Elemental Analysis in Action

Petrochemistry & Energy

PRESENTED BY

Kantima Sitlaothaworn

Chayabodee Sae-jea

SciSpec Co., Ltd.

Petrochemistry & Energy

- Elemental determinations are important in Quality Assurance and Quality Control (QA/QC) testing
  - CHNS/O content for the characterization of the products
  - Heat Values
  - CO_2 Emission
- Elemental Analysis can be used with solid, liquid, volatile, viscous and gas samples
- For example, Nitrogen-compounds are used as additives in lubricants and petrochemical companies need to evaluate these additives so they can assess quality of the final products.
- ASTM define methods and guidelines for the analysis of petrochemical and lubricant products

- Combustion (modified Dumas method)
- 24/7 Automatic operation
- Determine 1 to 5 elements (N, C, H, S,O)
- Analyze from few ppm to 100%

ASTM
(American Society for Testing Materials)

Method D 5291 – 09
Standard Test Methods for Instrumental Determination of Carbon, Hydrogen and Nitrogen in Petroleum Products and Lubricant

ASTM
(American Society for Testing Materials)

Method D 5622
Standard Test Methods for the Determination of Total Oxygen in Gasoline and Methanol Fuels by Reductive Pyrolisis

ASTM
(American Society for Testing Materials)

Method D 5373 – 02
Standard Test Methods for Instrumental Determination of Carbon, Hydrogen and Nitrogen in Laboratory Samples of Coal and Coke

A rapid, highly sensitivity, Easy operation and Accurate High Throughput

All-In-One-FlashSmart Elemental Analyzer

Sci Spec

ASTM D5291

Standard Test Methods for Instrumental Determination of CHN in Petroleum Products and Lubricants

Scope:

- ASTM method for simultaneous determination of carbon, hydrogen, and nitrogen in petroleum products and lubricants
- Three instrumental techniques : Combustion, separation, and detection.
- Applicable to crude oils, fuel oils, additives and residues
- Concentration range tested: 75-87 %C, 9-16 %H and <0.1-2 %N.
- Level of 0.1%N in lubricants could be determined.

The N test is not applicable for light materials or to samples containing <0.75 %N such as gasoline, jet fuel, naphta, diesel fuel, or chem. solvents. These methods are not recommended for volatile samples such gasoline.

Methods

- **Test Method** C*: By combustion produced gas stream, after full oxidation of component gases, is passed over heated copper to remove excess oxygen and reduce NOx to N2 gas. The gases are then passed through a heated chromatographic column to separate and elute N_2, CO_2, and H_2O in that order. The individual eluted gases are measured by a thermal conductivity detector.

- **Test Method D**:** The organic samples packed into lightweight containers are dropped at preset times into a vertical quartz, Inconel, or stainless steel reactor, a constant flow of helium is maintained. When the samples are introduced, the helium stream is temporarily enriched with pure oxygen. Flash combustion takes place primed by the oxidation of the container. Quantitative combustion is then achieved bypassing the gases over chromium trioxide and cupric oxide. The mixture of gases is transferred over copper at about 640 °C *(840 °C in a steel reactor)* to eliminate the excess of oxygen; then without stopping, it is introduced into the chromatographic column heated to about 120 °C (50 °C for Flash EA 1112 units). The individual components are then separated in the order nitrogen, carbon dioxide and water by a dedicated Poropak column (active carbon column for Flash EA 1112 units for nitrogen determination) and measured by a thermal conductivity detector. The instrument is calibrated with standard pure organic compounds. K-factors or linear regression can be used for instrument calibration. The typical operator analysis time for a single sample is about 4 min, and the total elapsed time is 8 min.

CHN determination in Lubricants

The CHN results can be used to estimate the processing and refining potentials and yields in the petrochemical industry.

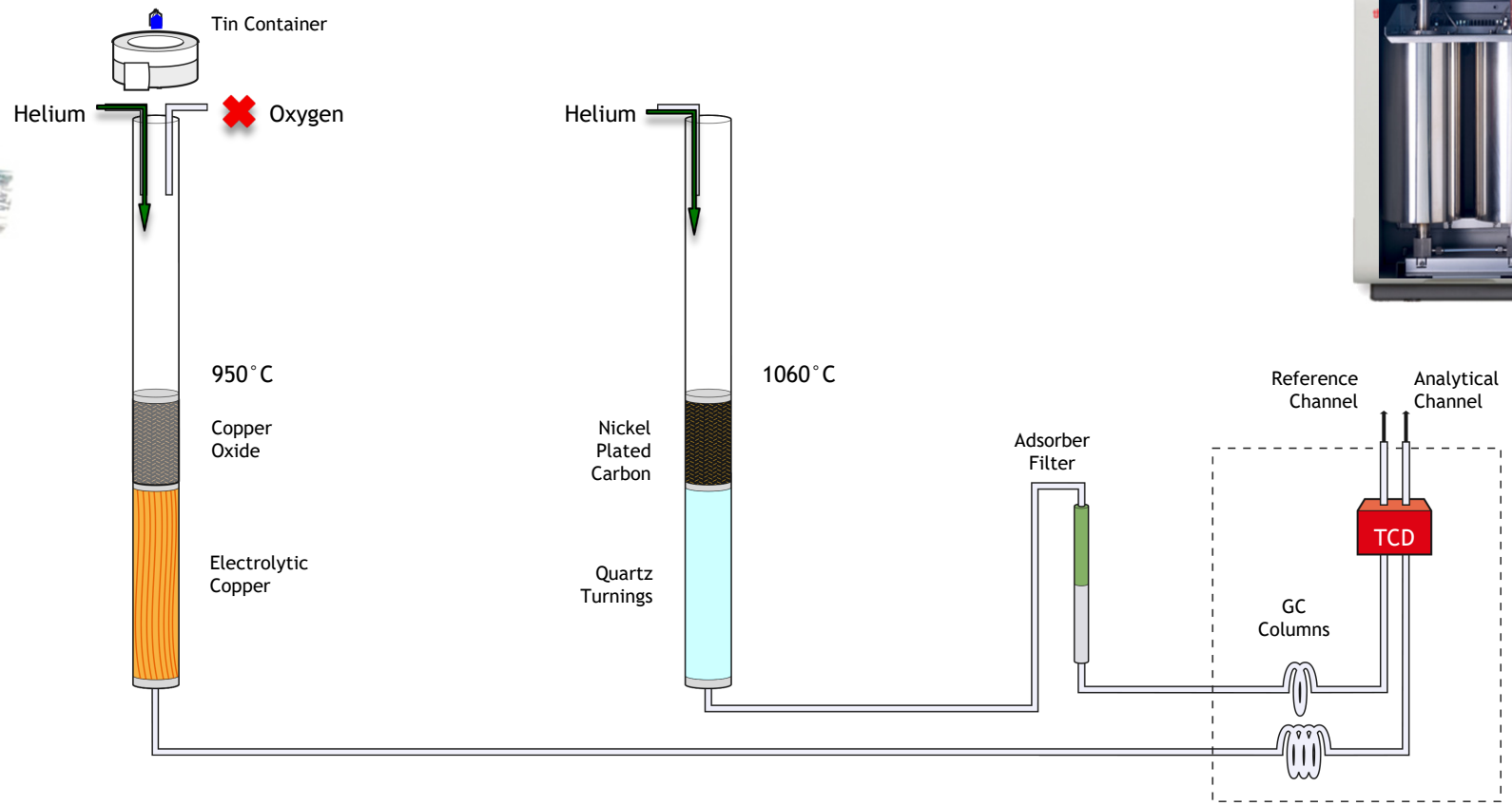
In a typical mineral oil production process, **N** content is periodically tested for quality control purposes. **N** determination marks the presence of **N** containing additives and from its concentration it is possible to predict the amount of nitrogen oxides yielded in the combustion process.

Hydrogen content in samples is helpful in addressing their performance characteristics. Hydrogen to carbon ratio is useful to assess the performance of upgrading processes.

TYPICAL NEEDS:

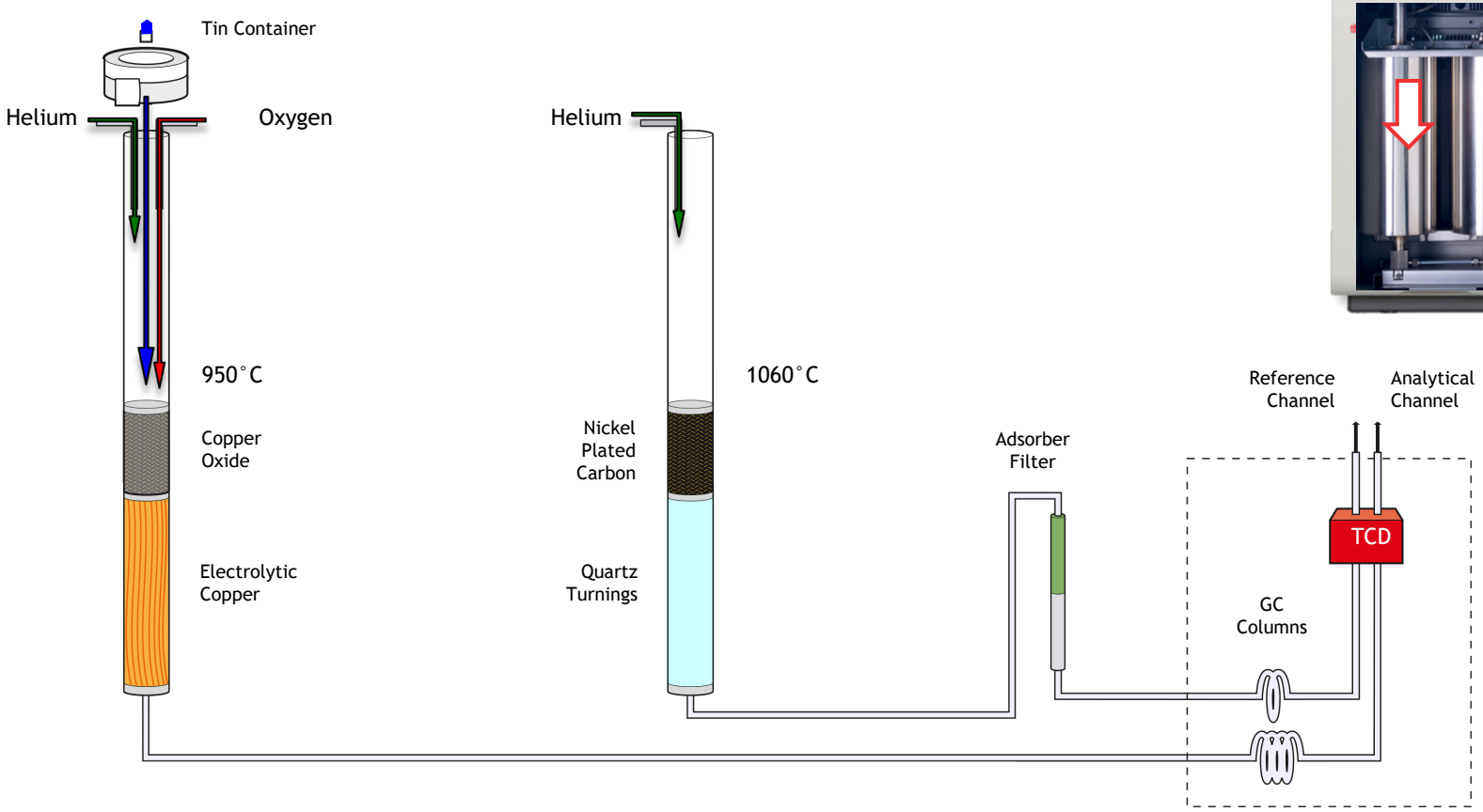
- High sample throughput
- Extremely good day-to-day reproducibility
- Fast analysis
- Fully automated and unattended operations
- Easy to use and maintain
- Low instrument downtime for maintenance
- Computer driven maintenance schedule

