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Control of Volatile Organic Compound Emissions from Batch Processes - Alternative Control Techniques Information Document

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Control of Volatile Organic Compound Emissions from Batch Processes

Alternative Control Techniques Information Document

Emission Standards Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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1.0 INTRODUCTION

The purpose of this document is to provide information on alternative control techniques for volatile organic compound (VOC) emissions from batch operations. Although the control techniques information applies to batch processing in all industries, the document focuses primarily on batch processes in the following six industries: plastic materials and resins (described by Standard Industrial Classification (SIC) Code 2821), pharmaceuticals (SIC 2833 and 2834), gum and wood chemicals (SIC 2861), cyclic crudes and intermediates (SIC 2865), industrial organic chemicals (SIC 2869), and agricultural chemicals (SIC 2879). This document contains information on emissions, controls, control options, and costs that States can use in developing rules based on reasonably available control technology. The document presents options only, and does not contain a recommendation on reasonably available control technology.

2.0 BATCH PROCESS DESCRIPTIONS

This chapter identifies and describes the most common unit operations found in batch processing and provides descriptions of industries that typically use batch processing. The unit operations section of this chapter provides descriptions of the equipment (i.e., reactors, filters, dryers, distillation columns, extractors, crystallizers, and storage/transfer devices) used to perform batch processing steps. In the industry description section, four industries were selected to illustrate how these unit operations are combined to produce polymers and resins, pharmaceutical products, pesticides, and synthetic organic chemicals.

Whereas the unit operations section provides general information on equipment operation and sources of VOC emissions, the industry description section focuses in detail on equipment arrangements, process flows, operating conditions, and sources of emissions. Whenever possible, information is provided that can be used, in conjunction with the procedures described in subsequent chapters, to estimate VOC emissions from the five example batch processes. Moreover, the readers may use these examples as a guide in evaluating emissions from other specific batch processes that use these same or similar unit operations.

2.1 UNIT OPERATIONS IN BATCH PROCESSING

The unit operations discussed are commonly used to produce, separate, and prepare chemical products or intermediates on a batch basis. For each unit operation, a discussion is provided of the equipment used to accomplish that operation, key equipment design considerations, principles of equipment operation, and factors affecting emissions.

2.1.1 Reactors

The heart of many batch production cycles is the reaction step. In this step, feedstocks are combined under the proper operating conditions and allowed to react to form a product. Catalysts may be used to initiate or accelerate the reaction or to optimize the generation of the desired product. Solvents are often used to provide a reaction medium for solid reactants or to ensure that the product remains in solution. Following the reaction step, the catalysts, solvents, byproducts, and excess reactants are usually separated from the desired product. The purpose of this section is to describe (1) the design and operation of the equipment used to accomplish the reaction step and (2) the emissions and factors affecting emissions from this equipment.

2.1.1.1 Reactors: Design and Operation. Kettle-type reactors are used often in batch production processes. Figure 2-1 shows a schematic of this type of reactor. These reactors may range from 10 gallons to thousands of gallons in volume. As can be seen from Figure 2-1, the reactors are equipped to provide a range of capabilities that may be required during the batch reaction step. This equipment includes: a jacket for heating and cooling, hookups for charging raw materials and for discharging the contents of the reactor, an agitator and recycle line for mixing, control systems for temperature and pressure, a condenser system for controlling vent losses, a return line for refluxing condensables, a steam ejector for vacuum operation, a nitrogen supply for padding and purging the reactor, and a manway for taking samples and adding solid catalysts, reactants, and other solid materials to the reactor.

A typical reaction cycle consists of the following steps: (1) charging solvents, catalysts, and reactant(s) to the reactor; (2) operating the reactor; and (3) discharging the contents of the reactor and preparing for the next reaction cycle. There are many variations to this typical reaction cycle. This description is not intended to address these many variations; instead, it is

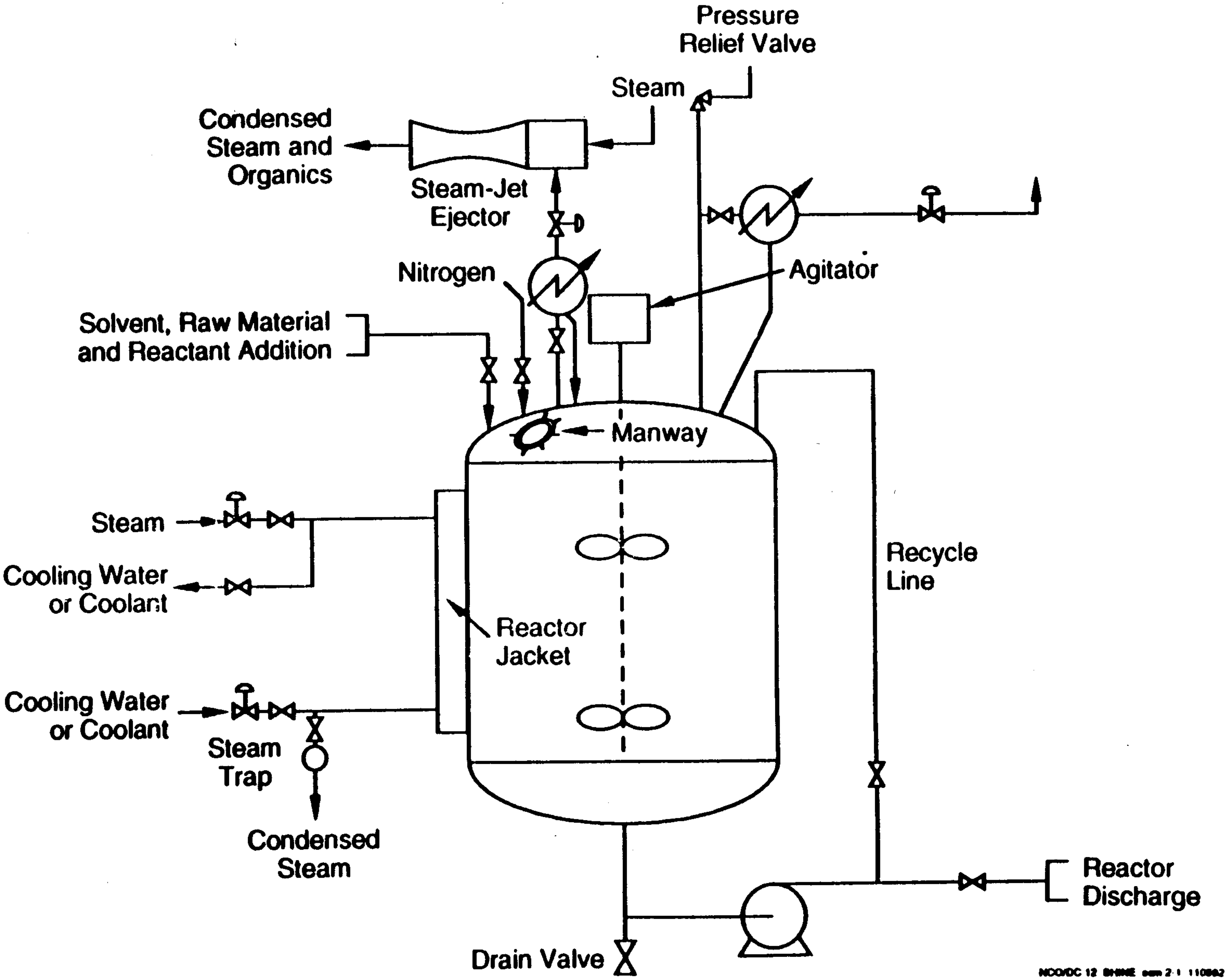


Figure 2-1. Basic design of a kettle-type batch reactor.

intended to provide a more general description of the operations involved in this stage of the process.

2.1.1.1.1 Reactor charging. The reaction cycle is normally initiated by charging solvents, catalysts, and raw materials into the reactor. For the purpose of this description, "raw materials" refers to compounds that are combined with other reactants to produce the desired product or intermediate. The initial charging step may be accomplished in many ways. If the reactor is tied into a vacuum system, the materials can be "pulled" into the reactor by reducing the pressure in the reactor below atmospheric. Steam jet ejectors, as shown in Figure 2-1, or vacuum pumps may be used for this purpose. The hookup connection for material addition is then used to introduce materials into the reactor. Drums containing solvents, catalysts, and raw materials can be hooked up to the reactor using flexible (i.e., flex) hoses. A dip-leg is inserted into the drum and connected to one end of the flex hose. The other end of the flex hose is connected to the reactor hookup connection. When the valve located at the reactor (in the hookup line shown in Figure 2-1) is opened, material in the drum flows through the flex hose and into the reactor due to the pressure differential.

Solvents, catalysts, and raw materials can also be pumped into the reactor through the hookup connection. Portable pumps are often used for this purpose. During the charging process, the valves in the vent line (the manual block valve and the control valve) are normally opened to prevent reactor pressure from increasing. The condenser is usually operated to reduce material losses through the vent line when volatile compounds are present in the reactor.

The manway may also be used to introduce materials into the reactor. Solid materials are usually added to the reactor in this manner. The manway normally contains bolts that can be removed to open it, but some manways have latches to allow for quick opening and closing. Solids are usually poured through the manway opening into the reactor. Once the transfer is complete, the manway is closed and bolted so that the reactor can be operated under pressure. In some cases, the middle part of the manway is constructed of heavy glass or plexiglass so the operator can view the inside of the reactor during operation.

The use of flexible hoses and quick-disconnect fittings are typical of manual-type operations where many different products may be manufactured in the same vessel. At other facilities where the same batch product is manufactured routinely in the same vessel, the reactor may be equipped with dedicated lines for transferring materials into the reactor. The dedicated lines connect the reactor with storage or weigh tanks containing solvents and raw materials. These storage tanks are often located at a higher level than the reactor so that material will flow by gravity into the reactor once valves in the transfer lines are opened. In some cases, a reactor may be equipped with dedicated lines for charging certain materials that are used often (e.g., common solvents) and also equipped with a general hookup line for less common materials.

2.1.1.1.2 Reactant addition and reactor operation. The most complex step in a typical batch reaction cycle is often the reactant addition step. This step involves the introduction of a reactant or reactants with the materials already charged into the reactor (e.g., solvents, catalysts, and initiators). The manufacture of some products involves only a single reactant addition step. The manufacture of other products is more complex, requiring several steps. In these cases, several intermediates may be generated during the reaction cycle, and different reactants may be reacted with each subsequent intermediate.

The operation of the reactor during the reactant addition step is affected primarily by two factors: (1) the kinetics of the specific reaction and (2) the capabilities of the reactor design. The reaction kinetics define the desired operating conditions. However, limits on the conditions that can be obtained during operation are often defined by the reactor design. Four important operating variables that are monitored and controlled during the reactant addition step are: the addition rate of the reactant, the reactor temperature, the reactor pressure, and the degree of mixing. The addition rate is closely tied to the reactant concentration, which optimizes the generation of the desired product. If undesirable by-products are generated when a reactant is available in excess, it would be necessary to monitor the addition rate closely to avoid operating with a reactant concentration that is too high. In other cases, the reactant concentration is not critical and, therefore, tight control of the reactant feed rate is not required.

The reactant addition step may be accomplished in the same way that materials are added to the reactor during the charging step. When the reactant feed rate must be tightly controlled, a metering pump is sometimes used. If the reaction rate is known, the reactant feed rate can be adjusted using the pump to maintain a proper concentration of the reactant. In other cases, operating parameters such as temperature and pressure determine how rapidly the reactant is added to the reactor. For example, if the reaction is exothermic, the cooling capacity of the reactor may determine how rapidly a reactant can be fed. The monitoring and control of operating variables other than the reactant addition rate are discussed in more detail below.

The reactor shown in Figure 2-1 is equipped with a typical temperature control system. The reactor is "jacketed" so that either cooling water or steam can be circulated around the shell of the reactor. For example, steam may be required initially to heat reactor contents to elevated temperatures due to kinetic considerations, while cooling water is required at a later time to quench or stop the reaction at a desired conversion level. A thermocouple is typically inserted into the side of the reactor and used to monitor the reactor temperature. The temperature read by the thermocouple is normally transmitted to controllers that manipulate the action of the automatic cooling water and steam valves.

Figure 2-1 also shows the scheme used to control the reactor pressure. A sensor located on top of the reactor measures pressure in the reactor headspace. This pressure reading is transmitted to controllers that operate flow valves on the vent line (during atmospheric pressure operation) or the ejector inlet line (during vacuum operation). Both lines may be fitted with condensers to minimize losses of volatile materials when they are purged from the reactor. The condensed materials are refluxed back to the reactor through the return line. As discussed earlier, the reactant addition rate is sometimes governed by operating variables such as the reactor pressure. The cooling capacity of the condenser and the sizing of the vent line both affect the operating pressure. In some cases, the reactant feed rate must be slowed to prevent overpressuring of the reactor or to reduce material losses through the vent line.

The degree of mixing is another operating variable that must be controlled during many reaction processes. The reactor shown in Figure 2-1 is equipped with an agitator for mixing. In some designs, a variable speed motor is installed so that the mixing rate can be adjusted. In addition to the agitator, mixing can be accomplished using the recycle line and the reactor transfer pump. The contents of the reactor are mixed by pumping material at the bottom of the reactor through the recycle line and back into the top of the reactor. The valve located in the recycle line can be manually throttled to control the recycle flow rate. This recycling process may be conducted with or without the agitator running, depending on the mixing needs of the specific reaction.

2.1.1.1.3 <u>Discharging reactor contents</u>. Once the reaction step is complete, product purification steps are usually required. These steps may involve a number of unit operations such as crystallization, distillation, filtration, and others. Some of these steps, such as solvent recovery, may be conducted in the reactor vessel. Other steps require more specialized equipment. These unit operations will be discussed in subsequent sections. For the purpose of this section, it is assumed that the contents of the reactor are discharged following the reaction step and the reactor is prepared for the next batch.

The contents of the reactor can be discharged by gravity or by using a transfer pump. If a pump is not available, nitrogen pressure or air pressure may be used to transfer material. Flex hoses can be used to connect the transfer line to the next equipment piece, such as a batch distillation column. At one end, the flex hose would be attached to the connection shown on the discharge side of the pump. On the other end, the flex hose would be attached to a similar connection on the distillation column. The contents of the reactor would be transferred to the still by opening valves in the transfer line at the reactor and distillation column and starting the transfer pump, if necessary.

After the contents have been transferred, it is often necessary to thoroughly clean the reactor. This cleanup is essential if a different product is to be produced in the next batch. If another batch of the same product is planned for the reactor, cleanup may not be required. In cases where the reactor needs thorough cleaning, it is often washed with water to remove residual product or catalyst. If water-insoluble compounds must be removed from the reactor, a solvent rinse is often required prior to starting the next batch. Both of these steps generate waste streams. Wastewater generated during water washing is often discharged to onsite wastewater treatment facilities; in some cases, it may be sent to the public sewer. Solvent from the reactor rinse step is usually collected and stored in waste solvent containers for disposal. The waste solvent may be disposed of by methods such as incineration or it may be purified for reuse by distillation. These operations may be conducted either onsite by the facility or the solvent may be sent to a commercial reclaimer.

Following the water wash or the solvent rinse, the reactor is heated until dry. Steam is used to heat the reactor jacket and evaporate residual water or solvent remaining on the inside reactor walls. If the reactor is washed in water, the evaporating water vapor may be allowed to flow out the vent line into the atmosphere. If a solvent rinse is used, normally the condenser is operated and the condensed solvent is reclaimed for disposal. In this case, some solvent may escape through the vent with noncondensables flowing out the vent line. Once the reactor is clean and dry, it can be closed and prepared for the next reactor charge.

2.1.1.2 Emissions and Factors Affecting Emissions From Reactors. The potential for VOC emissions exists during all steps of the reaction cycle that were discussed above. Emissions are discussed below in order according to the chronology of the steps presented above.

2.1.1.2.1 Charging. During the charging process, volatile compounds may be lost through the vacuum system, the vent line, or the manway.

Vacuum operation during charging. If materials are being charged into the reactor using a vacuum system, volatile compounds may be pulled into the vacuum system, which typically will be a steam jet ejector or a water seal vacuum pump. These compounds either leave the jet ejector system with the steam condensate, leave with vacuum pump seal water, or are vented from the vacuum system with noncondensables. The amount of materials lost through the vacuum system depends on the volatility of the compounds in the reactor and the duration of vacuum system operation. The steam condensate or pump seal liquid may be combined with other waste streams and treated onsite, or it may be discharged into a public sewer. Emissions may occur during the collection and treatment of these wastewater streams and are referred to as secondary emissions. A description of these emissions is discussed in this document.

Atmospheric venting during charging. If the reactor vent line is left open to the atmosphere during charging, volatile compounds may be vented along with the inert gases being displaced from the reactor through the vent line. As the material is pumped into the reactor, the rising liquid surface causes the displacement of the vapor occupying the shrinking headspace.

Manway emissions during charging. Emissions can also occur when the manway is open for charging solids into the reactor if volatile compounds have been previously charged into the reactor. These compounds will saturate the vapor space above the liquid in the reactor. If these vapors are less dense than air, they will flow from the reactor once the manway is opened due to the buoyancy effect. This buoyancy effect will be increased if the liquid in the reactor is warmer than room temperature. The longer the manway is left open, the greater the emissions will be during this step.

Nitrogen purging during charging. When toxic or ignitable material is contained in the reactor or is being charged into the reactor, the reactor headspace is often purged with an inert gas such as nitrogen. The purge may be carried out when the reactor vent is open to the atmosphere or prior to opening the manmay for solids addition. The purge reduces high concentrations of volatile material in the headspace that could harm workers in the immediate area or create an explosive mixture, but it increases the emissions of VOC's.

2.1.1.2.2 Emissions during reactant addition and reaction.

Reactant addition. The reactant addition step essentially is a charging step, except that the temperature of the material in the reactor may begin to increase as reactant is added. Emissions occur as a result of vapor displacement and increase with the rise in temperature because of increased volatilization of material in the reactor headspace. Emissions from reactant addition steps are normally emitted through the reactor vent line.

Reactor heatup. During the reaction, the contents of the reactor may begin to heat up, if the reaction is exothermic. External heating may also be applied to the reaction. Emissions of VOC's and air toxics occur during this step because of the expansion of headspace gas volume and because of the (increased volatilization of VOC's) due to temperature rise.

Additional load is placed on the condenser system if the reactor is purged with nitrogen during reaction. The nitrogen is routed through the vent line so that condensables in the purge gas can be refluxed back to the reactor. Since the nitrogen purge reduces the concentration of volatile organics flowing through the condenser, it lowers the dew point of the stream. In addition, the mass flow rate increases and the residence time decreases. This combination of effects can result in reduced condenser efficiency and, therefore, greater emissions of volatiles.

Pressure relief. Volatile organic compounds may also be emitted through the pressure relief valve during the reaction. This safety device is used to relieve overpressure in the reactor to prevent vessel rupture. The valve is set above any pressure that should normally be encountered during a normal reaction process.

2.1.1.2.3 Emissions from product purification and transfer.

Vacuum distillation. After the reaction is complete, excess solvent may be separated from the product by vacuum distillation. Emissions from this step will be limited by the exit conditions of the reactor condenser, or condensers, if a secondary condenser is used. Condensers work effectively in these situations since the uncontrolled streams contain high concentrations of volatile components that are easily condensed at moderate temperatures and atmospheric pressure.

Product transfer. Following reaction, the contents of the reactor are discharged for further processing and packaging. The transfer of the reactor material contents may be accomplished by gravity, by pumping, by pressurizing the reactor, or by depressurizing the receiver. The transfer step can create displacement emissions in the receiving vessel if the material transferred has a significant VOC concentration or if the receiving vessel contains VOC. If material is transferred using a vacuum pump, emissions may occur from the pump seal water, if the system is "once-through." The transfer of material using nitrogen or air pressure may cause VOC emissions, since the inert gas used as a carrier will in most cases be vented from the process lines after the transfer is complete. Depending upon the situation, this inert gas may contain significant amounts of entrained VOC's.

2.1.1.2.4 Reactor washing. As discussed earlier, wastewater and waste solvent streams may be generated during reactor washing. If the reactor is washed with water, the resulting wastewater stream will be directed either to a treatment facility (where secondary emissions may occur) or to a sewer. If the reactor is rinsed with a solvent, emissions may occur during the charging or disposal of the waste solvent. Emissions may also occur during subsequent drying steps. During drying, heat is applied to the reactor jacket to evaporate any residual solvent remaining on the inside reactor walls. The evaporating solvent may be routed through the condenser system for recovery.

2.1.2 Solid/Liquid Separation

Two general methods are available for the separation of a solid/liquid mixture--settling and filtration. Whereas settling relies on gravity to effect a separation, filtration uses external forces to separate the two phases. Specifically, filtration uses a permeable medium that retains the solid while allowing the liquid to pass through.

In order to force a liquid through a filter medium, a pressure drop must be applied. This pressure drop may be affected by gravity, centrifugal force, vacuum or positive pressure. Centrifugal separation is discussed in Section 2.1.2.2. The following section discusses batch filtration.

2.1.2.1 Batch Filtration. The two types of batch filtration systems most widely used are pressure and vacuum filters. Batch pressure filters are used more often than vacuum filters when filtering fine particles, because pressure filtration provides the driving force needed to achieve economical filtering rates. Batch pressure filters have the following advantages:

1. They allow for rapid filtration of fine slurries, which would otherwise be filtered at an uneconomically low rate;
2. They are compact and offer high filtering area per unit of plant space occupied; and

3. They are flexible in operation and provide this flexibility at a lower initial cost than other types of filters. However, a batch vacuum filter may be better suited for filtration applications that involve solvent vapors that produce highly combustible atmospheres.[1]

There are several types of batch pressure filters. Two common types are plate-and-frame and nutsche filters.

Plate-and-frame press. Figure 2-2 is a simple diagram of a plate-and-frame filter press, which consists of alternating solid plates and hollow frames. Plates and frames are separated by filter cloth. The feed slurry enters at the top of the frames, and the filter cake accumulates within the frames as the slurry flows downward. An open filtrate discharge allows the drain ports to empty into a trough. In closed discharge filters, drain ports are located in the corners of each plate. This drainage system allows the filtrate to flow in a channel along the length of the press.

Slurry is pumped into the filter press until the frames are full. This determination is made based on time, a decrease in feedrate or an increase in backpressure. Once the frames within the filter area are full, the discharge ports are opened. Filter cake forms on the cloth as the slurry liquid flows through the cloth.

The thickness of the filtercake depends on the purpose of the filtration. In purification of a dilute slurry to yield a clean filtrate, the filtercake is thin. In solids recovery, when slurries may be 40 percent solids, the frames are usually full after the cycle. Frames of varying thickness are available for different applications.

After the slurry has passed through the filter, a wash liquid may be applied. There are two different methods used for cake washing. In simple washing, wash liquid follows the same path as the slurry. In through washing, wash liquid enters alternate plates and is forced through the entire cake by alternately closed discharge ports. Cake characteristics

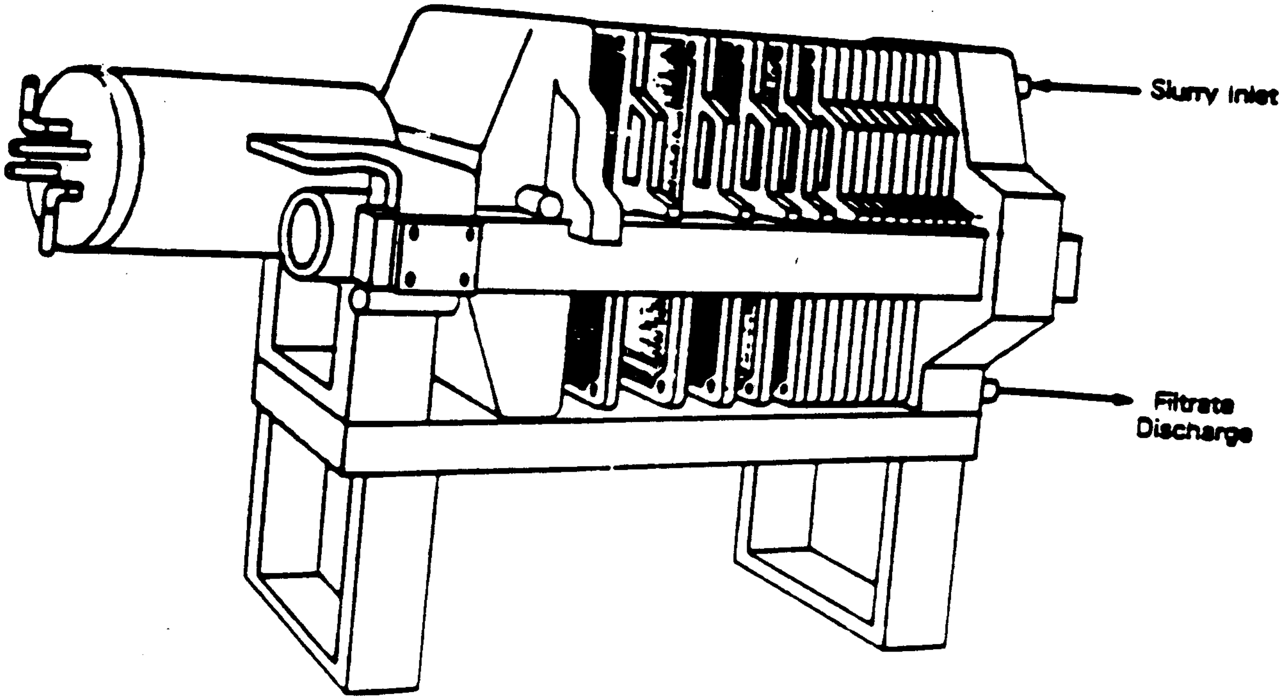


Figure 2-2. Plate-and-frame filter press.

determine the appropriate wash method. Compressed gas, such as air, may also be used to clean and dry the cake.

Solids are discharged by opening and separating the plates. Vibration and air blowing may be used to detach the filtercake from the cloth. These operations may be done manually or mechanically.

Nutsche filter. Another type of pressure filter, the nutsche filter, can either compress a slurry or apply vacuum to it in order to create a filter cake. A typical agitated nutsche filter is presented in Figure 2-3. The equipment not only acts as a filter but can also function as a product dryer after the slurry has been compressed and filtered into cake form.

The filter works by pressurizing the slurry with nitrogen to force the liquid through the filtering medium. The pressure needed to help maintain this process until enough liquid has been extracted is almost entirely a function of the specific particle characteristics of the product. Conversely, a vacuum may also be applied to the nutsche to draw the liquid down through the cake. Vacuum applications are usually limited to slurries with highly combustible atmospheres.[2] Because particles are spherical to irregular in shape and generally amorphous, the type of cake formation expected will determine the optimal pressure or vacuum needed to complete filtration. Experience has shown that filtration pressures generally range from 20 to 35 psig. Filters range in size from 1,000 to 2,000 gallons. Vacuum filtration occurs at pressures ranging from 3 to 20 psi. These filters also range in size from 1,000 to 2,000 gallons.

Upon completion of filtration, the filter may or may not go through a reslurry process, where it is washed and filtered again. This option is usually carried out when a highly specialized product requiring purity is desired or when solvents were not removed as part of the original slurry filtration process.

The nutsche filter is also capable of drying the filter cake and may be converted into a filter/dryer by only limited modifications. The actual drying process carried out in the

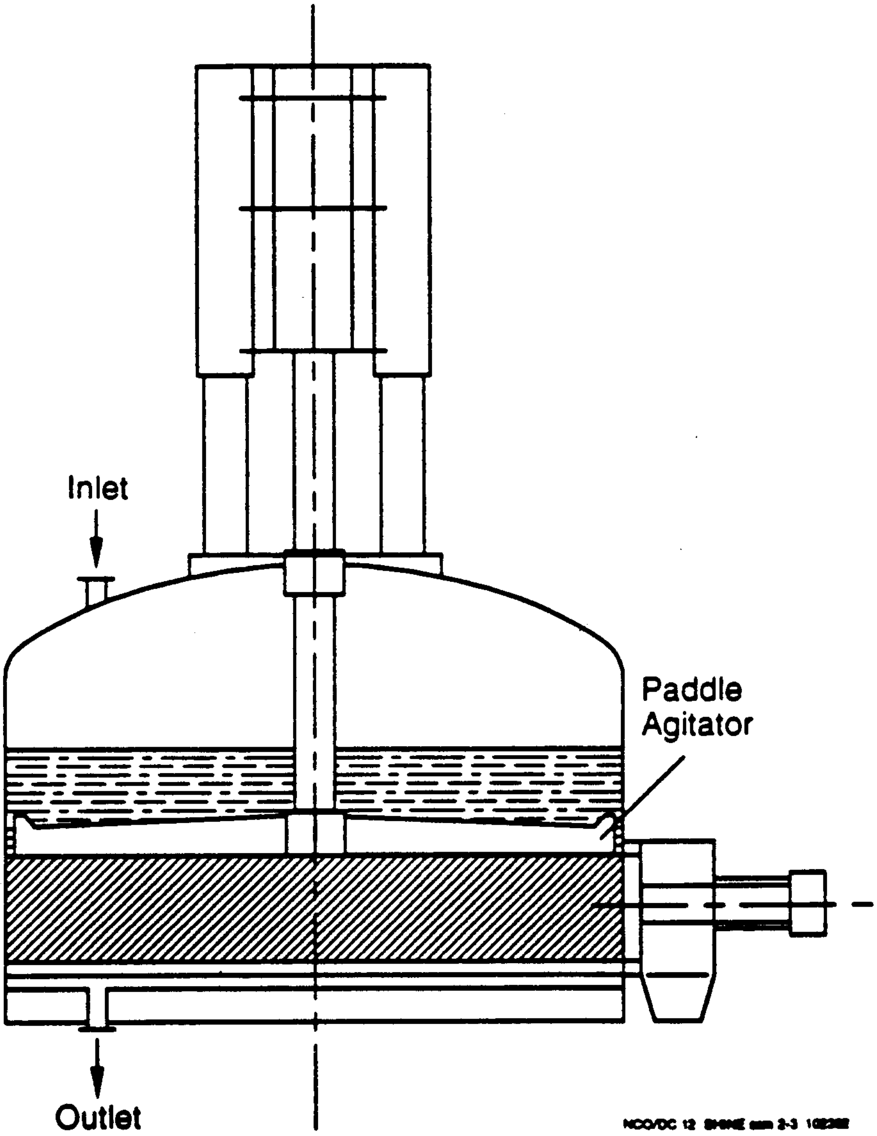


Figure 2-3. Agitated pressure Nutsche filter.

modified filter is usually convective. Heat is introduced to the filter/dryer through a hot gaseous medium (usually N_2) which is blown up through the cake until the desired level of dryness is achieved. The cake can be agitated or remain static, depending on the drying characteristics associated with the product.

2.1.2.1.1 Factors Affecting Emissions from Batch Filtration.

Plate and frame filters. Emissions from the plate-and-frame filter press can occur during filtration, washing, and discharge steps. The potential exists for VOC emissions during filtration and solvent washing from the trough used with open discharge, and the corner holes associated with closed discharge. Likewise, emissions can occur when the filter press is opened to remove solids. Vibration and air blowing to detach the solids can also increase the rate of emissions. The range of emissions will depend primarily on the vapor pressures and mole fractions of each VOC, the operating temperature of the filter, and air circulation rate. Because plate-and-frame filter presses offer no containment, it is also unlikely that material containing a high percentage of volatile or toxic solvent will be filtered using this type of device.

Nutsche filters. Pressure filters such as the nutsche filter shown in Figure 2-3 normally do not emit VOC's during actual filtration since they are fully enclosed. However, during slurry charging or vessel depressurizing, emissions of VOC can occur.

Emissions also can occur from all batch process filters if a compressed gas is used to purge the filter or dry the cake. The gas will entrain evaporated solvent and carry it to a vent. Emission rates will depend on the factors cited above and the compressed gas purge rate. Note also that if filtrate from either operation is discharged to wastewater treatment, there is also potential for emissions resulting from cross-media transfer effects.

2.1.2.2 Centrifugal Separation.

As mentioned in Section 2.1.2, filtration is used to separate a solid from a liquid. Centrifugal filters (basket centrifuges) make use of the outward (centrifugal) force that is exerted on an object during rotation. This centrifugal force pushes the liquid through the filter medium and presses the solids against the walls to form a cake. In a solid-bowl centrifuge the liquid is separated from the solid by centrifugal force and is continuously decanted off. The recovered solid accumulates on the sides of the bowl. Solid bowl centrifuges are used to recover small amounts of solids that are dispersed in large amounts of liquid. Catalysts, for example, often are recovered from liquid product in this manner.

2.1.2.3 Centrifugal Filters: Design and Operation. Centrifugal filters are cylinders which contain a rotating basket at the base of a vertical shaft. Figure 2-4 depicts a typical configuration for a basket centrifuge. The basket may be 0.8 to 1.2 m in diameter and 0.5 to 0.8 m deep. Its sides are perforated and covered with a filter medium such as fabric or woven metal. An inert gas such as nitrogen is often introduced into the chamber prior to the addition of slurry to avoid the buildup of an explosive atmosphere. Centrifuges must be carefully operated to avoid air infiltration by vortex entrainment. Therefore, they usually are operated under nitrogen blanket and kept sealed during operation.[3]

Feed slurry enters the chamber through an inlet pipe as the basket rotates at speeds of 600 to 1,800 revolutions per minute (rpm). Centrifugal force pushes the mixture towards the wall of the basket. The liquid passes through the filter medium and is discharged through a pipe. The solid particles form a filtercake on the sides of the basket.

After all of the slurry has been fed to the chamber, a wash liquid may be introduced to force the remaining slurry liquid through the cake and filter medium. The basket continues to spin in order to remove any residual liquid.

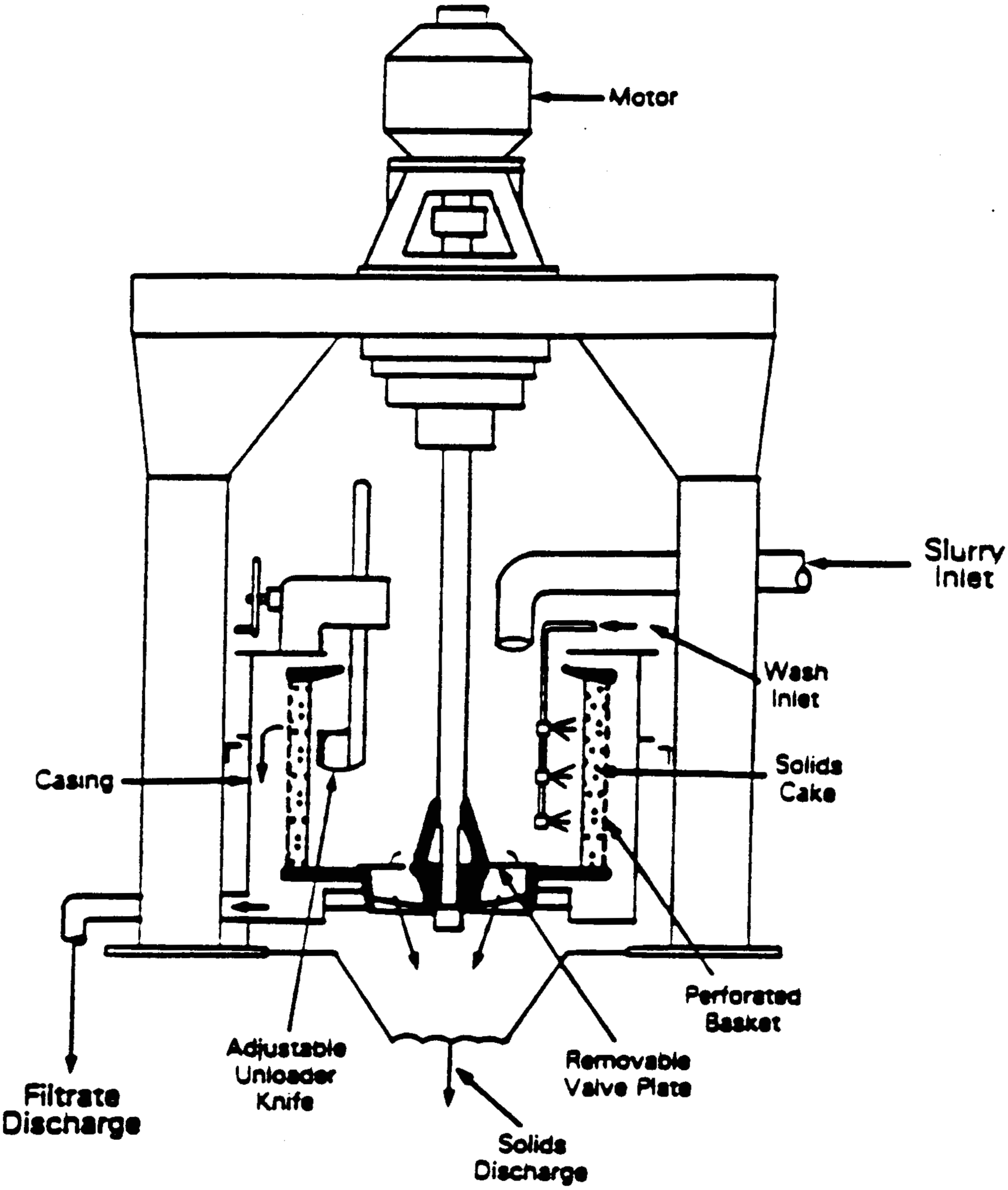


Figure 2-4. Top-suspended centrifugal filter.

At this point the motor speed is reduced, slowing the rotation to between 30 and 50 rpm. An adjustable knife is engaged to scrape the side of the basket and dislodge the filtercake. The cake material falls to the bottom of the chamber where it is discharged through an opening in the basket.

Manual dumping of filter cake from basket centrifuges also can occur, especially when top-unload centrifuges are used. Operators must "scoop out" product into a transfer vessel. The vessel is usually purged with high flow rates of inert gas just prior to this step.

Another type of basket centrifuge is the Heinkel centrifuge. The main feature that distinguishes the Heinkel centrifuge from other basket centrifuges is the inverting filter cloth the Heinkel employs. The inverting filter cloth allows top unloading in a simplified manner. Rather than scooping the contents out manually, the operator(s) can displace the entire filter cloth and empty its contents.[4]

2.1.2.4 Factors Affecting Emissions from Centrifugal Separation. Emissions from centrifuges may occur during initial vessel purging prior to the addition of slurry, and during discharge. A potential source of emissions from centrifuges is created by the inert gas blanket which is used to prevent the possibility of an explosive atmosphere. The inert blanket is especially necessary in bottom-discharge centrifuges because they contain metal knife scrapers that move the filtercake away from the walls. The mechanical friction associated with metal-to-metal contact and static electricity discharge are likely ignition sources.

The potential for an explosion depends on the type of centrifuge, the characteristics of the solvent vapor, and how the centrifuge is operated.[5] A centrifuge is difficult to blanket with an inert gas during discharge because it cannot stay sealed. During discharge, therefore, an inert gas purge is more effective in evading explosive conditions because of the higher flow rate associated with a purge. Note that during the actual centrifugation process, an inert gas blanket contributes significantly lower VOC emissions than a purge.

As mentioned, the much higher flow rates associated with inert gas purges will obviously induce greater emissions. Purges are used during bottom-discharge and prior to opening a top-unload centrifuge for sampling or unloading.

The solids removed from the centrifuge may still be "wet" with solvent and therefore be a source of emissions during unloading and transport to the next process step. Bottom-discharge centrifuges can minimize this problem if the solids are transferred to a receiving cart through a closed chute and the receiving cart is covered during transport. As with other filters, the emission rate from centrifugal filters will be influenced by operating temperature, VOC vapor pressures and mole fractions, inert purge gas flow rate, and the use of mitigating factors such as closed chutes and carts.

2.1.3 Drying

The term "drying" generally refers to the removal of liquid from primarily solid material. However, due to the large amount of solids (and sometimes a large portion of liquid) dryers can be large VOC emission sources. Dryers are used to remove liquids, usually residual solvent, from centrifuged or filtered product. This removal is accomplished by evaporating solvent into a gas stream. Solvent evaporation is accelerated by application of heat and/or vacuum to the wet solids. Circulation of warm air also speeds the drying process.

It is important to note the differences between dryers and evaporators. Whereas evaporators remove liquids as vapors at their boiling points, dryers remove the vapor into a gas stream at temperatures below its boiling point. Also evaporators are usually used to remove large amounts of liquid.

There are several different types of dryers being used by industry today. For example, tray, tunnel, rotary, drum and spray dryers are available. Selection of dryer type depends primarily on characteristics of the solid. Three dryer types that are commonly used in batch processes are tray, rotary, and double-cone dryers. The previous discussion on the converted nutsche filter/dryer is also considered relevant to this discussion.

2.1.3.1 Tray Dryers Figure 2-5 is a simplified diagram of a tray dryer. Tray dryers are among the simplest type of dryer, although they are labor intensive because of necessary manual loading and unloading. The product intended for drying is placed on trays that are stacked on shelves. After all the trays have been filled, the dryer door is closed and the shelves are heated. A vacuum is also pulled within the dryer to allow for drying at low temperatures. Typically, tray dryers contain 15 to 20 trays.[6]

2.1.3.2 Rotary Dryers: Design and Operation. Another important type of dryer is the rotary dryer. As shown in Figure 2-6, this dryer consists of a revolving cylinder that is slightly inclined to the horizontal. The diameter of the cylinder may range from 0.3 to 3 m, and the length may vary from 1 to 30 m.

Feed enters at the elevated end and is carried through the dryer by the rotation and slope of the cylinder. In direct-heat rotary dryers, the solids are dried by direct contact with a heated gas stream. This stream may consist of air or flue gas flowing at approximately 2.8 m^3 per minute. The flights shown in Figure 2-6 lift the solids and shower them through the gas stream. The solids and gas may flow cocurrently or countercurrently, with countercurrent flow having a greater heat-transfer efficiency.

Due to the nature of the equipment, the outlet stream for rotary dryers must be free-flowing and granular. Sticky feed materials may be dried if some of the granular product is recycled and mixed with the feed.

2.1.3.3 Tumble (Double-Cone) Dryers: Design and Operation. A batch double-cone dryer is shown in Figure 2-7. Material to be dried in this type of dryer must be manually loaded into the dryer and manually unloaded after the drying cycle is complete. Double-cone dryers may be operated under a vacuum in which a

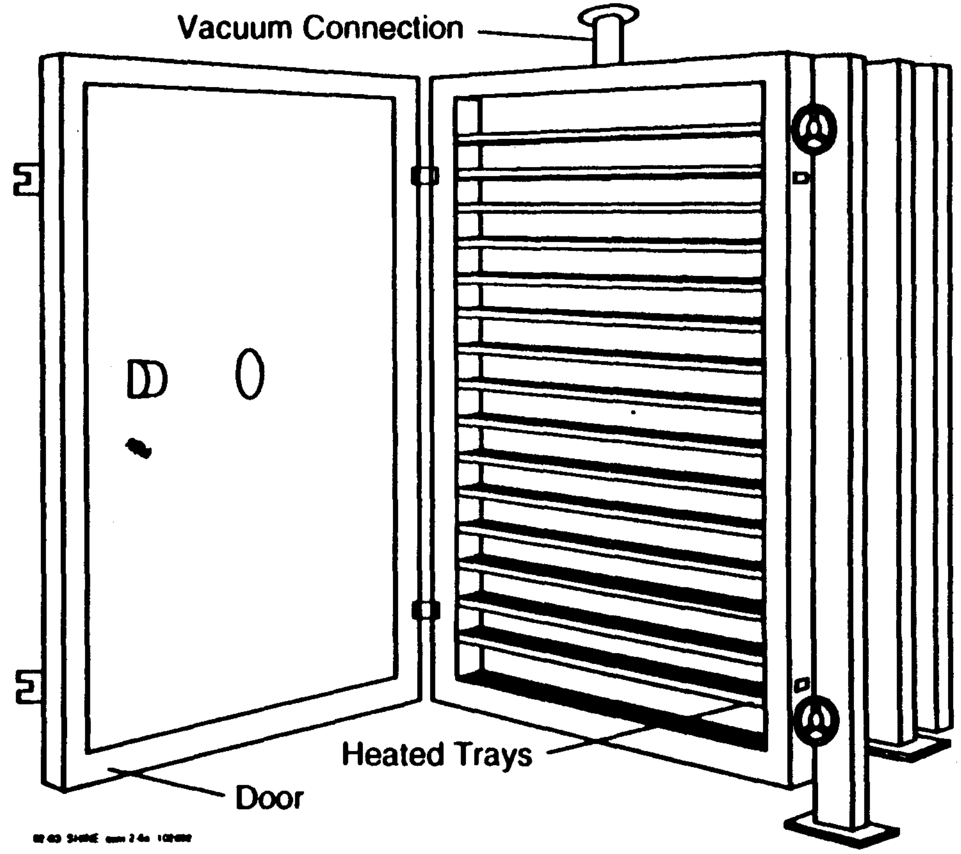


Figure 2-5. Vacuum tray dryer.

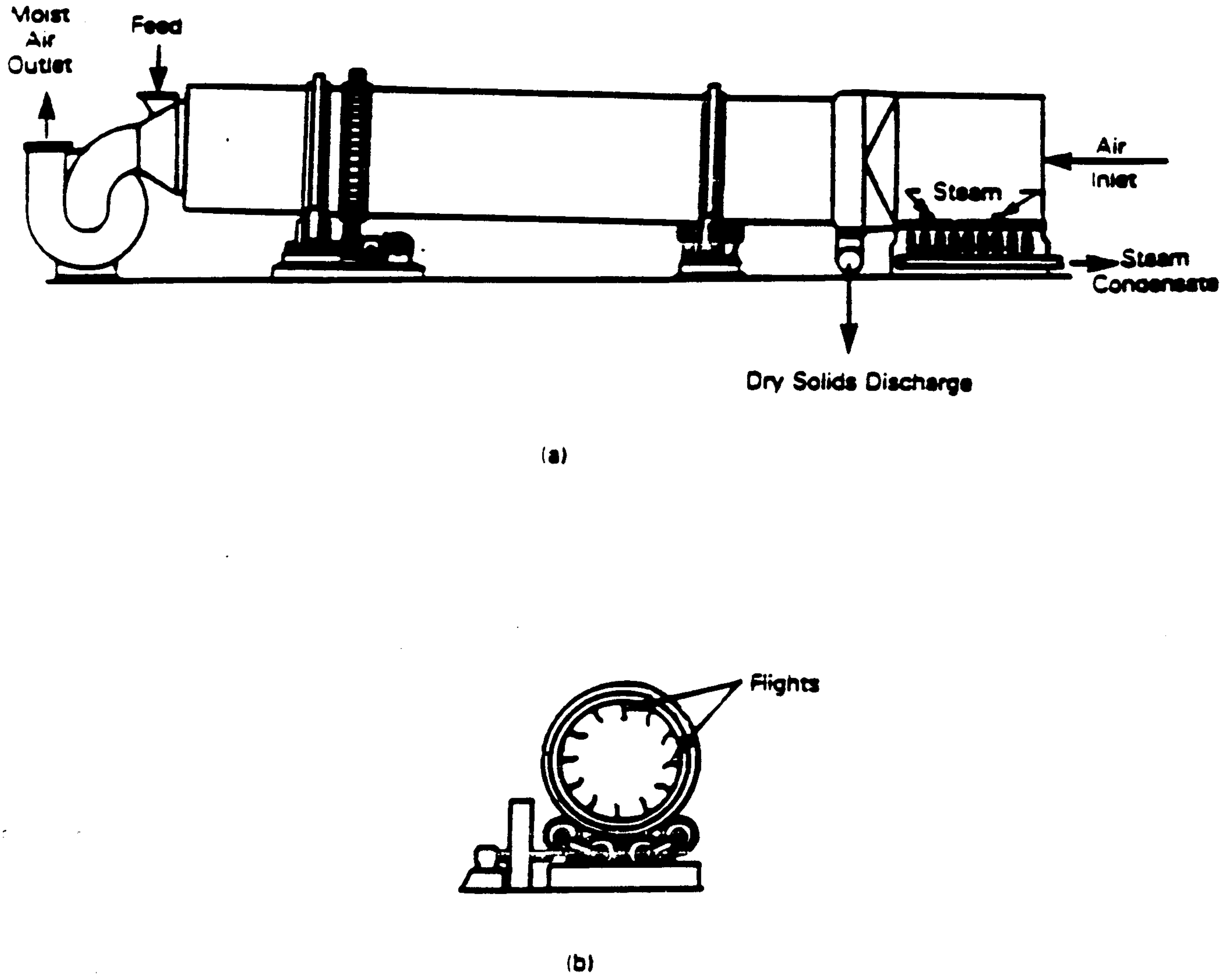


Figure 2-6. (a) Countercurrent air-heated rotary dryer.
(b) Cross-sectional view.

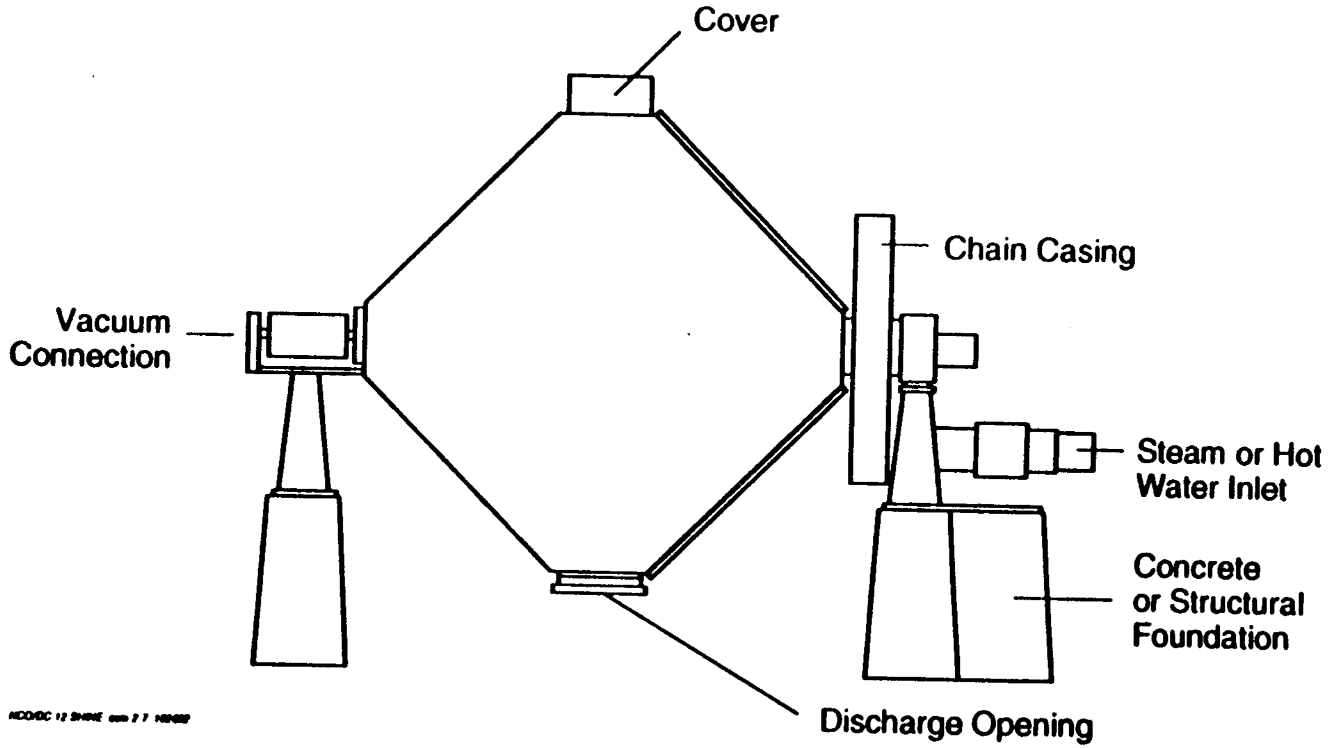


Figure 2-7. Tumble (double-cone) dryer.

small flow rate of air is allowed to leak in or occasionally may be used to dry material convectively with heated gas. Tumble dryers range in size from 20 to 100 gallons. Flow rates of drying gas and drying temperatures vary with product.

2.1.3.4 Factors Affecting Emissions from Dryers. Volatiles may be emitted at the feed inlet and product discharge areas of the dryers, as well as from the dryer exhausts. Tunnel, nutsche filter/dryers, and rotary dryers typically use a moving stream of heated air to dry the feed material. This mode of drying is termed "convective". Emission streams from convective dryers will have large volumes of noncondensable gases throughout the drying cycle.

Tray and double-cone dryers typically are operated under vacuum, in which the heat transferred to the material being dried will be through conduction from heated surfaces. Under vacuum, a smaller volume of air passes through the equipment due to inward leakage. This vacuum exhaust contains VOC's. The volume of noncondensables in vacuum dryer exhaust is small, compared to convective exhaust, and increases throughout the drying cycle.

Dryers are potentially large emission sources. Emissions vary according to dryer type, dryer size, number of drying cycles per year, and amount and type of solvent evaporated. Emission rates vary during a batch drying cycle: they are greatest at the beginning of the cycle and least at the end. The rate of VOC emissions from a given batch drying operation will be a function of the duration of the drying cycle and the amount of solvent in the material.

2.1.4 Distillation

Distillation is used to separate a mixture of liquids. The basis for this separation is the relative volatility (i.e., vapor-pressure and boiling point) of the components. Within refining and chemical manufacturing, distillation is the most commonly used method for separation and purification of liquids.

Separation is achieved by the redistribution of the components between the liquid and vapor phases. The more volatile component(s) concentrates in the vapor phase while the less volatile component(s) concentrates in the liquid phase. The two phases are generated by vaporization and condensation of the feed mixture.

