratory for the continuous analysis of the ions of heavy elements in aqueous flowing streams. The source of 60-kev gamma rays (λ= 0.21 A) is 10 mg of purified Am^{241} encapsulated in an Al container. The detector is a scanning gamma spectrometer in which a Tl-activated NaI crystal, optically coupled to a multiplier phototube, is used as a radiation transducer. Over the spectral range, continuous scanning rates of 1/10 and 1 cycle/min are available at count rates of up to 2×10^6 photons/min. Calibration curves are obtained by plotting concentration vs the logarithm of the 60-kev photopeak count rate. Linear calibrations were obtained for Pb^{++} in the concentration range of 0 to 300 g/liter, for UO_2^{++} in the range of 0 to 225 g/liter, and for Cd^{++} in the range of 0 to 50 g/liter. The flow rate of the solution in the range of 0 to 200 ml/min does not affect the results.

* * * *

The measurement of the attenuation of low-energy photon beams provides a sensitive method for determining the concentration of heavy elements in solutions. Several laboratory instruments(1,2) that use Am^{241} radiation sources have been designed for the rapid analysis of uranium or plutonium in solutions. A process-type instrument(3) for the continuous analysis of uranium solutions has been designed for use at the Savannah River Plant. In this paper a single-beam gamma absorptiometer is described that uses a small Am^{241} radiation source, (E_γ = 60 kev; λ = 0.21 Å), a NaI(Tl) scintillation detector, and a scanning gamma spectrometer with pulse-height discrimination, for the continuous monitoring of heavy-element ions in solution.

THEORY OF ABSORPTION

A gamma-ray differs from an x-ray only in the matter of its origin; both are electromagnetic radiation. The gamma-ray originates in the nucleus of an atom, whereas the x-ray arises from energy transitions involving the bound electrons of the atom. It is to be expected that the theory for absorption of gamma-rays will closely parallel that for x-ray absorption in matter.

A gamma-ray interacting with matter may lose energy by three different processes:

1. Photoelectric Effect
2. Compton Effect
3. Pair Production

A minimal energy of 1.02 Mev is required for the gamma-ray to lose energy through pair production. Americium^{241}, with a principal gamma-ray of 60 kev, will lose energy of the gamma-ray only through photoelectric absorption and Compton degradation, and of these two processes, the photoelectric loss is the greater.

In the photoelectric effect, the quantum of energy, hv, possessed by the gamma-ray is completely expended in the ejection of an electron from an atom or molecule of the matter with which the electromagnetic radiation interacts. The electron receives an energy, $E = hv - W_o$, where W_o is the binding energy of the electron. Momentum is conserved in the process through recoil of the atom or molecule. For an incident photon energy greater than that of the K-binding energy of the absorbing atom, photoelectric absorption takes place primarily in the K-shell, and is approximately proportional to Z^5,(4) where Z is the atomic number. It is for this reason that heavier atoms show an increased absorption for photons.

In the Compton Effect, the incident photon gives up only a part of its quantum energy to a bound electron. The electron may be freed, or can remain bound; the gamma-ray is degraded in energy, and is given a new course of direction. The Compton scattering coefficient is approximately proportional to Z,(5) the atomic number.

The processes of photoelectric absorption and Compton scattering involved in 60-kev gamma-ray interaction with matter lead to exponential attenuation:

$$I_t = I_o \mathcal{E}^{-\mu l} \qquad (1)$$

where,

I_t = transmitted intensity of the beam
I_o = incident intensity of the beam
l = length of path in the absorber
μ = linear absorption coefficient
$\mathcal{E}$ = 2.71828......

An expression for a mass absorption coefficient that is independent of the physical state of the absorbing species is obtained from:

$$I_t = I_o \mathcal{E}^{-\left(\frac{\mu}{\rho}\right) l \rho} \qquad (2)$$

where,

ρ = density
$\left(\frac{\mu}{\rho}\right)$ = mass absorption coefficient.

When concentrations are specified, the exponential attenuation equation becomes:

$$I_t = I_o \epsilon^{-\mu_m Cl} \qquad (3)$$

where,

μ_m = mass absorption coefficient
C = concentration.

If more than one absorbing species is present, the attenuation equation is:

$$I_t = I_o \epsilon^{-\sum^{i} \mu_{m_i} C_i l} \quad . \qquad (4)$$

It is important to emphasize that, for exponential attenuation to hold, monoenergetic gamma-rays should be used for the radiation source, and only these gamma-rays should be measured in the narrow transmitted photon-beam. Americium^{241} is an excellent source of 60-kev photons, and the gamma-ray spectrometer with its pulse-height discrimination and resultant narrow-band energy acceptance, an almost ideal detector for 60-kev photons in the emergent beam.

APPARATUS

The apparatus associated with the single-beam gamma absorptiometer consisted of the following:

1. Radiation source ..... 10 mg or 20 mg Am^{241}
2. Cell for the absorbing liquid
3. Scanning gamma-spectrometer
    a. NaI(Tl) crystal detector, 0.1 x 1.5-inch diam.
    b. Multiplier phototube......RCA 5819
    c. High-voltage power supply....(to -1250 v)
    d. Cathode-follower preamplifier
    e. Linear amplifier....ORNL Q-1593, with built-in Pulse-Height-Selector (PHS) circuit
    f. Count-rate meter
        Linear.....ORNL Q-1511
        Logarithmic.....ORNL Q-1454 B
    g. Recorder....10-mv Brown Recorder, chart speed, 60 in./hr.

RADIATION SOURCE

Americium^{241} is a desirable source material for a gamma-absorptiometric technique because of its spectral purity, low-energy value for a quantum (low-energy values enhance the probability of absorption), relatively high specific activity (4.8 x 10^7 photons/sec/mg), and long half-life ($t_{1/2}$ = 458 yr). The long half-life virtually eliminates decay corrections for the radiation source. Americium^{241} is obtained by chemical separation from Pu^{241} that has been aged to permit the daughter nuclide (Am^{241}) to grow in through β-decay of the parent. The alpha spectrum of Am^{241} shows six alpha-rays(6) with the principal particle (5.482 Mev) leading to a 59.6-kev energy level in the daughter nuclide, Np^{237}. The transition from the 59.6-kev level to the ground state in Np^{237} leads to the "60-kev" gamma-ray of Am^{241}. The 59.6-kev energy level in Np^{237} can be depopulated also by two cascading gamma rays of 26.4 kev and 33.2 kev, with only the former being observed. Almost all the transitions in Np^{237} pass through the 59.6-kev energy level.(7)

Approximately 40 photons of 59.6-kev energy and 2.8 photons of 26.4-kev energy are produced per 100 alpha disintegrations in Am^{241}. The 59.6-kev: 26.4-kev ratio should be approximately 14:1. The decay scheme for Am^{241} is shown in Figure 1. Fluorescent x-rays of Np^{237} are not included.

Two sources have been tried in the single-beam gamma absorptiometer; the first contained 10 mg Am^{241} as the oxalate embedded in a casting resin and encapsulated in an aluminum container with outside dimensions of 1/2- by 1-in. diameter. The aluminum container had a 6-mil window. The stainless steel construction and oxide form of the active material were adopted after the aluminum container displayed signs of impending rupture. The stainless steel capsule is shown in Figure 2. The sources were fabricated in the ORNL Analytical Chemistry Division by J. E. Strain.

The 20-mg Am^{241} source (stainless steel shell) has a measured gamma emission rate of 2.6×10^8 photons/sec which is 27% of the theoretical value for a 20-mg source. The measured biological hazard (at contact) is 350 mr/hr, with no detectable alpha contamination present on the surface of the stainless steel. An energy scan of the range of 0 to 100 kev for the 10-mg source is presented in Figure 3. The "escape peak" associated with the iodine K x-ray occurs at about 32 kev, and tends to obscure the 26.4-kev photopeak of the Am^{241}. The 13 and 17-kev x-rays of Np^{237} are probably responsible for the tailing out of this peak.

CELL FOR THE ABSORBING LIQUID

Cells for the absorbing liquid were constructed from Lucite, with path lengths of 1, 3 and 10 cm. Lucite exhibits little attenuation of the 60-kev energy. Swagelock fittings and polythene tubing conduct the flowing solution to the cell. The solution enters at the bottom of the cell in order to keep it filled with liquid. A centrifugal pump fabricated from stainless steel circulates the absorbing liquid through the loop at flow-rates from 0 to about 200 ml/min. A rotameter is used to measure the flow rates. Figure 4 is a diagram of the cell system.

DETECTOR

A thallium-activated sodium iodide scintillation crystal optically coupled to an RCA 5819 multiplier phototube is the radiation-sensing element. The detector crystal is 0.1-in. thick, and has a diameter of 1-1/2 in. The thickness was chosen to discriminate against hard background radiation. The total fractional transmission for Cs^{137} gamma-rays (662 kev) through 0.1 in. of sodium iodide is 0.94, whereas, the total fractional transmission for the 60-kev photons of Am^{241} through this same thickness of NaI is 0.004. Thus, the 0.1-in. thickness of NaI transmits 94% of the 662-kev photons of Cs^{137}, while stopping 99.6% of the 60-kev photons of Am^{241}.

The 0.1-in. crystal is shielded from the side because stray radiation traversing the 1-1/2-in. path in the crystal would create some response. The multiplier phototube is made light-tight by means of an aluminized sheath over the end surface, and by black, electrical, vinyl tape wrapped around the glass section of the phototube. A mu-metal shield that surrounds the phototube affords magnetic shielding.

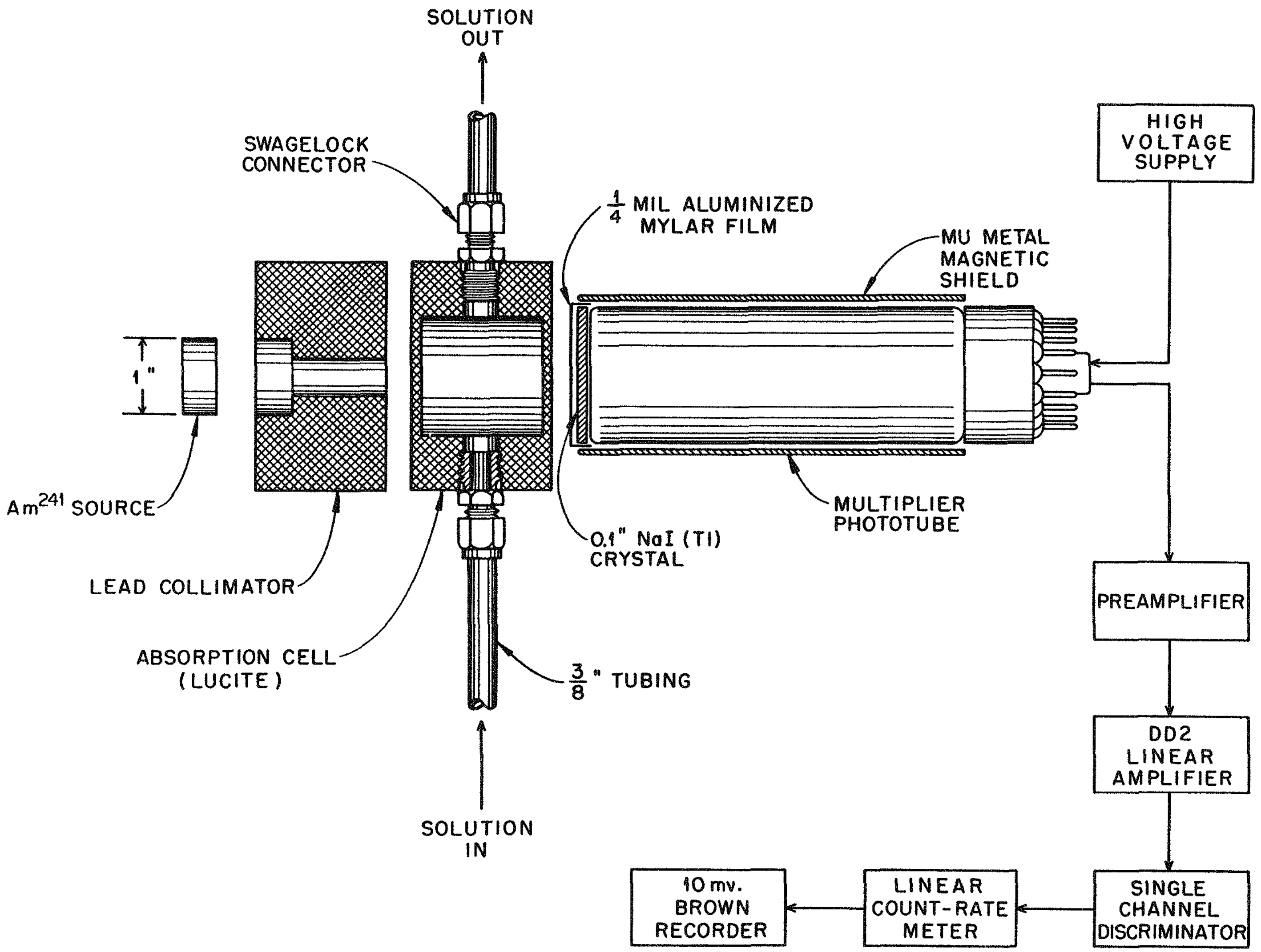

Figure 4. Single-beam gamma absorptiometer

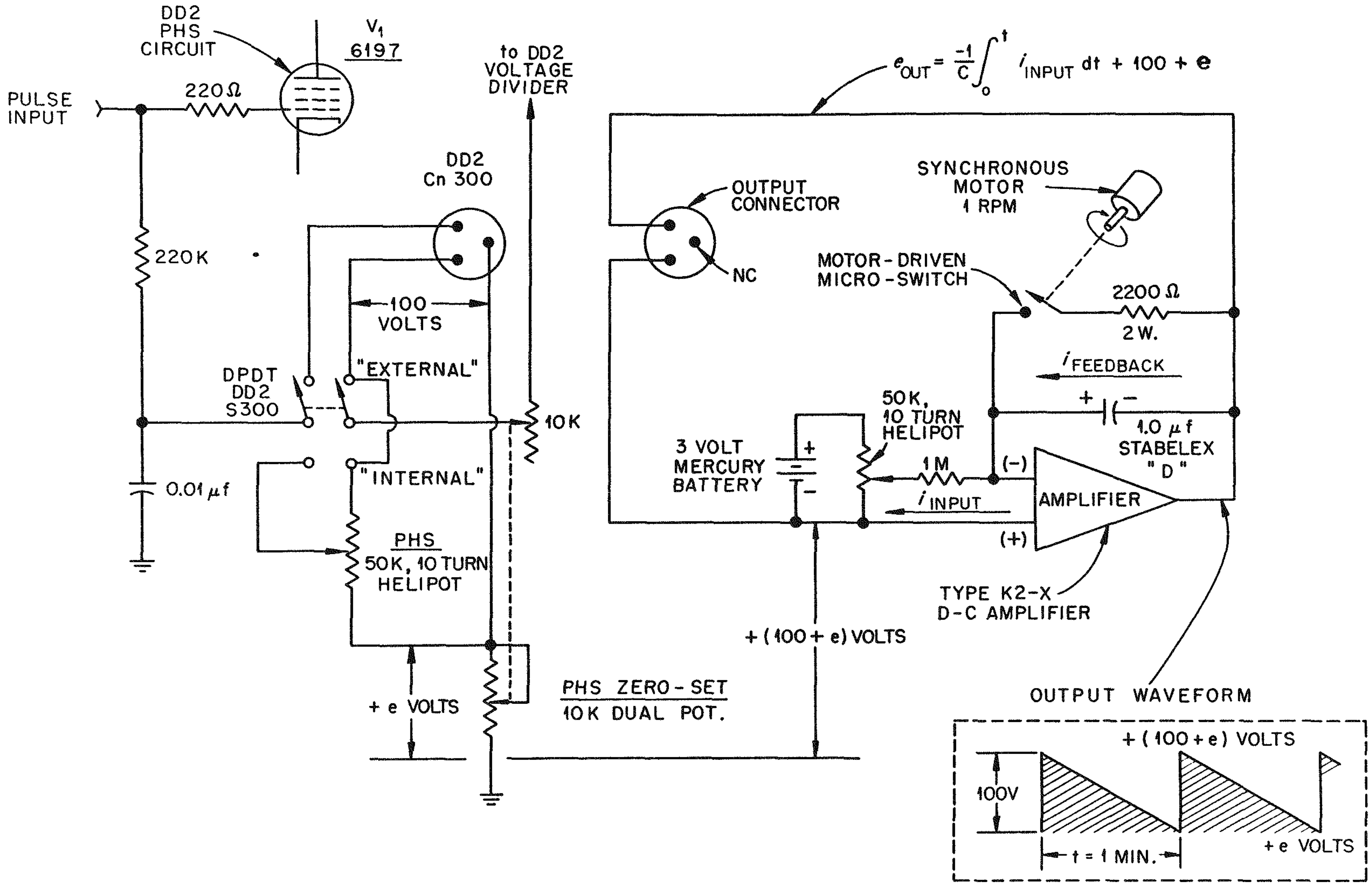

Figure 5. Integrator for rapid-scanning γ-spectrometer

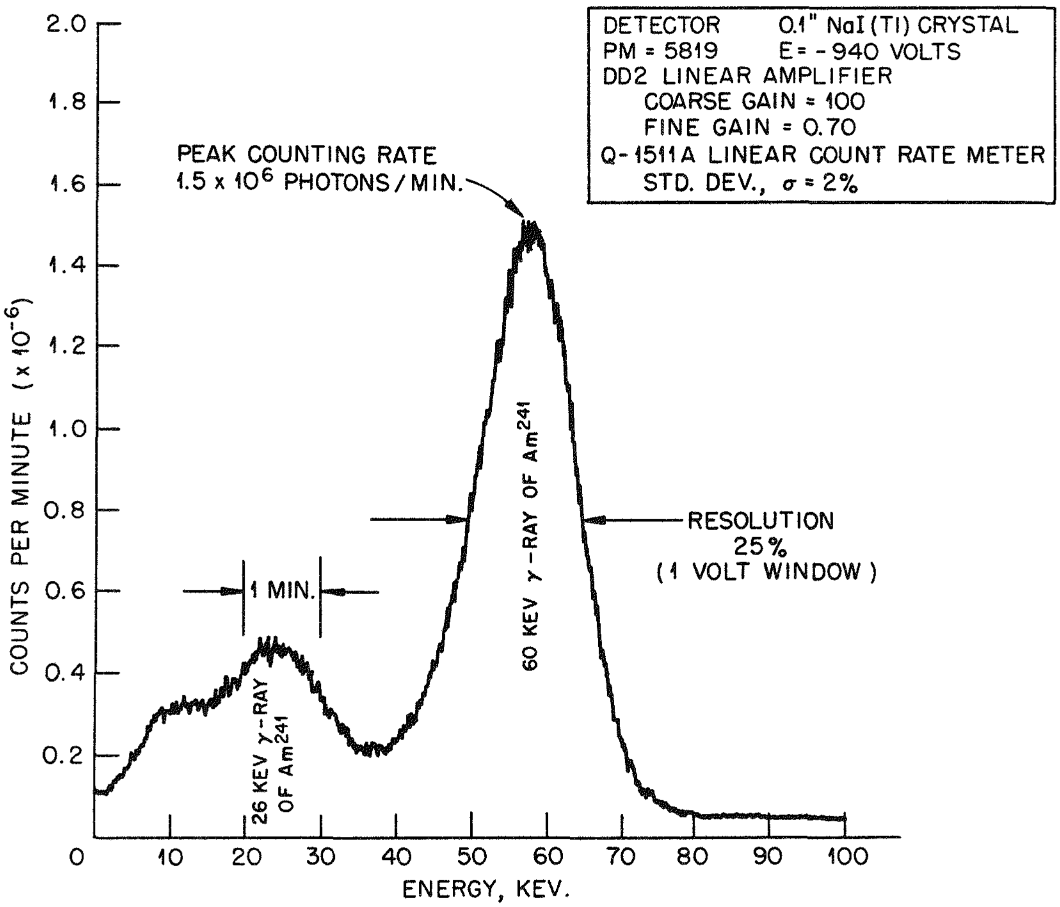

Figure 3. Gamma-ray spectrum for 10 mg Am^{241} source

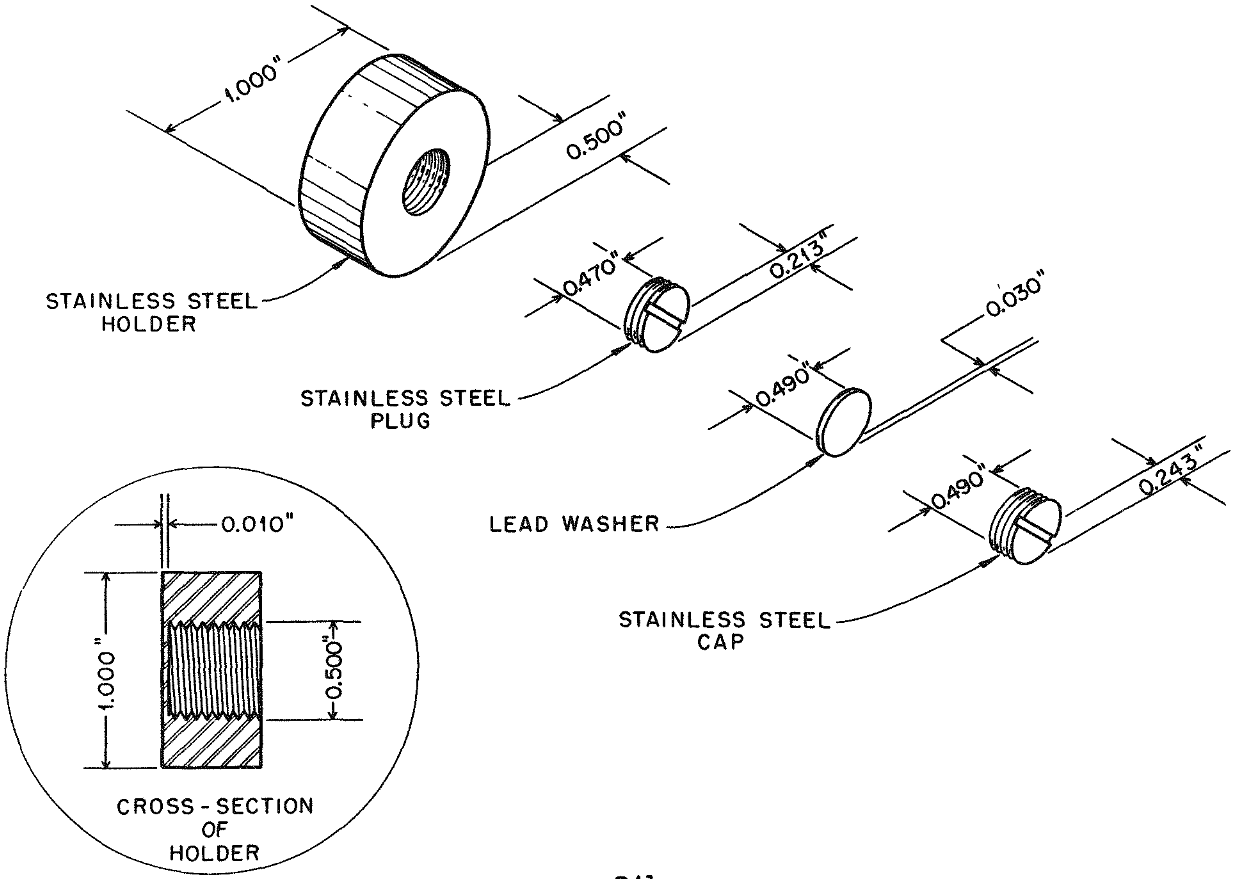

Figure 2. Am^{241} source holder

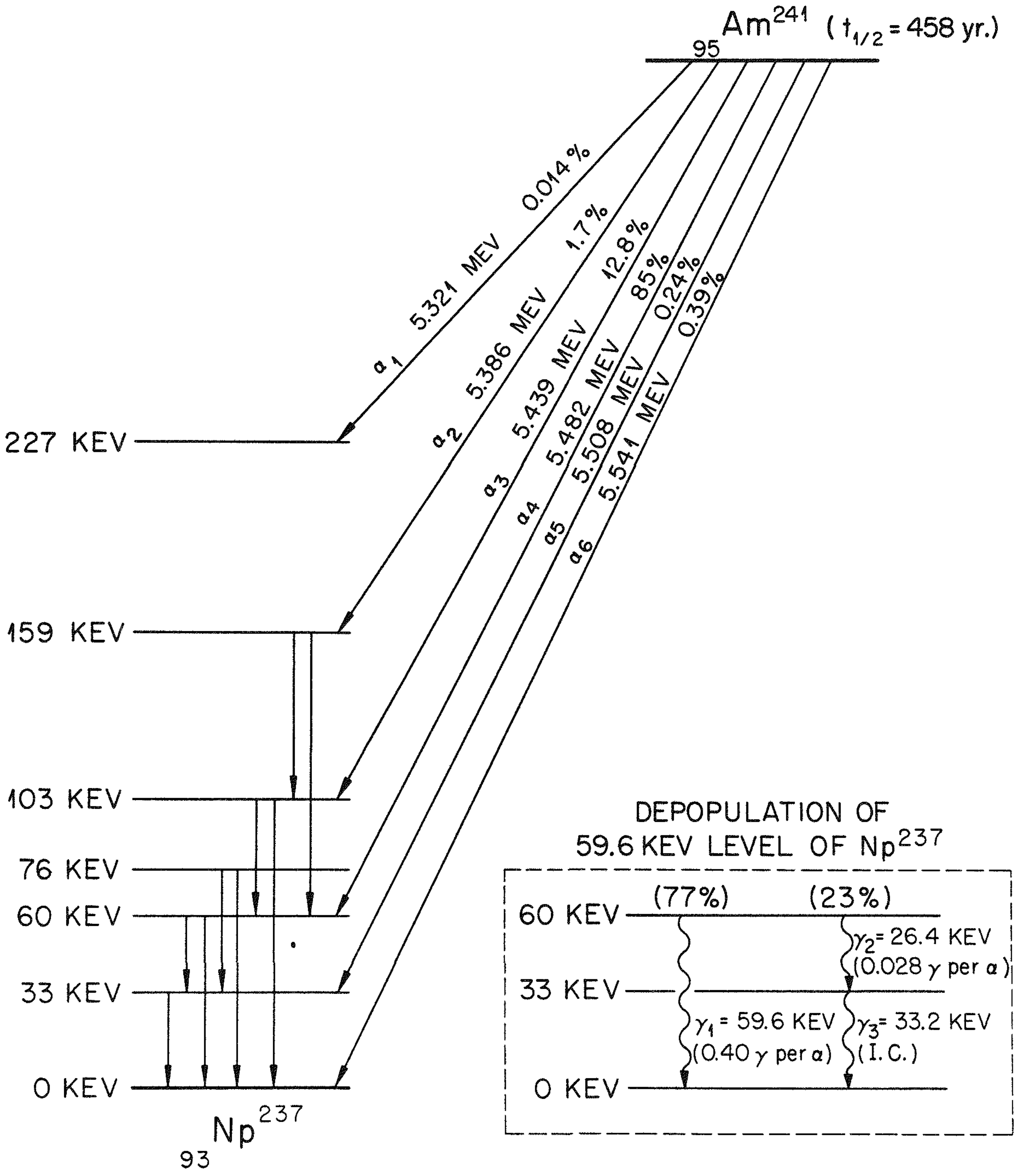

Figure 1. Decay scheme for Am^{241}

SCANNING GAMMA-SPECTROMETER

The scanning gamma-spectrometer was assembled from standard ORNL components, high-voltage power supply for the multiplier phototube, preamplifier, DD2 Linear Amplifier, Single-channel PHS with provision for differential and integral count-rates, count-rate meters, and a 10-mv Brown recorder. The recorder produces an energy scan voltage for the PHS circuits by means of a single-turn Helipot that is driven by a gear mechanism coupled to the chart-drive motor. The scan-rate is 10 kev/min in the 0 to 100-kev energy range.

A rapid-scanning feature was achieved by connecting an electrical integrator whose input is a constant current to the PHS circuit. The output voltage of the integrator decreases linearly from a value of +(100 + e) volts to + e volts in one minute; e is the zero-set voltage of the PHS circuit. At the end of one minute, the integrator capacitor is shorted through a 2.2 K resistor by a micro-switch that is actuated from a cam driven by a synchronous motor, and the circuit is automatically reset for another scan. The details of the integrator scan circuit and a diagram of the output waveform of the integrator are shown in Figure 5. Typical successive spectral scans for Am^{241} radiations through 3 cm of lead nitrate solution are displayed in Figure 6 to illustrate the reproducibility of the instrumentation.

CALIBRATION

Empirical calibration of the instrument is obtained by plotting on semilogarithmic graph paper the 60-kev gamma-ray count rate against known concentrations of the absorbing species. A calibration curve for uranium over the concentration range of 0 to 300 g/l, as typical of heavy-element attenuation, is presented in Figure 7. Lighter element attenuation, as represented by $CdCl_2$ solutions, is shown in Figure 8. Mass absorption coefficients, calculated from data taken in this fashion, tend to be on the low side of published values. The cause of the discrepancy is not known.

DISCUSSION

The single-beam gamma absorptiometric method offers a simple technique for monitoring the concentration of heavy metals in flowing streams, provided that variables other than the concentration of the desired absorbing species, such as temperature, presence of foreign ions, and undesired radiation, can be controlled. Temperature is a factor because of the volume expansion of liquids. The flow-rate of the solution through the absorption cell is not a factor (see Figure 9) if jet-streaming of the liquid through the cell is prevented. Precision of results is of the order of 5%.

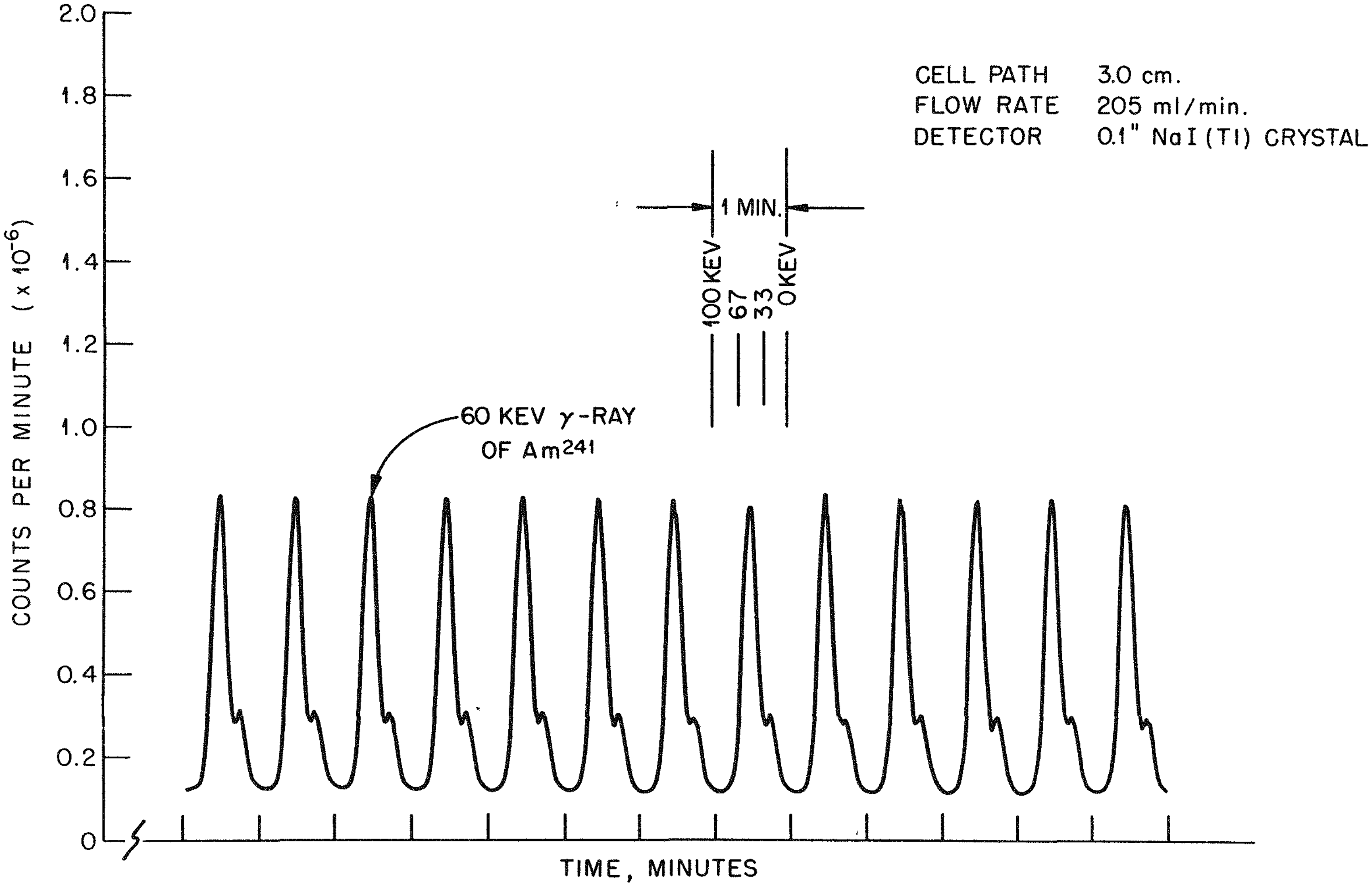

Figure 6. Consecutive spectral scans produced by a rapid-scanning single-beam gamma absorptiometer

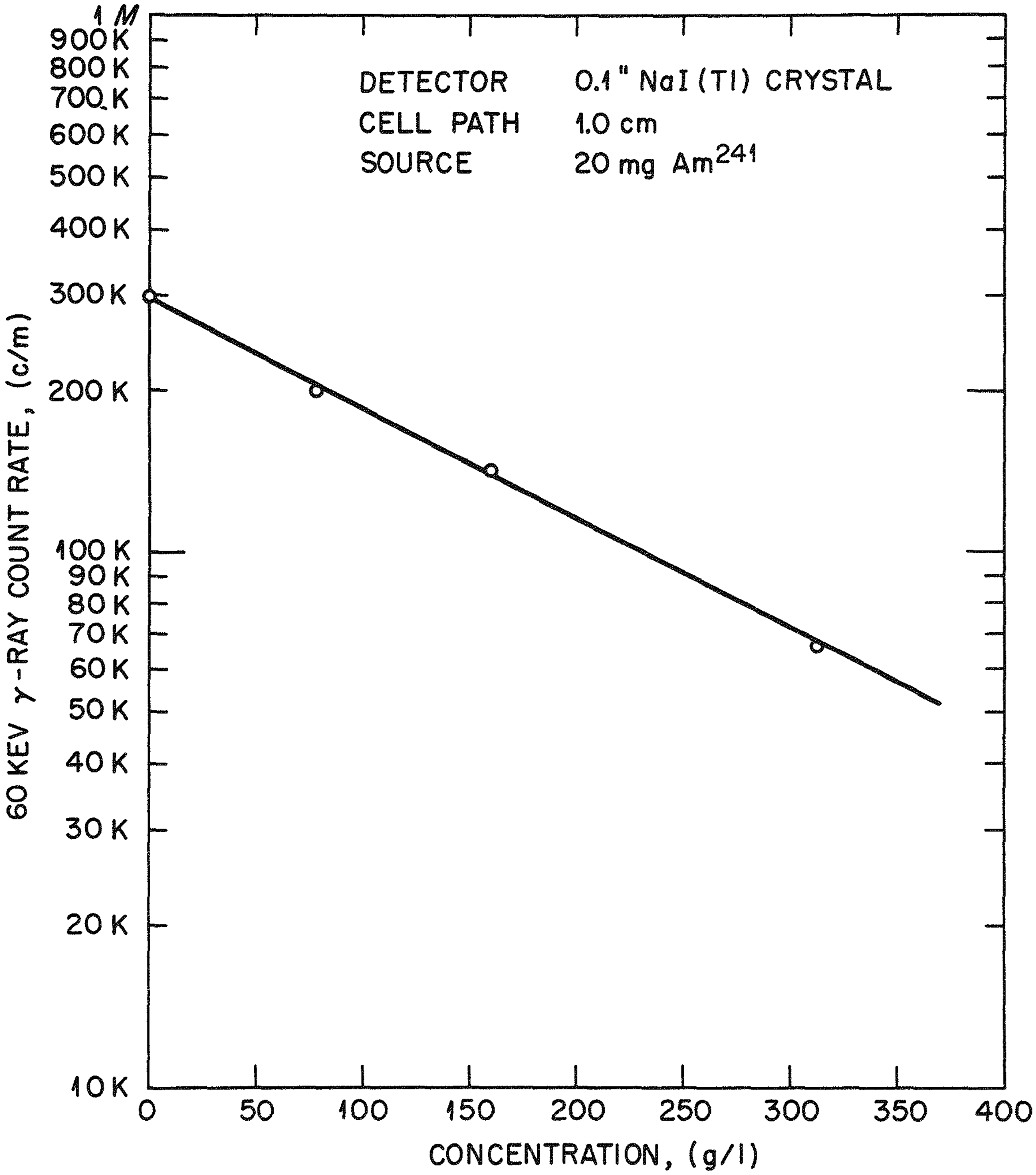

Figure 7. Calibration curve for uranium with single-beam gamma absorptiometer

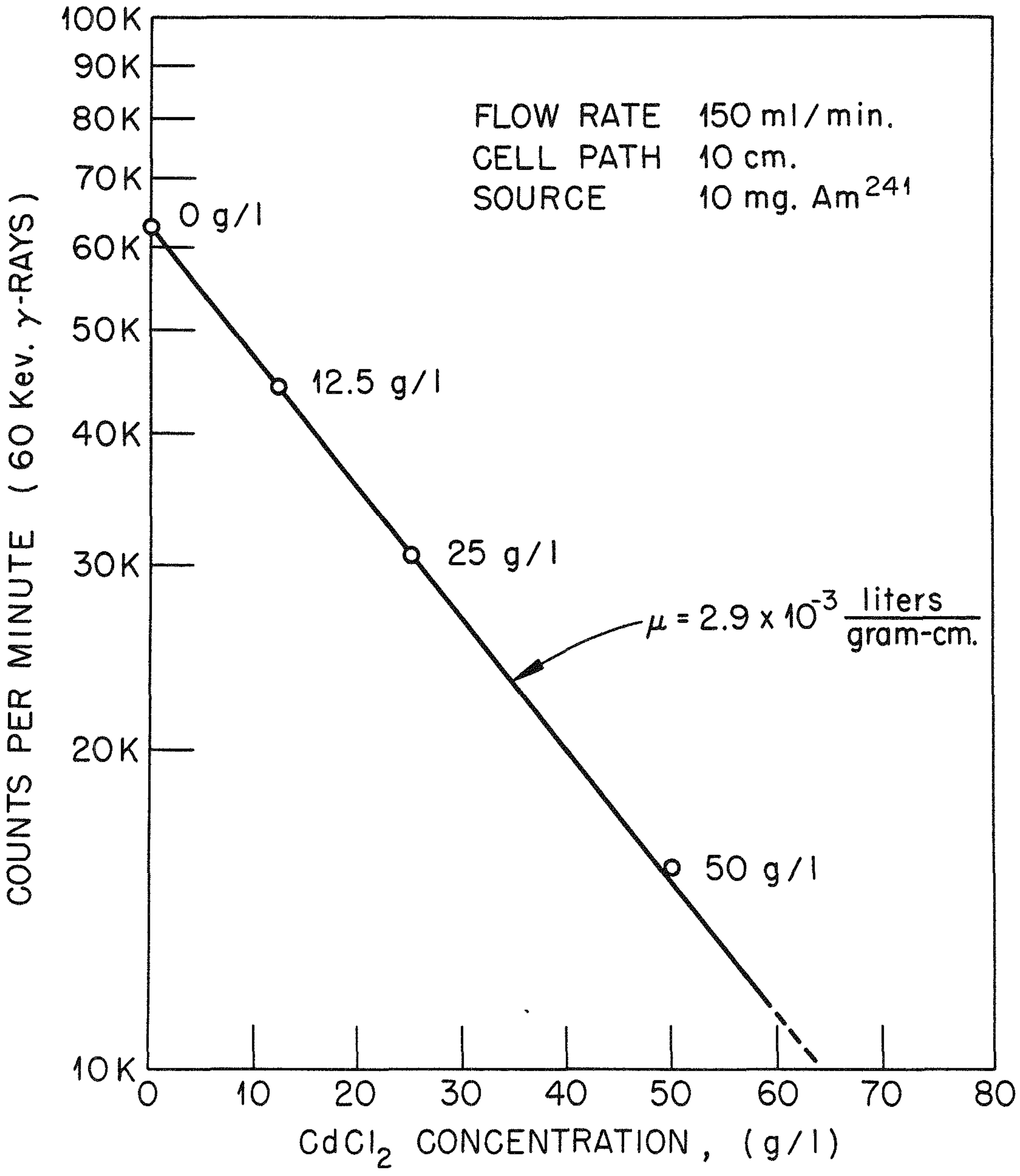

Figure 8. Attenuation of 60-kev γ-ray beam of Am^{241} by flowing $CdCl_2$ solutions

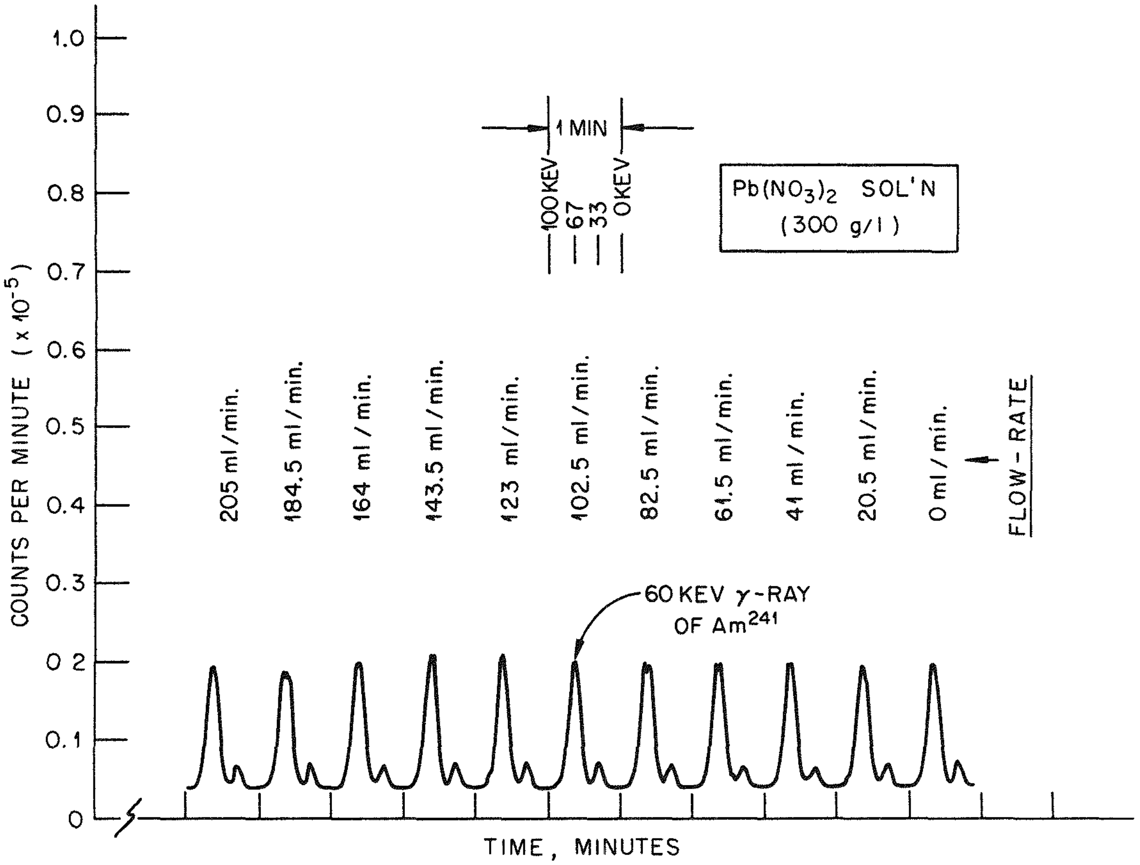

Figure 9. Effect of flow-rate when using a rapid-scanning single-beam gamma absorptiometer

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CONTINUOUS ANALYSIS OF RADIOACTIVE GAS AND LIQUID STREAMS

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ABSTRACT

Instrumentation for continuous analysis is a field which is increasing in scope every day. In the past, instruments for measuring the percentage ranges were needed, but in present-day processes, measurements in ppm and often ppb are required.