Flash*Smart* - CHNS Analytical configuration



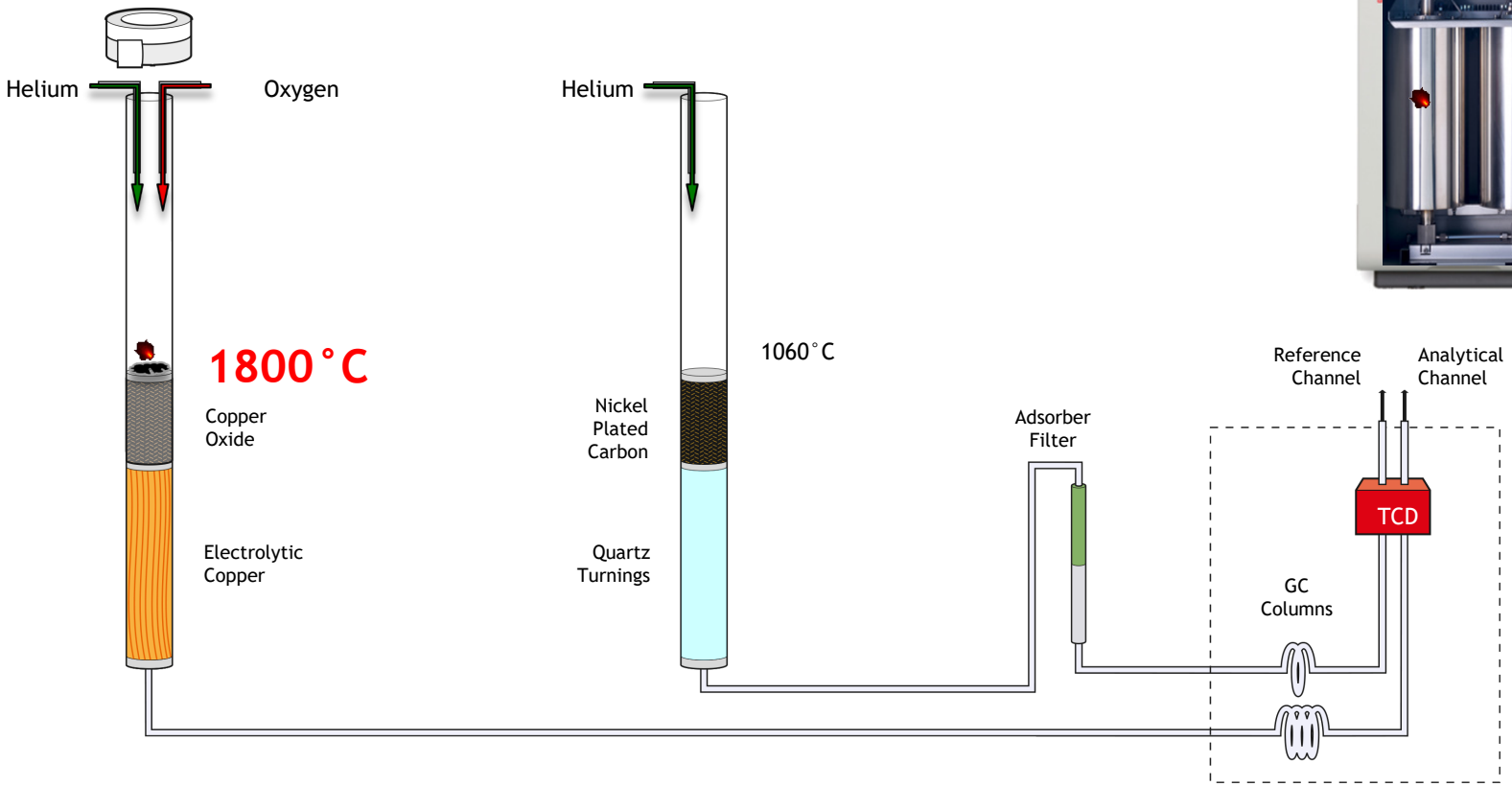
- Introduced into the combustion reactor by and auto sampler

Flash*Smart* - CHNS Analytical configuration



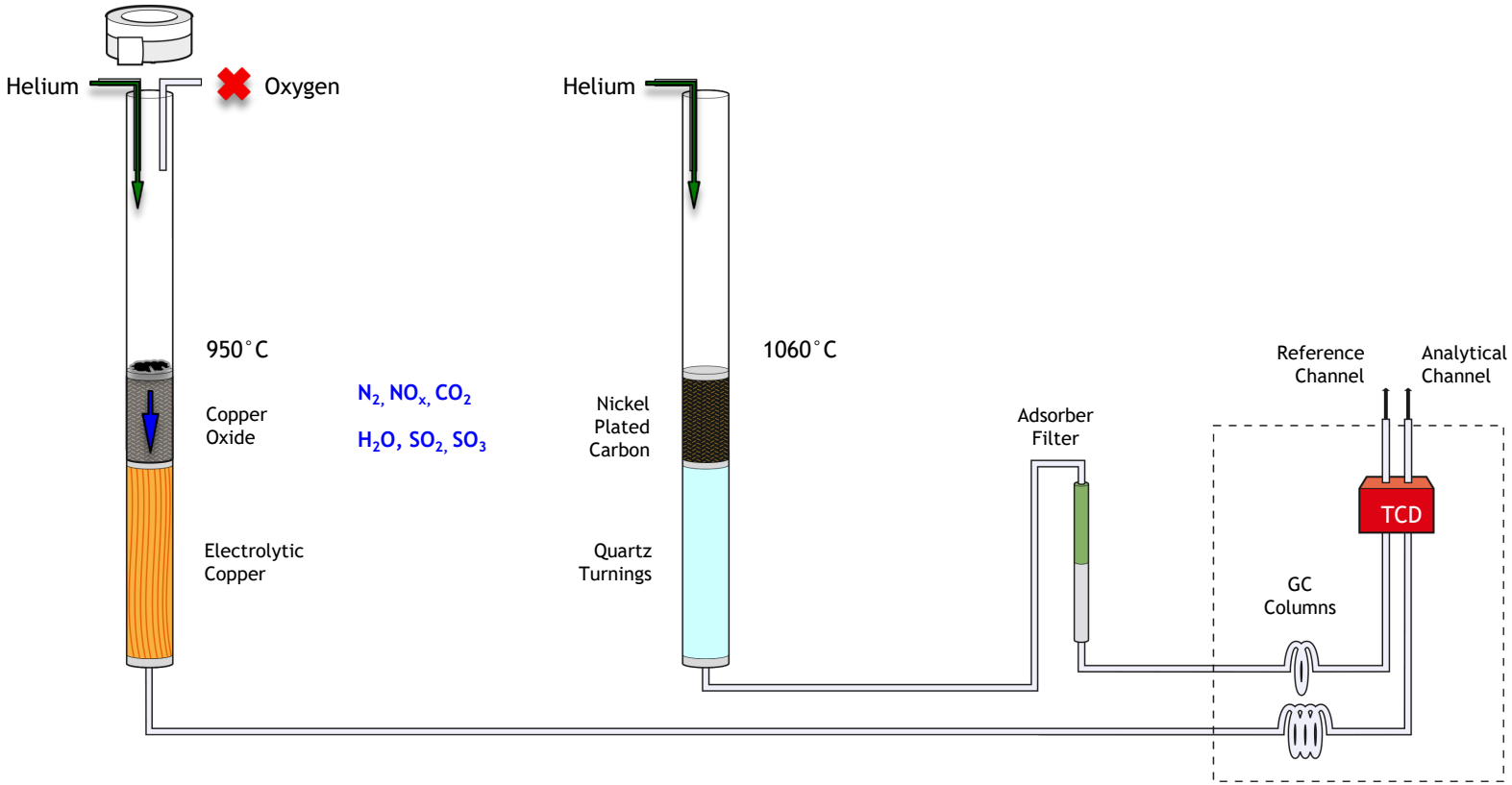
- Inserted in the special furnace heated at 950 °C
- A small volume of pure oxygen is added to the system and helps to burn the sample