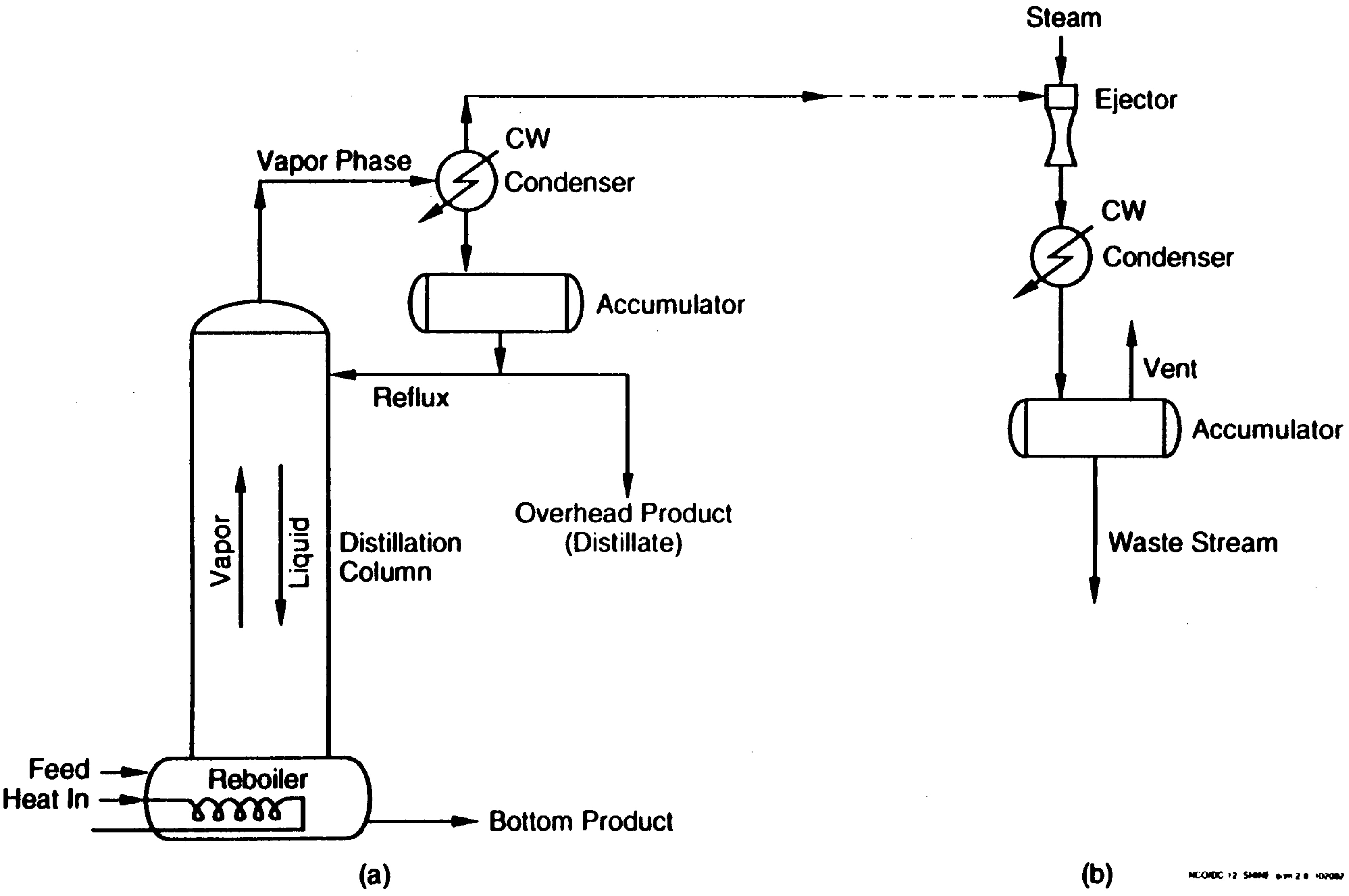
There are several different types of distillation operations. In simple operations, the feed is vaporized and condensed one time. This usually does not yield a clean separation. Fractional distillation involves repeated vaporization and condensation and results in a sharper separation.

2.1.4.1 Batch Fractionators: Design and Operation. The batch fractionator in Figure 2-8 consists of a reboiler and a sieve-plate column. The feed mixture is charged into the reboiler and heated until it begins to boil. The initial vapor that forms is richer in the more volatile component (A) than the liquid is. However, the vapor still contains a significant amount of both components. In order to increase the concentration of A in the vapor, the vapor stream enters the column where it is brought into contact with boiling liquid.

The vapor that exits the top of the column goes to a condenser and then to the accumulator (reflux drum). Some of the condensate in the reflux drum is returned to the column as reflux at the top of the column. As it flows down the column, the liquid contacts the vapors that are moving upward. Contact between the two phases occurs in a stagewise manner in a column which holds horizontal-stacked sieve trays. Vapor flows up through the perforations. Liquid flows down through pipes called downcomers.

The downcomers are located on alternating sides of each tray. Thus the liquid must flow across the tray. The top of the downcomer acts a weir, maintaining a minimum depth of liquid on the tray. The vapor bubbles up through the layer of liquid. This contact causes some of the more volatile component (A) to diffuse from the liquid, thus enriching the vapor.

The vapor leaving the top of the column is condensed; part of the condensate is returned to the column as reflux and the remainder is drawn off as product liquid, or distillate. This



(a)

(b)

Figure 2-8. (a) Batch fractionator with (b) vacuum generating equipment.

circulation continues until the desired separation is achieved, which is usually determined by the purity of the distillate. Specifications for this stream usually state a maximum concentration of the less volatile component.

The liquid leaving the reboiler is called the bottom product or bottoms. It is rich in the less-volatile component but is not as pure as the distillate. Whereas the vapor is enriched as it moves upward through the column, the equipment in Figure 2-8 does not provide for enrichment of the liquid stream. Thus, the condensed vapor product (distillate) will be more pure than the bottom product. Rectification of the liquid stream, to yield a nearly pure bottom product, requires a more complex column. Such columns are usually run on a continuous, rather than batch, basis.

The equipment shown in Figure 2-8 is a fairly simple arrangement. Variations are made based on the nature of the mixture and its components. Many batch processes involve a distillation in a reactor kettle or series of kettles (often called "still pots"), as opposed to a column. The distillation principles are the same regardless of whether the separation is conducted in kettles or columns. For example, operating pressures can be below atmospheric (vacuum), atmospheric, or above atmospheric (pressure). Figure 2-8 shows a possible arrangement for vacuum-generating equipment. Inert gas, especially steam, is often introduced to improve separation. If a mixture is particularly difficult to separate (i.e., azeotropic), other compounds may be added to aid in distillation.

2.1.4.2 Factors Affecting Emissions from Batch Fractionators. The gases and vapors entering the condenser can contain VOC, water vapor, and noncondensables such as oxygen (O_2), nitrogen (N_2) and carbon dioxide (CO_2). These vapors and gases originate from:

1. Vaporization of liquid feeds;
2. Dissolved gases in liquid feeds;
3. Inert carrier gases added to assist in distillation (only for inert carrier distillation); and

4. Air leaking into the column (in vacuum distillation).

The condenser cools most of the vapors enough that they can be collected as a liquid phase. The noncondensables (O_2, N_2, CO_2, and organics with low boiling points) are present as a gas stream and are vented from the condenser. Portions of this gas stream are often recovered in devices such as scrubbers, adsorbers, and secondary condensers.

Vacuum-generating devices (pumps and ejectors) might also affect the amount of noncondensables. Some organics can be absorbed by condensed steam in condensers located after vacuum jets. In the case of oil-sealed vacuum pumps, the oil losses increase the VOC content of the noncondensables exiting the vacuum pump. The noncondensables from the last piece of process equipment (condensers, pumps, ejectors, scrubbers, adsorbers, etc.) constitute the emissions from the distillation unit unless they are controlled by combustion devices such as incinerators, flares and boilers.

The most frequently encountered emission points from distillation operations are: condensers (which are described in Chapter 4), accumulators (losses are typical of vapor displacement, discussed in Chapter 3), steam jet ejectors (discussed in Chapters 3 and 4), vacuum pumps (discussed in Chapter 3 and 4), and pressure relief valves (discussed in Chapter 3). The total volume of gases emitted from a distillation operation depends upon:

1. The physical properties of the organic components (especially vapor pressure at the reflux drum temperature);
2. The efficiency and operating conditions of the condenser and other recovery equipment;
3. The volume of inert carrier gas used; and
4. Air leaks into the vacuum column (leaks are increased by both reduced pressure and increased column size).

2.1.5 Extraction

Liquid extraction is another method of separating a mixture of two liquids. Whereas distillation takes advantage of a difference in boiling point (vapor pressure), the principle of liquid extraction is based on a difference in solubility. In the extraction operation, a mixture of two liquids (A & B) is brought into contact with a third liquid called the solvent (S). The solvent preferentially combines with one of the components of the original mixture. The two resulting streams are:

1. Extract - mostly solvent and the liquid with which it preferentially combined (S + A); and
2. Raffinate - mostly residual liquid from the original mixture (B).

It is important to note that both exit streams will contain all three components (A, B and S). However, the raffinate will be primarily liquid B and the extract will be primarily a mixture of A and S.

There are three general types of equipment used for liquid-liquid extraction, although most batch extractions occur in mixer-settlers. In mixer-settlers, a mixer is used to contact the feed solution and solvent. A settling tank allows the two phases to separate by gravity. Stirred-tank reactors often serve as both mixer and settler.

2.1.5.1 Factors Affecting Emissions from Extractors. Emissions from mixer-settler extractors are similar to those from reactors (discussed in Section 3.1.1) in that they stem mainly from vapor displacement during purging, filling and cleaning of the vessel. Some VOC may also be emitted while the liquids are being agitated.

As discussed for reactors, the rate of VOC emissions will depend primarily on VOC vapor pressures at operating temperatures, liquid pumping rate during column filling, rate of sweep gas (if used) during purging, and equipment cleaning procedures.

2.1.6 Crystallization

Crystallization is a means of separating an intermediate or final product from a liquid solution. Solid particles (i.e., crystals) are formed from the homogenous liquid phase. This formation is accomplished by creating a supersaturated solution, in which the desired compound will form crystals. If performed properly and in the absence of competing crystals, crystallization can produce a highly pure product.

Four methods may be used to produce supersaturation. If solubility of the solute increases strongly with temperature, a saturated solution becomes supersaturated by simple cooling. If solubility is relatively independent of temperature or decreases with increased temperature, supersaturation may be generated by evaporating a portion of the solvent. Often a combination of cooling and evaporation is used.

If neither cooling nor evaporation is desirable, supersaturation may be induced by adding a third component. The third component forms a mixture with the original solvent in which the solute is considerably less soluble.

Batch crystallization usually relies on simple cooling or evaporation as the method for producing supersaturation. Batch crystallization is useful for low production rates and when the cooling range is wide, since it avoids the material shock that occurs in continuous crystallization equipment (i.e., metal stress) from mixing a hot solution with a cool mother liquor.[7] Figure 2-9 is a diagram of a batch vacuum crystallizer.

2.1.6.1 Vacuum Crystallizers: Design and Operation. In most vacuum crystallizers, supersaturation is generated by adiabatic evaporative cooling. The equipment mainly consists of a closed vessel with a conical bottom. A condenser and steam-jet vacuum pump maintain a vacuum within the crystallizer.

The feed solution is saturated and heated to a temperature greater than the boiling point at the crystallizer pressure. Upon entering the chamber, the solution cools spontaneously, and some of the solvent evaporates. The cooling and evaporation induce supersaturation, which initiates crystal formation. The mixture of mother liquor and crystals is referred to as "magma."

As crystals form and grow, they are drawn off by a discharge pipe. This pipe is located in the conical section of the vessel, above the downpipe that leads to the pump. The discharge stream will contain some mother liquor. Further processing (e.g., centrifugation) can separate the two components. Batch

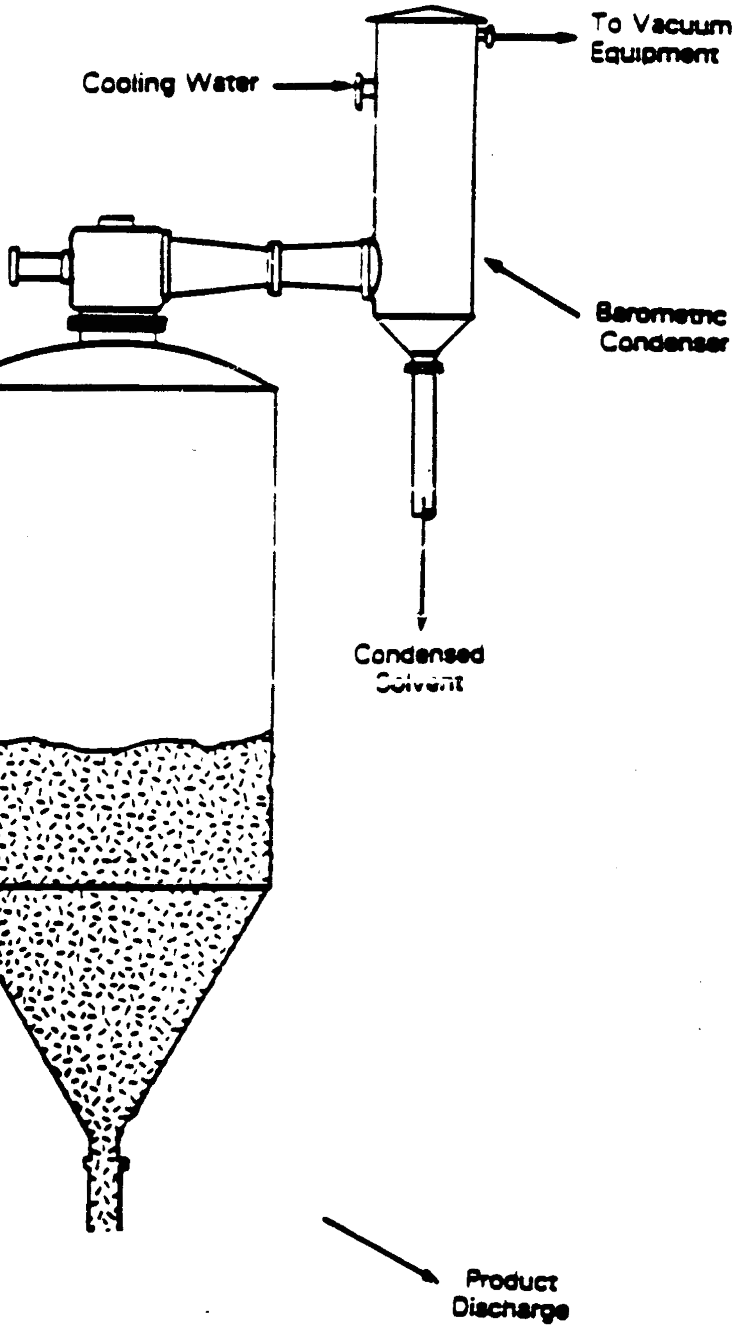


Figure 2-9. Vacuum crystallizer.

crystallization is usually performed with small amounts of material. Cycle times range from 2 to 8 hours.

2.1.6.2 Factors Affecting Emissions from Batch Vacuum Crystallizers. If crystallization is done mainly through cooling of a solution, there will be little VOC emission. In fact, the equipment may be completely enclosed.

However, when crystallization is done by solvent evaporation in a vacuum environment, there is a greater potential for emissions. The vapor over the magma is rich in solvent. Emissions will be significant if this evaporated solvent is vented directly to the atmosphere. The condenser and vacuum jet shown in Figure 2-9 reduce the amount of volatiles that actually leave the system. As with other vacuum operations, the rate of VOC emissions will depend primarily on the VOC vapor pressure at the crystallizer or condenser temperature, the absolute pressure of the system, and the air leak rate.

2.1.7 Storage

2.1.7.1 Storage Equipment: Design and Operation. There are three major types of vessels used to store volatile organic liquids (VOL's):

1. Fixed roof tanks;
2. External floating roof tanks; and
3. Internal floating roof tanks.

These tanks are cylindrical with the axis oriented perpendicular to the foundation and are almost exclusively above ground. This section addresses only the fixed roof type of storage tank.

Of currently used tank designs, the fixed-roof tank is the least expensive to construct and is generally considered as the minimum acceptable equipment for the storage of VOL's. A typical fixed roof tank consists of a cylindrical steel shell with a cone- or dome-shaped roof that is permanently affixed to the tank shell. A breather valve (pressure-vacuum valve), which is commonly installed on many fixed-roof tanks, allows the tank to operate at a slight internal pressure or vacuum. However, this valve prevents the release of vapors only during very small changes in temperature, barometric pressure, or liquid level.

Larger changes in these parameters can result in significant emissions from fixed roof tanks.

2.1.7.2 Factors Affecting Emissions from Storage Tanks. The major types of emissions from fixed-roof tanks are breathing and working losses. A breathing loss is the expulsion of vapor from a tank vapor space that has expanded or contracted because of daily changes in temperature and barometric pressure. The emissions occur in the absence of any liquid level change in the tank. The rate of VOC emissions from breathing losses is a function primarily of VOC vapor pressure (at the bulk liquid conditions), tank diameter, average vapor space height, and ambient temperature and pressure changes from day to night.

Working losses are associated with an increase in the liquid level in the tank. The vapors in the space above the liquid are expelled from the tank when, as a result of filling, the pressure inside the tank exceeds the relief pressure. Emptying losses occur when the air that is drawn into the tank during liquid removal saturates with hydrocarbon vapor and expands, thus exceeding the fixed capacity of the vapor space and overflowing through the pressure-vacuum valve. Combined filling and emptying losses are called "working losses." The rate of VOC emissions from these working losses is a function of VOC vapor pressure (at bulk liquid conditions), vapor space height, and turnover factor (i.e., the rate at which the tank is emptied and refilled). Information on emissions from storage tank working and breathing losses is detailed in EPA's AP-42 Compilation of Air Pollution Emission Factors.

2.1.8 Transfer Operations

Chemical transfer operations also contribute to plant VOC emissions. Common sources of transfer emissions are:

1. Manual transfer of chemicals from 55 gallon drums to receiving vessels; and
2. Transfer of final product from processes to receiving vessels.

Some chemicals are stored in 55-gallon drums. Transfer of chemicals from drums to process vessels is sometimes done through permanent piping; more commonly, however, it is done by opening the drum and manually pouring the contents. The manual pouring is a source of emissions, although a relatively small one on a "per drum" basis.

Emissions from transfer of final product from processes to receiving vessels occur frequently in batch processing. These emissions are analogous to vessel charging. The AP-42 emission factor handbook referenced earlier contains emission estimation methodologies for various loading mechanisms including splash loading and submerged filling.

2.1.9 Equipment Leaks

Pump seals, flanges, valve seals, agitator seals, and hose connections or couplings create VOC emissions when they leak. A protocol has been developed by EPA that can be used to develop emission factors for equipment leaks. However, if no other data is available, factors have been developed to estimate the amount of VOC that is leaking from a population of valves, seals, flanges, etc. These factors are known as synthetic organic chemical manufacturing industry (SOCMI) equipment leak factors. Note that the amount of time that the process components are in VOC service also plays a role in the amount of VOC that could be expected to leak. This is especially of concern in batch processes, where many components are not in service the majority of time and therefore should not be expected to leak as much material as components that are part of continuous processes. Note also that because of this reason it may be harder to detect leaking components in batch processes.

2.1.10 Wastewater

2.1.10.1 Generation. Wastewater may be generated from a number of activities that occur in batch processing, including equipment cleaning, vacuum ejector or pump once-through circulation using water, scrubber water discharging, steam stripping, or the discharging of water that was part of the process feedstock or that was generated in the process (i.e., a condensation reaction). Wastewater often contains dissolved VOC's or air toxics and may also carry large amounts of insoluble

VOC's or air toxics in emulsion-type multiple phase systems. Facilities often pretreat wastewater prior to discharge to publicly owned treatment plants, and this practice often is streamlined by isolating wastewater based on the degree of contamination and treating the various fractions accordingly.

2.1.10.2 Factors Affecting Emissions from Wastewater. The amount of VOC contained in the wastewater and the method of treatment of wastewater will affect the amount of VOC emissions. Treatment options include activated sludge without aeration and simple decantation and settling with the aid of flocculating agents. The EPA has published guidelines on air emissions from wastewater treatment systems. These guidelines examine various methods of wastewater containment, such as storage in open tanks and provide methodologies for estimation of emissions. For open tanks, the emission estimation discussion presented in Appendix B of this document is also relevant.

2.2 EXAMPLE INDUSTRY DESCRIPTIONS

The inherent diversity of batch manufacturing prevents a general description of this chemical industry segment. Instead, the following five industries have been selected as examples of the unit operation configurations, equipment operating conditions, and emission sources typically encountered in batch chemical processing: resin manufacturing, pharmaceuticals manufacturing, pesticides, and SOCMI. These processes were chosen because they contain high production volume batch processes, contain significant potential sources of VOC emissions, and illustrate the diversity of equipment configurations and process flows which characterize this type of industry.

For each of these batch processes, a detailed description is provided of the associated chemistry, equipment, and stream flows, including a process flow diagram. Each of the intermediate processing steps is discussed with an emphasis on process operating conditions wherever this information is available. A separate subsection for each process is devoted to

VOC emission sources and the factors that influence the extent of those emissions.

2.2.1 Synthetic Resin Manufacturing

The manufacture of synthetic resins is often accomplished using batch processes. In light of an ever-increasing demand for highly-specialized materials, batch processing offers flexibility in product specification and production rate, as well as a high degree of control over process variables. This industry description segment is intended to familiarize the reader with typical batch processing routes that are currently being used to manufacture resins. A specific process for the manufacture of epichlorohydrin-based nonnylon polyamide (wet strength) resin is described in detail below. In addition, information on sources of VOC and air toxics emissions from the process is presented following the process flow discussion. This process typifies the batch processes currently found in industry.

2.2.1.1 Process Flow. Figure 2-10 is a simplified flow diagram of a wet-strength resin production process. The batch process originates with the storage vessels. Material used as feedstock for the process is stored in some type of storage vessel. Vessel types range from 55-gallon drums to fixed or floating roof tanks to pressurized horizontal tanks. Underground tanks are typically not used for feedstock storage in this industry. At the beginning of the batch cycle, a quantity of material to be used as reactant feedstock is pumped from its storage container to a weigh tank, or charge tank. The volumes of weigh tanks range from a few hundred gallons for small batch processes to several thousand gallons for much larger batch processes. Weigh tanks, as the name implies, are used to measure the amount of material charged to the reactor. Several weigh tanks may be used for each reactor, depending on the required feedstock recipe.

Once the desired quantity of material has been obtained in the weigh tank(s), it is charged to the reactor, usually by gravity, as the weigh tanks in most cases are physically positioned above the reactors. Wet strength resins are formed by

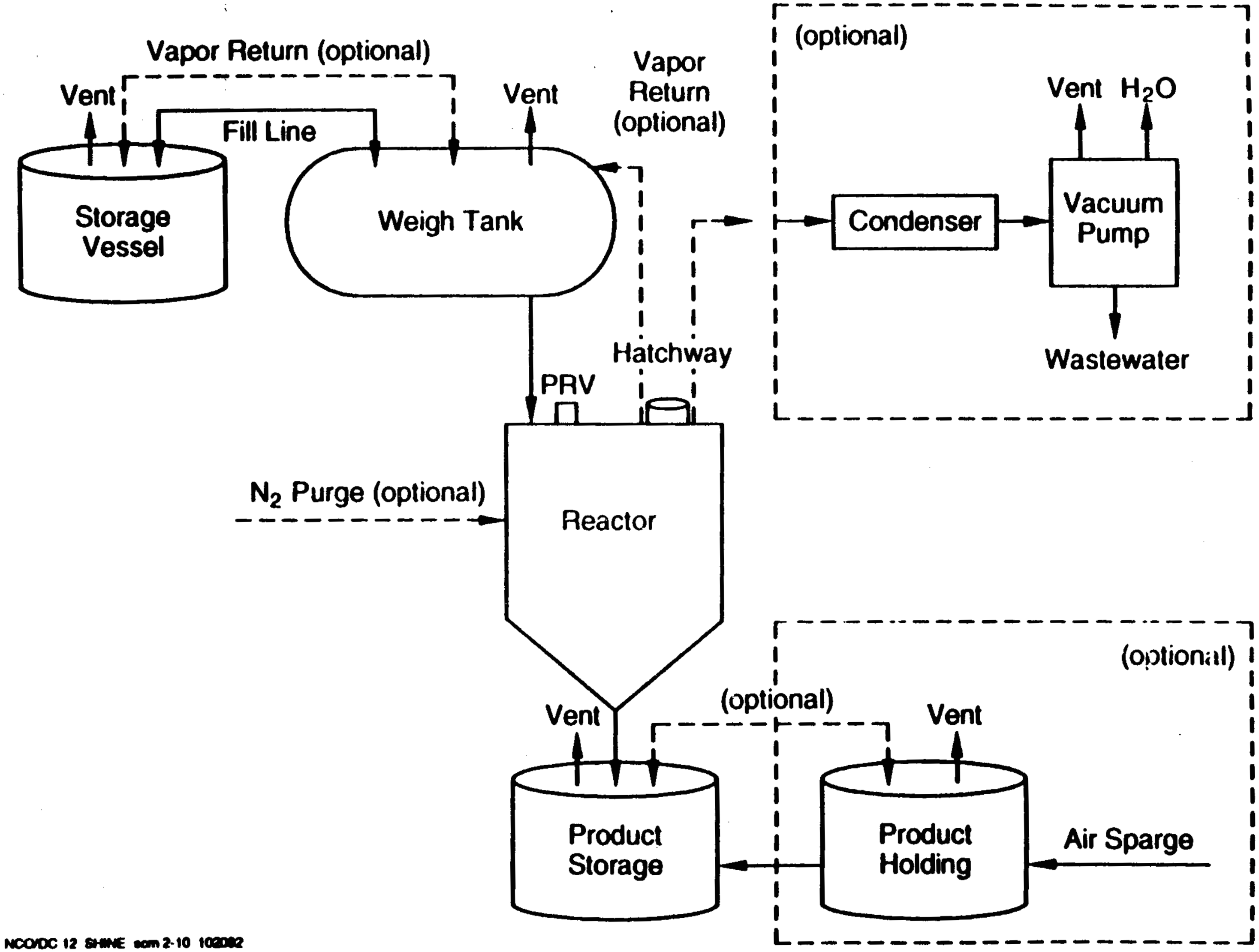


Figure 2-10. Wet-strength resins production.

reacting epichlorohydrin (EPI) with water and an inert amine-based polymer mixture. The amine polyer is in some cases manufactured onsite in much the same manner as is the cross-linked reaction production described below. Typical reactor sizes are on the order of 2,000 gallons. Reactors may also be charged by pumping the material from the weigh tanks by pressurizing the weigh tanks to push the material through to the reactor or by depressurizing the reactor vessel. Charging rates to the reactor typically are on the order of 50 gallons per minute, although some facilities report charging rates of greater than 200 gallons per minute.

Reactors are generally equipped with a temperature control jacket, an agitator, manholes for solids addition or sampling, and a pressure-relief valve. The manufacture of wet-strength resins involves an exothermic reaction which occurs at pressures at or close to atmospheric. Batch reaction times range from 2 to 24 hours, depending on the product. It is necessary in the manufacture of some products to halt polymer chain cross-linking reactions by adding acid when the resin viscosity reaches a certain point. Charging is usually conducted at ambient temperature. Temperatures during the reaction increase and may rise to as high as 70°C.

Some facility operating practices call for purging the reactors during feedstock addition and reaction stages with nitrogen to reduce the risk of explosion, and to dilute the vapor space concentration of toxic compounds in the reactor so that sampling and/or addition of solids may be done through the manhole without jeopardizing worker safety. Typical N_2 purge flow rates are on the order of 20 to 40 standard cubic feet per minute (scfm). Reactor vents typically are equipped with surface condensers, which operate at temperature ranges of 15° to 25°C and at atmospheric pressure. In these processes, a reflux stream from the condensers is routed back to the reactor primarily for temperature control. If the facility is using a nitrogen purge on the kettle, the exit gas containing nitrogen is sometimes routed through the condenser, although the effectiveness of condensing out such dilute concentrations of volatiles amid a significantly higher N_2 gas flow rate is questionable.

After the reactor stage of the manufacturing process ends, the crude product may be purified further by air sparging. Air sparging is the subsurface introduction of a gas intended to remove a more volatile minor component from a liquid. In this case, residual EPI may be removed to conform to product specifications. Condensers may be employed at this stage to recover solvent.

2.2.1.2 Emission Sources. Emission sources from the process described above are made up of the following: (a) storage tank working and breathing losses, (b) vapor displacement emissions resulting from material transfer or vessel evacuation, (c) reactor emissions due to heatup or purge, (d) sparging losses from finishing, and (e) equipment leak emissions from in-line process components such as pumps, valves, and flanges. The potential for wastewater emissions from reactor washing also exists.

2.2.1.2.1 Storage tank working and breathing losses. Storage tank working and breathing losses are typically no different for this industry than they are for any other industry. Working losses may usually be eliminated by equipping the tanks with a vapor return line back to the vessel being offloaded. Breathing losses, which are caused by temperature fluctuation and the subsequent expansion of vessel vapor space that must be relieved, may be partially abated by applying an inert gas blanket. Nitrogen typically is used for this purpose. Some facilities also store feedstock materials in sealed drums, so that there are no breathing or working losses associated with material storage. The charging of material from a drum to a vessel is sometimes accomplished by first evacuating a vessel to a slight vacuum prior to charge so that the material may simply be drawn into the vessel from the drum without forced displacement of any vapors in the receiving vessel. Emissions from drums typically are small enough so that the impact to the ambient concentration of VOC's/air toxics outside the plant boundary is negligible, although the airspace immediately surrounding the drum opening may contain enough VOC's/air toxics to have an impact on plant workers in the area.

Table 2-1 presents some typical emission stream characteristics from the emission events described for this process. Chapter 3 presents the methodologies used in calculating emissions from such events.

2.2.1.2.2 Vapor displacement. Vapor displacement losses are common types of emission events in this industry, since bulk material transfer from vessel to vessel occurs frequently. Vapor displacement losses from the general process described above would include weigh tank filling emissions and reactor filling emissions. Incoming material forces an equal volume of gas out of the vessel. This displaced gas contains a certain amount of volatile material. Vapor displacement losses can usually be abated by providing vapor return lines from the vessels being filled back to the vessels being emptied.

2.2.1.2.3 Reactor emissions. Reactors will have emissions created by charging of materials and subsequent vapor displacement. Following charging, reactor heatup emissions may occur at elevated temperatures, if no condenser is used and the reaction is exothermic. If a condenser is used, the concentration of VOC's will be equal to the 100 percent saturation concentration at the condenser outlet temperature. For situations in which a purge of inert gas is used concurrently with the reaction, emissions may be estimated by assuming that the purge stream is saturated to some degree with volatile material throughout the purge duration. Chapter 3 presents more detailed methodologies for estimating emissions from reactor heatup and purging events. The discharging of material from the reactor may create displacement emissions in the receiving vessel, as is shown in Figure 2-10.

2.2.1.2.4 Sparging emissions. Resin may be sparged with air or pure nitrogen during or following a reaction. Sparging is the use of compressed gas for the agitation of the material in the vessel and the stripping of trace amounts of volatiles in the

TABLE 2-1. SIMPLIFYING ASSUMPTIONS AND EMISSION STREAM CHARACTERISTICS FOR ESTIMATING EMISSIONS

Emission type	Flow rates, acfm	Percent saturation	Temperature	Duration of emissions
Storage tank				
Breathing losses	NA[a]	100	Ambient	Continuous
Working losses	10-20[b]	100	Ambient	Filling time
Vapor displacement	b	100	Ambient	Filling time
Reactor heatup				
With reflux condenser	0.1 - 5	100	Condenser temperature	Reaction time
Without reflux condenser	0.1 - 5	100	Elevated[c]	Reaction time
Reactor heating with purging				
With reflux condenser	10 - 200	< 100	Condenser temperature	Purge duration
Without reflux condenser	10 - 200	25	d	Purge duration
Product sparging	100 - 500	< 10	d	Air sparge duration

[a] Not applicable.

[b] The flow rate of displaced gas will equal the filling rate of liquid into the vessel.

[c] Depends on the reaction temperature, (typically 60° to 200°F).

[d] Determined by a heat balance around the entire contents of the emission stream, including the inert gas used as a purge or sparge. For dilute VOC streams, the exhaust temperature will closely approximate the purge gas temperature.

material, which is usually a liquid or slurry. The compressed air or nitrogen stream is introduced to the material through a perforated pipe located in the bottom of the sparging vessel. Another method of sparging is to use an air lift system, in which the compressed gas is introduced to the material through an opening in the middle of the longer leg of a "U-tube" having unequal legs. The air lift system is used less frequently than the perforated pipe. Emissions from this type of operation are governed by the amount of volatile material remaining in the product and whether this material may be easily stripped from the product. Further discussion of emissions due to gas sparging is presented in Chapter 3.

2.2.1.2.5 Emissions from equipment leaks. Leaking process components such as pumps, valves, flanges, sampling corrections, open lines, etc. are sources of emissions. Emissions may be calculated using the Synthetic Organic Chemical Manufacturing Industry (SOCMI) leak factors developed by EPA and multiplied by the fraction of time that the components are in VOC/air toxics service.

2.2.1.2.6 Wastewater emissions. Wastewater may be created from once-through vacuum pump seal water discharge or from scrubber water, if such a control device is used. In most cases, this water is discharged to the plant treatment system, since the concentration of pollutants in the water is low, precluding the option of solvent recovery. Further discussion of wastewater emissions is presented in Chapter 3.

2.2.2 Pharmaceuticals Industry Description

The pharmaceuticals industry uses predominantly batch processes to manufacture synthetic organic chemicals and to formulate finished pharmaceutical products. Most of the batch unit operations described earlier in this document can be found in these processes, which makes a discussion of this industry particularly relevant. Also, several characteristics of this industry make the control of VOC's and air toxics emissions particularly challenging.

First, the equipment used in processing is usually campaigned, meaning that it is not solely dedicated to the manufacture of just one product. Fluctuations in market demand often drive production schedules, more so than in any other industry. Since the characteristics of emission streams emanating from such equipment vary according to product, the devices used to control such streams must either be easily detached and moved or be capable of controlling streams that vary widely in solvent content, temperature, and pressure.

Such variation in emission stream characteristics also presents some difficulty to agencies responsible for issuing permits, since the actual emission levels of point sources such as reactor kettle condensers and the like will in some cases exceed the maximum permitted yearly emission rates because a different product is manufactured in the equipment. In most other industries, plant personnel would apply for a permit modification. However, the variability of equipment use and the short production runs characteristic of this industry make the application procedure and permit modification waiting period unrealistic.

A second characteristic of the pharmaceuticals manufacturing industry is the widespread use of higher volatility solvents such as methylene chloride (dichloromethane), which is extremely volatile low photochemically reactive solvent. Because of its high volatility, facilities that do not employ particularly stringent control techniques such as low-temperature refrigeration units, pressurized storage tanks, and closed-loop processing systems wherever applicable tend to emit large amounts of this solvent (for large facilities, these amounts can sometimes be in excess of 100 tons per year).[8]

The remainder of the discussion will revolve around actual processing characteristics associated with the pharmaceuticals industry. A typical simplified process flow diagram is included as an illustration of the type of equipment typically used in this industry and a typical processing route for a common pharmaceutical product. Due to the proprietary nature of information in the pharmaceuticals industry, it was not possible to present a process description of an unpublished process. Therefore, we have intended for the description of the manufacture of bulk aspirin to present the kinds of unit operations that occur in the pharmaceuticals industry. The process description is geared toward a general understanding of most pharmaceuticals manufacturing operations. Therefore, the discussion is also aimed at including other types of solvents, feedstocks, and operational practices that can be used in this equipment. Table 2-2 presents a summary of typical operating characteristics of batch equipment used in this industry. This summary can be used to characterize uncontrolled emission streams from various equipment. Process steps include product synthesis in reactors, purification in crystallizers and filters, and product finishing in dryers.

2.2.2.1 Process Description. Many pharmaceuticals manufacturing facilities make a distinction between the synthetic organic chemicals manufacturing processes that are used to produce active ingredients for their final products and those processes that are used to formulate the final product (pharmaceuticals processes). The process flow diagram illustrating chemicals manufacturing processes is for the manufacture of bulk aspirin. This process is both well known and appears to be simple, compared with processes that involve the manufacture of numerous intermediates which are reacted to yield final active ingredient. Note that the process flow diagram for the production of bulk aspirin includes the addition of salicylic acid in powder form, an active ingredient that must be manufactured prior to this process.

The fact that product or product intermediates are often in solid form brings up several elements that must be considered when evaluating the potential for VOC's or air toxics emissions. Solids must be filtered and dried at some point in the process. Emissions from dryers are considered to be the largest potential source of process emissions in the pharmaceuticals industry. When solids must be introduced into reactors, as is shown in the

TABLE 2-2. TYPICAL EQUIPMENT OPERATING CHARACTERISTICS

Equipment	Capacity, gallons	Purge/exhaust flow rates, acfm	Purge/exhaust duration. hours[a]	Temperature range, °F	P range, psia
Reactors	500 - 2,000	3 - 20/200[b]	3 - 15/0.05	80 - 200	14.7
Pressure filters	500 - 2,000	3 - 20	3 - 15	80 - 200	40 - 50
Crystallizers	500 - 2,000	0	3 - 20	30 - 50	10 - 14.7
Dryers					
- Tumble (double cone)	100 - 500	5 - 20	6 - 20	120 - 150	10 - 14.7
- Rotary	200 - 1.000	10 - 10,000	6 - 20	120 - 150	10 - 14.7
- Tray	100 - 300	1 - 50	6 - 20	20 - 100	1 - 14.7
Tablet covers					
- Rotating pan		500 - 1,500	2 - 3	80 - 450	14.7
- Fluidized bed		1.500 - 500	2 - 3	80 - 200	14.7
Extractors		0	--	80 - 200	14.7

[a] Residence time in equipment, if no purge or exhaust.

[b] 3-20 acfm during reaction; 200 for solids addition (2-3 min duration).

[c] High flow rate (20 acfm) used prior to addition of material and during filter cake scraping and discharge. Lower flow (3 acfm) during actual centrifugation.

bulk aspirin process flow diagram, emissions may occur as a result of the inert gas sweeping of the reactor vessel to reduce worker exposure and the possibility of explosion, if the vessel vapor space contains material in concentrations that approach explosive limits. Many processes now call for the addition of solids into the reactor prior to the addition of any other reagents. However, this practice may not always be practical, as solids tend to cling together and stick to the glass-lined surface of the bottom of the reactor. This practice also is not used if the solid reagent must be added over time.

2.2.2.2 Aspirin Process Description. This process description was originally described in the June, 1953, issue of Chemical Engineering. Although the actual process is outdated, this type of equipment is still in use today. The discussion below presents a brief synopsis of the process. A process flow diagram is presented in Figure 2-11.

According to the 1953 report, feedstocks to the reactor were acetic anhydride, mother liquor (containing appreciable amounts of acetic acid), and salicylic acid powder. The reaction occurred at temperatures of up to 90°C over a period of 2 to 3 hours. After reaction, the product (in liquid form) was pumped through a filter to remove impurities that may have been present in the feedstocks. Product liquid was routed to a crystallizer, where the liquid was cooled down to a temperature of 3°C over a period of about 16 hours. The slurry from the crystallizer was then transferred by gravity to a nutsche-type slurry tank, where a portion of mother liquor was decanted off to use in the next aspirin batch or distilled to recover acetic acid. The slurry was then transferred, again by gravity, to a centrifuge to separate the remaining mother liquor from the aspirin product. Product was scraped off the centrifuge walls, transferred to a dump cart, and then transferred to a rotary dryer for final drying. The remaining finishing steps included sifting, granulation, and tableting, which were not described in the article.

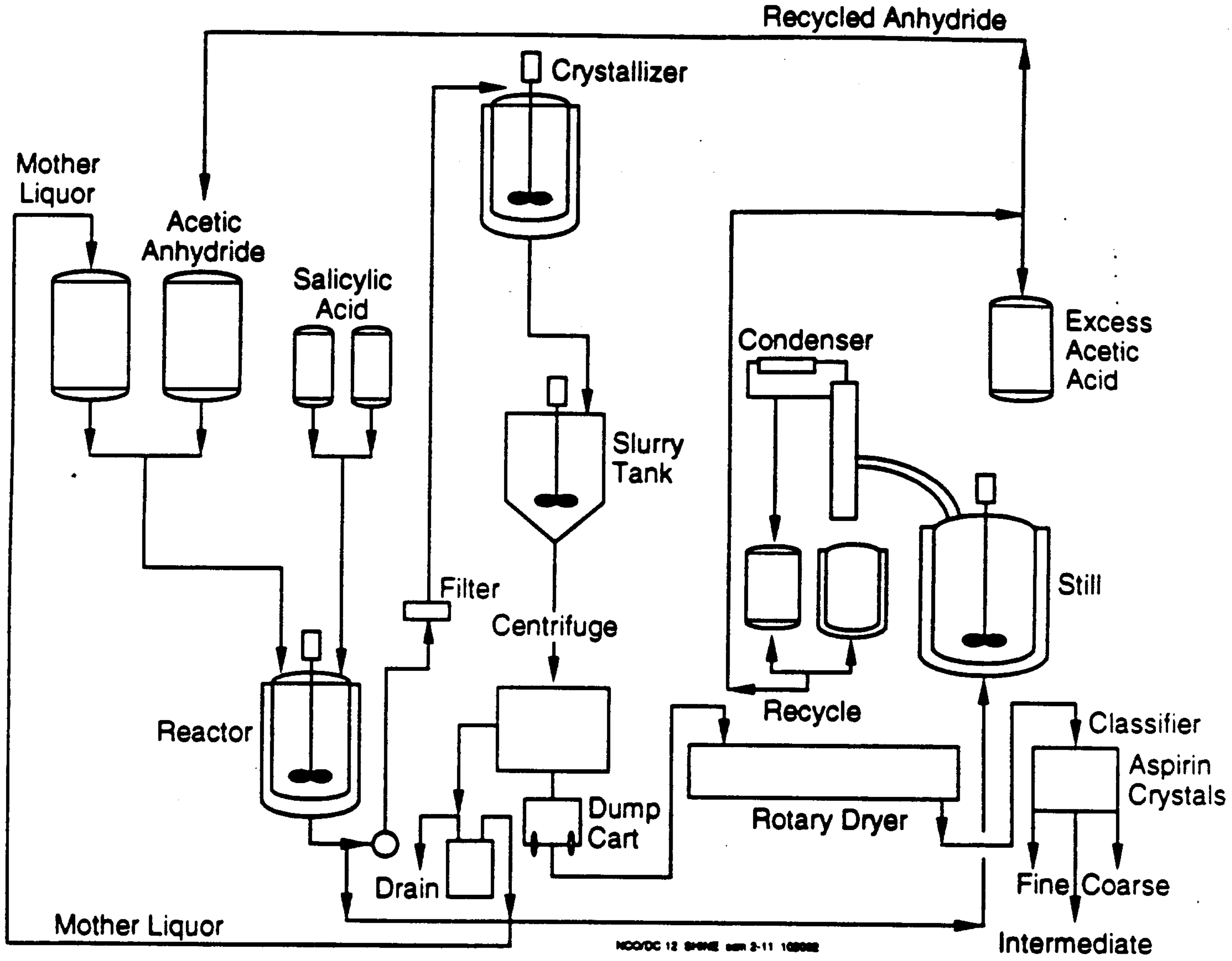


Figure 2-11. Aspirin Manufacturing
(Reprinted from Stern, Air Pollution, Volume VII, 1986).

The equipment described in this process is still used today to manufacture pharmaceutical products. Although instrumentation and some design characteristics have since been improved (i.e. bottom gravity discharge centrifuges), the equipment performs the same tasks in essentially the same way.

2.2.2.3 Emission Sources.

2.2.2.3.1 Process vents.

Vapor displacement. Many emissions from process vents in the pharmaceuticals industry come from vapor displacement events that are created during charging and transferring of material in all types of process vessels including reactors, surge or slurry tanks, and distillation kettles. All of the process vessels shown in Figure 2-11 undergo vapor displacement during material transfer. The extent of VOC and air toxic emissions from such events will depend on the material and quantity transferred, the material and/or vessel temperature, and the rate of transfer of the material, since this last parameter affects time allowed for equilibrium between the liquid and vapor phases. The vessel vapors that are displaced usually are assumed to be completely saturated with volatile material that is being charged or transferred.

2.2.2.3.2 Reactor emissions. Some reactors used in the pharmaceuticals industry are called autoclaves. Autoclaves are pressurized reactors. There are no emissions from such reactors because the systems are fully closed except during material transfer. In general emissions from reactors occur when atmospheric vents are present. If the material inside a vessel experiences an increase in temperature, two things occur: (1) the inert gas inside the vessel expands, causing a certain amount of gas to be displaced, and (2) the volatilization of liquid material increases. Emissions from reactors due to temperature increases occurs routinely. Reactors usually are equipped with condensers to reflux condensate during temperature increases, if the material inside the reactors is volatile.

Inert gas purges also may be employed to reduce the risk of explosion during reactions. In such cases, emissions are increased because of such purges since volatile material is swept out and the condensers that were installed to control condensables usually were not sized to abate the volume of gas that passes through as a result of the purge. Consequently, many facilities do not route the existing purge stream from reactor kettles through condensers because they are largely ineffective at controlling the relatively small amount of volatiles contained in the streams. Purge volumes are determined by the lower explosive limits of the material in the reactors, but generally range from 3 to 20 standard cubic feet per minute (scfm); although some facilities, especially prior to opening up manholes for solids addition, use purges on the order of 200 to 300 scfm. In these later cases, the purges are used to prevent workers who must manually add the solids from being exposed to toxic gases. These purges typically only last for periods of 2 to 5 minutes (the length of time that solids addition may take) as opposed to lasting the entire duration of reaction (as in lower-volume purges that are used to prevent explosions).[9] Chapter 3 details the methodology that should be used to calculate emissions from purges.

2.2.2.3.3 Emissions From Centrifuges, Filters, and Dryers. Centrifuges, filters, and dryers function by separating solvent from solid product. For some types of equipment, the majority of emissions will occur during unloading of the solid product from the process equipment. Older-style centrifuges, for example, must be unloaded manually by opening up the cover over the basket and scooping out product. Newer centrifuge designs use bottom unloading mechanisms that do not require manual unloading. Inert gas purging of the closed vapor space surrounding the centrifuge basket to reduce the possibility of explosion and reduce worker exposure increases VOC emissions.

Filters also separate solvent from solid product. Emissions from filters also occur mostly during unloading of the units, since they, like centrifuges, are enclosed during the actual separation operation. Some filters, such as nutsche filters, can be bottom-discharged so that solvent emissions from manual unloading may be minimized. Nutsche filters also are also capable of convectively drying product by passing a heated nitrogen stream through the filter cake after the filtration step is completed. Drying of product in the filter minimizes solvent emissions that will occur when the material is transferred from filter to dryer. Control systems also exist whereby the heated inert stream that passes through the cake in the drying step is compressed, condensed, and recirculated in a closed-loop system so that drying emissions are virtually eliminated. Chapter 4 presents a detailed description of this particular system.

Emissions from other types of dryers, such as tumble (double-cone) dryers, rotary dryers, and fluid bed dryers, occur when the solvent-laden drying stream exiting these enclosed process units are not contained or controlled. Since material to be dried often contains as much as 50 percent by weight solvent, controlling these emission streams will mean significant emissions reduction.

The characteristics of the emission streams from dryers depend largely on the flow rates and temperatures of drying streams and on the amount of solvent that must be removed. When the product is highly temperature-sensitive, a vacuum may be pulled on the drying vessel to allow volatilization at lower temperatures. A typical rotary dryer with a capacity of 20 ft^3 could operate at a vacuum of 4 to 5 pounds per square inch (gauge). The vacuum in this situation could be created with a liquid seal vacuum pump. Note that dryer emissions would be partly controlled by the vacuum pump, although contamination of seal water would exist.

Dryers that are used for tablet coating are also quite common in this industry. The two most common types of tablet coaters are rotating pan and fluidized bed coaters. A typical rotating pan tablet coater has a spray which coats tablets that are sitting in rotating open-ended pans while a stream of warm air (100°F) flows across the tablets at a typical rate of 1,000 acfm. Drying takes approximately 2 to 3 hours. Another process used for tablet coating, the wurster process, uses a fluidized bed in which the tablets are suspended in a vertical column while the spray solution is applied. The exhaust gas volume from the wurster process typically will be as high as 5,000 acfm. Coatings can be both water based and organic solvent based. A typical organic coating solution consists of 80 to 85 percent methylene chloride, 10 percent denatured ethanol or isopropanol, and 5 to 10 percent solids. One gallon of coating will generally process 25 pounds of tablets. Assuming that 600 pounds of tablets can be coated in each of the tablet coaters described above, as much as 250 pounds of methylene chloride could be emitted over the 2-3 hour drying span.[10] Example calculations of VOC emissions from dryers is contained in Chapter 3.

2.2.2.3.4 Emissions from extractors, distillation columns, and crystallizers. Emission streams from these pieces of equipment generally are less significant sources of VOCs and air toxics. Distillation columns and crystallizers are usually equipped with condensers for refluxing. Emissions from extraction columns are essentially vapor displacement emissions that occur while the columns and associated surge tanks are being filled or discharged.

2.2.2.3.5 Storage emissions. Storage vessels in the pharmaceuticals industry typically are on the order of 2,000 to 10,000 gallons. For highly volatile solvents such as methylene chloride, the tanks may be pressurized (to pressures of 100 psi) or refrigerated to eliminate breathing losses. Breathing and working losses may be calculated from the information contained in Chapter 3.

2.2.2.3.6 Emissions from equipment leaks. Fugitive emissions from leaking pumps, valves, flanges, and other process components may be calculated using the AP-42 SOCMI equipment leak factors.

2.2.2.3.7 Emissions from wastewater. Wastewater may be generated from vacuum pump seal water, scrubber discharge, or from condensation or feedstocks in the processes themselves. In cases where wastewater containing significant amounts of VOC's or air toxics is sent to the facility treatment system, emissions of VOC or air toxics may occur. Chapter 3 presents further discussion.

2.2.3 Pesticide Manufacturing

The manufacture of pesticides, the broad term for agricultural chemicals including herbicides, insecticides, nematicides, and fungicides, is often done using batch processes due to the low volume or complex processing required. The synthesis of the active ingredient, or "technical" product, is quite similar to the batch manufacture of any synthetic organic chemical with the notable exception that many pesticides have high mammalian toxicity. Therefore, higher levels of worker protection are required. The preparation of the final product for the end-user, called formulation, has other special processing requirements for the preparation of the solid substrates, diluents, "inert" ingredients, and product packaging. A preponderance of batch equipment may also be used in the formulation step.

The active ingredients of pesticides typically fall into two categories: low volatility (high boiling point) oils with limited solubility in water and solid organic compounds also typically with limited water solubility. There are some special cases where pesticides are high volatility liquids (or even gases), particularly in the case of fungicides, but these cases are unusual.

Limited solubility is desired in order to gain persistence in the target environment by minimizing washoff and leaching. However, this generally means that the manufacture takes place using organic solvents (in which the compounds are soluble), which are potential sources of VOC emissions. Due to the low vapor pressures (low volatility) of the active ingredients, the vaporization of the compounds themselves is not particularly a source of any significant VOC emission at the point of manufacture. Due to the toxicity of many compounds, however, worker exposure must be carefully controlled. At the point of use, typically outdoor agricultural activities, the active ingredients will vaporize over time and are a source of significant VOC emissions.

Some herbicides are salts of organic compounds and as such have significant water solubility. This makes the component "systemic" in that it can be absorbed by the plant and be transported even to the roots (e.g., for control of perennial weeds). These compounds use water as a solvent in at least a portion of their manufacturing.

The following is a generalized description of a one reaction step commercial synthesis of a "typical" liquid-type insecticide active ingredient. Due to the proprietary nature of the pesticide manufacturing industry, no particular commercial compound is being described, but this description provides a discussion of the types of process steps which might be used to manufacture an actual compound.

Raw material A, dissolved in low or moderate boiling point organic solvent, is charged to a 2,000 gal, glass-lined or stainless steel reactor. Initial reaction temperature is attained by admitting tempered water to the external heating jacket of the reactor. Prior to charging, the reactor had been purged with several volumes of nitrogen, and during the reaction a small purge flow is maintained to prevent the buildup of oxygen in the head space where flammable solvent vapors are present.

A second raw material, B, is introduced over a period of a couple of hours in order to conduct a "semibatch" reaction. The reaction produces heat which is removed by letting the solvent boil off and condensing and returning it to the reactor with the reflux condenser.

Following completion of the addition of B, the entire reactor contents are transferred hot to a second reactor for several hours of "cook out" where the final fraction of the reaction takes place. The crude product is then pumped through an in-line filter for removal of any solid catalyst that may have been used or for removal of solid by-products. By-product water or excess solvent may be removed as a lower layer using a decanter, and the mixture is pumped to a solvent removal system.

At this point, the batch process may be considered to be a continuous process because a feed or "equalization" tank will be constantly replenished with the product for each batch reaction. Due to the difficulty of startup and shutdown, a flash evaporator or distillation column or columns will typically be operated in a continuous mode. The final liquid active ingredient or "technical" product is recovered as the bottom product. Due to their low volatility, technicals are rarely distilled for final purification; they are recovered as "residue" products.

If only a small amount of solvent was used in the synthesis, a tank-based "drying" scheme may be used where the crude product is subjected to a vacuum for a period of time during which the volatile components "weather off" and are partially condensed with a vent condenser. The capacity of such a system may be enhanced using subsurface sparging of an inert gas.

The final liquid "technical" product may be packed out in drums or other bulk shipping containers for transport to the formulation plant. This plant is often at a different location and is likely be a different company.

The manufacture of a "typical" solid pesticide active ingredient, an herbicide, for example, is similar to the above except that some sort of solid-liquid separation equipment is required. Again, the following description is of no particular commercial compound, but merely provides a description of the types of process steps which might be used for the batchwise manufacture of a solid pesticide.

Raw material A is charged to a 5,000 gal stirred tank reactor which has already been filled with aqueous crystallization mother liquor from a previous batch. Raw material B is fed to the reactor over a period of a few hours; the reaction produces product C which, being only partially soluble, forms a slurry of fine crystals. Using a liquid ring vacuum pump, a vacuum is pulled on the reactor in order to promote the desorption of an acid gas by-product of reaction. The discharge of the vacuum pump is directed to a packed column vent scrubber using caustic and sodium hypochlorite as scrubbing liquid.

The reactor contents, a slurry, are pumped to a centrifuge feed tank, and the reactor is prepared for another batch. By using a bank of reactors, the centrifuge feed tank can be kept filled, and the rest of the process will operate nearly continuously.

An automatic-dump, basket-type centrifuge is used to separate the crystals of crude product from the mother liquor. The mother liquor goes to a holding tank from which a small bleed stream is discharged to wastewater treatment and the majority is returned to fill a reactor.

A bank of centrifuges is used so that the flow of wet cake into the blender is nearly constant. A portion of dried final product is fed to the blender for wet cake conditioning. The wet cake is then fed to a recirculating gas dryer.

The drying gas, heated nitrogen, is introduced into the bottom of the dryer. The drying gas conveys the product upward and carries moisture from the product. The hot, moist gas is then quench-cooled with water in a venturi scrubber. The scrubbing liquid, laden with dissolved product fines, is recycled to the mother liquor tank. The dry product, which is separated from the gas stream using a cyclone and bag filter arrangement, is pneumatically conveyed to interim product storage.

The "technical" solid will eventually be packed out into drums, tote bags, or other solids handling containers for shipping to the formulation plants.

The formulation of the pesticide active ingredients into a concentrate, powder, or granule that is more usable by the consumer also heavily utilizes batch processing techniques. Although there are no reactions, per se, the grinding, slurrying, mixing, coating, and drying steps all have the potential to produce VOC emissions. The following is a brief summary of the major types of pesticide formulations with a description of the unit operations that could be used to manufacture them. In general, they fall into the categories of sprays, dusts, and granules.