Gas- and liquid-stream analysis, actually, should be broken down into two separate categories, since sampling and measuring techniques vary widely in most instances. There are some methods of analyzing the two types of streams which do overlap in type of instrumentation but only in rare instances in technique as well.

The instruments for continuous gas analysis include on-stream analyzers for measurement of components in the following ranges:

Percentage. Methods of gas analysis, utilizing the thermal conductivity, thermal convection, and catalytic combustion properties of the gases or vapors are discussed briefly for general information purposes.

Parts per million. Methods of gas analysis utilizing the principles of infrared adsorption and gas chromatography are described with particular emphasis on the field of infrared analyzers.

Parts per billion. An analytical procedure making use of the ionization detector chamber for measurement of trace gas components is presented in some detail.

Instrumental methods for continuous liquid analysis cover component analysis in ranges as follows:

Percentage. Instruments making use of specific characteristics of the liquid such as refractive index, pH, and infrared adsorption are discussed with particular emphasis on refractive-index methods of analysis.

Parts per million. Methods of analysis, utilizing dielectric constants and infrared adsorption, are described with emphasis on the dielectric-constant method.

Parts per billion. A method of analysis will be considered for the measurement of dissolved elements such as Ba, B, Co, Pb, Na, and Sr in a liquid stream. Essentially any element which exhibits flame emission properties can be determined by this method of analysis.

In general, those methods of analysis are emphasized which deal with the determination of components in the ppm and ppb range. The analytical techniques cover measurement of gases in gas streams, gases in liquids, liquids in liquids, and dissolved solids in liquids.

It is generally known that the analysis of liquids is somewhat of a newcomer to the continuous analysis field; however, we believe it is on its way to becoming as well established as is gas analysis and that it may even surpass gas analysis in some areas. For this reason, much of this paper is devoted to the analysis of liquids as an upcoming method of continuous stream measurement.

INTRODUCTION

Continuous stream analyzers are being used more and more extensively in varying processes and especially in fields where human contact with the process materials or samples creates a hazard. Radioactive streams fall in this category as well as do toxic gases, combustible gases and corrosive gases or liquids. Continuous sampling instruments not only provide rapid, accurate analyses, but also eliminate the need for personal contact in collecting "grab" samples.

In the past, process requirements were generally such that analysis in the percentage range was sufficient. Present day requirements call for extremely accurate measurements in the parts-per-million and often parts-per-billion ranges. For this reason, new instruments capable of handling these problems, are being developed and produced as the need arises.

Since gas and liquid stream analyzers vary widely in most instances in sampling and measuring techniques, they should be broken down into two distinct categories. Although the principle of measurement used in some liquid analyzers is similar to that used in gas analyzers, and vice versa, enough difference exists in sampling techniques to allow this separation.

After establishing the need for two categories of "on stream" analyzers, it now becomes apparent that a further breakdown is necessary, either according to method, or range of measurement. For the purposes of discussion, separating the instrument groups by range seems the more feasible, since the range is more likely to determine what analyzer would be used for any given problem.

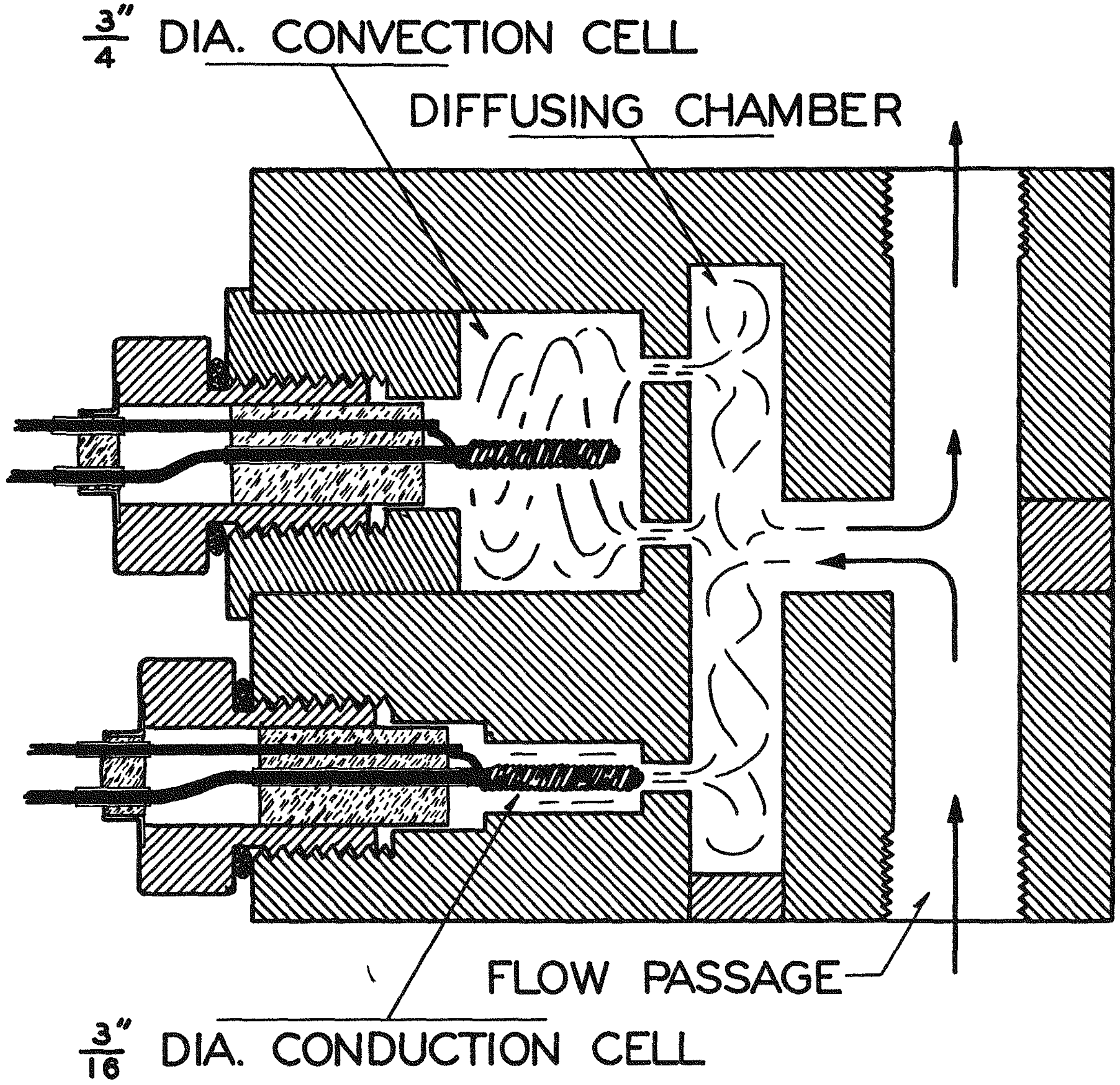


Figure 1. Thermal Conductivity Cells

CONTINUOUS GAS ANALYSIS

Analysis in the Percentage Range

When gas analysis is required in the percentage range, people in general think of thermal conductivity as an ideal method of inexpensive measurement. In the past, however, this type of instrument was confined to the measurement of binary streams only. In order to measure one component of a complex mixture, interfering components had to be "scrubbed" out or the sample otherwise altered to provide the detector with essentially a binary stream. For this reason, the field of application of this type of instrument was extremely limited. Recent developments in the design of thermal conductivity analyzers have somewhat expanded the applications of this instrument, however, and instruments are now available which are capable of measuring one component of a complex misture without the sample having been "scrubbed" or altered in any way.

Combining the principle that the optimum thermal convection loss for each gas is attained in wells of different diameters, with the principles of thermal conductivity, well diameters are first determined for the four filaments. (See Figures 1 and 2). By proper pairing of these wells as opposing arms of a Wheatstone bridge, the effects of background gases are annulled and the analyzer becomes specific for the gas of interest. Additional accuracy can also be obtained by incorporating annulling resistors in the bridge arms as required.

Where the gas or gases to be measured are combustible, a similar analyzer can be used which makes use of filaments in a closed chamber. Here the gas to be measured is burned catalytically on the surface of one filament, which is one arm of a Wheatstone bridge, causing that filament to increase in temperature and, hence, in resistance. This increase in resistance causes an unbalance of the bridge circuit proportional to the concentration of combustible gas being measured. For high concentrations of combustible vapors, above the L.E.L. or in an inert stream, dilution of the sample with air may be required.

Many other types of analyzers are suitable for measurement with considerable accuracy in the percentage range; some, however, are discussed further on since they are capable of lower ranges of measurement.

Analysis in the Parts-Per-Million Range

Infrared Analyzer. Where continuous analysis of one component, in a multicomponent stream, in the parts-per-million range is required, the most useful instrument which can be found is probably an infrared analyzer of the nondispersive type. There are essentially two kinds of nondispersive infrared analyzers available--positive and negative type instruments. Before going into the major differences between the two, it would seem best to explain a little of the theory of basic operation common to both the positive and negative type of systems.

In order to measure the concentration of one component in a mixture, an infrared analyzer essentially measures the amount of infrared absorption by

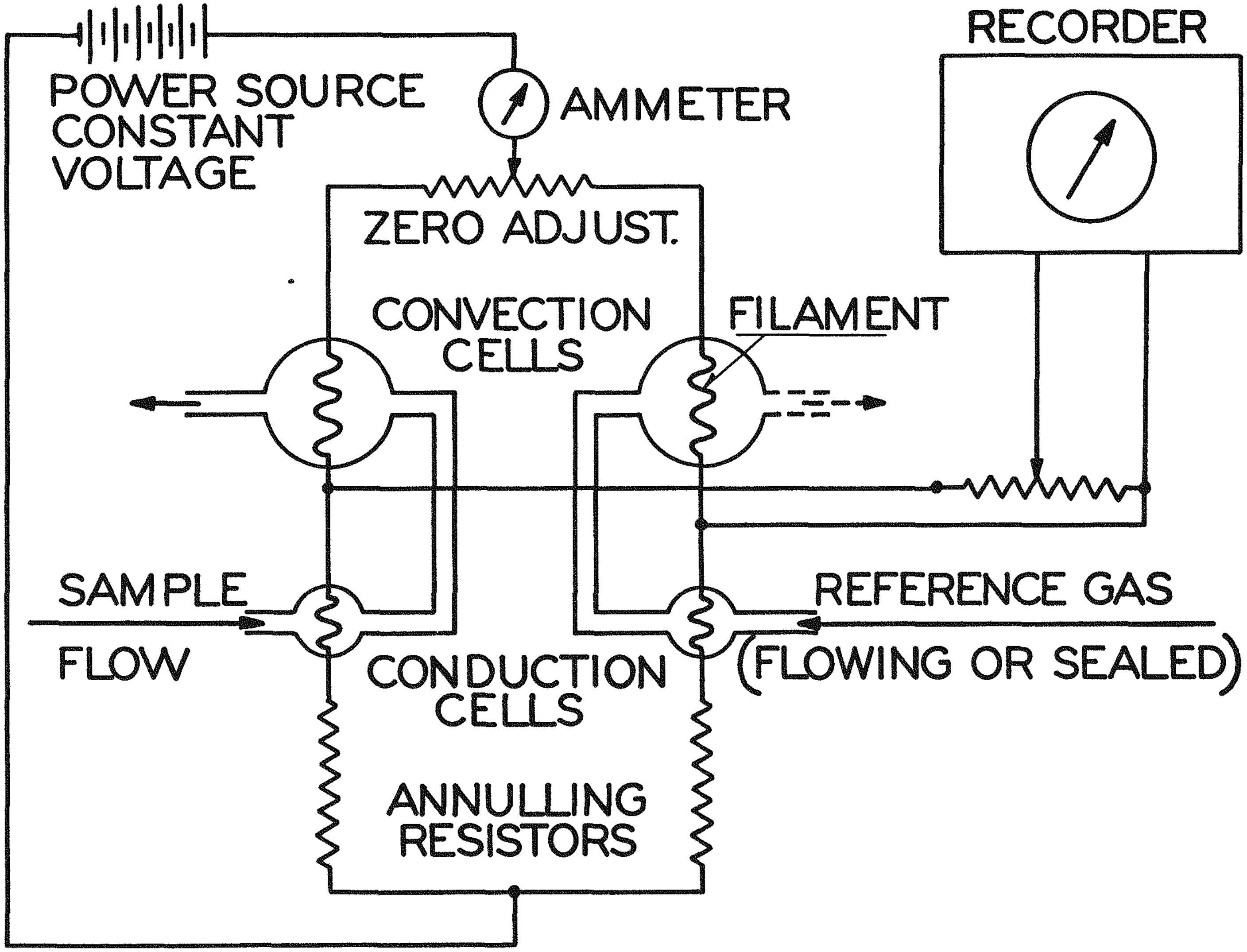


Figure 2. Diagram of Thermal Conductivity Apparatus

that component. The infrared absorption of a compound is a characteristic of the type and arrangement of the atoms composing its molecules.

Dissimilar compounds absorb in widely different spectral regions. For instance, carbon monoxide, carbon dioxide, and acetylene differ greatly in their absorption patterns (see Figure 3). On the other hand, similar compounds have similar spectra. The absorption spectra of methane, ethylene and butane are quite similar although there are regions in which the absorption differs (see Figure 4). These differences, fortunately, are sufficiently marked that it is possible to determine a small percentage of one of these gases in the presence of higher concentrations of the others.

There are certain gases such as hydrogen, argon, oxygen and nitrogen which do not absorb infrared energy and, therefore, their presence has no effect on an infrared analyzer.

To see what physically happens when a concentration of gas to be detected actually enters the infrared analyzer, refer to Figure 5. A voltage is impressed on two similar helices of nichrome wire. The wires are heated to a dull red color (1200°F), at which temperatures they emit infrared energy. This energy is channeled through the two parallel paths, the sample cell and the comparison cell, to a sensing element or detector. The detector transforms the optical signal to an electrical signal where it can be amplified and read out on a meter or recorder.

Between the nichrome filaments and the cells of a positive type analyzer, a rotating interrupter alternately blocks the radiation entering the sample cell and the comparison cell. When the beams are of equal intensity, an equal amount of radiation enters the detector from each beam. The amplifier is tuned so that only variations in infrared intensity occurring at the interrupting frequency produce an output signal. Therefore, when zero gas is flowing through the analyzer, the beams are equal and the output of the analyzer is zero.

When the gas to be analyzed is introduced into the sample cell, it absorbs some infrared energy and thus reduces the radiation reaching the detector from the sample beam. It must be remembered, at this point, that the detector sees only absorption by that gas for which it has been sensitized. As a result, the beams become unequal and the radiation entering the detector flickers as the beams are alternated. The detector gas in turn expands and contracts in accordance with this flicker as the temperature fluctuates.

As mentioned before, the principles of the positive and negative type infrared analyzers, although slightly different, are somewhat similar up to a point. We have now arrived at this point, that is, the point at which the two types differ to a marked degree. We have followed the principle of measurement by means of infrared energy up to where we now have (1) the pressure of the gas in the detector changing at a frequency equal to the frequency of rotation of the interrupter, and (2) the temperature changing at this same frequency.

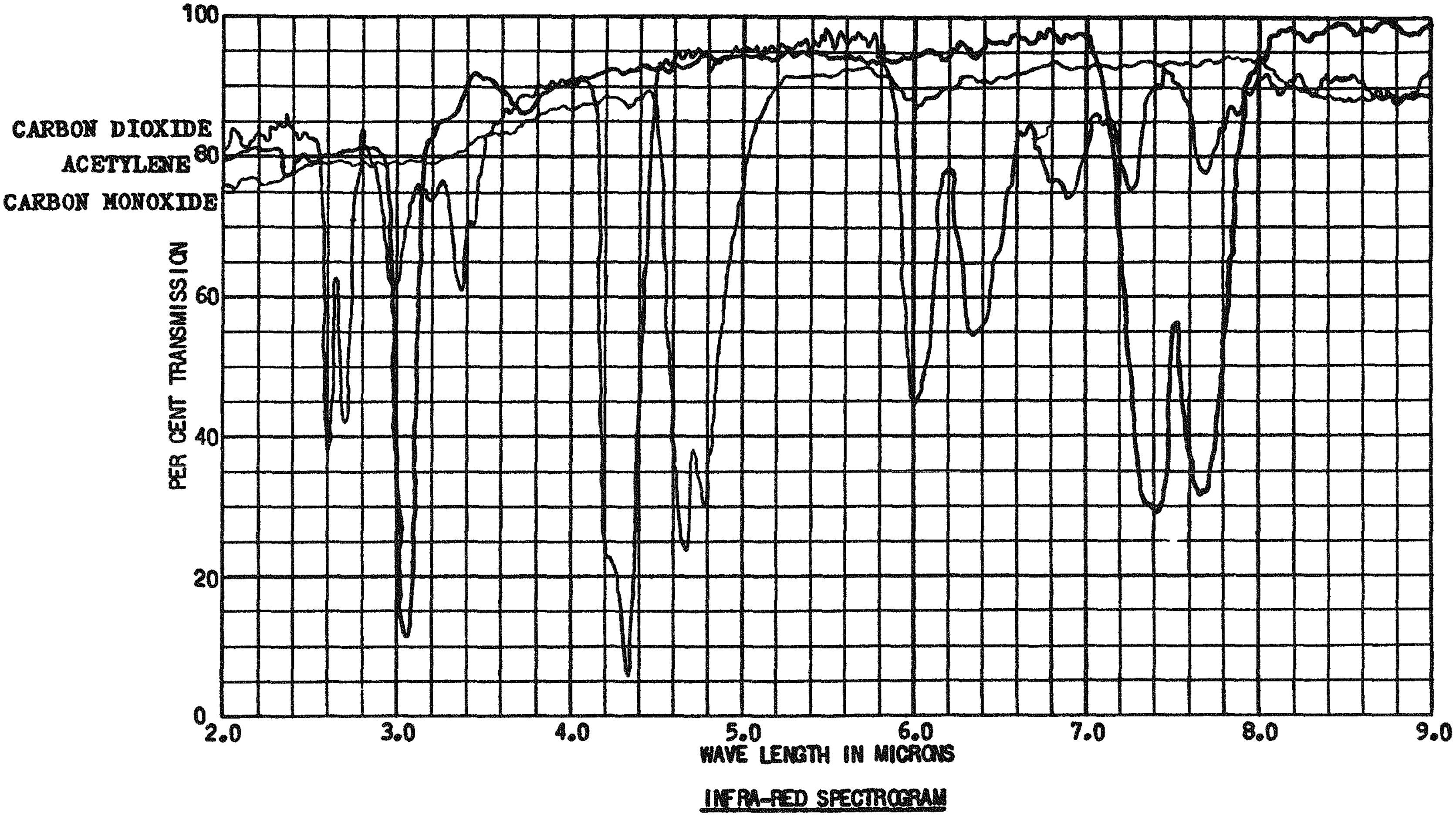


Figure 3. Infrared Spectrograms of Carbon Dioxide, Carbon Monoxide and Acetylene

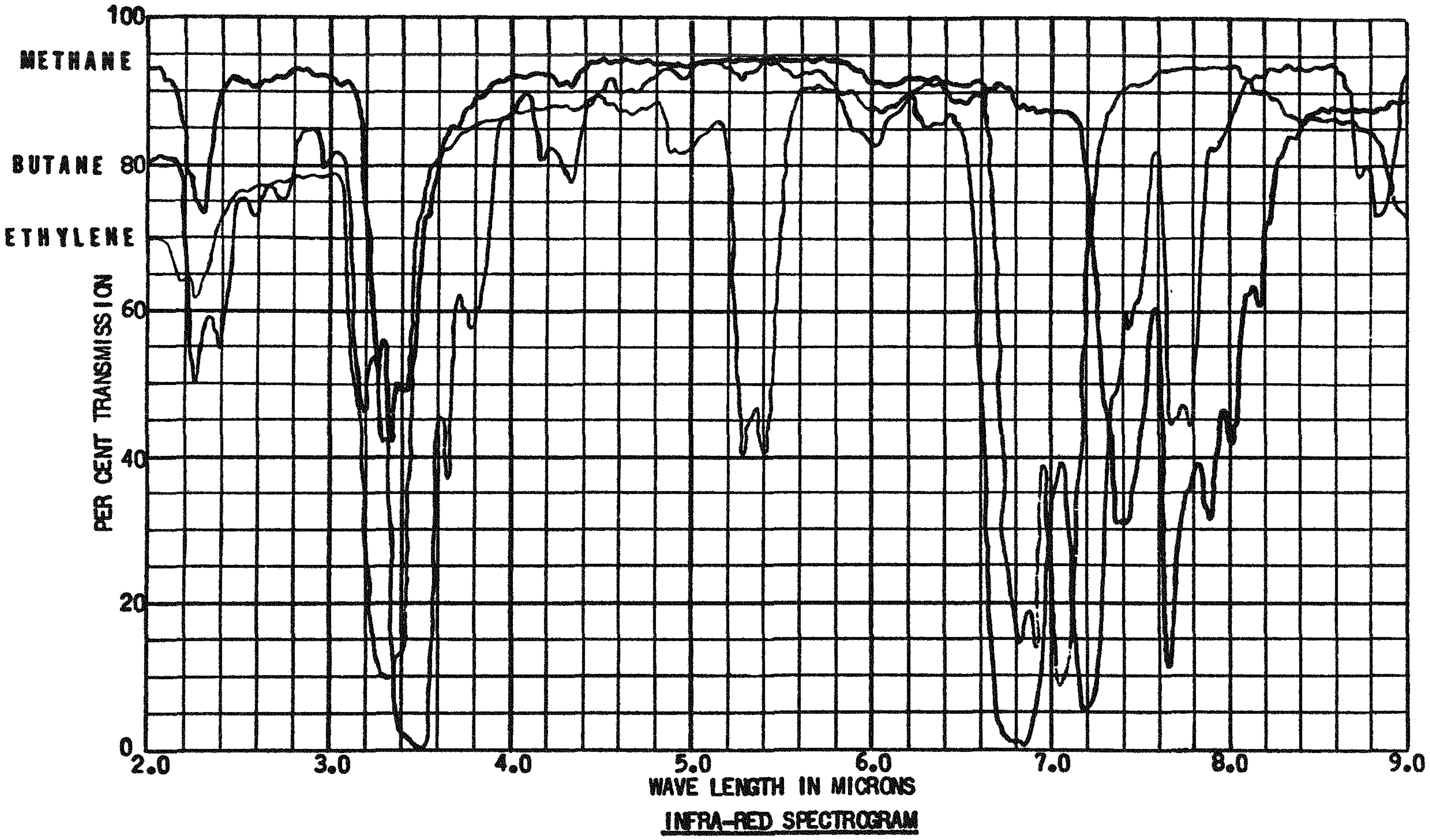


Figure 4. Infrared Spectrograms of Methane, Butane, and Ethylene

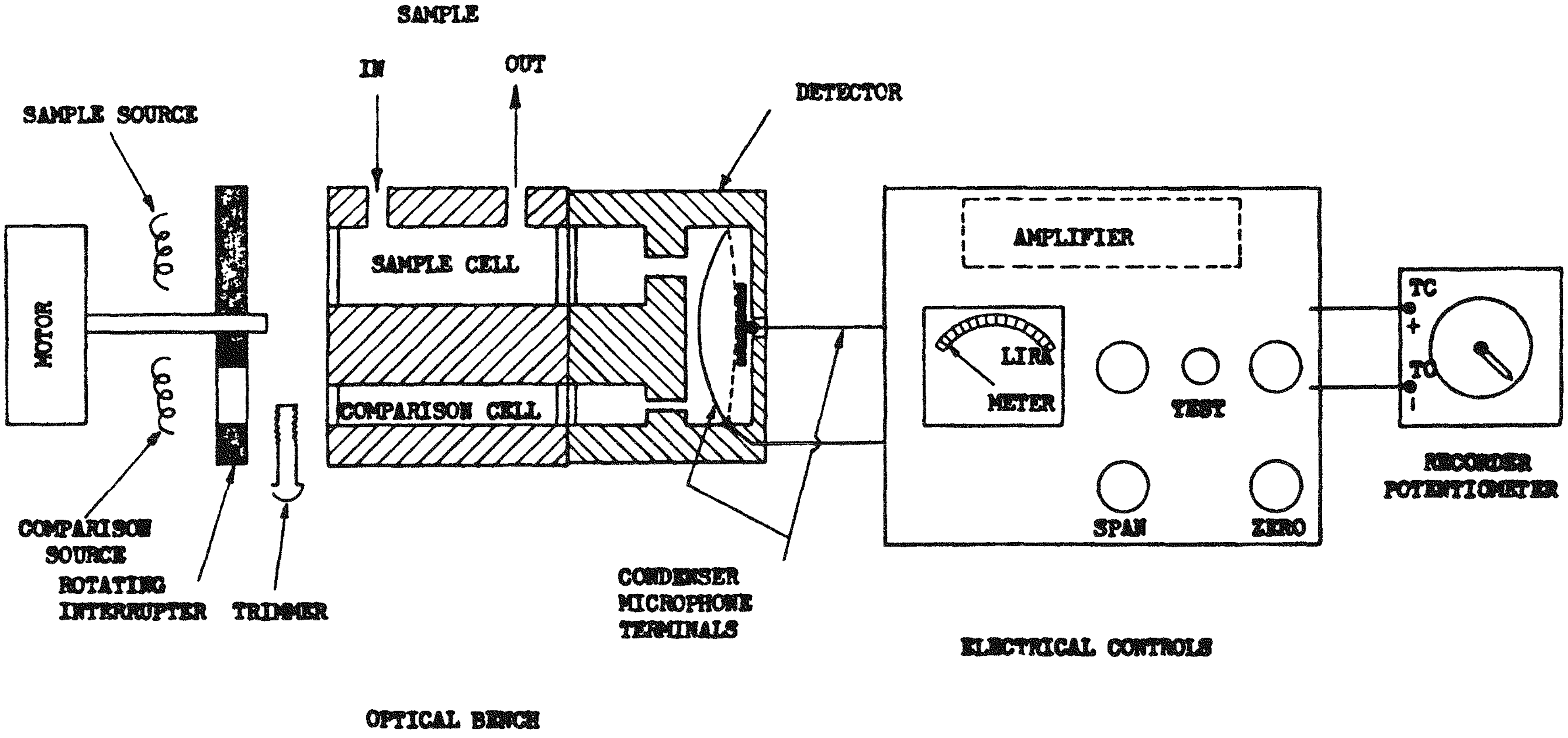


Figure 5. Schematic Diagram of an Infrared Analyzer, M.S.A. Model 200 LIRA

The negative type analyzer detects the changes in temperature by means of two sets of thermocouples located in the detector itself and thus changes the optical signal to an electrical signal. A flickering optical signal is not required. The major drawback of instruments of this type is the need for extremely close temperature control and thermostating of the entire analyzer.

In the most popular type of instrument in use, the pressure changes within the detector are used to move the membrane of a condenser microphone. This condenser microphone is incorporated into an oscillator network, providing an electrical signal which is amplified and fed to a meter or external recorder.

Gas Chromatography. Gas chromatography is the art of separating a mixture or complex stream of gas or vapor into its individual components or groups of components. This is accomplished by introducing a batch sample of gas into a stream of carrier gas and passing the resultant mixture through a column packed with suitable material. Since the rate of travel of each component through the packed column is dependent on its physical and/or chemical properties such as boiling point, acidity, basicity, asymmetry of molecules, etc., each component travels through the column and emerges at a different time. As the components emerge from the column, their concentration in the carrier gas is measured by a detector, the most common being a thermal conductivity cell. The readings obtained, if plotted on a recorder chart, produce a series of peaks, the location of which provides qualitative information as to what components are present in the sample. The height of the peaks provides the quantitative information or how much of each component is in the stream.

Although this type of analysis is not truly continuous, the proper selection of columns, and new modes of programming, such as tape, have made this type of instrument highly desirable from the standpoint of flexibility. Due to the fact that only one component is being measured at any one time, the only limitations on the gases or vapors which can be measured are that they have a coefficient of thermal conductivity which differs from that of the carrier-gas. Since a wide variety of carrier-gases are available, such as helium, hydrogen, nitrogen, argon, etc., (helium being the most common), no problem should exist in measurement of any gas or vapor. Actually, the biggest problem to be encountered is with high-boiling-point samples; however, chromatographic instruments are now available for continuous operation up to 450°F.

The field of gas chromatography is constantly changing and improving, as new means of detection, sampling, programming, etc., are developed, and should remain for some time as one of the most flexible means of process analysis.

Analysis in the Parts-Per-Billion Range

Ionization Detectors. Trace contaminants in a gas stream can be measured in the parts-per-billion range by conversion of the contaminant into submicron smoke particles and passing them into an ionization chamber. Such particles reduce the steady-state ion current by acting as recombination centers.

The sample is initially divided, one-half passing through a particle-forming agent, the other passing directly into a comparison chamber. The first portion of the stream, having formed a smoke, then passes into a detection chamber containing a source of alpha particles, and increases the rate of recombination, thus causing a decrease in ion current. The detector and compensator cells are incorporated as two arms of a Wheatstone bridge so that an unbalance of the conductance of the two cells is used as a measure of the contaminant to be determined. Figure 6 shows a typical flow system for this type of analyzer.

To produce the smoke particles, several means are at hand, depending on the contaminant to be measured:

1)	Pyrolysis	Example: Tetraethyl lead and nickel carbonyl react at high temperatures to form particles of lead and nickel.
2)	Hot Solid Reagents	Example: A copper oxide bed reacts with chlorinated hydrocarbons to form copper chloride particles.
3)	Gases	Example: Ammonia as a reagent will form ammonium chlorida.
4)	Aqueous Solutions	Example: Amines can be detected by bubbling air through acetic acid and reacting the vapors to form acetate particles.

These are only a few of the many ways to sensitize an instrument so that it is specific for one gas or group of gases to be detected.

<u>Note</u>: Unfortunately, this type of detector does not lend itself to measurements in highly radioactive streams; however, it is mentioned here as a method useful for trace analysis of many gases found in and around nuclear facilities.

CONTINUOUS LIQUID ANALYSIS

Analysis in the Percentage Range

Differential Refractometers. The need for more accurate means of analysis in the percentage range has brought about the development of several sensitive differential refractometers. A typical analyzer is shown in Figure 7.

In operation, a narrow beam of light is passed through a collimating lens and into the sample liquid. The light beam then passes through the sample liquid and the reference cell, which is filled with the reference liquid. It is then reflected from a mirror back through the cells and lens, and through a beam deflector to a detector cell. It is the double passage through the sample that gives this instrument extreme sensitivity.

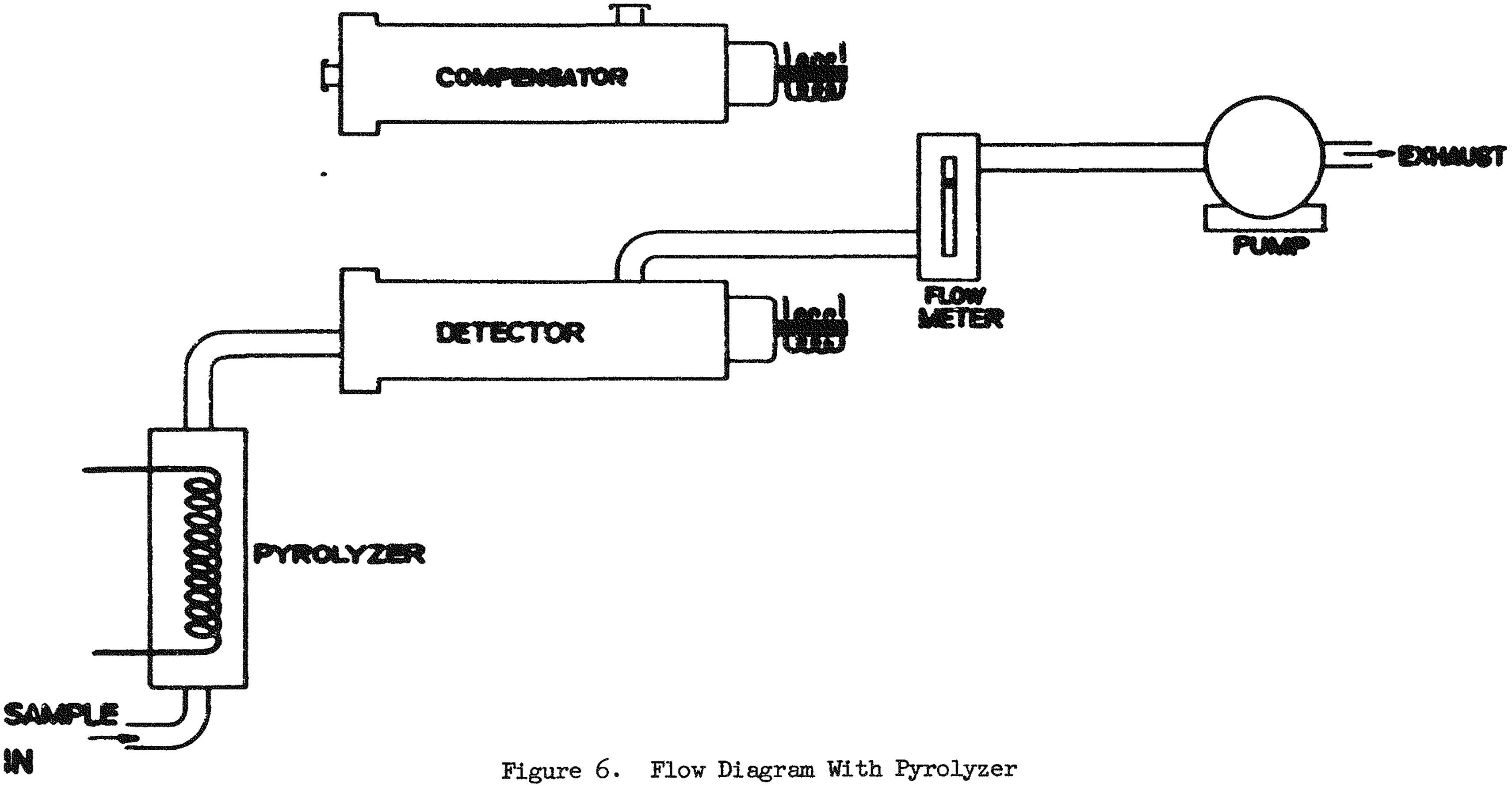


Figure 6. Flow Diagram With Pyrolyzer

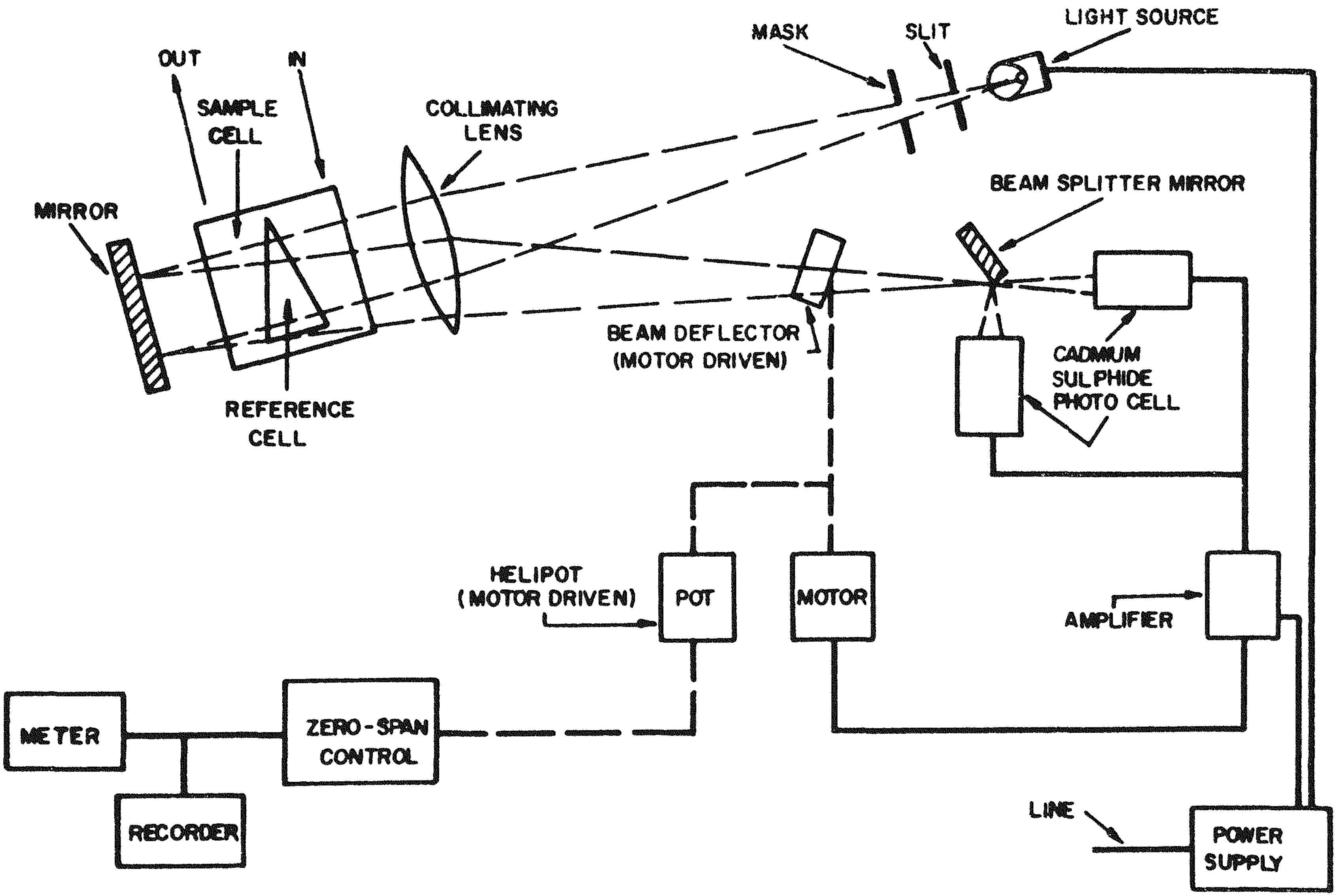


Figure 7. Schematic Optical System--
M.S.A. Process Refractometer

The detector cell is primarily a balancing network which takes the refracted light beam. splits it into two equal rays of light and directs them into matched photocells. If a change occurs in the composition of the sample stream, the refractive index will change. As a consequence, the angle of the refracted light will change and, hence, the light beam will not be split equally by the beam-splitter. More or less light now strikes the photocells, causing an unbalance which is amplified and fed to a servo motor. The servo motor re-positions the beam deflector until the light is once more split evenly so that the output from the photocells is balanced. This same servo motor also drives a helipot which produces a deflection in the meter or recording potentiometer.

A refractometer of the type described above is capable, in many cases, of determining a component in the concentration range from 0 to 1/2 per cent in 99.5-100 per cent of a second component. The limiting feature of course is the difference in refractive index over the full-scale range. The instrument described above can be used to measure a change as small as 0.0005 refractive index (RI) units for full scale, or as high as 0.2 RI units.

Let us consider a typical example of measuring from 0 to 20 per cent of toluene in benzene. The refractive index of a mixture of several components is:

$$R = A_{r_a} + B_{r_b} + C_{r_c} - \text{etc.} \qquad (1)$$

where A = % by volume of component A

r_a= RI of component A

B = per cent by volume of component B - etc.

RI of benzene = 1.50110

RI of toluene = 1.49693

According to (1) above, the RI of a 20-per cent mixture of toluene in benzene is:

$$R = 0.80\ (1.50110) + 0.20\ (1.49693) = 1.50027$$

Now, since the RI of benzene is 1.50110, the change in RI units caused by 0-20 per cent toluene is 1.50110 - 1.50027 = 0.00083 RI units. Since the instrument can handle anything over 0.0005 RI units full scale, it can be seen that this would be an easy problem to handle.

Should the above problem have been 0 to 5 per cent of toluene in benzene, the differential RI would be 0.00021 RI units which is too small to be handled by this instrument.

pH Analyzer. The pH value of a solution or merely its pH is defined as the logarithm of the reciprocal of the concentration (in moles per liter) of hydrogen ion which it contains. Mathematically this is expressed as $pH = \log \frac{1}{H^+} = -\log H^+$.

Hence, for pure water or a neutral solution in which the concentration of hydrogen ion is 1×10^{-7} mole per liter we have:

$$\log H^+ = \log(1 \times 10^{-7}) = -7$$

Hence, by measuring the difference between the pH of the pure sample stream and that of the contaminated stream, the amount of contamination can be determined.

Example: Impurity is HCl in water

pH reading is 4

Therefore, the Log $H^+ = -4 = \log(1 \times 10^{-4})$ or the concentration of hydrogen ion is 1×10^{-4} mole/liter. The solution is 0.0001 molar hydrochloric acid; this concentration can be converted to % by volume.

Both the refractometer and the pH meter are primarily for use on binary streams, since a third fluctuating component may neutralize the effect of the component which is being measured.

Infrared Analyzer. Where a complex mixture must be analyzed for one component, an infrared liquid analyzer may be used. Essentially the principle is the same as that discussed under gas analyzers, except that the sample cell is constructed differently and the detector must be filled with a gas which absorbs in the same region as the component being measured. Figure 8 shows the difference in cell construction and dimensions, while Figure 9 shows spectra of interest in relation to a problem of measuring water in alcohol. Figure 10 shows the spectral region chosen for use in the analysis, and the gas which is used in the detector. For the above problem and a range of 0 to 2 per cent water in alcohol, the instrument would be constructed as follows:

Sample cell - 0.0005 inches thick

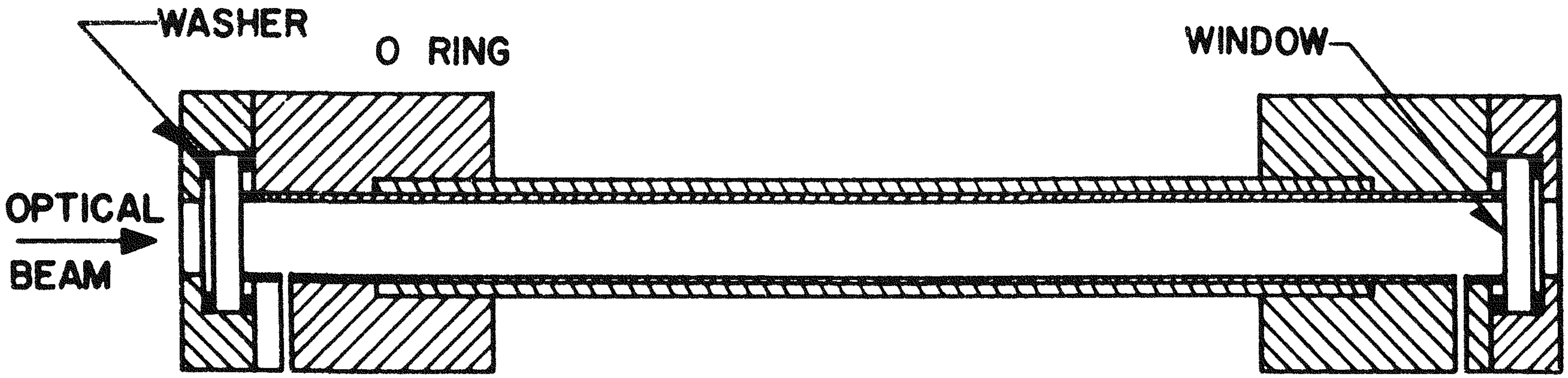
Detector fill - 100% carbon monoxide

Windows - calcium fluoride

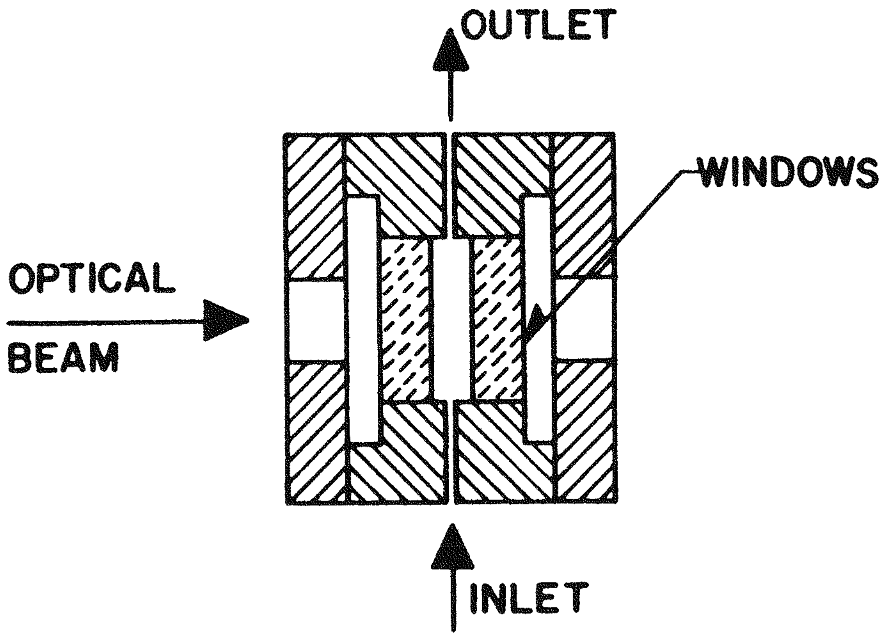
From the above discussion, it can be easily seen that refractometers and pH meters are designed for simple stream analysis, and infrared analyzers for the more complex streams.