Flash*Smart* - CHNS Analytical configuration

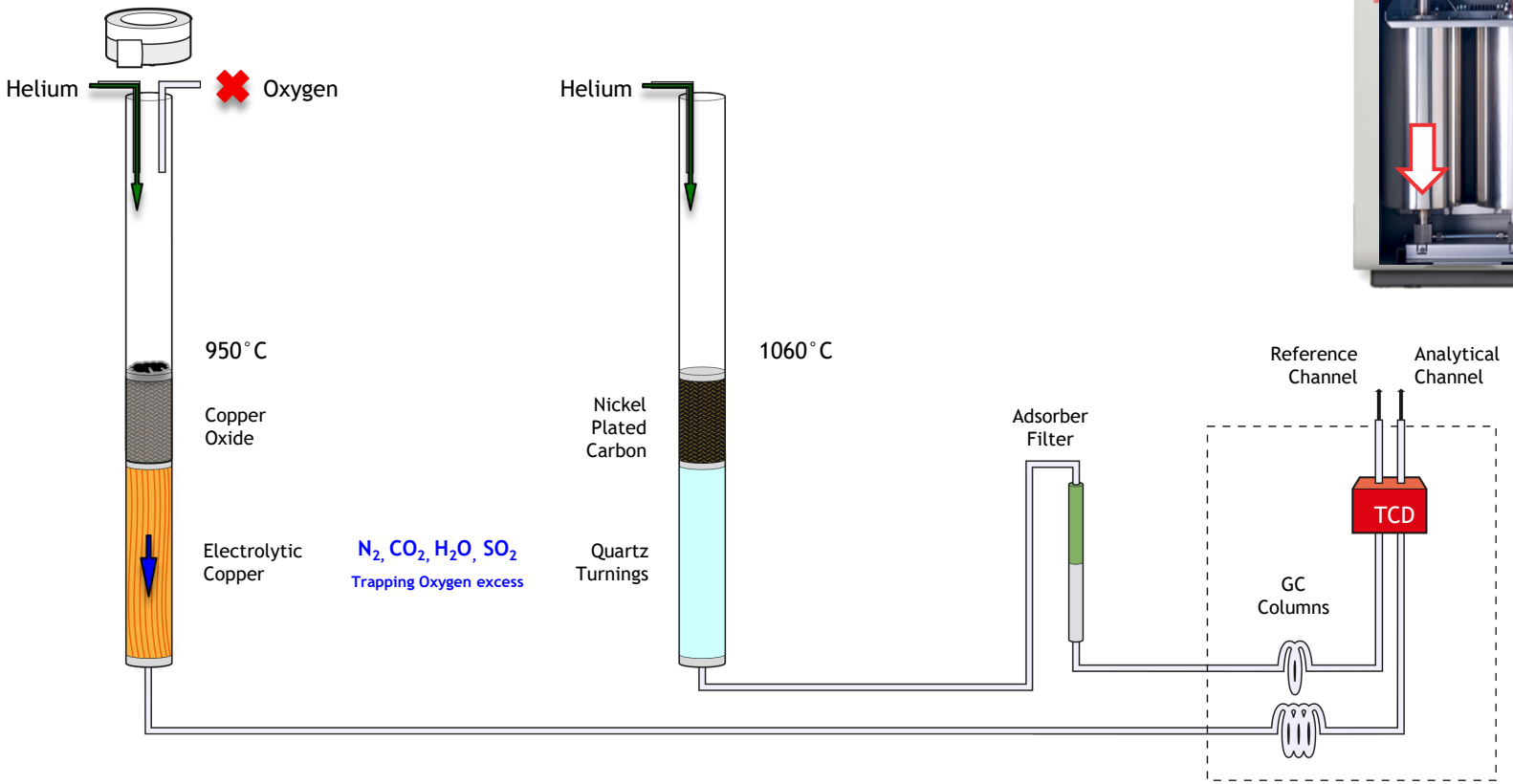


$O_2 + Sn \rightarrow SnO_2 + 1800\ ^oC$

Flash*Smart* - CHNS Analytical configuration

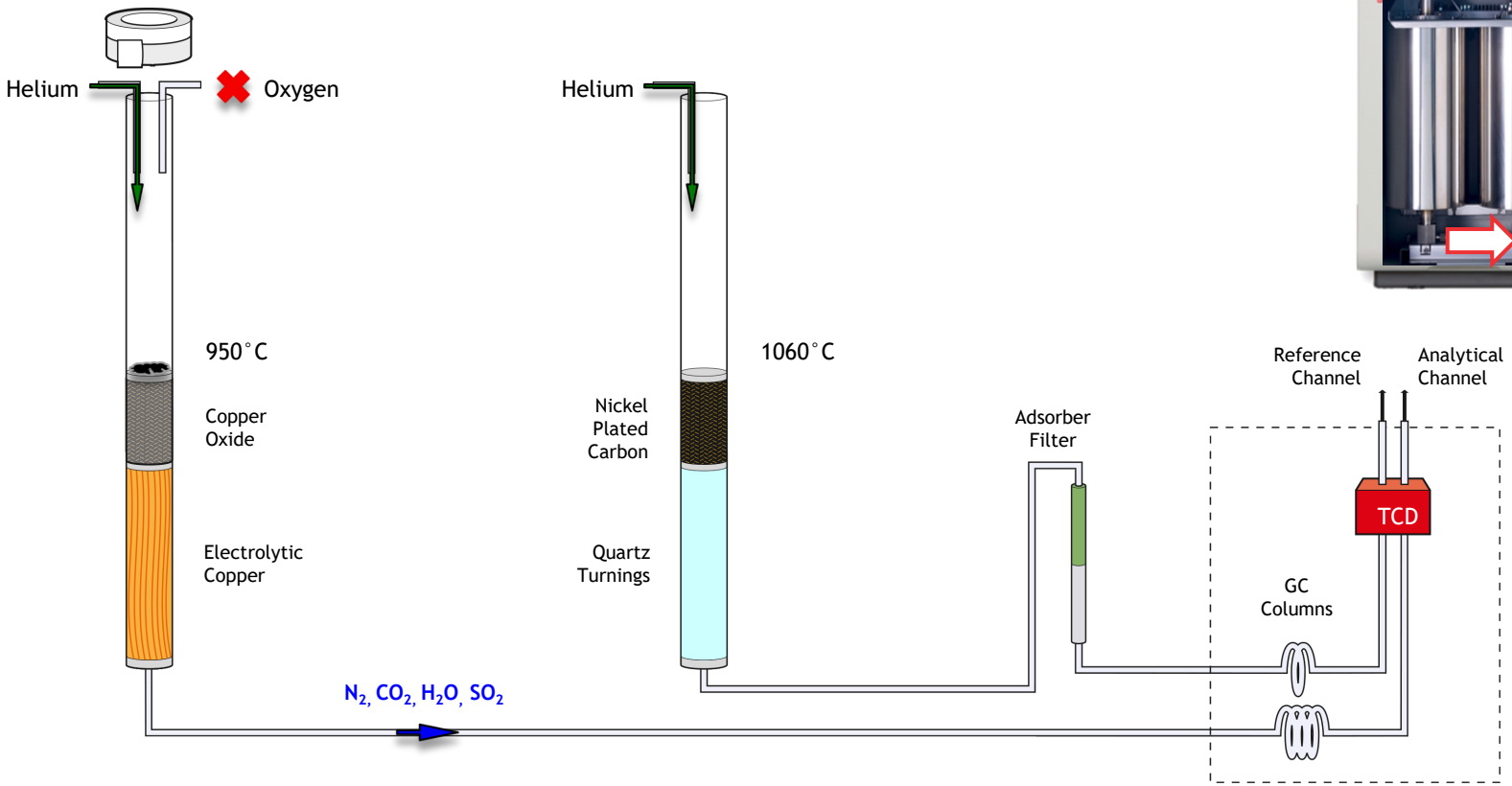


Flash*Smart* - CHNS Analytical configuration



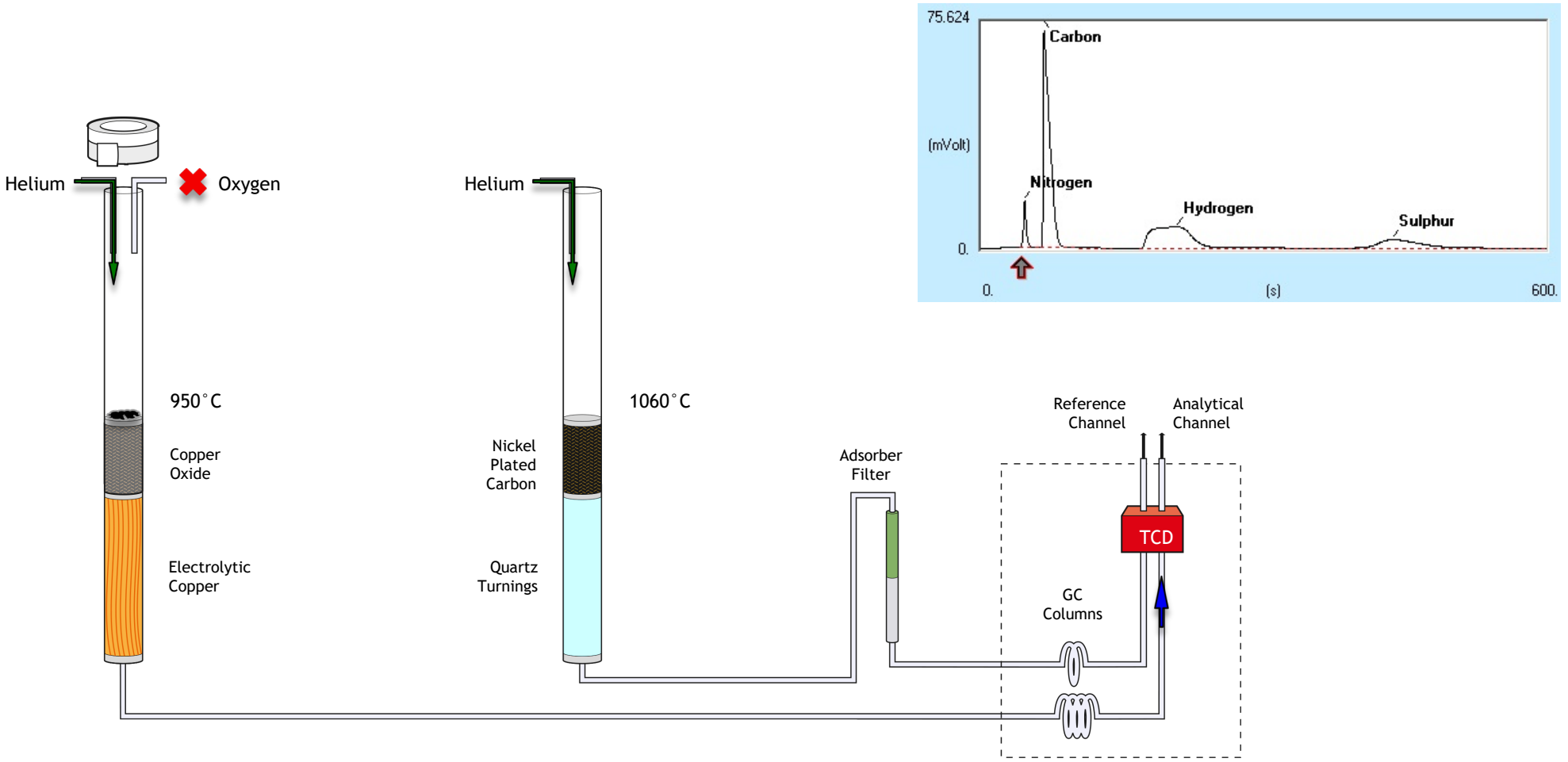
- Reduction “using Copper” converting the sample into element gases (reduce NOx to N2) and remove excess Oxygen