2.2.3.1 Sprays. A very common spray formulation type is the emulsifiable concentrate (EC) which is a concentrated oil solution of an active ingredient which is typically insoluble in water, but is soluble in petroleum solvents. The concentrated solution is then diluted with water in the field before application.

For liquid active ingredients, the manufacture of an EC formulation is straightforward in that only simple mixing is required. Dissolving solids into the organic solvent may require specialized agitation equipment, but it is still straightforward. Because of the need for rigorous quality control in the final product concentration, a reactor on weigh cells may be used, and the formulation ingredients, the oil, the emulsifier, and the "technical" active ingredient may be added by weight rather than volume. Each batch can then be assayed for the exact content of active ingredients; adjustments can be made before packing out into the final containers.

Potential VOC emissions arise from the purging of mix vessels, the filling of tanks and mix vessels, and from the hoods and vents provided for worker safety over the packaging lines.

Wettable powders (WP), another common type of spray formulation, are concentrated dusts of a solid active ingredient combined with a finely ground dry carrier, such as mineral clay, and a wetting agent. In use, the active ingredient gets suspended in the water in a well-agitated mix tank. The manufacture of these formulations usually requires fine grinding or milling of the active ingredients, and dry blending of the solid constituents. There is a significant risk of dust exposure associated with the manufacture of WP's but limited opportunities for VOC emission.

Water soluble powders are simple formulations for those active ingredients which are water soluble solids. As with wettable powders, fine grinding or dry milling and dry blending would be required, with dust hazards but little VOC emission potential.

Flowable formulations are very finely ground solid active ingredients in permanent suspension with liquid carriers and emulsifiers. The result is a "liquid" form of a water-insoluble pesticide without the use of organic solvents. There is, by definition, little potential for VOC emissions associated with flowable formulations.

Dry flowable formulations, also known as water dispersible granules, are small granules of a solid active ingredient and emulsifier. The manufacture of these granules may involve slurrying of the finely divided dry active ingredient followed by drying in special equipment (e.g., spray drying or a prilling tower) which is designed to form the desired granule size. There is a small potential for VOC emissions associated with the drying operation if organic solvents were used during the reslurrying, or if there is residual solvent present with the dry active ingredient that gets released with a secondary drying step.

Water soluble concentrates are true solutions of pesticides that are water soluble. With no solvents involved, there is little risk of VOC emissions from their manufacture.

2.2.3.2 Granules. Granular formulations are the other major type of formulations. Primarily intended for soil application, the granules consist of inert ingredients, usually clays plus binders, formed into pellets which are then sprayed with a solution of the active ingredient. The pesticide is thus deposited on the surface when the solvent dries, or depending on the porosity, the pellet may become impregnated with the pesticide. Granular formulations are a way to produce a solid end product from a liquid active ingredient, or by trapping the pesticide in the clay pellet, to produce an end product which is less hazardous to the user.

With typically low solubilities in water, the preparation of the solution for spraying on the pellets typically requires the use of an organic solvent. Obviously, there is a high potential for VOC emissions with the manufacture of granular formulations.

In order for the pellets to remain free flowing, the solvent must be completely evaporated from them before they can be packaged. In the case of dryers using purge gas, this implies low solvent loadings at the end of the drying cycle, with typically low efficiency of vent condensers. The dryer itself may be operated continuously whereas the preparation of the solutions and the substrates may be batchwise. Alternatively, a vacuum dryer may operate batchwise or continuously.

2.2.3.3 Heptachlor. Figure 2-12 is a simplified process schematic for the manufacture of heptachlor, a pesticide used to control termites in the soil subsurface. Because of proprietary concerns, operating characteristics of the equipment and other specific process information could not be included in this description. A simplified process description is presented below. A discussion of potential emission points of VOC's and air toxics follows the process description.

2.2.3.3.1 Process description. The process involves several steps. Hexachloropentadiene, heptane, cyclopentadiene, and propylene oxide are reacted to form heptachlor 237 intermediate. Carbon tetrachloride is added to the kettle as a solvent for the crude intermediate. The kettle contents are then charged to a chlorinator, where the crude intermediate is reacted with chlorine in the presence of catalyst to yield heptachlor. Acid gas from the chlorinator is routed to another process. The heptachlor/catalyst/solvent mixture from the chlorinator is then filtered. Solids from the filter (catalyst) are dried while the heptachlor (which is in liquid form) is sent to storage prior to packaging and shipment.[11]

2.2.3.3.2 Emission sources. Emissions of VOC's and air toxics from vapor displacement due to kettle charging and material transfer are expected to occur from all process vessels. Kettle reaction emissions are also expected. The acid gas stream from the chlorinator is pulled off for use in another process. It is unclear whether VOC's and air toxics that may be entrained in this stream are released at a point later on in the other

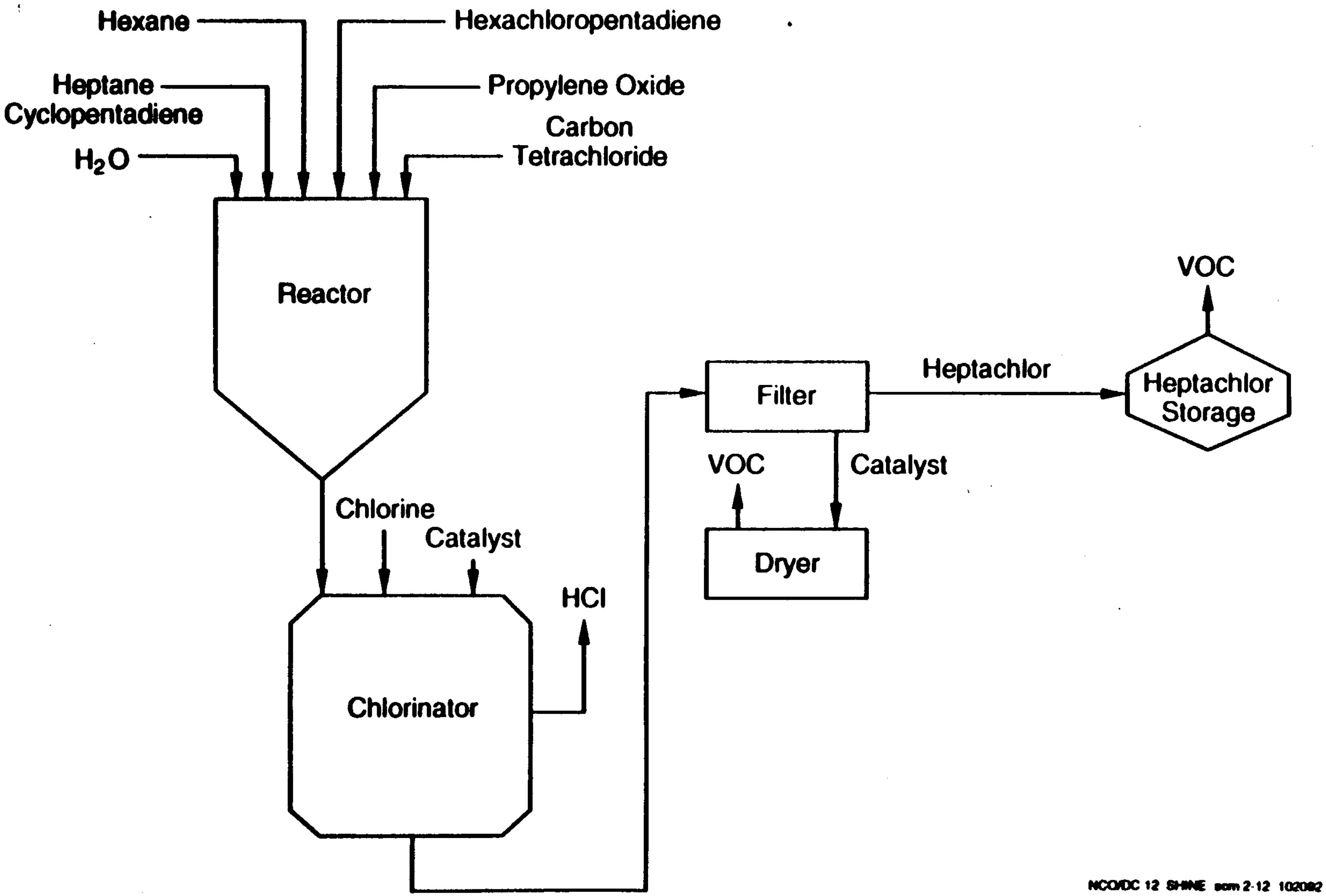


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Figure 2-12. Process schematic for Heptachlor.

(receiving) process. Emissions from the catalyst drying step are also expected.

2.2.4 Synthetic Organics Chemicals Manufacturing Industry (SOCMI)

The SOCMI uses both batch and continuous processes for the manufacture of various chemicals. Though most larger-volume chemicals are manufactured in continuous processing arrangements, some products are still manufactured on a batch basis. The manufacture of chlorendic anhydride was chosen to illustrate a batch process typical of this industry. Because of proprietary concerns, operating characteristics of the equipment and other specific process information could not be included in this description. A simplified process description is presented below. A discussion of potential emission points of VOC's and air toxics follows the process description.

2.2.4.1 Process Description. Figure 2-13 is a schematic of the chlorendic anhydride process. Maleic anhydride (melting point of 60°F) is reacted with hexachlorocyclopentadiene (HEX) to form chlorendenic anhydride. The chlorendenic anhydride exiting the reactor is routed to a crystallizer, where the addition of excess heptane and toluene produces chlorendenic anhydride crystals. The slurry from the crystallizer is then pumped to an agitated centrifuge head tank, which discharges the slurry by gravity to a centrifuge. The centrifuged liquid containing appreciable amounts of heptane and toluene solvent is recovered for further use. The chlorendenic anhydride from the centrifuge is loaded onto a solids conveyor and moved to a vacuum dryer to remove remaining solvents. From the dryer, the final product is loaded into drums for shipment.[12]

2.2.4.2 Emission Points. The potential for emissions of VOC's and air toxics exists for all process vessels shown in Figure 2-13. Because inert gas blanketing may be used to lower VOC concentrations in the process vessels, emissions are also expected from equipment openings, in which case the blanketing becomes a purge. Vapor displacement emissions would be expected from the various material transfer steps shown in the diagram.

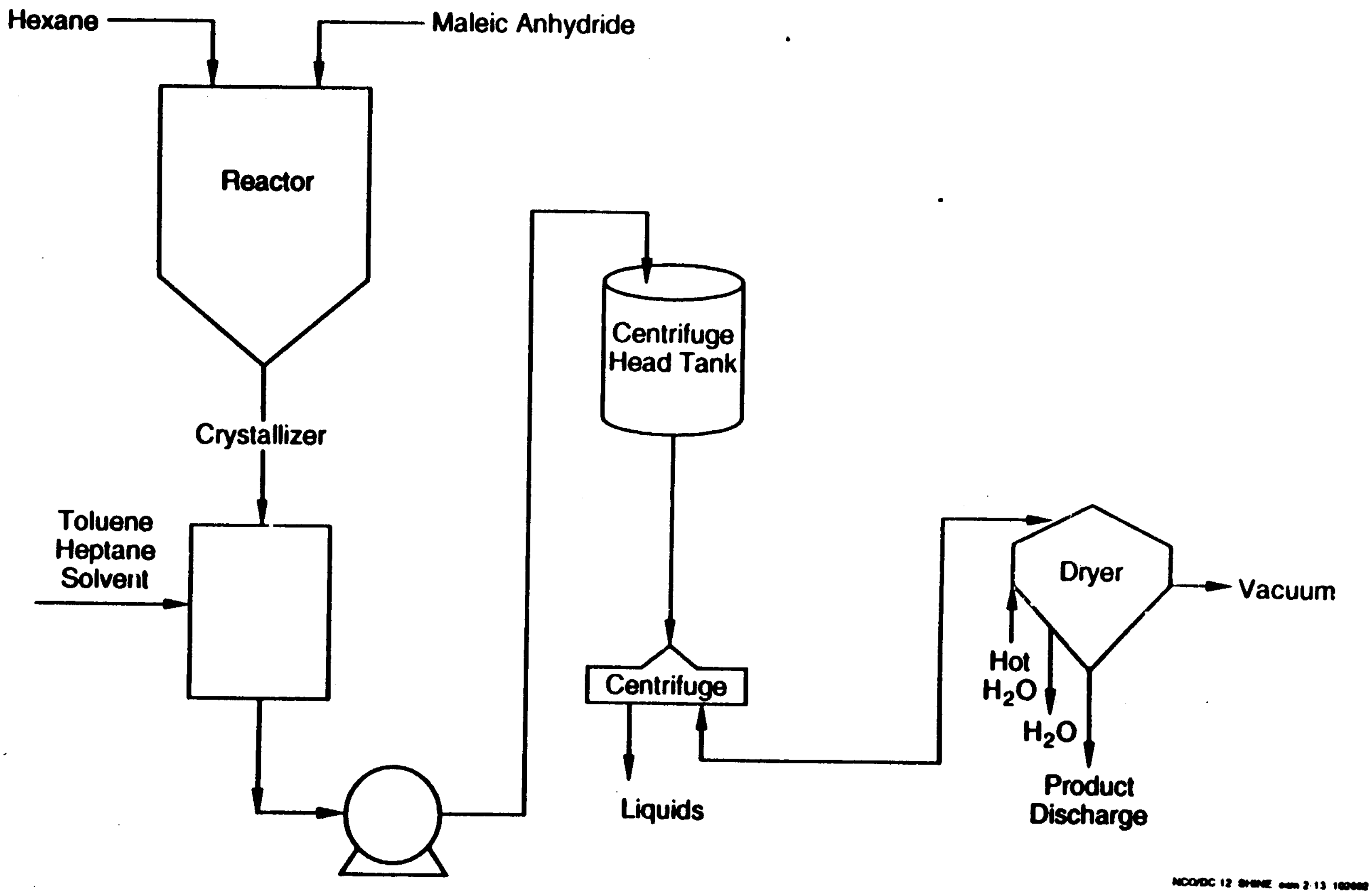

Figure 2-13. Process schematic for Chlorendic Anhydride.

The conveyer used to move material from the centrifuge to the dryer may also be a source of emissions. The dryer vacuum exhaust stream also would be a source of VOC and air toxics emissions.

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3.0 EMISSION ESTIMATION METHODOLOGIES

The methodologies presented in this chapter are based on the Ideal Gas Law and on fundamental vapor/liquid equilibrium relationships such as Henry's and Raoult's Law, unless otherwise specified. The equations are intended for use in estimating and characterizing uncontrolled emission streams from batch processes. Example calculations are presented in Appendix C. Significant errors may result in using the examples for situations that do not meet the conditions and/or assumptions that are clearly stated in the presentation of the methodologies. Chapter 4 presents a discussion on control efficiencies for various devices which may be used in conjunction with the characteristic streams presented in this chapter. Necessary constants and chemical data are presented in Appendix A. Appendix B discusses calculational issues and Appendix C contains example calculations for the methodologies described.

3.1 PROCESS VENT EMISSIONS

Process vent emissions may result from a number of different types of events. Methodologies for various emission events are presented in order of importance relative to the potential magnitude of their VOC emissions. Common process vents that occur in batch processing result from drying, tank and reactor inert gas purging, vapor displacement losses from material transfer, tank and reactor heating, gas evolution, gas sparging, batch pressure filtration, and vacuum generation. The discussion below presents the principles and methodology for estimating emissions from these events.

3.1.1 Drying

Two types of drying operations commonly occur in batch processing. These are conductive drying, in which heat is transmitted to the material to be dried by contact with heated surfaces, and convective drying, in which heat is transmitted by hot gases which are in contact with the material. Conductive drying may occur under vacuum conditions or at atmospheric pressure and in several types of dryers, including tray dryers, tumble (double-cone) dryers, pan dryers, and rotary dryers. Convective drying occurs at atmospheric conditions. Convective dryers include rotary dryers, fluid bed dryers, and spray dryers.

The methodology for calculating emissions from the types of dryers described above is essentially the same. In general, the rate of drying of the material depends on many factors associated with the specific drying situation (i.e., moisture or solvent content of material to be dried, heat and mass transfer parameters, drying period, etc.), but generally decreases with time so that a large percentage of liquid will be removed during the initial portion of the drying cycle.

Studies on the theory of drying of solids usually relate drying rate to moisture content of the solid[a]. Three distinct periods of drying can be observed: the constant-rate period where surface moisture is evaporated; the funicular state where capillarity of the liquid in the pores influences the drying rate; and the pendular state where the moisture content is so low that capillary action ceases and the liquid must diffuse through the pores of the solid. Each of these three periods of drying has successively lower rates of drying; the final drying rate, when the moisture content is zero, is of course also zero.[1]

Dryer design specialists, usually employed by the vendors of drying equipment, can relate the drying curve for solids to rate of drying expressed as a function of residence time. Laboratory or pilot-scale experiments are often needed to establish the

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[a] In dryer nomenclature moisture can also refer to organic solvent content, not just water content.

correct dryer size, operating temperature, gas flow rate, cycle time, etc. After a dryer is installed and operating correctly, the only data usually readily available are the cycle time, gas flow rates, and moisture content of the solid at the start and finish of the cycle. If very dry solids are produced, i.e., zero moisture content, it is clear that the drying rate at the end of the cycle will be asymptotic to zero. This end point condition, and a knowledge of the total solvent removed, can be used to estimate the emission characteristics of an existing, installed dryer.

In industrial practice, the filter cakes and centrifuged solids which must be dried often appear dry and free-flowing. In fact, they may contain as much as 50 percent solvent by weight. At the end of the drying cycle the solvent content is reduced to the percent or fractional percent level as required by the process. From a mass balance, the total amount of solvent emitted can be calculated.

In order to properly size emission control equipment for dryers, however, one must know the instantaneous emission stream characteristics throughout the cycle. Although the precise values can only be determined from extensive laboratory testing, a reasonable estimate can be obtained by assuming that the rate of decrease of drying rate is linear over the length of the drying cycle starting from the initial, highest value and declining to zero at the end of the cycle. From the material balance on solvent removed, the average drying rate can be calculated knowing the length of the cycle. From simple analytic geometry it is apparent that with a straight line relationship, and a final value of zero, the initial drying rate must be two times the average. Therefore, the drying rate, and hence the emission rate, can be estimated for any point in the drying cycle. The total emission stream can be calculated knowing the drying gas flow rate and conditions.

In the case of vacuum dryers, the emission stream contains a small amount of air due to leakage into the vacuum system, as well as any inert gas intentionally purged in. It is also worth noting that the vacuum-generating equipment (vacuum pump or steam ejector) itself may reduce, or may increase, the amount of VOC in the discharge stream (see description below.)

3.1.1.1 Vacuum Dryers. Tray dryers, double-cone dryers, pan dryers, and rotary dryers may be operated under vacuum conditions. Such vacuum dryers will have an inward leakage rate of air that will aid in carrying the VOC's and air toxics that have evaporated off the product out of the dryers. Vacuums in the range of 15 to 25 inches mercury are typical. Articles have been published which provide methods of estimating leakage rates for vacuum systems.[2] One such methodology is contained in Section 3.1.8. For a single dryer, the air leakage may range from 10 to 30 scfm depending on system design and vacuum level desired. An example calculation of vacuum dryer emissions is presented in Appendix C.

3.1.1.2 Atmospheric Dryers. While conductive dryers also may operate at atmospheric conditions, convective dryers operate at atmospheric pressure or above. Convective dryers include tray dryers and fluid bed dryers. The four types of conductive dryers discussed in the previous section, tray dryers, double-cone dryers, pan dryers and rotary dryers also may be operated at atmospheric conditions. A stream of air or inert gas is used to move the volatilized material from the dryer vessel in conductive drying. The gas stream is actually the heating mechanism in convective drying. In both of these situations, the calculation of total VOC content emitted during the drying cycle is identical to the vacuum drying method (a mass balance from initial cake concentration to final cake concentration). The estimation of the maximum dryer emission rate, which is used for sizing of equipment, is also analogous to the method presented for vacuum drying. The flow rate of gas through the system is the dryer exhaust gas rate. An example calculation of atmospheric dryer emissions is presented in Appendix C.

3.1.2 Tank and Reactor Purging

Consistent with batch processing there is frequently a need to use a gas stream to purge VOC vapors from either an empty tank or reactor vessel, or from the vapor space of a partially filled tank or reactor. Typical reasons for purging are to maintain product quality (e.g., by using a dry sweep gas to minimize water vapor in a system) or to reduce concentrations of flammable vapors below safety limits (by using an inert gas such as nitrogen or carbon dioxide).

3.1.2.1 Empty Tank Purging. Empty vessels may be purged intermittently (e.g., at startup and shutdown, or between batches) using a displacement purge to remove accumulated vapors. The estimation of VOC emissions in this case is fairly straightforward. Before the purge, the vapor space of an empty vessel can be assumed to be in equilibrium with the liquid which was removed. Thus, the starting concentration is known. The final concentration is a function of the number of volumes of purge gas used. This can be expressed as a power law when

$$\frac{C_f}{C_i} = x^n \qquad (3\text{-}1)$$

where:

n = the number of volumes of purge gas used;
x = the fractional dilution per volume change;
C_f = final concentration in vessel; and
C_i = initial concentration in vessel.

The fractional dilution per volume change assuming perfect mixing has been shown to be 37 percent. Thus, equation 3-12 becomes:

$$\frac{C_f}{C_i} = (0.37)^n \qquad (3\text{-}2)$$

This equation does not take into account evaporation of any residual liquid in the vessel, and assumes no free liquid. The equation was derived in the following way:

$$\frac{d\ (VCa)}{dt} = -qCa \qquad (3\text{-}3)$$

where: V = vessel volume
Ca = concentration of VOC species
q = volumetic purge rate
t = time

if: $q = 1\ ft^3/min$ and $V = 1\ ft^3$, then equation (3-3) reduces to:

$$\frac{dCa}{Ca} = -dt \qquad (3\text{-}4)$$

By integrating and setting the following boundary limits:

$t = 0 \quad Ca = C_i$
$t = 1 \quad Ca = C_f$, then equation (3-4) reduces to

$$\ln (C_f/C_i) = -1 \qquad (3\text{-}5)$$

Therefore, $C_f = 0.37\ C_i$

See Example 4 in Appendix C.

3.1.2.2 Filled Vessels. Filled or partially filled vessels are often "blanketed" with inert gas (or even air in the case of nonflammable solvents) using either "balanced pressure" or "trickle" control schemes.[3] With balanced pressure blanketing, there is no flow of gas unless the tank liquid level changes (during filling or emptying) or the pressure rises or falls due to thermal effects. The calculation of emissions from this type of blanketing is analogous to "working and breathing" losses addressed elsewhere in this document. For trickle blanketing, a constant flow of gas is maintained through the headspace. The flow rate may be quite low for storage tanks, but may be much higher for a reactor where removal of water vapor or excess solvent vapor is required. The higher flows have also been referred to as purges or sweeps.

Due to the lack of test data a traditional approach to calculating the volatile organic content of a purge gas stream is to assume that the gas is saturated with the vapors of the liquid over which it is flowing. This assumption is thought to be conservative or worst case in that the VOC content cannot possibly be greater than saturation (as long as there are no entrained droplets). For the purposes of calculating a maximum expected uncontrolled emissions rate, this approach is acceptable. However, as is shown in Appendix B, the actual VOC concentration of the exiting purge gas may be substantially below saturation. In fact, calculations show that the percentage saturation of an inert gas purge stream over a quiescent pool of liquid is expected to be no more than 10 percent. Likewise, the purging of equipment with turbulent liquid surfaces leads to higher saturation fractions, approaching 100 percent saturation at lower flowrates. Since most vessels will presumably be agitated, the assumption that the exiting purge gas is completely saturated with VOC is recommended. However, if the purge is greater than 100 scfm, a saturation factor of 25 percent is recommended.

Another assumption that must be made is that the displaced gas will fit the conditions of an ideal gas, and therefore, that the ideal gas law can be used. Most operations are run at conditions such as atmospheric pressure and relatively low temperatures, which allow the application of the ideal gas law. The VOC emission rate from purging may be estimated by first calculating the volumetric flow rate of the gas leaving the vessel, which is made up of noncondensables as well as the VOCs that have volatilized into the vapor space. The total rate of gas exiting a vessel is therefore:

$$Vr_2 = Vr_1 \left[\frac{P_T}{P_T - \sum (P_i x_i)} \right] \quad (3\text{-}6)$$

where:

Vr_2 = rate of gas displaced from the vessel, scfm

Vr_1 = rate of purge gas, scfm

P_T = vessel pressure, mmHg

$\Sigma(P_i x_i)$ = the sum of the products of the vapor pressures and mole fractions for each VOC, mmHg (see next section).

The emission rate of VOCs in this exit gas is then calculated using the following equation:

$$E_R = \frac{(y_i)(V_r)(P_T)(MW)}{(R)(T)} \quad (3\text{-}7)$$

where:

E_R = mass emission rate;

y_i = mole fraction in vapor phase, calculated in Equations 3-9 and 3-10.

V_r = volumetric gas displacement rate (equal to the total rate of gas exiting a vessel, Vr_2)

R = ideal gas law constant;

T = temperature of the vessel vapor space, absolute;

P_T = pressure of the vessel vapor space; and

MW = molecular weight of the VOC or air toxic.

Table A-4 of Appendix A contains values of the gas constant R. An example of a purging emission calculation is presented in Appendix C.

3.1.3 <u>Vapor Displacement Losses--Transfer of Material to Vessels</u>

Emissions occur as a result of vapor displacement in many batch operations. The transfer of liquids from one vessel to another vessel causes a certain volume of gas to be displaced in the receiving vessel. The VOC's that may be contained in this volume also are displaced. In many cases, the displaced gas is vented directly to the atmosphere. The amount of VOC's emitted during such an event is limited by the partial pressure of the components in the gas stream and the vessel pressure. Usually, vessel vapor spaces are filled with air (21 percent oxygen, 79 percent nitrogen) or almost pure inert gas, such as nitrogen.

The degree of saturation of the vent gas with the VOC's must be assumed or known before any calculations are done. As is normally the practice when permit levels are established, a conservative assumption usually is made to prevent underestimation of emissions. A conservative assumption in most vapor displacement calculations is to consider the gas being displaced to be 100 percent saturated with the volatile compounds that are entering the vessel. The following steps are involved in calculating emissions from vapor displacement events:

Step 1. Define the conditions of the displaced gas:

1. Temperature;
2. Pressure; and
3. Volumetric rate of displacement.

The rate of displacement of a gas from a vapor space is equal to the rate of filling of that vessel with a liquid. An example of this type of displacement event is the transfer of liquid material from one process vessel to another, such as the charging of a reactor with material from a weigh tank, and the subsequent emission of gas from the reactor that is saturated with the vaporized liquid.

Step 2. Calculate the mole fraction of components in displaced gas:

1. Determine or calculate the vapor pressure of the liquid compound of interest (for one specific component, such as an air toxic) or of the entire volatile component of the liquid (for total VOC emissions).

For one component, this can be done by consulting vapor pressure tables at the appropriate temperature (see Table A-1) or by using Antoine's equation, a form of which is presented below:

$$\ln P_i^* = A - [B/(T+C)] \quad (3\text{-}8)$$

where:

P_i^* = vapor pressure of component i (mmHg);

A,B,C = compound-specific constants; and

T = temperature of the liquid (K).

There are several forms of vapor pressure estimation equations and the reader should make sure that the constants correspond to the appropriate form and that the units are consistent. Most physical property handbooks contain the Antoine equation and the appropriate constants. Vapor pressures for some compounds are presented in Table A-1. Table A-2 contains vapor pressure equations for 120 compounds that use five constants.

If more than one compound is present in the liquid, the vapor pressures of all compounds in the mixture must be determined. After the vapor pressures have been determined, the partial pressure that the VOC vapor fraction exerts in the vessel vapor space may be determined by using Raoult's Law, which is a simple expression that describes equilibrium between an ideal vapor and an ideal liquid. The general equation for Raoult's Law is presented below:

$$y_i = \frac{P_i}{P_T} = \frac{x_i P_i^*}{P_T} \quad (3\text{-}9)$$

where:

y_i = mole fraction of i in the vapor;

P_i = partial pressure of component i;

x_i = mole fraction of component i in the liquid;

P_i^* = vapor pressure of component i at temperature T; and

P_T = the total pressure in the vessel vapor space.

Raoult's Law may be used for multicomponent systems, assuming the compounds are completely miscible in one another. If the compounds are not miscible, or are only partially miscible, then they are considered "nonideal" and Raoult's Law does not apply. At or above the solubility limit, each compound exerts a partial pressure in the vapor space which is equal to the vapor pressure at that temperature. Below the solubility limit, especially dilute solutions comprised of water and trace amounts of air toxics or VOC's, Henry's Law is used to describe the relationship between the mole fraction of the compound in the liquid and the vapor phase mole fraction. Henry's Law is presented below:

$$y_i = \frac{P_i}{P_T} = \frac{x_i\ H_i}{P_T} \qquad (3\text{-}10)$$

where:

x_i = mole fraction of component i in the liquid;
H_i = Henry's Law constant for i (at temperature T);
y_i = mole fraction of component i in vapor; and
P_T = the total pressure in the vessel vapor space.

This relationship is especially important in calculating evaporative losses from process wastewater. Henry's Law constants for some organic compounds at 25°C are presented in Table A-3. Also, a method of correcting the constants for different temperatures follows Table A-3 in Appendix A.

Step 3. Calculate the emission rate:

Once y_i, the mole fraction of component i in the vessel vapor space is known, the VOC or air toxic emission rate may be easily calculated by multiplying y_i by the vessel fill rate (which equals the gas displacement rate) and converting this volumetric rate to a mass emission using equation 3-7. Examples of vapor displacement emission calculations are presented in Appendix C.

3.1.4 Vessel Heating

When a process vessel partially filled with a VOC or a material containing a VOC is heated, the gas and vapors in the headspace expand and are discharged from the vent. An estimate of the emissions in the uncontrolled vent stream from such an event can be calculated based on application of the Ideal Gas Law and on vapor-liquid equilibrium principles.

The basis of the calculation is that the moles of gas displaced from a vessel are a result of the expansion of the noncondensable gas upon heating, and an increase in the VOC vapor pressure. The assumptions made for the calculations which follow are (1) atmospheric pressure of 760 mmHg and (2) the displaced gas is always saturated with VOC vapor in equilibrium with the liquid mixture.

The initial pressure of the gas (noncondensable) in the vessel is given by:

$$Pa_1 = 760 - \Sigma(P_i)_{T_1} \tag{3-11}$$

where:

Pa_1 = initial partial pressure of gas in vessel headspace, mmHg, and

$(P_i)_{T_1}$ = initial partial pressure of each VOC in vessel headspace, mmHg, at the initial temperature (T_1).

The choice of formula for calculation of P_i depends on which vapor-liquid equilibrium assumption is chosen (as discussed in Section 3.1.1). If the VOC species behaves "ideally" in the system under consideration, then Raoult's Law holds and

$$(P_i)_{T_1} = (P_i^*)_{T_1}X_i \tag{3-12}$$

where:

$(P_i^*)_{T_1}$ = vapor pressure of each compound at specified temperature, T_1, and

X_i = mole fraction of each compound in the liquid mixture.

If the VOC in question is present in very dilute concentrations in the liquid, then Henry's Law gives a reasonable estimate of the compound partial pressure if the empirically determined constant is available:

$$(P_i)_{T_1} = (H_i)_{T_1} X_i \qquad (3\text{-}13)$$

where:

H_i = Henry's Law Constant at T_1 in consistent units (atm/mole fraction); and

X_i = Mole fraction of each compound in the liquid mixture.

Note: If neither Raoult's Law nor Henry's Law is considered to be valid for the compound mixture being considered, a more complex procedure, beyond the scope of this document, must be used. Commercial computer programs are available to simplify the task of calculating vapor-liquid equilibria for nonideal mixtures.

The calculation of P_i is repeated at the final temperature conditions, T_2; and the final partial pressure of the gas in the vessel is calculated:

$$Pa_2 = 760 - \Sigma\ (P_i)_{T_2} \qquad (3\text{-}14)$$

By application of the Ideal Gas Law, the moles of gas displaced is represented by:

$$\Delta\eta = \frac{V}{R}\left[\left(\frac{Pa_1}{T_1}\right) - \left(\frac{Pa_2}{T_2}\right)\right] \qquad (3\text{-}15)$$

where:

$\Delta\eta$ = number of lb-moles of gas displaced;

V = volume of free space in the vessel ft^3;

R = Gas Law constant, 998.9 mmHg ft^3/lb-moles °K;

Pa_1 = initial gas pressure in the vessel, mmHg;

Pa_2 = final gas pressure, mmHg;

T_1 = initial temperature of vessel K; and

T_2 = final temperature of vessel, K.

The concentration of the VOC in the gas displaced at the beginning of the event is calculated assuming equilibrium at the initial vessel temperature. The final concentration of the VOC in the final amount of air displaced is calculated assuming equilibrium at the final vessel temperature. The VOC concentration in the displaced gas may be approximated by assuming it is equal to the average of the initial and final values. The number of moles of VOC displaced is equal to the moles of gas displaced times the average VOC mole fraction, as follows:

$$\eta_s = \frac{\dfrac{\Sigma(P_i)_{T_1}}{760-\Sigma(P_i)_{T_1}} + \dfrac{\Sigma(P_i)_{T_2}}{760-\Sigma(P_i)_{T_2}}}{2} \times \Delta\eta \qquad (3\text{-}16)$$

where:

η_s = lb-moles of VOC vapor displaced from the vessel being heated up.

The weight of VOC vented can be calculated by multiplying the number of moles by the molecular weight. The reader should note that, at the boiling point of the VOC, this equation goes to infinity. In a physical sense, the vessel vapor space is filled entirely with VOC during boiling; the rate of release of VOC is therefore equal to the total flow of VOC out of the kettle. Therefore, this equation is not valid at the boiling point of the VOC. An example of a vessel heatup calculation is presented in Appendix C.

3.1.5 Gas Evolution

When a gas is generated as a result of a chemical reaction, emissions may be calculated by assuming that the gas is saturated with any VOCs that are in contact with it at the exit temperature. Emission calculations are analogous to the filled vessel purging calculations and are calculated using the following formula to first calculate the rate of gas displaced:

$$V_2 = V_1 \left[\frac{P_T}{P_T - \sum (P_i x_i)}\right] \qquad (3\text{-}17)$$

when V_1 = initial volumetric rate of gas evolution

P_T = vessel pressure

$\Sigma (P_i x_i)$ = sum of the products of the vapor pressure and the mole fraction of each VOC at the exit temperature.

Once V_2 is known, it can be inputted into Equation 3-4 to calculate the emission rate. An example calculation of gas VOC emissions from gas evolution is presented in Appendix C.

3.1.6 Sparging

Sparging is the subsurface introduction of a gas (typically nitrogen or other inert gas) intended to remove by selective volatilization (stripping) a more volatile minor component from a liquid mixture of predominantly less volatile material. Common applications of sparging are the removal of trace quantities of water or volatile organic solvent from a low volatility (high boiling point) resin. The removal of low concentrations of organic solvents from wastewater also may be achieved using air sparging.

Sparging is a semibatch operation. The sparge tank is filled or discharged on a batch basis, while the gas is fed continuously at a steady flow rate for the duration of the sparge cycle. The subsurface sparger is designed to develop a mass of small diameter bubbles. The tank may be agitated as well in order to produce fine bubbles and increase the bubble residence time. These design features are intended to increase contact efficiency.

Utilizing fundamental chemical engineering principles and empirical correlations published in the literature it is possible to calculate the mass transfer coefficients encountered in sparging applications. The transfer rate of the component being stripped out is a function of temperature, composition, liquid diffusivity, gas rate and agitator power (which determine bubble size), and tank geometry (which, along with agitation power, determines residence time).

For the calculation of equilibrium concentration of VOC in the exiting sparge gas the earlier discussion of Raoult's Law and

Henry's Law applies. For simple sparging (low viscosity fluids; no solids) vapor concentration may approach 100 percent of the equilibrium value calculated. For complex sparging, an empirically determined lower value may need to be used.

Unlike continuous flow vapor-liquid separation processes, with batchwise sparging it is not possible to write a series of simple analytical equations which define the outlet gas concentration as a function of inlet concentration and thermodynamic properties of the compounds. This is because the liquid flow rate is zero and the composition changes with time. The problem of estimating the gas composition (hence, VOC emission rate) at any time during the sparge cycle, or of determining the amount of sparge gas and sparge time required to achieve a certain concentration reduction, can, however, be solved using simple numerical integration. One chooses a small time increment, one minute, for example, over which to calculate the gas flow and composition, making the simplifying assumption that the liquid composition does not change. From the inlet gas concentration (most likely zero) and the saturated exit gas concentration, the amount of volatile removed from the bulk liquid can be calculated, and a new estimate made for the liquid composition. The calculation of the vapor composition for the next time "slice" will be made based on this new liquid composition value. The cumulative quantity of volatile removed is used for subsequent estimates of the liquid composition.

A graphical representation of the vapor or liquid composition as a function of sparge time has a characteristic hyperbolic shape where the composition is asymptotic to zero. The initial composition is high, as is the stripping rate because the mass transfer is a function of the composition driving force. The final composition is low, but a long stripping time is required to achieve a small decrease in composition because the driving force is also very low. An example sparging volatilization calculation is presented in Appendix C.

3.1.7 Batch Pressure Filtration

Pressure filtration of nonaqueous, volatile, flammable, or hazardous slurries is typically conducted in a closed vessel. Generally, VOC's are not emitted during the filtration step, as there is no venting from the process vessel. However, during the gas blowing (cake-drying) step of the cycle, or during pressure release prior to cake discharge, venting occurs and there is potential for VOC emission.

The gas blowing step is intended to accomplish some preliminary cake drying by evaporating some of the liquid filtrate present in the filter cake. This operation is roughly equivalent to the constant-drying-rate period of operation of a dryer except that heated gas is not used (except in the case of some special purpose equipment where heated gas is, in fact, used). The blowing gas follows the same flow path as the filtrate, so that it could be vented through the receiving tank.

3.1.7.1 Filter Cake Purging. The emission rate in the vented purge/blowing gas can be calculated if the cake conditions at the start and end of this portion of the cycle are known. The filtrate will be evaporated at approximately a constant rate. Assuming that the filtrate is 100 percent VOC, the emissions rate is simply:

$$ER = \frac{W(X_i - X_f)}{t} \qquad (3\text{-}18)$$

where:

W = the dry weight of a batch of filter cake;

X_i = the weight fraction of filtrate at the start of the gas-blowing step;

X_f = the weight fraction of filtrate at the end of the gas-blowing step;

t = elapsed time of gas blowing; and

ER = emission rate in weight per unit time.

However, one key piece of data required for the above calculations, namely the filtrate content of the cake before the gas blowing, is not usually available. Therefore, this methodology is of only limited utility.

Since the blowing gas causes the VOC's in the filtrate to evaporate, the gas stream is partially saturated with vapor, and approaches vapor-liquid equilibrium as a limit. An assumption of percent saturation attained enables the calculation of emission rate.

An example calculation of estimating emissions from filter cake blowing is provided in Appendix C.

3.1.7.2 <u>Depressurization</u>. Prior to opening a batch pressure filter for solids discharges, the pressure must be relieved. In the case of a filter design utilizing a closed vessel, there is some compressed gas in the vapor space which will have some degree of vapor saturation of VOC from the filtrate. Upon depressurization, a fraction of the noncondensible gas along with the VOC vapor will be vented. The estimation of the emission rate from a depressurization event is a straightforward application of the Ideal Gas Law if certain simplifying assumptions are made.

If the vessel has been under pressure for some time during the filter cycle, and no additional noncondensable gas has been added, then it is reasonable to assume that the gas is saturated with the VOC vapor at the vessel temperature. To simplify the calculations, one assumes that the pressure decreases linearly with time once depressurization has begun, and that the composition of the gas/vapor mixture is always saturated with VOC vapor through the end of the depressurization. The estimation of the emission rate proceeds according to the following steps:

1. Calculate the mole fraction of each VOC vapor species initially present in the vessel at the end of the depressurization.

$$Y_i = \frac{x_i \ P_i}{P_1} \qquad (3\text{-}19)$$

where:

P_i = vapor pressure of each VOC component i;

P_1 = initial pressure of the process vessel in units consistent with P_i calculations; and

Y_i = mole fraction of component i initially in the vapor.

2. The moles of VOC initially in the vessel are then calculated using the ideal gas law as follows:

$$n_{voc} = \frac{(Y_{voc})(V)(P_1)}{R \quad T} \tag{3-20}$$

where:

Y_{voc} = mole fraction of VOC (the sum of the individual VOC fractions, ΣYi)

V = free volume in the vessel being depressurized

P_1 = Initial vessel pressure

R = Gas constant

T = Vessel temperature, absolute units

3. The moles of noncondensable gas present initially in the vessel are calculated as follows:

$$n_1 = \frac{VP_{nc_1}}{RT} \tag{3-21}$$

where:

V = free volume in the vessel being depressurized;

Pnc_1 = initial partial pressure of the noncondensible gas, $P_1 - \Sigma P_i$;

R = gas law constant, K; and

T = temperature, absolute units.

At the beginning of the depressurization, there are more moles of noncondensable gas in the vessel relative to the moles of VOC in the vessel than at the end of depressurization. At the beginning of the depressurization, there are:

$\frac{n_{voc}}{n_1}$ moles of VOC to noncondensables

5. At the end of depressurization, there are

$\frac{n_{voc}}{n_2}$ moles of VOC to noncondensables

where:

$$n_2 = \frac{V\ P_{NC_2}}{RT} \tag{3-22}$$

where:

V = Free volume in the vessel being depressurized;

P_{NC_2} = Final partial pressure of the noncondensible gas, $P_2 - \Sigma X_i P_i$;

R = Gas law constant, and;

T = temperature, absolute.

6. The moles of VOC for the duration of the depressurization may be calculated by taking an approximation of the average ratio of moles by VOC to moles of noncondensible and multiplying by the total moles of noncondensibles released during the depressurization, or:

$$\frac{\left[\frac{n_{voc}}{n_1} + \frac{n_{voc}}{n_2}\right]}{2} [n_2 - n_1] = N_{voc} \tag{3-23}$$

where: N_{voc} = moles of VOC emitted

7. The moles of VOC emitted can be converted to a mass rate using the following equation:

$$\frac{N_{voc} * MW_{voc}}{t} = Er_{voc} \tag{3-24}$$

where:

Er_{voc} = emission rate of the VOC

MW_{voc} = molecular weight of the VOC

t = time of the depressurization

An example calculation of emissions from vessel depressurization is provided in Appendix C.

3.1.8 Emissions from Vacuum Generating Equipment

Steam ejectors and vacuum pumps are used to pull vacuums on vessels and can be sources of VOC and air toxic emissions. Both come in contact with a stream of gas that potentially contains pollutants. A steam ejector consists essentially of a steam nozzle that produces a high-velocity jet across a suction chamber connected to the vessel being evacuated. The gas from the vessel is entrained into the motive steam as it passes across the suction chamber. Both gas and steam are usually routed to a condenser.

Conventional (mechanical-type) vacuum pumps use a high boiling point oil to lubricate the moving parts. The VOC's which are present in the gas on the suction side may be partially condensed in the elevated pressure inside the vacuum pump. This reduces the amount of VOC emitted in the gas discharge from the pump, but causes contamination (reduced lubricity) of the pump oil. For this reason, if a significant amount of VOC is expected in the gas being evacuated, a liquid ring vacuum pump may be selected.

In a liquid ring vacuum pump, the vacuum is created by the rotating motion of a slug of seal fluid inside the pump casing. The seal fluid is in intimate contact with the gas and VOC being evacuated. A portion of the seal fluid is ejected with the pump discharge, so a system for seal fluid recycle and makeup is required.

Because the seal fluid is in contact with the gas/VOC mixture, mass and heat transfer can occur inside the pump. The emissions from a liquid ring vacuum pump are, therefore, a function of the seal fluid temperature and composition, as well as the inlet gas composition. For purposes of calculation one may assume that the exiting gas is in equilibrium with the seal fluid. The seal fluid must be chosen to be compatible with the gas/VOC being evacuated. In some cases, the seal fluid itself is a VOC and equilibrium with the exiting gas may result in an increase in VOC level from that in the suction side. In other cases, the seal fluid can act to reduce the VOC level of the gas stream by absorbing (or condensing, in the case of a cooled seal fluid system) some of the VOC in the gas being evacuated.

3.1.8.1 Emission Estimation. Emissions from vacuum systems originate from two distinct sources: 1) the first is the gas at the vacuum system discharge, 2) the second is the seal fluid or motive steam. Calculating emissions from the gaseous discharge of systems that serve to induce vacuums on equipment involves the estimation of the amount of air that leaks into the equipment because of the pressure differential between the inside and outside of the vessel. Once this air leakage rate is known, the rate of VOC emissions may be calculated by knowing the vacuum system discharge outlet temperature and pressure.

The air leakage rate for the equipment may be estimated from the following equations, which correspond to the leakage created by metal porosity and cracks and leakage resulting from seals and components in a system for various vacuum pressure ranges:

1. Leakage from metal porosity and cracks

(For $1 \leq P \leq 10$ mmHg) $$W = 0.026\ P^{0.34}V^{0.60} \quad (3\text{-}25)$$

(For $10 \leq P \leq 100$ mmHg) $$W = 0.032\ P^{0.26}V^{0.60}D \quad (3\text{-}26)$$

(For $100 \leq P \leq 760$ mmHg) $$W = 0.106\ V^{0.60} \quad (3\text{-}27)$$

where:

P = system operating pressure, mmHg;

V = volume, ft^3; and

W = air leakage resulting from metal porosities and crack along weld lines, lb/hr.

2. Leakage from seals and components

(For $1 \leq P \leq 10$ mmHg) $$w = \pi D \theta P^{0.34} \quad (3\text{-}28)$$

(For $10 \leq P \leq 100$ mmHg) $$w = 1.20\ \pi D \theta P^{0.26} \quad (3\text{-}29)$$

(For $100 \leq P \leq 760$ mmHg) $$w = 3.98\ \pi D \theta \quad (3\text{-}30)$$

where:

D = sealed diameter, inches;

w = acceptable air leakage rate assigned to a system component, lb/yr; and

θ = specific leakage rate for components, lb/hr/in (presented in Table A-5 of Appendix A).

3. The total air leakage rate, in lb/hr, is merely the sum of the two components W and w.

$$La = W+w \tag{3-31}$$

Once the air leakage rate is known, the VOC emission rate, in lb/hr, may be calculated using the following equation from the 1978 Pharmaceuticals CTG:[4]

$$Se = MWs \frac{La}{29} \left(\frac{P_{system}}{P_{system} - P_i} - 1\right) \tag{3-32}$$

where:

Se = rate of VOC emission, in lb/hr;

P_{system} = absolute pressure of receiving vessel or ejector outlet conditions, if there is no receiver;

P_i = vapor pressure of the VOC at the receiver temperature, in mmHg;

La = total air leak rate in the system, lb/hr; and

29 = molecular weight of air, lb/lbmole.

An example calculation is provided in Appendix C.

Calculating emissions from seal fluid or motive steam is analogous to the calculations of VOC emissions from other sources of wastewater, which is discussed below.

3.2 EVAPORATIVE LOSSES FROM WASTEWATER

Evaporative losses from wastewater that is contaminated with VOC's has been examined in detail, but currently is not within the scope of this document. Several publications are available to aid the readers in calculating emissions from wastewater treatment systems which include surface impoundments, lagoons, and basins.[5,6,7]

3.3 STORAGE TANK EMISSIONS

In general, emissions of VOC's from storage tank working and breathing losses appear to be no different for continuous processes than they are for batch processes. Both types of losses usually are calculated using EPA-derived storage tank loss equations for three types of storage tanks: fixed roof, external floating roof, and internal floating roof. Fixed roof and horizontal pressure tanks appear to be the most common storage vessels used in batch processing. Estimation equations for these tank types and a detailed explanation of their use, may be found in an EPA reference.[8]

3.4 EQUIPMENT LEAKS

The calculation of emissions of VOC's from leaking process line components such as valves, pump seals, flanges, and sampling connections is no different for continuous processes than it is for batch processes. Emissions tend to be less because the amount of time that components are actually in VOC service is less for batch processes than it is for continuous processes.

In the event that no other specific data is available equipment leak emissions may be estimated using the equipment leak factors derived for the Synthetic Organic Chemical Manufacturing Industry (SOCMI). These factors are readily available, and are included in Appendix A in Table A-6.[9] It is also possible to develop unit-specific emission estimates according to an accepted EPA protocol. The methodology for developing a specific emission estimate for leaking components is contained in another reference.[10]

3.6 REFERENCES

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8. AP-42 Compilation of Air Pollution Emission Factors, Chapter 12.

9. EPA-453/R-93-026, Protocol for Equipment Leak Emission Estimates. June 1993.

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4.0 CONTROL TECHNOLOGIES

This chapter provides information on the types of emission control technologies currently available and in use on typical batch processes. The discussion is structured so that a general description of the theory and principles behind the effectiveness of various common control devices is presented first. Second, information is provided on the suitability of the various technologies for controlling VOC's from different batch unit operations, followed by a section discussing specific applications. Appendix D contains cost calculations and assumptions made in evaluating costs of thermal incineration and refrigeration systems for batch processing emissions.

Because the emission streams produced by batch unit operations are often of finite duration and the properties of these streams, such as flow rate, VOC content, temperature, and pressure, often change during the duration of the emission event, the system chosen for emission control ideally should be capable of handling both peak flow and nonpeak situations effectively. To that end, this chapter also addresses the relative importance of sizing equipment properly. The following control technologies are discussed: (1) condensers, (2) scrubbers, (3) carbon adsorbers, (4) thermal incinerators, (5) vapor containment systems such as vapor return lines, i.e., "vent-back" lines, and (6) operational practices that reduce emissions, such as reduced nitrogen use for blowing lines, elimination of transfer steps in product or intermediate handling, and elimination of vessel opening and purging steps.

4.1 CONDENSERS

Condensers can generally be classified as surface noncontact and barometric (direct-contact condensers). Surface condensers are usually shell-and-tube heat exchangers, in which the cooling fluid flows in tubes and the gas condenses on the outside of the tubes. Direct-contact condensers are those which allow for intimate contact between the cooling fluid and the gas, usually in a spray or packed tower. Although direct-contact condensers may also be part of a solvent recovery system, an extra separation step is usually involved in separating what was the cooling liquid from the newly formed condensate. An exception to this situation is the direct-contact condenser, which uses cooling fluid identical to the desired condensate; in this case, no separation is necessary.

In principle, condensers work by lowering the temperature of the gas stream containing condensables to a temperature at which the desired condensate's vapor pressure is lower than its entering partial pressure. Typical uses for condensers in batch processing are on reactors and vacuum-operated devices, such as distillation columns and dryers. Note that condensers servicing reactors and distillation columns often function in refluxing material. This refluxing is an integral part of the process, and therefore these condensers are often not considered to be emission control devices. Such applications often use secondary condensers, which operate at still lower temperatures and function primarily as control devices.

4.1.1 Design

The control efficiency attained by a condenser is a function of the outlet gas temperature. A typical exhaust gas from a batch reactor contains a large amount of noncondensable material, such as air or nitrogen, as well as some fraction of volatile material. Before this volatile material can condense, the entire contents of the gas stream must be cooled to the saturation point of the condensable material. Heat transferred from the gas stream during this stage is called sensible heat. Cooling the gas stream further after complete (100 percent) saturation is reached causes condensation of the volatile material. Heat removed from condensation is called latent heat. Both kinds of heat (which in refrigeration terminology usually are summed and reported as tons [each ton is 12,000 Btu/hr]) must be considered in the design of a condenser. Q, the heat requirement may be calculated by approximating the sensible and latent heat change when a gas stream containing condensable material is cooled:

$$Q = \dot{m}C_p\Delta T + \dot{m}\Delta hv \tag{4-1}$$

where:

Q = heat requirement;

$\dot{m}$ = mass flow rate of material;

C_p = heat capacity of material cooled;

ΔT = temperature difference between inlet material temperature and condensate temperature; and

hv = the latent heat associated with a phase change.

For a surface condenser, the heat transfer area requirement, A, may be approximated using the following equation:

$$A=\frac{Q}{U\Delta T_{LM}} \tag{4-2}$$

where:

A = heat transfer surface area;

Q = heat requirement;

U = overall heat transfer coefficient, which is based on the inside and outside heat transfer, and;

ΔT_{LM} = log mean difference in temperature between the cooling fluid and the exhaust gas at each end of the shell and tube exchanger.

Based on the above discussion, it is apparent that the amount of material that can be condensed from a gas is limited only by the following factors: (1) the inlet emission stream properties, including heat capacity and temperature, and (2) the heat transfer characteristics of the condenser, including surface area. By controlling these factors, it follows that nearly any amount of cooling can be imparted onto a gas stream.

In practice, however, the design of condensers and the amount of cooling that realistically occurs is based more on economics. Cooling fluid, for example, can range from water at ambient temperature to brine, which can be cooled to below the freezing point of pure water, to a low-temperature refrigerant. The colder the cooling liquid required, the more expensive the system becomes. In some applications, the condensing system is staged, so that certain condensables that may be present in the stream, i.e., water, will be condensed out at a higher temperature. The remainder of the gas can then be cooled further to condense out lower-boiling-point materials without the problem of ice formation and subsequent fouling of the heat-transfer surface. Note that the more elaborate a condensing system becomes, the higher the cost of operating that system.

It has generally been accepted that condensers are most effective when applied to gases that contain high percentages of condensables. This is because a large amount of sensible heat must be removed from a gas stream containing mostly noncondensable material in order for the stream temperature to decrease to the saturation temperature of the condensable. Obviously, the farther from saturation a gas stream is, the more sensible heat must be removed.

Verification of the expected control efficiency of a condenser is, especially for single-component systems, easier than the verification of other control technology efficiencies, such as carbon adsorption, gas absorption, incineration, etc., as these technologies require that the outlet gas pollutant concentrations be measured. To verify condenser efficiency, the outlet gas temperature is the only value that must be known in addition to the inlet conditions (including flowrate of noncondensables). By assuming that the vapor phase of the material is in equilibrium with the liquid at condenser outlet temperature, the percent by volume VOC discharged from the condenser may be calculated by dividing its partial pressure by the total pressure. In any case, if condenser efficiency cannot be calculated because the inlet gas conditions are not known, it is at least always possible to calculate the maximum VOC equilibrium concentration of the exit gas at outlet condenser conditions.

Another consideration that must be made when contemplating the use of a condenser for a particular application is whether there is an appreciable presence of water vapor in the stream. There are two reasons for concern in this situation. The first, which was touched on in the earlier discussion, is that a surface condenser cannot effectively function below the freezing point of the water, as ice will form and create an insulatory surface on the heat transfer surface, keeping the surface temperature above 32°F. The other consideration, which is more subtle but just as important to the overall effectiveness of the device, is whether the water will combine with the condensable material to form a low-boiling-point azeotrope. In such a situation, the saturation temperature of the azeotrope is lower than the condensing temperature of either pure compound, and the system must be designed accordingly.