Analysis in the Parts-Per-Million Range

Infrared Analyzer. The analyzer described above can in many instances be used for parts-per-million analysis, depending on the components and condition of the sample stream; however, since this type of analysis was



GAS CELL



LIQUID CELL

Figure 8. Liquid Cell for Use in Infrared Analyzer

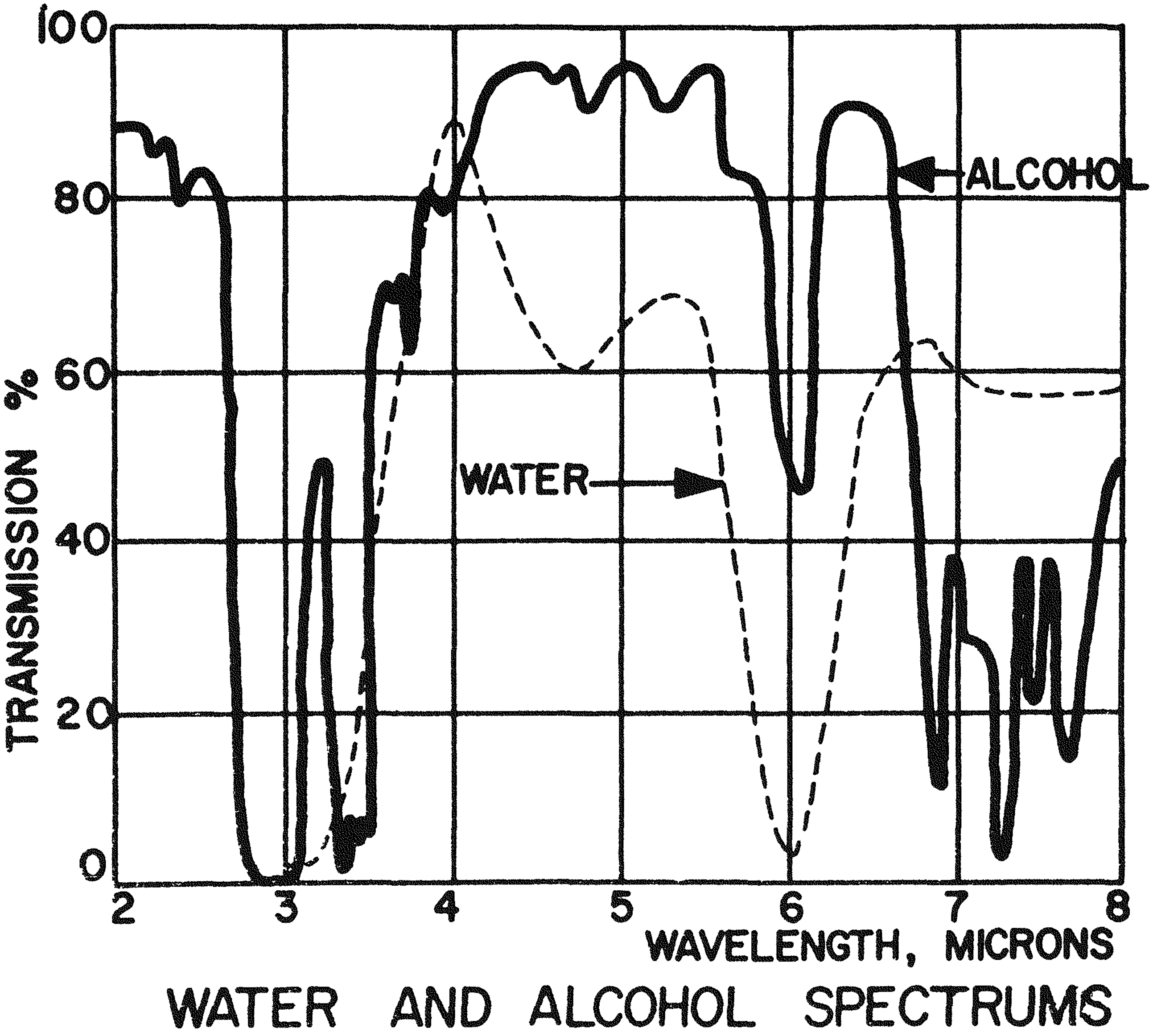


Figure 9. Water and Alcohol Spectra

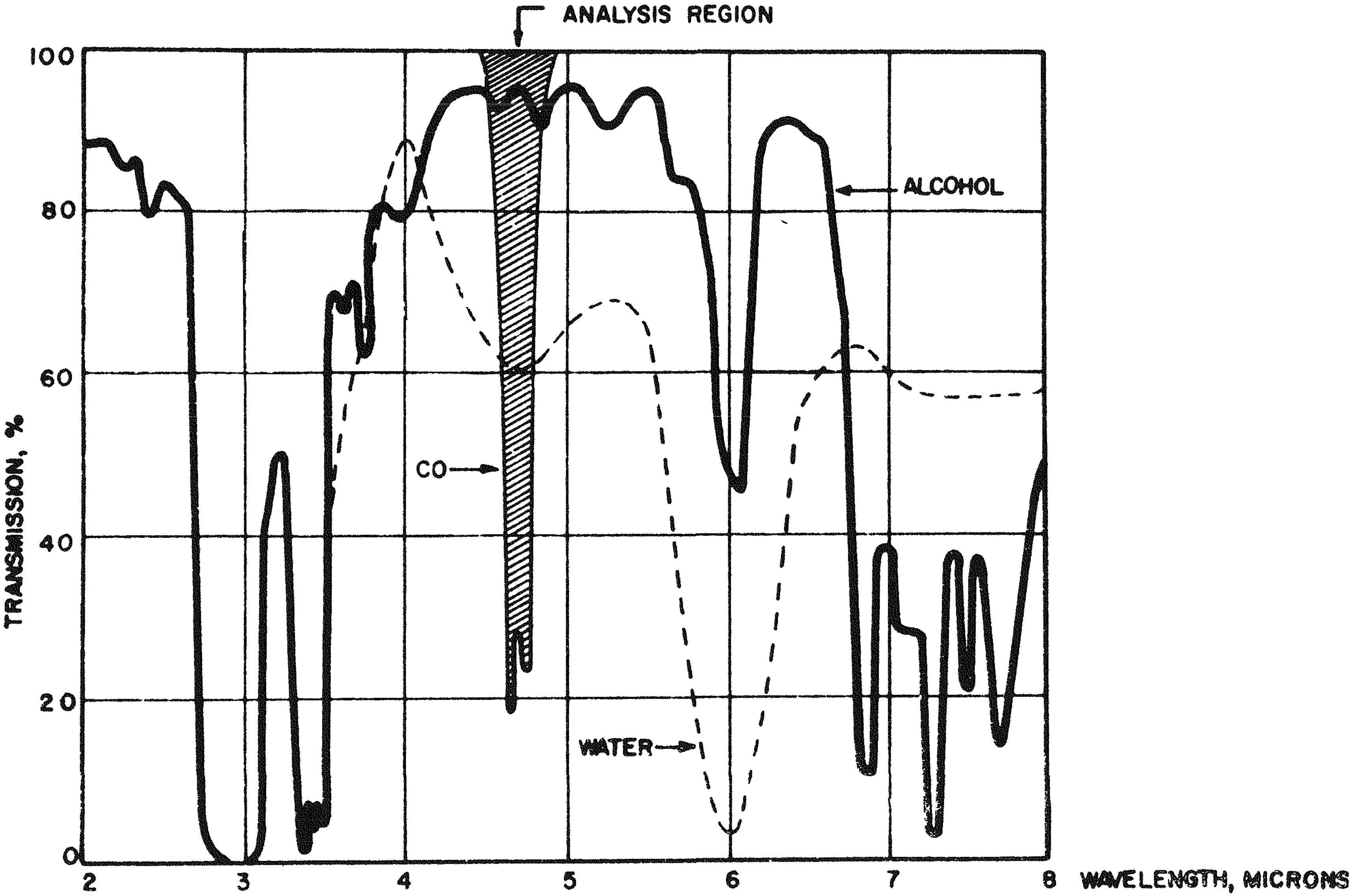


Figure 10. Water, Alcohol and Carbon Monoxide Spectra

discussed above, it would seem best to go on to other types at this time.

Dielectric Constant. Many binary sample streams can be measured accurately in the parts-per-million range by an analyzer of this type. Looking first at the basic formula for the dielectric constant, e, of a given medium, we find:

$$e = \frac{c}{c_o}$$

c = capacitance of condenser with a given medium between its plates

c_o= capacitance of condenser with vacuum between its plates

The measurement of water in organic streams, purity of acetone, toulene concentration in hydroformer distillates, etc., are only some of the many applications for which this analyzer can be used. In using this instrument to measure water in hydrocarbons, full scale deflections have been reported for water in the range 0 to 100 ppm by weight.

pH Meters. Again, pH meters can be used on binary streams to measure, in many cases, components in the parts-per-million range.

Analysis in the Parts-Per-Billion Range

Flame Photometer. This type of analyzer was developed to measure elements such as barium, boron, cobalt, lead, sodium, strontium, etc., dissolved in a liquid stream. This method of analysis can be used to measure essentially any element which exhibits flame emission properties. In following through the operation of this type of analyzer, let us assume that we are trying to measure sodium in water.

First, the sample is fed to a burner unit where it is aspirated into an oxyhydrogen flame. When sodium is present in the sample, the flame emits the characteristic yellow radiation of sodium. A grating monochromator isolates the yellow line of sodium from the background spectrum of the stream, where it is detected by a photomultiplier tube. An interrupter, located between the photomultiplier tube and the monochromator, alternately blocks and passes the light at a given frequency and eliminates dark current effects in the phototube. The output from the phototube is then amplified and rectified before being measured by a recording potentiometer. With this type of instrument, full-scale measurements can be made of sodium in a range as low as 0 to 10 parts per billion.

SUMMARY

The above instruments and methods of analysis are only a few of the many available for continuous gas and liquid analysis which are suitable for the analysis of radioactive streams. It is regrettable that all the instrumental methods useful for carrying out gas and/or liquid measurement could not be discussed herein, such as colorimetry, x-ray absorption, etc.; however, time did not permit this. It is hoped that close cooperation between the user and the manufacturers will continue as it has in the past, and will result in even newer instruments to help wage the never-ending battle for closer control in process streams.

A CORROSION-RESISTANT PIPETTER FOR REMOTE MEASUREMENT OF RADIOACTIVE SAMPLES

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ABSTRACT

In 1954-55, a remotely-controlled servo-operated pipetter was developed by the Analytical Instrumentation Group for use in the High Radiation Level Analytical Facility at Oak Ridge National Laboratory. In this device, a position servo remotely operates a positive displacement pipet designed so that it may also be cleaned remotely. These pipetters have been used to remotely measure highly radioactive reactor and process samples for two purposes: to determine sample density by the falling-drop method and to deliver known volumes of samples for quantitative dilution prior to analyses. Some of the samples for which the pipetter was designed contain nitric acid and so the construction materials of parts of the pipet in contact with the sample are stainless steel and Teflon. These pipetters have given satisfactory performance since 1955. For example, the relative standard deviation of successive deliveries of 100 microliter volumes is about 0.2 per cent.

In the near future, radioactive samples that must be remotely pipetted will contain one or more of the following corrosive chemicals: nitric acid, sulfuric acid, hydrochloric acid, hydrofluoric acid, or aqua regia. This has made it necessary to design and install a corrosion-resistant pipet in the standard remotely-operated servo unit of the pipetter in place of the original stainless steel-Teflon pipet.

A pipet has been designed that is not attacked by any of the above chemicals. It will also quantitatively deliver volumes of solutions made with certain organic solvents. It is possible to quickly substitute these

pipets in the servo assembly without varying the correlation between displacement-plunger position and control dial setting. The cost of manufacture of this pipet is estimated to be less than that of the original stainless steel-Teflon pipet. The useful delivery capacity of the pipet is about 700 microliters, but it would be possible to build smaller or larger pipets of this design. The pipet has a contained dynamic seal which can be recompressed if leakage develops due to wear.

Extensive seal, precision, corrosion, and life tests of pipets of this new design have been made. The precision of delivery of sample volumes is the same as that obtained with the stainless steel-Teflon pipet, 0.2 per cent relative standard deviation. Test results indicate that this pipetter will function reliably for thousands of pipettings of corrosive samples without retightening the dynamic-seal compression caps.

INTRODUCTION

In 1954-55, a remotely-controlled, position-servo-operated pipetter was developed by the Analytical Instrumentation Group at Oak Ridge National Laboratory. The purpose of this pipetter is to provide a precise, remotely-controlled means for sampling and pipetting highly radioactive solutions in order to avoid radiation exposure of the analytical chemist. The pipetter was developed through two prototype stages, with the assistance of the ORNL Engineering Department, from a pipetter that had been designed at ORNL for use in the Idaho Chemical Processing Plant.(13)

A pipetter of the 1954-55 design for the delivery of known volumes of samples for quantitative dilution prior to remotely-controlled analyses for free acid and uranium was built and demonstrated as a component of an adjunct to the Uranium Processing Exhibit of the ORNL Chemical Technology Division at the first International Conference on the Peaceful Uses of Atomic Energy, Geneva, August 3-20, 1955.(8) A photograph of this demonstration analytical cell for remotely-controlled analysis is published on the front cover of the June, 1957, issue of *Analytical Chemistry*. Subsequently, this pipetter was demonstrated at the Uranium Processing Exhibit in New York City, Oct. 20-Nov. 3, 1955, and at the Southwest American Exposition, Oklahoma City, April 22-29, 1956.

Pipetters of this design containing 1 ml or 0.1 ml stainless steel pipets have been in use in the High Radiation Level Analytical Facility(5,6) at Oak Ridge National Laboratory since 1955. A photograph of the operating face of this facility is published on the front cover of the November, 1957, issue of *Analytical Chemistry*. Satisfactory performance and minimum maintenance of the pipetter has been obtained. For example, the relative standard deviation of successive deliveries of 100-microliter volumes is about 0.2 per cent. These pipetters are used to remotely measure highly radioactive reactor and process samples for two purposes: to deliver 5-microliter drops of sample to determine sample density (or specific gravity) by the falling-drop method(1,2,6,7,9,10,11,14,15) and to deliver known volumes of samples for quantitative dilution prior to various subsequent analyses.(2,4,7,9,11,14)

The principles of operation of the stainless steel pipetter have been described.(4,9) In this device, a position servo remotely operates a positive displacement pipet designed so that it may also be cleaned remotely. The pipet is filled completely with sample so that it contains no air spaces. A position servomechanism drives a plunger of known and exactly machined diameter by precisely-controlled increments into this liquid so that increments of liquid of volume equal to the volume of plunger pushed into the liquid are extruded quantitatively from the delivery tip of the pipet. The volume extruded is directly proportional to the rotation of the driving leadscrew. The volume delivered is directly indicated in microliters on the control dial of the control unit by the incremental change in the setting of the dial. A complete description of the pipetter, including tabulations of mechanical and electronic drawings, has been published(4,9) and instructions have been prepared for its use and maintenance.(4) Because some of the samples for which this pipetter was designed contain nitric acid, the parts of the pipet in contact with the sample are fabricated from stainless steel and Teflon. A closeup photograph of this pipet is shown in Figure 1. A photograph of the assembly that is used for pipetting samples has been made (ORNL Photograph No. 17316). The assembly that is used for the determination of density by the falling-drop method has also been photographed (ORNL Photographs Nos. 17303 and 17525).

REQUIREMENTS FOR THE DESIGN OF A NEW CORROSION-RESISTANT PIPET

Recently, radioactive reactor and process samples, including those from Thorex, Darex, Zirflex, EBWR, and Sulfex programs, must be remotely pipetted that contain one or more of the following corrosive chemicals: nitric acid, sulfuric acid, hydrochloric acid, hydrofluoric acid, or aqua regia. Most of these samples cannot be pipetted with the stainless steel pipets that are installed in the High Radiation Level Analytical Facility. It was considered to be essential to design a new pipetting device that could withstand without damage any or all of these acids, high level radiation, and organic solvents such as acetone, 30-per cent TBP in Varsol, and 0.5 $\underline{M}$ TTA in xylene. Other desirable features would include a precision of delivery of about 0.2 per cent relative standard deviation, low maintenance requirements, rapid interchange of pipets without change of correlation between control dial setting and plunger position, low cost, provision to take up wear, and long, reliable life.

Some earlier related work had been done on the design of corrosion-resistant pipets. In September 1955, a fluorothene-lined pipet was built and used in the spectrographic cell of the High Radiation Level Analytical Facility. In November 1958, a plastic pipet was designed and built to replace the fluorothene-lined pipet. Provision was made for sealing the plunger-liner junction only above the intersection of the sidearm and the liner. Although a later modification of this pipet has been in use in the HRLAF spectrographic cell for a number of months, it has been found that it is difficult to fabricate successful replicates of this pipet.

It was decided on December 16, 1959, that the design and evaluation project described in this paper should be undertaken by the ORNL Analytical Instrumentation Group. The design decision was to develop a new corrosion-resistant pipet that could be substituted for the stainless steel pipets

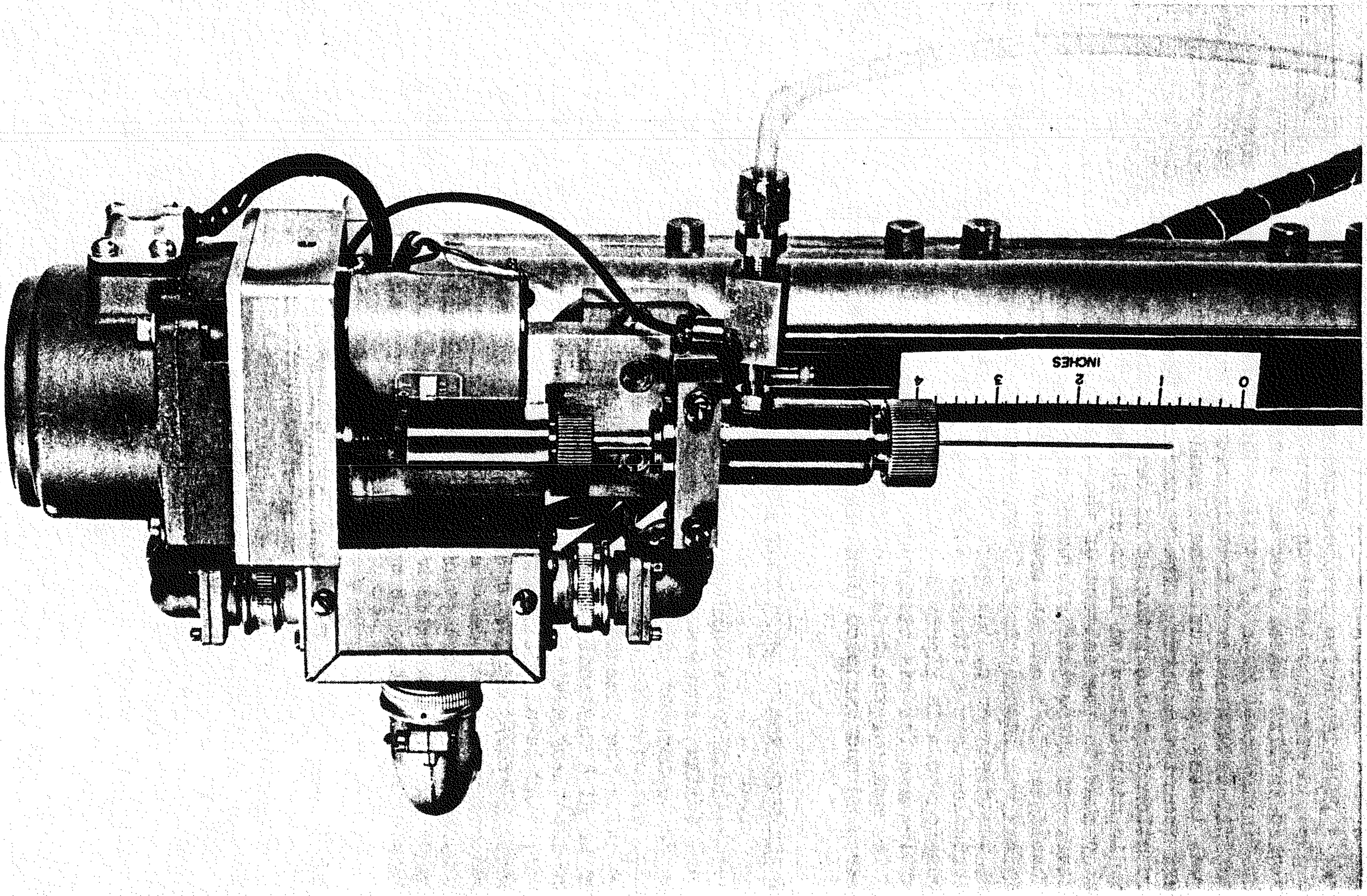

Figure 1. Photograph of Remotely Servo-Operated Stainless Steel-Teflon Pipetter

ORNL Photo. No. 14499

installed in the High Radiation Level Analytical Facility. That is, the new pipet was to be mechanically interchangeable with the stainless steel pipets and to be driven by the same position-servo system that was in use. The corrosive acids and organic solvents, considered as a whole, are almost the alchemical alkahest. Consequently, the selection of materials suitable for construction of the new pipet is a major portion of the problem.

MATERIALS OF CONSTRUCTION

A literature search was made in December 1959 to find materials having the required properties for construction of the new pipet. In essence, two materials were needed: a material that could be used for containment and to form a packing seal and a material that could be used to construct a displacement plunger.

Presumably, the packing material would have to be elastic or at least subject to controlled cold flow under contained compression. It was planned to design an improved type of dynamic seal.(12) The plastic, elastic materials that might be used are restricted in number because most are not sufficiently resistant to the combined attrition of organic solvents, concentrated oxidizing acids, mechanical friction and compression, and high-level radiation. Teflon is not perfectly elastic at normal temperatures and, therefore, does not recover completely when a deforming load is removed. However, Teflon does have an appreciable degree of elasticity, and its tendency to cold flow under load can be taken advantage of to form a very good dynamic seal, if the seal is properly contained. The other physical and chemical properties of Teflon are excellent for this purpose. Although Teflon has only a finite resistance to damage from radiation, it was known from experience with the stainless steel pipets that it is sufficiently radiation-resistant for the purpose. A high-density, low-void, virgin grade of Teflon is particularly suitable for precision machining. Teflon rods having these characteristics, designated as "TSI Grade" are extruded by Tri-Point Manufacturing, Inc., Albertson, L. I., New York. It was decided to use this material to form the contained dynamic seal and for the pipet liner.

The cylindrical displacement plunger must be machined to a calculated outside diameter with a tolerance of ± 0.0001 inches. One plunger was tested that had a taper of 0.001 inch over its working stroke. This amount of taper is intolerable because the Teflon seal is not elastic enough to recover from deformation by this much taper of the plunger. Also, the plunger must be hard, resistant to frictional wear, not cause galling or excessive wear of the Teflon seal, and must withstand various acids, solvents, and radiation. Various metals, including titanium, platinum, and tantalum, and various alloys, including iridium-rhodium, Hastelloys, Stellites, Inconels, and columbium-zirconium were considered but none were suitable. Many special alloys have been developed, each to resist a certain class of chemicals, but always some other chemical or acid will dissolve them. Glass cannot be used because it is attacked by hydrofluoric acid. Linde synthetic sapphire is probably suitable except for the fact that it is difficult to machine to precise tolerances and a plunger would therefore cost several hundred dollars. Because another suitable material has been found that is much less expensive to machine, no plunger has been fabricated from sapphire. Several plungers were fabricated from fluorothene. The chemical and radiation-resistance properties of fluorothene are very good for this application, but its physical properties are only fair; it is not as hard as it should be. This lack of rigidity results in some elastic deformation of a fluorothene plunger from the force of the servo drive so that liquid is ejected in increments rather than continuously and the precision (S) of delivery is degraded to about 0.4 per cent. Graphite cannot be used because it is porous and soaks up liquids in contact with it. National Carbon Company "Karbate" impervious graphites consist of graphite impregnated with various chemically-resistant synthetic resins. They have the required physical properties, but they are not recommended by the manufacturer for use with nitric acid more concentrated than 20 per cent, so these materials were not tested. A very satisfactory material for the pipet plunger is produced by The United States Graphite Company, Saginaw, Michigan: non-porous Graphitar Grade 14. This material is stated by the manufacturer to have an average Schleroscope hardness of 100, an average transverse breaking strength of 11,000 psi, an average compressive strength of 35,000 psi, and low friction. It may be machined to close tolerances and smooth finishes by grinding. The coefficient of friction of Graphitar is reduced by the addition of a fluid such as water. The coefficient of linear thermal expansion of Graphitar is extremely small. It is an electrical conductor which means that the standard conductometric fill-indicator circuit of the pipetter will function normally with a plunger made of Graphitar whereas two conductivity probes are required with non-conducting plungers. Tests of the new pipet have shown that the effect of thousands of strokes of a Graphitar Grade 14 plunger through a compressed, Teflon, contained dynamic seal is to lap the plunger surface to a higher degree of polish; the wear rate is very low. Thus, the physical properties of Graphitar Grade 14 are well suited to the requirements for the pipet plunger material, although Graphitar Grade 14 is not recommended by the U. S. Graphite Company for use in nitric acid above 30% concentration, nor in sulfuric acid above 96% concentration. Its resistance to attack by the chemicals that are anticipated to be present in samples for the High Radiation Level Analytical Facility, including all of those enumerated above, is excellent. For example, a Graphitar Grade 14 plunger was immersed in concentrated nitric acid at room temperature for seven days without measurable adverse effect; this plunger was subsequently tested for 6000 pipettings of various synthetic corrosive samples without wearing enough to cause detectable leakage of the pipet. The identity of the impregnating material is regarded as proprietary information and hence its resistance to cleaning or decontaminating solvents is not completely known to the authors. Based on the tests that have been made, Graphitar Grade 14 is the material preferred for construction of the pipet plunger.

The material chosen for construction of the pipet delivery tip and sidearm is fluorothene. These parts are screwed into the Teflon liner and have mating conical sealing surfaces. Fluorothene is harder than Teflon and this aids the vacuum-tight sealing process for these parts.

The two outer compression caps are fabricated of aluminum. The caps do not normally come into contact with the samples. Since many of the parts of the pipet servo drive mechanism are of aluminum, and have lasted in the High Radiation Level Analytical Facility for a number of years, it was decided to use aluminum for the caps of the new pipet.

DESCRIPTION OF NEW CORROSION-RESISTANT PIPET

An exploded-view photograph of the new corrosion-resistant pipet that has been built from these materials is shown in Figure 2. The Graphitar Grade 14 displacement plunger has the same design provision that was used

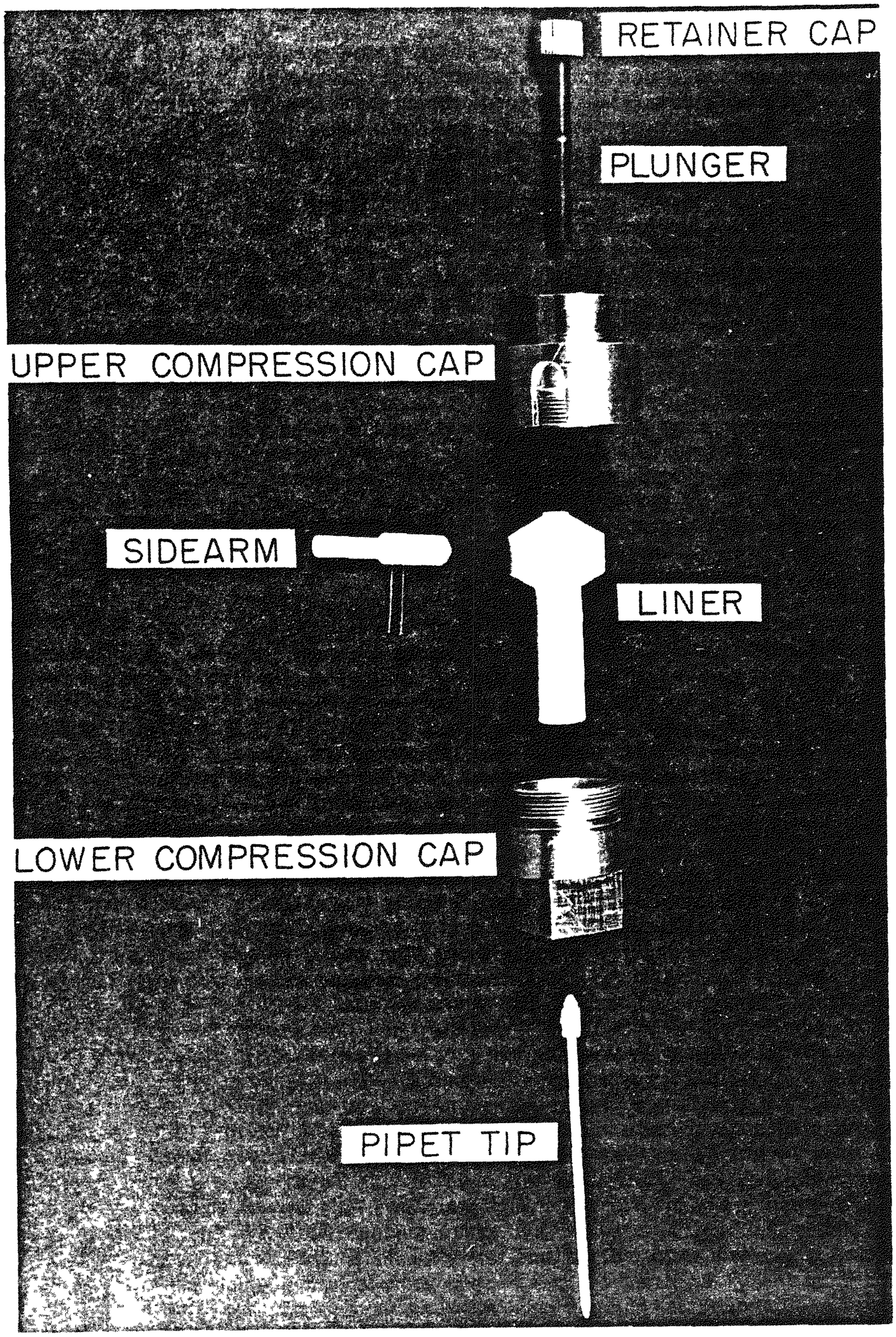

Fig. 2 - Exploded View Photograph of Corrosion-Resistant Pipet
ORNL Photo. No. 51524A

in the stainless steel pipet for complete air-free filling of the pipet and for remote cleaning and drying of the pipet by drawing solvents and air through the pipet. An 0.040-inch diameter hole extends upward 5/16 inch from the bottom of the plunger and is in vertical alignment with the axial passage in the sidearm when the plunger is in the fill position (setting of 50 on the control dial). An annular groove in the liner eliminates the need for angular alignment of the plunger hole with the sidearm passage. The plunger is joined to the position servo leadscrew by a knurled cap. The fluorothene sidearm is attached through traps to the house vacuum line and slurper system of the High Radiation Level Analytical Facility. It has two platinum conductivity probes so that a non-conducting plunger may be used. With the Graphitar Grade 14 plunger, either one of these probes is connected to the fill indicator circuit. The conical threaded end of the sidearm seals vacuum tight into the Teflon liner. The sidearm fits with clearance through a slot in the upper compression cap. There is no excessive torsion on the sidearm from tightening the lower compression cap because of appropriate specifications of relative areas and fits. The two aluminum compression caps have inner 30° conical surfaces which bear against the corresponding conical surfaces of the Teflon liner to form, under compression, a contained dynamic seal to the displacement plunger. The upper cap is clamped into the servo drive unit. The lower cap is tightened into the upper cap, with the liner in place, to a torque of 10 foot-pounds in order to compress the seal. The seal is formed both above and below the intersection of the sidearm and the plunger. There is 0.005 inch clearance between the plunger and the lower portion of the bore of the liner so that any solid particles that pass through the 0.013-inch orifice of the delivery tip will tend to wipe off from the plunger and not score the seal surface. This clearance also makes the requirement for concentricity of the bore of the liner and the vertical axis of the plunger less critical and tends to localize the seal at the proper site. Care is taken in the design so that the dynamic seal is entirely contained to prevent uncontrolled cold flow of the Teflon that would cause the pipet to develop a leak. Although no detectable seal wear was observed after 11,756 pipettings with one of these pipet assemblies, the compression caps may be retorqued to take up wear after it occurs. Liners were fabricated from virgin Teflon rods having a low void content and a high density ("TSI Grade" Teflon extruded by Tri-Point Manufacturing, Inc., Albertson, L.I., N.Y.). The conical threaded end of the fluorothene delivery tip seals vacuum tight into the Teflon liner. The orifice of the delivery tip is reduced by swaging to an inside diameter of 0.013 inch. The precision of delivery from an 0.013-inch orifice is better than that from an 0.040-inch orifice that was first used. A portion of an extruded drop may be removed from a delivery tip having an 0.013-inch orifice by momentarily dipping the pipet below the surface of the dilution liquid by means of the remote, screw-operated elevator, without appreciable loss of sample by diffusion from the delivery tip. This technique was also possible with the stainless steel pipet. Alternatively, the delivery tip may be touched to the side of the receiving vessel to remove all of the extruded sample. All passages above the orifice of the delivery tip, including the axial passage through the sidearm, have a greater diameter than 0.013 inch so that solid particles smaller in diameter than 0.013 inch that may be contained in the sample should not plug the pipet. To minimize danger of scoring the dynamic seal, however, it is recommended that, prior to pipetting, solid particles be removed from samples by centrifugation.

A photograph of an assembled corrosion-resistant pipet is shown in Figure 3. This new pipet is not attacked at room temperature by nitric, hydrochloric, hydrofluoric, or sulfuric acid, or aqua regia, or by organic liquids such as acetone. It will also quantitatively deliver volumes of samples made with organic solvents. It is possible to quickly substitute these pipets for the stainless steel pipets in the standard remotely-controlled position-servo assembly without losing the existing calibrated correlation between displacement-plunger position and control-dial setting. Provision is made to absorb dimensional tolerances during installation. The useful delivery capacity of the pipet is 700 microliters, but it would be possible to build smaller or larger pipets of this design. The pipet has a contained dynamic seal which can be recompressed if leakage develops due to wear. The principles of operation of the pipet are essentially the same as those of the stainless steel pipet.(4,9) The ORNL model Q-1348-A control unit has been modified from the original Q-1348 design so that it will automatically drive the pipet displacement plunger from the fill position (dial setting of 50) to the sealed position (dial setting of 250) when a conducting sample arrives at the conductivity probe in the sidearm. The drawing for construction of the new pipet was made December 23, 1959.(3) The first pipet (with a fluorothene plunger) was received from the ORNL Chemistry Division Shop February 23, 1960. Plungers fabricated from Graphitar Grade 14 were received April 12, 1960. The cost of fabricating one pipet has been estimated by the shop foreman to be substantially less than $200. Various minor modifications that were developed during the evaluation of the pipet from March through August, 1960, have been incorporated into a final mechanical drawing, ORNL Drawing No. D-CD-114.

PERFORMANCE OF PIPETTER WITH CORROSIVE LIQUIDS AND ORGANIC SOLVENTS

All tests of the corrosion resistance of the new pipetter were made at room temperature. The first tests of the performance of the new corrosion-resistant pipetter were made with pipet assemblies having a fluorothene displacement plunger. It was learned later that displacement plungers fabricated from Graphitar Grade 14 are superior to those fabricated from fluorothene, and so only the performance of the pipetter having a Graphitar Grade 14 plunger will be discussed in this paper.

In early tests with a Graphitar Grade 14 plunger, the orifice of the fluorothene delivery tip was 0.040 inch. A Beckman model K automatic titrator was used to titrate with sodium hydroxide successive 100 microliter deliveries of water-clear, C.P. reagent-grade, concentrated nitric acid. The relative standard deviation, S, of sets over the working stroke of these titrations ranged from 0.2 to 0.3 per cent. The same precision was obtained in titrations of 125 and 150 microliters of acid. A Graphitar Grade 14 plunger was immersed in concentrated nitric acid for seven days. There was no visual evidence of damage to the surface of the plunger. After assembly with a torque of 10 foot-pounds, no leakage of the pipet over its working stroke (dial setting from 250 through 950) could be detected with full vacuum (24 inches of mercury) applied to the sidearm. The precision of successive 100-microliter deliveries of a synthetic Darex-type solution (2.5 $\underline{N}$ HNO_3, 1.2 $\underline{N}$ HCl, 0.9 mg U/ml, 10 g 304L stainless steel/l) was S = 0.2 per cent (n = 14)

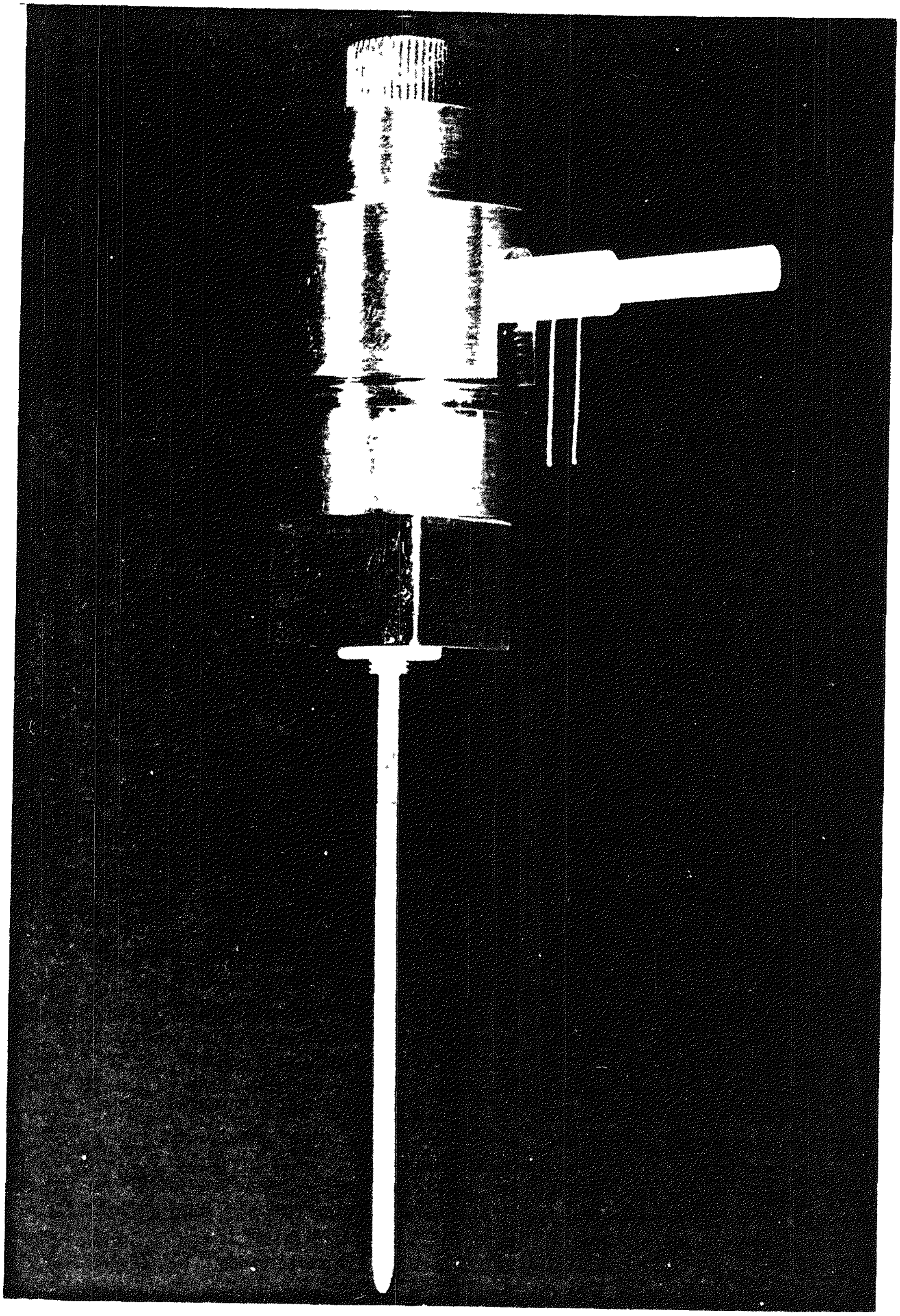

Fig. 3 - Photograph of Assembled Corrosion-Resistant Pipet

ORNL Photo. No. 51523

as determined gravimetrically. The pipet was then filled and left overnight with a Sulfex-type synthetic (6 M H_2SO_4, 50 mg 304L stainless steel/ml). The precision of delivery, subsequently determined gravimetrically, of 100-microliter portions of the Sulfex-type synthetic solution was S = 0.2 per cent (n = 14). No leakage could be measured of the pipet seal under full vacuum. The pipet was then tested with a synthetic EBWR solution (0.55 M Zr, 0.75 M Al, 1.4 M NH_4^+, 0.14 M Cr, 0.0018 M U, 3.6 M F^-, 1.1 M H^+) that contained both nitric and hydrofluoric acids. The precision, S, of delivery of 100-microliter portions, determined gravimetrically, was 0.3 per cent. Gravimetric test of the precision of delivery of 100-microliter portions of 0.5 M TTA in xylene gave an observed S of 0.4 per cent. The pipet was then left filled overnight with the synthetic EBWR solution. No leak was detected over the working stroke the next day. The precision of delivery of 100-microliter portions of 30-per cent TBP in Amsco was found gravimetrically to be S = 0.3 per cent.

Another Graphitar Grade 14 plunger was immersed for 24 hours in concentrated sulfuric acid and then for 24 hours in reagent-grade hydrofluoric acid. No damage to the plunger was observed in either case.

After completion of the above tests, the orifice of the delivery tip was swaged to an inside diameter of 0.013 inch. Titrations were made with sodium hydroxide of 100-microliter deliveries of concentrated nitric acid. The partial drop remaining on the tip was removed by touching the tip to the surface of the dilution liquid by means of an elevator. The relative standard deviation, S, of the titrations was 0.2 per cent. It was concluded that the smaller orifice, 0.013 inch instead of 0.040 inch in diameter, was superior because improved precision could be obtained even though the tip was immersed in the dilution liquid in order to remove the last extruded partial drop. With the larger orifice, it had been necessary, instead, to touch the delivery tip to the side of the receiving vessel. All subsequent tests, particularly, the dynamic tests, were made with delivery tips having an orifice with an inside diameter of 0.013 inch.

DYNAMIC TESTS OF PERFORMANCE OF PIPETTER WITH CORROSIVE LIQUID SAMPLES

The objective of dynamic tests with various corrosive liquids was to establish whether the seal in the pipet assemblies would develop a leak or whether an assembly would show a degradation in precision of delivery as a result of a large number of pipettings at room temperature of various corrosive liquids. At the time of assembly, the pipet compression caps were torqued to 10 foot-pounds. During the dynamic tests, the compression caps were never readjusted. Delivery tips were used that had orifices of 0.013-inch diameter. The position-servo control unit, ORNL model Q-1348-A, was modified in order to subject, successively, three pipet assemblies to dynamic tests with various corrosive liquids. The modification of the control unit consisted of wiring a Flexopulse timer into the circuit in such a manner that it caused the pipet displacement plunger to continuously recycle between positions corresponding to dial settings of 50 and 950. After each full cycle, consisting of a fill and an extrusion operation, a digital counter was automatically advanced by one unit. During the automatic recycling, the sidearm of the pipet was closed off and the delivery tip was immersed in turn for periods of time in various corrosive liquids so that the dynamic tests would include attrition from these liquids. Periodically, the Flexopulse timer was shut off so that the seal could be vacuum tested over the working stroke and so that the precision of delivery of 100-microliter portions of concentrated nitric acid could be determined by titration with sodium hydroxide by means of a Beckman model K automatic titrator. The deliveries of nitric acid for the precision determinations and the seal testing strokes were not included in the accumulated cycle record of the counter.