CHNS Analytical configuration

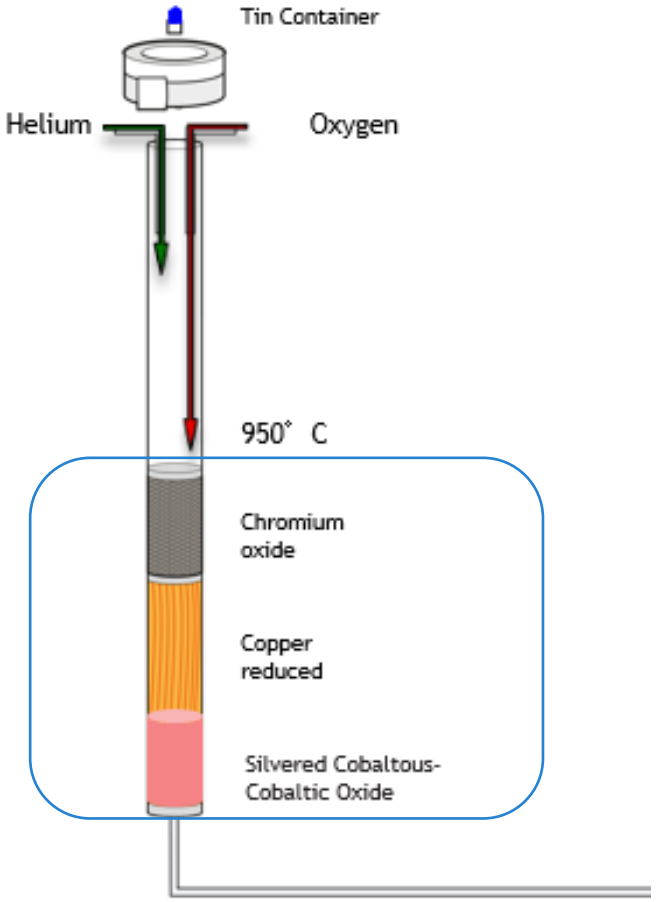


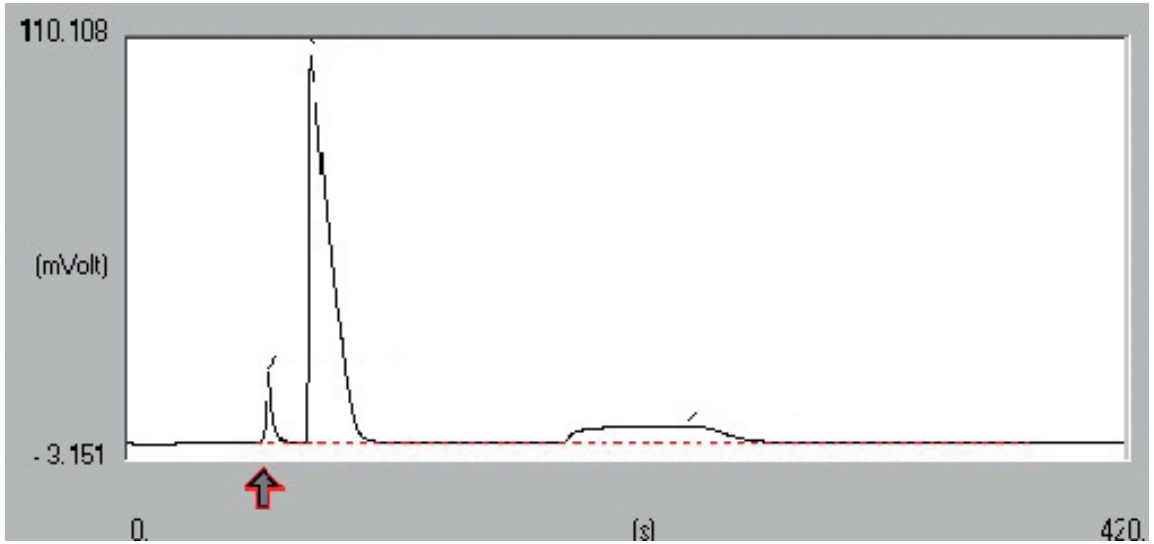
- A separation column and TCD detector allows the user to determine elements

CHNS Analytical configuration

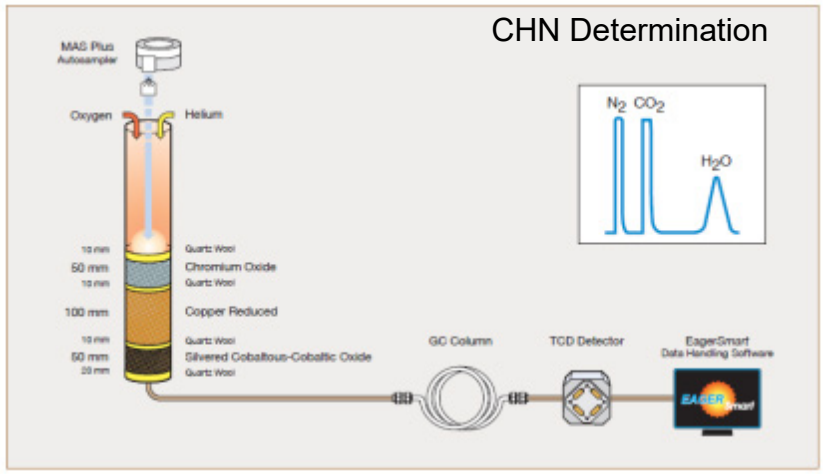


CHN Configuration





ASTM D5291 - CHN in Lubricant Reference Material

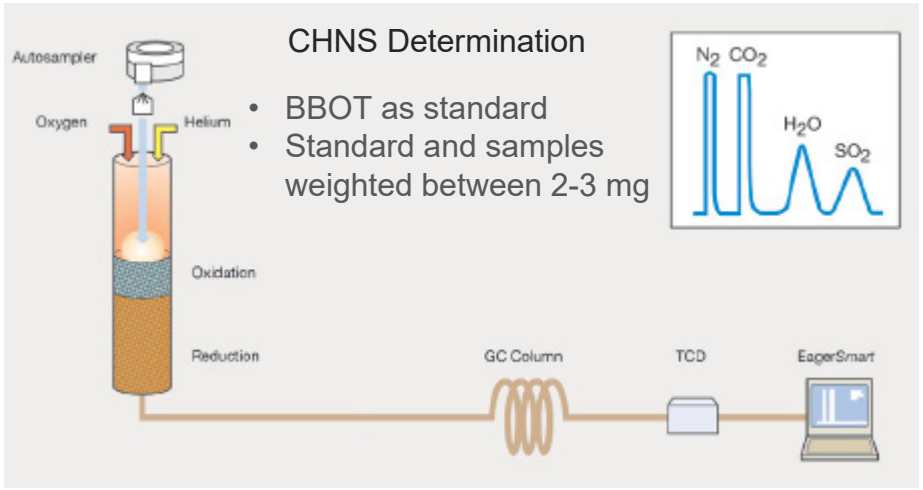


- Standard for Calibration : 2-3 mg Atropine (4.84 N%, 70.56 C%, 8.01 H%)
- Calibration method: K factor
- Lubricant sample weight: 2 – 3 mg

- Reactor Temperature: 950°C
- Oven Temperature: 65°C
- Helium Carrier Flow: 140 ml/min
- Helium Reference Flow: 100 ml/min
- Sample Delay: 12 sec
- Oxygen Flow: 250 ml/min
- Oxygen Injection Time: 5 sec
- Total Run Time: 420 sec

Element	N%	C%	H%
Data	1.14	82.50	13.84
	1.16	82.51	13.83
	1.16	82.29	13.82
	1.15	82.38	13.82
	1.14	82.40	13.86
	1.15	82.32	13.84
	1.17	82.42	13.73
	1.14	82.28	13.69
	1.15	82.26	13.86
	1.16	82.39	13.78
Av %	1.15	82.37	13.81
Std.Dev.	0.0100	0.0865	0.0561
RSD %	0.88	0.10	0.41
Acceptable range %	1.06 - 1.18	82.02 - 82.62	13.68 - 13.96

ASTM D5291 - CHNS in Crude Oil sample



CHNS Determination

- BBOT as standard
- Standard and samples weighted between 2-3 mg

CHNS repeatability of crude oils

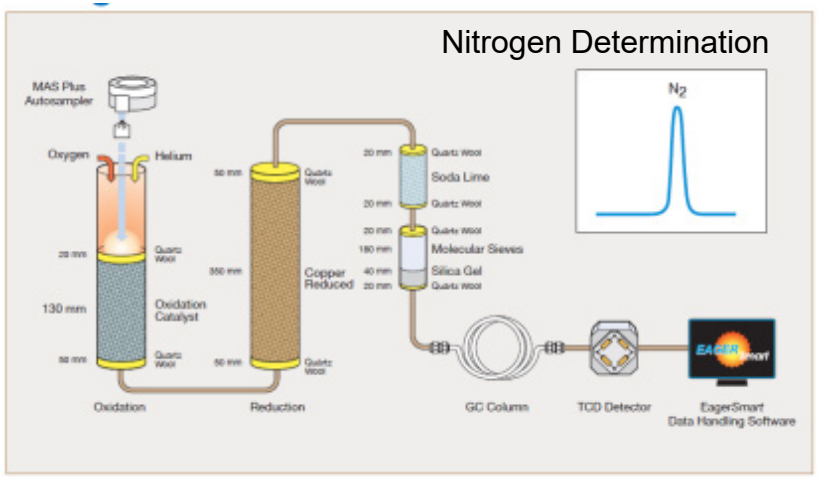
Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
Crude Oil 1	0.202 0.222 0.200 0.212 0.214	4.312	85.270 85.370 85.359 85.102 85.283	0.126	13.395 13.308 13.319 13.289 13.355	0.316	0.289 0.290 0.283 0.291 0.297	1.724
Crude Oil 2	0.270 0.282 0.271 0.279 0.270	2.071	85.425 85.770 85.547 85.377 85.752	0.212	11.919 11.925 11.894 11.794 11.870	0.446	2.028 2.018 2.015 1.985 2.018	0.810

Sulfur repeatability of oils

Sample	S%	RSD%
Model Oil	11.461 11.514 11.520 11.632 11.531	0.540
Crude Oil 1	8.534 8.573 8.499 8.645 8.471	0.796
Crude Oil 2	4.146 4.165 4.091 4.125	0.677
Residual Oil A	2.086 2.095 2.093	0.751
Residual Oil B	2.937 2.960 2.904 2.962	0.918
Residual Oil C	4.534 4.541 4.534 4.558	0.249

No matrix effect was observed when changing sample

ASTM D5291 - Nitrogen in Lubricant Reference Material using different standard for calibration



- Reactor Temperature: 950°C
- Reduction Reactor Temperature : 840°C
- Oven Temperature: 50°C
- Helium Carrier Flow: 140 ml/min
- Helium Reference Flow: 100 ml/min
- Sample Delay: 10 sec
- Oxygen Flow: 300 ml/min
- Oxygen Injection Time: 8 sec
- Total Run Time: 300 sec

- Standard for Calibration : 4-5 mg Atropine (4.84 N%), 4 – 4.2 mg, BBOT (6.51 N%), 9.5 – 10 mg tocopherol nicotinate (2.61 N%)
- Calibration method: K factor
- Lubricant Reference Material (acceptable N range: 1.06 – 1.18 N%), sample weight: 8 - 10 mg