4.1.2 Specific Systems and Applications

4.1.2.1 Reactor Vent Condensers. Several different types of condenser systems exist in batch processing applications. Probably the most common application is the use of the simple shell-and-tube heat exchanger to control reactor vents. As was noted in Chapter 2, emissions of VOC's occur from virtually all reactor processing and transfer steps, including charging, reaction, discharging, and cleaning. In many cases, these operations occur while a stream of noncondensable or inert gas is being used as a purge inside the kettle to keep the vapor phase from reaching explosive limits. This purge also takes away from the effectiveness of the condenser as a control device, since the vapor fraction of condensable material decreases with the addition of more noncondensable gas.

Condensers appear to be the most common control devices cited for reactors. It may be that these devices are relatively inexpensive and easy to use, since they are easily manifolded for the use of alternate cooling fluids that may be required for the diverse gas streams resulting from campaigned equipment.

4.1.2.2 Distillation Columns (Primary and Secondary Condensers). Shell-and-tube condensers usually are employed as refluxing devices on batch distillation units. In some cases, a secondary condenser is used to control the exhaust gas from the outlet of the reflux condenser. The EPA's OAQPS Guideline Series for the Control of Volatile Organic Emissions from Manufacture of Synthesized Pharmaceutical Products, December 1978, establishes the following guideline for surface condenser outlet gas temperatures on vents from reactors, distillation operations, crystallizers, centrifuges, and vacuum dryers that emit 6.8 kg/d (15 lb/d) or more of VOC:

-25°C when condensing VOC of vapor pressure greater than 5.8 psi (300 mmHg)
-15°C when condensing VOC of vapor pressure greater than 2.9 psi (150 mmHg)
0°C when condensing VOC of vapor pressure greater than 1.5 psi (77.5 mmHg)
10°C when condensing VOC of vapor pressure greater than 1.0 psi (52 mmHg)
25°C when condensing VOC of vapor pressure greater than 0.5 psi (26 mmHg)
35°C[a] when condensing VOC of vapor pressure between 0 and 0.5 psi (0 to 26 mmHg)

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[a] This requirement for material with a vapor pressure between 0 and 0.5 psi at 20°C was not part of the 1978 CTG but has been adopted by some States.

Based on a review of these guidelines, it becomes apparent that if the streams controlled are not completely saturated with VOC's, the guidelines offer very little control. The discussion below provides some basis for these conclusions.

Listed below are VOC's that typically are found in process vessels such as reactors, dryers, and distillation operations and their corresponding vapor pressures at 20°C. The corresponding condenser outlet temperature guidelines as established by the Pharmaceutical CTG are also listed.

	VP in mmHg at 20°C	Required condenser outlet, temp., °C	VP at outlet, mmHg	Percent volume at outlet
Methanol (MeOH)	95	0	31	4
Acetone	182	-15	30	4
Toluene	22	35	22[a]	3

[a] Because the required outlet temperature is higher than the inlet temperature, no cooling occurs and the stream remains at inlet conditions.

If the streams entering the condenser are at high temperatures, then the volume percent of VOC's entering can be high, maybe close to 100 percent vapor. For these situations, the condensers prove to be very effective. When a reflux condenser is used, the condenser isn't considered a control device, but an integral part of the process. The material being distilled off cannot be recovered without the cooling that is imparted on the gas stream from the condenser. If there are no noncondensables present (i.e., the steam is made up of 100 percent condensable vapors), there are essentially no emissions at the condenser outlet as long as the condenser is able to cool the stream below its boiling point temperature. Therefore, reflux conditions are not considered uncontrolled emission events. Atmospheric vent streams created by non-steady-state distillation operations, however, are.

During periods of unsteady-state operation, such as startup of an atmospheric distillation operation, there will be noncondensables present in the gas stream routed to the condenser. If distillation occurs under vacuum, then some amount of noncondensables will be present. This amount can be estimated by knowing or calculating the leak rate into the system (see Chapter 3 calculations).

A secondary condenser may be used to control the above-described emission events. For example, the volume percentage of a saturated methanol stream exiting a condenser is 95/760; or 12.5 percent by volume at 20°C. Dropping the temperature of this stream to 0°C and thereby reducing the outlet volume percentage to 4 percent yields a control of approximately 70 percent.

4.1.2.3 Dryers

4.1.2.3.1 Vacuum dryers. Batch dryer exhaust streams, especially vacuum dryer exhaust streams, have been reported to be controlled by condensers installed prior to the vacuum-generating devices (i.e., vacuum pumps, steam ejectors). The condensation of VOC prior to the vacuum-generating device also reduces the VOC wastewater load since the VOC is removed prior to the point at which the stream is contacted with the seal water or steam.

The emission stream parameters generally accompanying vacuum dryers include high concentrations and low flowrates. Over time the concentration of the emission stream drops off, while the flowrate usually remains constant.

To illustrate this situation, Figures 4-1 and 4-2 present typical drying rate curves for batch dryers. Figure 4-1 illustrates the cycle time dependency of the actual solvent content of the material drying. Figure 4-2 shows how the emission stream solvent content varies with time.

The curves illustrate that the majority of the solvent is removed from the material during the early stages of the batch drying cycle. The corresponding emission rate during these

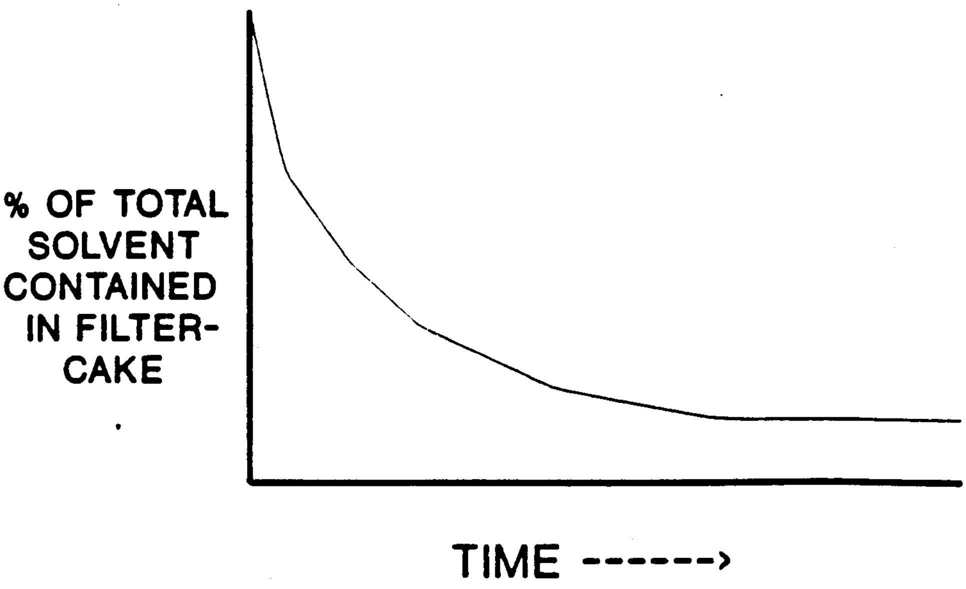

Figure 4-1. Filter cake drying curve.

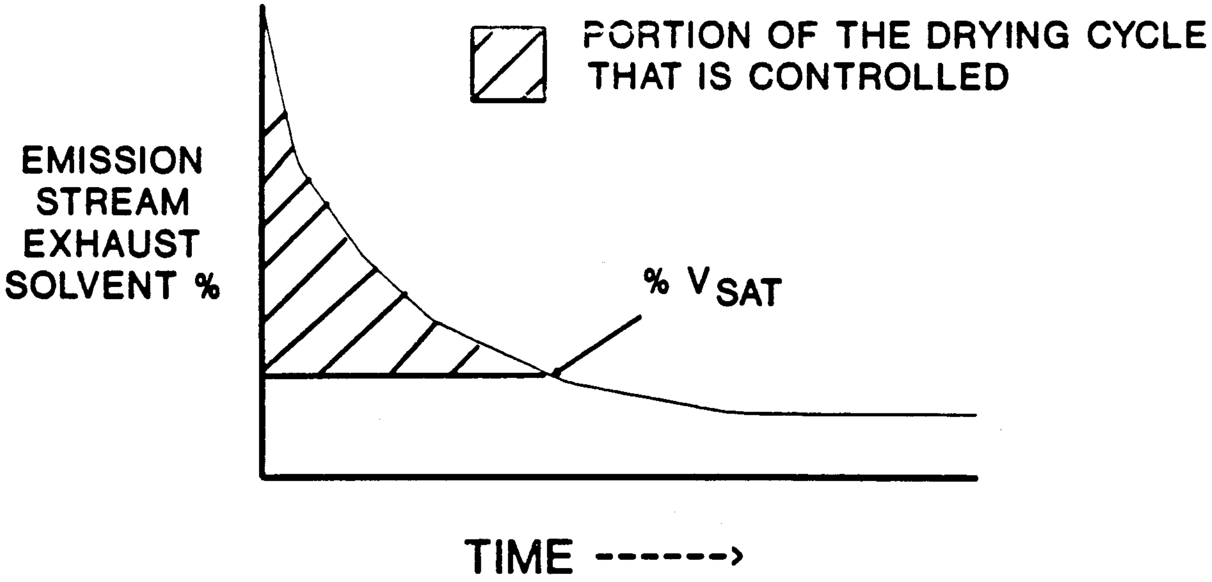

Figure 4-2. Dryer emission stream solvent content.

stages is also considerably higher. If a condenser is the device chosen for VOC control, it must be sized so that it can handle the peak VOC flow at the beginning of the cycle. Also note that the point marked VSAT in Figure 4-2 is the point in the cycle where the condenser is no longer effective. VSAT is the percent by volume of solvent in the gas stream corresponding to saturation at the condenser outlet temperature.

4.1.2.3.2 Convective dryers. The use of simple condensers for achieving high degrees of VOC control from convective dryers is also infeasible because the exhaust gas stream will have a higher volume percentage of noncondensable gas.

4.1.2.4 Crystallizers. Condensers may be used to control VOC emissions from crystallizers, especially batch vacuum crystallizers. Such crystallizers employ both surface condensers and barometric (direct-contact) condensers. Usually, a large amount of vacuum is necessary to produce crystals at low temperature. A typical batch vacuum crystallizer vacuum-generating system is essentially composed of a three-stage steam ejector system with an intercondenser (usually a barometric water condenser) after the first stage. Barometric condensers are used because they are inexpensive from an operating cost standpoint. However, if the material coming off the crystallizer will become a concern from the wastewater standpoint, the use of a surface condenser should be considered.

4.1.2.5 Refrigeration Systems for Manifolded Sources. Shell-and-tube condensers may be used to control VOC emissions from several combined events. Such applications are usually for solvent-recovery purposes, since it is often desirable to recover material that would otherwise be emitted as a VOC. This is especially true for industries such as the specialty chemicals and the pharmaceutical industries that require expensive feedstocks and solvents.

Vapor recovery systems are often designed so that the recovered material cost offsets the energy and capital costs of the systems themselves. In many cases, however, the recouped recovered material cost is insignificant compared to the cost of purchasing and operating the recovery systems. In such a case, the decision to install a solvent recovery system as opposed to another type of system is based on other factors, such as control effectiveness and concerns about waste handling and disposal.

While refrigeration systems are not often used solely to control single vapor displacement events such as reactor charging and extractor (mixer-settler) charging, they are often feasible for controlling collected displaced vapors from a number of sources.

Some facilities that have a large number of storage tanks, for example, are known to use staged refrigeration systems that employ pre-cooler sections. Often, the precooler operates at a temperature just above the freezing point of water. This condenser (usually an indirect shell-and-tube heat exchanger) rids the vapor stream of as much water as possible that would otherwise collect on heat transfer surfaces as ice and lower the heat transfer potential of colder surfaces. After the vapor passes through the initial indirect condenser (pre-cooler), it enters the main condenser section, which can cool the gas stream to very low temperatures, on the order of -100° to -160°F.

Low-temperature refrigeration systems such as the one described above are used to control vapor displacement emissions from multiple sources such as working losses from a tank farm. Often, the mixtures are separated by distillation although only one or two pure components may be recovered for reuse.

Perhaps the most important issue to consider when evaluating the need for such a system is the required size of the unit. For the tank farm situation described above or for a number of process vents from one manufacturing area, the system may be most effective when it can control the stream having the maximum vapor inlet loading at peak flow rate. Minimization of noncondensables in the displacement events is crucial to efficient operation, as is maintaining a fairly constant vapor loading rate to prevent cycling of the refrigeration system's compressors. Cycling also occurs if the system is oversized for the vapor load.

To prevent cycling and to optimize the efficiency of the system, the displaced vapors or process vents of finite duration must be staggered or controlled using orifices or flow controllers so that the system receives a fairly constant vapor inlet loading. One such system is currently being used by a large pharmaceutical manufacturing complex to control displaced vapors from a tank farm containing approximately 25 tanks. The emission rate of methylene chloride, the predominant stream component, has reportedly been reduced by more than 99 percent, from 357 lb/hr to 0.7 lb/hr.[1]

4.1.2.6 Combination of Vapor Compression and Condensation. In some situations, condensation is aided by compressing the gas stream containing VOC's to atmospheric pressure (if the stream is under vacuum) or to some elevated pressure prior to entering a condenser. The purpose of this compression step is to condense out the same amount of material at a higher temperature. For example, consider the simple calculation used to estimate the vapor phase mole fraction of the VOC:

$$Y_{VOC} = \frac{P_{VOC}}{P_{TOTAL}} \tag{4-3}$$

A low value of Y_{VOC} is desired at the outlet of the condenser. This can be achieved by reducing the numerator value, P_{VOC}, by lowering the gas temperature, or by increasing the denominator, P_{TOTAL}, by increasing the pressure of the system, or by a combination of both.

Most applications that use a combination vapor compression-condensation system use liquid ring compressors. These compressors are available for numerous ranges of flowrates and discharge pressures. Liquid ring compressor packages that include ring seal liquid recirculation systems are currently available and range in capital cost from approximately $75,000 for a system handling a flowrate of 150 scfm and discharging at a pressure of 40 to 60 psig to over $200,000 for a system handling 900 scfm at the same discharge pressure.[2] The systems are usually configured so that the pump comes before the heat exchanger. However, one pesticide manufacturer uses a high-pressure liquid ring compressor capable of compressing a gas to 100 psig in an application to recover methylene chloride from a solvent vacuum stripping process, following a heat exchanger that discharges its gases at 4°C. Plant personnel have stated that prior to installing such a system, the plant was discharging approximately 2 million lb of methylene chloride to the atmosphere each year, of which 85 to 90 percent is now recovered.[3]

There seem to be a number of applications that could make use of one form or another of these combination systems. One such application, which is commercially available, is used to retrofit a pressure (nutsche) filter to convert the filter to a dryer. This eliminates VOC emissions from associated transfer steps and essentially makes the drying process closed-loop, eliminating virtually all VOC emissions. This system is described below.

1. Description. Some pharmaceutical facilities make use of closed-loop drying systems to eliminate emissions of VOC's from drying steps.[4] Figure 4-3 presents a typical closed-loop drying system. One such system consists essentially of a high-pressure liquid ring pump in conjunction with two condensers. The system is designed to be used to dry a filtered product cake using a recirculating stream of heated inert gas. The most common application of the system is for recirculating exhaust from agitated pressure nutsche filters, although the system or some modification of this system could probably be adapted to use on most dryer exhaust streams and many streams that contain large amounts of noncondensables, such as inert purges.

2. Basic operation. Exhaust gas from the dryer or filter press is drawn into the liquid ring vacuum pump, which compresses the gas essentially to atmospheric pressure. The gas contacts

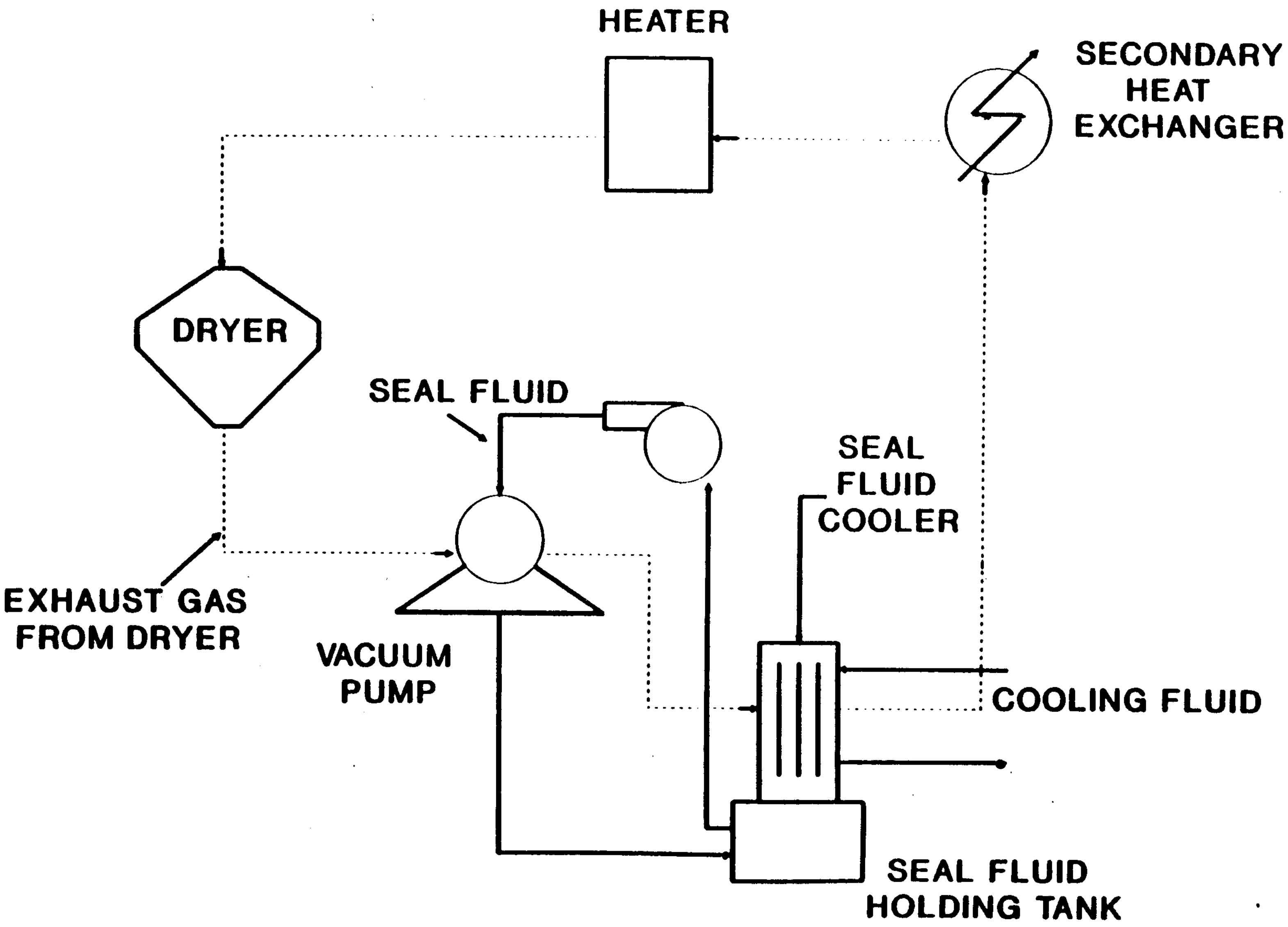

Figure 4-3. Closed-loop drying system.

the pump seal fluid in the vacuum pump. At this point, the pump acts as a contact condenser because the pump seal fluid is chilled. Pump seal fluid and condensed vapors flow into the seal fluid holding tank, which is kept cold by a ring liquid cooler positioned above the surface of the liquid in the tank headspace. The exhausted gases from the pump are also routed across the ring liquid cooler, which happens to be a noncontact vertical shell-and-tube heat exchanger. Some vapors may be condensed from the exhaust stream at this point since the temperature of the ring liquid cooler is slightly lower than the temperature of the fluid in the vacuum pump, especially at the outlet of the pump. Condensed vapors run down the outside of the tubes and shell walls to the seal liquid tank. The exhaust gas in the shell of the ring liquid cooler is routed to yet another shell-and-tube heat exchanger, which operates at a lower temperature than the ring liquid cooler. Condensed vapors from this second heat exchanger are also routed back to the ring liquid holding tank. The holding tank may be equipped with liquid level sensors and contain an overflow weir to remove excess ring liquid, which can ultimately be sent to a solvent recovery unit.

3. Adaptation to drying systems. This type of system may be fitted onto a pressure filter to dry a product cake, thereby eliminating some emissions that are created from product transfer. In addition, the gas stream used to move or vaporize volatiles, depending upon whether the drying is accomplished through conduction or convection (most agitated pressure filters will be more suitable for convective drying), can be recirculated so that there are no emissions to the atmosphere. In such a system, a heater would be added to the system after the exhaust gas cooler to heat the inert stream.

4.2 SCRUBBERS

4.2.1 General Gas Absorbers

Scrubbers, or gas absorbers, function by providing an intimate contacting environment for a gas stream containing material that is soluble in the contacting liquid. The rate of mass transfer from the gas to the liquid depends upon a driving force related to the actual VOC concentrations in the gas and liquid versus the equilibrium-defined VOC concentration in the two media at each point along the contacting path. The most common types of scrubbers found in batch processing industries are packed towers and spray chambers. For dilute concentrations of VOC's, impingement-plate towers, which disperse the vapor phase into a large number of tiny bubbles within the liquid phase and therefore increase the surface area contact between liquid and gas phases, are preferred.[5]

Gas absorbers are limited primarily by the solubility in the liquid stream of the material to be transferred to the liquid stream. Most of the scrubbers found in industry use water as the scrubbing medium, so the effectiveness of these devices depends largely on the solubility of the VOC's in water. In general, compounds containing nitrogen or oxygen atoms that are free to form strong hydrogen bonds and that have one to three carbon atoms are soluble; those compounds with four or five carbons are borderline; and those with six carbon atoms or more are insoluble.[6] Common solvents such as methanol, isopropyl alcohol, and acetone are very soluble in water. Toluene, on the other hand, is not. Although a scrubber could be designed to control a VOC such as toluene, the scrubbing medium would have to be a nonvolatile organic such as mineral oil. Although such systems do exist, their cost is relatively high, since it is energy-intensive to recover separate fractions of mineral oil and VOC, and the cost of mineral oil precludes the use of a once-through system.[7] Note that one of the considerations associated with the use of scrubbers is waste stream disposal and/or treatment.

Since there is usually the transfer of VOC's to the scrubber effluent stream when a water scrubber is used to control VOC emissions, regulators should consider the potential for emissions of VOC from the wastewater collection and treatment system when evaluating the control device effectiveness. When VOC loading is significant, steam stripping of the wastewater may be a viable and cost effective control. To estimate emissions and evaluate control effectiveness for wastewater, a recently revised publication entitled "Control of Volatile Organic Compound Emissions from Industrial Wastewater." Draft CTG can be used.[8]

Also existing for control of some pollutants are chemical scrubbers, which, instead of using a liquid medium to absorb material out of the gas phase, use the liquid medium to react with material in the gas phase. A good example is an emergency destruction scrubber for a compound such as phosgene ($COCl_2$). Phosgene, when reacted with slightly basic water, hydrolyzes to HCl and CO_2. Although these product gases still require control, their toxicity is much less than that of the initial reactant. Chemical scrubbers are often used as emergency back-up devices.

4.2.2 Design

The design of a scrubber involves the estimation of the ratio of gas-to-liquid mass flow rates and the appropriate amount of contacting area necessary to achieve the desired removal. A necessary piece of information, which can be difficult to obtain without experimental work, is the equilibrium curve depicting equilibrium mole fractions of the VOC in the solvent in the vapor and liquid phases at the contacting temperature. The equilibrium curve, as the name implies, is not a straight line, but approximations may be used and the curve may be assumed to be straight in some situations. For water scrubbers, the Henry's law constant at the water temperature is often used as the slope of the equilibrium curve.

The estimation of the physical properties of a scrubber design, such as the number of transfer units (N_{OG}) and the height of transfer unit (H_{OG}) for a packed tower, may be estimated based on the reported removal efficiency of a system and the reported liquid-to-gas mass velocities. The EPA publication EPA-450/3-80-027, Organic Chemical Manufacturing Volume 5: Adsorption, Condensation, and Absorption Devices, December 1980, contains the methodology that can be used to estimate such parameters.[9] Note that verifying the efficiency of a scrubber is more difficult than verifying the efficiency of condenser since there are more variables to consider and the equilibrium data for VOC in solvent at the required temperature are not always available. It is perhaps for this reason that unrealistically high scrubber efficiencies may sometimes be reported.

4.2.3 Specific Systems and Applicability

Scrubbers often are used in batch processing as secondary control devices to condensers. Scrubbers may be advantageous to use on streams that have discontinuous properties such as many of the emission streams from batch processes since scrubbers in most cases are not as expensive to operate during off-load times as other control devices. Although the control efficiency would decrease with decreasing gas flow rates during off-load times, the efficiency would pick up again with an increase in gas flow rate back up to the design value. The following paragraph describes one specific application for the control of the solvent isopropyl alcohol (IPA) with a water scrubber through convective drying.

A feasibility analysis of control devices was conducted on a dryer exhaust stream containing the solvent IPA. It was determined that a packed tower water scrubber could achieve at least 90 percent removal of IPA from the exhaust gas of an atmospheric dryer. Three meters of packing were determined to be required, and 0.4 m^3 of water per minute under peak conditions was determined to be necessary for a peak exhaust gas flow rate of 6,000 acfm with a 0.4 percent IPA concentration.[10]

4.3 CARBON ADSORPTION

Carbon adsorbers function by capturing material that is present in a gas phase on the surface of granular activated carbon. Adsorbers can be of the fixed-bed design or fluidized-bed design. Fixed-bed adsorbers must be regenerated periodically to desorb the collected organics from the carbon. Fluidized-bed adsorbers are continuously regenerated. Most batch industries that use carbon adsorbers use the fixed-bed type. Some use nonregenerative units, which are contained in 55-gallon drums and are used mostly for controlling odor from small process vents. Such units are returned to their distributors for disposal after they can no longer adsorb effectively.

4.3.1 Design

Carbon adsorption is usually a batch operation involving two main steps, adsorption and regeneration. This system usually includes multiple beds so that at least one bed is adsorbing while at least one other bed is being regenerated, thereby ensuring that emissions will be continually controlled. A blower is commonly used to force the VOC-laden gas stream through the fixed carbon bed. The cleaned gas is then exhausted to the atmosphere. A gradual increase in the concentration of organics in the exhausted gas from its baseline effluent concentration level signals it is time for regeneration. The bed is shut off and the waste gas is routed to another bed. Low-pressure steam is normally used to heat the carbon bed during regeneration, driving off the adsorbed organics, which are usually recovered by condensing the vapors and separating them from the steam condensate by decantation or distillation. After regeneration, the carbon bed is cooled and dried to improve adsorption. The adsorption/regeneration cycle can be repeated numerous times, but eventually the carbon loses its adsorption activity and must be replaced. Typically, facilities replace a portion of the carbon bed on an annual basis.

The efficiency of an adsorption unit depends on the type of activated carbon used, the characteristics of the VOC, the VOC concentration, and the system temperature, pressure, and humidity. Overall VOC removal efficiencies depend on the completeness of regeneration, the depth of the carbon bed, the time allowed for contact, and the effectiveness of recovery of desorbed organics. Carbon adsorption is not suitable for gas streams with a high concentration of organics, with organics with boiling points greater than 250°C or molecular weights greater than 200, with relative humidities greater than 50 percent, with high levels of entrained solids, or with temperatures over 100°F. Adsorbing organics from gas streams with high concentrations of organics may result in excessive temperature rise in the bed due to the accumulated heat of adsorption; this can be a serious safety problem. High-molecular-weight organics and organics with high boiling points are difficult to remove from the carbon under normal regeneration temperatures. The continuing buildup of these compounds on the carbon greatly decreases the operating capacity and results in frequent replacement of the carbon. Plasticizers or resins should also be prevented from entering the carbon bed, since they may react chemically on the carbon to form a solid that cannot be removed during regeneration. These problems can be controlled by the use of a condenser upstream of the carbon bed to remove the high-boiling-point components or a carbon bed guard that can be easily replaced on a regular basis. Entrained solids in the gas stream may cause the carbon bed to plug over a period of time. These solids are generally controlled by a cloth or fiberglass filter. Gas streams with high relative humidities affect the adsorption capacity of the bed. Humidity control can be achieved by cooling and condensing the water vapor in the gas stream. The relative humidity can also be decreased by adding dry dilution air to the system, but this usually increases the size and thus the cost of the adsorber required. The adsorption capacity of the carbon and the effluent concentration of the adsorber are directly related to the temperature of the inlet stream to the adsorber. Normally, the temperature of the inlet stream should be below 100°F or the adsorption capacity will be affected. Inlet stream coolers are usually required when emission stream temperatures are in excess of 100°F.

4.3.2 Applicability

Carbon adsorbers are often used as controls for batch process operations. At many facilities several VOC sources are ducted to a single adsorber, since most single emission streams from batch process operations do not warrant the sole use of an adsorber. Emissions from reactor vents, separation operations, dryers, and storage tanks may be often controlled by carbon bed adsorbers. In many of these applications, the adsorber is preceded upstream by a condenser. Since condensers are more efficient on saturated streams and carbon bed adsorbers are more efficient on dilute streams, a condenser followed by a carbon bed adsorber can be an effective control system.

Nonregenerative carbon adsorbers may also be useful for batch process operations. These systems are extremely simple in design. When the activated carbon becomes spent, it is replaced with a new charge. The spent carbon can be reactivated offsite and eventually reused. Carbon canisters, normally the size of 55-gallon drums, can be used to control small vent streams (less than 500 actual cubic feet per minute [acfm] <500 ft^3/min) with low organic concentrations. They are commonly used to control emissions from storage tanks and small reaction vents. One advantage of these systems is that they are immune to normal fluctuations in gas streams that are common to batch processes. In fact, most carbon adsorption systems are especially suited for batch processing, since the beds do not require continuous energy input (except for a fan to move the gas).

When designing and installing carbon bed adsorber systems, several safety factors need to be considered. Fixed carbon beds can spontaneously combust whenever the gas stream contains oxygen and compounds easily oxidized in the presence of carbon, such as ketones, aldehydes, and organic acids. Heat generated by adsorption or by oxidation of VOC in the bed is usually transported from the bed by convection. If less convection heat is removed than is generated, the bed temperature will rise. Higher temperatures will further increase the oxidation decomposition, and hot spots exceeding the autoignition temperature of the carbon may develop in the bed. If an adsorber is shut down for an extended period and not regenerated sufficiently upon startup, reintroduction of the VOC-laden stream may also lead to bed combustion. However, preventive measures can be taken to ensure safe operation of carbon adsorbers. Using adequate cooling systems, regularly inspecting valves to prevent steam leaks, and using adsorbers only on low-concentration streams all will ensure safe operation. In addition, beds used for adsorbing ketones should not be dried completely after regeneration. Although not drying them may reduce adsorption capacity somewhat, it is an effective safety measure because the water acts as a heat sink to dissipate the heat of adsorption and oxidation.

Carbon adsorption systems normally are designed for gas velocities between 80 and 100 ft/min.[11] The maximum rate of recovery of organics is dependent upon the amount of carbon provided and the depth of the bed needed to provide an adequate transfer zone. The required amount of carbon may be estimated from an adsorption isotherm, which is generally available for different compounds at various partial pressures.

For all practical purposes, it is difficult to estimate the efficiency of a carbon adsorption system. EPA has conducted several studies which show that a control efficiency of 95 percent is achievable for streams containing compounds that are considered appropriate (see above discussion) for adsorption, the actual control efficiency attained by a particular system is largely dependent upon the amount of time elapsed and the amount of material sorbed since the last regeneration or replacement.[12]

Note also that it is more difficult to predict the amount of material that has been sorbed for the intermittent streams with variable characteristics typical of batch processes than for continuous emission streams with constant properties. In some situations, the VOC's are sorbed out of the gas streams during peak loading periods and are reentrained during off-peak periods. In these situations, there is no net control of VOC by the carbon system. To prevent inadvertent stripping of VOC's during such periods, air flow should be diverted from the adsorber during periods of time when there are no VOC emissions.

As mentioned previously, most applications of carbon adsorbers follow condensers. Because of the highly flammable nature of many typical solvents, the industry trend is away from using these devices as primary control devices.

4.4 THERMAL DESTRUCTION

It is usually possible to route process vents to an incinerator or flare for control. Incineration systems are usually quite costly and must operate continuously; therefore the use of such systems is limited to those applications where a number of vents may be controlled. Note also that the byproduct combustion gases must also be controlled in most cases, thereby increasing costs.

4.4.1 Flares

Flaring is an open combustion process that destroys VOC emissions with a high-temperature oxidation flame to produce carbon dioxide and water. Good combustion in a flare is governed by flame temperature, residence time of components in the combustion zone, and turbulent mixing of components to complete the oxidation reaction.

4.4.1.1 Design. Flare types can be divided into two main groups: (1) ground flares and (2) elevated flares, which can be further classified according to the method to enhance mixing within the flare tip (air-assisted, steam-assisted, or nonassisted). The discussion in this chapter focuses on elevated flares, the most common type in the chemical industry. The vent stream is sent to the flare through the collection header. The vent stream entering the header can vary widely in volumetric flow rate, moisture content, VOC concentration, and heat value.

The knock-out drum removes water or hydrocarbon droplets that could create problems in the flare combustion zone. Vent streams are also typically routed through a water seal before going to the flare. This prevents possible flame flashbacks, caused when the vent stream flow rate to the flare is too low and the flame front pulls down into the stack.[13]

Purge gas (N_2, CO_2, or natural gas) also helps to prevent flashback in the flare stack caused by low vent stream flow. The total volumetric flow to the flame must be carefully controlled to prevent low-flow flashback problems and to avoid a detached flame (a space between the stack and flame with incomplete combustion) caused by an excessively high flow rate. A gas barrier or a stack seal is sometimes used just below the flare head to impede the flow of air into the flare gas network.

The VOC stream enters at the base of the flame where it is heated by already burning fuel and pilot burners at the flare tip. Fuel flows into the combustion zone, where the exterior of the microscopic gas pockets is oxidized. The rate of reaction is limited by the mixing of the fuel and oxygen from the air. If the gas pocket has sufficient oxygen and residence time in the flame zone, it can be completely burned. A diffusion flame receives its combustion oxygen by diffusion of air into the flame from the surrounding atmosphere. The high volume of flue gas flow in a flare requires more combustion air at a faster rate than simple gas diffusion can supply. Thus, flare designers add high-velocity steam injection nozzles to increase gas turbulence in the flame boundary zones, drawing in more combustion air and improving combustion efficiency. This steam injection promotes smokeless flare operation by minimizing the cracking reaction that forms carbonaceous spot. Significant disadvantages of steam use are increased noise and cost. The steam requirement depends on the composition of the gas flared, the steam velocity from the injection nozzle, and the tip diameter. Although some gases can be flared smokelessly without any steam, typically 0.01 to 0.6 kg of steam per kg of flare gas is required.

Steam injection is usually controlled manually by an operator who observes the flare (either directly or on a television monitor) and adds steam as required to maintain smokeless operation. Several flare manufacturers offer devices such as infrared sensors that monitor flame characteristics and adjust the steam flow rate automatically to maintain smokeless operation.

Some elevated flares use forced air instead of steam to provide the combustion air and the mixing required for smokeless operation. These flares consist of two coaxial flow channels. The combustible gases flow in the center channel and the combustion air (provided by a fan in the bottom of the flare stack) flows in the annulus. The principal advantage of air-assisted flares is that they can be used where steam is not available. Air assist is rarely used on large flares because airflow is difficult to control when the gas flow is intermittent. About 90.8 hp of blower capacity is required for each 100 lb/hr of gas flared.[14]

Ground flares are usually enclosed and have multiple burner heads that are staged to operate based on the quantity of gas released to the flare. The energy of the gas itself (because of the high nozzle pressure drop) is usually adequate to provide the mixing necessary for smokeless operation, and air or steam assist is not required. A fence or other enclosure reduces noise and light from the flare and provides some wind protection.

Ground flares are less numerous and have less capacity than elevated flares. Typically they are used to burn gas continuously while steam-assisted elevated flares are used to dispose of large amounts of gas released in emergencies.[15]

4.4.1.2 Factors Affecting Flare Efficiency.[16] Flare combustion efficiency is a function of many factors: (1) heating value of the gas, (2) density of the gas, (3) flammability of the gas, (4) auto-ignition temperature of the gas, and (5) mixing at the flare tip.

The flammability limits of the gases flared influence ignition stability and flame extinction. The flammability limits are defined as the stoichiometric composition limits (maximum and minimum) of an oxygen-fuel mixture that will burn indefinitely at given conditions of temperature and pressure without further ignition. In other words, gases must be within their flammability limits to burn. When flammability limits are narrow, the interior of the flame may have insufficient air for the mixture to burn. Fuels with wide limits of flammability (for instance, H_2) are therefore easier to combust.

The auto-ignition temperature of a fuel affects combustion because gas mixtures must be at high enough temperature and at the proper mixture strength to burn. A gas with a low auto-ignition temperature will ignite and burn more easily than a gas with a high auto-ignition temperature.

The heating value of the fuel also affects the flame stability, emissions, and flame structure. A lower-heating-value fuel produces a cooler flame that does not favor combustion kinetics and also is more easily extinguished. The lower flame temperature also reduces buoyant forces, which reduces mixing. The density of the gas flared also affects the structure and stability of the flame through the effect on buoyancy and mixing. By design, the velocity in many flares is very low; therefore, most of the flame structure is developed through buoyant forces as a result of combustion. Lighter gases therefore tend to burn better. In addition to burner tip design, the density of the fuel also affects the minimum purge gas required to prevent flashback for smokeless flaring.

Poor mixing at the flare tip or poor flare maintenance can cause smoking (particulate). Fuels with high carbon-to-hydrogen ratios (greater than 0.35) have a greater tendency to smoke and require better mixing if they are to be burned smokelessly.

Many flare systems are currently operated in conjunction with baseload gas recovery systems. Such systems are used to recover VOC from the flare header system for reuse. Recovered

VOC may be used as a feedstock in other processes or as a fuel in process heaters, boilers, or other combustion devices. When baseload gas recovery systems are applied, the flare is generally used to combust process upset and emergency gas releases that the baseload system is not designed to recover. In some cases, the operation of a baseload gas recovery system may offer an economic advantage over operation of a flare alone since sufficient quantities of useable VOC can be recovered.

4.4.1.3 EPA Flare Specifications. The EPA has established flare combustion efficiency criteria (40 CFR 60.18) which specify that 98 percent or greater combustion efficiency can be achieved provided that certain operating conditions are met: (1) the flare must be operated with no visible emissions and with a flame present; (2) the net heating value of the flared stream must be greater than 11.2 MJ/scm (300 Btu/scf) for steam-assisted flares and 7.45 MJ/scm (200 Btu/scf) for a flare without assist; and (3) steam-assisted and nonassisted flares must have an exit velocity less than 18.3 m/sec (60 ft/sec). Steam assisted and nonassisted flares having an exit velocity greater than 18.3 m/sec (60 ft/sec) but less than 122 m/sec (400 ft/sec) can achieve 98 percent or greater control if the net heating value of the gas stream is greater than 37.3 MJ/scm (1,000 Btu/scf). The allowable exit velocity for air-assisted flares, as well as steam-assisted and nonassisted flares with an exit velocity less than 122 m/sec (400 ft/sec) and a net heating value less than 37.3 MJ/scm (1,000 Btu/scf), can be determined by using an equation in 40 CFR 60.18.

4.4.1.4 Applicability. Although flares are not as widely used for controlling emissions from batch processes as other control devices--for example, condensers, adsorbers, and scrubbers--they are adjustable and can be useful for these processes. In many cases, however, they require a considerable amount of auxiliary fuel to combust gases that contain dilute concentrations of VOC's or VOC's that have low heats of combustion. Flares are capable of handling the highly variable flows that are often associated with batch process operations. Steam-assisted elevated flares may be used to control emissions from high-concentration, intermittent vent streams. In many facilities, elevated flares are used to control emissions during emergency venting or during process upsets, such as startup and shutdown. These intermittent emissions are characteristic of normal batch process operations with the exception that they may be more concentrated than normal batch emissions. Ground flares have less capacity than elevated flares and are usually used to burn gas continuously. They should also be easily accessible to batch processes because of the multiple burner head design, which can be stage-operated based on gas flow. Ground flares can operate efficiently from 0 to 100 percent of design capacity. The burner heads can also be specifically sized and designed for the materials in the flare gas.

4.4.2 Thermal and Catalytic Oxidizers

Thermal and catalytic oxidizers may be used to control emission streams of VOC's and air toxics, although they are not especially suited for intermittent or noncontinuous flows. Because they operate continuously, auxiliary fuel must be used to maintain combustion during episodes in which the VOC load is below design conditions. In some situations where VOC loading in the gas to be controlled is small, the environmental benefits of using fossil fuel and creating products of combustion in order to combust VOC's on an intermittent basis as opposed to releasing the uncombusted VOC's must be evaluated by considering the reduction of VOC compared to costs and production of other pollutants.

4.4.2.1 Thermal Oxidizer Design. Any VOC heated to a high enough temperature in the presence of enough oxygen will be oxidized to carbon dioxide and water. This is the basic principle of operation of a thermal incinerator. The theoretical temperature required for thermal oxidation depends on the chemical involved. Some chemicals are oxidized at temperatures much lower than others. However, a temperature can be identified that will result in the efficient destruction of most VOC's. All practical thermal incineration processes are influenced by residence time, mixing, and temperature. An efficient thermal incinerator system must provide:

1. A chamber temperature high enough to enable the oxidation reaction to proceed rapidly to completion;
2. Enough turbulence to obtain good mixing between the hot combustion products from the burner, combustion air, and VOC; and
3. Sufficient residence time at the chosen temperature for the oxidation reaction to reach completion.

A thermal incinerator is usually a refractory-lined chamber containing a burner (or set of burners) at one end. Discrete dual fuel burners and inlets for the offgas and combustion air are arranged in a premixing chamber to thoroughly mix the hot products from the burners with the process vent streams. The mixture of hot reacting gases then passes into the main combustion chamber. This chamber is sized to allow the mixture enough time at the elevated temperature for the oxidation reaction to reach completion (residence times of 0.3 to 1.0 second are common). Energy can then be recovered from the hot flue gases in a heat recovery section. Preheating combustion air or offgas is a common mode of energy recovery; however, it is sometimes more economical to generate steam. Insurance regulations require that if the waste stream is preheated, the VOC concentration must be maintained below 25 percent of the lower explosive limit to remove explosion hazards.

Thermal incinerators designed specifically for VOC incineration with natural gas as the auxiliary fuel may also use a grid-type (distributed) gas burner.[17] The tiny gas flame jets on the grid surface ignite the vapors as they pass through the grid. The grid acts as a baffle for mixing the gases entering the chamber. This arrangement ensures burning of all vapors at lower chamber temperature and uses less fuel. This system makes possible a shorter reaction chamber yet maintains high efficiency.

A thermal incinerator, handling vent streams with varying heating values and moisture content, requires careful adjustment to maintain the proper chamber temperatures and operating efficiency. Since water requires a great deal of heat to vaporize, entrained water droplets in an offgas stream can increase auxiliary fuel requirements to provide the additional energy needed to vaporize the water and raise it to the combustion chamber temperature. Combustion devices are always operated with some quantity of excess air to ensure a sufficient supply of oxygen. The amount of excess air used varies with the fuel and burner type but should be kept as low as possible. Using too much excess air wastes fuel because the additional air must be heated to the combustion chamber temperature. Large amounts of excess air also increase fuel gas volume and may increase the size and cost of the system. Packaged, single-unit thermal incinerators can be built to control streams with flow rates in the range of 0.14 scm/sec (300 scfm) to about 24 scm/sec (50,000 scfm).

Thermal oxidizers for halogenated VOC's may require additional control equipment to remove the corrosive combustion products. The halogenated VOC streams are usually scrubbed to prevent corrosion due to contact with acid gases formed during the combustion of these streams. The flue gases are quenched to lower their temperature and are then routed through absorption equipment such as packed towers or liquid jet scrubbers to remove the corrosive gases.

4.4.2.2 Thermal Incinerator Efficiency. The VOC destruction efficiency of a thermal oxidizer can be affected by variations in chamber temperature, residence time, inlet VOC concentration, compound type, and flow regime (mixing). Test results show that thermal oxidizers can achieve 98 percent destruction efficiency for most VOC compounds at combustion chamber temperatures ranging from 700 to 1300°C (1,300° to 2370°F) and residence times of 0.5 to 1.5 seconds.[18] These data indicate that significant variations in destruction efficiency occurred for C_1 to C_5 alkanes and olefins, aromatics (benzene, toluene, and xylene), oxygenated compounds (methyl ethyl ketone and isopropanol), chlorinated organics (vinyl chloride), and nitrogen-containing species (acrylonitrile and ethylamines) at chamber temperatures below 760°C (1400°F). This information, used in conjunction with kinetics calculations, indicates the combustion chamber parameters for achieving at least a 98 percent VOC destruction efficiency are a combustion temperature of 870° (1600°F) and a residence time of 0.75 sec (based upon residence in the chamber volume at combustion temperature). A thermal oxidizer designed to produce these conditions in the combustion chamber should be capable of high destruction efficiency for almost any nonhalogenated VOC.

At temperatures over 760°C (1400°F), the oxidation reaction rates are much faster than the rate of gas diffusion mixing. The destruction efficiency of the VOC then becomes dependent upon the fluid mechanics within the oxidation chamber. The flow regime must ensure rapid, thorough mixing of the VOC stream, combustion air, and hot combustion products from the burner. This enables the VOC to attain the combustion temperature in the presence of enough oxygen for sufficient time so the oxidation reaction can reach completion.

Based upon studies of thermal oxidizer efficiency, it has been concluded that 98 percent VOC destruction or a 20 ppmv compound exit concentration is achievable by all new incinerators. The maximum achievable VOC destruction efficiency decreases with decreasing inlet concentration because of the much slower combustion reaction rates at lower inlet VOC concentrations. Therefore, a VOC weight percentage reduction based on the mass rate of VOC exiting the control device versus the mass rate of VOC entering the device would be appropriate for vent streams with VOC concentrations above approximately 2,000 ppmv (corresponding to 1,000 ppmv VOC in the incinerator inlet stream since air dilution is typically 1:1). For vent streams with VOC concentrations below approximately 2,000 ppmv, it has been determined that an incinerator outlet concentration of 20 ppmv (by compound), or lower, is achievable by all new thermal oxidizers.[19] The 98 percent efficiency estimate is predicted on thermal incinerators operated at 870°C (1600°F) with 0.75 sec residence time.

4.4.2.3 Catalytic Oxidizer Design. Catalytic oxidation is also a major combustion technique examined for VOC emission control. A catalyst increases the rate of chemical reaction without becoming permanently altered itself. Catalysts for catalytic oxidation cause the oxidizing reaction to proceed at a lower temperature than is required for thermal oxidation. These units can also operate well at VOC concentrations below the lower explosive limit, which is a distinct advantage for some process vent streams. Combustion catalysts include platinum and platinum alloys, copper oxide, chromium, and cobalt.[20] These are deposited in thin layers on inert substrates to provide for maximum surface area between the catalyst and the VOC stream. The substrate may be either pelletized or cast in a rigid honeycomb matrix.

The waste gas is introduced into a mixing chamber, where it is heated to about 316°C (600°F) by contact with the hot combustion products from auxiliary burners. The heated mixture is then passed through the catalyst bed. Oxygen and VOC migrate to the catalyst surface by gas diffusion and are adsorbed in the pores of the catalyst. The oxidation reaction takes place at these active sites. Reaction products are desorbed from the active sites and transferred by diffusion back into the waste gas.[21] The combusted gas may then be passed through a waste heat recovery device before exhausting into the atmosphere.

The operating temperatures of combustion catalysts usually range from 316° to 650°C (600° to 1200°F). Lower temperatures may slow down and possibly stop the oxidation reaction. Higher temperatures may result in shortened catalyst life and possible evaporation or melting of the catalyst from the support substrate. Any accumulation of particulate matter, condensed

VOC, or polymerized hydrocarbons on the catalyst could block the active sites and, therefore, reduce effectiveness. Catalysts can also be deactivated by compounds containing sulfur, bismuth, phosphorus, arsenic, antimony, mercury, lead, zinc, tin, or halogens.[22] If these compounds exist in the catalytic unit, VOC will pass through unreacted or be partially oxidized to form compounds such as aldehydes, ketones, and organic acids.

4.4.2.4 Catalytic Oxidizer Control Efficiency. Catalytic oxidizer destruction efficiency is dependent on the space velocity (the catalyst volume required per unit volume gas processed per hour), operating temperature, oxygen concentration, and waste gas VOC composition and concentration. A catalytic unit operating at about 450°C (840°F) with a catalyst bed volume of 0.014 to 0.057 m^3 (0.5 to 2 ft^3) per 0.47 scm/sec (1,000 scfm) of vent stream passing through the device can achieve 95 percent VOC destruction efficiency. However, catalytic oxidizers have been reported to achieve efficiency of 98 percent or greater.[23] These higher efficiencies are usually obtained by increasing the catalyst bed volume-to-vent stream flow ratio.

4.4.2.5 Applicability of Thermal and Catalytic Oxidizers. Incinerators often are used to control multiple process vents that can be manifolded together. For example, processes that are contained within one building or processing area are sometimes tied together and routed to an incinerator. For some of these vents, a primary control device such as a condenser is located upstream. Note that the stack gases resulting from combustion often contain acid such as HCl and may require an exhaust gas control device such as a caustic scrubber.

There are also some incineration units that can handle low flow rates (in the range of 10 to 500 scfm). These units can be applied to single emission streams, such as reactor vent emissions. The presumably high destruction efficiency obtained for VOC's and air toxics using these devices makes their application attractive for very toxic substances.[24]

4.5 SOURCE REDUCTION MEASURES

4.5.1 Vapor Containment

Probably one of the less expensive and more effective methods of controlling displaced vapors from such events as vessel charging and from storage tank working losses is to use vapor return lines to vent the vapors back to the vessel from which the liquid was originally taken. Essentially 100 percent control of the vapors at the point source is achieved, and there do not appear to be many adverse effects from the standpoint of safety or convenience. However, the vessel which receives the "vent back" must also be controlled. Some facilities use vessels with flexible volumes, such as balloons, or traditional gas holders with self-adjusting diaphragms to contain vapors prior to a control device. Probably the biggest problem relative to batch processing is that there are many different possibilities at any given time for equipment configuration, and therefore a manifold-type system for venting back vapors to the appropriate vessels would have to be installed.

4.5.2 Limiting the Use of Inert Gas

Obviously, many applications in batch processing require the use of inert gas for blanketing and purging of equipment for safety purposes. Oftentimes, the distribution of the nitrogen is affected through continuous purging of equipment. While purging achieves the inert atmosphere desired, it is also a source of emissions because volatile compounds are stripped off and emitted along the same discharge pathway as the nitrogen exhaust stream. Limiting emissions from nitrogen purging is achieved by reducing the amount of nitrogen that is purged. An inert atmosphere can also be created by establishing, through a series of pressure transducers and distribution valves, a constant nitrogen, positive pressure "blanket." However, processing equipment that does not have the possibility of remaining airtight cannot be blanketed in this manner. The older style basket centrifuges requiring inertion during the separation of solid cake, for example, cannot be blanket-inerted. Therefore, it follows that limiting the distribution of nitrogen to constant positive pressure blanketing operations may require not only capital expenditures for the distribution system elements (i.e., the pressure transducers and distribution valves), but perhaps the replacement of some equipment.

There are other practices, however, such as the blowing of lines to move material and the sparging of large volumes of liquids that could be changed so as to reduce the amount of inert gases in the streams and thereby make the streams more suitable for control by devices such as condensers.

The blowing of lines with nitrogen to move material, for example, could be replaced by simple pumping and/or setting the lines on an incline. Blowing cannot be totally eliminated, however, because the vapor that may be contained in the vapor space in the lines may need to be purged at various times before maintenance.

Also, a recently developed technology for in-line stripping could conceivably replace the use of large volumes of inert gas used for sparging. Control of emissions from sparging, as is shown in Chapter 5, appears to be difficult because of the dilute volumes of VOC in the exhaust sparge gas. An in-line stripping system that is installed directly into process piping creates a large number of very tiny nitrogen bubbles, which results in maximum gas-liquid interface. One such system tested at a plant reduced the amount of nitrogen used for sparging from 38,400 to 1,150 scfm and was considerably more efficient.[25]

An added benefit of limiting the amount of nitrogen that is used in inerting processing equipment is that the volumetric flowrates of the exhausts will be diminished, and therefore VOC concentrations in the exhausts will be less dilute and may therefore be more cost effective to control or recover using add-on controls.

4.5.3 Use of Closed Processing Equipment

The retrofitting or replacement of older equipment with new airtight equipment is not only helpful to nitrogen blanketing applications, but perhaps more importantly, to the processing of material in entirely closed systems where the possibility of creating emissions is eliminated altogether. Batch processing appears to be gravitating to processing equipment that is versatile and therefore allows for numerous conventional unit operations such as mixing, reaction, filtration, and drying, to be conducted in the same vessel. Transfer losses, which can be very significant, are virtually eliminated, as are some cleaning operations that would otherwise be required in between processing runs.[26]

4.5.4 Material Substitution/Improved Separation Techniques

One of the more significant areas of material substitution in the batch manufacturing industry is the potential substitution of organic solvents with aqueous solvents, aqueous solvents with internally contained organic micelles, or supercritical fluids. Still in developmental stages, the use of aqueous polymeric systems having an internal micelle structure for hydrocarbons would allow for reactions to occur within the polymer micelles. Currently, the major problem with these polymers is that their solubility in water is still too low to be of any practical utility.[27]

The possibility of using supercritical fluids (SCF) in extraction and separation applications is becoming more of a reality. Supercritical fluids have been shown to be of utility in separation of organic-water solutions, petroleum fractions, and activated carbon regeneration. Additionally, a large body of experimental data has been accumulated on the solubility and extractability of natural products such as steroids, alkaloids, anticancer agents, oils from seeds, and caffeine from coffee beans in various supercritical fluids such as CO_2, ethane, ethylene, and N_2O. Currently, CO_2 is the most widely investigated SCF in these applications.

4.5.5 Improved Process Design

The elimination of intermediate isolation steps, if possible, can be a significant source of emissions reduction because filtration and drying steps are eliminated. It is also likely that some equipment cleaning steps can be eliminated without negative effects.

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5.0 ENERGY AND ENVIRONMENTAL IMPACTS

The energy and environmental impacts associated with applying various control options to VOC emissions from batch processes are presented in this chapter. The options are described in detail in Chapter 6.