One servo drive and control unit was used for all tests of the pipet assemblies, totaling about 24,000 complete pipetting cycles. Satisfactory performance was obtained and no maintenance was required.

The first pipet assembly to be tested dynamically was assembled with liner number 2. The Graphitar Grade 14 plunger in the pipet was the one that had been immersed prior to assembly for seven days in concentrated nitric acid and this pipet assembly was the one that had been used in the above series of tests with various corrosive liquids and organic solvents. Thus, the pipet had undergone considerable severe service testing prior to starting the dynamic test cycles. The data obtained are given in Table I. After 6000 cycles, pipetting various corrosive liquids, as tabulated, the tests of this pipet assembly were terminated. There was no leakage of the contained dynamic seal over the working stroke of the plunger with full vacuum (24 inches of mercury) applied to the sidearm and no indication of wear could be seen. The relative standard deviation, S, of the 84 titrations with sodium hydroxide of 100-microliter deliveries of concentrated nitric acid that were made at various intervals from 0 to 6000 cycles is 0.17 per cent. The dynamic performance of this pipet assembly is judged to be excellent.

The second pipet assembly to be tested dynamically included liner number 1B. The data obtained are given in Table I. During 6140 pipetting cycles, there was no leakage of the contained dynamic seal and no evidence of appreciable wear. The relative standard deviation, S, of 98 titrations of 100-microliter deliveries of concentrated nitric acid made at various times during the dynamic tests is 0.19 per cent. The dynamic performance of this pipet assembly is also considered to be excellent.

The third pipet assembly to be tested dynamically included liner number 1A. The data obtained are given in Table I. During 11,689 pipetting cycles, there was no leakage of the seal and no evidence of appreciable wear. The surface of the plunger had acquired a very high polish over its working stroke which indicates that the seal should last for very many more pipetting cycles. The relative standard deviation of 67 titrations by sodium hydroxide of 100-microliter deliveries of concentrated nitric acid is S = 0.16 per cent. The dynamic performance of this pipet assembly is also regarded to be excellent.

The overall results of the dynamic tests with three assemblies of the new corrosion-resistant pipetter are summarized in Table II. Since very satisfactory dynamic performance was observed, it was decided that sufficient testing had been made to terminate this phase of the evaluation program.

TABLE I. DYNAMIC TESTS OF PERFORMANCE OF PIPETTER WITH CORROSIVE LIQUID SAMPLES

PIPET ASSEMBLY, LINER NO.	TEST LIQUID	DYNAMIC PIPETTING CYCLES, NOTE 1		WEAR TEST NOTE 2	PRECISION NOTE 3 S, %
		FROM	TO		
2 (NOTE 4)	WATER	0	104	NEGATIVE	
	WATER	105	200	"	
	DAREX	201	318	"	
	DAREX	319	895	"	
	EBWR	896	1,005	"	0.17
	EBWR	1,006	2,002	"	0.21
	SULFEX	2,003	2,704	"	
	SULFEX	2,705	3,000	"	0.11
	DAREX	3,001	4,000	"	
	EBWR	4,001	5,076	"	
	SULFEX	5,077	6,000	"	0.19
1B	CONC. HNO_3	0	0	NEGATIVE	0.18
	WATER	0	103	"	0.18
	DAREX	104	1,000	"	0.18
	EBWR	1,001	2,000	"	0.18
	SULFEX	2,001	3,700	"	
	DAREX	3,701	4,475	"	0.21
	EBWR	4,476	6,140	"	0.22
1A (NOTE 5)	CONC. HNO_3	0	0	NEGATIVE	0.18
	SULFEX	0	2,326	"	0.16
	EBWR	2,327	8,874	"	0.13
	DAREX	8,875	10,563	"	0.17
	DAREX	10,564	11,689	"	0.16

EXPOSITION, TABLE I

Conditions:

Delivery tip orifice diameter,	0.013 in
Displacement plunger,	Graphitar Grade 14
Liner material,	extruded virgin Teflon having a low void content and a high density

Composition of corrosive test liquids:

Synthetic Darex; 2.5 $\underline{N}$ HNO_3, 1.2 $\underline{N}$ HCl, 0.9 mg U/ml, 10 mg 304L stainless steel/ml
Synthetic Sulfex; 6 $\underline{M}$ H_2SO_4, 50 mg 304L stainless steel/ml
Synthetic EBWR; 3.6 $\underline{M}$ F^-, 1.1 M H^+, 0.55 $\underline{M}$ Zr, 0.75 $\underline{M}$ Al, 1.4 $\underline{M}$ NH_4^+, 0.14 $\underline{M}$ Cr, 0.0018 $\underline{M}$ U

Notes

1. Cycles do not include pipetting strokes used to observe precision or test seal
2. Negative test means no leak with 24 in. Hg vacuum applied to sidearm, over working stroke, and no visual indication of wear of plunger
3. Relative standard deviation, S, of titrations with NaOH of 100-µl deliveries of concentrated nitric acid
4. Prior to these dynamic tests, the plunger in this pipet assembly had been immersed for 7 days in concentrated HNO_3 and had been extensively tested with various corrosive liquids
5. Plunger in this pipet assembly was machined by grinding

TABLE II. SUMMARY OF DYNAMIC PERFORMANCE OF PIPETTER WITH CORROSIVE LIQUIDS

PIPET ASSEMBLY, LINER NO.	NO. OF DYNAMIC PIPETTING CYCLES NOTE 1	WEAR TEST, END OF TEST PERIOD NOTE 2	OVER-ALL PRECISION OF DELIVERY NOTE 3	
			n	S, %
2	6,000	NEGATIVE	84	0.17
1B	6,140	NEGATIVE	98	0.19
1A	11,689	NEGATIVE	67	0.16

NOTES: 1. NUMBER OF CYCLES EXCLUSIVE OF PIPETTING STROKES TO MEASURE PRECISION OR TEST SEAL.

2. NEGATIVE TEST MEANS NO LEAK WITH 24 IN. Hg VACUUM APPLIED TO SIDEARM, OVER WORKING STROKE, AND NO VISUAL INDICATION OF PLUNGER WEAR.

3. RELATIVE STANDARD DEVIATION OF TITRATIONS WITH NaOH OF 100 μLITER DELIVERIES OF CONCENTRATED HNO_3.

STATIC TESTS OF CONTAINED DYNAMIC SEAL

As the components of the pipet are assembled, the compression caps are torqued to 10 foot-pounds. It was established experimentally that this is the proper torque value. The compression forms the contained dynamic seal both above and below the axial passage in the sidearm by controlled cold flow of Teflon. Dynamic and static tests were made to learn whether the seal, after formation, would be durable so that the compression caps would need retightening only after a reasonably large number of pipetting cycles result in appreciable wear of the seal surface. Most of the testing was done, as described, under dynamic conditions, where corrosive liquids were pipetted that were synthetics having essentially the same compositions as those of typical corrosive reactor and process samples that are expected to be remotely pipetted in the High Radiation Level Analytical Facility.

Several times during the dynamic tests of the performance of the pipetter with corrosive liquids and organic solvents the pipet was left empty over a weekend with the plunger at the fill position. In all cases, the pipet maintained its ability to seal, showing no leakage over the working stroke of the plunger with a full vacuum (24 inches of mercury) applied to the sidearm.

At the conclusion of the dynamic tests of three pipet assemblies, without retightening of the compression caps or other maintenance, the assemblies were stored empty with the plungers at a setting of 50. Periodically, the seal was vacuum tested over the working stroke. The test data are shown in Table III. No evidence was found of uncontrolled cold flow of the Teflon seal. It is concluded that the static performance of the contained dynamic seal is satisfactory.

CONCLUSIONS

From the data obtained in the evaluation testing of this pipet, it is concluded that the criteria that were established for the design of a corrosion-resistant pipet have been met. At the terminations of their respective dynamic and static tests, all three pipet assemblies are entirely satisfactory, without adjustment or other maintenance, for further service. On August 16, 1960, one of these pipet assemblies was installed for use in the High Radiation Level Analytical Facility. Additional pipets will be installed as needed.

ACKNOWLEDGEMENTS

During the design and fabrication of the new corrosion-resistant pipet, many contributions were made by Bryan Cook, foreman, Chemistry Staff Shop, Oak Ridge National Laboratory. Some information that was used for design purposes was obtained from W. R. Musick, Analytical Chemistry Division, Oak Ridge National Laboratory. During the initial work to evaluate the new pipet, some of the development work on this project was done by H. C. Jones, Analytical Instrumentation Group, Analytical Chemistry Division, Oak Ridge National Laboratory, including contributions to the improvements of the servo control unit circuitry.

TABLE III. STATIC TESTS OF CONTAINED DYNAMIC SEAL

PIPET ASSEMBLY, LINER NO.	TOTAL LENGTH OF TESTS, DAYS	RESULTS
2	20	NO LEAKAGE OVER WORKING STROKE AND NO EVIDENCE OF UNCONTROLLED FLOW OF TEFLON SEAL
1B	18	"
1A	62	"

NOTE: TESTS WERE ALSO MADE AT VARIOUS INTERVALS DURING EACH PERIOD.

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A CONTINUOUS STRIPPER FOR THE DETERMINATION OF DISSOLVED GASES AND FISSION-PRODUCT GASES IN HIGH-TEMPERATURE AND -PRESSURE WATER SYSTEMS

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ABSTRACT

A gas stripper device and procedure are described for making continuous, semicontinuous, and spot determinations of dissolved gases in high-temperature and -pressure water systems. Two of the gases, N_2 and H_2, are determined by gas chromatography, using a Vapor Fractometer. The concentrations of Xe^{133}, Xe^{138}, and Kr^{88} in the gases are determined by gamma-ray spectrometry. The techniques involved in these analyses are discussed.

Data are presented to show that 95% of the N_2 and H_2 plus 90% of the fission-product gases are removed by this continuous stripping process.

INTRODUCTION

Several closed circuit systems, called "loops", for circulating water at high temperature and pressure are in use in the NRX and NRU reactors at Chalk River. These loops are used to test potential reactor fuels under simulated pressurized-water, power reactor conditions.

In the past, the analysis of loop water for both dissolved gases such as H_2, O_2 and N_2 or for dissolved fission-product gases has involved taking a sample of loop water into an evacuated flask, pumping off the dissolved gas with a Toepler pump, measuring its volume, and then analyzing or counting an aliquot. Although satisfactory methods have been developed, they are all time consuming, the time being a minimum of one hour from sampling to final analysis or counting.

The gas stripper was developed to provide a continuous gas sample which could be analyzed or counted directly, thus eliminating the time normally required for sampling and removing the gases from water.

In this paper, studies are reported of the efficiency of the stripper and it is shown that gas concentrations measured in samples from the stripper, both for stable gases and fission-product gases, agree reasonably well with those determined by conventional methods.

It is hoped, in the future, that the apparatus can be adapted to continuous monitoring of stable gas and fission-gas concentrations in the loop water and eventually in the coolant of a power reactor such as NPD-2.

STRIPPER EQUIPMENT

Design

Basically, a gas stripper similar to that used in the NRU reactor(1) was desired, that is, a system whereby a stream of water is stripped of its dissolved gases by a counter-current stream of He. However, it was necessary to alter the NRU design so that higher efficiencies could be obtained and much lower flow rates of water and He could be used.

The factors which were considered for the design of a stripper, in this instance for the X-2 loop in NRX, were as follows:

(a) The water flow rate from the loop must not exceed the automatic make up rate to the loop; in this instance, 10 gal (UK)/hr.

(b) The water must not be removed from the loop at a rate which would affect the water conditions required for the test.

(c) The stripper should be large enough to provide the size of sample required for analysis.

(d) The flow rate of the loop water to the stripper should be such that the delay time from the test section in the reactor is long enough to permit decay of N^{16} ($t_{1/2}$ = 7.4 sec), and short enough to permit observation of the short-lived, fission-product gases with a half-life as short as 3 minutes.

(e) The flow rate of water and gas should be capable of accurate measurement and control. For instance, it was found difficult to control the water flow of 15 cm^3/min to the stripper within 20 per cent over long periods of time; however, the flow rate could be measured within ± 2 per cent with a small rotameter. The helium flow rate at 35 cm^3/min was easily controlled over long periods of time with a pressure regulator and needle valve, and could be measured within ± 3 per cent.

Description of the Stripper

The design of the stripper is shown in Figure 1. The body of the stripper consists of a glass tube 20 cm od, fitted to a stainless steel tube. The needle valve which controls the flow of water to the stripper is welded directly

A.E.C.L. Ref. # A-2625-K

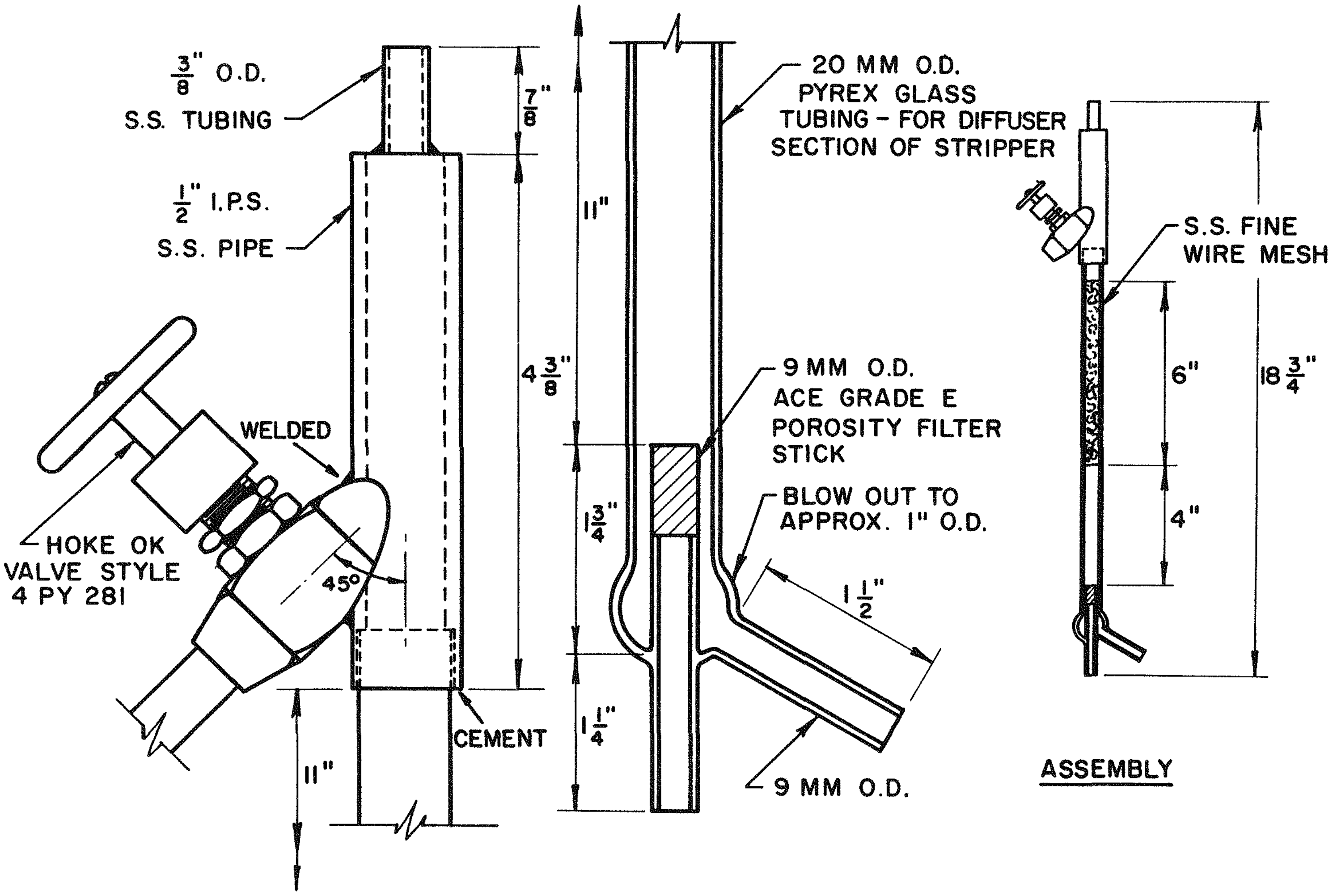

Fig. 1 - Gas Stripper

to the stainless steel tube. The top portion of the glass tube is packed with six inches of fine-grade, stainless steel (York Sheibel), wire-mesh packing.

The arrangement of the equipment is shown in Figure 2. The flow of water is controlled by the needle valve, and the loop water flows directly into the stripper. Any gases which exceed saturation concentrations at atmospheric pressure come out of solution as the water passes through the needle valve and also flow directly into the stripper. The water passes down through the packing and the dissolved gases are removed by a counter stream of He flowing from the diffuser. The He from the diffuser bubbles through 15 cm^3 of water which is maintained in the bottom of the stripper by a vented loop on the water outlet. The flow rate of the water is measured by a rotameter on the outlet of the stripper. The He flow is controlled by a pressure regulator and needle valve, the rate of flow being measured by a rotameter between the needle valve and the diffuser.

Sampling

Samples of the He stripping gas may be taken at the outlet of the stripper in two different ways. The gas may be passed directly through a sampling bulb until it is well flushed; then both ends of the bulb can be closed off and removed from the system. Alternately, the gases are passed through a long tube into which an evacuated bulb is connected as close as possible to the stripper. The sample bulb connector directs the gas flow up to the stop-cock on the evacuated bulb, completely flushing the connection (Figure 2). The evacuated bulb is opened for a few seconds to take the sample.

Installation

The stripper was installed in the sample station for the X-2 loop and was connected to a by-pass through which a fraction of the water from the loop is circulated. The water in the by-pass is cooled for monitoring, sampling and purification. The delay time from the test section in the loop to the stripper is dependent on the flow rate in the main loop circuit, the rate through the by-pass and the rate from the by-pass to the stripper. The delay time for this system, and for the flow rates used was 400 seconds. This delay time could be shortened to 130 seconds by reducing the length and diameter of the line from the by-pass to stripper, if required.

PROCEDURES AND RESULTS

Oxygen and Nitrogen Stripping

A series of experiments were conducted, using water saturated with air, to determine the flow rates required to give the most efficient stripping. The results, shown in Table 1, indicate that the best stripping efficiency was obtained with a He flow rate of 34 cm^3/min and a water flow rate of 16 cm^3/min.

Hydrogen and Nitrogen Stripping

The efficiency of the stripper for removing H_2 and N_2 from loop water was determined by measuring the concentrations of these gases in samples of

A.E.C.L. Ref. # A-2625-H

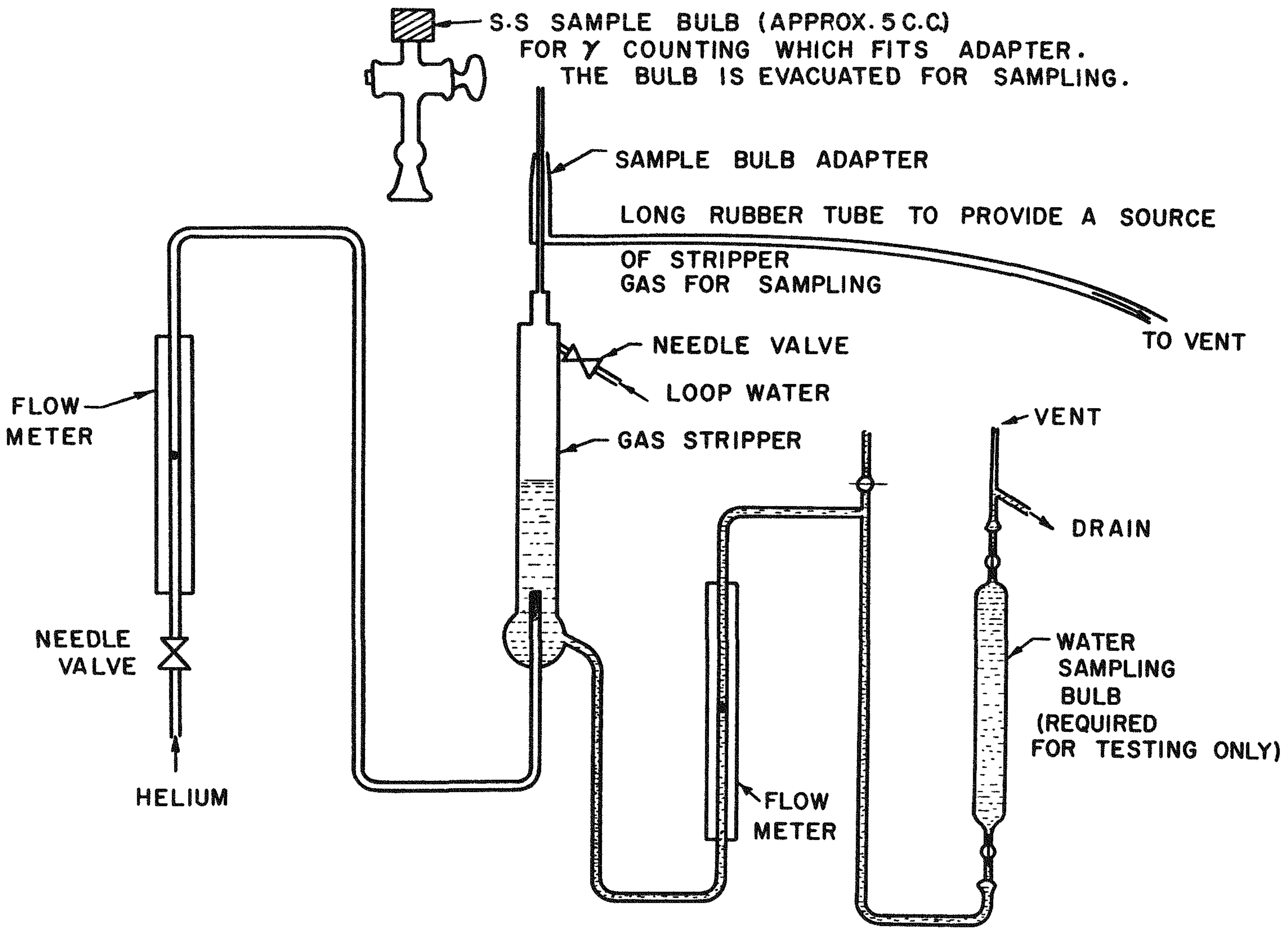

Fig. 2 - Schematic Flow Sheet of Gas Stripper

TABLE I

RESULTS OF TESTS TO DETERMINE THE FLOW RATES OF He AND WATER REQUIRED TO GIVE THE MOST EFFICIENT STRIPPING

Water flow	He flow	Water before stripping (saturated with air)		Water after stripping		Stripping Efficiency % removed	
cm^3/min	cm^3/min	O_2 cm^3/kg	N_2 cm^3/kg	O_2 cm^3/kg	N_2 cm^3/kg	O_2 %	N_2 %
25	10	6.0	11.7	0.6	1.08	90	90.8
25	60	6.0	11.7	0.39	0.82	93.5	93.0
16	34	6.0	11.7	0.17	0.37	97.2	96.8
16	30	6.0	11.7	0.18	0.37	97.0	96.8

the water before and after stripping. The concentrations were measured by removing the gases from water with a Toepler pump and then determining the H_2 and N_2 concentrations in an aliquot of the gases by conventional methods(2) and by gas chromatography. These measurements (Table II) indicate that up to 97.5 per cent of the N_2 and 99.8 per cent of the H_2 were removed from the water by the stripper.

The concentrations of H_2 and N_2 in the He stream were determined by gas chromatography, using a Perkin-Elmer Corporation Vapor Fractometer. The concentrations in the loop water were determined by multiplying the concentrations in the He stripping gas by the ratio of the He flow to the water flow to the stripper. In Table III, the results are compared with those obtained by sampling the loop water, pumping off the dissolved gas and analyzing an aliquot of the gas for H_2 and N_2.

The N_2 results from analysis of the He stream from the stripper are reproducible within 5 per cent and agree with values obtained in water samples. The H_2 results on the gas from the stripper are more erratic and the first values obtained were lower than those from water samples. It was suspected that the sample line to the stripper was not providing a representative sample or that the results from the gas chromatographic analysis were in error. The sample line was rerouted and the H_2 concentrations in the He were determined with a standardized Neir mass spectrometer. The H_2 results from the water samples and from the stripper gas were then observed to be in better agreement. The erratic H_2 results and the discrepancies are under investigation.

Stripping Efficiency for Fission-Product Gases

To measure the efficiency of the stripper for removing fission-product gases from water, the Xe^{133} concentrations were measured in samples taken before and after stripping. The Xe^{133} was pumped from these samples, using a Toepler pump.

The Xe^{133} was also measured in samples of the gas taken from the He stream of the stripper.

The gas samples were all counted in a standard-sized stainless steel bulb, using the same NaI crystal and pulse-height analyzer. The area under the 80-kev Xe^{133} peak was measured to determine the counting rate of the gas sample, so that all of the counting results were proportional to the actual Xe^{133} concentrations in the gas. The Xe^{133} concentrations were all converted to c/min/ml of water from the measured volumes of water samples and from the flow rates to the stripper. These results are shown on Table IV and indicate a stripping efficiency of approximately 90 per cent, assuming that the Toepler pump removes all of the Xe^{133} from the water samples.

Kr^{88} and Xe^{138} Determinations

The He from the stripper was sampled for Kr^{88} and Xe^{138} and subsequent γ-counting in an evacuated, standard-sized, stainless steel bulb(3)(5.74 cm^3).

TABLE II

THE EFFICIENCY OF THE STRIPPER FOR REMOVING HYDROGEN AND NITROGEN

(He flow rate 34 cm^3/min. H_2O flow rate 16 cm^3/min)

	Water before stripper cm^3/kg		Water after stripper cm^3/kg		Stripping efficiency %	
	H_2	N_2	H_2	N_2	H_2	N_2
	10.1	14.1	0.67	0.69	93.4	95.1
	12.4	13.7	0.4	1.1	96.8	92.0
	13.1	15.0	0.7	1.2	94.6	92.0
	13.5	14.7	0.75	0.4	94.4	97.3
	34.6	7.2	0.6	0.3	98.3	95.8
	34.6	7.2	0.7	0.0	98.0	100.0
*	45.0	18.05	0.19	.46	99.8	97.5
*	39.5	19.6	0.29	.52	99.3	97.3

* The H_2 and N_2 analysis by gas chromatography on samples of the gas pumped from the water.

TABLE III

COMPARISON OF TEST RESULTS FOR HYDROGEN AND NITROGEN

From analysis of water samples cm^3/kg		From analysis of He stream from stripper cm^3/kg	
H_2	N_2	H_2	N_2
11.7	8.05	4.7	10.3
9.7	10.7	2.8	10.25
10.3	10.3	5.5	8.9
45.0	18.05	33.4	19.4
		25.0	18.4
		33.2	19.2
39.5	19.6	26.2	18.2
		33.2	19.0
		30.2	18.3
41± 3	34± 4	*38± 3	35± 3
37± 1	26± 1	38± 1	30± 1

* Sampling line to stripper rerouted.

TABLE IV

EFFICIENCY OF STRIPPER IN REMOVAL OF XENON

Xe, cpm/ml water A In water before stripping	 B In water, calculated from count in stripping gas	 C In water, after stripping	Stripping Efficiency, % $\frac{B}{B + C} \times 100$
191	165	21	88.7
226	252	32	88.7
241	280	33	89.5
224	264	30	89.3

The sample was allowed to decay for 35 minutes to permit the Cs and Rb daughters to grow in. The sample bulb was then evacuated to remove the fission-product gases, and any Ar^{41}, which was found to interfere with the γ-counting. The Rb^{88} and Cs^{138} daughters remain on the walls of the stainless steel bulb for counting.

The bulb was counted on a 3 in. by 3 in. NaI (Tl) scintillation crystal coupled to the Chalk River transistorized, 100-channel, pulse-height analyzer.(4) The Kr^{88} and Xe^{138} activity was calculated from a measure of the Rb^{88} and Cs^{138} activity determined by summing the area under the 1.84-Mev Rb^{88} peak and the 1.43-Mev Cs^{138} peak. Although Rb-89 could cause some interference in this part of the spectrum, its effect is considered negligible due to the short half-life (3 min) of its parent Kr^{89} and the delay time in the system before sampling. A typical γ spectrum is shown in Figure 3.

To determine the actual disintegration rates of Kr^{88} and Xe^{138} by β-counting,(5) separate samples of the helium stream were taken in glass bulbs.

The samples for Xe^{138} were permitted to decay for 35 minutes from sampling time to allow the Cs^{138} daughter to grow to its maximum. Then the bulb was flushed with air and the Cs^{138} was washed out with hot 4 N HNO_3 containing a Cs carrier. The Cs^{138} was then precipitated as the chloroplatinate and counted on a β-counter of known geometry. The decay was followed to establish the half-life. The Xe^{138} disintegration rate at sampling time was then determined from the decay and growth curve for

$$Xe^{138} \xrightarrow[t_{1/2},\ 17\ \text{min}]{\beta} Cs^{138}$$

The Kr^{88} disintegration rates at sampling time were determined in the same manner with the exception that the sample bulb was flushed after 4 hours, to permit the Rb^{88} daughter to reach equilibrium with its parent Kr^{88} and to allow the Xe^{138} and Cs^{138} to decay to negligible amounts.

A summary of the results used to determine the factor to convert the γ-counting rates of Kr^{88} and Xe^{138} to disintegration rates are shown in Table V. The factor for Xe^{138} was determined within ± 4 per cent of the average and within ± 10 per cent for Kr^{88}.

The determinations of Xe^{138} and Kr^{88} by γ-counting on samples from the stripper on any one day were usually within 5 per cent; on one occasion only, was there a spread of 10 per cent.

Over the same period of time that the Kr^{88} and Xe^{138} concentrations in loop water were being determined by γ-counting of the gas samples from the stripper, samples of the water were being analyzed by other methods. The levels of activity, $(8 \pm 2) \times 10^4$ d/min/ml for Kr^{88} and $(1.2 \pm 0.2) \times 10^5$ d/min/ml for Xe^{133}, determined by both methods agreed, when the differences in decay time between samples and the differences in efficiencies of gas removals from water were accounted for.

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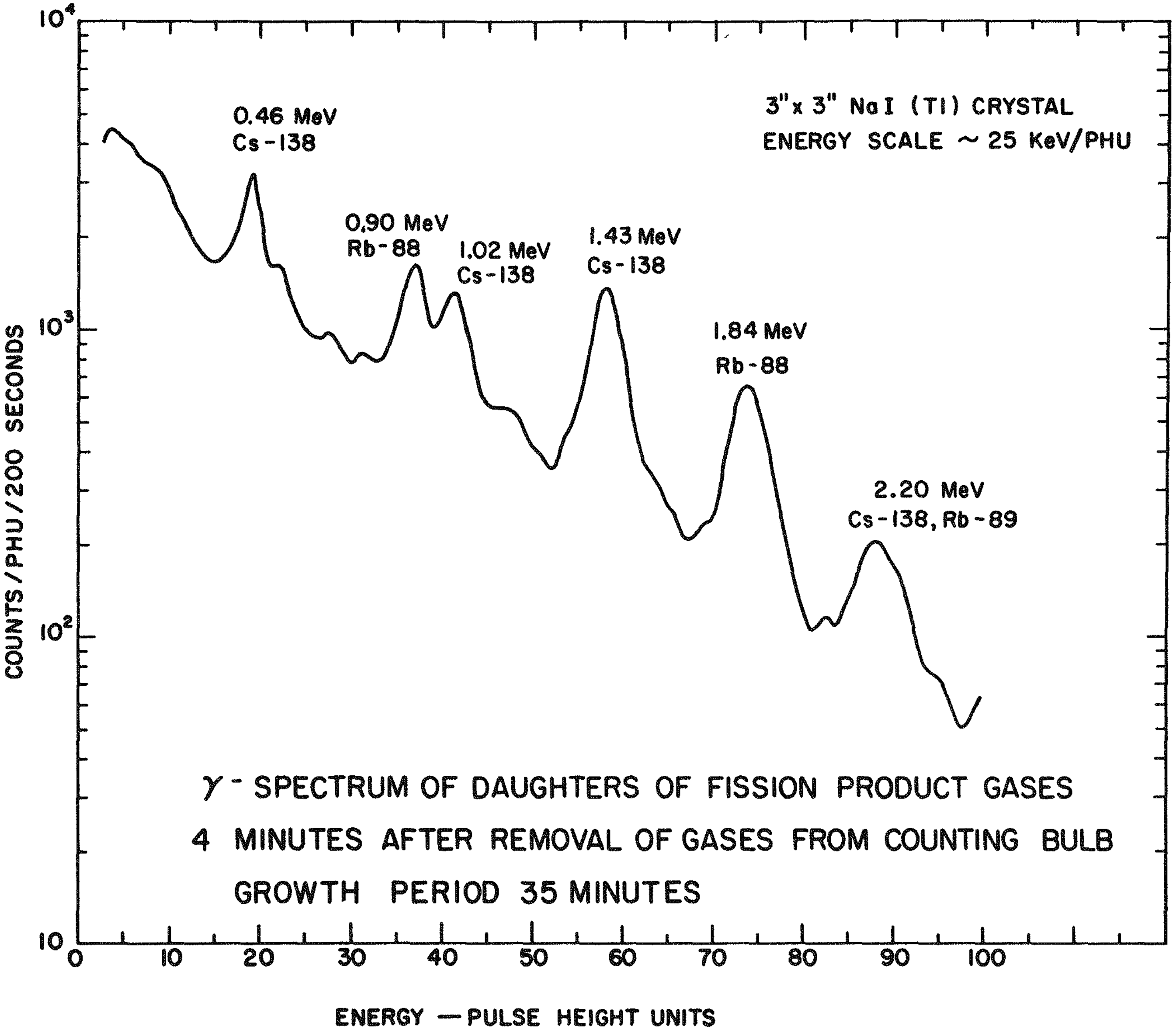

Fig. 3 - Gamma Spectrum of Daughters of Fission-Product Gases

TABLE V

SUMMARY OF STANDARDIZATION RESULTS

	Xe-138					Kr-88				
Date	γ count cpm/ml water	average	From β count dpm/ml water	average	Conversion factor dpm/cpm	γ count cpm/ml water	average	From β count dpm/ml water	average	factor dpm/cpm
Aug. 18/60	1.04×10^3 1.16×10^3 1.13×10^3 1.13×10^3	1.12×10^3	8.17×10^4 7.83×10^4	8.0×10^4	71.4	232 246 238 244	240	6.85×10^4 6.75×10^4	6.80×10^4	284
Sept. 9/60	1.62×10^3 1.71×10^3	1.67×10^3	1.28×10^5 1.19×10^5	1.24×10^5	74.3	290 325	308	9.22×10^4 9.68×10^4	9.45×10^4	307
Sept. 12/60	1.23×10^3 1.19×10^3 1.08×10^3 1.29×10^3	1.20×10^3	8.67×10^4 7.87×10^4	8.27×10^4	68.8	252 234 217 240	236	6.38×10^4 6.42×10^4	6.40×10^4	271
Sept. 15/60	1.23×10^3 1.17×10^3 1.32×10^3 1.21×10^3	1.23×10^3	6.55×10^4 1.09×10^5	8.70×10^4	70.5	213 246 239 222	230	6.00×10^4 5.88×10^4	5.94×10^4	258
Sept. 16/60	1.00×10^3 1.00×10^3 $.995 \times 10^3$	1.00×10^3	6.95×10^4 7.45×10^4	7.20×10^4	72.0	209 202 202	204	5.11×10^4 5.11×10^4	5.11×10^4	251

SUMMARY

This gas stripper provides a method for efficiently separating the dissolved gases from water. The gas samples from the stripper can be counted directly in the sample bulb to determine fission-product gases by γ-ray spectrometry, and the stable gases can be measured, using chromatographic techniques.

The results are reproducible within 10 per cent. This reproducibility is adequate for control and monitoring purposes, and the results compare well with those obtained by other methods.

Further development of the stripper is under way to improve the accuracy and precision of the results.

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We wish to acknowledge the co-operation and help of A. R. Colp (Chemical Operations) and I. H. Crocker.

RECENT IMPROVEMENTS IN THE X-RAY ABSORPTION-EDGE METHOD OF ANALYSIS

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ABSTRACT

Several improvements have been made in the x-ray absorption-edge method of analysis in the past year. It was known that, with the exception of direct absorption-edge interference, there was little interference from other elements. It has been shown that in determining elements near Zr in the periodic table, matrix elements from Ni to Sn in the periodic table give no interference within the limits of error of the method. Large amounts of elements with low atomic numbers will cause the answers to be slightly high. This effect can be compensated for by inserting an Ag foil in the beam. Large amounts of elements with high atomic numbers will cause the answers to be slightly low. With the U concentration about 90 times that of Zr, the results for Zr were observed to be in error by 2%. When very accurate work is required, it will be necessary to correct for the presence of these heavy elements.

The method of calculation has been improved. By treating the data in a different manner, some of the corrections that were used previously were eliminated. The method of obtaining the blank ratio-curves was also improved. A new curve can now be made in less than a half day, whereas previously two days or more was required. In the past, slow instrumental drifts were encountered which occasionally required the preparation of a new blank ratio-curve.

Several improvements have been made in the instrument. It was found that changes in the temperature of the water used to cool the head of the x-ray tube caused an error in the analysis. The tap-water cooling system was replaced with a recirculating radiator cooling system. Other instrumental improvements were made; these will be discussed.

MATHEMATICAL RESOLUTION OF COMPLEX OVERLAPPING SPECTRA AND SPECTRAL FINE STRUCTURE BY MEANS OF HIGH-SPEED DIGITAL COMPUTING(a)

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SUMMARY(b)

The Oak Ridge National Laboratory is currently engaged in a program whose aim is the spectrophotometric study of solution chemistry at temperatures up to at least 330°C and at pressures up to 200 atmospheres. It is anticipated that the necessary measurements can be made up to near the critical point (~370°C) in both water and deuterium oxide systems. One of the advantages of the spectrophotometric technique at high temperatures and pressures is that it provides a means of determining not only equilibrium conditions but also chemical kinetics without the complexity and uncertainties that are associated with a method that requires withdrawing a large number of samples. In view of the spectral character and considerable fine structure exhibited by members of the actinide, lanthanide, and transition metal groups, it again appears to be one of the best techniques for the simultaneous determination of many constituents. We have made extensive studies on the uranyl ion system, from near 0° to 100°C.

The complicated spectrum that is observed for the uranyl ion between 3500 and 5000 Å arises from a vibrationally perturbed electronic absorption and exhibits some twelve transitions in this frequency interval. Each band overlaps two or three other bands on both the high and low frequency side of the band center, and results in the rather ill-defined summed spectrum that is observed. This overlapping, coupled with the fact that the individual transitions react in different ways to change in temperature or solution parameters,

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(a) This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

(b) Editor's Note. A condensed version or summary of this paper is presented herein; the complete paper is to be published elsewhere.

complicates the spectra even further. With this overlapping it is impossible to measure with any reasonable certainty the parameters (position or frequency, intensity, and width) of a single absorption band. Even under conditions where hydrolysis effects were minimal, changes are observed in all three parameters of each band. The spectra obtained for the uranyl ion in sulfate systems represent the summed absorption (for each transition) of the possible species: uncomplexed UO_2^{++}, UO_2SO_4, $UO_2(SO_4)_2^{-2}$, $UO_2(SO_4)_3^{-4}$, and any hydrolyzed species present.

It has become clear that the success of analyzing large multicomponent systems, especially those containing uranium, and of measuring the metal-ion concentrations (and individual valence states) under variable conditions such as changing temperature, etc., would require a more detailed knowledge than is now available of the parameters of the electronic transitions and vibrational bands that compose the spectrum. From an analysis of all the necessary equations that relate to the light absorption parameters of all species considered to be present, it has become evident that one should be able to calculate from accurate spectral data alone, the concentrations of the species, and their dissociation constants.

It has been found that analysis and interpretation of the system are possible if high-speed digital computing techniques are used. An iterative, generalized, least-squares fitting routine that was written for x-ray and neutron-diffraction data analysis on the ORACLE (the high-speed digital computer at ORNL) was modified for the purpose of resolving the complex spectra into their components; a similar, though not as versatile, program is available for the IBM-704 (and -7090) computers. A Gaussian-type function was found to be the single function that best represents the shape of a single spectral band. A resonance-type function was evaluated and found not to be as satisfactory. A more nearly theoretically correct model would probably be a function combining a Gaussian function with a small contribution from a resonance function. A more fundamental program of study of the most appropriate functions for representing the shapes of various single spectral bands, of the factors that contribute to the broadening of the "line" into a band in the condensed systems that liquids represent, and of spectral band structure, is underway. The ORACLE program can be used to analyze up to 21 overlapping absorption bands.

The least-squares fitting errors for the parameters of the resolved bands are as follows: intensity parameter, approximates the experimental error of about ±0.002-0.003 absorbancy units; half-band width parameter, about ±2 to 20 cm^{-1} (400 to 800 cm^{-1} range), depending upon peak sharpness and overlap; position, about ±1 to 60 cm^{-1} (30,000-20,000 cm^{-1} range), depending upon peak position and sharpness. This computing technique has been successfully applied to plutonium and transition-group elements and to mixtures of various elements that exhibit complex spectra. The resolved bands permit one to study various parameters of individual transitions without interference from overlapping near-by bands. Results for the $UO_2(ClO_4)_2$ system are shown in Figure 1.

The significant features of the computer programs, automatic curve plotting programs, and the mode of operation of the program will be briefly discussed. Results for the resolution of the uranyl sulfate, perchlorate,

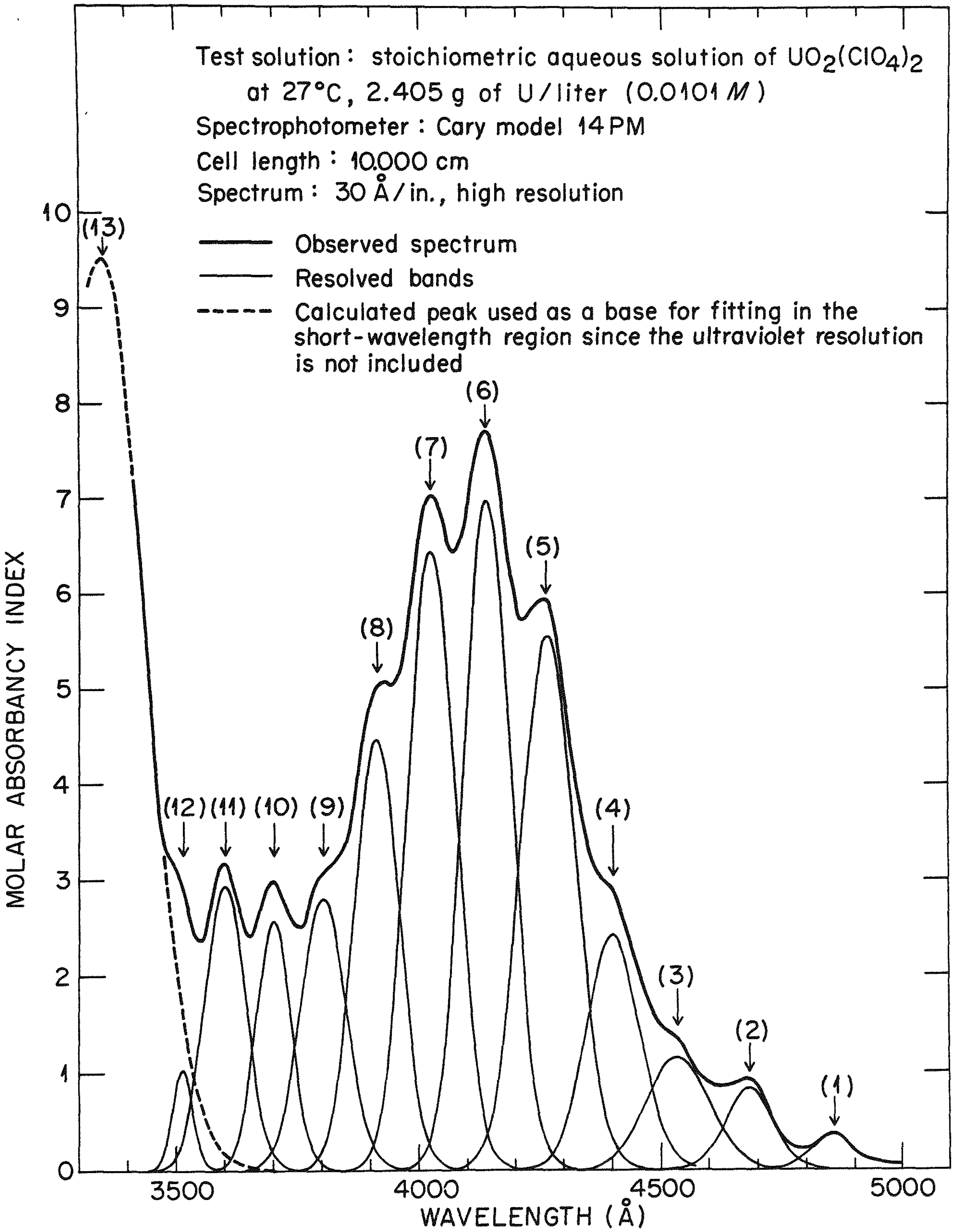

Figure 1. Observed Spectrum of $UO_2(ClO_4)_2$ and the Individual Bands Resolved by Use of the ORACLE

and other spectra systems will be shown, along with the resolved spectra plotted by the computer. This generalized technique has also been applied to other types of summed curve systems, e.g., gas chromatograms, and is potentially useful for many others. This will also be discussed, along with other aims of the overall program. At the present time an automatic digital data read-out system is being designed for IBM punched card output with data points obtainable at wavelength intervals as close as 1 angstrom.