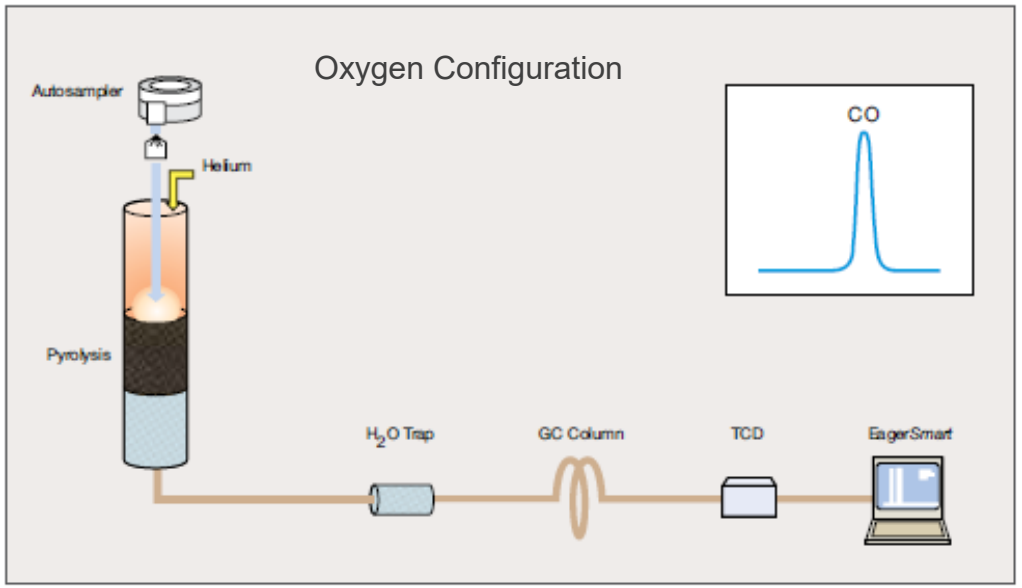
Run	TS Lubricant Ref. Mat. (1.12 N% ± 0.10)	Atropine Std.	BBOT Std.	Tocopherol Nicotinate Std.
	Weigh (mg)	N %	N%	N%
1	8.105	1.11	1.10	1.10
2	8.856	1.10	1.09	1.09
3	8.848	1.11	1.10	1.10
4	8.901	1.11	1.10	1.10
5	8.585	1.11	1.10	1.10
6	9.001	1.10	1.10	1.10
7	8.698	1.10	1.09	1.09
8	9.836	1.11	1.10	1.10
9	12.529	1.10	1.10	1.10
10	9.313	1.09	1.09	1.09

Average N %	**1.10**	**1.10**	**1.10**
SD	0.007	0.005	0.005
RSD %	0.63	0.44	0.44

ASTM D5622 – Determination of Total Oxygen in Gasoline and Methanol Fuel by Reductive Pyrolysis

ASTM D 5622-95 Method Requirements (Test method A)

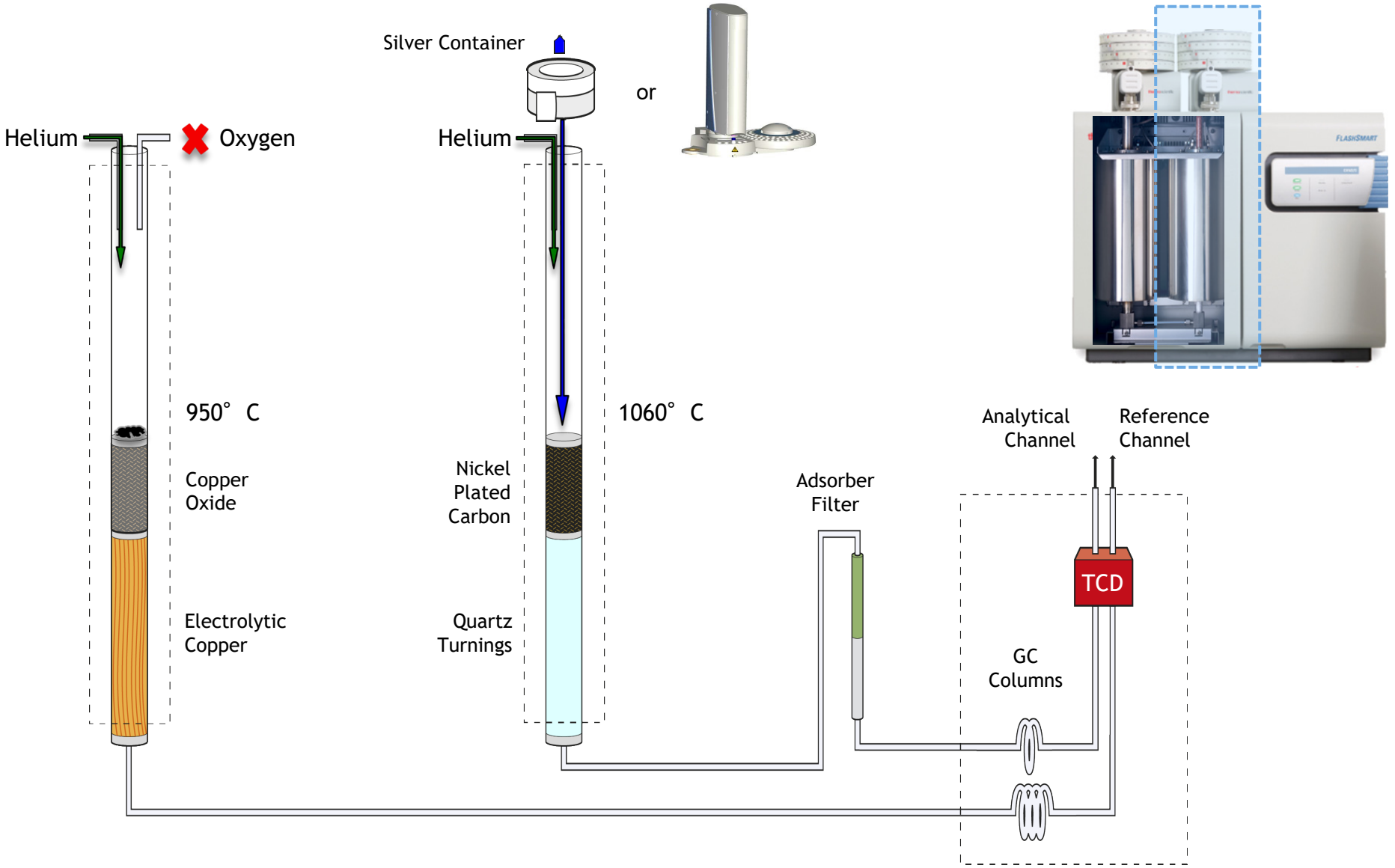
1. Calibration: Analyze two times the standard NIST SRM 1837 (6.57% O)
2. Quality control: analyze twice the standard NIST SRM 1838 (3.95% O), the results obtained must be within 2% relative with the certified value
3. Repeatability: the difference between two consecutive test results must not exceed 0.06 for samples with 1.0 to 5% O.



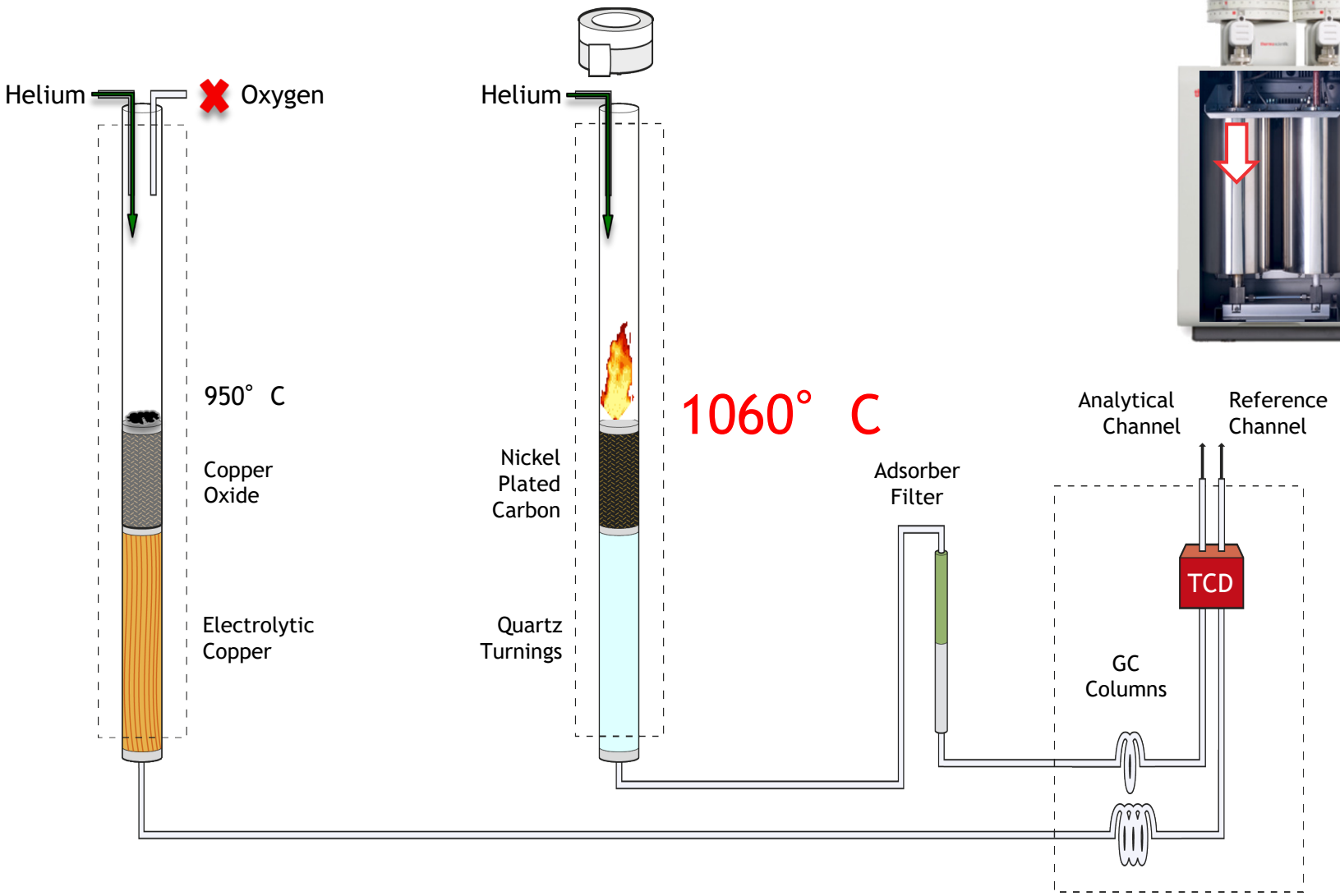
- Furnace Temperature: 1060°C
- Oven Temperature: 65°C
- Helium Carrier Flow: 140 ml/min
- Helium Reference Flow: 100 ml/min
- Standard : Solution n-hexane/ethanol, NIST SRM 1837
- Sample Volume Injected : 2-3 µL
- Total Run Time: 5 mins