The environmental impacts analysis considers the national energy burden of operating the control devices used to meet various options, as well as the national estimate of NO_x produced from the incineration of selected model process emission streams and from the generation of electricity. Solid waste and wastewater impacts were not evaluated because the effects resulting from the operation of these control devices are considered negligible.

5.1 ENERGY IMPACTS

Table 5-1 presents the national estimate of energy usage for each of the options described in Chapter 6. The energy burden was calculated by estimating the amount of fuel and electricity required to operate the thermal incinerator and the electricity requirement for the refrigerated condenser systems for the applicable model streams. Approximately 10 percent of the total energy burden shown for each of the options in the table is related to the condenser systems. The remainder is associated with the natural gas requirements of the thermal incinerator. Energy usage for model streams and plants was extrapolated to a nationwide estimate by considering the number of facilities in the batch industries covered by this document. Note that there is no discernable difference in energy between the 98 percent and 95 percent options. This effect occurs because the thermal

TABLE 5-1. ENERGY AND ENVIRONMENTAL IMPACTS

Option	Description of option	Uncontrolled emissions, 1,000 Mg/yr	Baseline emissions, 1,000 Mg/yr	Nationwide emission reduction from baseline, 1,000 Mg/yr	Energy burden, 10^{13} Btu/yr	NO_x emissions, 1,000 Mg/yr[a,b]
1	98% control of aggregated process vents that are not exempt per regression lines 1, 4, 7	210	77	65	5	5
2	90% control of process vents	210	77	52	2	2
3	95% control of process vents	210	77	63	5	5

[a] Emissions of NO_x are from incinerator exhaust and from power plants used to generate the electrical power fraction of the energy burden.

[b] NO_x emission factors:

Incinerators: 200 ppm NO_x in exhaust for streams containing nitrogen compounds, and 21.5 ppm NO_x in all other streams (based on test data).

incinerator is the significant energy using device and it was assumed to control emission streams by 98 percent in all cases. The energy difference in using refrigerated condensation systems operating at 98 percent and 95 percent efficiency was insignificant compared to the incinerator energy requirements.

5.2 AIR QUALITY IMPACTS

The NO_x emissions from thermal incinerators were estimated assuming that the incinerator flue gas flow rate contained 50 ppm NO_x. This value is in the range of concentration observed for emission streams from incinerators (see footnote b, Table 5-1). An alternative emission factor which could have been used is 0.133lb NO_x per million Btu of natural gas.[1]

The NO_x emissions from energy generation were calculated because condensers also use power. Several assumptions were required. Since the majority of electrical power comes from coal combustion, and the majority of coal used is bituminous, an emission factor was developed to related electrical power, in kilowatt-hours (kWh), to NO_x generation. This factor was developed using an AP-42 emission factor for NO_x generation from bituminous coal combustion. This factor is 14 lb NO_x/ton coal[2]. The average net heating value of bituminous coal is 14,000 Btu/lb.[3] It was also assumed that coal-fired power plants are about 35 percent efficient. The emission factor is therefore 5×10^{-3}lbs NO_x/kwh, or:

$$\text{kWh}\ \frac{3{,}412\ \text{Btu}}{\text{kWh}}\ \Big|\ \frac{}{0.35}\ \Big|\ \frac{\text{lb}_{\text{coal}}}{14{,}000\ \text{Btu}}\ \Big|\ \frac{\text{ton}}{2{,}000\ \text{lb}}\ \Big|\ \frac{14\ \text{lb}\ NO_x}{\text{ton}}$$

Offsets for individual cases can be calculated using the emission factors presented above.

5.3 WASTEWATER AND SOLID WASTE IMPACTS

Wastewater and solid waste impacts are not expected to be significant for this source category. Thermal incineration for halogenated compounds will yield acid gases which typically are neutralized using caustic scrubbers. The number of streams from batch processing emissions that potentially would be halogenated and incinerated was not estimated, however. For refrigeration systems, wastewater could be generated from humid waste gas streams, but this quantity also is not expected to be significant.

5.4 REFERENCES FOR CHAPTER 5.0

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6.0 DESCRIPTION OF CONTROL OPTIONS

6.1 TECHNICAL BASIS FOR CONTROL OPTIONS

6.1.1 Approach

The methodology used in developing control options is based on an evaluation of the technical feasibility and costs of controlling any vent stream that could be emitted to the atmosphere from a batch process. In order to be able to apply the options and to defend the rationale that was used to develop the options for a wide variety of stream characteristics, factors such as cost effectiveness and control device applicability were examined for all potential variations in duration of emission events and emission stream characteristics of flow rate and VOC concentration. This section presents a discussion of batch processing emissions and describes the methodology for developing the options.

6.1.1.1 Batch Processing Emission Stream Characteristics. In general, there are two qualities that differentiate batch processing emissions from those of sources operating continuously. First, batch emission stream characteristics (e.g., flow rate, concentration, temperature, etc.) are never constant. Second, the emissions are released on an intermittent basis. To illustrate these ideas, consider the batch process shown in Figure 6-1. Emissions of VOC's will occur from this process from start to finish in the order that the bulk flow of material and energy occurs. For example, the process begins with the charging of a VOC material from storage into the weigh tanks. A displacement of air from the weigh tanks occurs at this point as a result of being pushed out by the incoming volume of material. Through vaporization of the VOC liquid across the liquid-air interface, this air contains some amount of VOC and thus constitutes an emission event. The event is short-lived, however, lasting only the time of the charge; the concentration of VOC's in the displaced flow rate will increase to a point close to saturation by the time the last of the displaced air

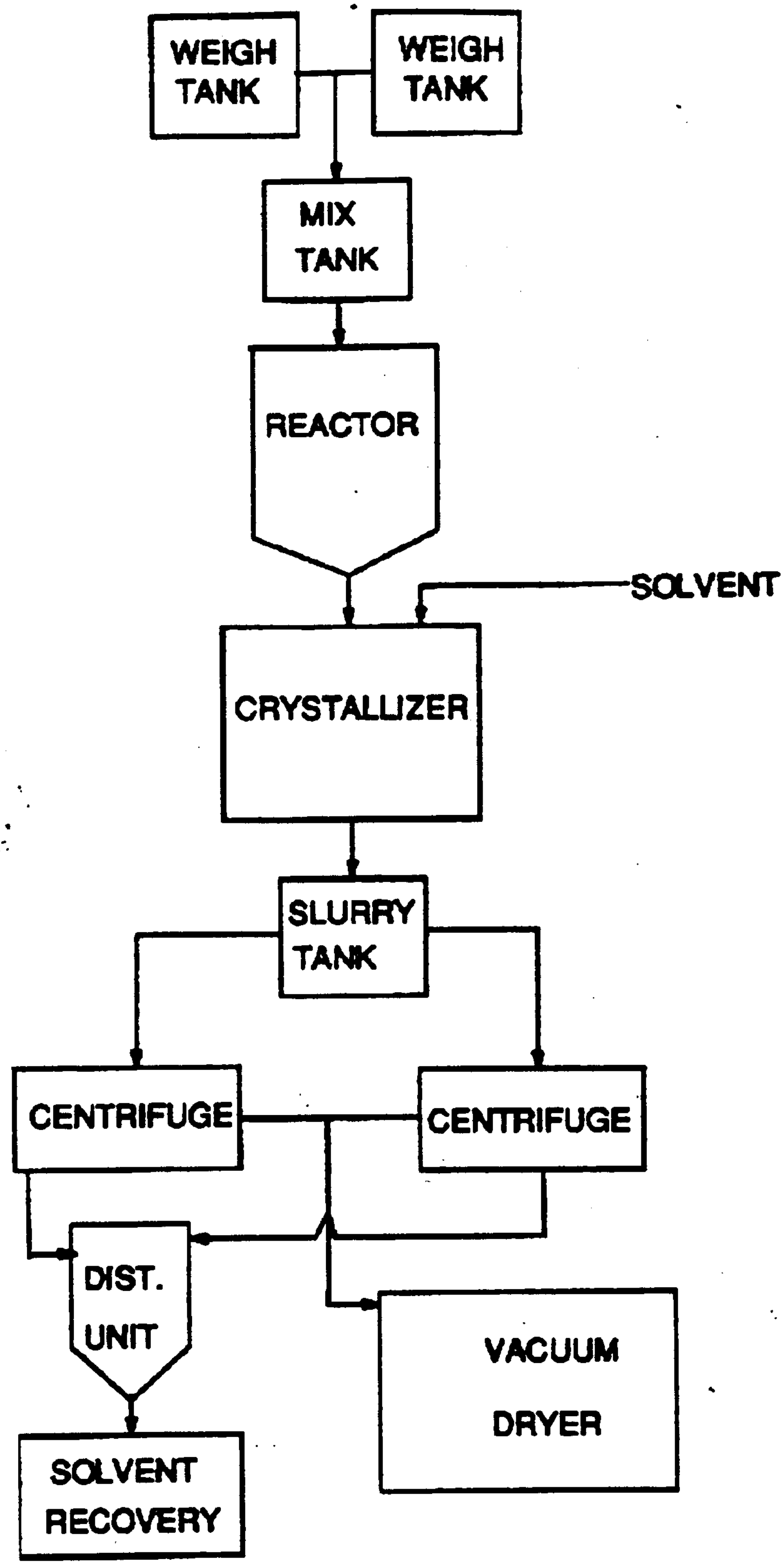

Figure 6-1. Model Batch Process

leaves the charge tank. As the material moves from the weigh tanks to the reactor, another displacement occurs that contributes to emissions of VOC's. This emission event is very similar to the event created by filling the weigh tank. Similarly, as the material flows through the process, each piece of equipment becomes a contributor to VOC emissions through a distinct series of finite emission events. In some equipment, such as the reactor, more than one type of emission event occurs; for example, an event results from charging, heatup, and kettle purging from this piece of equipment.

In the example process shown in Figure 6-1, consider the movement of a highly volatile solvent such as diethyl ether through the process; the emission events that occur as a result of air displacement have concentrations of VOC's in excess of 50 percent by volume. For the reactor purging event, however, the concentration of VOC drops as the emission stream is diluted by high flows of inert gas into and out of the kettle. The largest source of uncontrolled emissions in this process is the vacuum dryer, whose emission stream is characterized by an decrease in VOC concentration and a somewhat steady flow rate over the course of its drying cycle.

Figures 6-2 and 6-3 present the fluctuations in flow rate and concentration, respectively, that will occur during the batch cycle. The result of combining the flow rate and concentration profiles is presented in Figure 6-4, the emissions profile. In order to give a more vivid illustration of how flow rate, concentration, and emissions vary in such a batch process, Figures 6-2, 6-3, and 6-4 have all been placed on the same page, resulting in Figure 6-5. Note that the time scale for all these figures is the same. Close inspection of Figure 6-5 reveals that the concentration and flow rate characteristic of the process vents vary independently from each other; although there appears to be a slight trend for the concentration to change inversely with flow rate.

The reason for presenting these profiles is to introduce the idea that the variable emission stream characteristics of batch

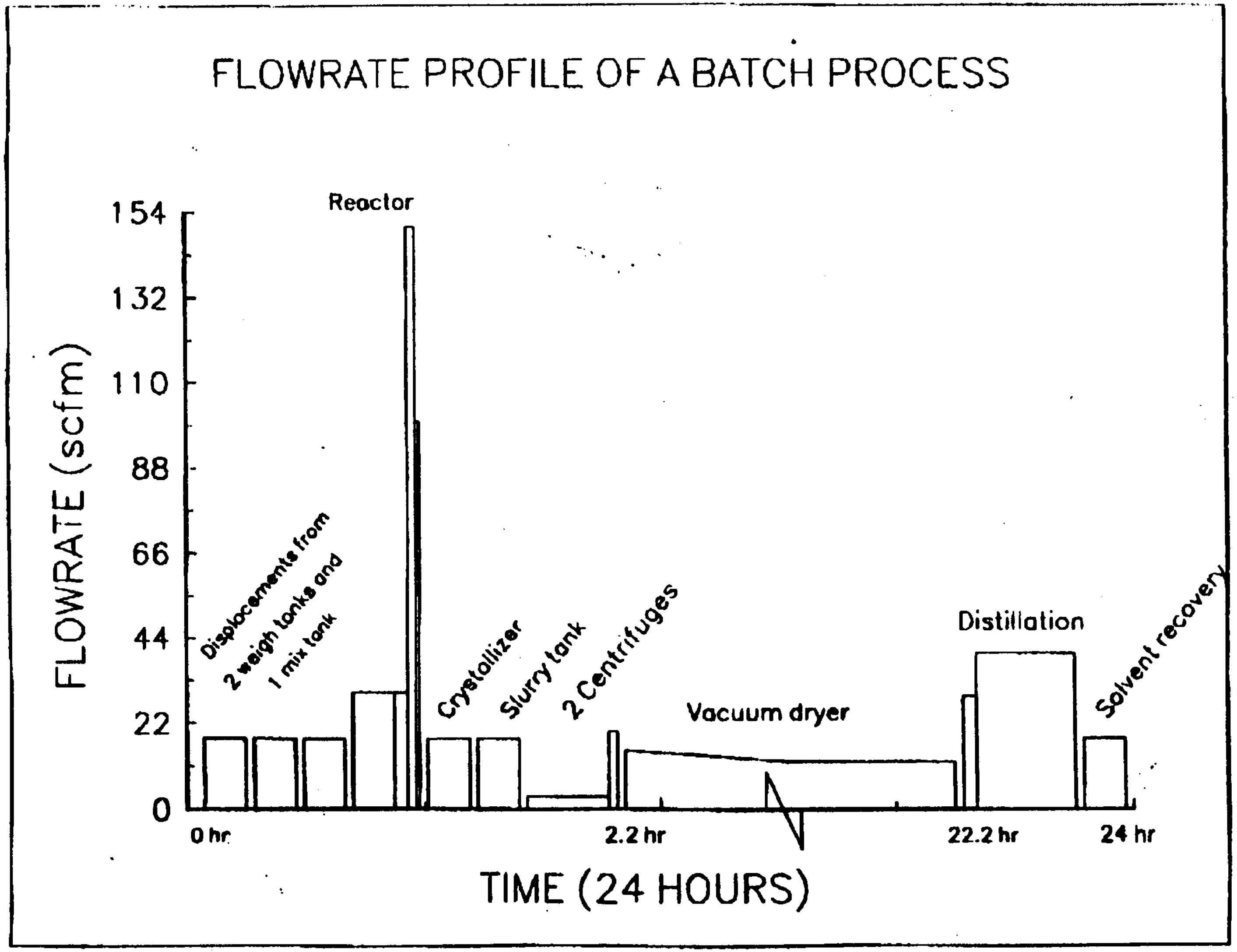

Figure 6-2. Flowrate profile

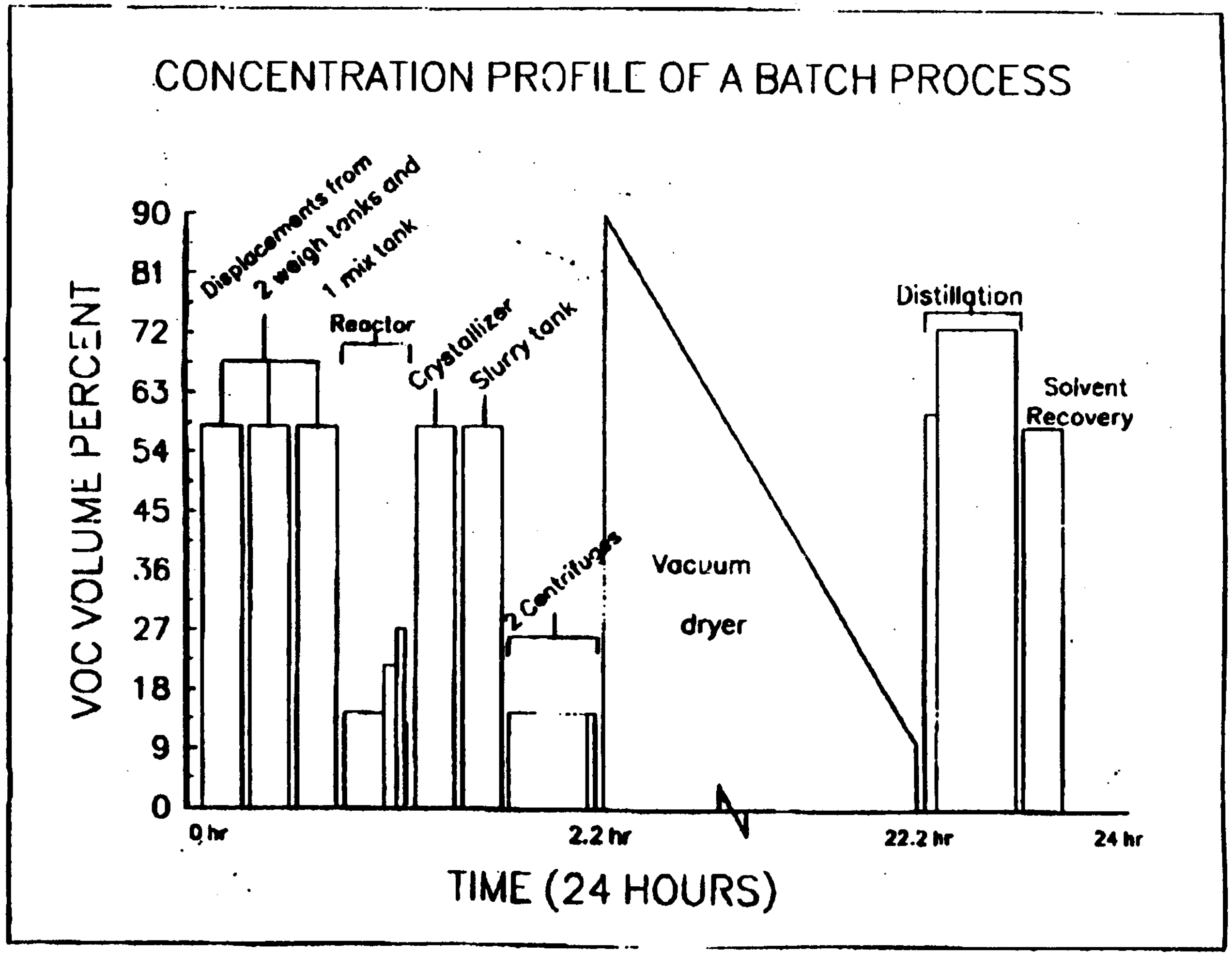

Figure 6-3. Concentration profile

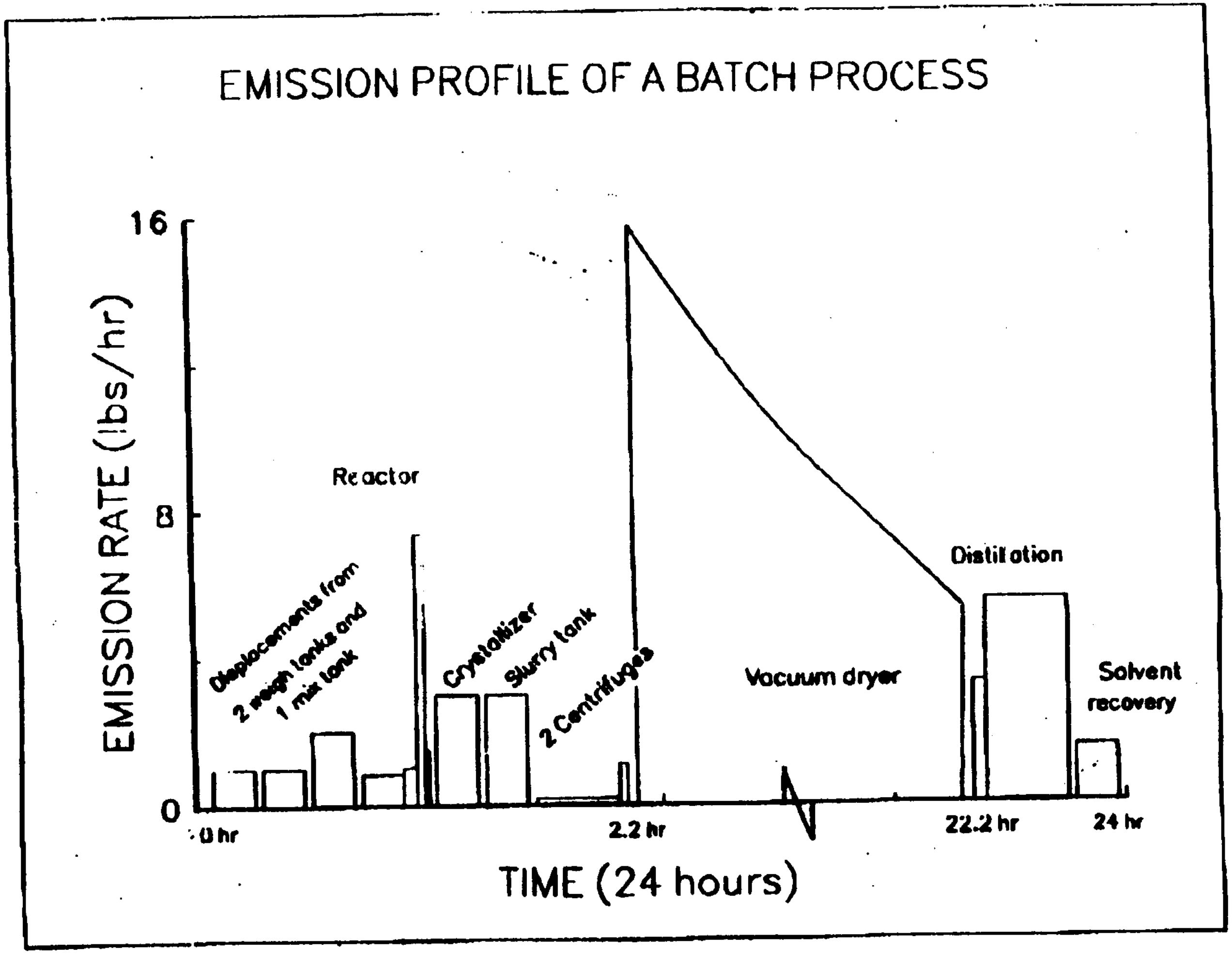

Figure 6-4. Emissions profile

process vents affect the feasibility of using control devices currently available in industry. These attributes also potentially create confusion on the part of plant operators and regulators concerning how to describe the emission characteristics (e.g., instantaneous maximums, 8-hr averages, 24-hr averages, or batch cycle averages). In light of these considerations, it follows that the methodology for development of options would address questions of control device applicability, as well as provide meaningful criteria for determining which streams should be recommended for control. The methodology development is described below.

6.1.1.2 Control Devices Examined. The cost and feasibility of controlling typical batch emission streams was examined by applying typical add-on control devices that are found in industry. All currently available types of control devices were examined, including thermal destruction (thermal, catalytic oxidizers and flares), refrigeration (condensers), gas absorption (water scrubbers), and carbon adsorption systems. The final cost analysis, however, was done based on thermal incineration and condenser systems. These devices were used exclusively in examining cost because, among other factors, they can be applied to a universe of compounds. In many cases, other control devices might prove to be more cost effective, but generally, they can not be used universally and therefore the cost impacts of the option would not be supported for streams containing wide ranges of compounds. A case in point is the use of a water scrubber to control steams containing water-soluble VOC's. The cost and cost effectiveness of this device may be considerably better than that of an incinerator or refrigeration system affording the same level of control, but the costs of the option could not be based on this device because it would only be available for a segment of potential emission streams. Likewise, carbon adsorption, which is less costly than thermal incineration and condensation in many cases, will not control some types of VOC's and therefore it was also ruled out as a test case for the feasibility analysis.

Although thermal incineration and condensation systems are limited in the types of streams that each can feasibly control, these limitations are based more on concentration and less in terms of compound specificity. Additionally, the two devices complement each other in being able to handle ranges of emission stream parameters. For example, the condenser option ideally would be used to control richer streams (>10,000 ppm) while the thermal incinerator could handle streams that were more dilute (<10,000 ppm) and largely infeasible to consider for control with a condenser system. Minor limitations to compound specificity associated with burning halogenated compounds were considered by adding the cost of caustic scrubbing and lowering waste gas heat contents (it was later concluded that this incremental cost was within the margin of error of the study estimate), while compound specificity did not appear to be a problem with refrigeration systems.

Note that although the thermal incinerator and condenser were used to establish control cost effectiveness curves, the options are not equipment-based, only performance-based. Therefore, an emission limit would specify a control level (e.g., 98 percent, 95 percent, 90 percent) and not a particular control device. Therefore, an operator could elect to use a water scrubber to meet control requirements in cases where a water scrubber would achieve the required level of control.

6.1.1.3 Considerations. The first issue considered in developing options was the sensitivity of the costs of each control device to the intermittency of emission events. The primary indicator of cost is cost effectiveness in units of dollars per megagram VOC controlled ($/Mg). This cost effectiveness value is obtained by dividing the annualized cost of the control device ($/yr) by the annual emissions reduction (Mg/yr). The cost effectiveness decreases (values become higher) as the amount of time that the emission stream is released to the atmosphere (on-stream duration) is reduced. This trend is readily obvious from Figure 6-6, which is a graphical presentation of cost effectiveness versus vent stream flow rate

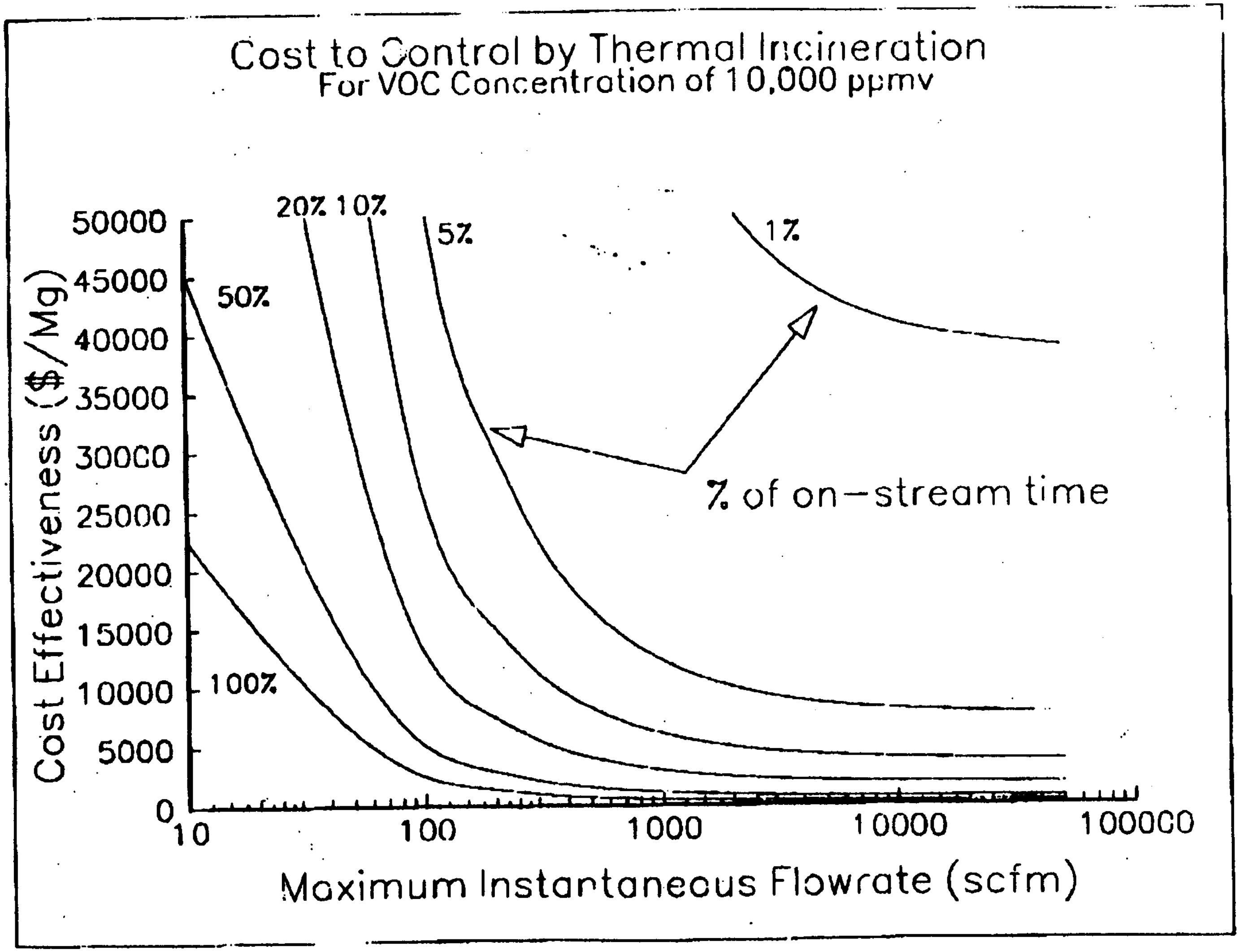

Figure 6-6. Dependence of control device cost on emission intermittency

at a set annual emission rate and set VOC concentration for different on-stream durations. Notice that the on-stream duration is directly related to flow rate when the annual emission rate is constant. Figure 6-6 is based upon a thermal oxidizer with an assumed control efficiency of 98 percent. The use of a thermal oxidizer for the analysis presented in Figure 6-6 is meant only to illustrate the sensitivity of cost effectiveness with on-stream duration (intermittency). Other devices, such as condensers and carbon absorbers, also exhibit similar sensitivity with varying on-stream durations.

Because each control device is often sized according to the maximum possible flow rate and VOC concentration, devices used in batch process emission control are usually oversized for the majority of the time that they are in service. Also, for devices such as incinerators and condensers, the annualized cost of maintaining proper operating conditions (e.g., maintaining incineration and condenser temperatures) when there is no material being vented to the devices drives up the cost of control. Consequently, the cost effectiveness of controlling batch emissions is generally lower (values are higher) than the cost of controlling continuous emissions for similar stream characteristics.

The second consideration that was made in developing the options was to limit the number of parameters necessary to determine which streams should be required to be controlled. Because there is inherent variation in the characteristics of flow rate and VOC concentration during batch emission events, eliminating as many parameters as possible (especially those that vary) will minimize confusion in compliance determinations. For example, an owner or operator could choose to report an average concentration of a VOC emission stream, rather than a 'peak' concentration in order to fall below a concentration cutoff. By eliminating concentration as a parameter used to determine applicability, this problem would be circumvented.

6.1.1.4 Approach. The approach chosen uses uncontrolled annual VOC emissions (expressed as lb/yr) and average flow rate (scfm) to define which streams should be controlled and the level of control required. This approach considers the impact of varying VOC concentrations and frequency of emission events, but does not require their use as parameters to determine applicability. Generally, the uncontrolled annual emission total of VOC's from a particular source is more readily available from material balance and other calculational approaches than is a detailed minute-by-minute concentration and flow profile, as is an average flow rate.

6.1.2 Control Options Methodology

6.1.2.1 Cost-Effectiveness Curves. The methodology that was used to develop the options utilizes the parameters of annual emissions and average flow rate to identify which streams are reasonable to control from a cost and technical feasibility standpoint. Note that the volatility of components of concern is a sensitivity which requires consideration for design and cost of the condenser systems. Hence, three regions of volatilities were considered in the analysis. Low volatility materials are defined for this analysis as those which have a vapor pressure less than or equal to 75 mm Hg at 20°C; moderate volatility materials have a vapor pressure greater than 75 and less than or equal to 150 mm Hg at 20°C and high volatility materials have a vapor pressure greater than 150 mm Hg at 20°C. In determining applicability of the requirements to multicomponent VOC streams, a weighted average of the VOC volatilities should be used to determine the appropriate volatility range. This weighted average volatility is defined in Chapter 7 under 'Definitions', and is ultimately used to determine which equation to use.

Figures F-1 through F-54 of Appendix F show cost effectiveness versus flow rate for annual emissions of 30,000, 50,000, 75,000, 100,000, 125,000, and 150,000 lb/yr for various control levels (i.e., 90, 95, or 98 percent) and volatilities. Each graph represents the full range of concentrations of VOC's that might be expected in any given emission stream (from 100 ppm to 100,000 ppm [the upper concentration examined for toluene, a low volatility material, is 37,000 ppm]); for simplicity, we can call this the "envelope." Note that the 100 ppm line is not graphed in the curves presented in Appendix F. This line typically falls between the 1,000 and 10,000 ppm curves, but ends as the envelope narrows. The width of each envelope is an indication of how much the cost effectiveness varies with concentration.

Figure 6-7 is an example of the curves contained in Appendix F. The figure shows the cost effectiveness of controlling any stream having a single component or group of components with a total vapor pressure in the moderate volatility range (from 75 to 150 mm Hg at 20°C). There are four curves on the graph: Two of the curves show the cost effectiveness versus flow rate for control by thermal incineration (abbreviated as "throx") at concentrations of 1,000 ppmv and 8,750 ppmv. The other two curves are for condenser control of streams with concentrations of 10,000 ppmv and 100,000 ppmv. Points along the curves were established by inputting a constant mass emission total and a constant concentration into the condenser and thermal incinerator spreadsheets and plotting the resulting flow rate and cost effectiveness values corresponding to various durations.

Since the annual emissions are constant at 50,000 lb/yr, the flow rate (x-axis) values at any point along the curves are an indicator of the duration of the emission events. For example, the left-hand endpoints of the curves represent streams that are continuous (i.e. in order to emit 50,000 lb/yr from an emission point at a concentration of 100,000 ppmv, the minimum flow rate for the stream, if it is venting continuously, is around 5 scfm). As the curves move from left to right (increasing flow rates), the duration of the emission events decrease, so that points along the right hand edges of the curves represent short duration events in which large amounts of VOC's are released at high flow rates. These "bursts" of emissions are not surprisingly more expensive to control because they must be sized for large flows, yet they will only control emissions for short durations. For some concentrations, points on the upper-right corner of the

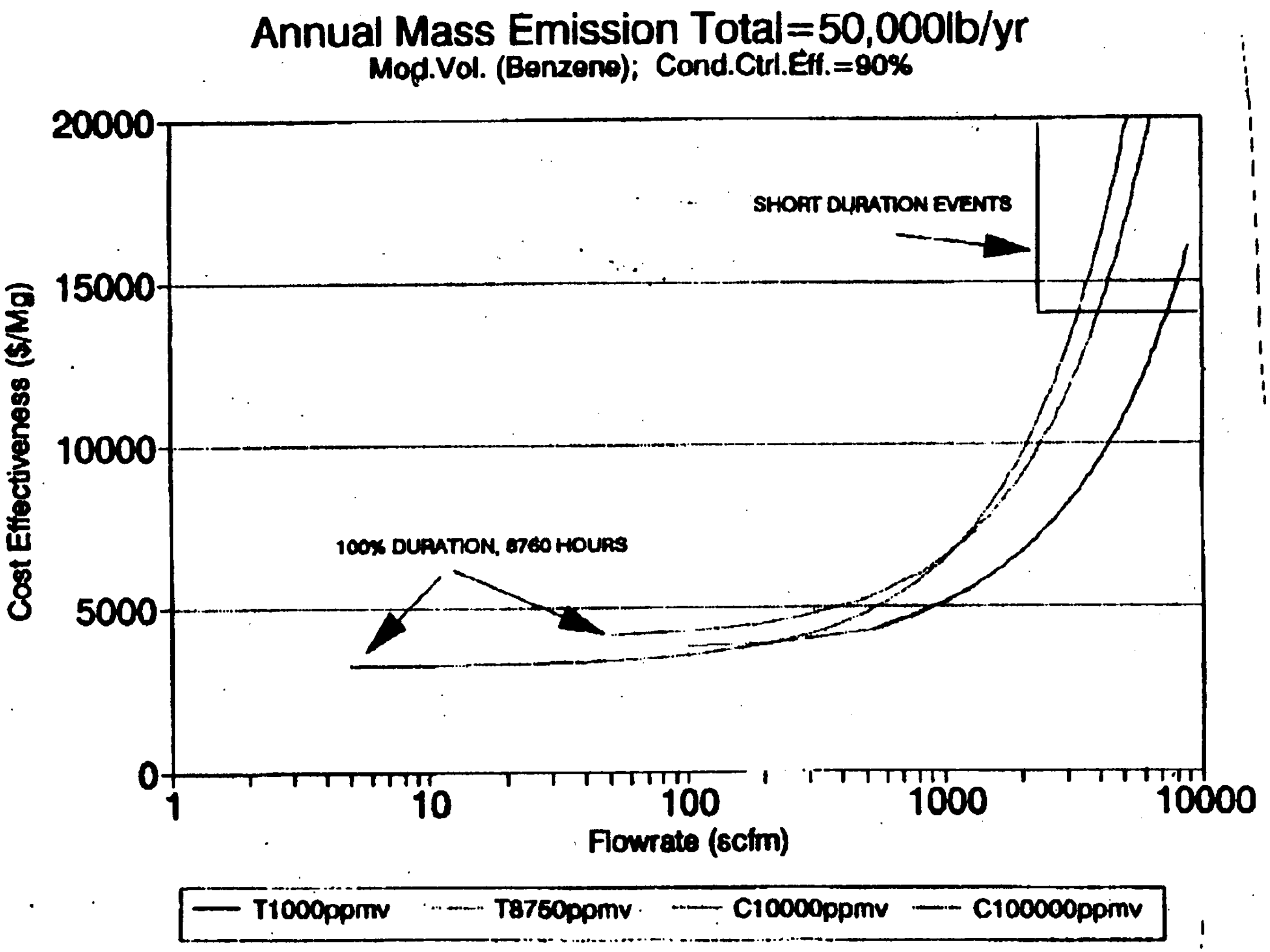

Figure 6-7. Annual mass emission total = 50,000 lb/yr Mod. Vol. (Benzene); Cond. Crtl. Eff. = 90 percent.

graph may occur less than 10 hours per year; these streams resemble emergency releases.

Based on the above discussion, it can be seen from Figure 6-7 that for a process vent emitting 50,000 lb/yr of VOC, the cost effectiveness of control is a maximum of $5,000/Mg for a maximum flow rate of about 400 scfm or less, regardless of concentration, regardless of duration. At higher flow rates, the curves begin to rise sharply and the cost effectiveness values become higher (indicating that they are less feasible to control from a cost standpoint).

This discussion, then, forms the basis for setting up option requirements based on annual emissions and flow rate. By establishing a number of curves for different annual emission totals (i.e., 30,000, 50,000, 75,000, 100,000, 125,000 and 150,000 lb/yr), values of flow rate were obtained for an optimum cost effectiveness range, considering impacts. These annual emissions, and corresponding flow rates were used as data points (x was annual emissions and y was flow) for simple regression analysis to define the line that will represent optional cutoffs for applicability that could be included in standards.

Note also that the subheading for Figure 6-7 states that condenser control efficiency is 90 percent. Since both the thermal incinerator and the condenser cost algorithms were used to construct each graph contained in Appendix F, there were varying levels of control efficiency that could be achieved by the condenser; the thermal incinerator was assumed to be effective to 98 percent all the time. Therefore, for curves containing condenser control efficiencies less than 98 percent (i.e. 90, 95 percent), the overall control level is limited by the condenser efficiency.

6.2 PRESENTATION OF FLOW RATE REQUIREMENTS

Table 6-1 presents the regression line and data points obtained from Appendix F graphs for various control levels. Note that the graphs presented in Appendix F resemble the graph shown in Figure 6-7. However, the labor and maintenance costs for graphs shown in Appendix F are for 1 shift per day only, as

TABLE 6-1. SUMMARY OF CONTROL OPTION REGRESSION LINE DATA

Volatility	Control level %	Flow rate data points (scfm) for annual mass emissions, lb/yr[a]						No.	Regression line	No. flow value lb/yr[b]
		30,000	50,000	75,000	100,000	125,000	150,000			
Low	98	757	1,787	3,076	4,363	5,652	6,939	1	FR = (0.052)AE-789	15,173
	95	866	2,452	4,043	5,600	7,158	8,717	2	FR = (0.065)AE-895	13,769
	90	449	1,634	3,324	5,113	6,954	8,826	3	FR = (0.07)AE-1,821	26,014
Moderate	98	251	612	1,063	1,514	1,965	2,416	4	FR = (0.018)AE-290	16,111
	95	515	1,034	1,682	2,330	2,978	3,627	5	FR = (0.026)AE-263	10,115
	90	334	1,082	1,833	2,776	3,319	4,062	6	FR = (0.031)AE-494	15,935
High	98	208	517	904	1,290	1,677	2,063	7	FR = (0.015)AE-256	17,067
	95	215	544	955	1,366	1,777	2,188	8	FR = (0.016)AE-278	17,375
	90	-	369	704	1,039	1,374	1,709	9	FR = (0.013)AE-301	23,153

[a] This field lists y-coordinates for the corresponding x-coordinates of 75,000, 100,000, 125,000, and 150,000 lb/yr.

[b] Annual mass emissions below this value no control required, regardless of flow rate.

[c] The regression line equations presented here can be incorporatedinto regulations as "cut-offs." As cutoffs, they would be used to determine what streams should be contolled, given an annual mass emission (AE) total and an average flow rate(FR). If the flow rate calculated by the "cutoff" line equation (when annual mass emission is inputted) is higher than the average flow rate of the stream, then control would be required to the level specified (98,95, or 90 percent).

opposed to 3 shifts per day labor and maintenance costs assumed in the construction of Figure 6-7. By using the line equations presented in Table 6-1, average flow rates can be established using the annual emission total. Comparison of this "cutoff" with the actual flow rate of the emission source would determine whether control is required.

The options that were further evaluated for nationwide impacts based on the curves in Appendix F are presented in Table 6-1. The regression lines can be used to determine what streams should be controlled, given an annual mass emission total and an average flow rate. If the flow rate calculated by the "cutoff" line equation (when annual mass emission is inputted) is higher than the average flow rate of the stream, then control would be required to the level specified (98, 95, or 90 percent). The assumptions used to arrive at the baseline and uncontrolled emission numbers, and the industries affected as shown in Table 6-2 are discussed in the next section.

6.2.1 Discussion of Additional Issues

6.2.1.1 Single stream versus aggregation. The annual emission total and flow rate cutoffs can be applied either to single streams or to emission streams resulting from aggregated sources. Costs for manifolding sources have been considered in the design and cost calculations. For example, total purchased equipment costs for the condenser systems were multiplied by an additional 25 percent to account for manifolding whereas a 300-foot collection main with 10 takeoffs and an auxiliary collection fan was costed out in the incinerator cost calculations.

An additional analysis was undertaken to identify whether there is a level at which the incremental cost of manifolding individual emission sources is unreasonable compared with the emission reduction achieved. Simply stated, what level of emissions would rule out including a source into an aggregate pool of sources, based on a measure of control achieved over the cost of manifolding the small source to the central process control device. This level is identified as the "deminimis" level for purpose of the applicability analysis. A deriation of this deminimis level is presented in Appendix B.

6.2.1.2 Halogenated Compounds. The cost-effectiveness curves shown in Figures F-1 through F-54 are for thermal incinerators and condensers. The costs are based on using an incinerator operating at 1600°F, with fractional heat recovery, and not equipped with an emission control device. For halogenated compounds, such an incinerator might not achieve a control level of 98 percent, and additionally, acid gas would be emitted from the combustion process. Consequently, the cost analysis was repeated using costs based on an incinerator designed to control halogenated compounds. Such an incinerator would maintain combustion temperatures at 2000°F, have no fractional heat recovery, and would be equipped with a caustic scrubber to control acid gases.

From the curves, the increase in cost effectiveness values associated with using a thermal incinerator equipped to control halogenated compounds appears to be approximately 1 to $5K/Mg more costly than using the nonhalogenated compound incinerator.

6.3 IMPACTS OF APPLYING OPTIONS

A model plant approach was used to examine the impacts of applying the options to industry on a nationwide basis. For the industries assumed to be covered, emissions streams from small, medium, and large model plants were evaluated to determine the level of control required based on the annual emissions and flow rates specified by various control option regression lines. Emission reductions over baseline control were evaluated for each model plant and were extrapolated to a nationwide basis using Census of Manufacturers Industry Profile data. The nationwide impacts development is outlined below.

6.3.1 Industries Covered

While the information contained in this document is generally applicable for batch processes in all or most industries, the impacts presented are only for selected industries. These industries and their corresponding Standard Industrial Classification (SIC) codes are presented in Table 6-2.

TABLE 6-2. PERCENTAGE OF EMISSIONS FROM BATCH PROCESSES

SIC code	SIC description	<7800 (hrs/yr)	>0 (hrs/yr)	% Batch
2821	Plastics materials and resins	14,396	124,547	12%
2834	Pharmaceutical preparations	8,432	15,459	55%
2861	Gum and wood chemicals	2,287	20,415	11%
2865	Cyclic crudes and intermediates	223	8,365	3%
2869	Industrial organic chemicals	17,060	173,167	10%
2879	Agricultural chemicals	92	3,912	2%

NOTE: Emissions data was obtained from AIRS facility subset data base search

Note that facilities that make up the industries listed also potentially use continuous processes; in order to assess what proportion of emissions generated in these industries is from batch processes, the Aerometric Information Retrieval System (AIRS) Facility Subsystem data base was accessed. For each applicable SIC code, emissions from process vents were totaled. Then, a subset of these data, those emissions that were reported to have durations of less than 7,800 hours per year, were totaled and divided by the total vent emissions for those SIC codes. The resulting fraction was taken to be the percentage of total emissions for each SIC code that would result from batch processing. From the table, the percentages of emissions considered "batch" may appear lower than expected; one of the limitations of using the AIRS database is that only sources with greater than 100 tons per year are listed. Because many batch industries are for low-volume chemicals, basing these percentages on AIRS data probably biases the percentages low.

6.3.2 Model Processes

Figures E-1, E-2, E-3, and E-4 of Appendix E present model batch processes that are typically found in batch industries. These model processes were recommended by an industry trade association for use in evaluating impacts.[1] Tables E-1, E-2, E-3, and E-4 of Appendix E are summaries of emission streams characteristics resulting from the unit operations shown in the model batch processes for low, moderate, and high volatility materials. Emission stream characteristics were calculated based on data, where possible, and from the vapor-liquid equilibrium assumptions described Chapter 3. Appendix E also contains all the calculations and assumptions used to develop model emission streams, from which only a few were selected to make up the model batch processes. The emission rates for all unit operations within the model processes were tabulated for each volatility. The small, medium, and large model plants are based on multiples of these model process emission totals. Three model processes were assumed to represent the small plant, 10 model processes were assumed to represent the medium-sized plant, and 30 model processes were assumed to represent the large plant. A list of assumptions made in developing each of the model plants is presented in Tables E-5 through E-8.

6.3.3 Baseline Assumptions/Extrapolations

The baseline used in estimating nationwide impacts for process vents corresponds to the level of control achieved by the Pharmaceutical CTG. Emissions from the number of batch facilities in SIC Code 2834 (Pharmaceutical Preparations) were subject to this control level. The Pharmaceutical CTG contains condenser exit temperature requirements for five classes of volatility, and requires 90 percent control on dryers emitting more than 330 lb/d. The facilities in the remaining five SIC codes, 2821, 2861, 2865, 2869, and 2879, were assumed to be subject to no VOC emission controls for process vents.

Essentially, two extrapolations were done in order to arrive at nationwide impacts. The first was to evaluate the control option impacts from the model batch processes and extrapolate to the small, medium, and large model plants. The second was to extrapolate the impacts from the small, medium, and large model plants to the total number of facilities conducting batch processes nationwide. These extrapolations are discussed in more detail below.

6.3.3.1 Model Plants. As mentioned before, the small model plant was assumed to contain three model batch processes; the medium model plant was assumed to contain 10 model batch processes, and the large model plant was assumed to contain 30 model batch processes. These values fall within ranges recommended by an industry trade association.[3] Tables E-9 through E-12 of Appendix E present model plant emission totals for the small, medium, and large model plants assuming (1) no control at all, and (2) current pharmaceutical control for low, moderate, and high volatility materials.

Because the model processes are grouped into model plants that only contain multiples of single processes, the model plants are not entirely reflective of the batch industries. It is expected, for instance, that actual plants will have combinations of different processes. However, because the estimation of nationwide impacts is based on an evaluation of the flow rate and annual emission total of individual processes exclusively, the groupings are used exclusively to extrapolate nationwide numbers. Therefore, these "unreflective" groupings do not affect the correctness of the impact.

6.3.3.2 Nationwide Facilities. Table 6-3 presents data taken from industry profiles contained in the Census of Manufacturers and from EPA data on county ozone nonattainment status. This information was used to extrapolate the model plant emission totals (under no control, current pharmaceutical control, and for the various options) to a nationwide basis.

Emissions from the batch industries represented by the SIC codes in Table 6-3 were estimated by assuming that model processes 1 through 3 (solvent reaction with atmospheric dryer [model process 1], solvent reaction with vacuum dryer [model process 2], and liquid reaction [model process 3]) were evenly used among the industries covered. The impacts assume that low, moderate, and high volatility materials are evenly distributed among the model processes (i.e., 1/3 of the processes use low volatility materials, 1/3 use moderate volatility materials, and 1/3 use high volatility materials). Nationwide emissions were estimated by multiplying the census size groupings by employee number (i.e., small plant--0 to 19 employees) by model emission totals to estimate small, medium, and large plant emissions. Only the total number of facilities located in nonattainment areas (excluding marginally nonattainment) were considered. The formulator model process (Figure E-8) was not included in the nationwide impacts, but is found in some SOCMI batch operations.

6.4 SUMMARY OF OPTIONS AND IMPACTS

Table 6-4 presents the overall reduction in VOC that can be expected from various options and the national costs associated with applying the options on a nationwide basis. Options are for aggregated sources controlled to 98 percent, 95 percent, and 90 percent overall, respectively.

REFERENCES

1. Letter from Synthetic Organic Chemical Manufacturers Association (SOCMA) to Randy Mcdonald, EPA/ESD/CPB, providing comments and recommendations on the Batch CTG. Dated April 19, 1991.

2. Reference 1.

7.0 FACTORS TO CONSIDER IN IMPLEMENTATION OF A RULE BASED ON THE OPTIONS PRESENTED IN THIS DOCUMENT

This chapter presents information for State and local air quality management agencies to use in developing enforceable regulations to limit emissions of VOC's from batch processing operations. The information presented here assumes that the Agency adopts one of the options presented in Chapter 6. The information is the same regardless of the option selected.

A unique approach has been developed to determine the applicability and optimum level of control required for batch emission sources. Additionally, a model rule with blanks to allow for choices of options, is included in Appendix G. This chapter is divided into the following sections: (1) Definitions and Applicability, (2) Format of the Standards, (3) Testing, (4) Monitoring Requirements, and (5) Reporting/Recordkeeping Requirements.

7.1 DEFINITIONS AND APPLICABILITY

7.1.1 Definitions

The agency responsible for developing a standard must define the terms that appear in the language for the standard. The source category of batch processes, for example, requires a definition of the term "batch" as it is used to describe the mode of operation of equipment and processes. Another term that will likely require defining is "vent". The feasibility analysis that has been described in Chapter 6 applies to any type of gaseous emission stream (continuous or batch) containing VOC's, as long as the flowrate and annual mass emission total requirements are met. Finally, the terms "flowrate" and "annual mass emissions" also should be defined clearly. Provided below is a listing of definitions for terms as they are used in this CTG and which are recommended for State-adopted rules.

Aggregated means the summation of all process vents containing VOC's within a process.

Annual mass emissions total means the sum of all emissions, evaluated before control, from a vent. Annual mass emissions may be calculated from an individual process vent or groups of process vents by using emission estimation equations contained in Chapter 3 of the Batch CTG and then multiplying by the expected duration and frequency of the emission or groups of emissions over the course of a year. For processes that have been permitted, the annual mass emissions total should be based on the permitted levels, whether they correspond to the maximum design production potential or to the actual annual production estimate.

Average flowrate is defined as the flowrate averaged over the amount of time that VOC's are emitted during an emission event. For the evaluation of average flowrate from an aggregate of sources, the average flowrate is the weighted average of the average flowrates of the emission events and their annual venting time, or:

$$\text{Average Flowrate} = \frac{\sum \text{(Average Flowrate per emission event)(annual duration of emission event)}}{\sum \text{(annual duration of emission events)}}$$

Batch refers to a discontinuous process involving the bulk movement of material through sequential manufacturing steps. Mass, temperature, concentration, and other properties of a system vary with time. Batch processes are typically characterized as "non-steady-state."

Batch cycle refers to a manufacturing event of an intermediate or product from start to finish in a batch process.

Batch process train means an equipment train that is used to produce a product or intermediate. A typical equipment train consists of equipment used for the synthesis, mixing, and purification of a material.

Control devices are air pollution abatement devices, not devices such as condensers operating under reflux conditions, which are required for processing.

Emissions before control means the emissions total prior to the application of a control device, or if no control device is used, the emission total. No credit for discharge of VOC's into wastewater should be considered when the wastewater is further handled or processed with the potential for VOC's to be emitted to the atmosphere.

Emission events can be defined as discrete venting episodes that may be associated with a single unit of operation. For example, a displacement of vapor resulting from the charging of a vessel with VOC will result in a discrete emission event that will last through the duration of the charge and will have an average flowrate equal to the rate of the charge. If the vessel is then heated, there will also be another discrete emission event resulting from the expulsion of expanded vessel vapor space. Both emission events may occur in the same vessel or unit operation.

Processes, for the purpose of determining control applicability, are defined as any equipment within a contiguous area that are connected together during the course of a year where connected is defined as a link between equipment, whether it is physical, such as a pipe, or whether it is next in a series of steps from which material is transferred from one unit operation to another.

Semi-continuous operations are conducted on a steady- state mode but only for finite durations during the course of a year. For example, a steady-state distillation operation that functions for 1 month would be considered semi-continuous.

Unit operations are defined as those discrete processing steps that occur within distinct equipment that are used to prepare reactants, facilitate reactions, separate and purify products, and recycle materials.

Vent means a point of emission from a unit operation. Typical process vents from batch processes include condenser vents, vacuum pumps, steam ejectors, and atmospheric vents from reactors and other process vessels. Vents also include relief valve discharges. Equipment exhaust systems that discharge from unit operations also would be considered process vents.

Volatility is defined by the following: low volatility materials are defined for this analysis as those which have a vapor pressure less than or equal to 75 mmHg at 20°C, moderate volatility materials have a vapor pressure greater than 75 and less than or equal to 150 mmHg at 20°C; and high volatility materials have a vapor pressure greater than 150 mmHg at 20°C. To evaluate VOC volatility for single unit operations that service numerous VOCs or for processes handling multiple VOCs, the weighted average volatility can be calculated simply from knowing the total amount of each VOC used in a year, and the individual component vapor pressure, as shown in the following equation:

$$\text{Weighted Average Volatility} = \frac{\sum_{i=1}^{n}\left[(\textit{Vapor pressure of VOC component } i)\,\frac{(\textit{mass of VOC component } i)}{(\textit{molecular weight of VOC component } i)}\right]}{\sum_{i=1}^{n}\left[\frac{(\textit{mass of VOC component } i)}{(\textit{molecular weight of VOC component } i)}\right]}$$

7.1.2 Applicability

The analysis on which options are based was performed over a number of industries thought to manufacture a significant percentage of total production on a batch basis. These industries, identified by 4-digit SIC codes, are presented in Chapter 6. They are: plastic materials and resins (SIC 2821), pharmaceutical preparations (SIC 2834), medical chemicals and botanical products (SIC 2833), gum and wood chemicals (SIC 2861), cyclic cruds and intermediates (SIC 2865), industrial organic chemicals (SIC 2869), and agricultural chemicals (SIC 2879). Although the impacts in this document were evaluated based on a scope limited to these industries, any batch emission point of VOC's from presumably any industry could be subjected to these requirements. Note that there are two CTG's, the Air Oxidation CTG and the Reactor Processes and Distillation Operations CTG, that cover synthetic organic chemical emissions from continuous processes. The CTG's also exempt batch or semi continuous processes. The information in this document applies to the processes that are exempted because they are not continuous. This includes semi continuous processes.