UTILIZATION OF COMPUTERS IN RADIOCHEMICAL ANALYSIS

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ABSTRACT

This paper describes a computer program designed to reduce the gamma spectral data obtained with a 200-channel pulse height analyzer in the assay of radionuclide mixtures. With this program, the radioactivity associated with each photopeak observed in the spectrum of a multicomponent mixture can be calculated. The analysis of the spectral data by means of statistical techniques is described. While this program was specifically designed for use in radioactivation analysis, it can also be used in analyzing radionuclide mixtures. Typical examples of its application are cited.

EDITOR'S NOTE

This paper is omitted from the *Proceedings* because it is to be submitted to *Analytical Chemistry* for publication.

Facilities for the Analysis of Reactor Materials

FACILITIES FOR CHEMICAL ANALYSIS AT THE AUSTRALIAN ATOMIC ENERGY COMMISSION RESEARCH ESTABLISHMENT

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ABSTRACT

Organization and facilities for chemical analysis suitable for smaller atomic energy research establishments are dealt with in some detail. This information may be of value to countries in the process of establishing similar research organizations. It was formerly the rule rather than the exception for the research worker to undertake his own chemical analyses, or at least to have within his immediate team several members provided with basic equipment for such work. However, the present need for highly refined and complex chemical analysis has placed the means for obtaining much analytical data beyond the reach of the individual or small team in a research organization. In order to conserve staff, avoid unnecessary duplication of equipment, ensure effective organization and record keeping, promote close liaison and interchange of ideas within the various branches of analytical chemistry, and ensure adequate knowledge of analytical chemistry literature and research work, it was decided in the early stages of planning to organize one central analytical chemistry service and research group for the whole research establishment. The group is organized around major items of instrumentation, closely integrated with conventional methods of gravimetric and volumetric analysis, which often precede an instrumental method. The more important facilities available in the group include: spectrometry (emission, infrared, mass, and x-ray); electrochemistry (polarography, coulometry, titrimetry); ultraviolet and visible spectrophotometry; chromatography (including gas chromatography); a wide range of counting equipment (including vacuum-fusion analysis of gases in metals); and instrumentation associated with techniques of solvent extraction, ion exchange, and the analysis of highly active solutions.

Details are given of simple records and literature reference systems maintained by the group. Staff requirements, service and research work loadings, and some of the current analytical chemistry work in relation to the current program of the research establishment are also presented in some detail.

INTRODUCTION

The organization and operation of an analytical chemistry service for the Australian Atomic Energy Commission Research Establishment at Lucas Heights, Sydney, Australia, is described in this paper. The present strength of this research establishment is approximately 700, of whom 160 are graduates of recognized universities and colleges.

The organization and operation of an analytical chemistry service is dealt with in some detail, since the information may be of value to countries in the process of establishing similar research organizations.

NEED FOR INSTRUMENTATION

It has become increasingly evident during the past 10 years that the demand by many research workers for a wide range of chemical analyses (often involving complex instrumentation and other facilities) necessitates careful consideration of the most efficient means of obtaining such analyses without undue duplication of equipment or laboratories. It was formerly more commonplace for the research worker to undertake his own chemical analyses, or at least to have within his own immediate team several members provided with basic equipment for such work. However, the present need for highly refined and complex analysis has placed the means for obtaining much analytical data beyond the reach of the individual or small team. While it is often convenient to carry out a range of routine chemical analyses within the research team or project, one has to ensure that the best methods have been selected rather than expedients based on simple equipment immediately available.

The question of how to organize facilities for chemical analysis in the smaller atomic energy research establishments is an important one, since the cost of necessary instrumentation may range from 50,000 to over 100,000 pounds (Australian) equivalent to 100,000 - 200,000 dollars. For a narrow and rather restricted program the cost will be closer to the lower figure. If the program involves reactor development the higher figure will most certainly be exceeded. This necessity for comprehensive instrumentation for chemical analysis is not restricted to atomic energy research. Lewin(1) in an article entitled: "Modern Instrumentation May Spell the End of Small Company Research" - states that . . . . "a minimum of about $91,000 in electronic and optical instrumentation alone is necessary to do chemical research effectively. A well-equipped laboratory contains more like $180,000 worth of such instruments."

ORGANIZATION

An early idea put into practice at the A.A.E.C. Research Establishment, was that staff carrying out chemical analyses with the aid of comprehensive instrumentation (closely integrated with the more familiar "bench methods), may be used very effectively as a group around the instrumentation. The structure of such a group can be varied to suit the overall research programs or to include the routine chemical control of pilot or large-scale plants or research reactors. Such a group can be fully effective only when sufficient staff are available to provide:-

(1) individual technical staffs responsible for each major instrument or group of instruments;

(2) a basic staff to cover normal analytical laboratory operations;

(3) staff for research and development;

(4) staff for attachment or secondment to project teams, processes, etc., and

(5) a small staff responsible for records.

In such a scheme it is essential that a staff be "attached" to each instrument or group of instruments. In this way the chemist becomes thoroughly familiar with the particular instrument and is able to obtain more reliable and rapid results and carry out research more effectively than a colleague using the equipment intermittently or even for the first time.

It is well known that the familiar volumetric, gravimetric, ion-exchange and other procedures often precede an instrumental method. The chemists associated with such procedures need not feel isolated from instrumentation, for it is often quite feasible for them to work with the instrument operator, particularly in the final stages. In this way all analytical chemists in a group can obtain an appreciation of instrumental methods without endeavoring to acquire the experience and skill of the specialist. It is clear that while the specialist in a particular instrumental field may be termed the "operator" for convenience, in practice, operation is merely one aspect of the broad field which includes much research.

DIFFICULTIES

Many research workers are familiar with the delays which follow the provision of a basic service. The problems of a chemical analysis service, which endeavors to return the results of analyses within the shortest possible time, are not greatly different from those of a group providing any form of service. From the viewpoint of the individual research worker, the prime consideration is how soon a reliable result can be returned. While time can be saved with an efficient organization and records system (which may include data processing equipment), the time saved is often small compared with the time necessary for research and development of a new method or the adaptation of an existing method. It must be admitted that no service provides the perfect answer to all the problems. It is useful, however, to ask certain questions regarding the service.

(1) Are all requests for chemical analyses really necessary or pertinent to the investigation? While the individual research worker can often defend the number and complexity of chemical analyses requested, there is no doubt that careful planning of the experiment with full cooperation of the analyst in the early stages, can result in considerable savings. In many cases obtaining the analytical chemistry data constitutes the major effort in the research.

(2) How soon can the individual research worker have the results of the chemical analyses? While the project or experiment is of prime concern to the individual research worker and the results of chemical analyses may be required

before proceeding to the next experiment, the overall effort of the service in relation to the research institute or organization requires some consideration. The overall service should be considered from the viewpoint of what is expected of it from the various research projects. It is possible that a service which may return say 80% of all results of chemical analyses within one week of receipt of the samples is satisfactory. With some research projects this may not be satisfactory - the majority of results may be required in one day. The remedy may lie in the direction of additional staff or instrumentation, a redistribution of effort, or by the assistance of the research group requiring the analyses. The responsibility of the planners of research projects is clearly not to assume that the chemical analyses will be a matter of routine.

While duplication of facilities may be undesirable for the smaller research establishment, it is possible that some decentralization of analytical chemistry is necessary when the strength of an establishment approaches 2,000. This could be achieved by having a central analytical chemistry research and development group with specialized service groups serving individual sections or projects. The inevitable duplication of staff and equipment following on decentralization would be less serious than in the case of a smaller research establishment. However, no hard and fast arrangement should be aimed at. At the present time we have found that some decentralization of routine chemical analysis is advantageous. An example is the routine chemical control of effluent operations which is carried out by the Operations Division using methods developed and tested by the central analytical chemistry group.

A.A.E.C. FACILITIES

The organization of analytical chemistry at the A.A.E.C. Research Establishment is shown in Figure 1. At the present time the Research Establishment is organized into a number of sections. Each section consists of groups and sub-groups which are the main research units. With expansion of the Research Establishment it is probable that the larger sections will become divisions. The Analytical Chemistry Group is at present responsible for nearly all analytical chemistry research and service work of 10 sections at the Research Establishment. Currently 800 samples a month (involving approximately 1,500 chemical analyses) are examined by a staff of 29. The number of samples examined is increasing at the rate of approximately 80% per annum as the Research Establishment's programs gather momentum. Research and development of new methods of chemical analysis and other collaboration in research projects, occupies approximately 30% of the total time.

A simple yet adequate records and literature reference system is maintained by the group. The records system is based on two kinds of 6 in. by 4 in. cards. Figure 3 shows the front and reverse sides of a pink-colored, request-for-chemical-analysis card. The reverse side of this card has space for details of the results of chemical analysis - the original card being returned to the originator of the request. Figure 4 shows the front and reverse sides of the white analysis-record card. These cards are maintained in storage cabinets - each card bearing a consecutive number. When a request for a chemical-analysis card is received in the group leader's office it is allocated a record-card number. For example: 60/2500 refers to request number 2500 in 1960. The details on the front of the request card are transferred to the white record card. The pink request card is then forwarded to one of the sub-groups. A sample involving separate chemical analyses

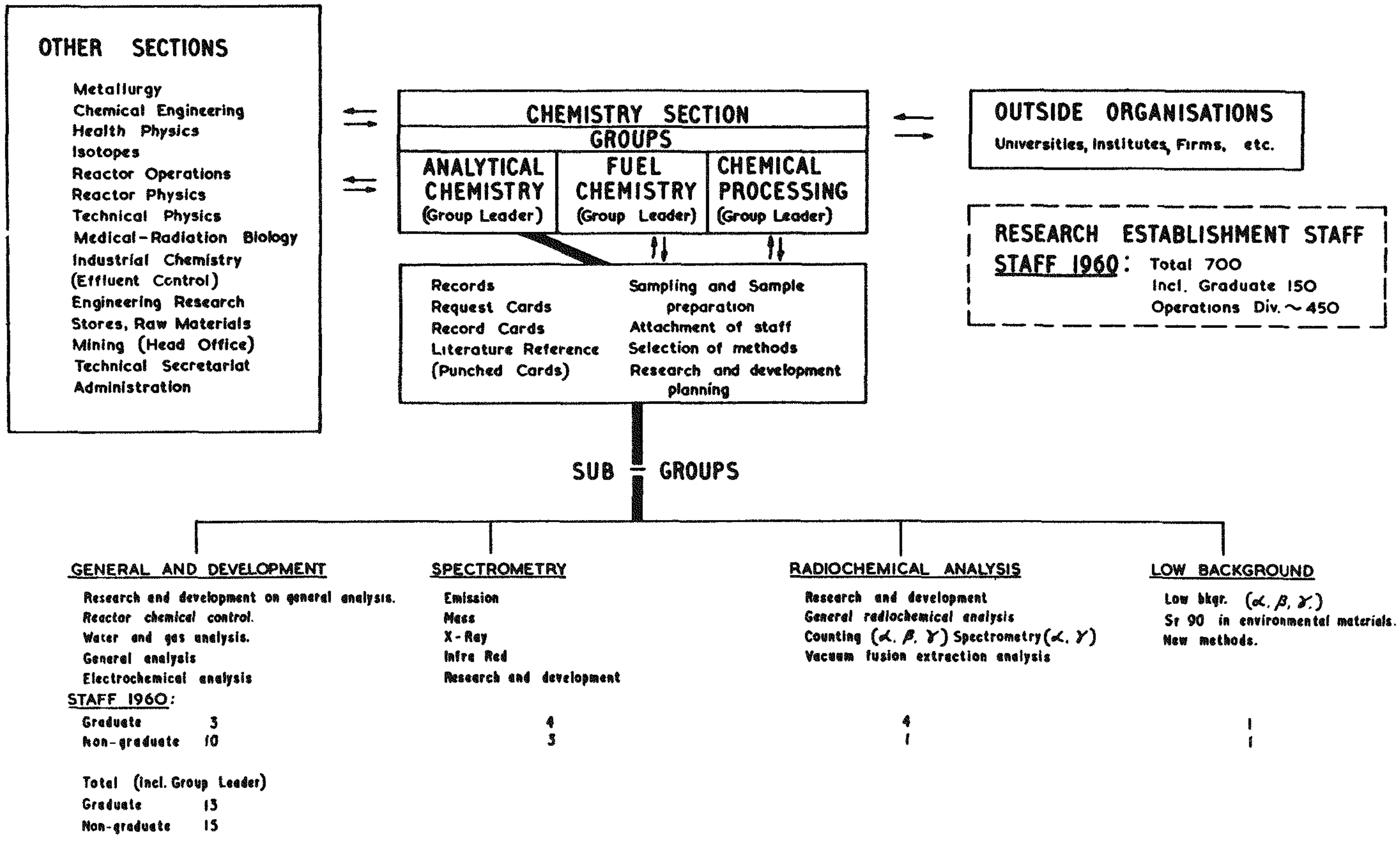
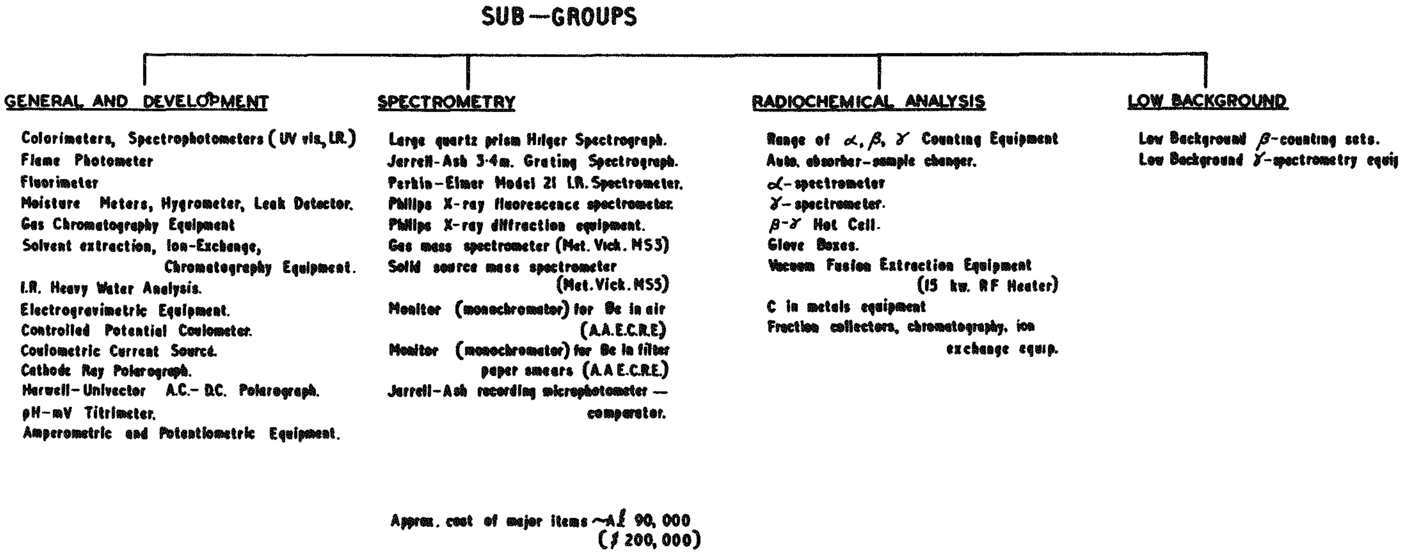


Figure 1. Analytical chemistry at AAEC research establishment.



SUB—GROUPS

GENERAL AND DEVELOPMENT

- Colorimeters, Spectrophotometers (UV vis, I.R.)
- Flame Photometer
- Fluorimeter
- Moisture Meters, Hygrometer, Leak Detector.
- Gas Chromatography Equipment
- Solvent extraction, Ion-Exchange, Chromatography Equipment.
- I.R. Heavy Water Analysis.
- Electrogravimetric Equipment.
- Controlled Potential Coulometer.
- Coulometric Current Source.
- Cathode Ray Polarograph.
- Harwell-Univector A.C.- D.C. Polarograph.
- pH-mV Titrimeter.
- Amperometric and Potentiometric Equipment.

SPECTROMETRY

- Large quartz prism Hilger Spectrograph.
- Jarrell-Ash 3·4m. Grating Spectrograph.
- Perkin-Elmer Model 21 I.R. Spectrometer.
- Philips X-ray fluorescence spectrometer.
- Philips X-ray diffraction equipment.
- Gas mass spectrometer (Met. Vick. MS3)
- Solid source mass spectrometer (Met. Vick. MS5)
- Monitor (monochromator) for Be in air (A.A.E.C.R.E)
- Monitor (monochromator) for Be in filter paper smears (A.A.E.C.R.E.)
- Jarrell-Ash recording microphotometer — comparator.

RADIOCHEMICAL ANALYSIS

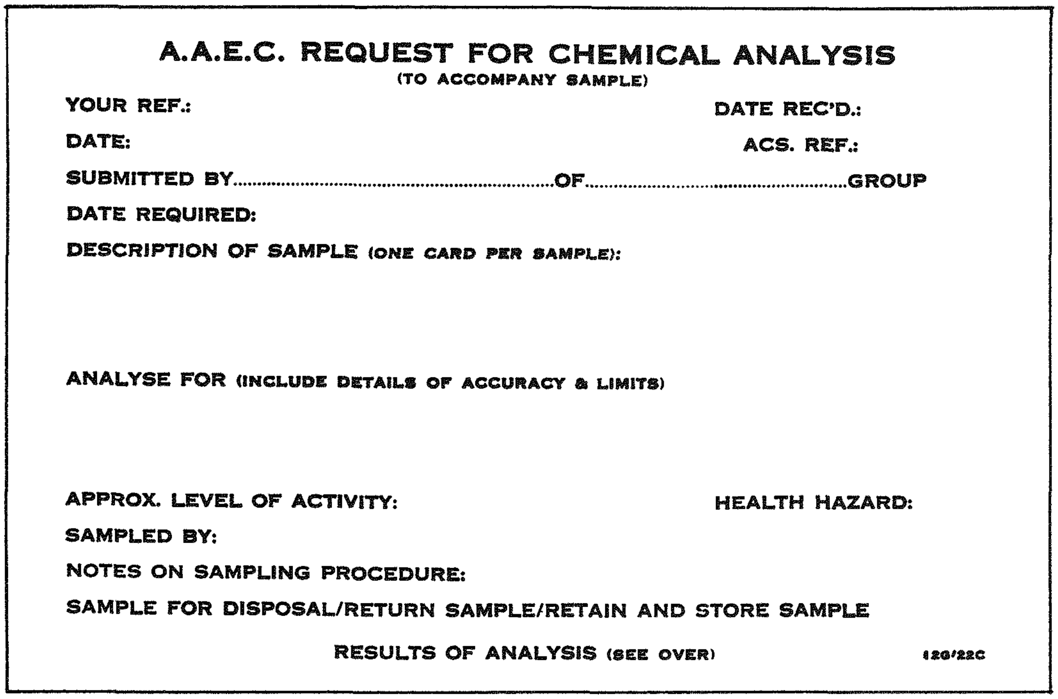
- Range of α, β, γ Counting Equipment
- Auto. absorber-sample changer.
- α- spectrometer
- γ- spectrometer.
- β-γ Hot Cell.
- Glove Boxes.
- Vacuum Fusion Extraction Equipment (15 kw. RF Heater)
- C in metals equipment
- Fraction collectors, chromatography, ion exchange equip.

LOW BACKGROUND

- Low Background β-counting sets.
- Low Background γ-spectrometry equi

Approx. cost of major items ~A£ 90, 000 ($ 200, 000)

Figure 2. Major items of analytical chemistry equipment at AAECRE.



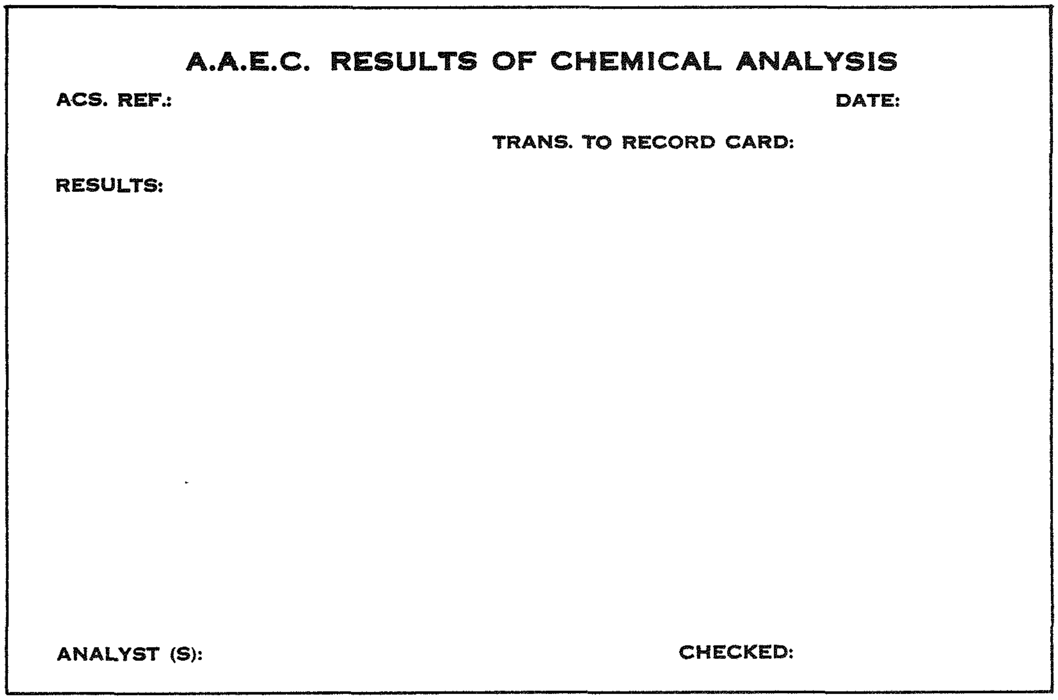
A.A.E.C. REQUEST FOR CHEMICAL ANALYSIS
(TO ACCOMPANY SAMPLE)

YOUR REF.: DATE REC'D.:
DATE: ACS. REF.:
SUBMITTED BY.......................................OF.......................................GROUP
DATE REQUIRED:
DESCRIPTION OF SAMPLE (ONE CARD PER SAMPLE):

ANALYSE FOR (INCLUDE DETAILS OF ACCURACY & LIMITS)

APPROX. LEVEL OF ACTIVITY: HEALTH HAZARD:
SAMPLED BY:
NOTES ON SAMPLING PROCEDURE:
SAMPLE FOR DISPOSAL/RETURN SAMPLE/RETAIN AND STORE SAMPLE
RESULTS OF ANALYSIS (SEE OVER) 126/22C

(A)



A.A.E.C. RESULTS OF CHEMICAL ANALYSIS

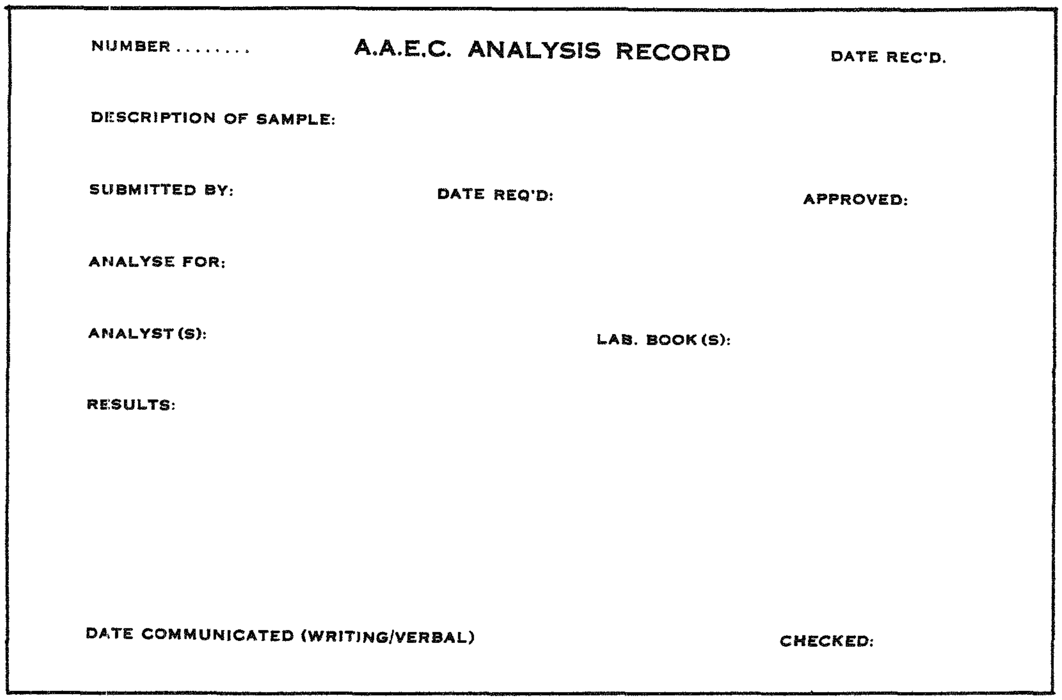
ACS. REF.: DATE:
TRANS. TO RECORD CARD:
RESULTS:

ANALYST (S): CHECKED:

(B)

Figure 3. "A.A.E.C. request for chemical analysis" card (pink).

(A) front
(B) reverse side



NUMBER........ **A.A.E.C. ANALYSIS RECORD** DATE REC'D.

DESCRIPTION OF SAMPLE:

SUBMITTED BY: DATE REQ'D: APPROVED:

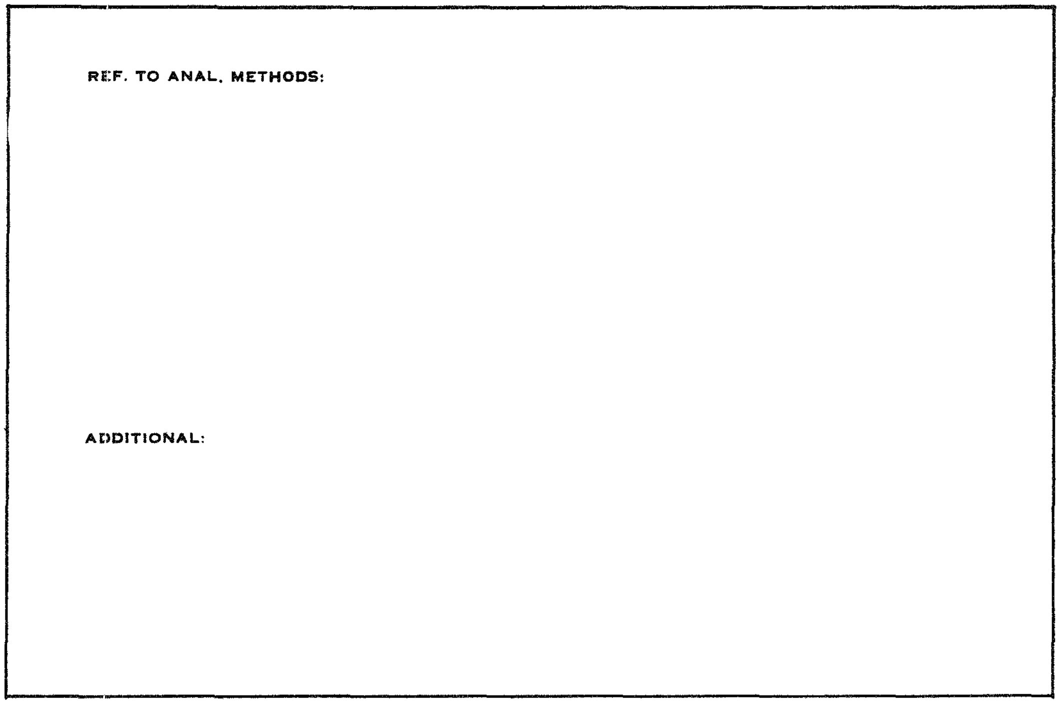
ANALYSE FOR:

ANALYST (S): LAB. BOOK (S):

RESULTS:

DATE COMMUNICATED (WRITING/VERBAL) CHECKED:

(A)



REF. TO ANAL. METHODS:

ADDITIONAL:

(B)

Figure 4. "A.A.E.C. analysis record" card (white).

(A) front
(B) reverse side

by more than one sub-group is transferred with the card to each sub-group in turn. Results are transferred to the white record cards and any necessary checks are made or problems are discussed prior to returning the completed card to the originator. Under this system samples do not always accompany the card. Active samples may be retained by the originator until collected, or forwarded to a depot in the various active areas. Other chemical analyses may be undertaken at the site of the experiment. In such cases the work is recorded in laboratory notebooks and a block of numbers from the white record cards are used for these samples. On completion of all necessary chemical analyses, the request cards bearing the results are forwarded to the Group Leader's office. With this simple system the research worker can maintain individual files of completed chemical analyses. Lost request cards can also be duplicated from the record cards at any time.

The literature reference system is based on punched keysort cards (Figure 5). A panel of 10 abstractors from the group's graduate staff covers a selection of 100 journals considered important in the broad field of analytical chemistry. Each abstractor is responsible for abstracting all the important analytical chemistry papers from approximately 10 journals, irrespective of his own interests. Every month the cards are collected and coded by a selected member of the non-graduate staff trained for this purpose. The same staff member also undertakes reference card searches on behalf of graduate staff. It may be thought that the literature reference system duplicates existing library services and abstracting journals. However, we have found the punched card system to be more selective than systems with broader interest such as the typical library catalog. In addition, the abstracting panel are able to maintain close contact with the original papers and reports. A further advantage is the rapid reference which is possible to abstracts of official reports in the field of atomic energy.

Figure 2 shows the major items of analytical chemistry equipment or instrumentation currently in use by the Analytical Chemistry Group of the A.A.E.C. Research Establishment. The equipment is predominantly of British or U.S. manufacture and considerable care was taken with its selection. The group is housed in 14 laboratories occupying some 7000 square feet of actual laboratory space, exclusive of office accommodation. The Chemistry-Chemical Engineering Building (Figure 6) has an area of approximately 47,000 square feet and cost 1,000,000 Australian pounds ($2,000,000). This building has been described.(2)

The present work of the group can be considered in the light of the main program of the Research Establishment which concerns high-temperature, gas-cooled reactor system development. The initial research program is shown in Table I.

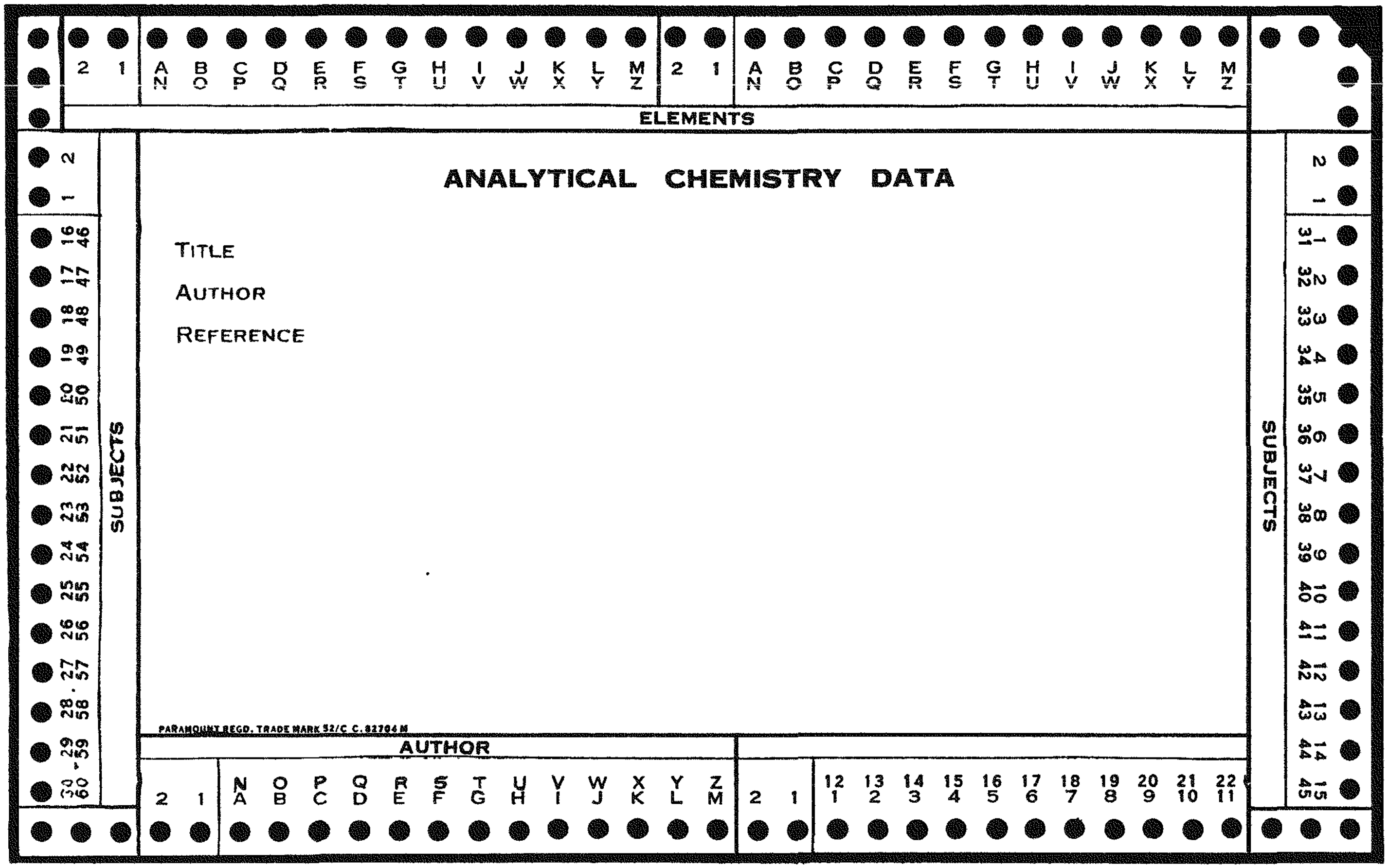


Figure 5. "Analytical chemistry data," punched keysort card.

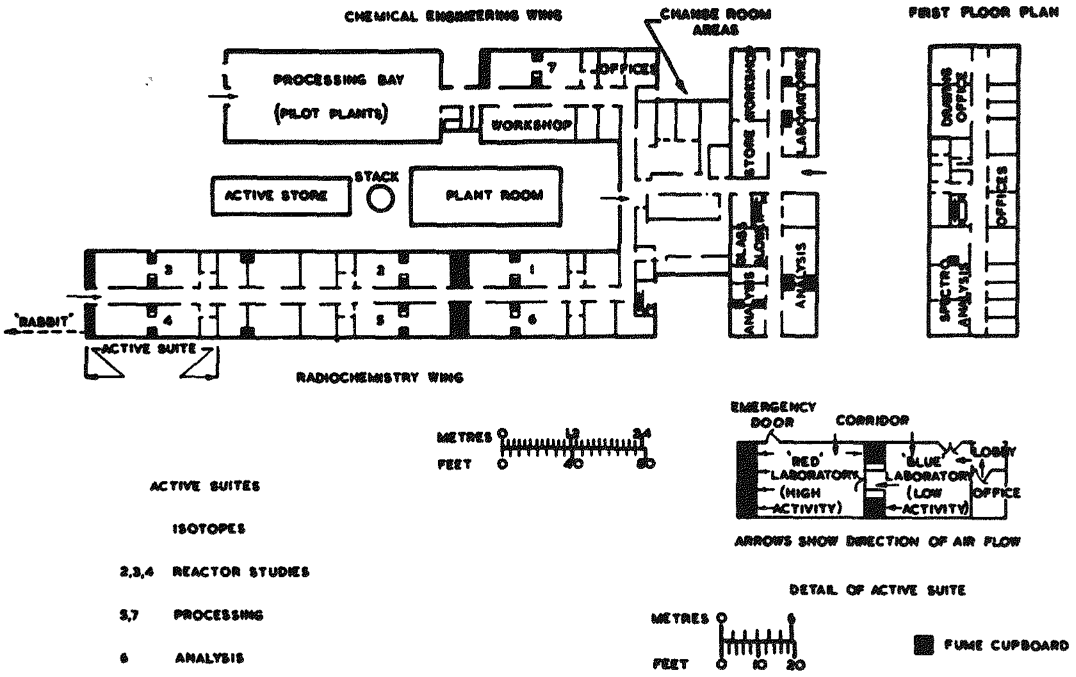


Figure 6. Diagram of chemistry-chemical engineering building.

TABLE I

A.A.E.C. RESEARCH PROGRAM

	Initial Research Program	Possible Alternatives
Coolant	Carbon dioxide	Helium
Moderator	Beryllia, beryllium	Graphite
Reflector	Beryllia	Graphite
Fuel cycle	U^{233} - thorium	Other fuel cycles at reduced conversion factor
Fuel element and diluent	1. Intermetallic: U-Be_{13}, Th-Be_{13} in Be 2. Oxide: UO_2, ThO_2 in BeO 3. Carbide: UO_2, ThO_2 in graphite	
Canning material	Beryllium	1. Graphite 2. Ceramic 3. Stainless steel

The main program consequently necessitates a wide range of chemical analyses related to materials technology development. Work has commenced on the problems of the preparation, purification, fabrication and studies of the properties of beryllium metal, beryllia and graphite. Irradiated fuel element specimens are currently being examined after irradiation in the "HIFAR" materials-testing reactor. This is a 10 Mw reactor almost identical in design with the "DIDO" reactor at A.E.R.E., Harwell. A second reactor, "MOATA," is being installed early in 1961. This latter reactor of the UTR-10 type provides a neutron flux of about 10^{11} neutrons/cm^2/sec and has a thermal power of about 10 Kw. The Analytical Chemistry Group is also assisting in more basic or pure research in such fields as chemistry and metallurgy.

CURRENT ANALYTICAL CHEMISTRY STUDIES

Some of the current analytical chemistry studies are as follows:

(1) Polarography of the lanthanides (see paper presented at this conference).

(2) X-ray fluorescence method for determination of strontium in acid solutions in the range 0.01-1 mg/ml. Used in conjunction with low-background Sr^{90} determinations.

(3) Determination of low levels of Ra in effluent. Lead sulphate-EDTA method.

(4) Fusion-extraction gas analysis of irradiated fuel and other materials (e.g. U-Th Be_{13} alloys, Be, etc.).

(5) Radiometric titration method for Be, using inactive phosphate and carrier-free Be^7.

(6) Metal: oxygen ratios in oxide fuel samples.

(7) Radiometric precipitation in filter paper. Based on the precipitation of µg quantities of metal ions in discs of filter paper which are immersed in buffered solutions of active reagents.

(8) Differential spectrophotometric method for U analysis in (U-Th)-Be_{13} alloys.

(9) Development of reliable methods for the estimation of submicrogram amounts of Be in sea water, river water, soils and rocks, from environmental surveys.

(10) Ion-exchange method for separation of traces of Sr^{90} from environmental materials (see publication list).

(11) Radioactive isotope dilution method using Sr^{85} for determination of stable Sr content of environmental materials. Used in conjunction with (2).

(12) Microbiology of heavy water in "HIFAR" reactor.

(13) Development and construction of an air monitor for Be.

(14) Development and construction of a filter paper smear monitor for Be.

(15) Improved methods for the volumetric determination of Be.

(16) Separation of Be on diallyl phosphate complexing resin.

(17) Coprecipitation methods for Sr separation.

(18) Monitor for the determination of deuterium and oxygen in helium.

(19) Determination of traces of permanent gases by gas chromatography, using molecular sieves.

SOME RECENT PUBLICATIONS

Some recent analytical chemistry publications by the group include:

(1) de Bruin, H. J. and Smythe, L. E., "Determination of Traces of Oxygen in Sodium by Infrared Spectrophotometry," Nature 182, (1958).

(2) Palmer, A. R., "The Thorium-APANS Complex. A Spectrophotometric Study," Anal. Chim. Acta 19, 458 (1958).

(3) Florence, T. M., "Estimation of Traces of Nickel in Sodium Metal," Anal. Chim. Acta 19, 548 (1958).

(4) de Bruin, H. J. and Smythe, L. E., "The Determination of the Oxygen Content of Sodium Metal by the Butyl Bromide Method," Analyst 83, 242 (1958).

(5) Florence, T. M., "A Rapid Method for the Determination of Sub-microgram and Microgram Amounts of Beryllium in Filter Paper," Anal. Chim. Acta 20, 472 (1959).

(6) Davis, P. S., "Separation of Strontium-90 from Calcium," Nature 183, 674 (1959).

(7) Florence, T. M., "A Specific Method for the Determination of Uranium in Ores by Cathode Ray Polarography," Anal. Chim. Acta 21, 418 (1959).

(8) de Bruin, H. J., "Determination of Traces of Oxygen in Sodium Metal by Infrared Spectrometry," Anal. Chem. 32, 360 (1960).

(9) Davis, P. S., "Determination of Traces of Oxygen in Gases-Methylene Blue Method," Metallurgia 62, 49 (1960).

(10) Smythe, L. W. and Whittem, R. N., "Analytical Chemistry of Beryllium," Analyst (In Press).

(11) Florence, T. M. and Smythe, L. E., "Use of Azo Dyestuffs for the Polarographic Determination of the Lanthanides," Nature 187, 771 (1960).

(12) Davis, P. S., "The Estimation of Sr^{90} by an Ion-Exchange Method," Proc. 3rd Australasian Radiobiology Conference," Sydney, Aug. 15-18 (1960).

(13) Smythe, L. E. and Davis, P. S., "Results of Sr^{90} Determinations on Samples from Lucas Heights and Richmond, N.S.W. 1950-60," Proc. 3rd Australasian Radiobiology Conference, Sydney, Aug. 15-18 (1960).

(14) Thackray, M., "Radiometric Precipitation in Filter Paper," submitted to Nature.

(15) Florence, T. M., "The Direct Determination of Uranium in Concentrates by Spectrophotometric Titration," Anal. Chim. Acta (In Press).

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1. Lewin, S. Z., Chem. and Eng. News 36, 35, March 24, 1958.

2. Miles, G. L. and Watson-Munro, C. N., "The Design and Construction of Research Facilities for a Power Development Programme." Proceedings of the Second Geneva Conference on the Peaceful Uses of Atomic Energy, 1, 102 (1958).

CALDER-HALL TYPE REACTOR COOLANT: ANALYTICAL REQUIREMENTS AND PROBLEMS

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F. J. Woodman

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ABSTRACT

Calder-Hall type reactors using CO_2 as gaseous coolant call for (a) analytical control of the quality of the liquid CO_2 used as the raw feed material and (b) subsequent analysis of the circuit gas under startup, shutdown, and normal operating conditions.

An outline is given of sampling techniques and analytical procedures both for the examination of the feed gas and for the circuit gas; methods for B, moisture, oil, C^{14}, CO, and other gaseous impurities are described briefly, and some typical analytical data are presented. Techniques involved include mass spectrometry, gas chromatography, liquid scintillation beta counting, and infrared absorption.