Thermo Scientific™ AS 1310 Liquid Autosampler

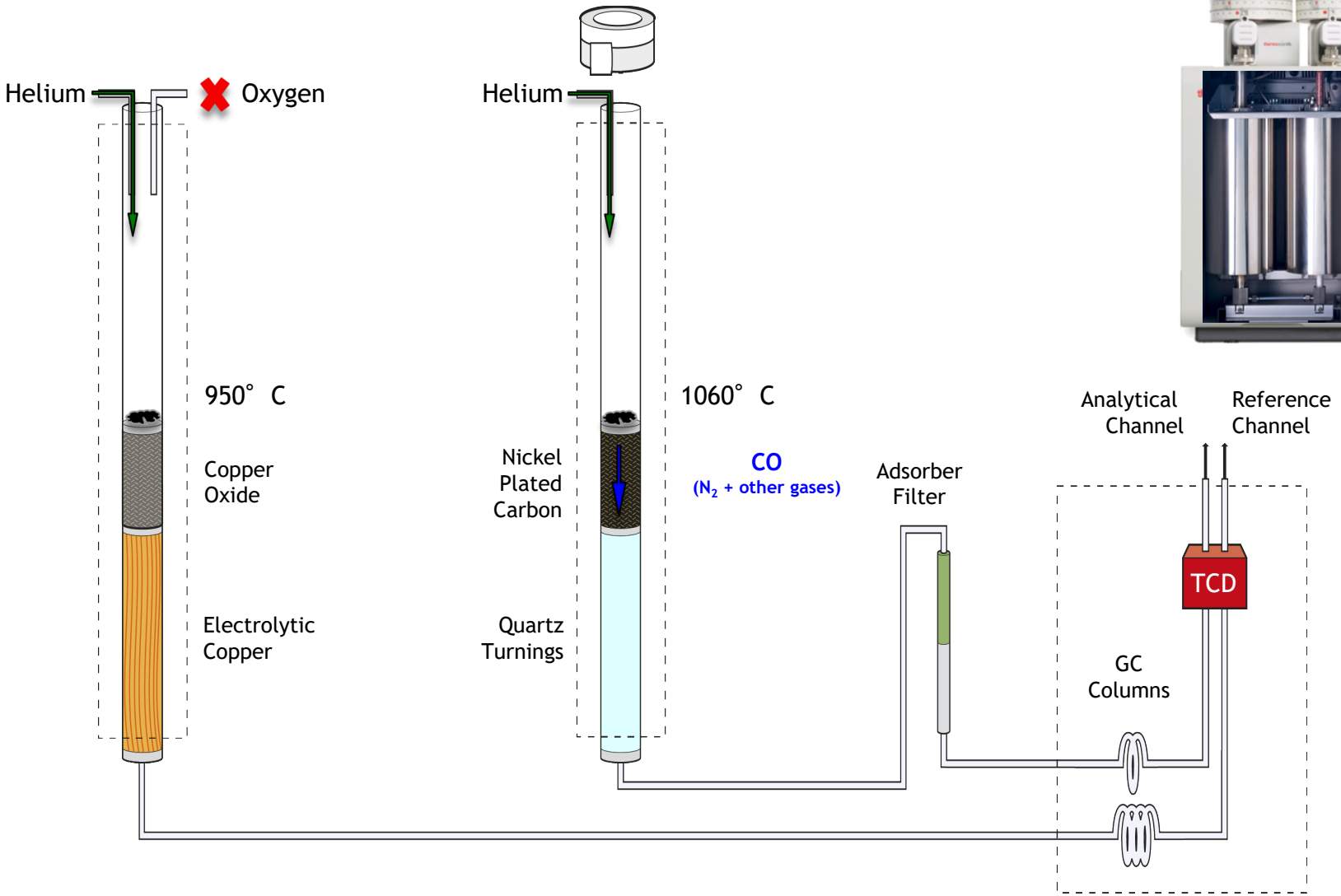
Oxygen Analytical configuration



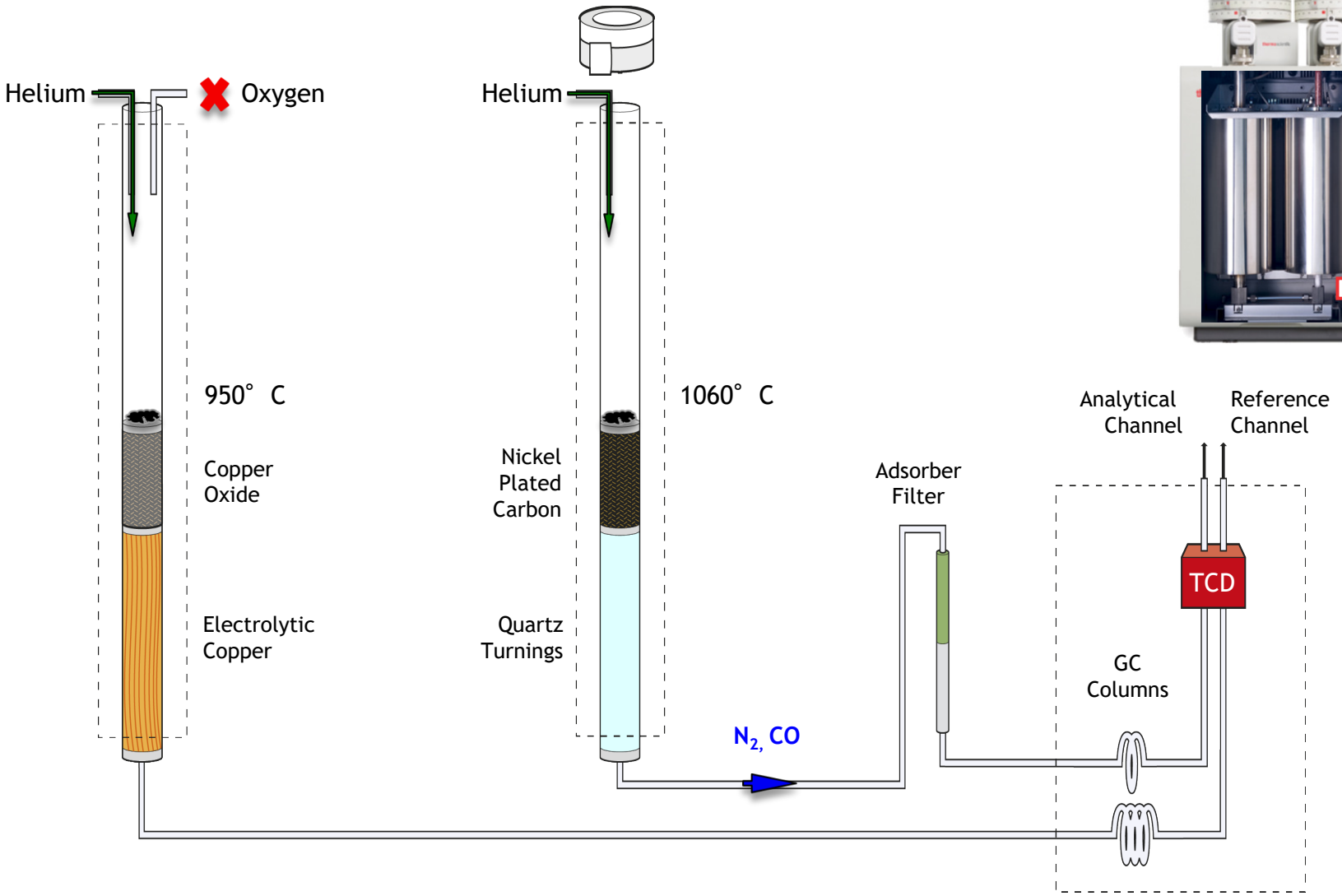
Oxygen Analytical configuration



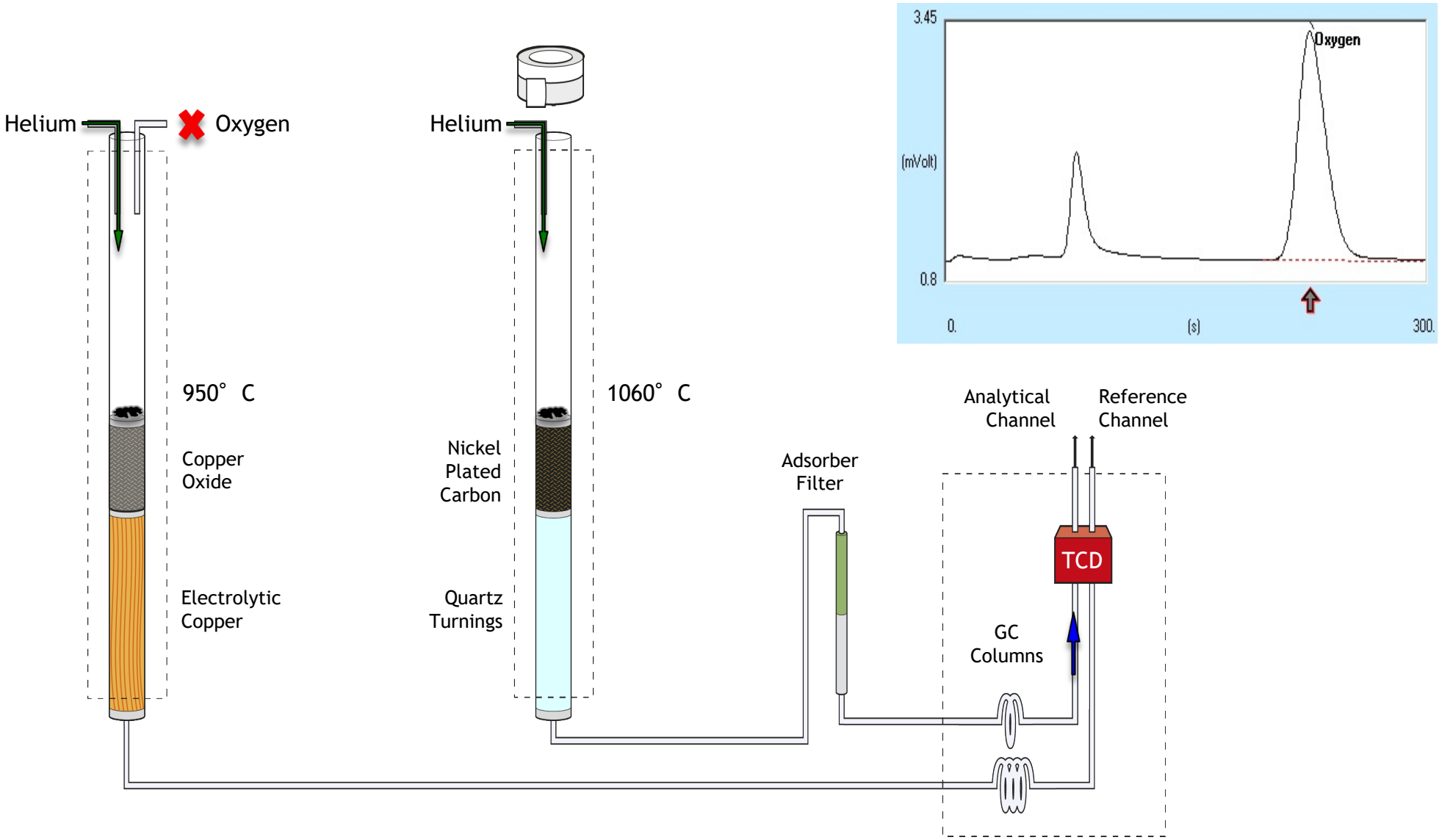
Oxygen Analytical configuration



Oxygen Analytical configuration



Oxygen Analytical configuration



ASTM D5622 – Determination of Total Oxygen in Gasoline and Methanol Fuel by Reductive Pyrolysis