The control option requirements presented in Chapter 6 apply to (1) individual batch VOC process vents to which the annual mass emissions and average flowrate cutoffs are applied directly, and (2) aggregated VOC process vents for which a singular annual mass emission total and average flowrate cutoff value is calculated and for which the option is applied across the aggregate of sources. The applicability is discussed in more detail below.

Sources that will be required to be controlled by a control device will have an average flowrate that is below the flowrate specified by the cutoff equation (when the source's annual emission total is input). The applicability criteria is implemented on a two-tier basis. First, single pieces of batch equipment corresponding to distinct unit operations shall be evaluated over the course of an entire year, regardless of what materials are handled or what products are manufactured in them, and second, equipment shall be evaluated as an aggregate if it can be linked together based on the definition of a process.

To determine applicability of a cutoff option in the aggregation scenario, all the VOC emissions from a single process would be summed to obtain the yearly emission total, and the weighted average flow rates from each process vent in the aggregation would be used as the average flow rate.

All unit operations in the process, as defined for the purpose of determining cutoff applicability would be ranked, in ascending order, according to their ratio of annual emission divided by average flow rate. Sources with the smallest ratio would be listed first. This list of sources constitutes the "pool" of sources within a process. The annual emission total and average flowrate of the pool of sources would then be compared against the cutoff equations to determine whether control of the pool is required. If control were not required after the initial ranking, unit operations having the lowest annual emissions/average flowrate would then be eliminated one by one, and the characteristics of annual emissions and average flowrate for the pool of equipment would have to be evaluated with each successive elimination of a source from the pool. Control of the unit operations remaining in the pool to the specified level would be required once the aggregated characteristics of annual emissions and average flowrates met the specified cutoffs.

By aggregating unit operations, the annual emission totals are more easily achieved at better cost effectiveness values. However, a unit operation may have a high emissions to flowrate ratio, albeit low actual emissions and the cost effectiveness of controlling such a unit operation may not be reasonable. Such cases have been evaluated using the cost analysis of ductwork. Essentially, the costs of ducting can be shown to be dependent on flowrate of the emission stream and required length of ducting. The incremental cost analysis for manifolding single unit operations to a control device are contained in Appendix B.

7.2 FORMAT OF THE STANDARDS

The control options are performance-based standards in the format of a percent reduction. The cutoff is applied using the annual mass emission total and an average vent stream flowrate (in scfm). These parameters were chosen to determine the applicability of the cutoff because they were considerably easier to deal with than concentration or duration of emission events. Concentration and duration are extremely dynamic variables in typical batch processing emissions, and, while flowrate and yearly vent emissions also are dynamic, these parameters are usually more available. The flowrate from a vent is sometimes known because the gas-moving equipment (i.e., compressors, vacuum pumps) that is used to create the venting must be sized. Flowrates from other batch emission events, such as displacements and material heating, may be estimated using the Ideal Gas Law. Specific situations and equations are presented in Chapter 3.

The annual mass emission total also is required for application of the cutoff to vents. Annual uncontrolled emissions are frequently reported to State agencies for the purposes of permit review, State emission inventories, or Federal programs, such as the Superfund Amendments and Reauthorization Act (SARA) 313 reporting requirements. For batch process vents, however, the task of estimating annual emissions may be complicated by several factors; among them are venting configurations from multipurpose equipment and variations in flow, concentrations, and emission stream duration. In such situations, owners or operators may elect to use material balances in conjunction with control device efficiencies to determine potential VOC emissions.

7.3 TESTING

Source testing to measure annual mass emissions and maximum flowrate for the purpose of determining applicability of a cutoff is much more complex for batch processes (which have noncontinuous and, often, multicomponent vent streams) than it is for continuous processes. The intermittent vent streams also present serious problems for testing the performance of the control devices. Each step in a batch process, such as charging the reactor or operating the dryer, generates gaseous streams with independently defined characteristics. This is illustrated in Chapter 6, where the emission stream characteristics of flowrate, temperature, duration, and VOC concentration are given for a model batch process. The gaseous streams from each step may be vented separately, some or all streams may be combined before venting to the atmosphere, and some operators may have the flexibility of using different vents for the same equipment.

In addition to the inherent problems of stack testing at batch processing facilities, these industries tend to be reactive to market demands and change product lines much more often than continuous processing plants. Vent stream characteristics change with the production of new products. This not only affects the emission inventory for the plant; it can also affect the performance of the control device.

Testing may be more realistic for facilities that have all vents from a single product processing area manifolded together, and the common vent has a continuous, positive flow. If measurement of more typical batch process vents (in which flow and concentration vary independently with time) is required, several considerations related to measurement techniques must be made.

In the presence of unsteady or transient gas flows typical of those found in batch gas streams, gas mass flow measurement uncertainty can be decreased by utilizing measurement approaches that separate density effects from velocity effects. In addition, electronic flow measurement (EFM) must be utilized to allow mass flow averaging over the event time. Typical inexpensive gas flow measurement techniques (orifice meters and pitot-type probes) are velocity head devices. They measure differential pressure as a function of both the gas density and the stream velocity. In transient batch-type situations where density may be changing independent of velocity, this type of gas flow measurement couples the effects and can potentially introduce larger uncertainties into the velocity measurement. In addition, for velocity head devices, EFM systems must be utilized to eliminate the errors associated with pressure averaging prior to velocity calculations. This error, often referred to as "square root" error, arises from the nonlinear dependence of the measured variable (pressure) on the stream velocity. In all measurement devices where this occurs (orifice meters, pitot tubes, annubars), the time-averaged value of the square root of the pressure signal does not equal the square root of the time averaged value of the pressure signal. This inequality introduces positive bias errors into the flow measurement and can be eliminated by the use of EFM.

Probes that are most suited for transient batch flow systems are probably insertion turbine meters and ultrasonic probes. Both of these probes can have turn-down ratios (ratio of maximum to minimum measurable flow velocity) of 10-15 to 1 and are true velocity measurement devices. Both of these probes can be hot-tapped into existing gas streams, and their uncertainty levels are equal to or better than pitot tubes in steady flows. The insertion turbine meter, like all pitot probes, requires a traverse, which limits its application to transient flows.

However, ultrasonic meters, which are used extensively in chemical plants, return an average velocity flow across the gas stream. For this reason, ultrasonic probes can track shorter transients with less uncertainty because of the elimination of the need for a traverse at each sample interval.

Simultaneous concentration measurements may be made using EPA Method 25A, a semicontinuous Method 18 (at close intervals), or perhaps by using Fourier Transform Infrared (FTIR) technology (for which no EPA method currently exists), an emerging technology that has experimentally been demonstrated to measure multicomponent volatile compounds from a noninvasive standpoint.

The use of EFM's to combine the flow and concentration measurements and obtain instantaneous mass emissions, as well as batch mass emissions (integrated over the batch cycle time) appears to be indispensable for accurate emission measurements of batch emission streams. However, this testing is more sophisticated and presumably more expensive than emissions measurement for continuous, steady-state emission streams.

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The use of EFM's to combine the flow and concentration measurements and obtain instantaneous mass emissions, as well as batch mass emissions (integrated over the batch cycle time) appears to be indispensable for accurate emission measurements of batch emission streams. However, this testing is more sophisticated and presumably more expensive than emissions measurement for continuous, steady-state emission streams.

Another alternative is to measure emissions from a single step in the process to confirm emission estimates based on equations in Chapter 3. This method also can be costly if testing is required for the entire duration of the step, from startup to completion. Sampling periodically throughout the step may be sufficient to characterize emissions and confirm emission estimates in some situations.

saturation). Note that under these conditions, the unit also will perform at maximum efficiency because the emission stream is completely saturated. In some cases, the varying incoming emission stream characteristics make it impossible to meet an instantaneous control efficiency value, but overall control efficiency value can be met by controlling the richer peak load (at higher efficiencies) and by not controlling the emission streams when the VOC concentration begins to taper off. If vent stream characteristics or worst-case conditions are known, the condensation unit can be designed to meet a standard, and a performance test may not be necessary. Monitoring can be relatively simple. Temperature monitors can be mounted at the coolant inlet to the vapor condenser or the gas outlet, and temperature can be recorded on a strip chart. Flowmeters can also be incorporated.

Carbon adsorbers are another vapor recovery device that can be used to meet rule requirements, and if vent stream characteristics or worst-case conditions are known, a performance test may not be necessary. Again, a monitoring device should be used to indicate and record the VOC mass emissions in the exhaust gases from the carbon adsorber. Of particular concern when using carbon adsorption systems to control batch emission streams is the desorption of VOC compounds from the carbon bed to the gas exhaust when the VOC concentration in the entering gas stream decreases as it might during a batch emission event. The adsorber may handle the peak VOC emissions only to desorb them out during non-peak events, thereby producing an outlet stream that is more uniform in concentration. Thus, there may be no net control from the device.

7.5 REPORTING/RECORDKEEPING REQUIREMENTS

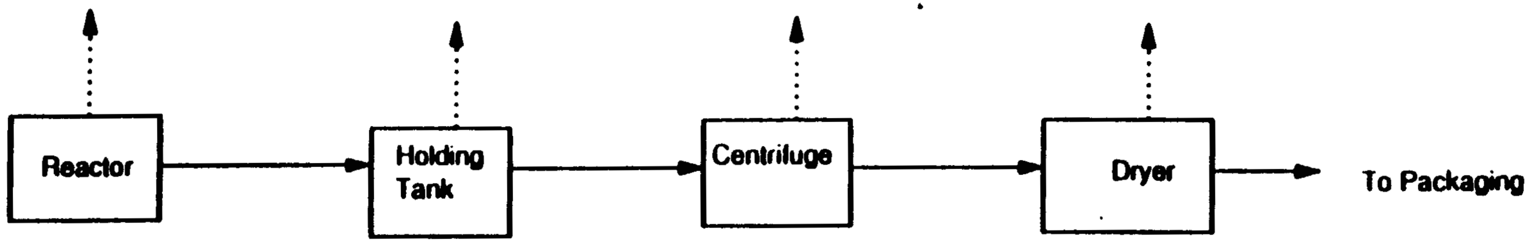
Records should be kept that record the characteristics of each process vent or group of process vents subject to a rule that indicate average flowrate and annual mass emission total. Note that the annual mass emission total combines the mass emission potential for each emission event with the number of potential emission events in a year. If there is no permitted value, owners and operators must keep records of the number of emission events that will occur in a year in order to obtain an accurate mass emission total.

Each facility required to control process vents should keep a copy of the operating plan for each control device in use. The operating plan should identify the control method and parameters to be monitored to ensure that the control device is operated in conformance with its design. Each facility should keep a record of the measured values of the parameters monitored. Any exceedances of the design parameters should be recorded along with any corrective actions. The air pollution control agency should decide which of the recorded data should be reported and what the reporting frequency should be.

7.6 EXAMPLE APPLICATION

Figure 7-1 presents an example analysis. Individual unit operations, as well as the aggregate process are evaluated using the regression equations to determine whether control at an example level (90 percent) is required. The results indicate that the dryer requires control of 90 percent, as does the overall process. The uncontrolled annual mass emissions from the dryer are 36,000 lb/yr. At this level, emission sources with flowrates less than 167 scfm (regardless of volatility) would be required to be controlled to 90 percent. Similarly, the uncontrolled emissions from the aggregated process are 47,700 lb/yr. Processes with an average flowrate of 319 scfm or lower would require control at 90 percent, again regardless of volatility. In this situation, operators might choose to control the dryer emissions to a level in excess of 90 percent in order to meet the overall process control requirement.

Figure 7-1. Example Analysis



Individual

Unit Operation	Average Flowrate	hrs/batch	Lbs VOC/batch	lbs/yr (@300 days/yr)	FR
React	20 scfm	3	6	1800	-
Holding Tank	10 scfm	.25	4	1200	-
Centrifuge	30 scfm	.5	29	8700	-
Dryer	30 scfm	6	120	36000	1002 (low vol) 622 (mod vol) 167 (hi vol)
			159 lbs/batch		

Aggregated

@ 1 batch/day, 300 days/yr, 47,700 lbs/yr

$$\text{Average Flowrate} = \frac{((20)(3)(300)+(10)(.25)(300)+(30)(.5)(300)+(30)(6)(300))}{((3)(300)+(.25)(300)+(.5)(300)+(6)(300))}$$

$$= 26 \text{ scfm}$$

90 % control:

		@47700 lbs/yr FR
FR = .07(lbs/yr) - 1821	low vol	1518
FR = .031(lbs/yr)-494	mod vol	985
FR = .013(lbs/yr)-301	hi vol	319

Conclusions: Would require control of dryer at 90% and overall process at 90%

APPENDIX A

PHYSICAL DATA

TABLE A-1. PHYSICAL PROPERTIES OF COMMON AIR SUBSTANCES

Organic liquid	Vapor molecular weight	Liquid density, lb/gal at 60°F	Condensed vapor density, lb/gal at 60°F	True vapor pressure in psia at:						
				40°F	50°F	60°F	70°F	80°F	90°F	100°F
Petroleum liquids[b]										
Gasoline RVP 13	62	5.6	4.9	4.7	5.7	6.9	8.3	9.9	11.7	13.8
Gasoline RVP 10	66	5.6	5.1	3.4	4.2	5.2	6.2	7.4	8.8	10.5
Gasoline RVP 7	68	5.6	5.2	2.3	2.9	3.5	4.3	5.2	6.2	7.4
Crude oil RVP 5	50	7.1	4.5	1.8	2.3	2.8	3.4	4.0	4.8	5.7
Jet Naphtha (JP-4)	80	6.4	5.4	0.8	1.0	1.3	1.6	1.9	2.4	2.7
Jet kerosene	130	7.0	6.1	0.0041	0.0060	0.0085	0.011	0.015	0.021	0.029
Distillate fuel No. 2	130	7.1	6.1	0.0031	0.0045	0.0074	0.0090	0.012	0.016	0.022
Residual oil No. 6	190	7.9	6.4	0.00002	0.00003	0.00004	0.00006	0.00009	0.00013	0.00019
Volatile organic liquids										
Acetone	58.1	6.6	6.6	1.7	2.2	2.9	3.7	4.7	5.9	7.3
Acetonitrile	41.1	6.6	6.6	0.6	0.8	1.1	1.4	1.9	2.5	3.1
Acrylonitrile	53.1	6.8	6.8	0.8	1.0	1.4	1.8	2.4	3.1	4.0
Allyl alcohol	58.1	7.1	7.1	0.1	0.2	0.3	0.4	0.5	0.7	1.0
Allyl chloride	76.5	7.9	7.9	3.0	3.8	4.8	6.0	7.4	9.1	11.0
Ammonium hydroxide 28.8 percent solution	35.1	7.5	7.5	5.1	6.6	8.5	10.8	13.5	16.8	20.7
Benzene	78.1	7.4	7.4	0.6	0.9	1.2	1.5	2.0	2.6	3.3
n-Butyl chloride	92.6	7.4	7.4	0.7	1.0	1.3	1.7	2.2	2.7	3.5
Carbon disulfide	76.1	10.6	10.6	3.0	3.9	4.8	6.0	7.4	9.2	11.2
Carbon tetrachloride	153.8	13.4	13.4	0.8	1.1	1.4	1.8	2.3	3.0	3.8
Chloroform	119.4	12.5	12.5	1.5	1.9	2.5	3.2	4.1	5.2	6.3
Chloroprene	88.5	8.0	8.0	1.8	2.3	2.9	3.7	4.6	5.7	7.0

TABLE A-1. (continued)

Organic liquid	Vapor molecular weight	Liquid density, lb/gal at 60°F	Condensed vapor density, lb/gal at 60°F	True vapor pressure in psia at:						
				40°F	50°F	60°F	70°F	80°F	90°F	100°F
Cyclohexane	84.2	6.5	6.5	0.7	0.9	1.2	1.6	2.1	2.6	3.2
Cyclopentane	70.1	6.2	6.2	2.5	3.3	4.2	5.2	6.5	8.1	9.7
1,1-Dichloroethane[c]	99.0	9.9	9.9	1.7	2.2	2.9	3.7	4.7	5.9	7.4
1,2-Dichloroethane[c]	99.0	10.5	10.5	0.6	0.8	1.0	1.4	1.7	2.2	2.8
cis-1,2-Dichloroethylene	97.0	10.8	10.8	1.5	2.0	2.7	3.5	4.4	5.6	6.8
trans-1,2-Dichloroethylene	97.0	10.5	10.5	2.6	3.4	4.4	5.5	6.8	8.3	10.0
Diethyl ether	74.1	6.0	6.0	4.2	5.7	7.0	8.7	10.4	13.3	Boils
Diethylamine	73.1	5.9	5.9	1.6	2.0	2.9	3.9	4.9	6.1	7.5
Diisopropyl ether	102.2	6.1	6.1	1.2	1.6	2.1	2.7	3.5	4.3	5.3
1,4-Dioxane	88.1	8.7	8.7	0.2	0.3	0.4	0.6	0.8	1.1	1.5
Dipropyl ether	102.2	6.3	6.3	0.4	0.6	0.8	1.1	1.4	1.9	2.3
Ethyl acetate	88.1	7.6	7.6	0.6	0.8	1.1	1.5	1.9	2.5	3.2
Ethyl acrylate	100.1	7.8	7.8	0.2	0.3	0.4	0.6	0.8	1.1	1.5
Ethyl alcohol	46.1	6.6	6.6	0.2	0.4	0.6	0.9	1.2	1.7	2.3
Freon 11	137.4	12.5	12.5	7.0	8.8	10.9	13.4	16.3	19.7	23.6
n-Heptane	100.2	5.7	5.7	0.3	0.4	0.5	0.7	1.0	1.2	1.6
Hexane[c]	86.2	5.5	5.5	1.1	1.5	1.9	2.4	3.1	3.9	4.9
Isobutyl alcohol	74.1	6.7	6.7	0.06	0.1	0.1	0.2	0.3	0.4	0.5
Isopropyl alcohol	60.1	6.6	6.6	0.2	0.3	0.6	0.7	0.9	1.3	1.8
Methyl acetate	74.1	7.8	7.8	1.5	2.0	2.7	3.7	4.7	5.8	7.0
Methyl acrylate	86.1	8.0	8.0	0.6	0.8	1.0	1.4	1.8	2.4	3.1
Methyl alcohol	32.0	6.6	6.6	0.7	1.0	1.4	2.0	2.6	3.5	4.5

TABLE A-1. (continued)

Organic liquid	Vapor molecular weight	Liquid density, lb/gal at 60°F	Condensed vapor density, lb/gal at 60°F	True vapor pressure in psia at:						
				40°F	50°F	60°F	70°F	80°F	90°F	100°F
Methylene chloride	84.9	11.1	11.1	3.1	4.3	5.4	6.8	8.7	10.3	13.3
Methyl cyclopentane	84.1	6.3	6.3	0.9	1.2	1.6	2.2	2.9	3.6	4.5
Methyl ethyl ketone	72.1	6.7	6.7	0.7	0.9	1.2	1.5	2.1	2.7	3.3
Methylmethacrylate	100	7.9	7.9	0.1	0.2	0.3	0.6	0.8	1.1	1.4
Methyl propyl ether	74.1	6.2	6.2	3.7	4.7	6.1	7.1	9.4	11.6	13.7
n-Pentane[c]	72.2	5.3	5.3	4.3	5.5	6.8	8.5	10.5	12.8	15.6
n-Propylamine	59.1	6.0	6.0	2.5	3.2	4.2	5.3	6.5	8.0	9.6
Propyl chloride[c]	78.5	d	d	2.8	3.5	4.5	5.6	7.0	8.7	10.6
Tertbutyl alcohol	74.1	6.6	d	0.2	0.3	0.4	0.6	0.9	1.2	1.7
1,1,1-Trichloroethane	133.4	11.2	11.2	0.9	1.2	1.6	2.0	2.6	3.3	4.2
Trichloroethylene	131.4	12.3	12.3	0.5	0.7	0.9	1.2	1.5	2.0	2.0
Toluene	92.1	7.3	7.3	0.2	0.2	0.3	0.4	0.6	0.8	1.0
Vinylacetate	86.1	7.8	7.8	0.7	1.0	1.3	1.7	2.3	3.1	4.0
Vinyledene chloride	96.5	10.4	10.4	5.0	6.3	7.9	9.8	11.8	15.3	23.2

[a] RVP = Reid vapor pressure.

[b] Vapor pressures calculated from pages D-212 through D-215 of "Handbook of Physics and Chemistry," 67th Edition.

[c] Data unavailable.

Source: Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)--Air Emission Models. EPA-450/3-87-026. December 1987.

TABLE A-2. VAPOR PRESSURE - EQUATION CONSTANTS

$\ln P = A + B/T + C \ln T + D T^{E}$ (P - mm Hg, T - K)

NO	FORMULA	NAME	A	B	C	D	E	TMIN	TMAX
1	C2H4O	ACETALDEHYDE	201.1772	-8.4786E+03	-3.1548E+01	4.6314E-02	1	150.15	461.00
2	C2H5ON	ACETAMIDE	127.5872	-1.1961E+04	-1.6068E+01	1.1880E-05	2	354.15	494.30
3	C2H3N	ACETONITRILE	53.4092	-5.3856E+03	-5.4954E+00	5.3634E-06	2	229.32	545.50
4	C8H8O	ACETOPHENONE	127.9772	-1.0385E+04	-1.7284E+01	1.4779E-02	1	292.80	701.00
5	C3H4O	ACROLEIN	133.5072	-7.1227E+03	-1.9638E+01	2.6447E-02	1	185.45	506.00
6	C3H5NO	ACRYLAMIDE	39.1412	-1.0231E+04	-1.7139E+00	----	-	357.65	465.75
7	C3H4O2	ACRYLIC ACID	53.0992	-7.2180E+03	-4.8813E+00	1.0060E-03	1	286.65	615.00
8	C3H3N	ACRYLONITRILE	82.7112	-6.3927E+03	-1.0101E+01	1.0891E-05	2	186.63	535.00
9	C3H5CL	ALLYL CHLORIDE	38.1982	-4.3084E+03	-3.1322E+00	1.1171E-17	6	138.65	516.15
10	C6H7N	ANILINE	286.3872	-1.6504E+04	-4.2763E+01	3.9918E-02	1	267.13	699.00
11	C7H9NO	O-ANISIDINE	----	----	----	----	-	---	---
12	C6H6	BENZENE	73.1572	-6.2755E+03	-8.4443E+00	6.2600E-06	2	278.68	562.16
13	C7H5CL3	BENZOTRICHLORIDE	50.6272	-7.4190E+03	-4.6513E+00	1.7396E-18	6	268.40	737.00
14	C7H7CL	BENZYL CHLORIDE	49.8582	-7.1698E+03	-4.4836E+00	1.3858E-18	6	234.15	686.00
15	C12H10	BIPHENYL	122.1472	-1.2321E+04	-1.4955E+01	5.6056E-06	2	342.37	780.26
16	C2H4CL2O	BIS(CHLOROMETHYL)ETHER	56.1552	-6.3984E+03	-5.4972E+00	8.2034E-18	6	231.65	579.00
17	CHBR3	BROMOFORM	53.1752	-6.7653E+03	-5.0514E+00	2.9653E-18	6	281.20	696.00
18	C4H6	1,3-BUTADIENE	69.2092	-4.5800E+03	-8.2922E+00	1.1820E-05	2	164.25	425.37
19	C6H11ON	CAPROLACTAM	69.2792	-1.0469E+04	-6.8944E+00	1.2113E-18	6	342.36	806.00
20	CS2	CARBON DISULFIDE	57.9042	-4.7063E+03	-6.7794E+00	8.0195E-03	1	161.11	552.00
21	CCL4	CARBON TETRACHLORIDE	73.5462	-6.1281E+03	-8.5763E+00	6.8461E-06	2	250.33	556.35
22	C2H3CLO2	CHLOROACETIC ACID	98.2572	-1.0585E+04	-1.1348E+01	4.1635E-06	2	333.15	686.00
23	C8H7CLO	2-CHLOROACETOPHENONE	----	----	----	----	-	---	---
24	C6H5CL	CHLOROBENZENE	44.7492	-5.9408E+03	-3.9391E+00	1.1617E-06	2	227.95	632.35
25	CHCL3	CHLOROFORM	130.3672	-7.4746E+03	-1.8700E+01	2.1909E-02	1	209.63	536.40
26	C4H5CL	CHLOROPRENE	42.9902	-4.7595E+03	-3.7996E+00	1.1726E-17	6	143.15	525.00
27	C7H8O	M-CRESOL	242.9872	-1.6060E+04	-3.5083E+01	2.8800E-02	1	285.39	705.85
28		CRESOLS/CRESYLIC ACID(ISOMERS & MIXTURES)	----	----	----	----	-	---	---
29	C7H8O	O-CRESOL	205.9872	-1.3928E+04	-2.9483E+01	2.5182E-02	1	304.19	697.55
30	C7H8O	P-CRESOL	282.9872	-1.7540E+04	-4.1637E+01	3.6171E-02	1	307.93	704.65
31	C9H12	CUMENE	82.7612	-8.3340E+03	-9.3567E+00	1.3600E-17	6	177.14	631.15
32	C6H4CL2	1,4-DICHLOROBENZENE	83.4172	-8.4634E+03	-9.6308E+00	4.5833E-06	2	326.14	684.75
33	C4H8CL2O	DICHLOROETHYL ETHER	----	----	----	----	-	---	---
34	C3H4CL2	1,3-DICHLOROPROPENE*	44.1267	-5.3347E+03	-3.9572E+00	6.9674E-18	6	191.50	577.00
35	C4H11NO2	DIETHANOLAMINE	281.1172	-2.0360E+04	-4.0422E+01	3.2378E-02	1	301.15	542.04
36	C8H11N	N,N-DIMETYLANILINE	46.4592	-7.1600E+03	-4.0127E+00	8.1481E-07	2	275.60	687.15
37	C4H10O4S	DIETHYL SULFATE	86.4342	-9.2791E+03	-1.0340E+01	6.8675E-03	1	248.00	483.00
38	C14H20N	DIMETHYLBENZIDINE	----	----	----	----	-	---	---
39	C3H7N	DIMETHYL FORMAMIDE	110.7172	-9.8538E+03	-1.3393E+01	2.1867E-17	6	212.72	647.00
40	C2H8N2	1,1-DIMETHYLHYDRAZINE	----	----	----	----	-	---	---
41	C10H10O4	DIMETHYL PHTHALATE	66.1802	-1.0534E+04	-6.4298E+00	1.0804E-18	6	272.15	766.00
42	C2H6SO4	DIMETHYL SULFATE	78.1512	-8.8719E+03	-8.5921E+00	1.8941E-06	2	241.35	758.00
43	C6H3N2O4	2,4-DINITROPHENOL	----	----	----	----	-	---	---
44	C7H6N2O4	2,4-DINITROTOLUENE	26.7022	-6.9259E+03	-1.6468E+00	3.6725E-03	1	343.00	814.00
45	C4H8O2	1,4-DIOXANE	47.3782	-5.6777E+03	-4.3645E+00	1.9626E-06	2	284.95	587.00
46	C12H12N2	1,2-DIPHENYLHYDRAZINE	89.6402	-1.2785E+04	-9.5673E+00	1.6660E-18	6	404.15	573.00
47	C3H5CLO	EPICHLOROHYDRIN	57.0212	-6.6420E+03	-5.6252E+00	1.2280E-06	2	215.95	610.00
48	C5H8O2	ETHYL ACRYLATE	126.6672	-8.2672E+03	-1.7694E+01	1.8538E-02	1	201.95	553.00
49	C8H10	ETHYLBENZENE	83.3532	-7.6911E+03	-9.7970E+00	5.9310E-06	2	178.15	617.17
50	C2H5CL	ETHYL CHLORIDE	65.2652	-4.7867E+03	-7.5387E+00	9.3370E-06	2	134.80	460.35

From "Henry's Law Constant for HAP's." Carl Yaws. Prepared for the U. S. Environmental Protection Agency. Final Report. September 30, 1992.

TABLE A-2. (continued)

NO	FORMULA	NAME	A	B	C	D	E	TMIN	TMAX
			ln P = A + B/T + C ln T + D T^E				(P - mm Hg, T - K)		
51	C2H4BR2	ETHYLENE DIBROMIDE	38.8582	-5.5877E+03	-3.0891E+00	8.2664E-07	2	282.85	650.15
52	C2H4CL2	ETHYLENE DICHLORIDE	111.4972	-7.3230E+03	-1.5370E+01	1.6794E-02	1	237.49	561.00
53	C2H6O2	ETHYLENE GLYCOL	189.7672	-1.4615E+04	-2.5433E+01	2.0160E-05	2	260.15	645.00
54	C2H4O	ETHYLENE OXIDE	91.9272	-5.6330E+03	-1.2517E+01	1.6080E-02	1	160.71	469.15
55	C2H4CL2	ETHYLIDENE DICHLORIDE	76.8602	-6.0103E+03	-9.1334E+00	8.5960E-06	2	176.19	523.00
56	CH2O	FORMALDEHYDE	96.6172	-4.9172E+03	-1.3765E+01	2.2031E-02	1	181.15	408.00
57	C4H10O2	ETHYLENE GLYCOL DIMETHYL ETHER	80.1902	-6.3722E+03	-1.0083E+01	9.9699E-03	1	215.15	536.15
58	C4H10O2	ETHYLENE GLYCOL MONOETHYL ETHER	266.7972	-1.3845E+04	-4.0900E+01	6.8096E-02	1	183.00	569.00
59	C8H16O4	DIETHYLENE GLYCOL MONOETHYL ETHER ACETATE	105.8972	-9.9058E+03	-1.3729E+01	1.2203E-02	1	248.15	660.00
60	C6H12O3	ETHYLENE GLYCOL MONOETHYL ETHER ACETATE	79.6572	-8.6783E+03	-8.7264E+00	1.0459E-17	6	211.45	597.00
61	C6H14O3	DIETHYLENE GLYCOL MONOETHYL ETHER	250.9672	-1.7164E+04	-3.4699E+01	2.5107E-05	2	250.00	632.00
62	C5H10O3	ETHYLENE GLYCOL MONOMETHYL ETHER ACETATE*	80.0053	-8.6783E+03	-8.7264E+00	1.0459E-17	6	211.45	597.00
63	C8H18O3	DIETHYLENE GLYCOL MONOBUTYL ETHER	173.6772	-1.5712E+04	-2.1908E+01	2.8569E-17	6	205.15	654.00
64	C6H14O3	DIETHYLENE GLYCOL DIMETHYL ETHER	78.2492	-8.2848E+03	-8.6687E+00	1.9629E-17	6	203.15	432.91
65	C3H8O2	ETHYLENE GLYCOL MONOMETHYL ETHER	353.1672	-1.6390E+04	-5.5450E+01	6.6861E-02	1	225.00	564.00
66	C6H12O2	ETHYLENE GLYCOL MONOPROPYL ETHER	65.3342	-7.7712E+03	-6.6964E+00	2.2398E-17	6	183.15	582.00
67	C8H10O2	ETHYLENE GLYCOL MONOPHENYL ETHER	----	----	----	----	-	---	---
68	C5H12O2	DIETHYLENE GLYCOL MONOMETHYL ETHER	428.7372	-2.1730E+04	-6.6416E+01	6.9903E-02	1	250.00	630.00
69	C8H18O3	DIETHYLENE GLYCOL DIETHYL ETHER	71.5962	-8.5825E+03	-7.6847E+00	3.6009E-06	2	228.85	624.00
70	C6H14O2	ETHYLENE GLYCOL MONOBUTYL ETHER	110.6072	-1.0705E+04	-1.3140E+01	2.9781E-17	6	203.15	600.00
71	C8H18O4	TRIETHYLENE GLYCOL DIMETHYL ETHER	98.8572	-1.1633E+04	-1.1067E+01	6.2208E-18	6	229.35	651.00
72	C8H15O3	ETHYLENE GLYCOL MONOBUTYL ETHER ACETATE	----	----	----	----	-	---	---
73	C6CL6	HEXACHLOROBENZENE	158.3372	-1.8324E+04	-1.8899E+01	2.3902E-18	6	501.70	825.00
74	C4CL6	HEXACHLOROBUTADIENE	81.9512	-9.5280E+03	-9.0606E+00	1.3588E-06	2	252.15	741.00
75	C2CL6	HEXACHLOROETHANE	430.2172	-2.7220E+04	-6.0495E+01	3.0865E-05	2	459.95	512.25
76	C6H14	HEXANE	160.5772	-8.3533E+03	-2.3927E+01	2.9469E-02	1	177.84	507.43
77	C6H6O2	HYDROQUINONE	105.9772	-1.2856E+04	-1.2677E+01	6.9120E-03	1	444.65	822.00
78	C9H14O	ISOPHORONE	78.1382	-8.1126E+03	-9.5117E+00	8.1784E-03	1	265.05	715.00
79	C4H2O3	MALEIC ANHYDRIDE	63.9872	-7.7226E+03	-7.2087E+00	7.0169E-03	1	326.00	710.00
80	CH4O	METHANOL	105.0372	-7.4713E+03	-1.3988E+01	1.5281E-02	1	175.47	512.58
81	CH3BR	METHYL BROMIDE	67.6932	-4.6986E+03	-7.9966E+00	1.1553E-05	2	179.47	467.00
82	CH3CL	METHYL CHLORIDE	59.2372	-4.0301E+03	-6.7151E+00	1.0210E-05	2	175.43	416.25
83	C2H3CL3	METHYL CHLOROFORM	84.1522	-6.5442E+03	-1.0205E+01	8.5368E-06	2	242.75	545.00
84	C4H8O	METHYL ETHYL KETONE	109.8472	-7.1300E+03	-1.5184E+01	1.7234E-02	1	186.48	535.50
85	CH6N2	METHYL HYDRAZINE	----	----	----	----	-	---	---
86	C6H12O	METHYL ISOBUTYL KETONE	147.8072	-1.0034E+04	-1.9766E+01	1.6353E-05	2	189.15	571.60
87	C2H3NO	METHYL ISOCYANATE	41.7632	-4.4556E+03	-3.6339E+00	1.5024E-17	6	256.15	505.00
88	C5H8O2	METHYL METHACRYLATE	246.1372	-1.2144E+04	-3.7654E+01	4.2873E-02	1	224.95	564.00
89	C5H12O	METHYL TERT-BUTYL ETHER	50.9812	-5.1301E+03	-4.9617E+00	1.9765E-17	6	164.55	497.10
90	CH2CL2	METHYLENE CHLORIDE	74.9742	-5.7947E+03	-8.8015E+00	7.6432E-06	2	178.01	510.00
91	C15H10N2O2	METHYLENE DIPHENYL DIISOCYANATE	78.9502	-1.3604E+04	-7.8629E+00	6.0025E-18	6	311.20	609.00
92	C13H14N2	4,4-METHYLENEDIANILINE	----	----	----	----	-	---	---
93	C10H8	NAPHTHALENE	80.3972	-9.0622E+03	-9.0648E+00	3.5805E-06	2	353.43	748.35
94	C6H5NO2	NITROBENZENE	85.5522	-9.7448E+03	-9.5228E+00	7.5659E-18	6	---	---
95	C6H5NO3	4-NITROPHENOL	----	----	----	----	-	---	---
96	C3H7NO2	2-NITROPROPANE	51.5512	-6.2903E+03	-4.8462E+00	9.2273E-18	6	181.83	594.00
97	C6H6O	PHENOL	54.1872	-8.0500E+03	-4.8990E+00	2.800E-06	1	314.06	694.25
98	C6H8N2	P-PHENYLENEDIAMINE	79.0322	-1.1341E+04	-8.1769E+00	1.5761E-18	6	413.00	796.00
99	COCL2	PHOSGENE	107.4272	-5.6774E+03	-1.5351E+01	2.1250E-02	1	145.37	455.00
100	C8H4O3	PHTHALIC ANHYDRIDE	70.5352	-8.9302E+03	-7.8671E+00	5.9603E-06	2	404.15	791.00

TABLE A-2. (continued)

$\ln P = A + B/T + C \ln T + D\,T^{E}$ (P - mm Hg, T - K)

NO	FORMULA	NAME	A	B	C	D	E	TMIN	TMAX
101	C3H4O2	BETA-PROPIOLACTONE	59.6992	-7.8204E+03	-5.7808E+00	3.0689E-18	6	239.75	685.00
102	C3H6O	PROPIONALDEHYDE	60.2442	-5.3095E+03	-6.5289E+00	5.8611E-06	2	193.15	496.00
103	C3H6CL2	PROPYLENE DICHLORIDE	49.2312	-5.6774E+03	-4.6063E+00	9.0212E-18	6	172.71	572.00
104	C3H6O	PROPYLENE OXIDE	88.7372	-6.0580E+03	-1.1104E+01	1.2670E-05	2	161.22	482.25
105	C6H4O2	QUINONE	----	----	----	----	*	---	---
106	C8H8	STYRENE	128.6272	-9.2655E+03	-1.7609E+01	1.5391E-02	1	242.54	648.00
107	C2H2CL4	1,1,2,2-TETRACHLOROETHANE	129.4872	-1.0273E+04	-1.6556E+01	9.3081E-06	2	229.35	645.00
108	C2CL4	TETRACHLOROETHYLENE	53.8712	-6.1912E+03	-5.3312E+00	2.1269E-06	2	250.80	620.00
109	C7H8	TOLUENE	78.4662	-6.9950E+03	-9.1635E+00	6.2250E-06	2	178.18	591.79
110	C7H10N2	2,4-TOLUENE DIAMINE	100.9772	-1.2648E+04	-1.1672E+01	2.9007E-06	2	371.29	804.00
111	C9H6N2O2	2,4-TOLUENE DIISOCYANATE	95.0812	-1.1659E+04	-1.0583E+01	4.1543E-18	6	287.06	737.00
112	C7H9N	O-TOLUIDINE	222.3572	-1.4424E+04	-3.2263E+01	2.8462E-02	1	249.47	694.15
113	C6H3CL3	1,2,4-TRICHLOROBENZENE	35.9082	-6.6591E+03	-2.5549E+00	4.6936E-04	1	290.15	725.00
114	C2H3CL3	1,1,2-TRICHLOROETHANE	57.7592	-6.3017E+03	-5.9182E+00	2.7261E-06	2	236.50	302.00
115	C2HCL3	TRICHLROETHYLENE	54.5102	-5.4716E+03	-5.8275E+00	4.5098E-03	1	188.40	571.15
116	C6H3CL3O	2,4,5-TRICHLOROPHENOL	----	----	----	----	*	---	---
117	C6H15N	TRIETHYLAMINE	51.6572	-5.6819E+03	-4.9815E+00	1.2363E-17	6	158.45	535.15
118	C8H18	2,2,4-TRIMETHYLPENTANE	115.9172	-7.5500E+03	-1.6111E+01	1.7099E-02	1	165.78	543.96
119	C4H6O2	VINYL ACETATE	43.0492	-5.2462E+03	-3.6360E+00	6.5798E-18	6	180.35	524.00
120	C2H3CL	VINYL CHLORIDE	121.9572	-5.7601E+03	-1.7914E+01	2.4917E-02	1	119.36	431.55
121	C2H2CL2	VINYLIDENE CHLORIDE	67.7482	-5.4481E+03	-7.5697E+00	7.0922E-17	6	10.59	482.00
122		XYLENES (ISOMERS & MIXTURES)	----	----	----	----	*	---	---
123	C8H10	M-XYLENE	79.8542	-7.5941E+03	-9.2570E+00	5.5500E-06	2	225.30	617.05
124	C8H10	O-XYLENE	85.7512	-7.9608E+03	-1.0126E+01	6.0150E-06	2	247.98	630.37
125	C8H10	P-XYLENE	138.2772	-9.2470E+03	-1.9441E+01	1.9084E-02	1	286.41	616.26

* - Estimated values for coefficients in vapor pressure equation.

ln = natural logarithm

Primary data source: Daubert, T. E. and R. P. Danner, DATA COMPILATION OF PROPERTIES OF PURE COMPOUNDS, Parts 1,2,3 and 4, Supplements 1 and 2, DIPPR Project, AIChE, New York, NY (1985-1992).

$\log P = A - B/(T+C)$ (P - mm Hg, T - C)

NO	FORMULA	NAME	A	B	C	TMIN	TMAX
11	C7H9NO	O-ANISIDINE	8.30799	2475.780	237.134	61	218
33	C4H8CL2O	DICHLOROETHYL ETHER	7.69239	1990.755	235.347	23	178
40	C2H8N2	1,1-DIMETHYLHYDRAZINE	7.58826	1388.510	232.537	-35	20
67	C8H10O2	ETHYLENE GLYCOL MONOPHENYL ETHER	7.15937	1767.871	168.070	25	245
72	C8H15O3	ETHYLENE GLYCOL MONOBUTYL ETHER ACETATE	7.21589	1659.242	191.339	25	192
85	CH6N2	METHYL HYDRAZINE	6.84297	1115.190	191.648	2	25
116	C6H3CL3O	2,4,5-TRICHLOROPHENOL	7.82316	2420.564	237.476	72	252

log = logarithm to base 10

Primary data source: Ohe, S., COMPUTER AIDED DATA BOOK OF VAPOR PRESSURE, Data Book Publishing Company, Tokyo, Japan (1976).

Primary data source for 67 and 72: Curme, G. O., editor, GLYCOLS, Reinhold Publishing Corp., New York, NY (1953).

TABLE A-3. SUMMATION OF DATA FOR HENRY'S LAW CONSTANT

			Henry's Law Constant,	H - atm/mol fraction
NO	FORMULA	NAME	H @ 25 C	BASIS
1	C2H4O	ACETALDEHYDE	4.8730000	Experimental
2	C2H5ON	ACETAMIDE	0.0000986	UNIFAC
3	C2H3N	ACETONITRILE	1.1076388	VLE Data
4	C8H8O	ACETOPHENONE	0.5089400	Solubility Data
5	C3H4O	ACROLEIN	4.5711400	Solubility Data
6	C3H5NO	ACRYLAMIDE	0.0000145	UNIFAC
7	C3H4O2	ACRYLIC ACID	0.0223962	VLE Data
8	C3H3N	ACRYLONITRILE	5.4484900	Solubility Data
9	C3H5CL	ALLYL CHLORIDE	515.4180500	Solubility Data
10	C6H7N	ANILINE	0.0977600	Solubility Data
11	C7H9NO	O-ANISIDINE	0.0092393	UNIFAC
12	C6H6	BENZENE	308.3400000	Experimental
13	C7H5CL3	BENZOTRICHLORIDE	54.5177107	UNIFAC
14	C7H7CL	BENZYL CHLORIDE	17.7286753	UNIFAC
15	C12H10	BIPHENYL	22.6700000	Experimental
16	C2H4CL2O	BIS(CHLOROMETHYL)ETHER	-------	Reaction with water
17	CHBR3	BROMOFORM	29.5600000	Experimental
18	C4H6	1,3-BUTADIENE	3961.1653000	Solubility Data
19	C6H11ON	CAPROLACTAM	0.0001639	UNIFAC
20	CS2	CARBON DISULFIDE	1064.0713500	Solubility Data
21	CCL4	CARBON TETRACHLORIDE	1677.7900000	Experimental
22	C2H3CLO2	CHLOROACETIC ACID	0.0036272	UNIFAC
23	C8H7CLO	2-CHLOROACETOPHENONE	1.5713000	Solubility - Estimated
24	C6H5CL	CHLOROBENZENE	209.4500000	Experimental
25	CHCL3	CHLOROFORM	221.3300000	Experimental
26	C4H5CL	CHLOROPRENE	51.6355560	UNIFAC
27	C7H8O	M-CRESOL	0.0394800	Solubility Data
28		CRESOLS/CRESYLIC ACID(ISOMERS & MIXTURES)	-------	
29	C7H8O	O-CRESOL	0.0911500	Solubility Data
30	C7H8O	P-CRESOL	0.0396800	Solubility Data
31	C9H12	CUMENE	727.7800000	Experimental
32	C6H4CL2	1,4-DICHLOROBENZENE	176.1100000	Experimental
33	C4H8CL2O	DICHLOROETHYL ETHER	1.1390000	Solubility Data
34	C3H4CL2	1,3-DICHLOROPROPENE	197.2200000	Experimental
35	C4H11NO2	DIETHANOLAMINE	0.0000001	UNIFAC
36	C8H11N	N,N-DIMETYLANILINE	0.7701322	UNIFAC
37	C4H10O4S	DIETHYL SULFATE	0.3405000	Solubility Data
38	C14H16N2	DIMETHYLBENZIDINE	0.1780100	Solubility - Estimated
39	C3H7NO	DIMETHYL FORMAMIDE	0.0098341	VLE Data
40	C2H8N2	1,1-DIMETHYLHYDRAZINE	0.0910756	VLE Data
41	C10H10O4	DIMETHYL PHTHALATE	0.0548542	UNIFAC
42	C2H6SO4	DIMETHYL SULFATE	0.2226700	Solubility Data
43	C6H3N2O4	2,4-DINITROPHENOL	0.4756000	Solubility Data
44	C7H6N2O4	2,4-DINITROTOLUENE	0.3996900	Solubility Data
45	C4H8O2	1,4-DIOXANE	0.3079797	VLE Data
46	C12H12N2	1,2-DIPHENYLHYDRAZINE	0.0135700	Solubility - Estimated
47	C3H5CLO	EPICHLOROHYDRIN	1.8590400	Solubility Data
48	C5H8O2	ETHYL ACRYLATE	14.1169500	Solubility Data
49	C8H10	ETHYLBENZENE	437.8100000	Experimental
50	C2H5CL	ETHYL CHLORIDE	672.2200000	Experimental

To convert from H in atm/vol fraction to:
H in atm/ (mol/m3), divide by 55,556
H in mmHg/mol fraction, multiply by 760
H in psia/mol fraction, multiply by 19.7
H in kPA/mol fraction, multiply by 101.325
H in kPa/mol/m^3), multiply by 101.325/55,556
Source: Carl Yaws, "Henry's Law Constant for HAPs", Final Report. September 30, 1992.

TABLE A-3. (CONTINUED)

			Henry's Law Constant,	H - atm/mol fraction
NO	FORMULA	NAME	H @ 25 C	BASIS
51	C2H4BR2	ETHYLENE DIBROMIDE	36.1100000	Experimental
52	C2H4CL2	ETHYLENE DICHLORIDE	65.3800000	Experimental
53	C2H6O2	ETHYLENE GLYCOL	0.0001051	VLE Data
54	C2H4O	ETHYLENE OXIDE	13.2280793	VLE Data
55	C2H4CL2	ETHYLIDENE DICHLORIDE	312.2300000	Experimental
56	CH2O	FORMALDEHYDE	0.0187000	Experimental
57	C4H10O2	ETHYLENE GLYCOL DIMETHYL ETHER	1.9471264	VLE Data
58	C4H10O2	ETHYLENE GLYCOL MONOETHYL ETHER	0.0409170	VLE Data
59	C8H16O4	DIETHYLENE GLYCOL MONOETHYL ETHER ACETATE	0.0358406	UNIFAC
60	C6H12O3	ETHYLENE GLYCOL MONOETHYL ETHER ACETATE	0.0986300	Solubility Data
61	C6H14O3	DIETHYLENE GLYCOL MONOETHYL ETHER	0.0026793	UNIFAC
62	C5H10O3	ETHYLENE GLYCOL MONOMETHYL ETHER ACETATE*	0.1218685	UNIFAC
63	C8H18O3	DIETHYLENE GLYCOL MONOBUTYL ETHER	0.0012481	UNIFAC
64	C6H14O3	DIETHYLENE GLYCOL DIMETHYL ETHER	0.0837496	UNIFAC
65	C3H8O2	ETHYLENE GLYCOL MONOMETHYL ETHER	0.0405801	Correlation
66	C6H12O2	ETHYLENE GLYCOL MONOPROPYL ETHER	0.0474169	UNIFAC
67	C8H10O2	ETHYLENE GLYCOL MONOPHENYL ETHER	0.0037600	Solubility Data
68	C5H12O2	DIETHYLENE GLYCOL MONOMETHYL ETHER	0.0022577	UNIFAC
69	C8H18O3	DIETHYLENE GLYCOL DIETHYL ETHER	0.1189224	UNIFAC
70	C6H14O2	ETHYLENE GLYCOL MONOBUTYL ETHER	0.0292288	VLE Data
71	C8H18O4	TRIETHYLENE GLYCOL DIMETHYL ETHER	0.0025951	UNIFAC
72	C8H15O3	ETHYLENE GLYCOL MONOBUTYL ETHER ACETATE	0.2746400	Solubility Data
73	C6CL6	HEXACHLOROBENZENE	94.4500000	Experimental
74	C4CL6	HEXACHLOROBUTADIENE	572.2300000	Experimental
75	C2CL6	HEXACHLOROETHANE	463.8900000	Experimental
76	C6H14	HEXANE	42667.0100000	Experimental
77	C6H6O2	HYDROQUINONE	0.0000800	Solubility Data
78	C9H14O	ISOPHORONE	0.3682100	Solubility Data
79	C4H2O3	MALEIC ANHYDRIDE	0.0121651	UNIFAC
80	CH4O	METHANOL	0.2885032	VLE Data
81	CH3BR	METHYL BROMIDE	381.0578800	Solubility Data
82	CH3CL	METHYL CHLORIDE	490.0000000	Experimental
83	C2H3CL3	METHYL CHLOROFORM	966.6700000	Experimental
84	C4H8O	METHYL ETHYL KETONE	7.2200000	Experimental
85	CH6N2	METHYL HYDRAZINE	0.0248008	UNIFAC
86	C6H12O	METHYL ISOBUTYL KETONE	21.6700000	Experimental
87	C2H3NO	METHYL ISOCYANATE	-------	Reaction with water
88	C5H8O2	METHYL METHACRYLATE	7.8317700	Solubility - Estimated
89	C5H12O	METHYL TERT-BUTYL ETHER	30.8401800	Solubility Data
90	CH2CL2	METHYLENE CHLORIDE	164.4500000	Experimental
91	C15H10N2O2	METHYLENE DIPHENYL DIISOCYANATE**	0.0026600**	Solubility - Estimated
92	C13H14N2	4,4-METHYLENEDIANILINE	0.0284900	Solubility Data
93	C10H8	NAPHTHALENE	26.8300000	Experimental
94	C6H5NO2	NITROBENZENE	1.3300000	Experimental
95	C6H5NO3	4-NITROPHENOL	0.0064600	Solubility Data
96	C3H7NO2	2-NITROPROPANE	6.6111800	Solubility Data
97	C6H6O	PHENOL	0.0722000	Experimental
98	C6H8N2	P-PHENYLENEDIAMINE	0.0007700	Solubility Data
99	COCL2	PHOSGENE**	780.0225300**	Solubility Data
100	C8H4O3	PHTHALIC ANHYDRIDE	0.0441500	Solubility Data

TABLE A-3. (CONTINUED)

			Henry's Law Constant, H = atm/mol fraction	
NO	FORMULA	NAME	H @ 25 C	BASIS
101	C3H4O2	BETA-PROPIOLACTONE	0.0063801	UNIFAC
102	C3H6O	PROPIONALDEHYDE	3.3224900	Solubility Data
103	C3H6CL2	PROPYLENE DICHLORIDE	158.7100000	Experimental
104	C3H6O	PROPYLENE OXIDE	19.7742986	VLE Data
105	C6H4O2	QUINONE	0.0576800	Solubility Data
106	C8H8	STYRENE	144.7155400	Solubility Data
107	C2H2CL4	1,1,2,2-TETRACHLOROETHANE	13.8900000	Experimental
108	C2CL4	TETRACHLOROETHYLENE	983.3400000	Experimental
109	C7H8	TOLUENE	356.6700000	Experimental
110	C7H10N2	2,4-TOLUENE DIAMINE	0.0000742	UNIFAC
111	C9H6N2O2	2,4-TOLUENE DIISOCYANATE**	0.0091900**	Solubility - Estimated
112	C7H9N	O-TOLUIDINE	0.1344600	Solubility Data
113	C6H3CL3	1,2,4-TRICHLOROBENZENE	106.6700000	Experimental
114	C2H3CL3	1,1,2-TRICHLOROETHANE	45.7700000	Experimental
115	C2HCL3	TRICHLOROTHYLENE	566.6700000	Experimental
116	C6H3CL3O	2,4,5-TRICHLOROPHENOL	0.4841100	Solubility Data
117	C6H15N	TRIETHYLAMINE	6.9428000	Solubility Data
118	C8H18	2,2,4-TRIMETHYLPENTANE	185451.3318600	Solubility Data
119	C4H6O2	VINYL ACETATE	28.2111800	Solubility Data
120	C2H3CL	VINYL CHLORIDE	1472.2300000	Experimental
121	C2H2CL2	VINYLIDENE CHLORIDE	1438.9000000	Experimental
122		XYLENES (ISOMERS & MIXTURES)	-------	
123	C8H10	M-XYLENE	413.3400000	Experimental
124	C8H10	O-XYLENE	270.5600000	Experimental
125	C8H10	P-XYLENE	413.3400000	Experimental

Notes:

1. * - Estimated values for coefficients in vapor pressure equation.

2. ** - Reacts with water.

3. For basis of UNIFAC, the estimation of the activity coefficient at infinite dilution makes use of the group contribution contribution method using the UNIFAC equations (Gmehling, J., P. Rasmussen and A. Fredenslund, Ind. Eng. Chem. Process Des. Dev., 21, 118 (1982)).

4. For basis of Solubility - Estimated, the estimation of water solubility makes use of experimental data which is available on reference compounds that are very close in molecular structure to the compound of interest. The addition of a molecular group (or groups) to the reference compound then provides a molecular structure that is identical to the molecular structure of the compound of interest ($\log S = \log S_{ref} + \Delta Group$).

TABLE A-4. VALUES OF THE GAS CONSTANT R IN PV = n RT

N	Temp.	Pressure	Volume	R	n	Temp.	Energy	R
gm mol	K	atm	liter	0.082057477	gm mol	K	calorie	1.9859
gm mol	K	atm	cm^3	82.057	gm mol	K	joule	8.3145
gm mol	K	mm Hg	liter	62.364				
gm mol	K	bar	liter	0.083145	lb mol	°R	Btu	1.9859
gm mol	K	kg/cm^2	liter	0.084784	lb mol	°R	hp-h	0.00078048
gm mol	K	kPa	m^3	0.0083145	lb mol	°R	Kw-h	0.00058200
lb mol	°R	atm	ft^3	0.73024	lb mol	°R	ft-lb	1545.3
lb mol	°R	in. Hg	ft^3	21.850				
lb mol	°R	mm Hg	ft^3	554.98				
lb mol	°R	$lb/in.^2$	ft^3	10.732				
lb mol	°R	lb/ft^2	ft^3	1545.3				
lb mol	K	atm	ft^3	1.3144				
lb mol	K	mm Hg	ft^3	998.97				

Source: Engineering Data Book. Gas Processors Suppliers Association, Ninth Edition.