A short description is given of "in-line" instrumentation for the continuous measurement of moisture and CO.

Finally, a summary is given of work, still in progress, on the application of gamma-spectrometry to the study of radioactive species, some very short lived, that are present in the circuit-gas; the development of preliminary separation and concentration procedures, using, for example, Molecular Sieve materials, is also outlined.

* * * *

The Nuclear Power Stations operating at Calder Hall and Chapelcross each comprise four pressurized, carbon dioxide-cooled, graphite-moderated reactors, fueled with natural uranium. Each of these eight reactors has a normal operating thermal power of 200 Mw. The charge of gaseous coolant for each reactor is approximately 25 tons. In addition to this pair of four-reactor stations owned and operated by the U.K.A.E.A., eight other stations owned and to be operated by Electricity Generating Boards with designed power totalling several thousand Mw are in course of construction or design and all of these are basically of the Calder Hall type, using carbon dioxide coolant. From this it will be appreciated that the analytical control of the feed gas and the circuit gas are important topics and the need for cheap, simple, robust methods and instrumentation is apparent. It is the purpose of this paper to summarise analytical control requirements on the feed material and on the circuit gas and to outline the results of investigations in progress on the analysis of the coolant for various radioactive components, some of which have very short half-lives.

The gaseous coolant in a reactor must, of course, possess a number of characteristics in addition to the important requisite of good heat-transfer properties and this situation is reflected in some of the analytical requirements. Neutron economy considerations, for example, dictate that the coolant itself shall have a low absorption cross-section and that impurities with high cross-sections shall be kept below specified, very low concentrations. It is clearly important that the coolant shall have high radiation stability and that it shall be chemically compatible with other materials in the reactor; analyses throwing light on radiation breakdown and interaction with, say, the graphite moderator, are, therefore, likely to be called for.

ANALYTICAL CONTROL OF FEED GAS

Supplies of raw feed carbon dioxide are derived from several sources: (a) chemical process by-product, (b) fermentation process by-product, (c) air/coke reaction. The gas is delivered to the reactor site in road tankers of 10-ton capacity in the liquid form. Samples are taken from each tanker on arrival and rapidly examined to determine the percentage of gas not absorbed by a solution of potash; this gives a quick measure of the purity of the gas before it can be cleared for feeding into the storage tanks. The liquid carbon dioxide is sampled by flowing it through a copper spiral immersed in hot water which gives continuous gasification under controllable conditions. It is, of course, important to sample the liquid and not the gaseous ullage since fractionation is known to occur. A measured volume of the gas is then collected over brine and absorbed in a potash solution; the residual gas is measured in a calibrated portion of the absorption vessel and removed, if required, for subsequent analysis by mass spectrometry or gas chromatography.(1) For more accurate assessment, mercury is used instead of brine.(2)

The analysis of the residual gas includes the determination of argon, hydrogen, oxygen, nitrogen, methane, ethane, propane and ethylene; the most important of these is argon since argon-40 has a capture cross-section of 0.53 b for thermal neutrons, yielding argon-41 which decays with a half-life of 1.8 hours with 1.28 Mev gamma emission. The presence of argon, therefore, has significant influence on shielding problems when the gas is fed into the circuit as a coolant. Initially, argon was determined by neutron-activation analysis(3) but it was soon found more convenient to analyse the residual gas by conventional mass spectrometric techniques along with all the other gaseous impurities listed above. It is now found satisfactory to analyse only occasional consignments in detail in this way, since the quality of the raw material supply is very good.

Another impurity which could have profound effects on the performance of the coolant is, of course, boron. This is determined on the feed gas by absorption in sodium hydroxide and subsequent distillation as methyl borate, followed by absorptiometric estimation of the boron with curcumin.(4)

Moisture is determined on the feed gas by the conventional magnesium perchlorate absorption method.(5)

We have found that gas chromatographic analysis of residual gas samples has been, on occasions, of use as a complementary technique to conventional mass spectrometry; for example, the chromatographic approach enabled us to characterise and estimate traces of dimethyl ether in the ppm region when present as an unexpected impurity. In fact, it is quite feasible to dispense with mass spectrometry as a control technique and use the much cheaper gas chromatographic method.(6)

Figures 1 and 2 illustrate the arrival of a 10-ton road tanker and the performance of the acceptance analysis before feeding the carbon dioxide to the storage tanks; Figure 3 is a view of the storage tanks. Table I summarises a typical feed gas analysis.

TABLE I

TYPICAL FEED GAS ANALYSIS

Component Determined	Typical Result
	ppm
A	3
H	< 1
O	35
N	75
CH_4	< 1
C_2H_6	< 1
C_3H_8	1
C_2H_4	5
H_2O	40
B	< 0.1
	% v/v
Residual Gas	0.02

CIRCUIT GAS ANALYSIS

The main sampling points are shown in Figure 4, which diagramatically represents the gas circuit. Sampling of the circuit gas has to be carried out at pressures of the order of 100 lbs per square inch and at a temperature of about 150°C. This is fairly readily accomplished by using a cylinder fitted with a valve at each end coupled to the sampling point by means of a flexible pressure line incorporating a T-piece and valve. The line and cylinder are flushed out with the sample gas and the cylinder is finally filled with gas at the pressure of the system being sampled.(7)

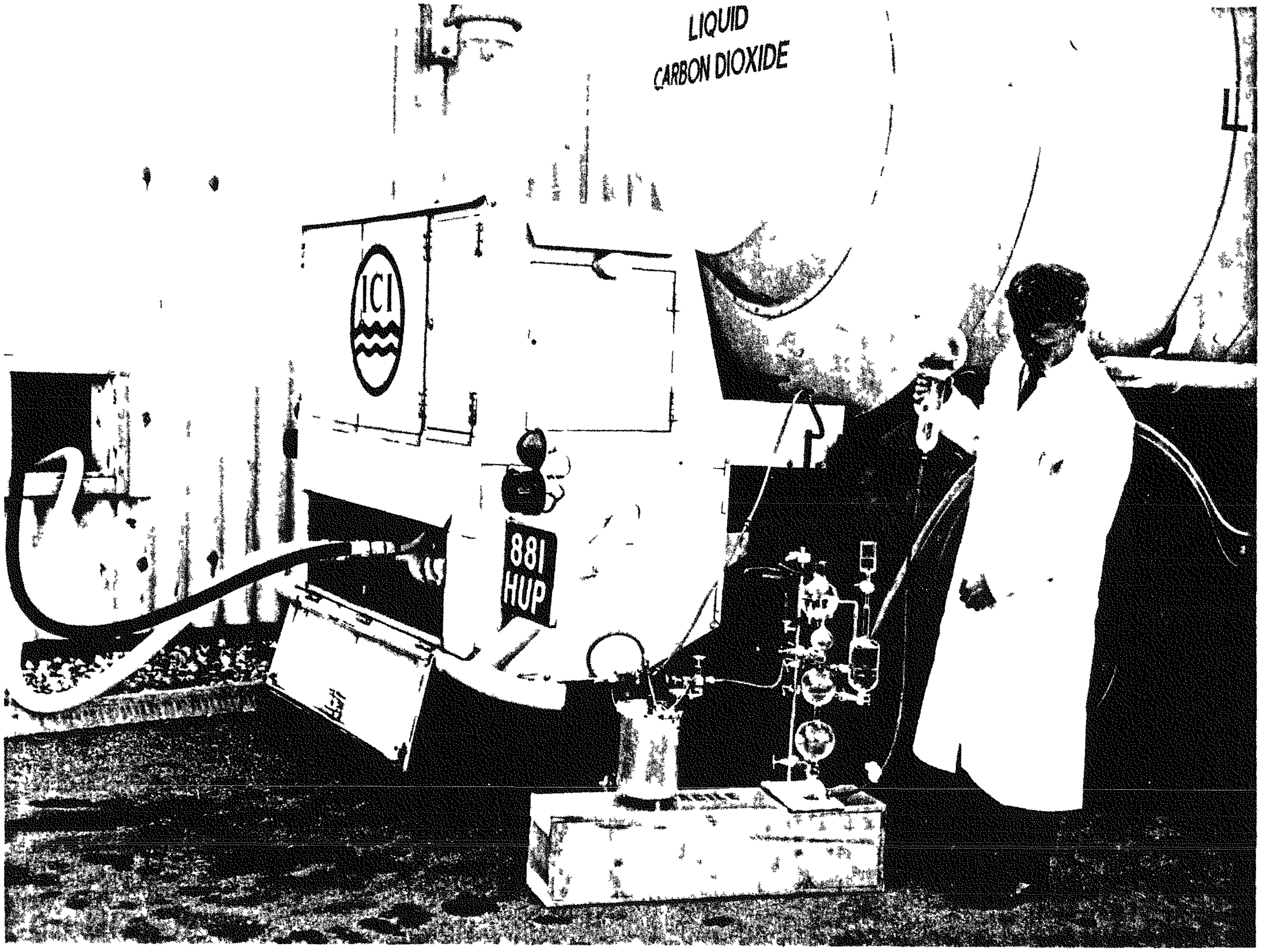


Fig. 1 - Sampling of CO_2 Supply Tankers

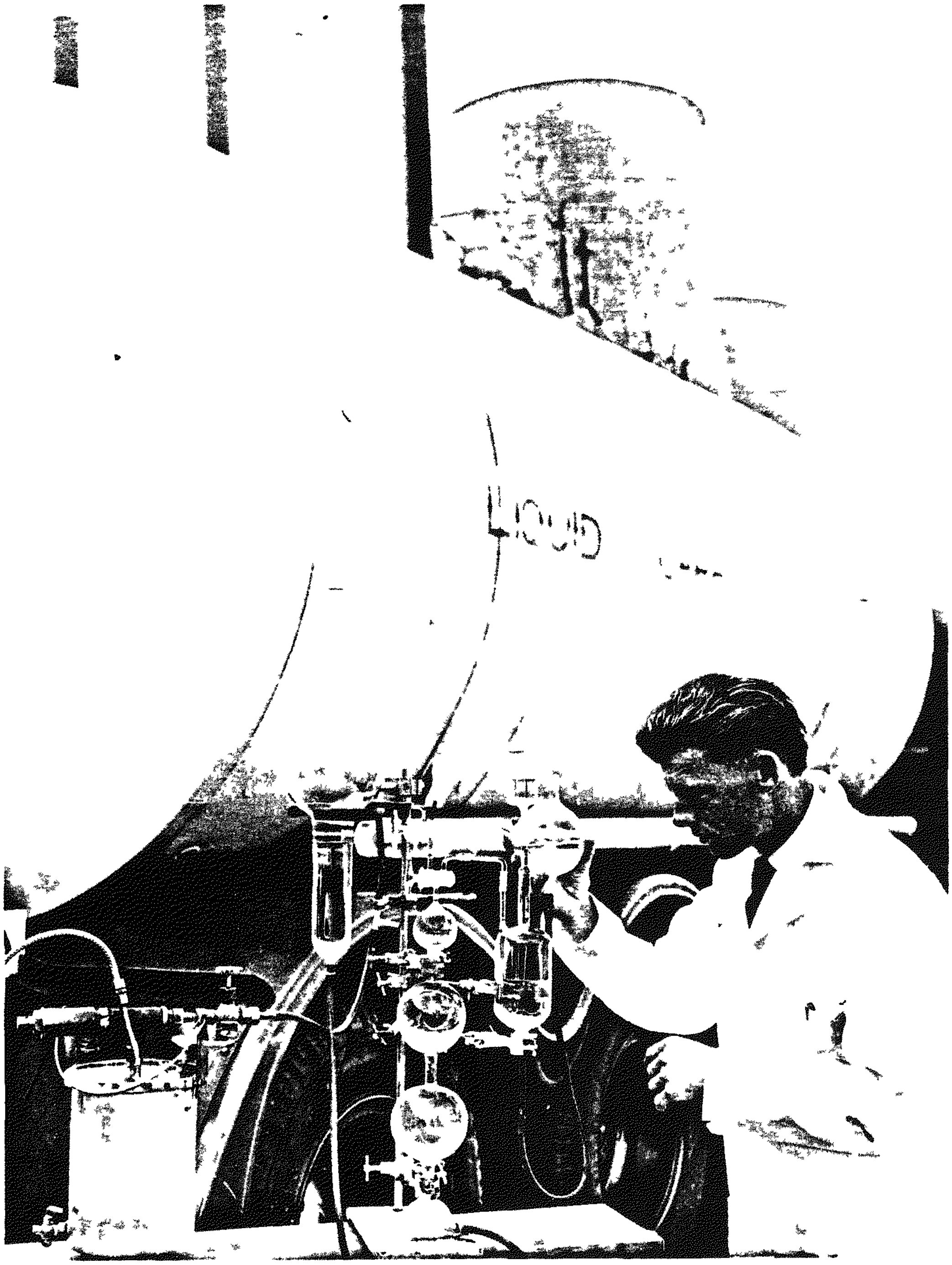


Fig. 2 - Sampling of CO_2 Supply Tankers

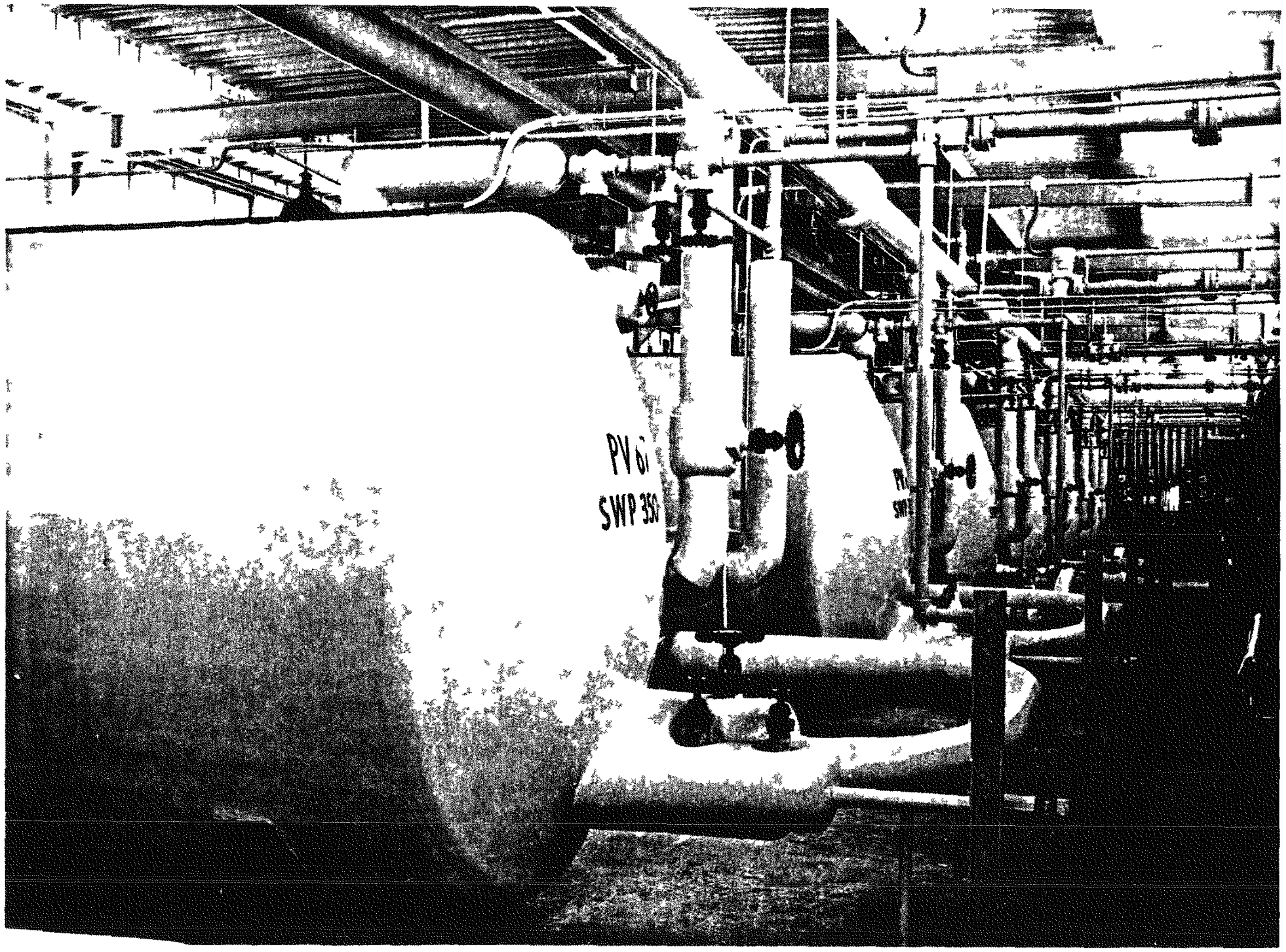


Fig. 3 - CO_2 Storage Tanks at Calder Hall

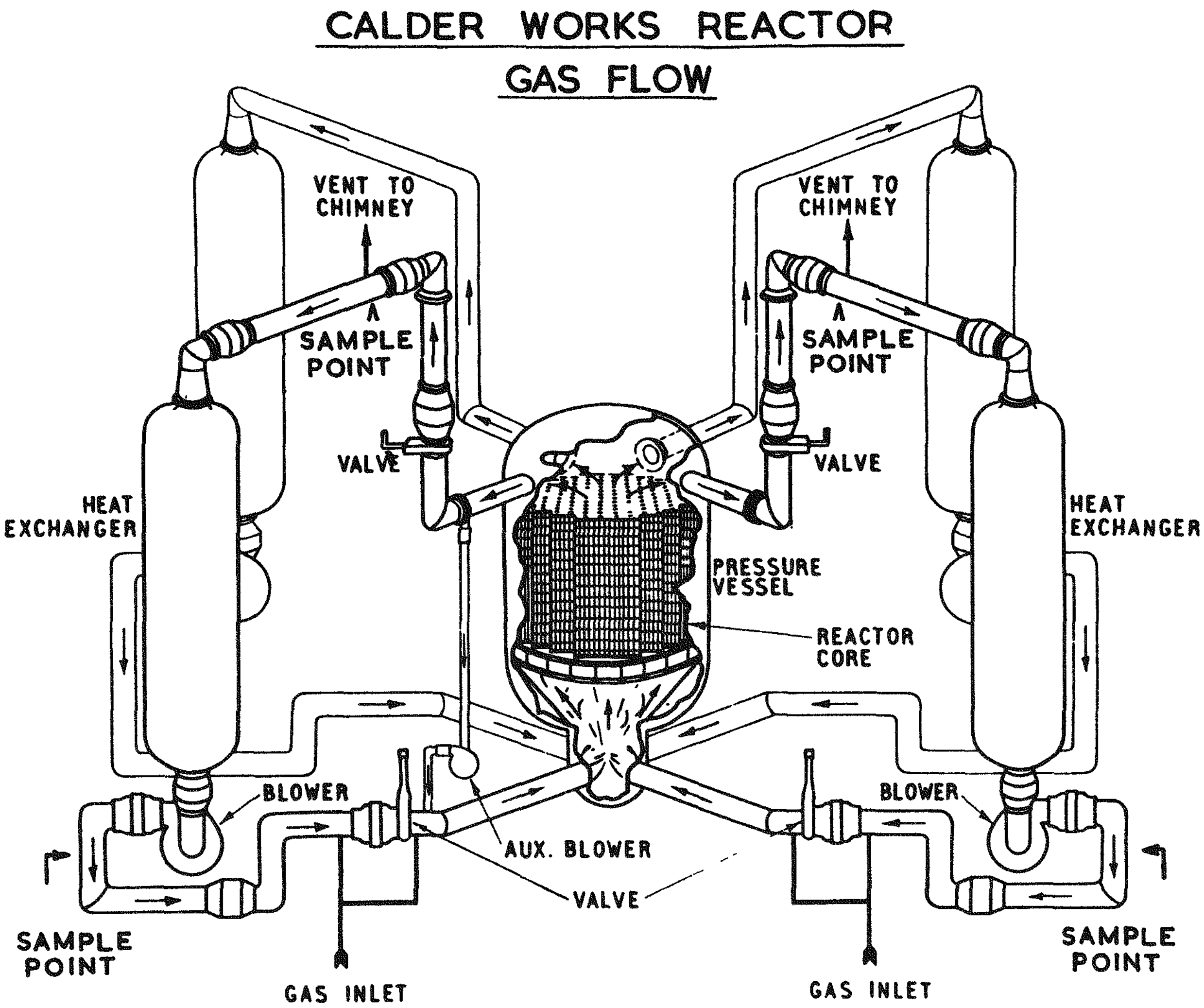


Fig. 4 - Position of Sampling Points on a Calder Hall Type Reactor

Following a fresh charge of gas to a reactor, a periodic determination is usually made of "residual gas," i.e., the percentage of gas not absorbed in potash(1) in the carbon dioxide in circuit as supporting evidence of normal satisfactory start-up. Carbon monoxide determinations are made for a similar reason; the method is basically the conventional iodine pentoxide procedure. The gas sample is dried by passage through silica gel, anhydrone, and then through iodine pentoxide at 140° to 150°C; the resulting iodine is absorbed in potassium iodide and titrated with sodium thiosulphate.(8)

Carbon monoxide can also be determined by infrared monitors installed on a limited scale in the reactors. More important, perhaps, than continuous monitoring of the coolant for carbon monoxide is the application of the infrared analyser to the detection of combustion.(9) For this purpose, the instruments have been modified to allow differential measurements to be made of gas leaving a channel against the bulk gas entering the bottom duct to the reactor. By utilizing this technique, it is possible to distinguish between an ordinary burst without combustion and a burst with combustion; instrument sensitivity is such that an increase of 150 ppm above a background of several thousand ppm of CO would give full-scale deflection.

Mass spectrometric analysis of the "residual gas" enables one to follow the changes in level of other gaseous impurities, in particular the fall in nitrogen and argon contents soon after start-up; the initial start-up values and the time taken for the levels to fall to those of the feed gas obviously depend on the degree of purging before final pressurizing of the gas circuit and the rate of any leakage of coolant from the reactor.

Figure 5 shows the build-up of "residual gas" and carbon monoxide as a reactor is started up. Figure 6 illustrates the changes in level in some impurities with time.

Moisture determinations are frequently carried out during start-up, and under normal operating conditions. A variety of methods have been assessed and are available. As reference method we prefer the anhydrone absorption procedure.(5) A modification of the Karl Fischer method has been used.(10) It, however, is subject to interference from some impurities likely to be present in circuit gas, involves manipulative difficulties, is rather slow and generally is less suitable. For quick "spot checks" on moisture one of the commercially available hygrometers, such as the "Alnor" hygrometer has been found quite satisfactory. For continuous monitoring of moisture level, we have installed infrared instrumentation ("IRGAS" - Infra Red Gas Analysers) supplied by Messrs. Grubb-Parsons. Preliminary vibration troubles have been overcome and these monitors are now useful in that they would give immediate warning of ingress of water due, for example, to sudden failure in a heat-exchanger element; their present lower limit of detection is about 20 ppm w/w. Normal operational levels after start-up fall well below this limitation, usually not exceeding 10 ppm w/w. Improved infrared instrumentation with a greater sensitivity is to be tested shortly. Other commercially available instrumental procedures based on the electrolytic procedure of Keidel have been examined and offer promise as continuous monitoring systems. The principle of operating the infrared gas analyser which was installed is shown in Figure 7. It is similar to the Perkin-Elmer TRI-NON instrument and utilises, as does that model, the principles laid down by Luft in Germany in 1943.

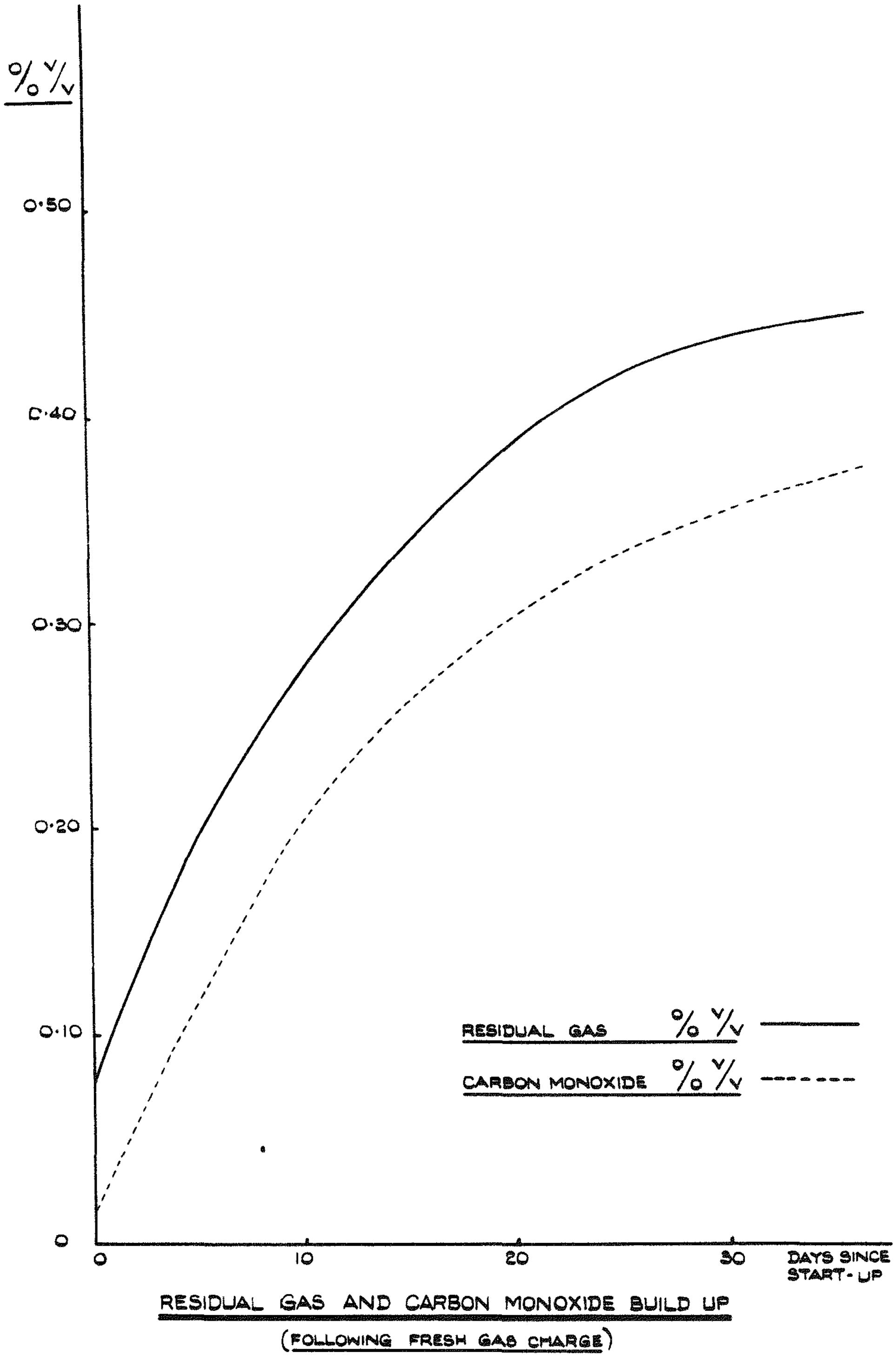


Fig. 5 - Build up of Carbon Monoxide and Residual Gas in Calder Type Reactor

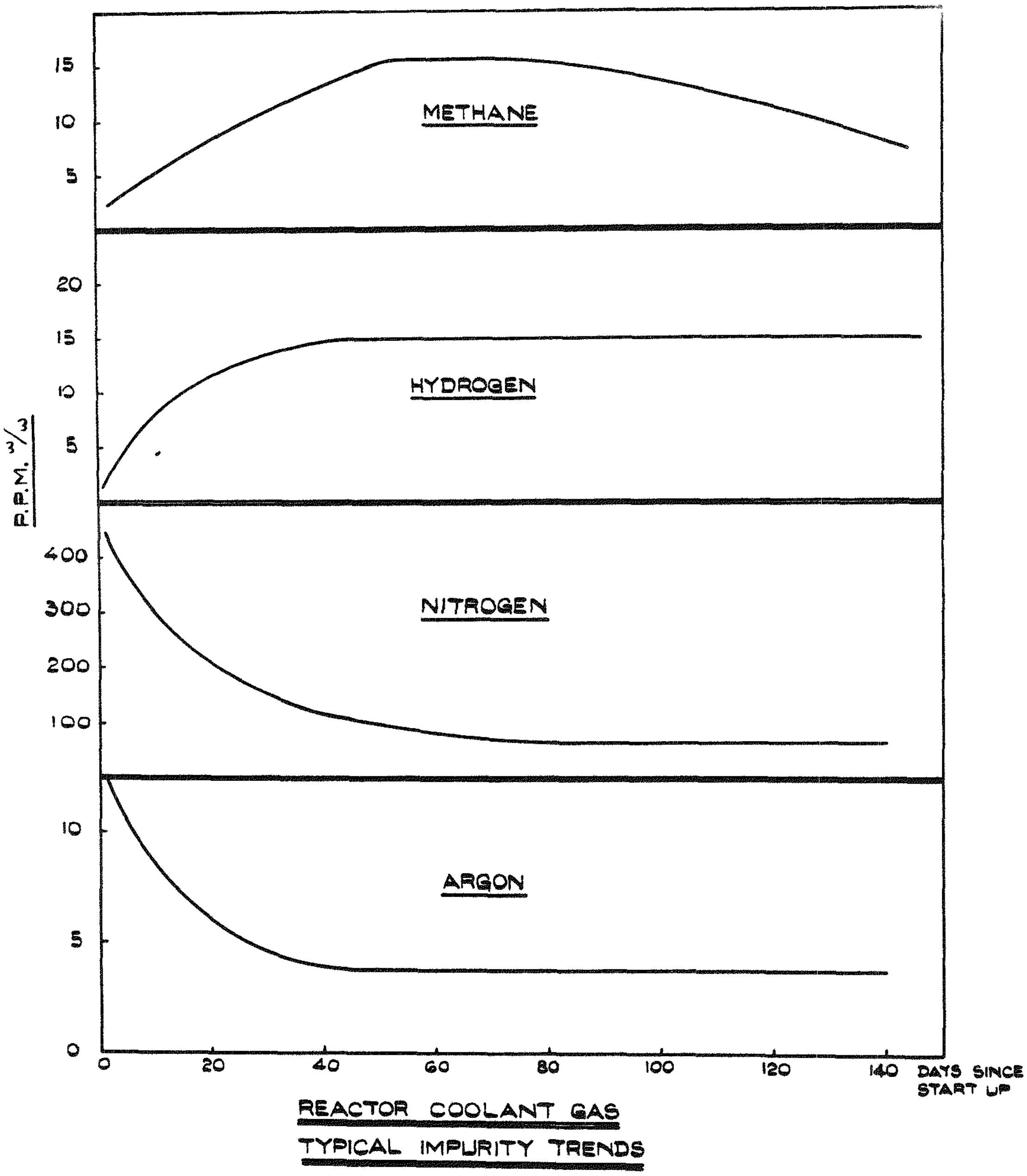


Fig. 6 - Impurity Trends in Reactor Coolant Gas

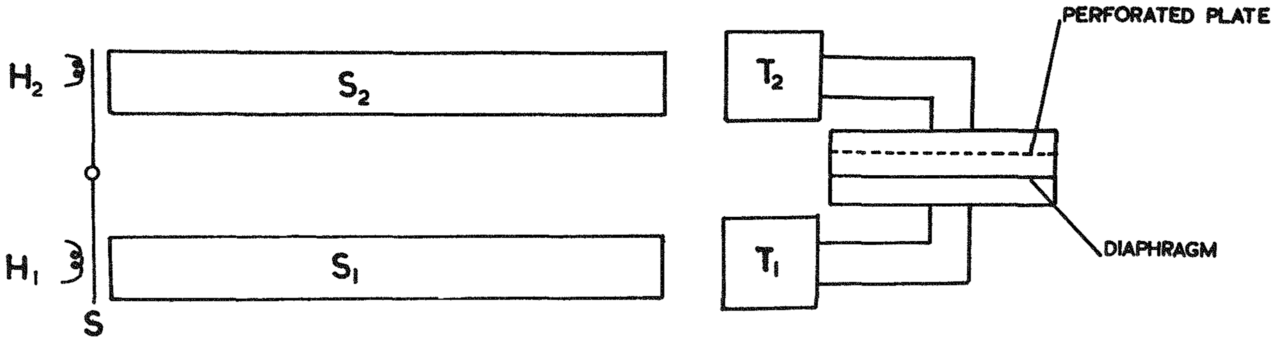
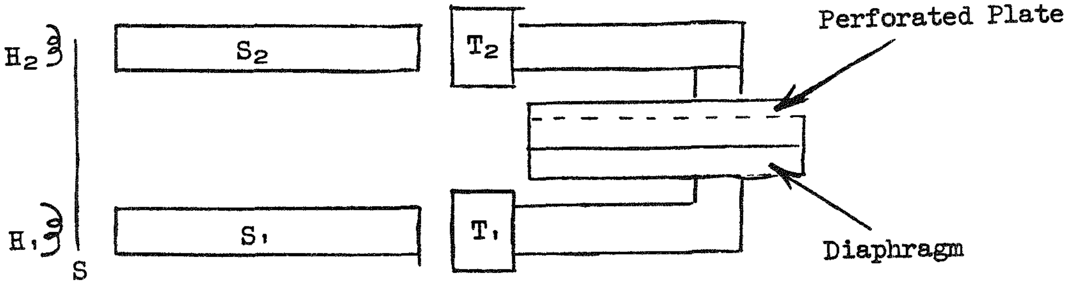


Fig. 7 - Basic Arrangement of Infra Red Gas Analyzer

The gas to be analysed is passed continuously through the sample tube S_1. Absorption in S_1 is compared with the absorption in a similar tube (S_2) mounted parallel to S_1 and usually filled with dry air. Energy from two nichrome heaters, H_1 and H_2, is passed through both tubes and the portion transmitted is received by the two chambers T_1 and T_2 which contain a pure sample of the gas to be measured.

The chambers T_1 and T_2 are separated by a thin diaphragm which forms one electrode of an electrical condenser. The other electrode is in the form of a closely adjacent insulated, perforated, metal plate. Radiation transmitted by the tubes S_1 and S_2 is absorbed by the gas in T_1 and T_2, causing a temperature increase with a resultant increase in pressure. If the transmission through both S_1 and S_2 is identical, the diaphragm remains stationary; when, however, a sample of gas containing the gas to be detected is introduced into S_1, the transmission balance is broken and the diaphragm is displaced, producing a corresponding change in the capacitance of the condenser. The application of a polarising potential to the condenser converts the capacitance change to a current change which is amplified to provide an indication related to the pressure difference between T_1 and T_2.

In order to obtain measurements free from zero drift, a rotating shutter S interrupts the radiation from heaters H_1 and H_2 at a frequency of ca. six cycles per second, allowing pressure changes to be directly related to temperature changes which are themselves related to the differences in absorption of energy in S_1 and S_2. Any other gas also present in the sample will not affect the result unless it has absorption bands which overlap those of the gas being determined. In this event, filter tubes containing the interfering gas or gases can be included in the two optical paths.



Other views of the actual instrument used are shown in Figures 8 and 9.

The carbon-14 content of circuit gas is of interest for two reasons. Firstly, it is necessary to evaluate the activity due to carbon-14 prior to the occasional release of the reactor coolant and, secondly, it is of interest in the study of coolant-moderator reactions. As indicated earlier, the carbon monoxide builds up after start-up to a level of the order of 0.3 - 0.4 per cent (v/v) and we have established, somewhat surprisingly, that the carbon-14 level in the carbon monoxide is consistently some twenty times higher than it is in the carbon dioxide. This presumably follows from the reaction of the fresh coolant carbon dioxide with graphite moderator rich in carbon-14 and implies that subsequent exchange is very slow. The result of this observation is the continuing need for an analytical procedure for the determination of carbon-14 separately in the monoxide and dioxide; this is readily achieved by absorbing the carbon dioxide in potash (with subsequent regeneration of the carbon dioxide into baryta) while the residual carbon monoxide is oxidised by iodine

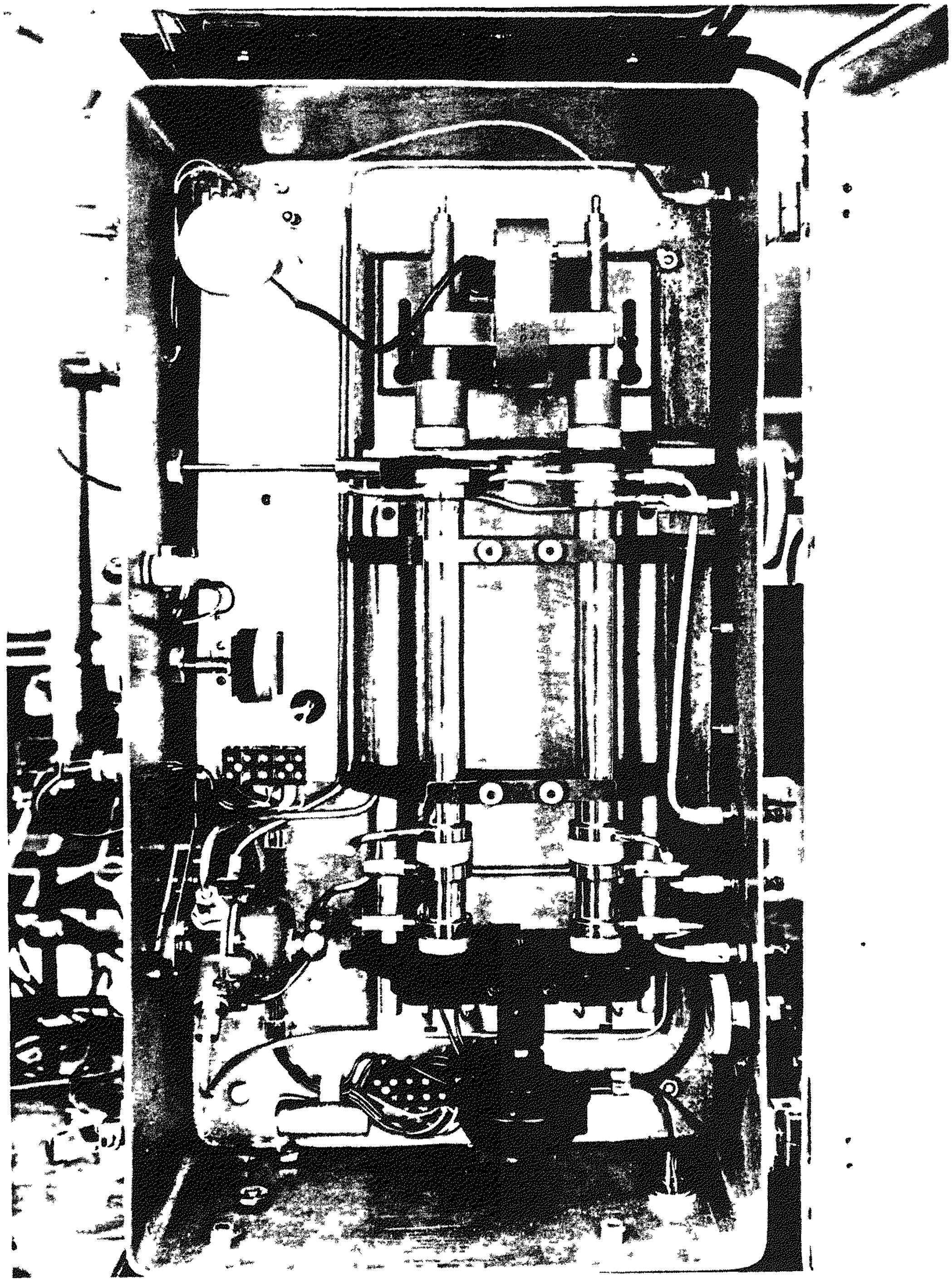


Fig. 8 - Infra Red Gas Analyzer

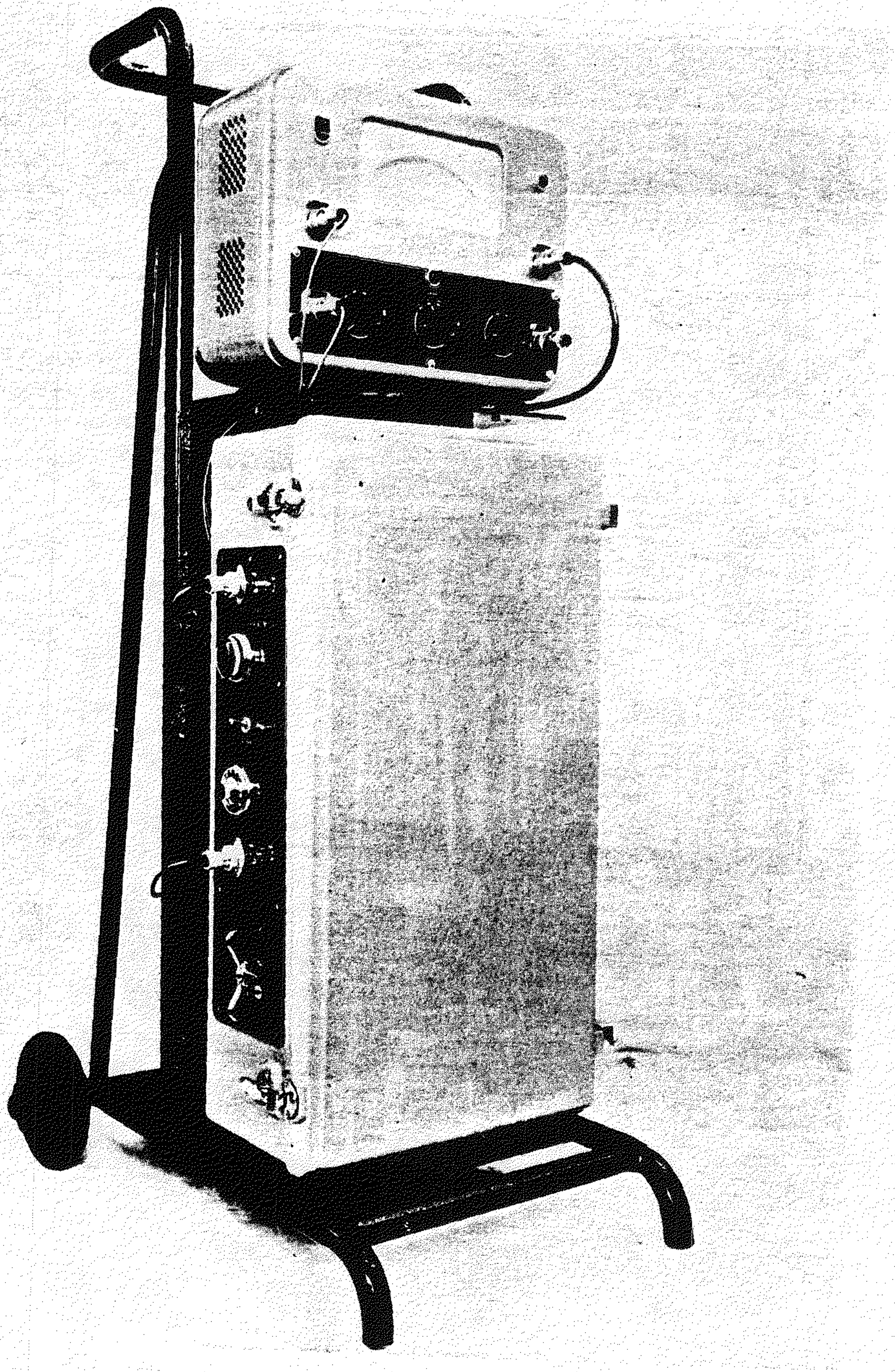


Fig. 9 - Infra Red Gas Analyzer. Complete Assembly

pentoxide to the dioxide which is in turn absorbed in baryta. The resulting barium carbonate precipitates are filled with an organic scintillant and the carbon-14 contents are evaluated conventionally in a liquid scintillation counter.(11) A typical figure for the carbon-14 content of coolant carbon dioxide is 1 dpm/ml.

One other determination in the circuit gas worth mentioning is that of traces of oil derived, for example, from a faulty seal in the blower. The sampling technique,(12) which is not perhaps ideal, is designed to collect oil, both in the form of fine droplets and as a vapor; it involves the insertion of a specially designed sampling tube with a 1/16-inch hole drilled in the side 1/8 inch from the end; a needle valve leads to a copper cooling spiral and two absorption vessels containing carbon tetrachloride. After six hours sampling at one liter per minute, the tube complete with head is detached and rinsed with carbon tetrachloride; the washings are combined with the main absorbant and the oil content is assessed by a conventional infrared absorption procedure.(13) The measurements are at 2890 cm^{-1} (3.46μ) (attributed to the C-H stretching frequency of hydrocarbons), using as standard the actual oil used in the blowers. The limit of detection is 5 ppm w/w and on only one occasion in four years operation has this figure been exceeded. We regard this largely as a qualitative technique, bearing in mind that oil ingress would also be rapidly indicated by carbon monoxide increase and hydrocarbon increase in the "residual gas."