Sample	Data	Test 1		Test 2		Test 3		Test 4	
		Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
NIST SRM 1837 (6.57 O)	Area mv/sec	390510	380352	388289	379413	389888	379269	385273	384467
NIST SRM 1838 (3.95 O%)	Av.%	3.92		3.89		3.89		3.96	
	Difference from certified value	0.03		0.06		0.06		0.01	

The results of the SRM 1838 met the certified value within 2% RSD

Calibration response of SRM 1837 and accuracy of SRM 1838

Oxygen analysis of a solution of n-hexane/ethanol (4.5 O%)

Injection Mode	AS 1310 Autosampler	Manual Injection
Oxygen %	4.4902	4.5184
	4.4962	4.4436
	4.5290	4.5320
	4.4721	4.5802
	4.5387	4.4841
	4.5172	4.4840
	4.4895	4.5303
	4.5371	4.4854
	4.5200	4.5642
	4.5132	4.4828
	4.4774	4.4832
	4.5346	4.4886
	4.5366	4.5421
	4.5029	4.5132
	4.4985	4.5402
Mean Oxygen %	4.5102	4.5115
Std. Dev.	0.0226	0.0367
RSD %	0.5019	0.8150

Sample	Test A		Test B		Test C	
	O%	RSD%	O%	RSD%	O%	
1	2.723–2.713	0.275	2.742–2.741	0.013	2.763–2.766	
2					.537	
3					.954	0.642
4	3.084–3.090	0.141	3.076–3.069	0.146	3.052–3.077	0.573
5	2.027–2.012	0.519	2.027–2.008	0.672	2.016–2.021	0.166
6	2.654–2.645	0.225	2.640–2.632	0.212	2.625–2.620	0.113

Repeatability: the difference between two consecutive test results must not exceed 0.06 for samples with 1.0 to 5% O

Repeatability of oxygen analysis in gasoline

ASTM D5373 - Determination of CHN in coal

Coal mine
Representative sample of 20-50 tons

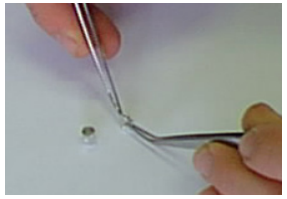
Take 1 kg

Broken by
a hammer

Homogenization by
a ball mill (<0.2 mm)

Dry aprox.
1 gram in an
oven at 105° C

Analysis



Weight the sample
in a tin container

Take the weight by
Microbalance

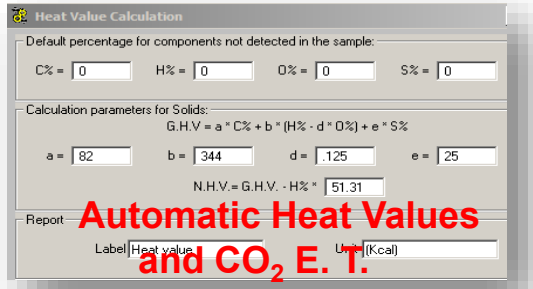
Introduce the sample into
the MAS Plus Autosampler

Analysis by Flash*Smart* EA
CHNS/O configuration

CHNS det.
by combustion

Oxygen det.
by pyrolysis

Heat Values (GHV and NHV) by
Eager*Smart* software

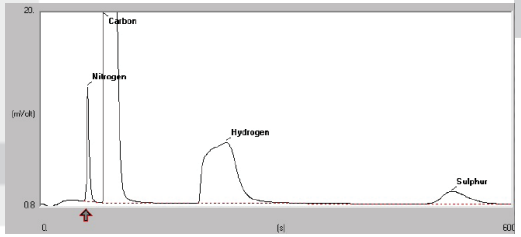


Automatic Heat Values and CO_2 E. T.

CHNS/O determination and Heat Values calculation of coal

CHNS Repeatability of 10 determinations of coal samples

Sample	A				B			
Element	N%	C%	H%	S%	N%	C%	H%	S%
	1.93	88.48	3.76	4.16	1.15	81.54	4.18	0.41
	1.95	88.51	3.76	4.19	1.15	82.45	4.17	0.41
	1.94	88.34	3.76	4.21	1.14	82.53	4.17	0.41
	1.93	88.21	3.75	4.20	1.14	82.36	4.17	0.40
	1.93	87.95	3.74	4.21	1.13	81.99	4.17	0.41
	1.95	88.49	3.75	4.20	1.14	82.14	4.16	0.40
	1.93	88.21	3.74	4.20	1.13	81.86	4.16	0.40
	1.94	88.45	3.75	4.21	1.14	82.60	4.18	0.40
	1.94	88.46	3.76	4.21	1.13	81.59	4.14	0.41
	1.94	88.04	3.73	4.18	1.14	82.02	4.16	0.41
Mean %	1.94	88.31	3.75	4.20	1.14	82.11	4.17	0.41
RSD %	0.41	0.23	0.28	0.39	0.65	0.46	0.28	1.27



Authors
Dr. Liliana Krotz, Dr. Francesco Leone and Dr. Guido Giazzi
Thermo Fisher Scientific, Milan, Italy

Keywords
Coal, CHNS/O, Elemental Analysis, CO_2 Emission Trade, Heat Value

Goal
This application note reports nitrogen, carbon, hydrogen, sulfur and oxygen data in coal samples, the relative Heat Values and CO_2 Emission Trade Evaluation according to ASTM D5373-02 Method.

Introduction
Coal is the largest source of energy worldwide but it is also considered as a source of pollution since various toxic chemicals are released in the environment as by-products during the coking process. Environmental pollutants such as sulfur dioxide, sulfuric acid and hydrogen sulfide are related to sulfur concentration on coal. The composition of coal varies depending on the place where it formed and which kind of soil or rock determined its formation. This means that its composition and properties affect its final use and its impact on the environment.

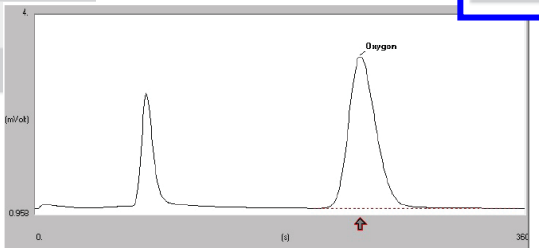
Given environmental concerns and regulations, the elemental analysis of coal is important for its quality control. In particular sulfur quantification helps identify pollutants. The method for CHN determination is described in ASTM D5373-02 Method. The method covers the analytical determination of nitrogen, carbon and hydrogen in coal and coke samples.

As the demand for improved sample throughput and reduction of operational costs increases, an automated technique, providing analysis with excellent reproducibility is needed. The Thermo Scientific™ FlashSmart™ Elemental Analyzer (Figure 1) enables the fast quantitative determination of the elements in large concentrations with no need for sample digestion. The system, which operates with dynamic flash combustion of the sample, provides automated

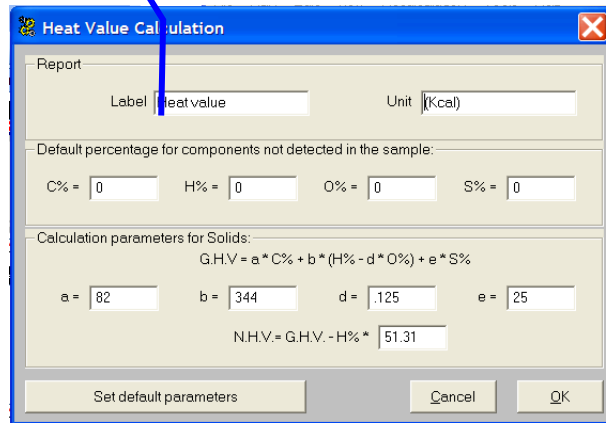
ThermoFisher SCIENTIFIC

Oxygen determination of coal samples in triplicate.

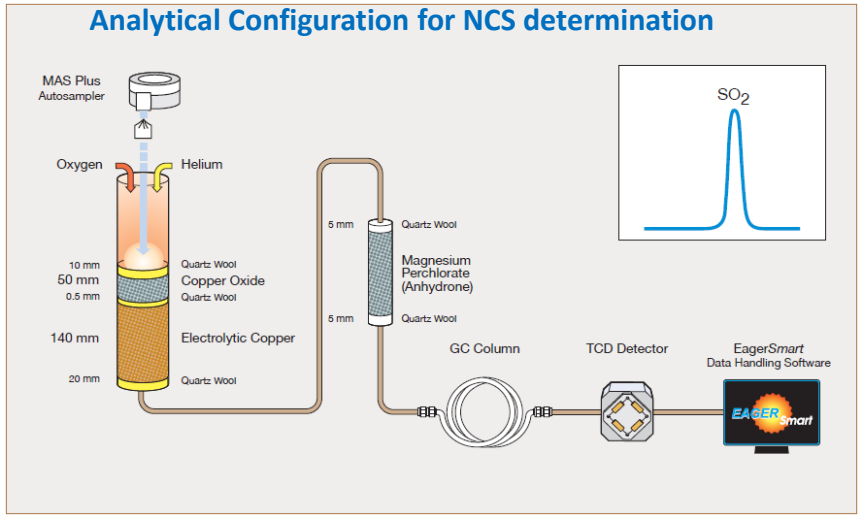
Sample	A	B
Oxygen %	1.10	3.42
	1.11	3.44
	1.09	3.43
Av. Oxygen %	1.10	3.43
RSD %	0.91	0.29



Sample	A	B
GHV (kcal/kg)	8589	8030
NHV (kcal/kg)	8397	7816
CO_2 E.T.	92.07	91.97



Catalyst : Activated Alumina



- The calibration was performed with 2 – 2.5 mg BBOT as standard us
- BBOT, acetanilide and Thermo Scientific Soil Reference Material wer
- Standards and samples were weighed with the addition of about 10 r
- Samples were analyzed in triplicate.