TABLE A-5. SPECIFIC LEAK RATES FOR ROUGH VACUUM SYSTEM COMPONENTS

Component	θ = specific leak rate, lb/h/in.
Static seals	
O-ring construction	0.002
Conventional gasket seals	0.005
Thermally cycled static seals	
t<200°F	0.005
200<t<400°F	0.018
t>400°F	0.032
Motion (rotary) seals	
O-ring construction	0.10
Mechanical seals	0.10
Conventional packing	0.25
Threaded connections	0.015
Access ports	0.020
Viewing windows	0.015
Valves used to iolate system	
Ball	0.02
Gate	0.04
Globe	0.02
Plug-cock	0.01
Valves used to throttle control gas into vacuum system	0.25

[a] Assumes sonic (or critical) flow across the component.

Source: Chemical Engineering, 88:78, December 14, 1981.

TABLE A-6. AVERAGE EMISSION FACTORS FOR FUGITIVE EMISSIONS IN SOCMI[a]

Equipment component	"Average" SOCMI factors, Kg/h/source
Pump seals	
Light liquid	0.0199
Heavy liquid	0.00862
Valves	
Gas	0.00597
Light liquid	0.00403
Heavy liquid	0.00023
Compressor seals	0.228
Safety relief valves--gas	0.104
Flanges	.00183
Open-ended lines	0.0017
Sampling connections	0.0150

[a] These factors are appropriate for estimating emissions when no other data (i.e., leakage rates) are available.

Source: EPA-953/R-93-026. June 1993.

APPENDIX B.

CALCULATIONAL ISSUES

APPENDIX B.

CALCULATIONAL ISSUES

This appendix contains calculational issues encountered during the development of this document. An examination of the degree of saturation with VOC of a purge gas stream exiting a vessel containing VOC, and a discussion of an incremental cost analysis of manifolding single unit operations to a control device is provided below.

Calculational Issue 1: Degree of Saturation of a Purge Gas Stream. The degree of saturation was examined for purges of quiescent vapor-liquid interfaces and agitated gas sparging. Based on the results obtained from various mass transfer correlations, the expected saturation fraction ranges from 0 to 100 percent for the range of conditions examined. The calculations show that typical batch purging (at flowrates of 20 to 30scfm) over quiescent surfaces yields fractional saturation values of less than 10 percent, whereas purging of agitated sparging yields values of 80% or better. The discussions below present the theory and calculations relating to these findings.

I. General

If the vaporized liquid is a single component, or for dilute concentrations in a solvent, then the rate of mass transfer of the liquid across the liquid-vapor interface will only be a function of the diffusion through the vapor "boundary layer" film. The mass transfer is said to be "gas phase controlled."

As the purge gas passes over the surface of the volatile liquid, vapor will diffuse into the bulk of the gas where it will mix by convection and eddy currents. The driving force for diffusion is the concentration difference of the interface (which is the saturation or equilibrium concentration in the vapor) and the bulk gas phase. The resistance is the diffusivity of the VOC in the gas. The flux, or flow of material across the interface is the rate of vaporization and becomes the VOC content of the exiting purge gas. The flux (I) is related to the diffusivity and the concentration driving force as follows:

$$I = (D_v \rho_m / B_T)(y_i - y) \qquad \text{(B-1)}$$

where:

I = flux, gmol/m^2 hr

B_T = the thickness of the boundary layer, m

D_v = the diffusivity, m^2/hr

ρ_m = the molar gas density, gmol/m^3

$(y_i - y)$ = the concentration difference in mole fraction.

Since B_T is not usually known, other forms of this equation are more convenient where a term k is defined as the mass transfer coefficient, and is empirically related to diffusivity, viscosity, density, and the geometry of the system. The governing equation then becomes

$$I = N/A = k(y_i - y) \qquad (B\text{-}2)$$

where N is the number of moles of VOC transferred across the interface of area A per unit of time, in the previous units, N would be in gmols/hr.

II. Inert N_2 Purging of Quiescent Solvent Pools

The geometry of the headspace of a storage tank or reactor with contents at rest, where the purge gas is moving across a quiescent surface of liquid, resembles evaporation from an open pool. MacKay and Matsugu determined an empirical correlation for the mass transfer coefficient for evaporation from a pool where one of the terms is windspeed. In the case of tank purging, this would be analogous to the superficial velocity of the sweep gas across the liquid pool surface.

The k value calculated by the MacKay and Matsugu correlation has units corresponding to the following equation for mass transfer flux:

$$I = N/A = k[(p_i - P)/RT] \qquad (B\text{-}3)$$

where k = m/hr in this example, and the term $[(p_i - P)/RT)$ reduces to p_i/RT to maximize the concentration driving force; this term is in units of gmols/m^3.

This equation is based on a moles per volume concentration gradient driving force rather than a mole fraction (y_i, y) driving force. The equation for k, the mass transfer coefficient, in m/hr, is as follows:

$$k = .029\ U^{.78} D^{-.11} N_{Sc}^{-.67} \qquad (B\text{-}4)$$

where:

N_{Sc} = the dimensionless Schmidt number which relates the diffusivity and gas viscosity, calculated to be 1.86 for nitrogen at these conditions.

$N_{Sc} = \mu/\rho D_v$

μ = viscosity, g/m · hr (multiply Centipoise [CP] by 3,600 to obtain this value;

ρ = density g/m^3;

D_v = diffusivity, m^2/hr;

U = the wind velocity (meters/hr) equal to the purge rate in m^3/hr, divided by [(.707)(tank diameter,m) (vapor space height,m)]; and

D = the pool diameter (meters).

To use this equation for evaporation in a tank head space, the pool diameter was taken to be the tank diameter.

The average velocity across the surface of the liquid is calculated to equal the flowrate divided by the term [(.707)(diameter)(height)]. The correction of .707 was calculated to account for tank geometry. It describes the average velocity of the material as it passes through the average available cross-sectional area.

Figures B-1 and B-2 are the graphical presentation of the results of using the MacKay and Matsugu correlation for estimating the rate of vaporization of toluene into a nitrogen purge gas stream for several different tank sizes and at two different temperatures. The composition of the exiting purge stream was calculated by material balance; the percent of saturation level is also shown. Even for a low purge rate of only 0.1 acfm across a small head space of an 8 ft diameter tank (typical for 3,000 to 6,000 gal storage), only 5 percent of saturation is attained.

Based on using the MacKay and Matsugu method it is clear that purge gas streams are substantially below the saturated level of VOC. Therefore, the assumption of saturation predicts much higher VOC loadings to the control device than could realistically be expected.

In a variation from the MacKay and Matsugu approach, the geometry of the vapor space of a purged tank may also be considered to be similar to that of a wetted wall column where the area of wetting is the surface area of the tank contents, and the diameter of the column would become the <u>effective</u> diameter (not the pool diameter) of the cross-section of the tank head space through which the purge gas sweeps at a calculated superficial velocity. Gilliland and Sherwood proposed the following correlation for wetted-wall columns

$$N_{Sh} = 0.023\ N_{Re}^{0.81} N_{Sc}^{0.44} \qquad \text{(B-5)}$$

where:

$N_{Sh} = kD_e\bar{M}/\rho D_v$ (N_{Sc}) as defined above

$N_{Re} = D_e V_s \rho/\mu$

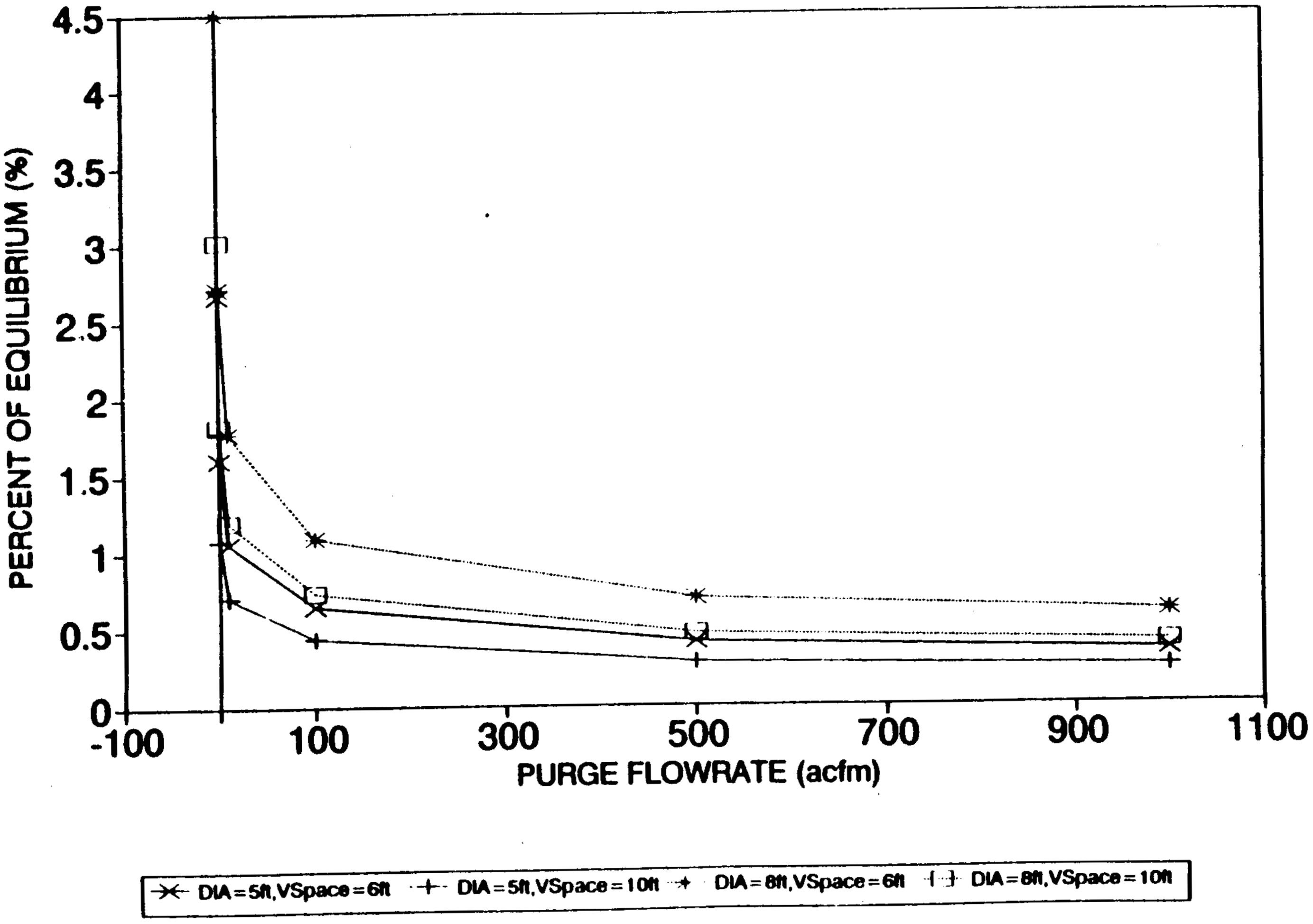


Figure B-1. Mackay/Matsugu method for toluene at 25C, Vp=29.9mmHg.

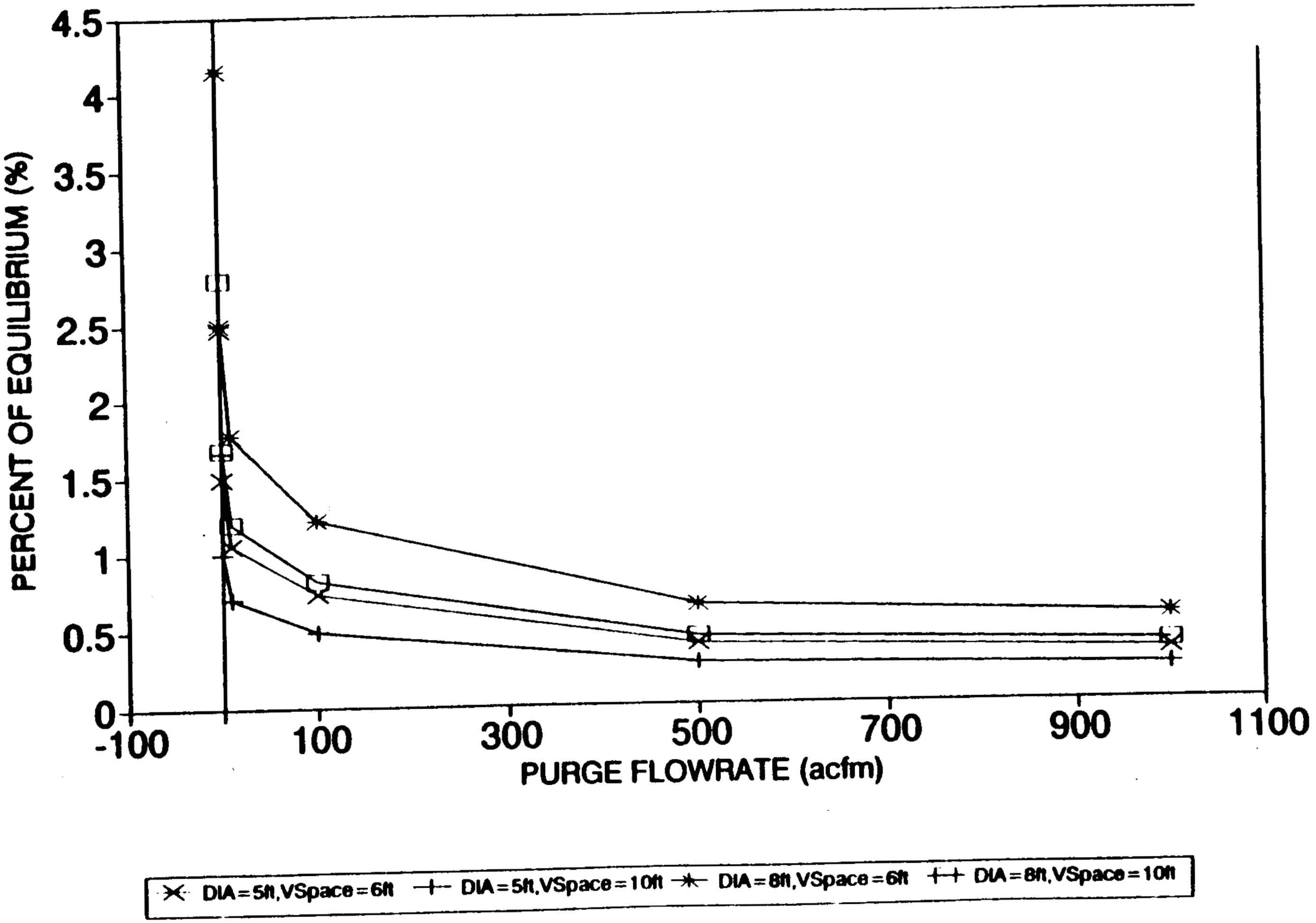


Figure B-2. Mackay/Matsugu method for toluene at 50C, VP=94.3mmHg.

The mass transfer coefficient, k, is contained in the Sherwood Number, N_{Sh}, which relates equivalent diameter, D_e; gas molecular weight, M; gas density, p; and vapor diffusivity, D_v. The Gilliland-Sherwood equation can be rearranged to solve directly for k; the units are moles per area per time.

The area of mass-transfer is the area of the surface of the tank contents. The driving force is the difference between the vapor concentration at the interface (assumed to be the saturation value) expressed as a mole-fraction, and the bulk gas composition (which is essentially zero). The rate of evaporation is thus expressed as

$$N/t = kA(y_i - y) \qquad \text{(B-7)}$$

Knowing the purge gas flow rate and evaporation rate, the composition of the exit gas can be calculated by material balance and compared to saturation composition.

A series of calculations were done using the wetted wall correlation for a storage tank of toluene being purged with nitrogen. Figures B-3 and B-4 are the graphical representations of the data. As with the MacKay and Matsugu approach, very low values of percent of saturation are obtained. For example, a low purge rate of 0.1 acfm across a small head space of an 8 foot diameter tank results in only 7.3 percent of saturation.

The calculated percentages of saturation equilibrium for most flowrates and vessel vapor spaces using both the wetted wall equations and the MacKay-Matsugu correlation yield low values, in the range of 0 to <10 percent, with most values below 5 percent. A conservative assumption for calculating the purge equilibrium fraction, therefore, would be to assume 10 percent. Note that, as the superficial velocity increases, k increases. As flow rate is increased, velocity also increases, but more inert gas is introduced to the system, thereby decreasing the percent equilibrium.

We can consider both equations bounded by the realistic superficial velocity across the liquid surface. Figure B-5 shows graphically the differences in values obtained for percent equilibrium for the MacKay-Matsugu correlation versus the Wetted Wall method. As the vapor space decreases (increasing superficial velocity), the percentage of equilibrium increases, especially in the low purge rate range. For vapor space values of 0.5 feet or less, the equations begin to approach higher values as the superficial velocity increases. In most purge situations, however, the vapor space above the vessel will be greater than 0.5 feet and the assumed 10 percent equilibrium fraction will be realistic.

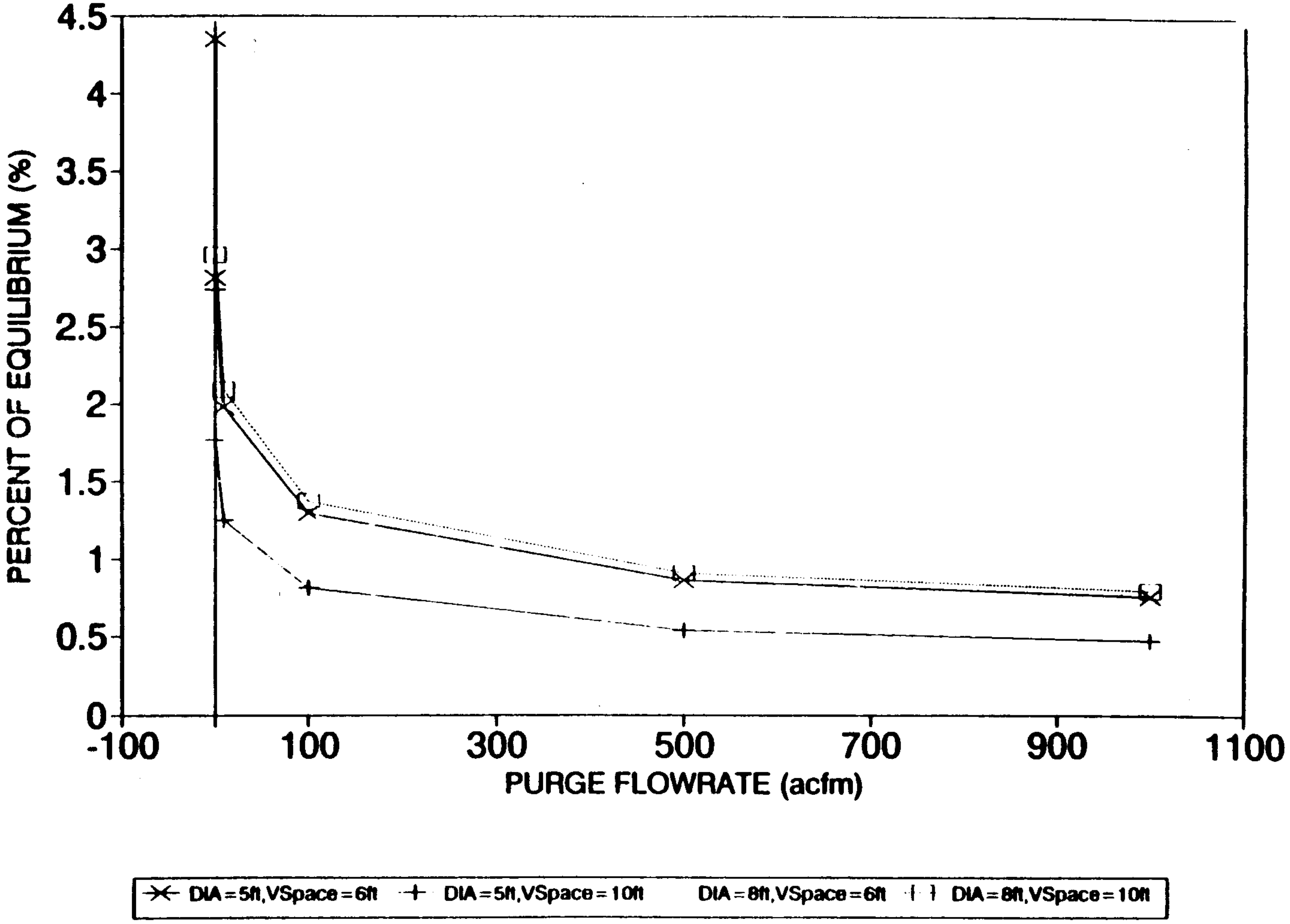


Figure B-3. "Wetted Wall" method for toluene @ 25C, VP=29.9mmHg.

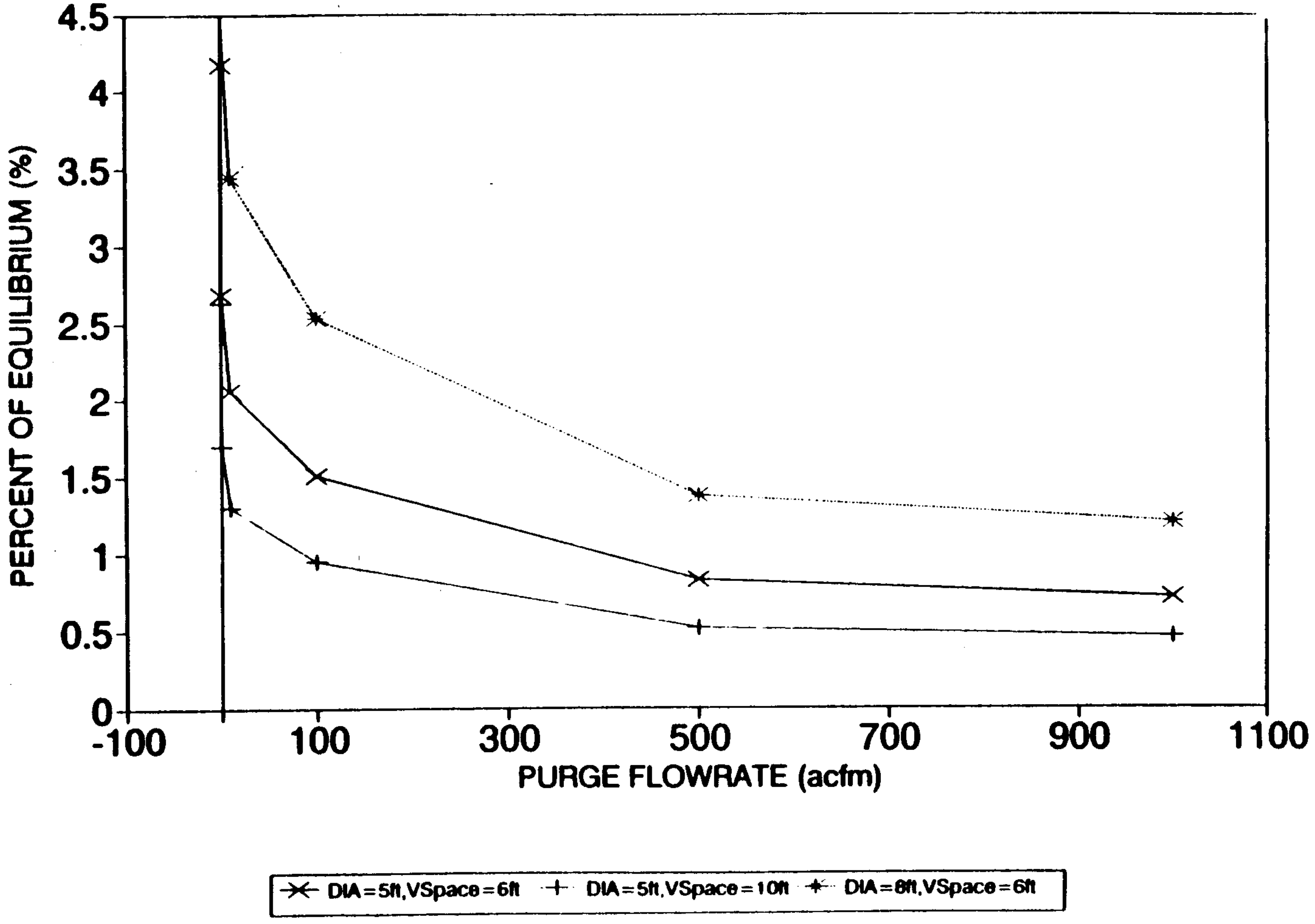


Figure B-4. "Wetted Wall" method for toluene @50C VP @ 50C=94.3mmHg.

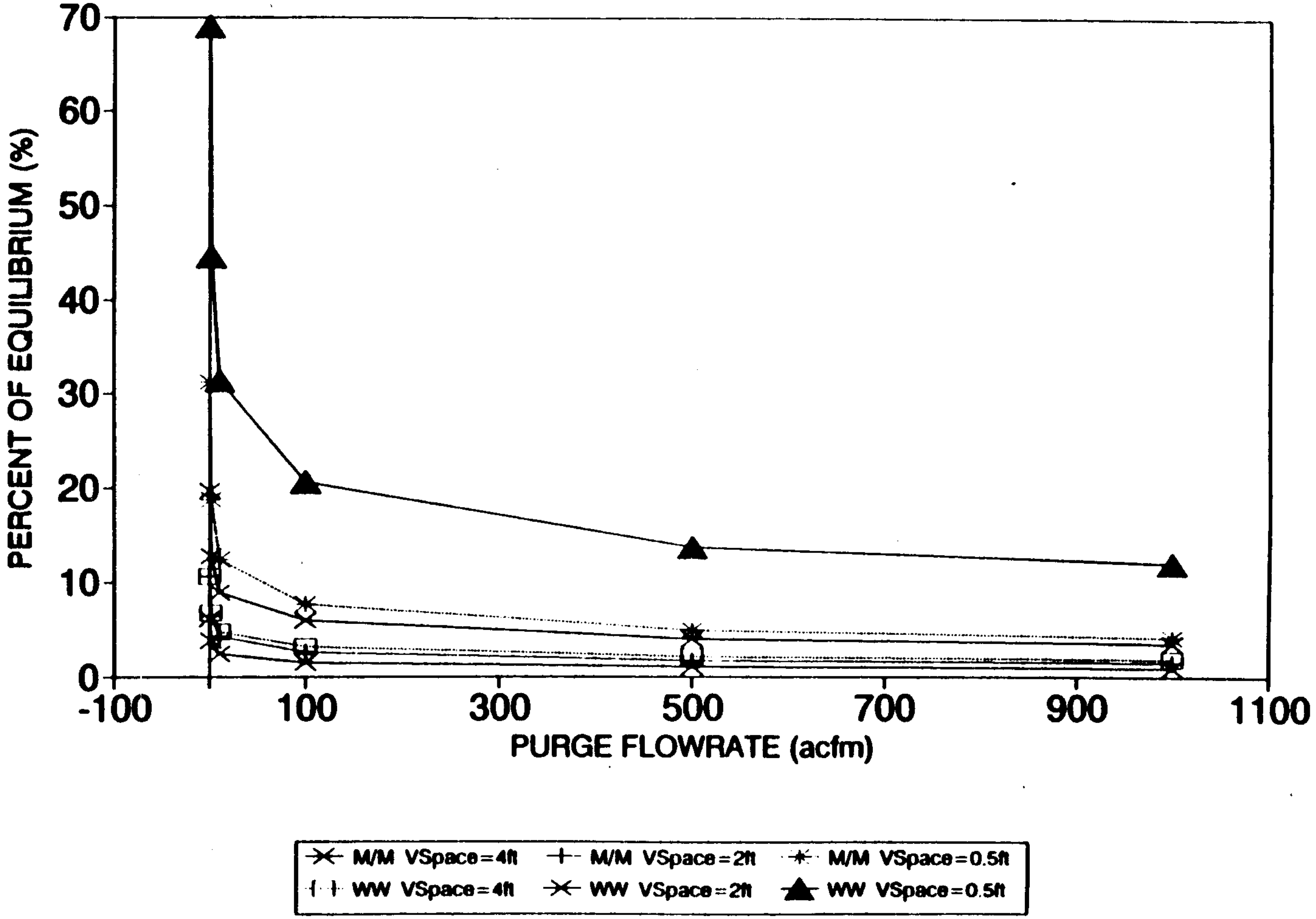


Figure B-5. Mackay/Matsugu "Wetted Wall" toluene at 25C=29.9 mmHg, diameter=8 ft.

In the case of mixed liquids (two or more components) the estimation of the mass transfer rate is somewhat more complex as it requires calculation of both the gas phase mass transfer coefficient, as explained above, and a liquid phase mass transfer coefficient. The liquid phase coefficient takes into account the rate of diffusion of the more volatile component through a film of the less volatile component, to the vapor-liquid interface where it can evaporate.

Furthermore, with binary or multicomponent liquid mixtures the mass transfer driving force is no longer simply expressed as the pure component vapor pressure divided by the total pressure. The equilibrium partial pressure is the driving force, but the calculation of that term is related to the liquid composition. The simple correction factor implied by Raoult's Law is to multiply the vapor pressure by the mole fraction in the liquid. However, in many real situations (e.g., dilute aqueous solutions of sparingly soluble organic solvents), the materials are highly nonideal, and application of Raoult's Law leads to substantial under estimation of the equilibrium vapor concentration of minor components.

The use of empirically determined Henry's Law constants for the estimation of vapor phase concentrations is a practical way to approach calculation of a realistic mass transfer driving force. This methodology is described in previous sections. In extreme cases of nonideality, the partial pressures of a mixture of compounds is greater than the vapor pressure of any of the pure compounds. This phenomenon is more readily observed where a mixture forms a low-boiling azeotrope. Obviously, in such cases application of empirical correlations (such as Henry's Law) is necessary for an accurate calculation of driving force.

But, in the case of purging of mixed liquids a second component in the liquid phase seriously decreases the value of the liquid mass transfer coefficient. Therefore, although the actual mass transfer driving force may be somewhat greater than estimated for a pure component, the overall mass transfer rate will not be, and the use of the fractional approach to equilibrium will be valid.

III. Inert N_2 Purging of Agitated Vessels

A. Sparging

Agitated vessels can be evaluated in the same way using mass transfer coefficients for stirred tanks. The coefficient of mass transfer through broken interfaces during sparging is given by the equations:

(B-8)

$$k_L = 1.0 \frac{(\epsilon V)^{0.25}}{N_{Sc}^{0.67}}$$

where:

(B-9)

$$\epsilon = \frac{4N^3D_i^3Y_N}{\pi} \left(\frac{D_i}{D_T}\right)^2 \left(\frac{D_i}{H_L}\right)$$

k_L = mass transfer coefficient, m/s;

V = m/s;

N_{Sc} = Schmidt No. of the sparge gas;

N = impeller speed, RPS;

D_i = impeller diameter, m;

Y_N = impeller power factor;

D_T = tank diameter, m; and

H_L = liquid depth, m.

Notice that mass transfer at this interface is liquid-phase controlled.

The amount of mass transfer that can occur is a function of the characteristics of the agitation scenario, including impeller size and speed. As an approximation, the tank with a five-foot diameter and a 6 ft. vapor space height containing toluene at 25°C was assumed to have an agitator with a 1 ft diameter impeller rotating at 0.5 revolutions per second. In absence of real data the power number was assumed to be 1.6, corresponding to a typical value in solid-liquid dispersion.

Using the sparge velocity as in other examples for purge velocity (i.e., flowrate divided by area of flow), much higher values of mass transfer coefficients are obtained. Saturation values for low sparge rates are considerably higher. For 100 acfm, the expected fraction of saturation was calculated to be 30 percent. Figure B-6 illustrates the values of percent equilibrium verses purge flowrate for this agitated sparge system. Table B-1 is the data in tabular form.

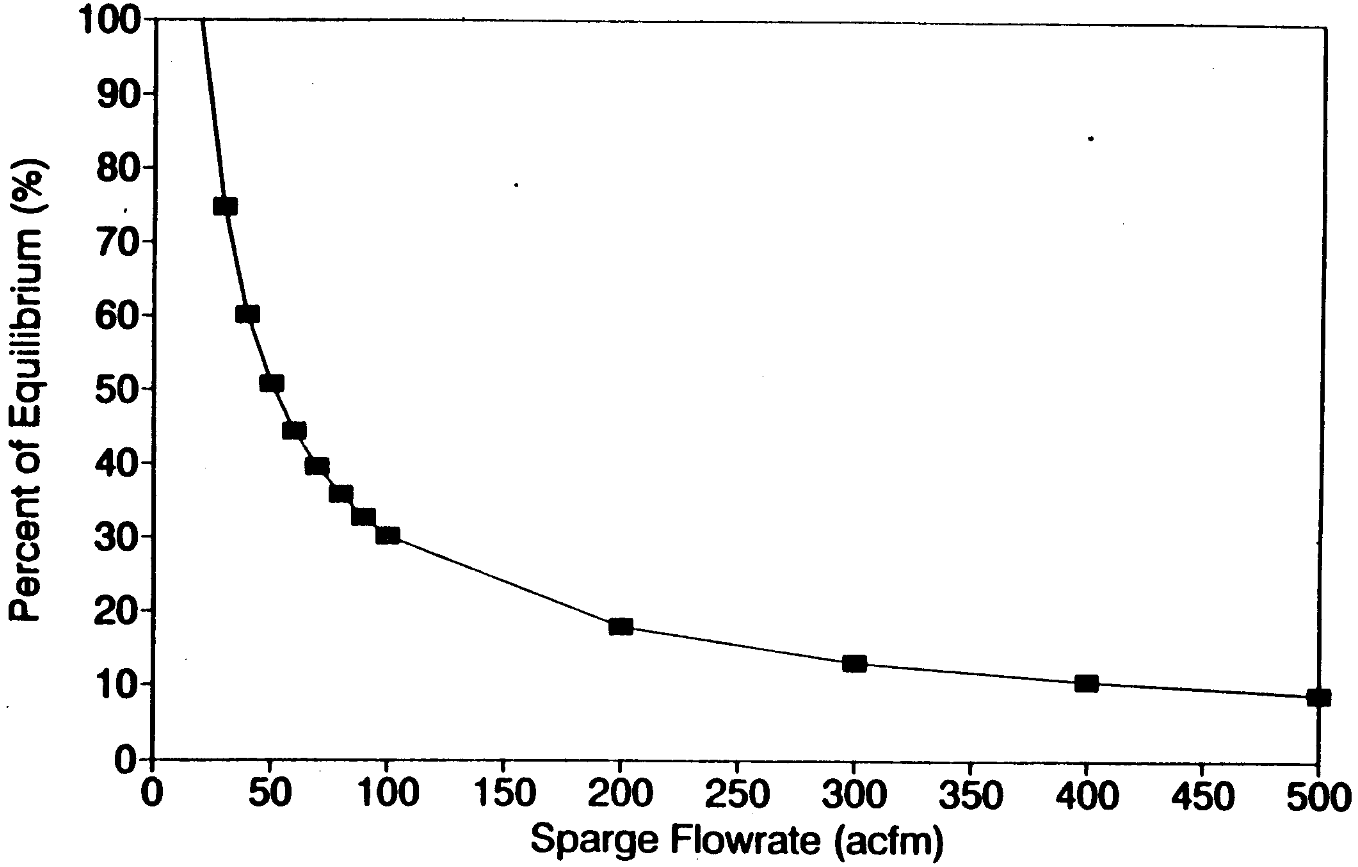


Figure B-6. Agitated Purging.

TABLE B-1. PURGE EQUILIBRIUM CALCULATION RESULTS FOR FIGURE B-6.

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Mass Transfer Through Broken Interfaces (Agitated Purge)
With Gas Sparging

Vessel Configuration:		**Process Liquid:**			**Impeller Diam (m):**	0.3048	**Liquid Depth (m):** 3
Diam.	5 ft	Name:	TOLUENE		**Power Number:**	1.6	
Vap Space	6 ft	Temp	25	Deg C	**Agit Speed (rps):**	0.5	
Agitator Power		VP	28.9	mm Hg			
		NSc	1.66				

Purge Flow Rate ACFM	Super. Veloc. ft/sec	SV^0.78 m/hr	De ^-0.11 m	NSc Ratio	NScR ^0.67	km m/hr	I gmol/m2/hr	N lbmol/hr	Purge lbmol/hr	y @ exit mol fr	y equil mol fr	Percent of Equil.	Percent of Stream	Epsilon (m2/sec3)	k (m/s)	k (m/hr)
0.1	0.0001	0.1479	0.955	1.452	1.284	0.0027	8.0628	0.0324	0.0153	2.11687	0.03934	5381	87.91655	8.29E-07	0.001393	5.014002
1	0.0008	0.8910	0.955	1.452	1.284	0.0161	14.3361	0.0676	0.1531	0.37644	0.03934	957	27.31875	8.29E-07	0.002477	8.916297
10	0.0079	5.3988	0.955	1.452	1.284	0.0987	25.4972	0.1025	1.5312	0.06694	0.03934	170	6.274136	8.29E-07	0.004404	15.85567
20	0.0157	9.2189	0.955	1.452	1.284	0.1695	30.3214	0.1219	3.0623	0.03980	0.03934	101	3.827989	8.29E-07	0.005238	18.85567
30	0.0236	12.6482	0.955	1.452	1.284	0.2325	33.5561	0.1349	4.5935	0.02937	0.03934	75	2.87268	8.29E-07	0.005796	20.86723
40	0.0314	15.8300	0.955	1.452	1.284	0.2910	36.0564	0.1450	6.1247	0.02367	0.03934	60	2.312015	8.29E-07	0.006229	22.4233
50	0.0393	18.8398	0.955	1.452	1.284	0.3463	38.1271	0.1533	7.6558	0.02002	0.03934	51	1.982710	8.29E-07	0.006586	23.70975
60	0.0471	21.7166	0.955	1.452	1.284	0.3992	39.9052	0.1604	9.1870	0.01746	0.03934	44	1.716161	8.29E-07	0.006838	24.61546
70	0.0550	24.4835	0.955	1.452	1.284	0.4502	41.4731	0.1667	10.7182	0.01556	0.03934	40	1.531678	8.29E-07	0.007164	25.79046
80	0.0629	27.1822	0.955	1.452	1.284	0.4997	42.8809	0.1724	12.2494	0.01407	0.03934	36	1.387730	8.29E-07	0.007407	26.66595
90	0.0707	29.7978	0.955	1.452	1.284	0.5477	44.1624	0.1775	13.7805	0.01286	0.03934	33	1.271601	8.29E-07	0.007629	27.46262
100	0.0786	32.3500	0.955	1.452	1.284	0.5947	45.3411	0.1823	15.3117	0.01190	0.03934	30	1.1784	8.29E-07	0.007832	28.19581
200	0.1572	56.5492	0.955	1.452	1.284	1.0211	53.9199	0.2166	30.6234	0.00709	0.03934	18	0.702844	8.29E-07	0.009314	33.53065
300	0.2357	78.2130	0.955	1.452	1.284	1.4008	59.6722	0.2399	45.9351	0.00522	0.03934	13	0.519507	8.29E-07	0.010308	37.10777
400	0.3143	96.3853	0.955	1.452	1.284	1.7534	64.1219	0.2578	61.2468	0.00421	0.03934	11	0.416106	8.29E-07	0.011076	39.87469
500	0.3929	113.5197	0.955	1.452	1.284	2.0867	67.8007	0.2726	76.5585	0.00356	0.03934	9	0.354751	8.29E-07	0.011712	42.16257
1000	0.7858	194.9282	0.955	1.452	1.284	3.5832	80.6291	0.3241	153.1169	0.00212	0.03934	5	0.21124	8.29E-07	0.013928	50.14002

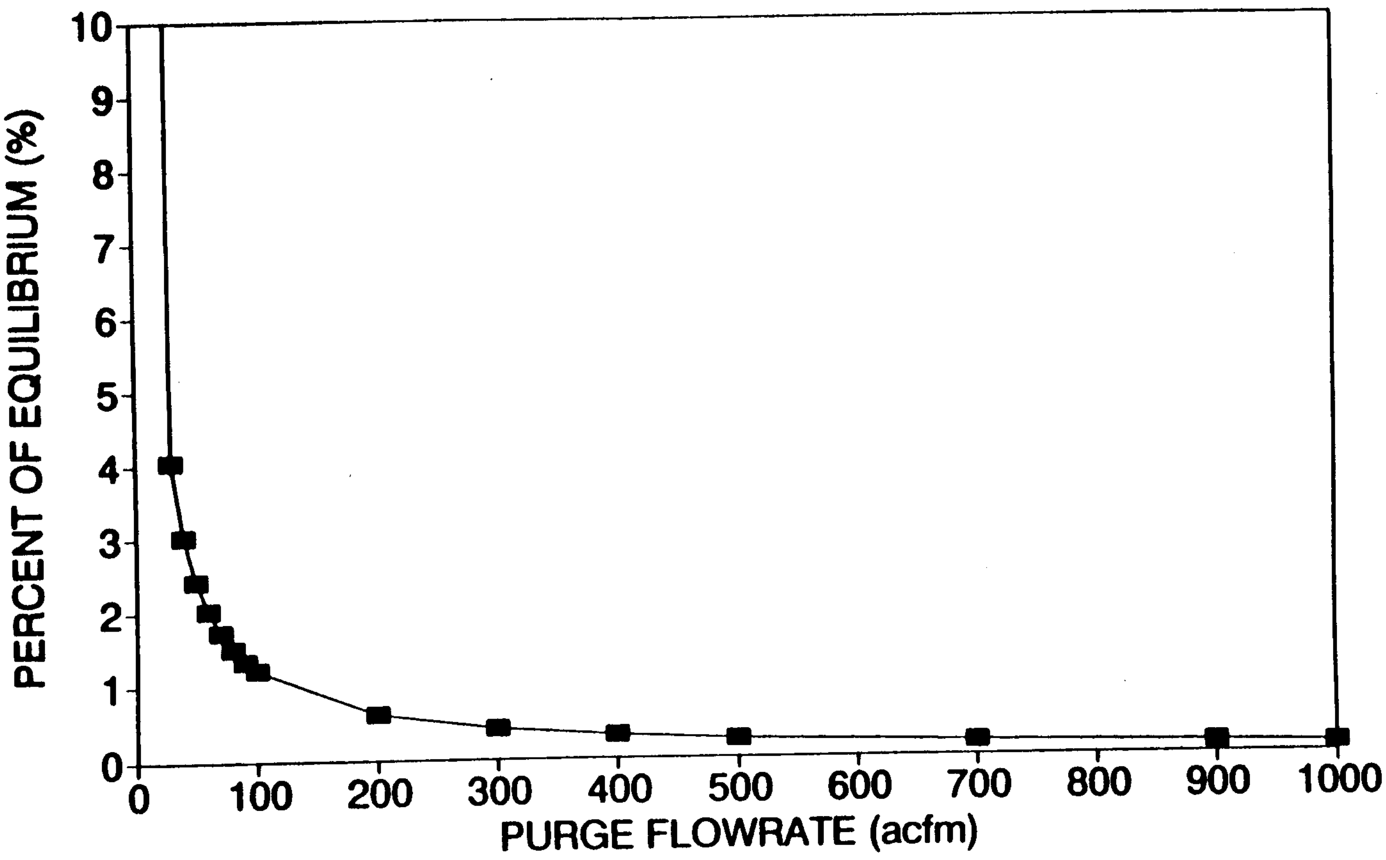

Figure B-7. Non-Sparge Agitated purge typical impeller scenario.

B. Agitated Purging

Mass transfer at gas-liquid agitated interfaces during nitrogen purging was also examined using the following liquid phase mass transfer coefficient:

$$k_L = \frac{.0256\ (\epsilon D_T)^{1/3}}{N_{Sc}^{1/2}} \qquad \text{(B-10)}$$

Figures B-7 and B-8 are the results of examining two different agitation scenarios. The first scenario, labelled the "typical" impeller scenario, is identical to the sparge impeller example discussed previously. It considers the use of a 1-foot diameter impeller rotating at .5 revolutions per second. Y_N, the power factor, is 1.6. The second scenario, presented in Figure B-8, considers the use of a 2-foot diameter impeller, rotating at 2 revolutions per second. The power factor also is higher, at 6.6. This scenario is termed "worst case", as an approximation of the maximum turbulence encountered during such a situation. Notice that values approaching 80% saturation are shown corresponding to typical purge flowrates of 20 to 30 scfm in Figure B-8 (data in Table B-3). Saturation values are much lower for the typical impeller scenario in Figure B-7 (data in Table B-2).

IV. Conclusions

The degree of saturation with VOC of a purge gas stream exciting a vessel containing VOC is highly dependent upon specific vessel geometries and liquid-vapor interface conditions. Values approaching complete saturation are not unrealistic for systems utilizing severe agitation or sparging, while much lower fractional saturation levels are expected for non-agitated purging events.

In order to provide a conservative, yet realistic approach to estimating the degree of saturation of an inert gas purge, the following guidelines are recommended:

1) for purge flowrates less than 100 scfm, assume that the vent streams exiting streams are completely saturated with VOCs.

(2) for purge flowrates greater than 100 scfm, assume that the vent streams exiting the vessel are 25% saturated with VOCs.

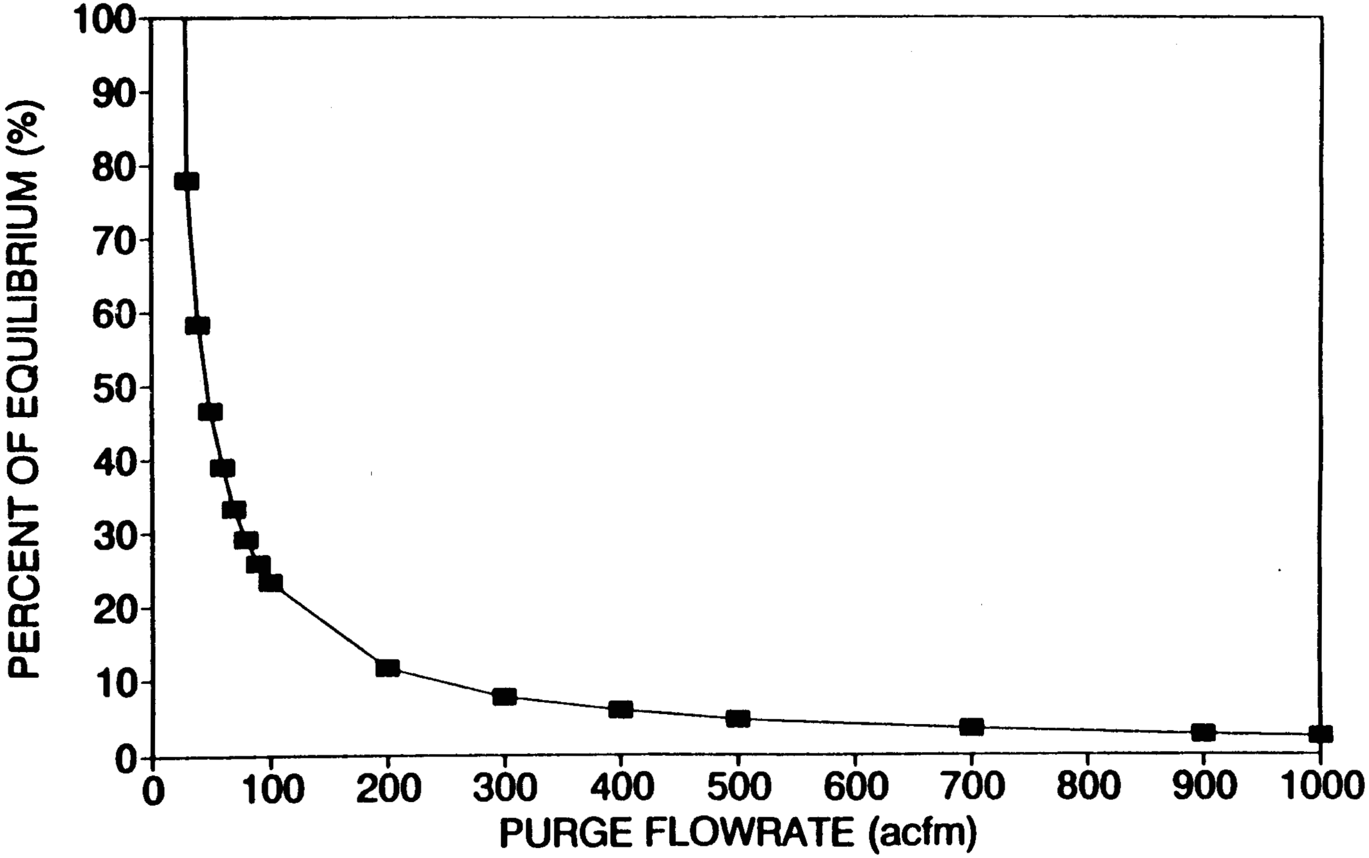

Figure B-8. Non-Sparge Agitated Purge worst case impeller scenario.

TABLE B-2. PURGE EQUILIBRIUM CALCULATION RESULTS FOR FIGURE B-7.

File:PURGEGAS

01-Dec-92

Mass Transfer Through Broken Interfaces (Agitated Purge)
Without Gas Sparging: Typical

Vessel Configuration:			**Process Liquid:**			**Impeller Diam (m):**	0.3048	**Liquid Depth (m):**	3
Diam.	5	ft	**Name:**	TOLUENE		**Power Number:**	1.6		
Vap Space	6	ft	**Temp**	25	Deg C	**Agit Speed (rps):**	0.5		
Agitator Power			**VP**	29.9	mm Hg				
			NSc	1.86					

Purge Flow Rate ACFM	Super. Veloc. ft/sec	SV^0.78 m/hr	De ^-0.11 m	NSc Ratio	NScR ^0.67	km m/hr	l gmol/ m2/hr	N lbmol/ hr	Purge lbmol/ hr	y @ exit mol fr	y equil mol fr	Percent of Equil.	Percent of Stream	Epsilon (m2/sec3)	k (m/s)	k (m/hr)
=====	=====	=====	====	====	====	=====	=====	=====	=====	=====	=====	=====	======			
0.1	0.0001	0.1479	0.955	1.452	1.284	0.0027	1.2291	0.0049	0.0153	0.32269	0.03934	820	24.39651	8.29E-07	0.000212	0.764321
1	0.0008	0.8910	0.955	1.452	1.284	0.0164	1.2291	0.0049	0.1531	0.03227	0.03934	82	3.126029	8.29E-07	0.000212	0.764321
10	0.0079	5.3688	0.955	1.452	1.284	0.0987	1.2291	0.0049	1.5312	0.00323	0.03934	8	0.321652	8.29E-07	0.000212	0.764321
20	0.0157	9.2189	0.955	1.452	1.284	0.1695	1.2291	0.0049	3.0623	0.00161	0.03934	4	0.161085	8.29E-07	0.000212	0.764321
30	0.0236	12.6482	0.955	1.452	1.284	0.2325	1.2291	0.0049	4.5935	0.00108	0.03934	3	0.107446	8.29E-07	0.000212	0.764321
40	0.0314	15.8300	0.955	1.452	1.284	0.2910	1.2291	0.0049	6.1247	0.00081	0.03934	2	0.080608	8.29E-07	0.000212	0.764321
50	0.0393	18.8398	0.955	1.452	1.284	0.3463	1.2291	0.0049	7.6558	0.00065	0.03934	2	0.064499	8.29E-07	0.000212	0.764321
60	0.0471	21.7196	0.955	1.452	1.284	0.3992	1.2291	0.0049	9.1870	0.00054	0.03934	1	0.053753	8.29E-07	0.000212	0.764321
70	0.0550	24.4935	0.955	1.452	1.284	0.4502	1.2291	0.0049	10.7182	0.00046	0.03934	1	0.046077	8.29E-07	0.000212	0.764321
80	0.0629	27.1822	0.955	1.452	1.284	0.4997	1.2291	0.0049	12.2494	0.00040	0.03934	1	0.04032	8.29E-07	0.000212	0.764321
90	0.0707	29.7978	0.955	1.452	1.284	0.5477	1.2291	0.0049	13.7805	0.00036	0.03934	1	0.035842	8.29E-07	0.000212	0.764321
100	0.0786	32.3500	0.955	1.452	1.284	0.5947	1.2291	0.0049	15.3117	0.00032	0.03934	1	0.032259	8.29E-07	0.000212	0.764321
200	0.1572	55.5482	0.955	1.452	1.284	1.0211	1.2291	0.0049	30.6234	0.00016	0.03934	0	0.016132	8.29E-07	0.000212	0.764321
300	0.2357	76.2130	0.955	1.452	1.284	1.4009	1.2291	0.0049	45.9351	0.00011	0.03934	0	0.010755	8.29E-07	0.000212	0.764321
400	0.3143	95.3853	0.955	1.452	1.284	1.7534	1.2291	0.0049	61.2468	0.00008	0.03934	0	0.008067	8.29E-07	0.000212	0.764321
500	0.3929	113.5197	0.955	1.452	1.284	2.0867	1.2291	0.0049	76.5585	0.00006	0.03934	0	0.006453	8.29E-07	0.000212	0.764321
1000	0.7858	194.9282	0.955	1.452	1.284	3.5832	1.2291	0.0049	153.1169	0.00003	0.03934	0	0.003227	8.29E-07	0.000212	0.764321

TABLE B-3. PURGE EQUILIBRIUM CALCULATION RESULTS FOR FIGURE B-8.