DETERMINATION OF RADIOACTIVE COMPONENTS OF CIRCUIT GAS

It is of great interest and some importance to determine the radioactive components of circuit gas in prototype power reactors during normal operation for several reasons. Firstly, from the aspect of shielding studies, much valuable guidance can be obtained by characterization of the various active species present. Secondly, from the health physics standpoint it is important to have a knowledge of the activities present in circuit gas before a discharge "blow-down" can be authorised. Thirdly, from the point of view of the continuing satisfactory operation of burst-cartridge detection gear, data on activities other than fission-product activities, is clearly useful. Finally, from the more fundamental aspect of reactor studies, including coolant-moderator interactions and canning material performance, information on the active species present is important.

Two active components have already been mentioned (argon-41 and carbon-14) but, in addition, it would be expected that nitrogen-16 and oxygen-19 would be present. The modes of formation and half-life data for these radionuclides are summarised for convenience in Table II.

TABLE II

METHODS OF FORMATION AND HALF-LIVES OF FOUR RADIONUCLIDES IN CIRCUIT GAS

Isotope	Method of Formation	Half-Life
A^{41}	A^{40} (n,γ)	110 min.
C^{14}	C^{13} (n,γ) N^{14} (n,p)	5568 yr.
N^{16}	O^{16} (n,p)	7.4 sec.
O^{19}	O^{18} (n,γ)	29 sec.

Preliminary measurements of the absolute activities of A^{41}, N^{16}, and O^{19} in the coolant gas have been made by R. L. D. French(14) as part of a reactor shielding study, by flowing the gas from a duct sampling point, along a delay line and through a flow-through Geiger tube. Total β-counts were taken at various gas flow rates, and by plotting log count rates against delay time (i.e. reciprocal flow rate) a composite decay curve is obtained. It is possible, from this, to deduce the absolute activities by successive subtraction of the various components in order of decreasing half-life.

All series of measurements taken so far show some evidence of a short-lived component with a half-life of the order of one second. No information appears to be available in the literature on such a gaseous isotope which might be expected in reactor coolant gas but N^{18} would appear to be the most probable isotope. A check on the β energy of the isotope, which is being undertaken, will be necessary to determine whether or not it is N^{18}.

The separate determination of A^{41} in the gas has reached a more advanced stage.(15) The problem is far simpler than that for the shorter-lived isotopes, since normal gamma-spectrometric techniques can be used. The gas sample is contained in a container 4 in. high and 1-1/2 in. in diameter situated on a 1 in. by 1-1/2 in. NaI (Tl) crystal. The counting efficiency of this system has been calculated mathematically and for gas containing 4 ppm w/w of natural argon, a typical value of A^{41} activity of 10 dps/cc (at NTP) is obtained.

The A^{41} content of shield-cooling air has also been measured in a similar manner, but due to the lower activities in this case, a much larger container had to be used (1 foot in diameter by 1 foot in height). This was calibrated against the smaller container, using normal coolant gas.

This γ-spectrometric study of the activity of the coolant gas using a 100-channel γ spectrometer, confirms the presence of N^{16}, A^{41}, and O^{19} with their main energies at 6.13 Mev, 1.29 Mev, and 0.20 Mev, respectively. This can clearly be seen in Figure 10. Gamma spectra obtained from circuit gas filter samples are typical of irradiated graphite associated with traces of activated corrosion products of constructional materials, e.g., activated iron rust.

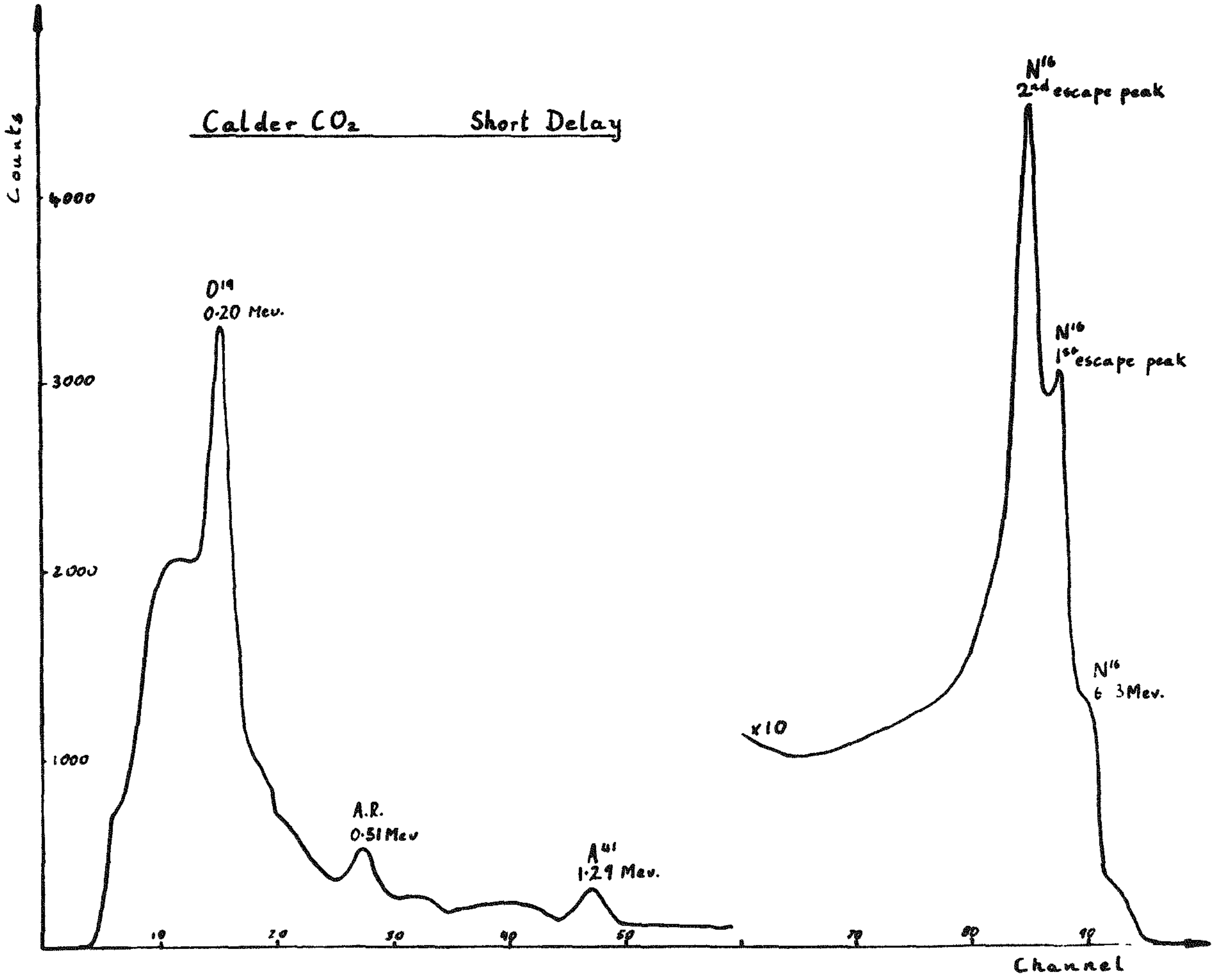


Fig. 10- γ Spectrum of Circuit Gas With Short Delay Before Counting

Some very small contribution to the gas activity comes occasionally from fission-product gases released into the coolant from burst cartridges or from cartridge contamination, and some knowledge of these is very useful in the understanding and improvement of methods for the detection of burst cartridges. The examination of a sample of gas from a channel containing a burst cartridge gives initially the same γ-spectrum as Figure 10. If, however, a "residual gas" sample from this channel is scanned, the spectrum will consist essentially of only the A^{41} peak, as can be seen in Figure 11. Cooling for 10 hours, however, will give a completely different spectrum, shown in Figure 12, consisting of peaks of 0.081, 0.15, 0.19 and 0.25 Mev due to the fission product gases Xe^{133} (5.3 days), Kr^{85m} (4.4 hours), Kr^{88} (2.8 hours) and Xe^{135} (9.2 hours), respectively. These peaks had originally been 'lost' under the background due to the shorter-lived isotopes, and it is, therefore, obvious that in order to study the fission-product gases in the coolant without too great a delay, it is necessary to separate the A^{41} from the Xe and Kr isotopes by some rapid physical means.

We have examined several techniques and the most encouraging method investigated so far is that of passing the gas through a gas chromatographic column containing Linde 5A Molecular Sieve material of 36-42 mesh, BSS.

The carrier gas used in these experiments has been hydrogen, flowing at a rate of 120 ml per minute. This gas is passed through a water cooler and Molecular Sieve purifier. It will be possible, using this technique, either to separate the gases and count them individually, or to remove the A^{41} with the oxygen and scan the rest of the sample as a mixture of the xenon and krypton. Figures 13 and 14 show the apparatus used for this work and some of the results. In the most recent experiments, we have used a plastic column six feet long spirally wound to give a coil about 4 inches in diameter which can be fitted directly over a 3 in. by 3 in. sodium iodide crystal. After removal of all CO_2 and CO from the gas sample, 100 to 200 ml of residual gas are treated chromatographically and as soon as the A^{41} plus oxygen peak is completed, the spiral column is detached for gamma-spectrometric scanning for xenon and krypton; a very similar result is then obtained to that shown after 10 hours decay, except, of course, that it has been achieved very much more quickly. This work is still in progress but it seems clear that extension and development of this approach should eventually provide the answer to the problem.

Summarizing, we can say that normal analytical control of the feed and circuit gas presents no special problems now, but the investigation of short-lived induced activities and fission product activities in circuit gas, although well advanced, is not yet a completely solved problem from the analytical standpoint.

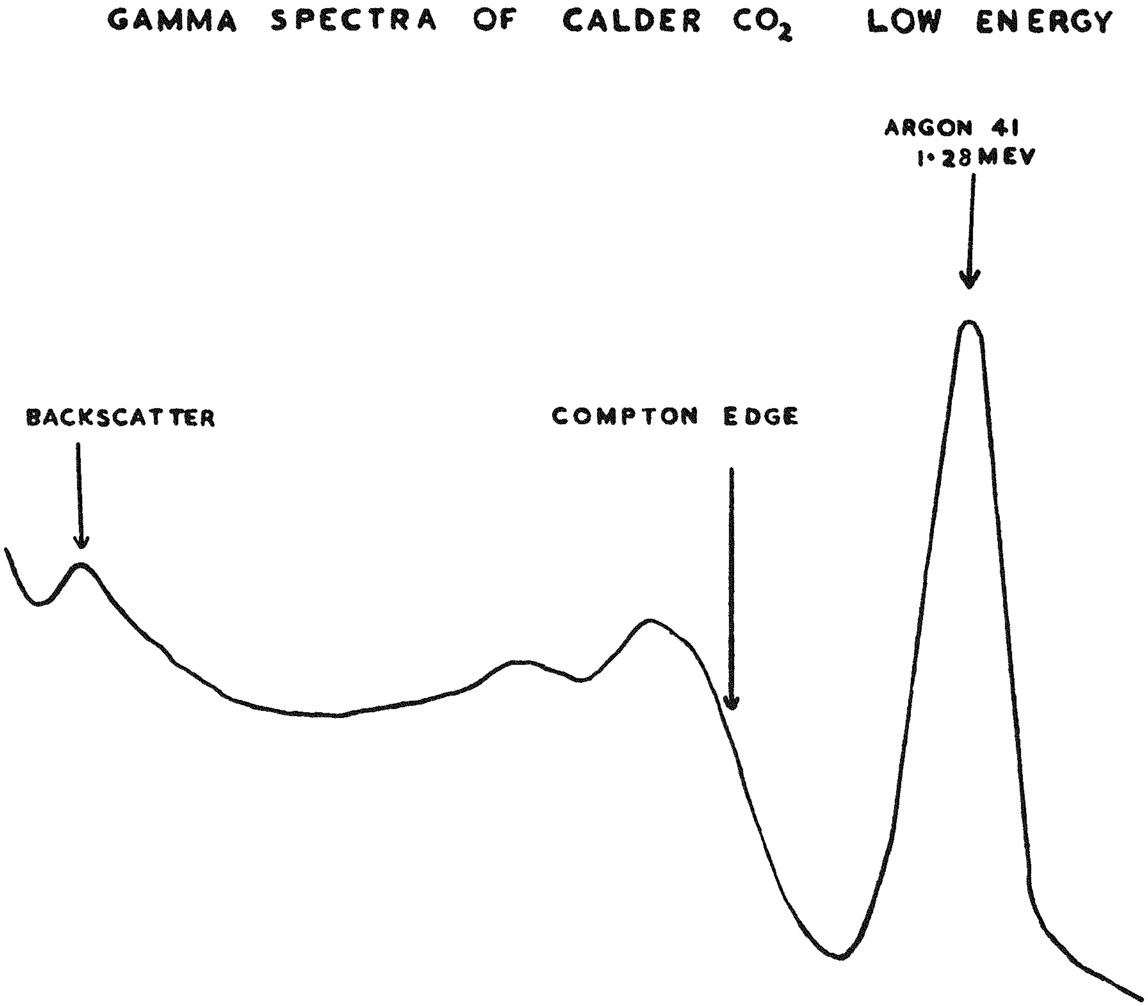


Fig. 11 - Residual Gas γ Spectrum

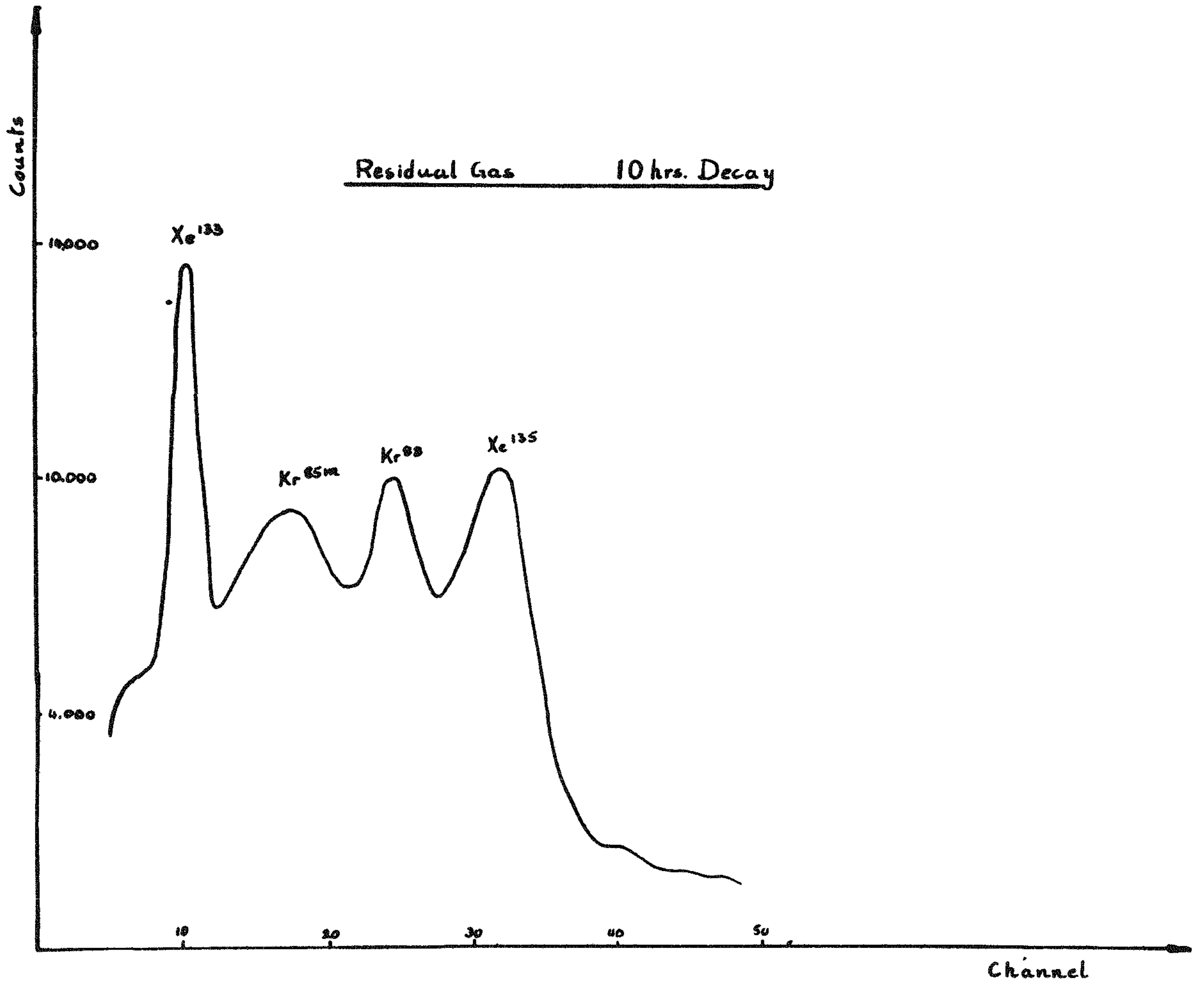


Fig. 12 - γ Spectrum of Residual Gas After 10 Hours Delay

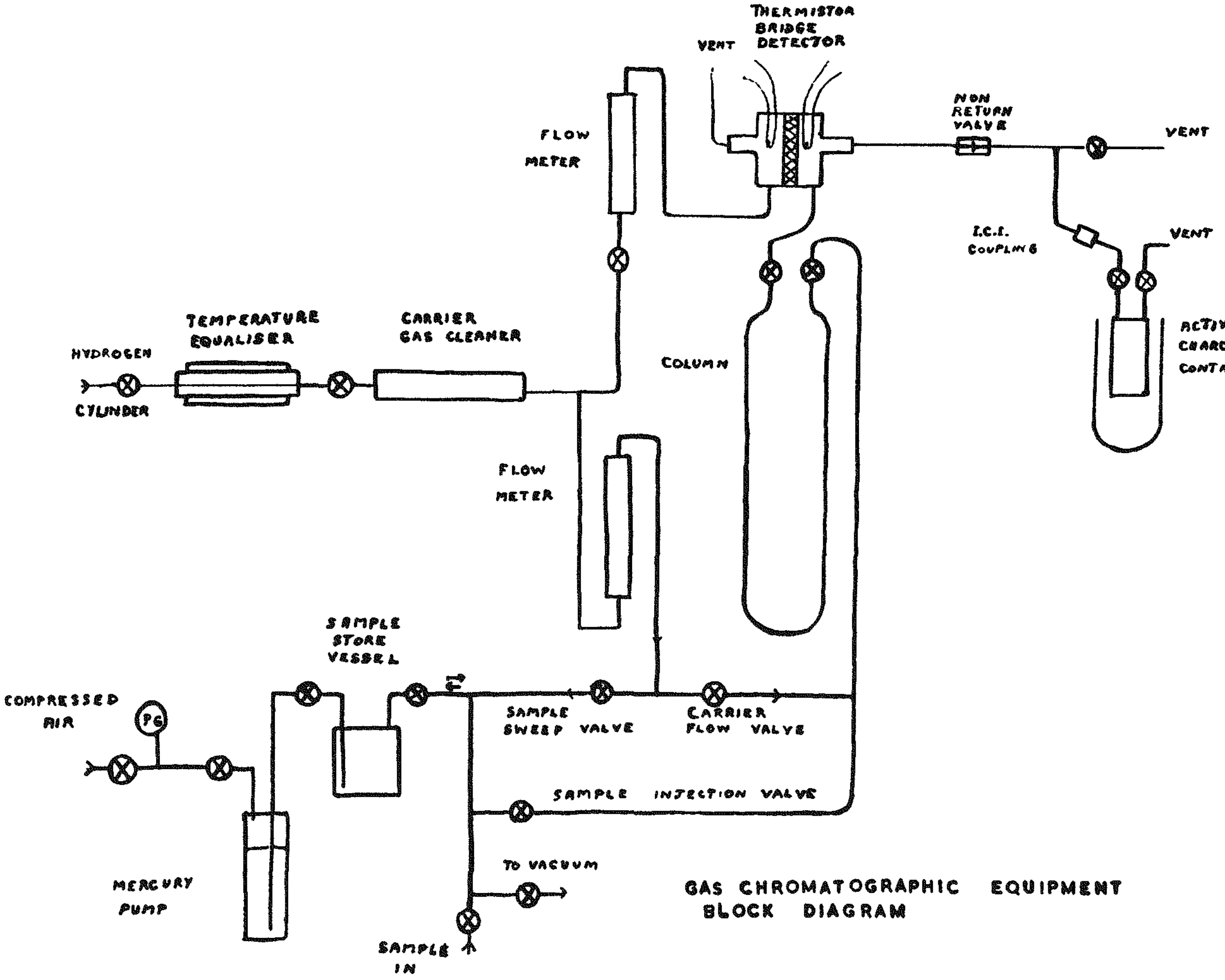


Fig. 13 - Gas Chromatographic Equipment. Block Diagram

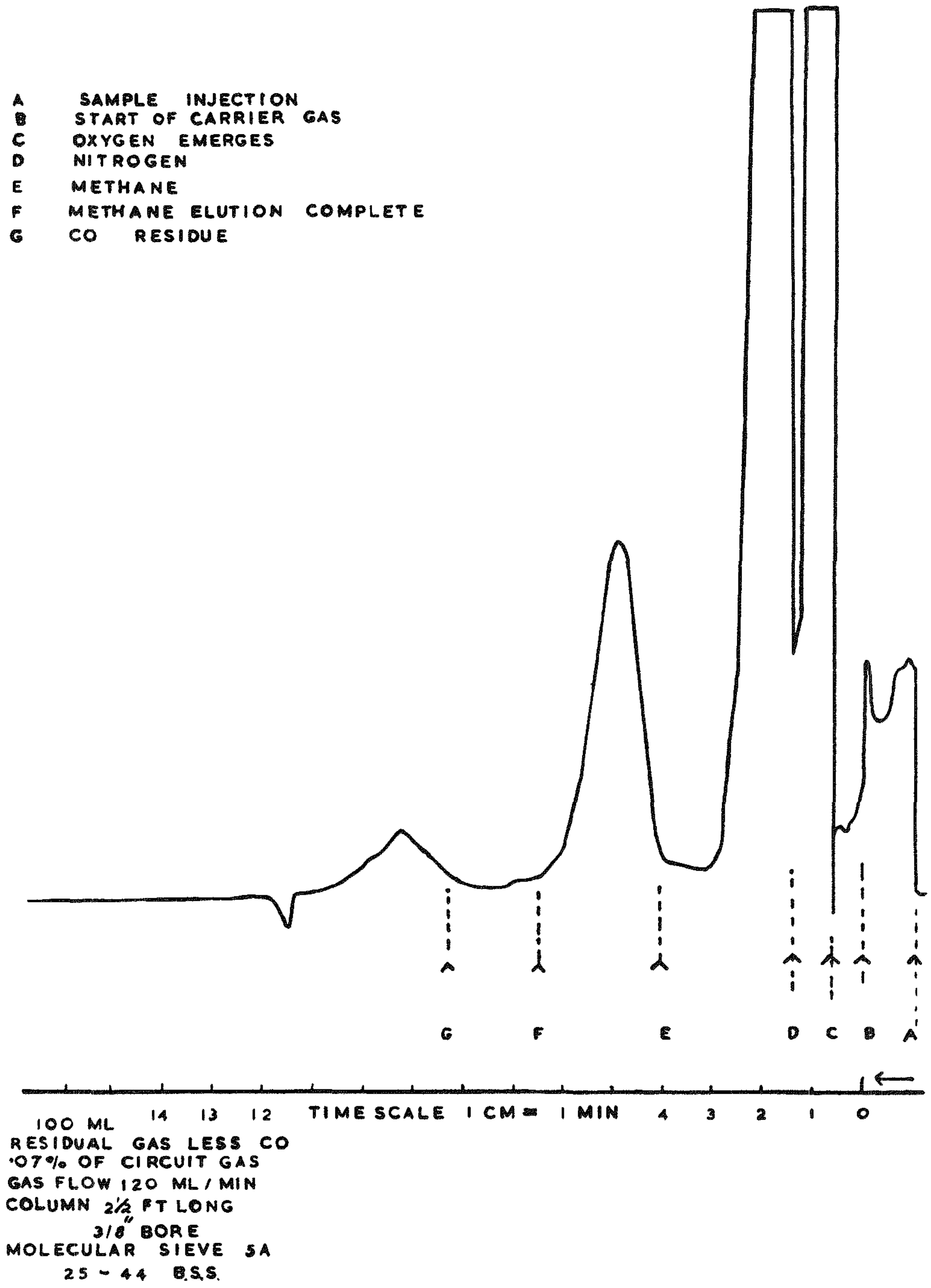


Fig. 14 - Gas Chromatographic Separation of Residual Gas

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EDITOR'S NOTE

All IGO-AM/W (No.) references are issued under the corporate author,

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Standards for the Chemical Analysis of Nuclear Materials

THE USE OF ATOMIC WEIGHTS IN URANIUM MEASUREMENTS*

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ABSTRACT

Uranium accountability at large installations, such as those operated by Union Carbide Nuclear Company, requires many measurements of U, both chemical and isotopic. These measurements are obtained for materials being processed in the plant as well as for all incoming and outgoing streams. If the shipper's basis of measurement differs from that of the receiver, undesirable discrepancies will result. A source of differences of this kind has been the nonuniform application of atomic weights, particularly of U, by U.S. Atomic Energy Commission installations.

Union Carbide Nuclear Company and Goodyear Atomic Corporation have recently abandoned the old chemical atomic weight for U in favor of a scheme based upon the physical atomic weights of the individual isotopes. Not only is this new method more accurate but it can be applied in a uniform manner to the analysis of U of any isotopic composition. It will eliminate biases due to atomic weight discrepancies among the participants. The U. S. Atomic Energy Commission is considering adopting it for use at all of its installations.

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*This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation for the U. S. Atomic Energy Commission

Thousands of analytical measurements of uranium are made daily in this country to evaluate process efficiency, follow development programs, and provide the necessary accountability for uranium being transferred from one account or location to another, and the atomic weight of uranium is used in each of these measurements. It will seem strange to most chemists, who are unaccustomed to questioning the validity of atomic weights, to learn that uranium atomic weights are not uniformly applied. Some installations handle natural uranium only and use the atomic weight established by the International Commission on Atomic Weights. Others use this value for natural uranium and values based upon nuclidic masses for isotopically altered material. Still others ignore the International Commission's value and use nuclidic masses altogether. Each of these schemes differs from the others, as will be shown later. We who are engaged in making highly precise uranium measurements should therefore be interested in using the most precise and accurate atomic weights possible. It is also of great importance to adopt a uniform practice in the application of uranium atomic weights or systematic discrepancies will certainly arise if the shipper of material bases his measurements upon values different from those of the receiver.

Many years ago, before the existence of isotopes was known, atomic weights were considered unchanging values and therefore it was believed the only improvement possible was through the use of more accurate and precise methods for their determination. More than 60 elements, including uranium, are now known to occur in nature in two or more isotopic forms. The isotopic composition of several of these elements is known to vary considerably, depending upon the source of the element. This means that the true atomic weight varies from sample to sample. There is evidence that indicates a slight variation in the isotopic composition of natural uranium. The uranium atomic weight picture becomes much more complicated if isotopic abundances are appreciably altered from the natural range. The addition of artificial isotopes to the mixture only adds to the confusion. Within the activities of the Atomic Energy Commission a very large effort, the gaseous diffusion process, is operated in order to make uranium richer in the isotope 235. Conversely, the rejected portion is depleted in U^{235} or enriched with respect to U^{238}. The atomic weight of the uranium near the top of a gaseous diffusion cascade has, therefore, been made smaller, while that near the bottom has been made larger.

Another large scale effort that changes the atomic weight of uranium is that of nuclear reactor operation. In a reactor, U^{235} is burned through fission and the uranium is, therefore, depleted with respect to U^{235} or, conversely, enriched with respect to U^{238} by the process. Also, during reactor operation, artificial uranium isotopes are formed from the natural isotopes by nuclear processes. These are U^{236} formed when U^{235} captures a neutron; U^{237} which can be formed by the n, 2n reaction from U^{238}; U^{239} which can be formed by the n, γ reaction from U^{238}; and U^{240} formed by the second order n, γ reaction with U^{238}. Other uranium isotopes from U^{227} to U^{240} are formed from nuclear reactions with other elements. Of particular interest to the chemist is the isotope 236 because its abundance is often high enough to materially change the atomic weight of the sample, and its long half-life (about 2.46×10^{7} years) assures us that the problem refuses to go away.

Considerable intermingling of gaseous diffusion and reactor materials has occurred so that a very large portion of the uranium we have today has not only been altered with respect to the abundance of its natural isotopes, but has additionally been contaminated by artificial isotopes, principally U^{236}.

The chemical atomic weight of natural uranium approved by the International Commission on Atomic Weights is 238.07. This is the value of Hönigschmidt and Wittner(1) and was determined upon uranium from several sources. These brilliant experimentalists, in one of the most precise chemical measurements yet made, compared UCl_4 to Ag and AgCl and UBr_4 to Ag and AgBr to give the value 238.074 ± 0.004 for 41 determinations. However, (Figure 1) since no artificial isotopes are recognized in this value, it cannot be used in their measurement or in the measurement of uranium containing them. It is therefore inapplicable to a very large percentage of the uranium analyses at AEC installations.

Another basis for measurement is the nuclidic mass or atomic mass of each isotope. Since muclidic masses are usually stated in the physical scale, they must be converted to the chemical scale for the chemist. As you know, the physical scale is related to the oxygen isotope 16 as exactly 16 while the chemical scale is related to "natural oxygen" as exactly 16. Obviously, the fathers of the chemical scale were not aware of the variability of the O^{18}/O^{16} ratio from source to source or "natural oxygen" would never have been chosen as the basis for a scale of atomic weights. In 1950, Nier(2) determined the ratio of the chemical scale to the physical scale to be 1.0002783 when atmospheric oxygen was used for the investigation. On the other hand, when water or iron ore was used as a source of oxygen the ratio was 1.000268 (see Figure 2). The difference in conversion factors thus determined from two sources of oxygen is due to a four per cent variation in the O^{18}/O^{16} abundance ratios. Nier said at this time that "...the accuracy of measurement has now reached the stage where it is meaningless to speak of precise atomic weights unless the source of material is clearly defined." Actually, neither of these values is commonly used today but rather an intermediate figure of 1.000275. Wichers(3) therefore says that "...natural oxygen has become effectively defined, by usage of the International Commission on Atomic Weights, as that mixture of isotopes whose atomic weight is 1.000275 times the nuclidic mass of oxygen isotope 16." One can see then that, through practice, the chemical scale of atomic weights is, in reality, related to the nuclidic mass of the oxygen 16 isotope rather than to "natural oxygen" as the classic definition says it is. The value of 1.000275 is widely used today as the factor relating the two scales of atomic weights.

Since it is impossible to measure all uranium relative to the natural material, other bases of measurement must be examined. The International Commission's atomic weight could be used for natural uranium and nuclidic masses for all other uranium if no significant difference existed between the two. Unfortunately, this is not the case (see Figure 3). Using the latest values for nuclidic masses and isotopic abundances, the computed atomic weight for natural uranium is 238.039, which is significantly different

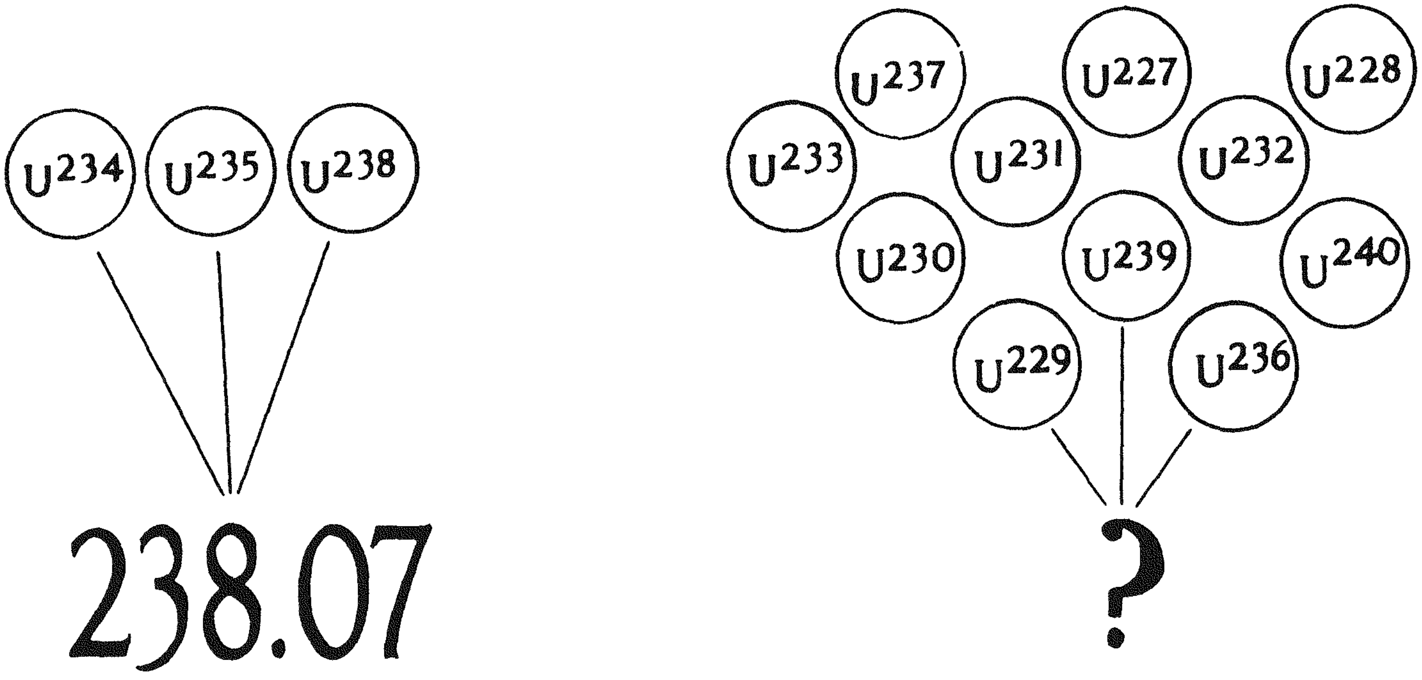

Fig. 1 - Artificial Isotopes are not recognized in the International Commission's Atomic Weight

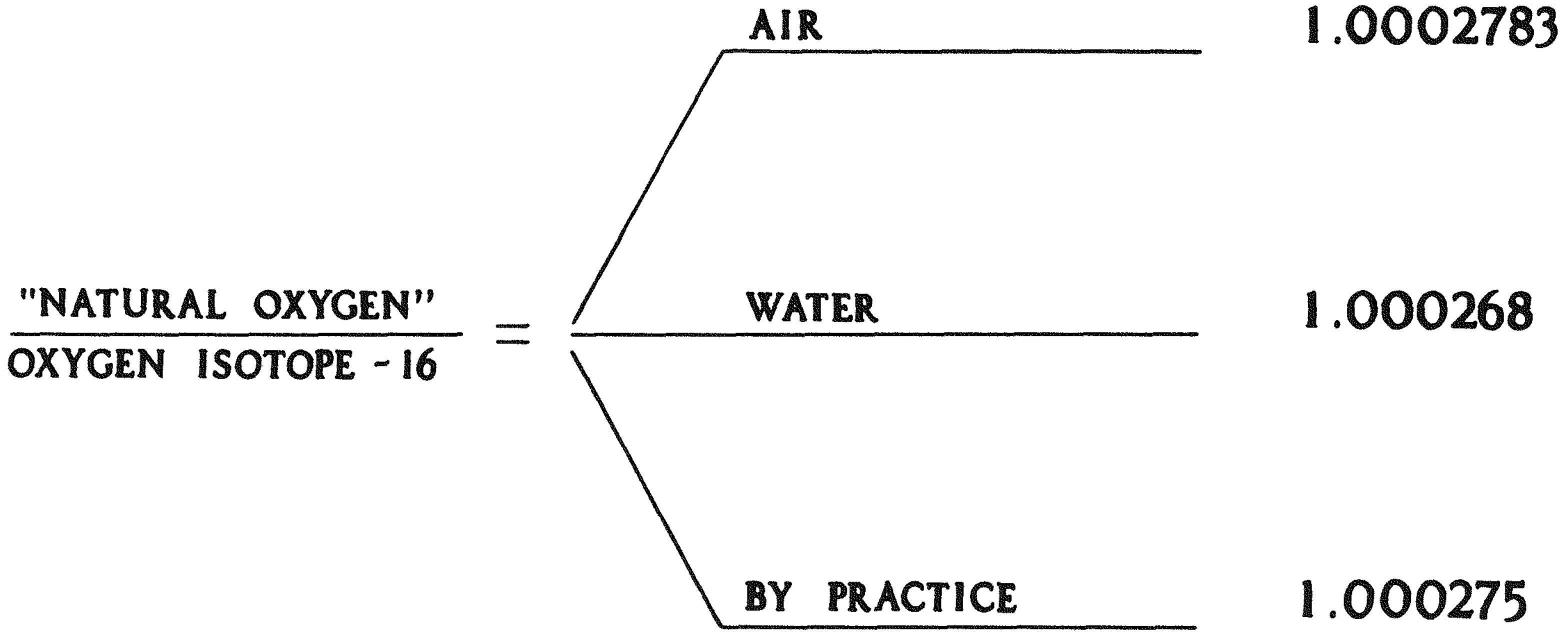

Fig. 2 - "Natural Oxygen," the Basis for Chemical Atomic Weights, Varies Considerably

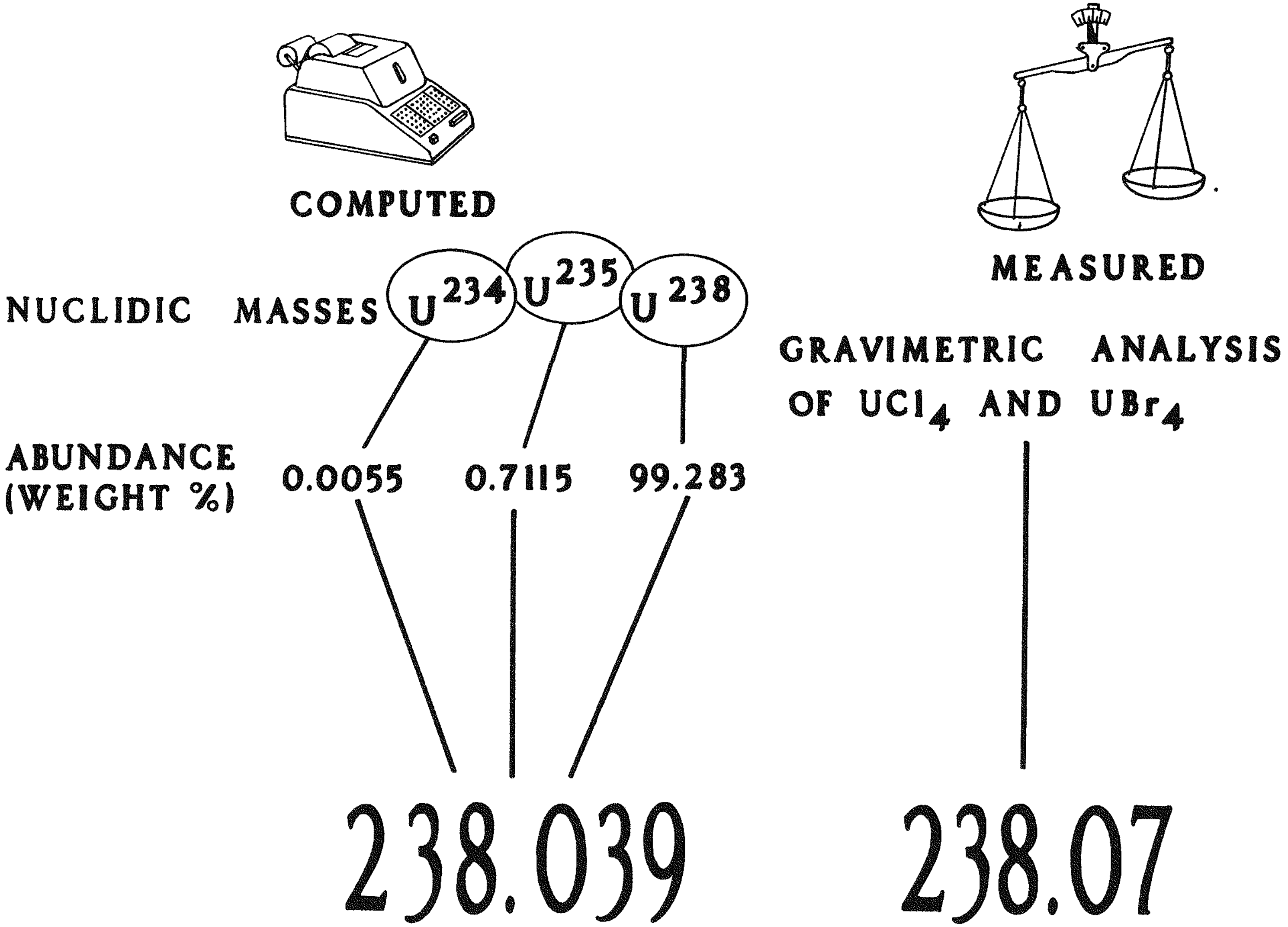

Fig. 3 - Atomic Weight of "Natural Uranium"

from 238.07. If this dual system were employed, natural uranium would be debited to a system at a relatively higher uranium content than either enriched or depleted material would be credited (see Figure 4). It is easily seen then that such a system is untenable.

The only remaining basis is adoption of the nuclidic mass values, which were determined by physical measurements, for the computation of the atomic weight of all uranium. This step has been proposed by Union Carbide Nuclear Company(4) to the Atomic Energy Commission for Commission-wide adoption, and is now under study by the Commission.

Precise nuclidic masses are calculated from the kinetic energies associated with radioactive disintegrations and nuclear reactions or by studies of mass differences of "doublets" with the mass spectrometer. Both these methods are highly precise as can be adjudged from the great precision to which nuclidic mass values are stated. Certainly for elements with few isotopes and for elements with a strongly predominant isotope, the mass spectrometric values should be more accurate than those determined chemically through stoichiometric relationships. As we have seen, nuclidic masses are the only basis of measurement applicable to all the isotopes of uranium. They provide the only means of positively avoiding discrepancies from atomic weight differences in uranium accountability within and between installations.

In order to assure uniformity of treatment by all installations, a statement of the basic considerations in the case and some rules of computation are in order:

A. Basic Considerations

1. All uranium is considered to be a mixture of individual uranium isotopes. (Figure 5)
2. The chemical atomic weight of uranium in any sample is computed from the nuclidic mass and abundance of each isotope in the mixture. (Figure 6)
3. The chemical atomic weights used for all other elements, except the transuranic elements, are those accepted by the International Commission on Atomic Weights at its last meeting (Paris, July 1957).(5)

B. Rules of Computation

1. Compute the nuclidic mass on the chemical scale for each uranium isotope by dividing the nuclidic mass, based on the physical scale,(6) by 1.000275, retaining all digits.
2. The chemical atomic weight is the average of the nuclidic masses on the same scale weighted according to the abundance of each isotope in the mixture.

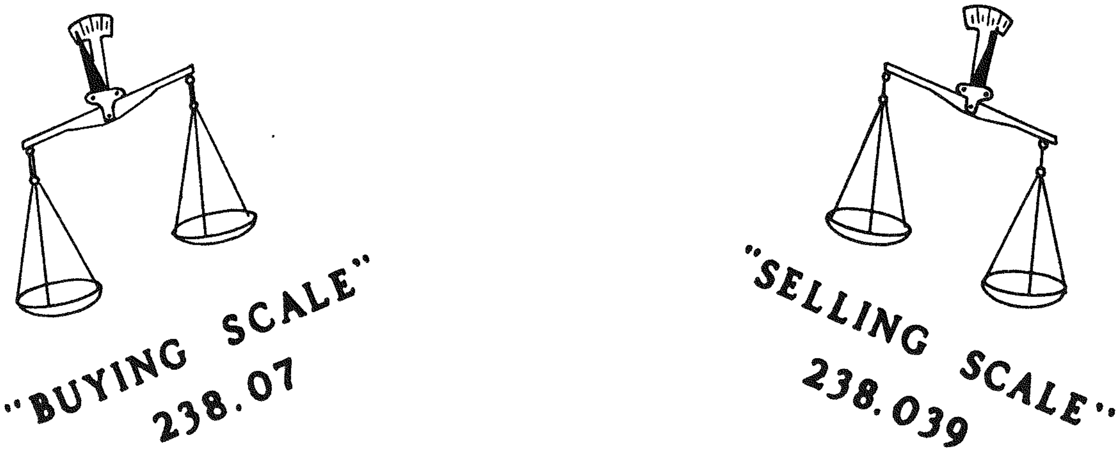

Fig. 4 - A Dual System is Untenable:Somebody Loses !!