Samples were homogenized with homogenizer

Sample Name	Replicate	Weight (mg)	Nitrogen	Carbon	Sulphur
BBOT		2.485	6.51	72.64	7.44
Acetanilide		2.469	10.34	70.99	0
Sample A	1	10.102	0.0218	0.456	0.501
	2	10.84	0.0219	0.433	0.503
	3	10.288	0.0214	0.436	0.500
%RSD			**1.22**	**2.83**	**0.30**
Sample B	1	10.304	0.0237	2.55	0.432
	2	10.177	0.0251	2.55	0.436
	3	10.326	0.0230	2.52	0.432
%RSD			**4.47**	**0.68**	**0.53**
Sample C	1	11.233	0.0117	4.60	0.417
	2	10.084	0.0115	4.64	0.412
	3	10.318	0.0117	4.59	0.414
%RSD			**0.99**	**0.57**	**0.61**
Sample D	1	4.303	0.0154	3.07	6.40
	2	4.303	0.0154	3.07	6.42
	3	4.210	0.0153	3.06	6.41
%RSD			**0.65**	**0.68**	**0.16**
Sample E	1	4.141	0.0085	3.31	7.70
	2	4.303	0.0085	3.34	7.73
	3	4.207	0.0081	3.36	7.72
%RSD			2.76	0.75	0.20
Sample F	1	4.110	0.0099	4.96	9.00
	2	4.239	0.0099	4.95	8.99
	3	4.055	0.0099	4.94	8.99
%RSD			**0.00**	**0.20**	**0.06**
Acetanilide		2.372	10.34	71.04	0
Soil reference material		15.454	0.211	2.25	0.0260
BBOT		2.348	6.51	72.81	7.45

The results of the QC check met the certified value

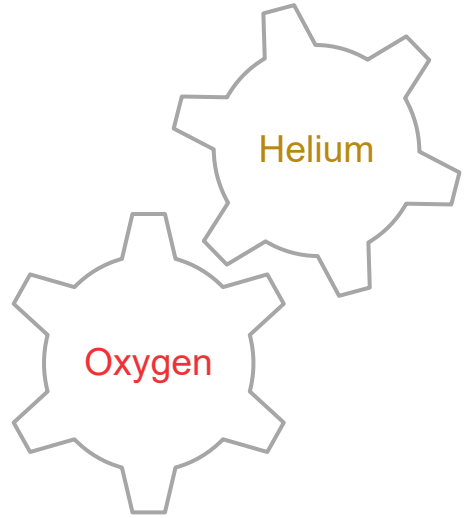
Application Note

Elemental Analysis: Nitrogen determination of lubricants with different pure organic calibration standards

- AN 42151 Biomass and Bio-fuels characterization
- AN 42152 Diesel and bio-diesel characterization
- AN 42169 Petrochemical Compounds Characterization
- AN 42182 Organic Elemental Analysis for Carbon characterization
- AN 42216 Characterization of Lubricants and oils
- AN 42218 Characterization of Coals
- AN 42222 Total Oxygen determination in Gasoline
- AN 42238 Characterization of Carbon Black
- AN 42240 Characterization of Lubricants and Oils using He and Ar as Carrier Gases
- AN 42263 Fully Automated Double Channel Analysis for Petrochemical Applications

Helium and Oxygen Consumption

Helium consumption	Always Ready	Option 1 Standby-mode	Option 2 Switch to N2 gas and Standby- mode
Configuration	All	All	All
Per working day – 8 working & 16 Standby hours	345 L	134 L	115 L
Per one week - 5 working day	2149 L	729 L	576 L
Per month – 4 weeks	9676 L	2918 L	2310 L
Lifetime / week	~ 3	~ 9	~12



*Flow 250 ml/min, 5 sec

The analytical times are taken as **8 hours per day for 5 days** and all other time the Analyzer is in Stand-By Mode.

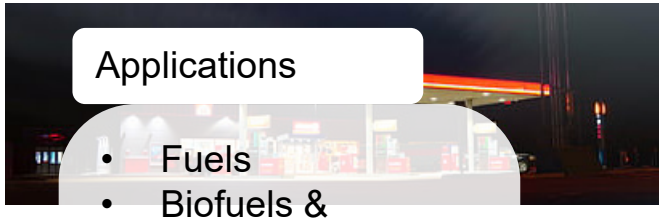
The values are calculated from a *carrier gas flow of 140 ml/min and reference flow of 100 ml/min* during analysis times and carrier gas flow of 10 ml/min and reference flow of *10 ml/min during Stand-By Mode.*

Helium bottle 7,000 liters

Configuration	CHN/CHNS/NCS
Oxygen consumption / Sample	120.8 mL
Oxygen consumption / 100 Sample per day	12.08 L

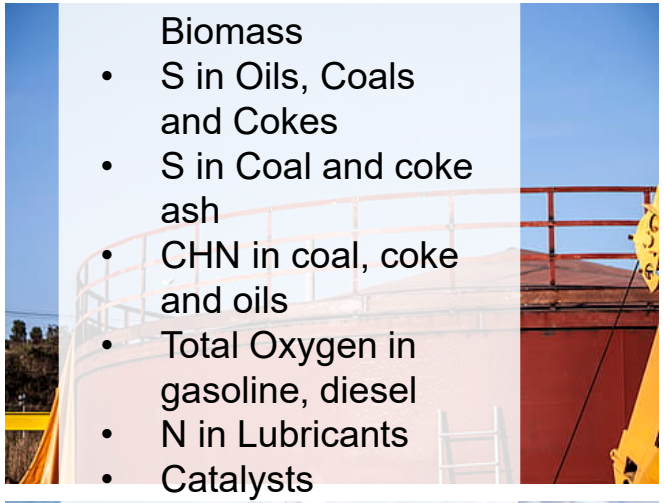
* Oxygen Flow Split / Sample: 100 mL

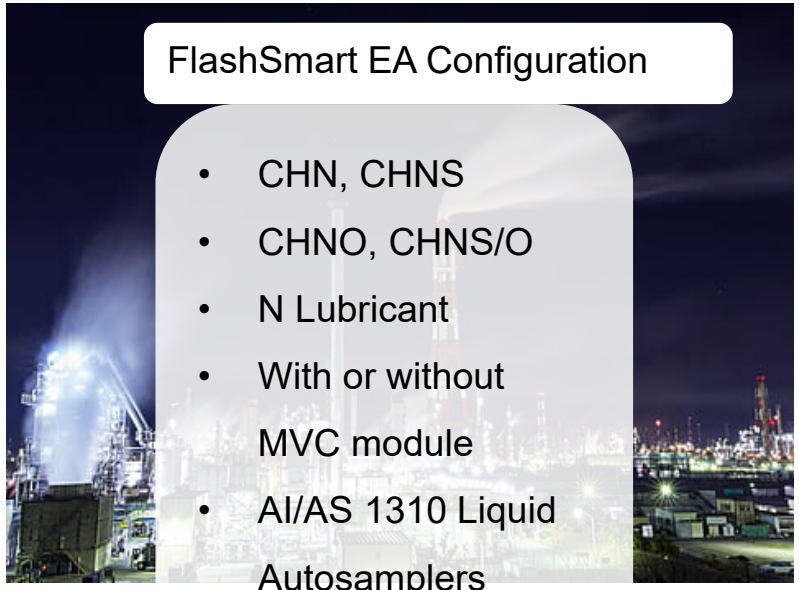
All-In-One-Flash*Smart* Elemental Analyzer



Applications

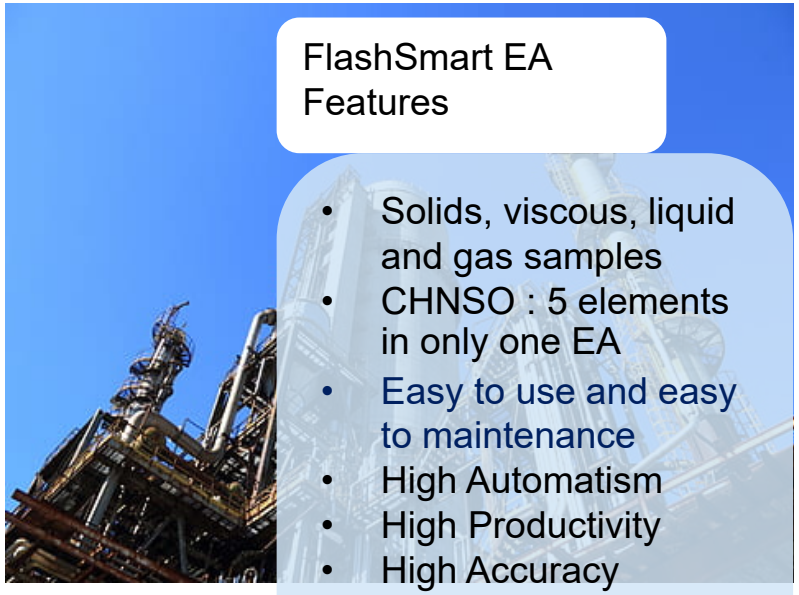
- Fuels
- Biofuels & Biomass
- S in Oils, Coals and Cokes
- S in Coal and coke ash
- CHN in coal, coke and oils
- Total Oxygen in gasoline, diesel
- N in Lubricants
- Catalysts





FlashSmart EA Configuration

- CHN, CHNS
- CHNO, CHNS/O
- N Lubricant
- With or without MVC module
- AI/AS 1310 Liquid Autosamplers
- FPD detector



FlashSmart EA Features

- Solids, viscous, liquid and gas samples
- CHNSO : 5 elements in only one EA
- Easy to use and easy to maintenance
- High Automatism
- High Productivity
- High Accuracy
- High Precision
- Reduced He and O2 consumption
- Automatic Heat Values and CO2, E.T.

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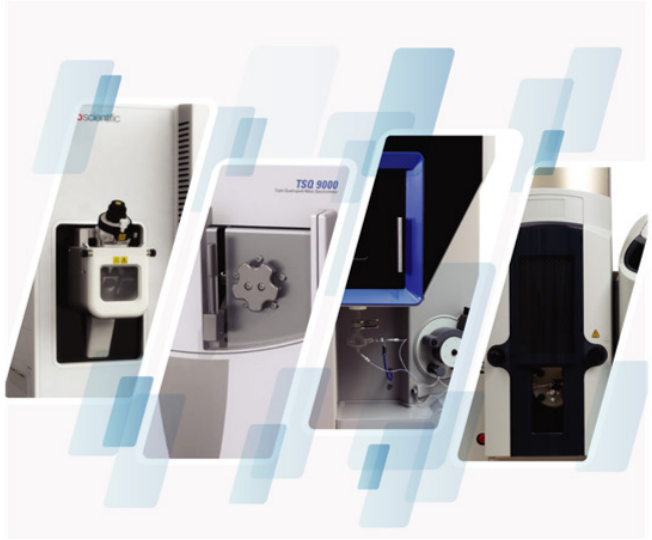

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Thank You

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