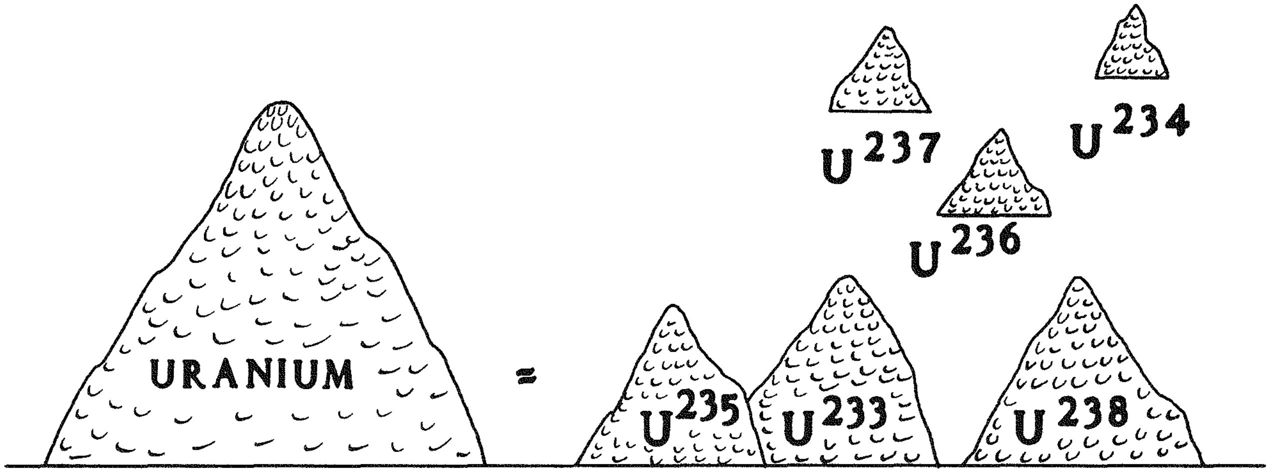

Fig. 5 - Consider All Uranium a Mixture of Individual Isotopes

$$\sum \left[\frac{\text{NUCLIDIC MASS}}{\left(\text{EACH ISOTOPE}\right)} \right] \left[\frac{\text{ABUNDANCE}}{\left(\text{EACH ISOTOPE}\right)} \right] = \underline{\text{ATOMIC WEIGHT}}$$

Fig. 6 - Equation for Computing Atomic Weight for Each Mixture

$$\text{Atomic Weight} = \cfrac{100}{\cfrac{\text{Wt. \% } U_A}{\text{Nuc. Mass, Chem., } U_A} + \cfrac{\text{Wt. \% } U_B}{\text{Nuc. Mass, Chem., } U_B} + \ldots}$$

3. The nuclidic mass, chemical scale, of each uranium isotope is rounded to six digits as follows:

In rounding off,(7) if left-most discarded digit is:

a) Less than 5,	Leave right-most retained digit unchanged.
b) Greater than 5, or is a 5 followed by digits not all of which are zero,	Increase right-most retained digit by one.
c) 5, followed only by zeros,	Leave right-most retained digit unchanged, or increase by one, whichever is necessary to make it an even number.

4. Where desired, compute gravimetric factors from chemical atomic weights retaining all digits, and round the gravimetric factor to five digits using the rules described in 3 above.

Of course, these computations would be simpler and less confusing if, instead of a physical scale and a chemical scale, we had a single unified scale.(8) There is a good likelihood that a unified system based upon the carbon isotope-12(8,9) as exactly 12 will be adopted at the next meeting of the International Commission on Atomic Weights. Adoption of a C^{12} system, or any other system, will not eliminate discrepancies resulting from the use of the chemically-measured atomic weight of uranium. The problem lies in the fact that nuclidic masses must be used for all uranium which contains artificial isotopes and that the international value is incompatible with the best nuclidic mass values.

As measurement methods are improved and more and more variations in natural isotopic composition are measured, and as the separation of natural isotopes and the presence of artificial ones become more common, the International Commission on Atomic Weights, or a similar authoritative body, will need to take on the job of international approval of nuclidic masses which will, in an increasing measure, replace atomic weights as applied to the naturally occuring element.

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APPENDIX A

NUCLIDIC MASSES OF URANIUM ISOTOPES

Nuclide	Trilinear Chart of Nuclides (a)		Unpublished Values (b)	
	Physical Scale	Chemical Scale (c)	Physical Scale	Chemical Scale(c)
U^{227}	227.1020	227.0396	227.103100	227.040664
U^{228}	228.10262	228.03991	228.103773	228.041062
U^{229}	229.10499	229.04200	229.106100	229.043113
U^{230}	230.10595	230.04269	230.107058	230.043796
U^{231}	231.10863	231.04509	231.109780	231.046242
U^{232}	232.10980	232.04599	232.110936	232.047123
U^{233}	233.11240	233.04831	233.113585	233.049496
U^{234}	234.11408	234.04972	234.115310	234.050946
U^{235}	235.11750	235.05286	235.118658	235.054018
U^{236}	236.11959	236.05467	236.120776	236.055861
U^{237}	237.12275	237.05756	237.123942	237.058751
U^{238}	238.12522	238.05975	238.126440	238.060973
U^{239}	239.12916	239.06342	239.130320	239.064577
U^{240}	240.13181	240.06579	240.132880	240.066862

(a) Sullivan, W. H., Trilinear Chart of Nuclides, Union Carbide Nuclear Company, Oak Ridge National Laboratory, January 1957.

(b) Unpublished values furnished the author by Ralph J. Jones, U. S. Atomic Energy Commission, Washington, D. C. These values are attributed to Everling, Konig, Mattauch, and Wapstra and will be published soon in Nuclear Physics.

(c) Nuclidic Mass, Chemical = $\frac{\text{Nuclidic Mass, Physical}}{1.000275}$

STANDARDIZATION IN RADIOISOTOPES AT THE INTERNATIONAL LEVEL

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ABSTRACT

The need for standards in the nuclear field has become more and more apparent during recent years with the increasing use of nuclear reactors and radioisotopes. Standardization groups in individual countries have met and are continuing to meet this problem on a national level; in addition, many are attempting to work out international solutions by acting through the International Standards Organization (ISO) which is the international representative of many national organizations. There are in addition a number of other organizations (e.g., the International Commission on Radiochemical Units of Measurement, International Union on Pure and Applied Physics, World Health Organization, and International Atomic Energy Agency) which are active in this work, often only in a specialized area, however. The work of a number of these organizations will be discussed briefly together with a somewhat more detailed account of the program of the ISO for setting standards in nuclear nomenclature, reactor safety, radiation protection, and radioisotopes.

* * * *

The need for standardization in scientific and engineering work now appears so obvious that no one questions it. Yet such was not always the case even in matters affecting our every-day living. For example, less than 70 years ago there were no standard time zones in the United States, with the result that a traveler going from one location to another was never sure whether he would find his arrival time to be before or after dinner. With increased speed of transportation and communication and with increased industrialization the necessity

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* Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

for standardized time and measurement units became obvious. About 1900 Frederick Taylor in the U.S.A. and Henri Fayol in France attempted to set standards of work by using time and measurement units. These methods were the beginning of a new aspect in standardization-time and motion studies or, as the practitioners themselves prefer to express it, the profession of efficiency engineering was born.

It comes as somewhat of a surprise to many persons to learn that there is a veritable catalog of human movements, lifting, turning, raising, lowering, etc., each with a "standard time." This type of attempt at standardization has led to some unpleasant and unfortunate labor-management relations, and is certainly not the type of standardization under discussion today.

Science has always prided itself on being truly international, so it is not surprising to find the formation of international standardizing bodies such as the International Bureau of Weights and Measures in Paris. This group, formed in 1875, is the custodian of the international standards of mass and length, and serves as the official arbiter in matters of units.

Actually, by act of Congress in 1832 standard units of weight and measures were set up in the U.S.A. In 1893, definitions and relationships between the U.S. system and the metric system were defined. But as industrialization increased, the need for standard practices and standard equipment in factory operation became apparent. Early attempts at standardizing led to the realization that a national organization with national interests was the only really sensible way to handle this problem.

The American Engineering Standards Committee which was set up to study these problems led in 1918 to the formation of the American Standards Association (ASA), whose sponsorship is industry and discipline wide. The ASA is concerned with standards in such diverse fields as safety engineering practice, manufacture, shipping, and testing, to mention but a few. The concern is of a more applied nature than that of, say, the National Bureau of Standards (NBS), which is interested in the fundamental and scientific aspects of standardization.

In the specific field of radioactivity, the NBS has been charged with the responsibility of maintaining and measuring standard solutions or samples of radioactive materials. Historically these were radium standards; indeed the fundamental unit, the curie, was originally defined as the number of disintegrations occurring in one gram of radium. With the advent of artificial radioactivity and controlled nuclear fission, the numbers and quantities of radioactive isotopes haye greatly increased. The NBS continues to make fundamental measurements of disintegration rates for standardization, but again expanded technology demands standardization in many aspects of radioisotope production, measurement, distribution and use which the NBS has little interest or reason to become active in. Just as the American Standards Association (ASA) and its many sponsoring organizations such as the ASTM, ACS, ASME, etc., were called upon to set standards for safety, methods, shipping, handling, measurement, etc., for other industries previously, just so has it been called upon to do a similar task for the nuclear industry. The Nuclear Standards Board of the ASA was set up some four years ago to handle these problems. The board has 31 member organizations representing 11 professional groups, 11 individual organizations, 7 governmental agencies and two other groups, The National Safety

Council and the AFL-CIO. The board has set up 7 projects denoted as committees N1 through N7; the title of each is tabulated below:

N-1 Definitions and Term

N-2 General and Administrative Standards

N-3 Nuclear Instrumentation

N-4 Electrical Apparatus and Systems

N-5 Chemical Engineering

N-6 Reactor Safety

N-7 Radiation Protection

In addition, there are a number of other groups such as the American Society for Testing Materials, American Nuclear Society, etc., which are active in this field. Most of these groups are sponsors of ASA and work through it.

Rapid expansion of nuclear technology has truly made nuclear science an international technology. Nations which have essentially no heavy industry - chemical, manufacturing, or fabricating - are building reactors, producing radioisotopes, and handling considerable amounts of radioactive materials. So the problem of standardizing methods, techniques, safety requirements, etc., has become an international one. The creation by the United Nations of numerous sponsoring, consulting, and advisory groups such as the International Atomic Energy Agency, United Nations Technical Assistance Administration, the UNESCO organization, to name but a few, points up the importance placed on international cooperation in technical fields. The United States government has, in addition, a number of programs of its own which are carried out through treaty and agreement with other national groups. The Organization of American States is an example of such a group. Last year, for example, excluding contributions to U.N. and other inter-governmental organizations, the United States spent 130 million dollars on technical assistance. We sent 4300 experts to 60 countries and trained 8300 persons from other countries here. A considerable amount of this assistance was in the nuclear field, so this is a very real international program.

Two of the outstanding scientific groups active in the standardization field are the International Union of Pure and Applied Physics (IUPAP), and the International Commission for Radiological Protection (ICRP). The IUPAP works in the field of physics, preparing reports and tables of physical constants. It attempts to secure international agreement on constants, nomenclature and related matters. The ICRP deals with radiation protection and publishes recommendations concerning the same.

The International Standards Organization (ISO) serves as the primary supernational group in the area of standardization. With National Standards bodies in 40 countries as members, the ISO has as its aims the development of standards in the world with a view to facilitating international exchange of goods and services and to developing mutual cooperation in the spheres of intellectual, scientific, technological and economic activity. The American Standards

Association is the American representative to this group; Canada is included in the U. S. representation. Since the sponsors of ASA include 62 groups such as technical societies (The American Chemical Society, American Nuclear Society, American Medical Society), industrial organizations (Atomic Industrial Forum, Electric Light and Power Group, American Iron and Steel Institute), government (National Bureau of Standards, USAEC, U. S. Department of Labor), and labor (AFL-CIO, International Brotherhood of Electrical Workers, International Association of Machinists), it genuinely represents the entire spectrum of interested groups in American business and professional life. Unlike other more specific international organizations, the ISO represents no one faction, and has no aim other than that of promoting international standards. The present effort in the field of radioisotopes and radioactivity is strongly oriented toward immediate practical, fundamental goals:

1. definitions, symbols and terminology
2. radiation protection
3. reactor safety
4. handling, packaging, and measurement of sealed and unsealed sources

In general, the procedure used by ISO member bodies is as follows:

For a particular problem a working group is set up. One nation is given responsibility (the secretariat) for the group and all interested nations are invited to participate. Each national representation brings to the group conference the national standards (if such exists) at present in effect in his country.

Different aspects of the problem may be assigned to various member groups, but in the end an effort is made to produce a standard or recommendation which will be acceptable to all nations. Because of language barriers, differences in national regulations and regulating procedures, and human contrariness, a satisfactory solution to some apparently even simple problems is often quite difficult. Because the standards recommended must be universally applicable, it is often difficult and exasperating work. The problems are often more complicated because of conflict of interests occasioned by other supernational groups.

The World Health Organization (WHO), for example, which is a UN-sponsored group, has broad interests in the fields of medicine and public health. Through concern for fall-out and general radiation protection, WHO has interests in radioisotopes. Recently WHO published a book of analytical procedures which lists standard methods to be used in radiochemical analysis.

The International Labor Organization (ILO) is also interested in safety and protective measures concerning radioactivity.

The International Atomic Energy Agency (IAEA), created by the U.N. to accelerate and enlarge the contribution of atomic energy to peace and prosperity, is also vitally concerned in international standards, although primarily it serves as a consultive and educational medium throughout Europe and Asia. The

ILO and the IAEA have recently proposed a change in the well-known "trefoil" basic ionizing radiation symbol. The "trefoil" which was designed and first put into use at the University of California has been almost universally adopted. At the recent International Standards Organization (ISO) meeting, however, the adoption of this symbol was blocked, and future adoption made uncertain because of the proposal by ILO and the IAEA that a "skull and cross-bones" type symbol be used.

The ILO is also concerned with the transportation and shipping of radioisotopes. Proposals concerning transportation have been made by international organizations (other than ISO) which would make it difficult or impossible by the U.S.A. to comply with these international agreements and our own ICC regulations.

The progress which has been made in ISO has been mainly (as might be expected) in areas in which considerable national progress has been made: reactor safety, radiation protection, terminology, definitions, and symbols.

Since the ISO represents the ASA, which in turn reflects the views, programs, and accomplished work of its sponsoring organizations, it seems that certain admonitions, encouragements, and requests would not be out of place here.

First, it behooves each and every person working in the nuclear field to see that American methods and techniques, radiation protective measures, and proved equipment and devices for handling or transporting radioactivity be recorded promptly in the literature or placed in the hands of the proper professional group concerned with the particular problem. This cannot be emphasized too greatly. In order for Americans to propose an international standard, some sort of an American standard or standardization technique is essential. European scientists and engineers respect American know-how; but it must be formalized, not word of mouth. In this respect, the present state of affairs leaves much to be desired, but the situation is improving. The ORNL Master Analytical Manual; the work of ASTM subcommittees such as that on radioactivity in industrial water, dosimetry, and applications of radioactivity; and the recently-begun National Research Council Monographs on radiochemistry, give us a literature of standard methods from which to work.

Second, familiarize yourself with procedures and practices from overseas. It is often quite enlightening.

Third, in our associations with foreign visitors at our laboratories or at meetings, let us not be too quick to deprecate the methods and techniques of others.

Neither let us be too self-complacent or boastful concerning our own. After all, if we have the better method, it will prove itself.

In conclusion, may I say that standardization on the international level has just begun; we have a long, tough road ahead. The progress that is made on the international level is determined to a very great degree by the progress and results that are obtained by all of us at our own laboratory level.

PROBLEMS IN GRAVIMETRIC DETERMINATION OF URANIUM IN URANIUM TRIOXIDE*

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ABSTRACT

Large accountability and monetary discrepancies in the Atomic Energy Commission's operations can result from several major sources of error in the gravimetric determination of the uranium in uranium trioxide. These sources of possible bias are 1) the atomic weight used for uranium, 2) absorption of moisture, and 3) use of the incorrect gravimetric factor for uranium in the black oxide. Errors from these sources can be minimized by using physical measurements converted to the chemical atomic weights; a dry atmosphere for blending, subsampling, and weighing; and a gravimetric factor based on titration.

* * * *

Each year the installations of the Atomic Energy Commission receive and ship very large quantities of uranium as the trioxide. Some of these transactions involve purchases; others are inter-installation transfers. There are several prominent sources of bias in the gravimetric measurement of the uranium in this material, any one of which can lead to large accountability and monetary discrepancies. A very small bias of 0.05% in the uranium content of the trioxide represents a discrepancy of one pound for each ton of uranium which is equivalent to about $10 per ton in the purchase price.

The major sources of error or bias in the gravimetric method are 1) use of the atomic weight for uranium derived from chemical measurements, 2) absorption of atmospheric moisture by the trioxide, and 3) use of an incorrect gravimetric factor for uranium in the black oxide produced by ignition. Studies have been made of these sources of error; the findings will be discussed individually.

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* This document is based on work performed at the Oak Ridge Gaseous Diffusion Plant operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

ATOMIC WEIGHTS

Some installations and laboratories are still using 238.07(3) for the atomic weight of natural uranium. This value was determined by chemical methods and is 0.013% greater than the value of 238.04(7,8) which is derived by converting the physical measurements of the nuclidic masses to the chemical scale. Since the atomic weights of the isotopes of uranium have not been measured by chemical methods, the atomic weight of uranium at all isotopic enrichments should be calculated from the physical measurements of the nuclidic masses as recommended by Barton.(1)

ABSORPTION OF ATMOSPHERIC MOISTURE

The literature contains meager information on the hygroscopic nature of uranium trioxide. Katz and Rabinowitch(4) mention the hydrates and that the trioxide absorbs some water from the air to form the dihydrate.

The yellow uranium trioxide(5) is so hygroscopic that a 5-gram sample, exposed to the usual room atmosphere, cannot be weighed accurately on an analytical balance as it will not reach a rest point. This rapid increase in the weight of the sample was measured using an automated chain-o-matic balance attached to a calibrated pen recorder. The data are shown in Table I.

TABLE I

INCREASE IN WEIGHT OF A FIVE-GRAM SAMPLE EXPOSED TO ATMOSPHERIC MOISTURE

Time		Weight Increase	
Minutes or	Hours	mg	Per Cent
0	0	0	0
1.5	0.025	0.6	0.010
3	0.05	1.1	0.019
6	0.10	2.0	0.035
9	0.15	2.7	0.047
12	0.20	3.5	0.061
15	0.25	4.1	0.072
18	0.30	4.8	0.084
21	0.35	5.4	0.095
24	0.40	5.9	0.103
30	0.50	6.9	0.121
60	1.00	10.5	0.184
120	2.00	16.3	0.286
180	3.00	22.1	0.388
240	4.00	27.1	0.476
300	5.00	31.5	0.553

These data show that the trioxide absorbs moisture immediately upon being exposed to the atmospheric moisture.

Approximately 1-1/2 minutes are required to weigh a sample during which time the sample increases in weight by 0.01%. Most samples are blended in the laboratory which require a minimum of 30 minutes and, if done in the usual room atmosphere, the increase in weight will be at least 0.12% and possibly more as the additional agitation may increase the exposure to the atmosphere. The subsampling for specification analyses also takes several minutes and during this exposure to the atmosphere there will be an additional increase in weight of 0.03 to 0.04%. An increase in the weight of the sample results in an apparent decrease in the uranium content which will be reflected as a bias in the analysis. Thus, a dry atmosphere is needed for the blending, subsampling, and weighing of samples.

PROTECTION FROM ATMOSPHERIC MOISTURE

The trioxide is transferred in a dry box to the shell of a Patterson-Kelley Twin Shell Blender. The shell is sealed, removed from the dry box, and rotated. Subsampling from the shell and weighing of the sample are also performed in the dry box.

The trioxide increases in weight when stored with the usual desiccants, such as Drierite or calcium chloride, even in a plastic vial within a desiccator. Samples are prepared for storage by transferring the oxide in a dry box to glass jars which are closed with a metal cap and taped. The jars are removed from the dry box and sealed immediately with paraffin.

USE OF INCORRECT GRAVIMETRIC FACTOR FOR URANIUM IN BLACK OXIDE

The nonstoichiometry of the uranium-oxygen system is discussed by Katz and Seaborg(6) with special emphasis on the uranium(IV,VI) oxide. Brouns and Mills(2) have reported that ignition of uranium trioxide at 800° C for many hours produces an oxide which has less than the theoretical amount of uranium required for the oxide, U_3O_8.

The usual procedure in the gravimetric method is to ignite the yellow uranium trioxide for one hour at 850° C and apply the stoichiometric gravimetric factor to the weight of the black oxide formed. Samples of trioxide from a production source were ignited under these ignition conditions and the percentage of uranium in the oxide formed was determined by titration to be 84.74% which is approximately 0.06% less than the percentage of uranium in the stoichiometric compound. The use of the stoichiometric factor of 84.80% for natural uranium would thus bias the analysis high by 0.06%. The ignition was continued for 80 hours, during which time the oxide composition did not reach the theoretical value, as shown in Figure 1. The ignition of samples for one hour at 900° C produces an oxide, as shown in Figure 2, containing only 84.76% uranium. Thus, a method is needed to provide either a stoichiometric compound or an oxide having a reproducible uranium value.

PROCEDURES FOR OBTAINING THE STOICHIOMETRIC COMPOUND

Samples of trioxide when ignited for 80 hours at 900° C form an oxide which is stoichiometric and the theoretical value can be used in the analysis. A stoichiometric oxide is also produced by ignition of samples at 1000° C for about eight hours, as shown in Figure 3, but these ignition conditions are so

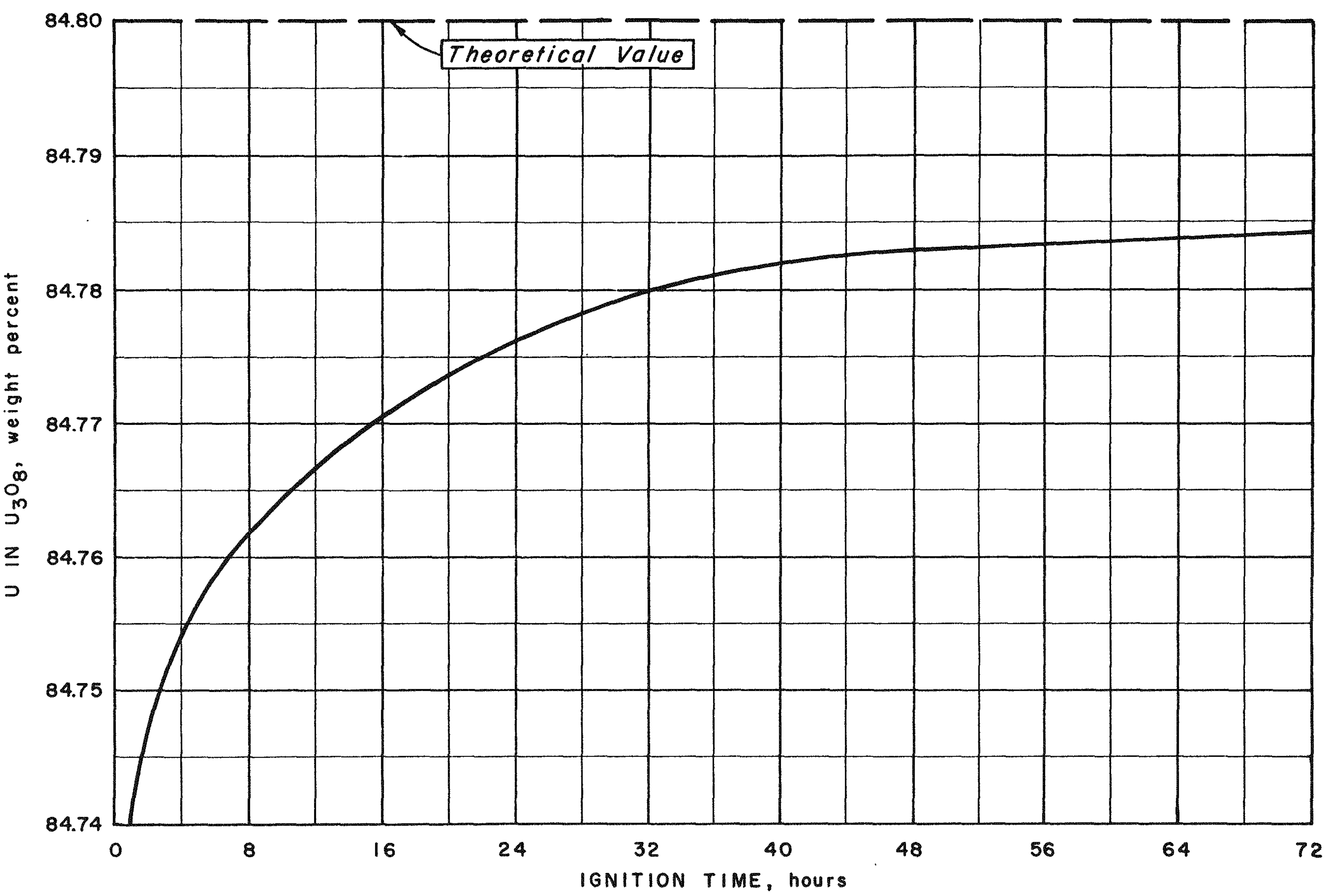

Figure 1. Ignition of UO_3 at 850° C

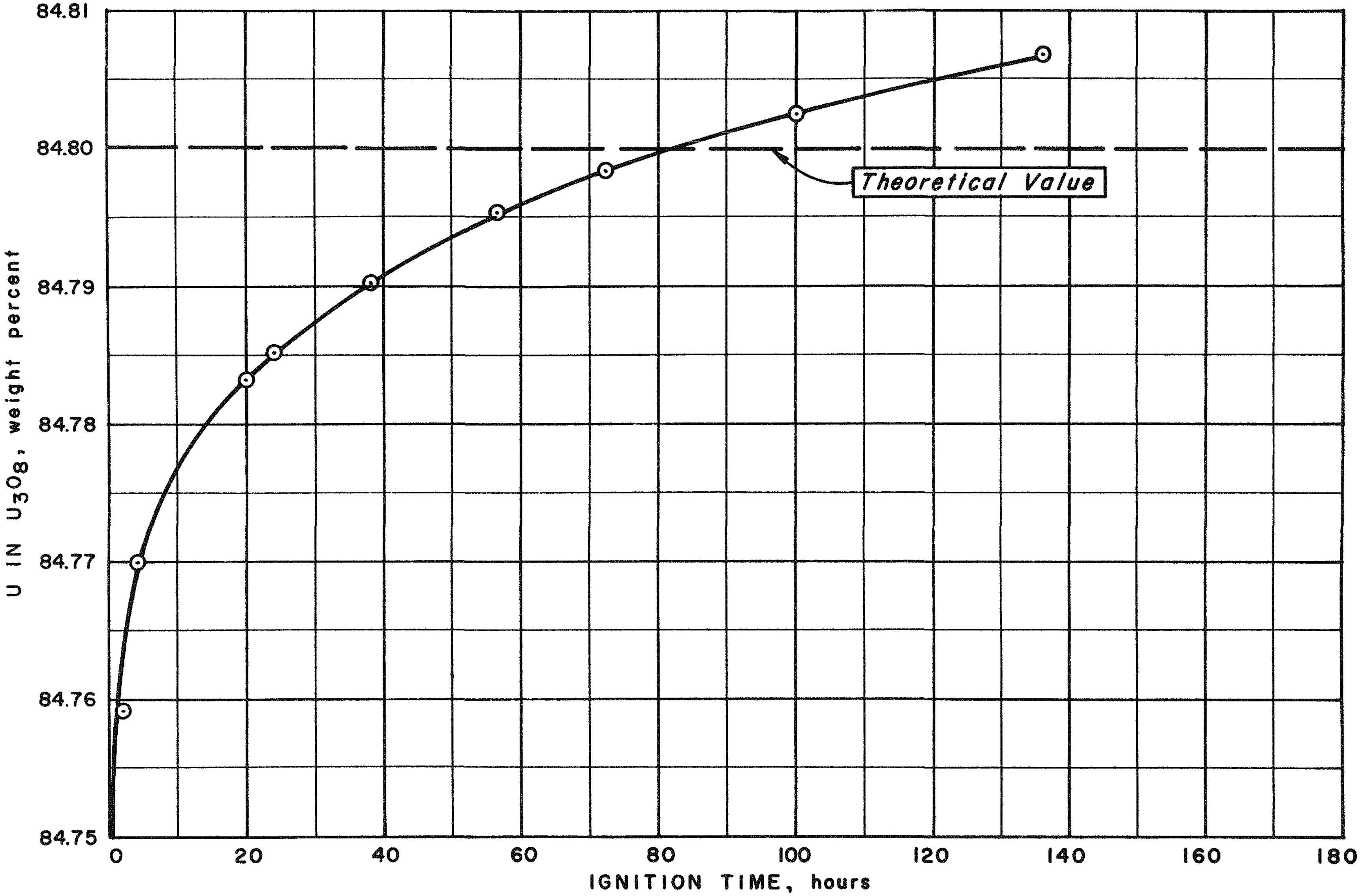

Figure 2. Ignition of UO_3 to U_3O_8 at 900° C

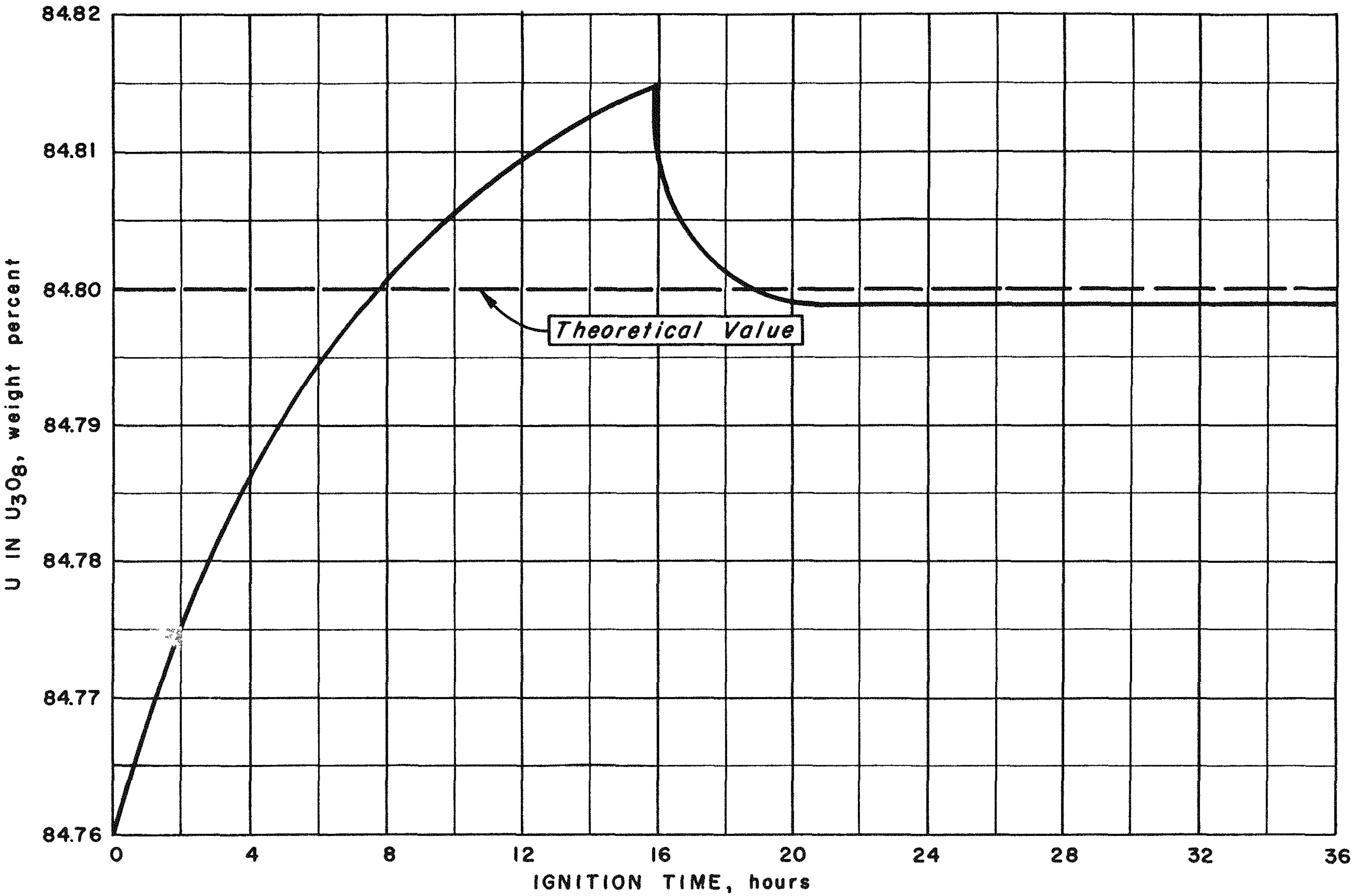

Figure 3. Ignition of UO_3 at 1000° C; followed by ignition at 850° C

critical that slight variations in the temperature and/or period of ignition may vary significantly the composition of the oxide. The preferred procedure is to ignite the trioxide for 16 hours at 1000° C and then at 850° C for four hours. Another method is to add hydrogen fluoride to the trioxide, evaporate to dryness, and then ignite at 850° C for 16 hours (the first hour in a steam atmosphere to prevent loss of uranium by volatilization), as shown in Figure 4.

PREPARATION OF OXIDE WITH CONSTANT GRAVIMETRIC FACTOR

Long periods of ignition are not practical and it is not necessary to ignite the oxide to the stoichiometric form so the theoretical gravimetric factor may be used without bias in the calculations. Samples with the same history of preparation when ignited under identical conditions produce a black oxide which has a uranium value that is constant though usually less than the theoretical value. The percentage of uranium in the oxide is determined by the precise potentiometric titration method developed by Voss and Greene(9) and the resultant gravimetric factor is applied to the weight of oxide formed to obtain the true uranium content.

OXIDE COMPOSITION VARIES WITH IGNITION TEMPERATURES

Black oxide which has previously been ignited for several hours at 850° C shows a weight loss of 0.01 to 0.02% with a corresponding increase in uranium content when ignited at 900° C for two hours, as shown in Figure 5. A loss in weight or an apparent increase in the uranium content was observed when the oxide was ignited at 1000° C for two hours, after the initial ignition of 850° C. These data show the necessity for using furnaces in which the temperature is measured with a calibrated potentiometer and accurately controlled. The temperature near the door of the standard muffle furnace is usually 50-100° C less than at other locations in the furnace. Samples should always be ignited at a fixed temperature and for a constant period of time to minimize variations in the oxide composition.

GRAVIMETRIC FACTOR FOR OXIDES CONTAINING SULFUR

Some of the Commission's trioxide contains up to 3000 ppm of sulfur, added as sulfamic acid, to increase the reactivity of the uranium during reduction and fluorination. While most of the sulfur is lost during ignition, the uranium content of the resulting oxide is considerably lower than theoretical even though the actual amount of sulfur may be less than 100 ppm.

The percentage of uranium in the black oxide produced by ignition at 850° C for one hour of a sample containing 3000 ppm of sulfur is 84.68%. The difference in this gravimetric factor and the stoichiometric one represents a bias of 0.14% in the analysis. If the ignition conditions and the sulfur concentration remain reasonably constant, an unbiased gravimetric factor can be determined by titration and applied.

CONCLUSION

Methods and techniques which are recommended in the gravimetric determination of uranium are 1) use of the atomic weight of uranium derived by converting the physical measurements of the nuclidic masses to the chemical scale; 2) blending, subsampling, and weighing of the trioxide in a dry atmosphere; and

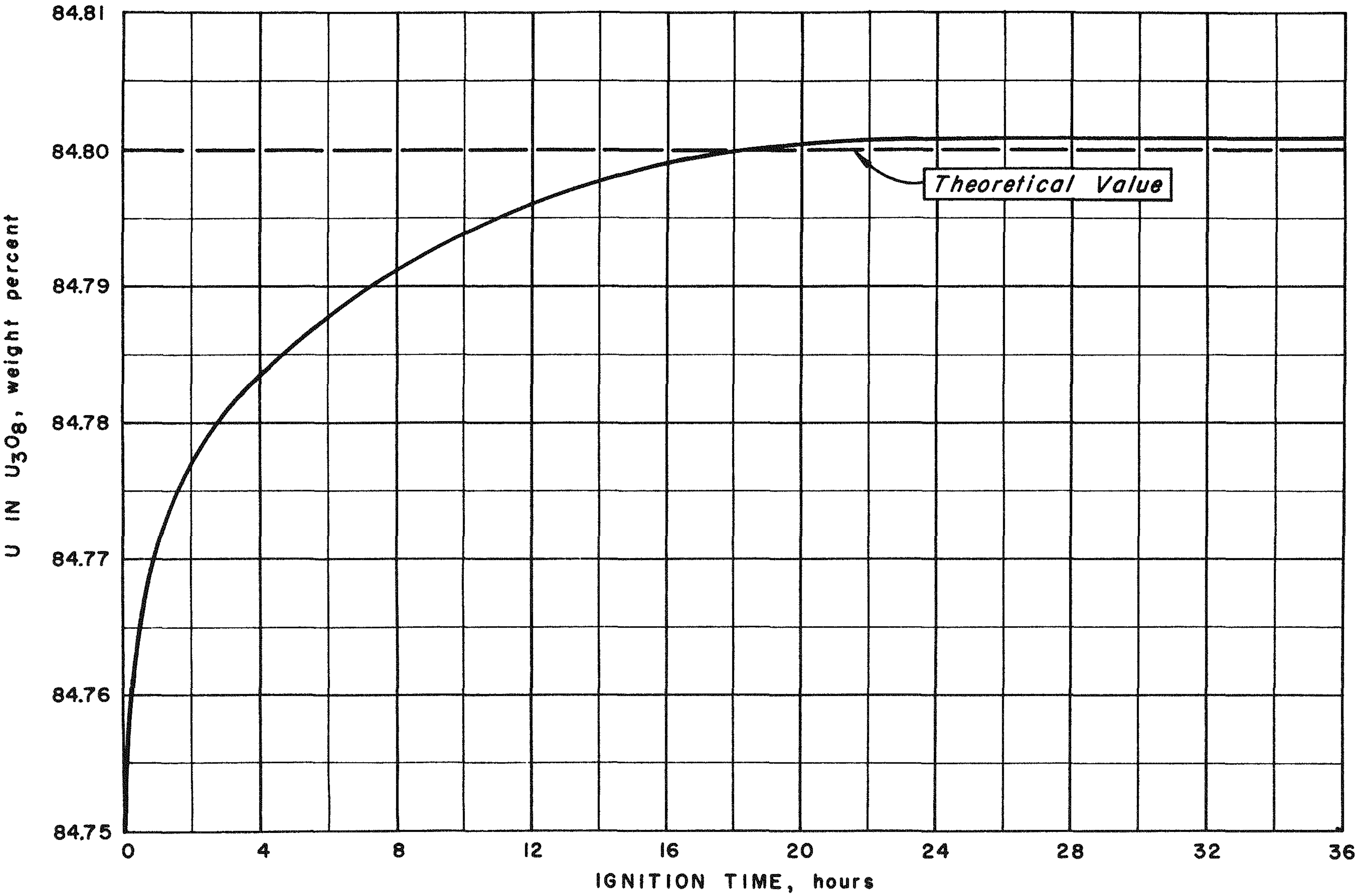

Figure 4. UO_3 treated with HF before ignition at 850° C

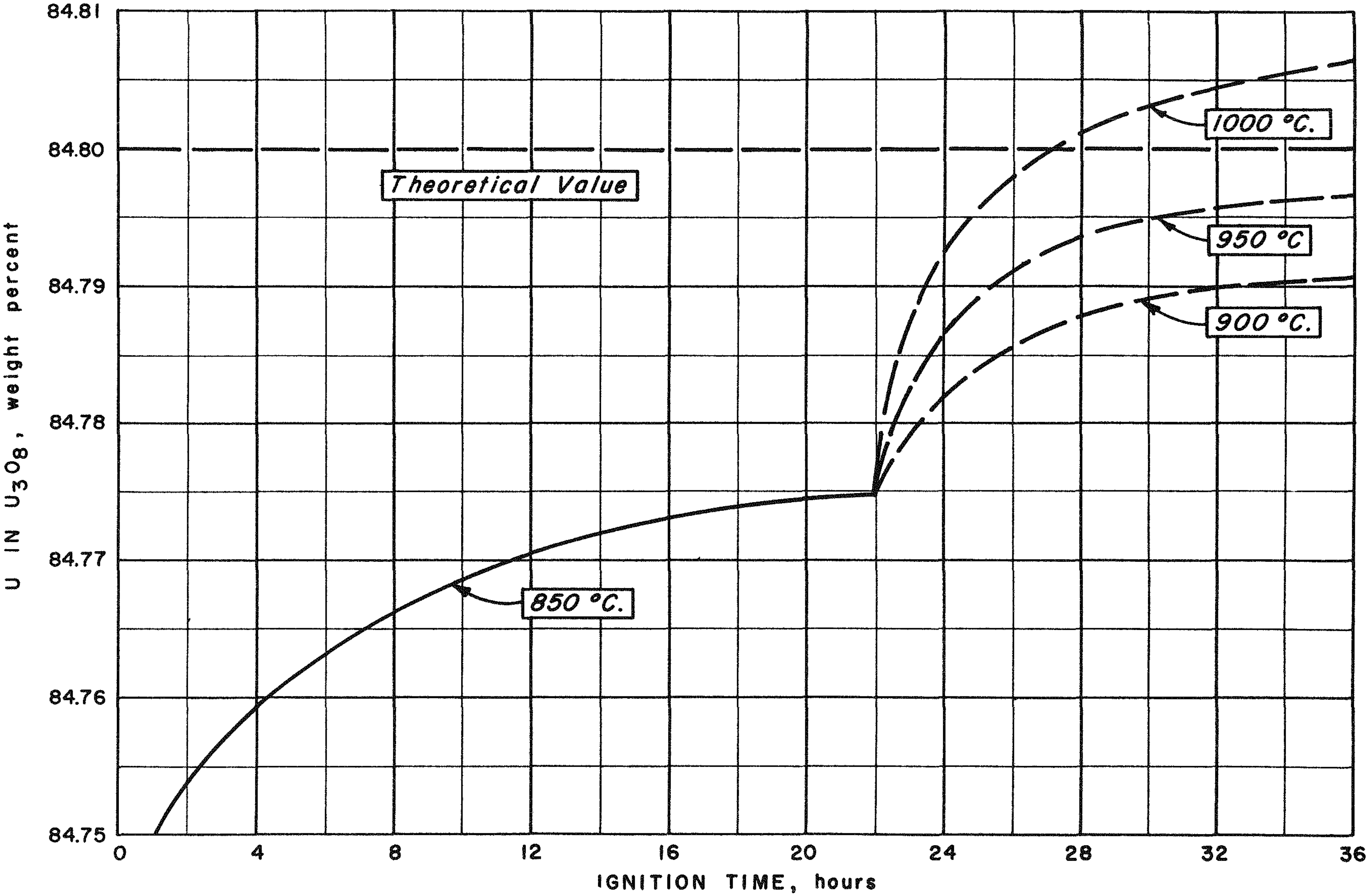

Figure 5. Temperature effect on oxide composite

3) determination of the gravimetic factor for the uranium in the black oxide by titration. The adoption and application of these practices should minimize or eliminate discrepancies in the accountability of trioxide between installations and reduce significant biases between laboratory methods.

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