File:PURGEGAS 01-Dec-92

Mass Transfer Through Broken Interfaces (Agitated Purge)
Without Gas Sparging: Worst Case

Vessel Configuration:			**Process Liquid:**			**Impeller Diam (m):**	0 61	**Liquid Depth (m):**	3
Diam.	5	ft	Name:	TOLUENE		Power Number:	6.6		
Vap Space	6	ft	Temp	25	Deg C	Agit Speed (rps):	2		
Agitator Power			VP	29.9	mm Hg				
			NSc	1.86					

Purge Flow Rate ACFM	Super. Veloc. ft/sec	SV^0.76 m/hr	De ^-0.11 m	NSc Ratio	NScR ^0.67	km m/hr	I gmol/ m2/hr	N lbmol/ hr	Purge lbmol/ hr	y @ exit mol fr	y equil mol fr	Percent of Equil.	Percent of Stream	Epsilon (m2/sec3)	k (m/s)	k (m/hr)
0.1	0.0001	0.1479	0.955	1.452	1.284	0.0027	24.3154	0.0977	0.0153	6.38366	0.03934	16227	66.45696	0.007024	0.0042	15.1206
1	0.0008	0.8910	0.955	1.452	1.284	0.0164	24.3154	0.0977	0.1531	0.63839	0.03934	1623	36.9644	0.007024	0.0042	15.1206
10	0.0079	5.3686	0.955	1.452	1.284	0.0987	24.3154	0.0977	1.5312	0.06384	0.03934	162	6.000796	0.007024	0.0042	15.1206
20	0.0157	9.2189	0.955	1.452	1.284	0.1695	24.3154	0.0977	3.0623	0.03192	0.03934	81	3.093207	0.007024	0.0042	15.1206
30	0.0236	12.6482	0.955	1.452	1.284	0.2325	24.3154	0.0977	4.5935	0.02128	0.03934	54	2.083621	0.007024	0.0042	15.1206
40	0.0314	15.8300	0.955	1.452	1.284	0.2910	24.3154	0.0977	6.1247	0.01596	0.03934	41	1.570889	0.007024	0.0042	15.1206
50	0.0393	18.8396	0.955	1.452	1.284	0.3463	24.3154	0.0977	7.6558	0.01277	0.03934	32	1.26066	0.007024	0.0042	15.1206
60	0.0471	21.7186	0.955	1.452	1.284	0.3992	24.3154	0.0977	9.1870	0.01064	0.03934	27	1.052779	0.007024	0.0042	15.1206
70	0.0550	24.4935	0.955	1.452	1.284	0.4502	24.3154	0.0977	10.7182	0.00912	0.03934	23	0.903741	0.007024	0.0042	15.1206
80	0.0629	27.1822	0.955	1.452	1.284	0.4997	24.3154	0.0977	12.2494	0.00798	0.03934	20	0.791666	0.007024	0.0042	15.1206
90	0.0707	29.7976	0.955	1.452	1.284	0.5477	24.3154	0.0977	13.7805	0.00709	0.03934	18	0.704324	0.007024	0.0042	15.1206
100	0.0786	32.3600	0.955	1.452	1.284	0.5947	24.3154	0.0977	15.3117	0.00638	0.03934	16	0.634336	0.007024	0.0042	15.1206
200	0.1572	55.5492	0.955	1.452	1.284	1.0211	24.3154	0.0977	30.6234	0.00319	0.03934	8	0.318178	0.007024	0.0042	15.1206
300	0.2357	76.2130	0.955	1.452	1.284	1.4309	24.3154	0.0977	45.9351	0.00213	0.03934	5	0.212344	0.007024	0.0042	15.1206
400	0.3143	96.3853	0.955	1.452	1.284	1.7534	24.3154	0.0977	61.2468	0.00160	0.03934	4	0.159343	0.007024	0.0042	15.1206
500	0.3928	113.5187	0.955	1.452	1.284	2.0867	24.3154	0.0977	76.5585	0.00128	0.03934	3	0.127515	0.007024	0.0042	15.1206
1000	0.7858	194.9282	0.955	1.452	1.284	3.5832	24.3154	0.0977	153.1169	0.00064	0.03934	2	0.063798	0.007024	0.0042	15.1206

Calculational Issue 2: Incremental Cost Analysis of Manifolding Single Unit Operations to a Control Device

I. General

The incremental cost effectiveness of manifolding single unit operations to a control device was examined. Ductwork diameter for an emission source to a control device was estimated by assuming an average surficial velocity through the duct to be 2,000 ft/min. The duct costs are based on stainless steel, circular duct prices. The analysis describes ductwork cost as a function of length of ducting and emission source flowrate. Calculations are provided below. The results of the analysis show a minimum level of 500 pounds per year of VOC emissions is necessary to yield an incremental cost effectiveness comparable to the average cost effectiveness of RACT. This is the deminimis level for applicability of RACT to any single unit operation. Figure B-9 shows the incremental ducting analysis results for 0 to 300 feet of duct versus mass emissions. Table B-4 is the cost analysis data.

Calculations

Assume:

$$\text{Velocity} = 2{,}000 \text{ ft/min}$$

$$\text{Flowrate} = (\text{Area})(\text{velocity})$$

$$\text{Flowrate} = (\pi r^2)(2{,}000 \text{ ft/min})$$

$$\frac{\text{Flowrate}}{2{,}000 \text{ ft/min}} = \pi \frac{d^2}{4}$$

$$d(\text{ft}) = \sqrt{(0.0064)(\text{Flowrate})}$$

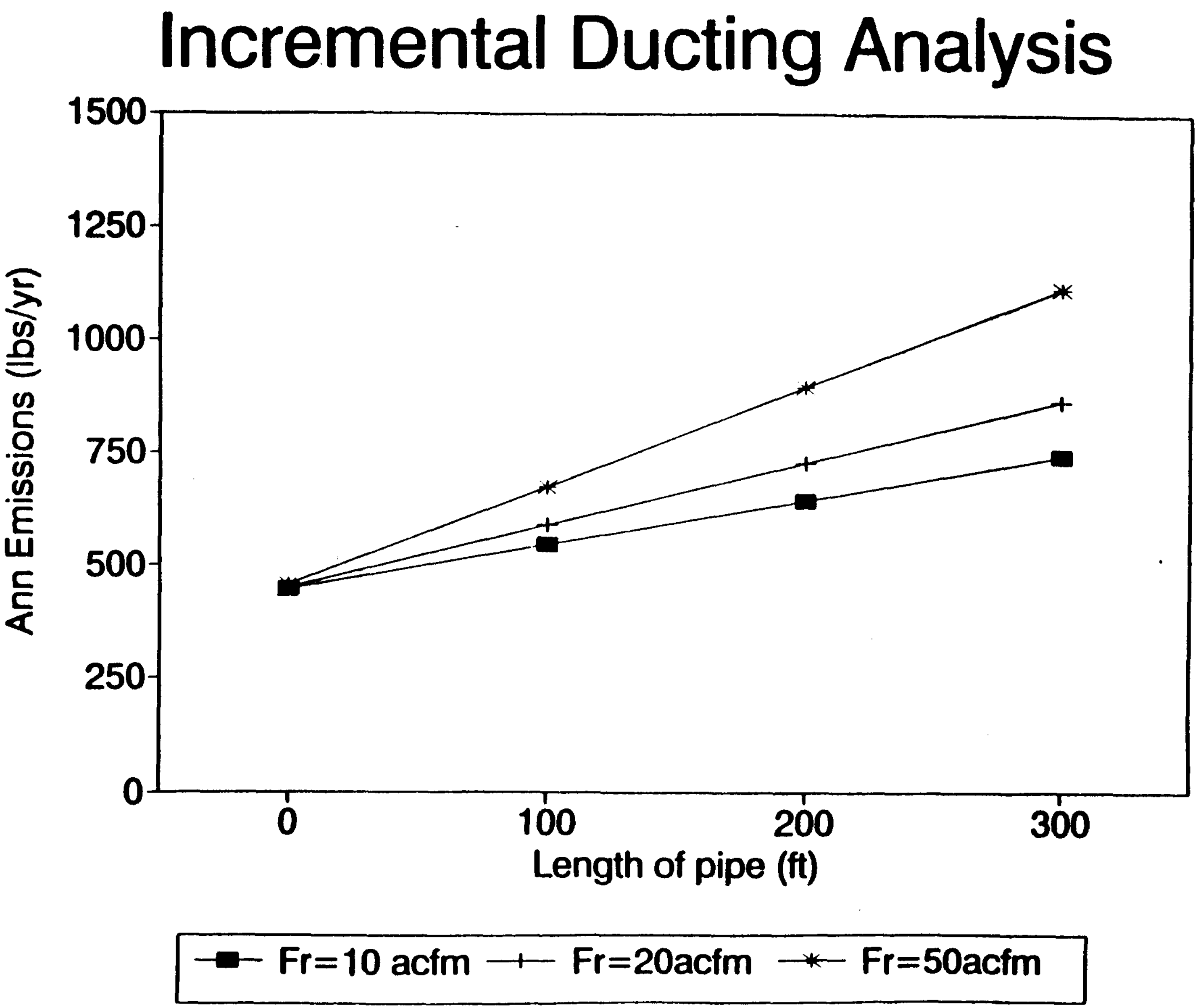

Figure B-9. Incremental Ducting Analysis Results

TABLE B-4. COST ANALYSIS DATA

Cost Analysis -- Manifolding Cost Analysis

Flowrate (acfm)	Length (ft)	FOB Cost Total (June 92 $)	TCI (June 1992)	Annualized	Mg Cap	Lbs
10	0	1174.385	2009.372	407.4002	0.2037	448.6787
10	100	1430.529	2447.636	496.2581	0.248129	546.5398
10	200	1686.674	2885.899	585.116	0.292558	644.4009
10	300	1942.818	3324.162	673.9738	0.336987	742.2619
20	0	1182.414	2023.111	410.1857	0.205093	451.7464
20	100	1544.657	2642.908	535.8497	0.267925	590.1428
20	200	1906.9	3262.706	661.5137	0.330757	728.5393
20	300	2269.143	3882.504	787.1777	0.393589	866.9358
50	0	1198.346	2050.369	415.7124	0.207856	457.833
50	100	1771.102	3030.356	614.4046	0.307202	676.6571
50	200	2343.859	4010.342	813.0969	0.406548	895.4811
50	300	2916.615	4990.328	1011.789	0.505895	1114.305

Costs

Manifold costs include ductwork, damper, and elbows. Below are the costs for the individual components for a manifold.

Stainless Steel Round Duct

A 0.25 inch-thick stainless steel duct is the first component of the manifold. The cost of this duct is based on the amount of steel required, as decided in Chemical Engineering magazine.[5]

$$\text{Volume} = 2\pi RL(t)$$

$$= (2\pi)\left({}^{D}/2\right)(L)\left({}^{0.25}/12\right)$$

$$\text{Specific Gravity Stainless} = .29\text{lb/in}^3$$

$$= \left(\frac{.25\pi DL}{12}\right)\left(\frac{.29\,lb}{\text{inches}^3}\right)\left(\frac{12\text{inches}}{\text{ft}}\right)^3$$

$$\text{lbs steel} = (32.8)(D)(L)$$

where,

$$D = \sqrt{(0.00064)(\text{Flowrate})}$$

So,

$$\$/ft = (32.8)(\sqrt{0.00064\ \text{Flowrate}})$$

The price of stainless steel is \$1.03/lb

$$= (32.8)(\$1.03/\text{lb})(0.0253)(\text{Flowrate})^{.5}$$

$$= 0.85\ (\text{Flowrate})^{0.5}$$

This cost is adjusted to June 1992 dollars by the ratio of indices of $^{359.6}/376.3$.[6]

$$\$/\text{ft} = 0.81\ (\text{Flowrate})^{0.5}$$

Damper:

The cost of a stainless steel circular damper was estimated from a graph in the EAB Cost Manual.[7] Several points were taken from the graph of diameter of damper, versus dollars. These points were:

D(in)	$
20	2,300
30	3,200
40	4,000
50	5,000
60	6,300

A regression line was developed from this data.

$$Y = 98(D) + 240$$

This line was multiplied by a factor, 3, to get the cost for a stainless steel damper, in accordance with the referenced manual.

$$Y = 294(D) + 720$$

Cost was adjusted to June 1992 dollars from December 1978 dollars using appropriate indices.[8]

$$Y = 294(D) + 720 \left({}^{358.7}/223.7\right)$$

$$Y(\$/\text{damper}) = 471(D) + 1{,}155, \text{ where D is in inches}$$

$$D(ft) = \sqrt{0.00064 \text{ Flowrate},}$$

So,

$$\$/\text{damper} = (471)\sqrt{\frac{0.00064}{12}(\text{Flowrate})}+1{,}155$$

$$= (3.45)(\text{Flowrate})^{0.5} + 1{,}155$$

Elbows

Two elbows are assumed to be needed for each source. Costs were based on Chemical Engineering Magazine article.[5]

$$\$/\text{elbow} = (0.81)(1.65)(\text{Flowrate})^{0.5}$$

$$= 1.34\ (\text{Flowrate})^{0.5}$$

Total cost of manifold is therefore:

$$\boxed{\begin{array}{l} \$ = [.81\ (FR)^{.5}]_{5} \bullet \text{ (Feet of Duct)} \\ \quad + 1.34\ (FR)^{.5}\ (2) + 3.45\ (FR)^{.5} + 1{,}155 \end{array}}$$ (Free on Board)

FOB Prices are corrected to Total Capital Investment (TCI) using the following elements:

Inst, Sales Tax, Freight = (.18)(FOB$); Purchased Equipment Cost (PEC) = (1.18 FOB)

Direct Costs:[9]

Foundation	(.08)	(PEC)
Handling	(.14)	(PEC)
Electrical	(.04)	(PEC)
Piping	(.02)	(PEC)
Insulation	(.01)	(PEC)
Painting	(.01)	(PEC)

= .3 (PEC)

Indirect Costs:[10]

Engineering = (.10)(PEC)

Construction and Field Expense = (.05)(PEC)

= .15(PEC)

$$\therefore \text{TCI} = (FOB) + (.18)(FOB) + (.3)(1.18)(FOB) + (.15)(1.18FOB)$$
$$\text{TCI} = FOB\ (1 + .18 + .354 + .177)$$
$$\text{TCI} = 1.711\ FOB$$

Indirect Annual Costs[11]

Admin.	2% TCI
Prop. Tax	1% TCI
Insurance	1% TCI
Cap Rec.	(.16275) (10 yrs, 10%)

REFERENCES FOR APPENDIX B

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4. Agitation in Multiphase Systems, Hydrocarbon Processing, July 1979.

5. Chemical Engineering, May 1990, p. 127.

6. Chemical Engineering, September 1992, cost index.

7. Neveril, R. B., Gard, Inc. Capital and Operating Costs of Selected Air Pollution Control Systems. EPA450/5-80-002. December 1978.

8. Reference 6.

9. OAQPS Control Cost manual, EPA 450/3-90-006, January 1990.

10. Reference 10.

11. Reference 10.

APPENDIX C.

SAMPLE CALCULATIONS

Example 1. Vapor displacement of a single component liquid

Example 2. Vapor displacement of a homogenous mixture

Example 3. Tank/reactor heatup losses

Example 4. Empty tank and reactor purging

Example 5. Filled tank and reactor purging

Example 6. Sparging volatilization

Example 7. Vacuum dryer emissions

Example 8. Atmospheric dryer emissions

Example 9. Vessel Depressurization

Example 10. Emissions from a steam ejector

Example 11. Emissions from equipment leaks

Example 1. Vapor displacement of a homogenous liquid

A 5,000-gallon reactor is to be filled at ambient conditions (25°C and 1 atm) with 3,600 gallons of benzene. The fill rate is 60 gallons per minute and the reactor vent is open to the atmosphere. Calculate VOC emissions from this event.

Solution
Step 1. Define the conditions of the displaced gas:

Temperature = 298K (25°C - ambient)

Pressure = 1 atmosphere (760 mmHg, 14.7 psia)

Volumetric rate of displacement = 60 gallons/minute

Step 2. Calculate the vapor phase mole fractions of the components in the displaced gas:

In this situation, benzene is the only component in the liquid, therefore x_i in equation 3-9 is 1.

Using Raoult's Law:

$$y_i = \frac{x_i P^*}{P_T}$$

where:

$x_i = 1$
P^* (vapor pressure of benzene at 25°C [77°F]) = 1.9 psia.
(From Table A-2.)
P_T = 1 atm (14.7 psia)

$$y_i = \frac{(1)(1.9 \text{ psia})}{(14.7 \text{ psia})} = 0.13$$

Therefore, the gas in the vapor space will be 13 percent by volume benzene.

Step 3. Calculate the emission rate:

$$E_R = \frac{(y_i)(\dot{V})(P_T)(M_w)}{(R)(T)}$$

$$E_R = \frac{(0.13)\ (60\ \text{gal/min})\ (1\ \text{atm})\ (78\ \text{lbmol})\left[\dfrac{\text{ft}^3}{7.48\ \text{gal}}\right]}{(1.3144\ \text{atm ft}^3/\text{lbmol K})\ (298\text{K})}$$

E_R = 0.21 lb/min benzene

Since there are 3,600 gal of benzene to be charged, the event will take

$$\frac{3{,}600\ \text{gal}}{60\ \text{gal/min}} = 60\ \text{min}$$

Therefore, total benzene emissions for this event are:

(0.21 lb/min)(60 min/event) = 12.6 lb/event

Example 2. Vapor displacement of a homogenous (miscible) mixture

A 50-50 volume percent solvent mixture of heptane and toluene is charged to a surge tank at the rate of 300 gal/min. A total of 1,500 gal is charged. The mixture temperature is 20°C. Calculate emission rates for both mixture components.

Solution

Step 1. Define conditions of the displaced gas:

1. Temperature of displaced gas: 20°C;
2. Pressure = 1 atm (14.7 psia, 760 mmHg); and
3. Rate of displacement = 300 gal/min.

Step 2. Calculate vapor phase mole fraction:

VOC	Molecular weight, lb/lbmole	Density, lb/gal	Gallons charged	Pounds	lbmoles	x_i
Heptane	100	5.7	750	4,275	42.8	0.42
Toluene	92	7.3	750	5,475	59.5	0.58
				TOTAL	102.3	1.0

P* heptane @ 20°C (68°F) = 0.7 psia

P* toluene @ 20°C (68°F) = 0.4 psia

$$y_i = \frac{x_i (P^*)}{P_T}$$

$$\text{Heptane: } \frac{(0.42)(0.7 \text{ psia})}{(14.7 \text{ psia})} = 0.020 = y_{heptane}$$

$$\text{Toluene: } \frac{(0.58)(0.4 \text{ psia})}{(14.7 \text{ psia})} = 0.016 = y_{toluene}$$

Step 3. Calculate emission rate:

$$E_{R_{heptane}} = \frac{(y_{heptane})\dot{V}(P_T)(M_w)}{R_T}$$

$$E_{R_{heptane}} = \frac{(0.020)\ (300\ gal/min)\ (1\ atm)\ (100\ lb/lbmol)\ \left[\frac{ft^3}{7.48\ gal}\right]}{1.3144\ atm\ ft^3/lbmol\ K)\ (293K)}$$

$$E_{R_{heptane}} = 0.21\ lb/min$$

$$E_{R_{toluene}} = \frac{(y_{toluene})(\dot{V})(P_T)(M_w)}{R_T}$$

$$E_{R_{toluene}} = \frac{(0.016)\ (300\ gal/min)\ (1\ atm)\ (92\ lb/lbmol)\ \left[\frac{ft^3}{7.48\ gal}\right]}{\left[\frac{1.3144\ atm\ ft^3}{lbmol\ K}\right]\ (293K)}$$

$$E_{R_{toluene}} = 0.15\ lb/min$$

Therefore, total emissions for the event

Heptane: (0.21 lb/min)(5 min) = 1 lb

Toluene (0.15 lb/min)(5 min) = 0.75 lb

Example 3. Tank/reactor heatup losses

A 2,000 gal reactor, 75 percent full of a solution of a raw material in toluene is heated from 20°C to 70°C. The reactor is vented to the atmosphere during the heatup; how much toluene will be emitted?

Solution

Since the liquid is mostly toluene, a simplifying assumption is that the partial pressure of toluene in the headspace is equal to the vapor pressure. At 20°C, the vapor pressure of toluene is 22 mmHg; at 70°C it is 200 mmHg. The head space of the reactor is 500 gal or 66.8 ft^3. The temperatures must be expressed in absolute units K. The gas constant, R_1 in appropriate units (from Table A-3) is 998.9 mmHg-ft^3/lbmol-°K. The weight of toluene emitted is then directly calculated:

$$\Delta\eta = \left[\frac{66.8\ \text{ft}^3}{998.9\ \frac{\text{mmHg ft}^3}{\text{lbmol K}}}\right]\left[\left(\frac{760-22\ \text{mmHg}}{(273+20)\ \text{K}}\right) - \left(\frac{760-200\ \text{mmHg}}{(273+70)\ \text{K}}\right)\right]$$

$$\Delta\eta = 0.0592\ \text{lbmoles non-VOC gas displaced}$$

$$\eta_S = \frac{\left(\frac{22\ \text{mmHg}}{760-22\ \text{mmHg}}\right) + \left(\frac{200\ \text{mmHg}}{760-200\ \text{mmHg}}\right)}{2}\ (0.0592\ \text{lbmoles gas})$$

$$\eta_S = 0.01195\ \text{lbmoles toluene}\ (92.13\ \text{lb toluene/lbmole})$$
$$= 1.06\ \text{lb toluene}$$

Example 4. Empty tank and reactor purging

A 2,000 gallon reactor vessel was cooled to 20°C and the contents, in acetone solvent, were pumped out leaving only vapors. If this vessel is then purged with 1,000 scf of nitrogen at 20°C, how much VOC (acetone) will be contained in the vented nitrogen?

Solution

At 20°C the vapor pressure of acetone is 182 mm Hg. Thus, the initial concentration can be calculated from Ideal Gas Law:

$$PV = nRT$$

$$n/V = P_{acetone}/RT$$

Concentration of acetone $= P_{acetone}M_W/RT$

$MW = 58.08$ lb/lbmol

$R = 998.9$ mmHg ft^3/lbmol K

$T = 273+20 = 293$K

$P_{acetone} =$ 182 mmHg (partial pressure of acetone equals vapor pressure, since acetone is the only component)

$$C_i = \frac{(182\ \text{mmHg})(58.08\ \text{lb/lbmol})}{(998.9\ \text{mmHg ft}^3/\text{lbmol K})(293\text{K})} = 0.036\ \text{lb/ft}^3$$

(C_i = Initial concentration in the reactor vessel)

The number of volume changes of inert gas is as follows:

[1,000 scf][(273+20)/273] = 1,073 acf

(2,000 gal)(ft^3/7.48 gal) = 267 ft^3
1,073/267 = 4 (vessel volume changes = 4.0)

Plugging the values back into equation 3-14 yields:

$C_f/C_i = (0.37)^{4.0} = 0.0187$ lb/ft^3

Thus, $C_f = 0.0187(0.036) = 0.000673$ lb/ft^3

Emissions = (vessel volume)($C_i - C_f$)
= 267 ft^3 (0.000673 lb/ft^3)
= 9.43 lb

Example 5. Filled Tank and Reactor Purging

A tank containing methanol at 25°C is purged with a 30 scfm stream of nitrogen. Calculate the emission rate of methanol during the purge.

VP_{MEOH} at 25°C = 128 mmHg

$$\frac{\eta_{MEOH}}{\eta_{N2}} = \frac{128}{760-128} = .20$$

$$(30 \text{ scfm}) \left(\frac{1 \text{ mole}}{359 \text{ scfm}}\right) \left[\frac{.20 \text{ moles MEOH}}{\text{lb mole } N_2}\right] \left(\frac{32 \text{ lb}}{1 \text{ mole}}\right) = .5 \text{ lbs/min MEOH}$$

Example 6. Calculation of Sparging Volatilization

A 1,000-gal tank of wastewater containing 0.025 wt% toluene is to be air sparged to remove the toluene to a concentration level of less than 20 ppb (by weight) to permit discharge to a municipal sewer system. Ambient air is to be used; the design temperature is 20°C. Toluene-water vapor-liquid equilibrium at 20°C can be approximated using a Henry's Law constant of 370 atm (Henry's Law constants are listed in the Appendix).

Approach: Use 1 minute time slices, assume a sparge rate, calculate time required to achieve concentration objective, adjust sparge rate until reasonable cycle time is calculated. Because of standard geometry of 1,000-gal tank, and modest gas rates, 100 percent of equilibrium concentration can be assumed. Table C-1 summarizes the results of the calculations made using a personal computer spreadsheet program. With 75 acfm of sparge gas, the desired concentration of 20 ppb toluene is achieved in 55 minutes of sparging. The table clearly shows that the bulk of the VOC is removed during the early part of the cycle: one-half of the total toluene is removed in the first 3 minutes, and 90 percent is removed after 13 minutes. This typical concentration profile for batch sparging makes the selection of control technology (described elsewhere in this report) somewhat challenging.

TABLE C-1. SPARGING VOLATILIZATION

*Tank Volume	1000 Gal
Moles of H2O	462.26 lb-mol
*Sparge Rate	75 acfm
	0.19465 lbmol/min
*System Temp	20 Deg C
*Pressure	760 mm Hg
*Dissolved VOC	Toluene
*Initial Conc'n	0.025%wt %
Moles of VOC	0.02260147
	0.005%mol %
*MW of VOC	92.14
*Henry's Const.	370 atm
*Exit Gas Equil.	100.00%
*Time Slice	1 min

Time Increment	x-bulk	y-exit	#mols out	cum out	new x-b	wt fr	Percent Removal
	------	------	------	------	------	------	------
0	0.000048	0.018090	0.003521	0.003521	0.000041	2.11E-04	15.580%
1	0.000041	0.015271	0.002972	0.006494	0.000034	1.78E-04	28.733%
2	0.000034	0.012892	0.002509	0.009003	0.000029	1.50E-04	39.837%
3	0.000029	0.010883	0.002118	0.011122	0.000024	1.27E-04	49.210%
4	0.000024	0.009188	0.001788	0.012910	0.000020	1.07E-04	57.123%
5	0.000020	0.007756	0.001509	0.014420	0.000017	9.05E-05	63.804%
6	0.000017	0.006548	0.001274	0.015695	0.000014	7.64E-05	69.443%
7	0.000014	0.005527	0.001076	0.016771	0.000012	6.45E-05	74.204%
8	0.000012	0.004666	0.000908	0.017679	0.000010	5.44E-05	78.223%
9	0.000010	0.003939	0.000766	0.018446	0.000008	4.60E-05	81.616%
10	0.000008	0.003325	0.000647	0.019093	0.000007	3.88E-05	84.480%
11	0.000007	0.002807	0.000546	0.019640	0.000006	3.28E-05	86.898%
12	0.000006	0.002370	0.000461	0.020101	0.000005	2.77E-05	88.939%
13	0.000005	0.002000	0.000389	0.020491	0.000004	2.33E-05	90.663%
14	0.000004	0.001689	0.000328	0.020819	0.000003	1.97E-05	92.118%
15	0.000003	0.001425	0.000277	0.021097	0.000003	1.66E-05	93.346%
16	0.000003	0.001203	0.000234	0.021331	0.000002	1.40E-05	94.382%
17	0.000002	0.001016	0.000197	0.021529	0.000002	1.19E-05	95.258%
18	0.000002	0.000857	0.000166	0.021696	0.000001	1.00E-05	95.996%
19	0.000001	0.000724	0.000140	0.021837	0.000001	8.45E-06	96.620%
20	0.000001	0.000611	0.000119	0.021956	0.000001	7.13E-06	97.147%
21	0.000001	0.000516	0.000100	0.022057	0.000001	6.02E-06	97.591%
22	0.000001	0.000435	0.000084	0.022141	9.94E-07	5.08E-06	97.967%
23	9.94E-07	0.000367	0.000071	0.022213	8.39E-07	4.29E-06	98.283%
24	8.39E-07	0.000310	0.000060	0.022273	7.09E-07	3.62E-06	98.551%
25	7.09E-07	0.000262	0.000051	0.022324	5.98E-07	3.06E-06	98.777%
26	5.98E-07	0.000221	0.000043	0.022368	5.05E-07	2.58E-06	98.967%
27	5.05E-07	0.000186	0.000036	0.022404	4.26E-07	2.18E-06	99.128%
28	4.26E-07	0.000157	0.000030	0.022435	3.60E-07	1.84E-06	99.264%
29	3.60E-07	0.000133	0.000025	0.022461	3.04E-07	1.55E-06	99.379%
30	3.04E-07	0.000112	0.000021	0.022482	2.56E-07	1.31E-06	99.475%
31	2.56E-07	0.000094	0.000018	0.022501	2.17E-07	1.11E-06	99.557%
32	2.17E-07	0.000080	0.000015	0.022516	1.83E-07	9.35E-07	99.626%
33	1.83E-07	0.000067	0.000013	0.022530	1.54E-07	7.89E-07	99.684%
34	1.54E-07	0.000057	0.000011	0.022541	1.30E-07	6.66E-07	99.734%
35	1.30E-07	0.000048	0.000009	0.022550	1.10E-07	5.62E-07	99.775%
36	1.10E-07	0.000040	0.000007	0.022558	9.28E-08	4.75E-07	99.810%
37	9.28E-08	0.000034	0.000006	0.022565	7.84E-08	4.01E-07	99.840%
38	7.84E-08	0.000028	0.000005	0.022570	6.62E-08	3.38E-07	99.865%

TABLE C-1. (Continued)

39	6.62E-08	0.000024	0.000004	0.022575	5.58E-08	2.86E-07	99.886%
40	5.58E-08	0.000020	0.000004	0.022579	4.71E-08	2.41E-07	99.904%
41	4.71E-08	0.000017	0.000003	0.022583	3.98E-08	2.04E-07	99.919%
42	3.98E-08	0.000014	0.000002	0.022585	3.36E-08	1.72E-07	99.931%
43	3.36E-08	0.000012	0.000002	0.022588	2.84E-08	1.45E-07	99.942%
44	2.84E-08	0.000010	0.000002	0.022590	2.39E-08	1.22E-07	99.951%
45	2.39E-08	0.000008	0.000001	0.022592	2.02E-08	1.03E-07	99.959%
46	2.02E-08	0.000007	0.000001	0.022593	1.71E-08	8.73E-08	99.965%
47	1.71E-08	0.000006	0.000001	0.022594	1.44E-08	7.37E-08	99.971%
48	1.44E-08	0.000005	0.000001	0.022595	1.22E-08	6.22E-08	99.975%
49	1.22E-08	0.000004	0.000000	0.022596	1.03E-08	5.25E-08	99.979%
50	1.03E-08	0.000003	0.000000	0.022597	8.67E-09	4.43E-08	99.982%
51	8.67E-09	0.000003	0.000000	0.022598	7.32E-09	3.74E-08	99.985%
52	7.32E-09	0.000002	0.000000	0.022598	6.18E-09	3.16E-08	99.987%
53	6.18E-09	0.000002	0.000000	0.022599	5.21E-09	2.67E-08	99.989%
54	5.21E-09	0.000001	0.000000	0.022599	4.40E-09	2.25E-08	99.991%
55	4.40E-09	0.000001	0.000000	0.022599	3.72E-09	1.90E-08	99.992%
56	3.72E-09	0.000001	0.000000	0.022600	3.14E-09	1.60E-08	99.994%
57	3.14E-09	0.000001	0.000000	0.022600	2.65E-09	1.35E-08	99.995%
58	2.65E-09	0.000000	0.000000	0.022600	2.24E-09	1.14E-08	99.995%
59	2.24E-09	0.000000	0.000000	0.022600	1.89E-09	9.65E-09	99.996%
60	1.89E-09	0.000000	0.000000	0.022600	1.59E-09	8.15E-09	99.997%
61	1.59E-09	0.000000	0.000000	0.022600	1.35E-09	6.88E-09	99.997%
62	1.35E-09	0.000000	0.000000	0.022600	1.14E-09	5.81E-09	99.998%
63	1.14E-09	0.000000	0.000000	0.022601	9.59E-10	4.90E-09	99.998%
64	9.59E-10	0.000000	0.000000	0.022601	8.09E-10	4.14E-09	99.998%
65	8.09E-10	0.000000	0.000000	0.022601	6.83E-10	3.49E-09	99.999%
66	6.83E-10	0.000000	0.000000	0.022601	5.77E-10	2.95E-09	99.999%
67	5.77E-10	0.000000	0.000000	0.022601	4.87E-10	2.49E-09	99.999%
68	4.87E-10	0.000000	0.000000	0.022601	4.11E-10	2.10E-09	99.999%
69	4.11E-10	0.000000	0.000000	0.022601	3.47E-10	1.77E-09	99.999%
70	3.47E-10	0.000000	0.000000	0.022601	2.93E-10	1.50E-09	99.999%

Example 7. Vacuum dryer emissions

Example: Consider the following example of a double-cone dryer operating at 15 inches of mercury, with an air-leakage rate of 15 scfm. The temperature inside the dryer is 60°F. Three hundred pounds of product cake, initially containing 25 percent by weight acetone are dried to less than 1 wt% solvent over the course of 8 hours. Calculate the maximum VOC emission rate.

Solution. The total amount of acetone dried from the product cake is:

$$\frac{300\text{ lb cake}}{} \left| \frac{0.25\text{ lb acetone}}{\text{lb cake}} \right. = 75\text{ lb acetone (initially)}$$

$$\therefore 300-75 = 225\text{ lb product in cake}$$

The amount of acetone remaining at the end of the cycle is:

$$\frac{x}{225+x} = 0.01$$

$$x = (0.01)(225+x)$$
$$x = 2.25*0.01x$$
$$0.99x = 2.25$$
$$x = 2.3\text{ lb acetone (at end of cycle)}$$

$\therefore$ Therefore, the total amount of acetone removed from the drying cycle is:

$$75-2.3 = 72.7 \sim \underline{73\text{ lb}}$$

Average emission rate over the drying cycle is:

$$(73\text{ lb}/8\text{ h})(1\text{ h}/60\text{ min}) = \underline{0.15\text{ lb/min}}$$
average dryer emission rate

The initial drying rate is two times the average rate, assuming a straight-line decline.

Maximum (initial drying rate)

$$(2)*(0.15) = 0.30\text{ lb/min}$$

$$MW_{acetone} = 58\text{ lb/lbmol}$$

Therefore, the molar flow of acetone is

$$(0.30\text{ lb/min})(\text{lbmol}/58\text{ lb})(60\text{ min/hr}) = 0.31\text{ lbmol/h}$$

The airflow (leakage) is given as 15 scfm where 359 scf (at 0°C and 1 atm) is 1 mole. Therefore, the airflow is

(15 scf/min)(lbmol/359 scf)(60 min/h) = 2.51 lbmol/h

Therefore, the uncontrolled emission stream at the start of the drying cycle is estimated to be:

Component	lbmol/h	mole fraction
Acetone	0.31	0.110
Air	2.51	0.890
TOTAL	2.82	1.000

This rate represents the maximum VOC emission rate during the cycle.

Example 8. Atmospheric dryer emissions

Example. A tray dryer uses 6,000 acfm of heated air (65°C) over a period of 6 hours to remove isopropyl alcohol (IPA) from a batch of solids. Each batch consists of 1,000 pounds of material containing 40 percent (by weight) solvent. The final product contains less than 0.6 percent solvent. Calculate the total uncontrolled VOC emissions per drying cycle and the maximum VOC emissions rate.

Mass balance over the drying cycle:

(1,000 lb cake)(0.40 lb IPA/lb cake) = 400 lb IPA initially

Quantity of bone-dry solids = 1,000-400 = 600

Amount of IPA remaining:

$x/600+x = 0.006$

$\therefore$ x = 3.6 lb IPA

Amount of IPA removed is:

400-3.6 = 396 lb (MW = 60.09)

Average emission rate = 396 lb/6 h = 66 lb/h

Assume initial rate = 2* average rate

= (2)(66) = 132 lb/h

(132 lb/h)(lbmol/60.09 lb) = 2.20 lbmol/h

Calculate composition of uncontrolled emission stream at start of drying cycle:

Airflow:

(6,000 acf/min)(60 min/h)(lbmol/359 scf)(273/273+65)scf/acf = 810 lbmol/h

Component	lbmol/h	mole fraction
IPA	2.20	0.0027
Air	810.00	0.9973
TOTAL	812.2	1.0000

Knowledge of, or an estimate of (as above) the uncontrolled outlet stream composition is necessary to select an appropriate control technology. One should note that the mole fraction of the VOC is considerably lower (approximately two orders of magnitude) in the convective oven exhaust than in the vacuum oven (previous example).

Example 9. Vessel Depressurization

A 1,000 gallon nutsche filter is used to compress a slurry containing acetone and inerts at 80°F (26.7°C). A pressure of 35 psig is imparted onto the slurry until the desired filtration is achieved (approximately 40 minutes). The nutsche filter is then depressurized prior to discharging of its contents. Calculate the emission rate of acetone resulting from this step.

Step 1. Ratio of acetone to air initially present in the vessel and after depressurization:

$$35\ psig = 49.7\ psia \left(\frac{760\ mmHg}{14.7\ psia}\right) = 2,570\ mmHg$$

$$\frac{n_{acetone}}{n_{air}} = \frac{(246\ mmHg)}{(2,570-246\ mmHg)} = .106\ (initially)$$

$$\frac{n_{acetone}}{n_{air}} = \frac{246}{760-246} = 0.48\ \text{(after depressurization)}$$

Step 2. Calculate moles noncondensable gas in the vessel initially and after depressurization:

(Assume free volume equals 1/2 of the total volume)

$$n_1 = \frac{(500\ gallons)\left[\frac{ft^3}{7.48\ gal}\right](2.570\ mmHg - 246\ mmHg)}{998.9\frac{mmHg * ft^3}{lbmol\ K}(300K)}$$

N_1 = 0.523 lbmol

Moles of noncondensable gas at the end of depressurization:

$$n_2 = \frac{(500\ gallons)\left[\frac{ft^3}{7.48\ gallons}\right](760-246\ mmHg)}{\left[\frac{998.9\ mmHg * ft^3}{lbmol\ K}\right](300K)}$$

n_2 = 0.11 lbmoles of noncondensable gas

Step 3. Average ratio of $\frac{\text{moles acetone}}{\text{moles air}}$ throughout the depressurization:

$$\frac{0.106 + 0.48}{2} = 0.293$$

Step 4. Calculate lb acetone emitted:

Total moles noncondensable (non-acetone) released:
0.52 - 0.11 = 0.41 lb moles

Total lb acetone released:

$$0.41\ moles\ non\ acetone \left(\frac{0.293\ moles\ acetone}{moles\ non\text{-}acetone}\right)\left(\frac{58\ lb\ acetone}{moles\ acetone}\right)$$

$$= 7\ lb/event$$

$$= 0.17\ lb/\text{min}\ (1\ event = 40\ minutes)$$

Example 10. Emissions from a Steam Ejector

A double-cone batch dryer (volume of 20 ft^3) operates at 74 mmHg. A steam ejector is used to pull a vacuum on the dryer. System components are listed below. A solvent recovery condenser operating at 20°C precedes the ejector. The solvent is methanol.

W leakage

$W = 0.032\ P^{0.26}\ V^{0.60}$ $P\ [=]\ \text{torr}$

$W = 0.032(74)^{0.26}\ (20)^{0.60}$ $V\ [=]\ ft^3$

$W = 0.59\ \text{lb/h}$ $W\ [=]\ \text{lb/h}$

W leakage (see Table A-9 for component-specific leak rates)

Assume system has:

2 seals (rotary) @ 0.10	0.20
10 threaded connections @ 0.015	0.15
2 access ports @ 0.020	0.04
1 view window @ 0.015	0.015
10 valves @ 0.03	0.30
1 control gas valve @ 0.25	0.25
	0.955 lb/h/in.

For 4 in. fittings:

$W = 1.2\ \pi D \theta P^{0.26}$

$W = 1.2\ \pi(4)(0.955)74^{0.26}$

$W = 44\ \text{lb/h}$

$\therefore$ Total in-leakage (La) = 44+0.59 = 44.6 lb/h

as cfm if (379 scf/mol)(mol/29 lb) = >582.8 ft^3/h
= 9.7 scfm

VOC emissions:

$$S_E = MW_s \frac{La}{29}\left[\frac{P_{system}}{P_{system}-P_s} - 1\right]$$

$$S_E = \left(\frac{32\ lb\ MeOH}{lbmol}\right)\left(\frac{44.6\ lb\ air/h}{29\ lb\ air/lbmol}\right)\left(\frac{760}{(760-95)} - 1\right)$$

(VP_{MeOH} at 20°C = 95 mmHg)

$\therefore\ S_E = 7.03$ lb MeOH/h

Example 11. Calculation of Emissions from Equipment Leaks

Estimate VOC emissions from a facility process having the following components in light liquid service 100 percent of the time.

- 1 pump
- 18 flanges
- 1 gas valve
- 5 liquid valves
- 1 sampling connection
- 3 open-ended lines

Solution

Multiply by equipment leak factors found in Table A-6.

Equipment leaks	kg/h
1 pump	
(0.0199 kg/h)(1) 100 percent service	0.0199
18 flanges	
(0.00183)(18) 100 percent service	0.0329
1 gas valve	
(0.00597)(1) 100 percent service	0.00597
1 S.C.	
(0.0150)(1) 100 percent service	0.0150
3 O.E.L.	
(0.0017)(3) 100 percent service	0.0051
	0.07887

0.07887 kg/h (h/3,600 s) = $2.2\text{x}10^{-5}$ kg/s

APPENDIX D.

COST CALCULATIONS

Background Information/Introduction to Control Device Model Calculations

The attached documentation details the calculations and assumptions that were used to arrive at the control device cost effectiveness curves used to set RACT. The documentation requires some preliminary discussion of certain issues because of the complexity of the approach. This preface is intended to provide this necessary background. Note also that the basis for much of the assumptions used in estimating costs is the fourth edition of the OAQPS Control Cost Manual, prepared by the Emission Standards Division of the Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, NC 27711.

Discussion

Time Variation

One of the major ideas behind RACT for batch processes is the consideration of on-stream emission event duration. The calculations assume a certain mass emissions value, in lbs/year. Mass emissions is really the annual VOC emission rate from the batch process vent(s) considered to be controlled. By making mass emissions an input variable, and by setting the VOC concentration and the emission stream flowrate (i.e., these parameters are also input), the models are designed to calculate a value of on-stream emission event duration, which we call "time var." This "time var" value is used throughout the model to calculate control device costs and cost effectiveness. The "time var" or time variation field should not be confused with the initial duration input as 60 minutes. It was assumed that each event took 60 minutes initially to calculate emissions per event and heat load per event, but considered the number of events per year that would actually be occurring using time var (which is the fraction of continuous emissions). Note, also, that operation and maintenance costs are calculated on a per shift basis.

For those combinations of mass emissions and flowrate that yielded time var values of less than .33, only 1 shift per day was assumed. For time var between .33 and .66, 2 shifts per day were assumed, and 3 shifts per day were assumed for time var >.66.

Condenser Model Calculations

The calculations below can be cross-referenced with the example condenser model spreadsheet, which is included as an attachment to this set of calculations.

1. Input Variables - Emission Stream Characteristics

Example Inputs		Cell I.D.
1,000	a. Flowrate, (acfm):	H7
25	b. Temperature, (°C):	H8 (Default is 25°C)
760	c. Pressure, (mmHg):	H9 (Default is 760 mmHg)
60	d. Duration, (min):	H10 (Default is 60 minutes)
30.37	e. VOC volume percent*:	H11 (Default is saturation)
90	f. Required condenser control efficiency, (%):	J6
100,000	g. Mass emissions, (lb/yr):	M14

*This field is considered an input field although the spreadsheet is designed to calculate this value for saturation. In our analysis, we multiplied the saturation value by a fraction that would result in our desired concentration values (i.e., 1,000, 8,750, 10,000, and 100,000ppmv for the cost effectiveness curves).

For example, volume percent is calculated in the example in the following manner:

`10 ^ ($BW$11 - ($BX$11/(H8+$BY$11)))/H9` (1)

where:

$BW$11 = 7.117 (Antoine Coeff 'a' for acetone);
$BX$11 = 1210.595 (Antoine Coeff 'b' for acetone); and
$BY$11 = 229.664 (Antoine Coeff 'c' for acetone).

where:

the Antoine's equation is of the form:

$$\log_{10} P_a^* = a - \frac{b}{c + t}$$

where:

P_a^* = vapor pressure of component a, mmHg
a, b, c = Antoine's coefficients for component a
t = temperature, °C

Equation 1 is the vapor pressure/total pressure where vapor pressure equals:

10^ [$\log_{10}$Pa* = a - b/(c + t)]

Pa* = 10^ [a - b/(c + t)]

So, 10^ [$BW$11 - ($BX$11/(H8 + $BY$11))) = Pa*

Volume percent = [Pa*/total pressure (H9 = 760)]

= H11 = 30.37% (in the example)

Non-condensable Volume Percent, (%): (Cell H16)

Because the gas stream contains a portion that is condensable material and a portion that is noncondensable material and the fraction of the stream that is condensable material was calculated above the remaining portion of the stream is easily calculated as below:

= 1 - H11

= 1 - Volume percent (calculated above)

= 1 - .3037 = .6963 = 69.63%

Emissions, (lbs/event): (Cell H17)

This equation uses the ideal gas law to estimate the emissions of the VOC (acetone in the example) per event before the condenser is applied.

H11 * H10 * H7 * H9/(998.97 * (H8 + 273))*$BZ$11

where:

$BZ$11 = Molecular weight of VOC; acetone = 58 lb/lbmol; and
998.97 = Universal gas constant, (mmHg ft^3/lbmol K).

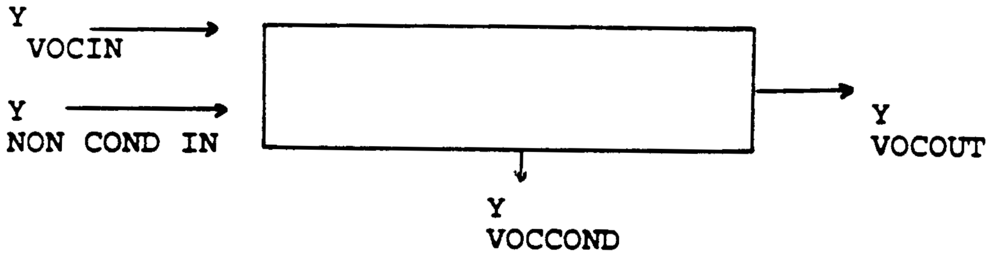
= .3037*60 min*1,000 acfm*760 mmHg/(998.97*(25+273))*58

= 2,702 lbs/event

Partial Pressure at Exit Stream, (mmHg): (Cell J9)

The above calculations are used to estimate the uncontrolled waste gas composition. The spreadsheet will estimate control costs for a desired control efficiency or exit condenser temperature, if specified. If control efficiency is specified, as it was in this cost analysis, the spreadsheet calculates the required exit partial pressure of the waste gas, which is the saturation vapor pressure at the exit condenser temperature.

For this example, the condenser control efficiency, J6 = 90% 90 percent control for a condenser means the following:



[YVOC IN] [FLOWRATE]/RT = <u>MOLES VOC IN</u>

[1 - Y VOC IN] [FLOWRATE]/RT = MOLES NONCONDENSED

MOLES VOC OUT = (1-CONTROL EFF.)(MOLES VOC IN)

After manipulation and cancelling these equations are reduced to:

$$Y_{VOCOUT} = \frac{(1 - \text{CONT. EFF})(Y_{VOCIN})}{1 - Y_{VOCIN} * \text{CONT. EFF}}$$

This is the same equation as the one contained in cell J9, except that the equation in cell J9 is multiplied by 760 mmHg, the assumed total pressure of the system, atmospheric in thsi case. The resulting value is the partial pressure of the VOC component.

= 760 mmHg*(.3037(1-.9))/(1-.3037*.9)

= 31.77 mmHg

<u>Required Condenser Exit Temperature, (C): (Cell J12)</u>

Substituting the partial pressure back into Antoine's equation, yields a temperatuere at which 90 % control is achieved.

$$\log p^* = a - \frac{b}{t + c}$$

$$t = \frac{-b}{(\log P^* - a)} - c \quad \text{or} \quad t = \frac{b}{(a - \log P^*)} - c$$

The formula in cell J12 is:

(($BX$11/($BW$11-LOG(J9))-$BY$11))

So, substituting the values from the example condenser model spreadsheet into this equation:

= ((1210.595/(7.117-LOG_{10}(31.77))-229.664))

= 14.06 C

Condenser Exit Flowrate (variable), (ft^3/min): (Cell H18)

This formula takes into account the ratio of the volume percent of noncondensables entering the condenser and the volume percent of noncondensables exiting the condenser along with the equation: $P_1V_1/T_1 = P_2V_2/T_2$. Solving for V_2.

The formaula in cell address H18 is:

H7 * H16 * (((1.8 * $CE$6) + 32) + 460)/(((1.8 * H8) + 32)
+ 460) * H9/$CH$6/(1-H19)

where:

$CE$6 = Condenser Exit Temperature, (C);
$CH$6 = Compressor Pressure, (mmHg); and
H19 = Condenser Exit Volume Percent, (%).

So, substituting the spreadsheet values into this equation: is

= 1,000 acfm*.6963*(((1.8*(-14.06 C))+32)+460)/(((1.8*
25 C)+32)+460)*760 mmHg/760 mmHg/(1-.0418)
= 631 cfm

Condenser Exit Volume Percent, (%): (Cell H19)

This field substitutes back into Antoine's equation the required exit condenser temperature, which is given in $CE$6.

$$P_{partial}/P_{total} = Y_{out}$$

10^($BW$11 - ($BX$11/($CE$6 + $BY$11)))/$CH$6

where:

$CH$6 = Total Pressure, (mmHg).

So, substituting the values from the example condenser model spreadsheet into this equation:

= 10^(7.1175-(1210.595/(-14.06 C+229.664)))/760 mmHg

= .0418 = 4.18%

Constant Properties Exit, (lbs VOC/event): (Cell H20)

Using the ideal gas law this equation calculates the emissions per event after the condenser:

H19 * H18 * $CH$6 * $BZ$11/(998.97 * $CF$6) * H10 where:

$CF$6 = Condenser Exit Temperature, K.

So, substituting the values from the example condenser model spreadsheet into this equation:

= (.0418*631 cfm*760 mmHg*58 lb/lbmol)/(998.97*258.94)*60
= 270 lbs VOC/event

Condenser Control Efficiency, (%): (Cell H21)

This cell provides for the calculation of the condenser control efficiency, but it is not used in this example because the efficiency was input in the analysis.

Condenser Heat Load, (BTU/event): (Cell H22)

Cell H22 calculates the condenser heat load, in terms of sensible heat and latent heat of cooling the stream down to the desired temperature.

Heat load is made up of: (1) latent heat of condensation for the material condensed, (2) sensible heat of cooling of the noncondensables, and (3) sensible heat of cooling of the condensables.

Sensible heat is calculated as $\overset{\circ}{m}\ Cp\ \Delta T$

Latent heat is calculated as $\overset{\circ}{m}Hv$

where:

$Q_{sensible} = m\ C_p\ \ T$; and
$Q_{latent} = m\ H_v$.

where:

m = mate rate;
C_p = heat capacity;
H_v = heat of vaporization; and
T = range of cooling.

1st Term: (Sensible and latent heat of condensables)

((H17 - H20) * ($CB$11 + $CA$11 * (H8 - $CE$6) * 1.8))

where:

H17 - H20 = lb VOC condensed = 2702 - 270.2 = 2431.8 lb/event;

$CB$11 = 220 (BTU/lb, H_{vap} of acetone); and

$CA$11 = 0.3 (Cp acetone, BTU/lb°F), assumed constant.

So, substituting these values into the 1st part of the equation in cell H22:

Heat load (condensed) = (2702 - 270.2) [220 (BTU/lb)

+ 0.3 BTU/lb°F (25-(-14.06))*1.8] = 586,288 BTU/event

2nd Term: (Sensible heat of condensables that were not condensed, calculated in Cell H20)

The 2nd part of the heat load equation as it appears in the condenser model is:

(H20*$CA$11*(H8-$CE$6)*1.8)

So, substituting the correct values into the equation:

= (270.2*0.3(25-(-14.06))*1.8) = 5699 BTU/event

3rd Term: (Sensible heat of noncondensables)

The 3rd part of the heat load equation as it appears in the condenser model is:

= H18*(1-H19)*H9/(998.97*($CE$6+273)*29*H10)*$CA$20*(H8-$CE$6)*1.8))

where:

$CA$20 = BTU/lb°F for air, .24.

So,

= 631 cfm*(1-0.0418)*760 mmHg/(998.97*(-14.06+273)*29*60)*.24 *(25-(-14.06)*1.8))

= 52,517 BTU/event

Therefore the sum of the three terms is 586,288 + 5,699 + 52,517 = 644,504 BTU/event. The spreadsheet calculated a slightly different value, 644,613 BTU/event. However, rounding is the reason for the difference in the values.

Condenser Heat Load During Non-Events, (BTU/event): (Cell H23)

Assumed 10 percent of heat load during events to keep the heat exchanger surfaces cold and to account for heat losses.

Tons: (Cell H24)

Calculated Annual Refrigeration requirements based on on-stream time.

$$[644{,}613\ \frac{\text{BTU}}{\text{event}}\ \frac{\text{event}}{60\ \text{min}}]\ [\frac{60\ \text{min}}{\text{hr}}]\ [8{,}760]\ [\text{Time Var}]$$

$$+\ [64{,}461\ \frac{\text{BTU}}{\text{event}}\ \frac{\text{event}}{60\ \text{min}}]\ [\frac{60\ \text{min}}{\text{hr}}]\ [8{,}760]\ [1\text{-Time Var}]$$

where:

Time Var = .00415.

$$= \frac{(\text{BTU})}{\text{yr}}\ \text{x}\ \frac{\text{yr}}{8{,}760/12{,}000\ \text{BTU/hr/ton}}$$

= tons refrigeration used to calculate annual energy costs = 5.57

Refrigeration Unit Cost (DIFF TEMP), ($): (Cell H27)

The refrigeration cost is based on the heat load and temperature. The cost for a refrigeration unit are given in 10°F increments from 40°F to -70°F, and a 30°F increment between -70°F to -100°F. A Quattro Pro macro that checks the required condenser exit temperature appears on the right side of the condenser model spreadsheet underneath the "\t\". The group of numbers under the macro are the refrigeration unit costs given the calculated tons of refrigeration required. Below are the actual equations that produce the Purchased Equipment Cost (PEC) for refrigeration units at different temperatures.

Temp., °F	Cost Equation
40	1,451(Tons) + 10,817
30	1,820 (Tons) + 11,064
20	2,340 (Tons) + 11,021
10	3,197 (Tons) + 13,972
0	4,013 (Tons) + 14,427
-10	5,582 (Tons) + 13,431
-20	7,560 (Tons) + 13,451
-30	4,334 (Tons) + 40,089
-40	5,459 (Tons) + 40,082
-50	6,704 (Tons) + 39,993
-60	7,152 (Tons) + 43,640

-70	8,938 (Tons) + 41,713
-100	17,798 (Tons) + 46,906

The required condenser exit temperature for the stream contained in the example condenser model spreadsheet is -14.06°C which equals approximately 7°F. So, the equation for 0°F would be used to estimate the PEC of the refrigeration unit as below:

4,013 (Tons) + 14,427

where:
Tons = the tons of refrigeration required during an event

Sizing the condenser refrigeration unit based on the heat load calculated during an event provides the "worst-case" costs because this would be the maximum heat load encountered by the condenser during any given time throughout the year.

So,

4,013 (H22/H10*60/12,000) + 14,427

Substituting the values in the example into this equation:

= 4,013 (644,613/60*60/12,000) + 14,427

= $229,996

Total System Costs (1.25*Unit Cost), ($): (Cell H32)

1.25 * PEC, to account for precooler and auxiliary equipment.

= 1.25 * $229,996 = $287,495

Total Capital Investment (TCI), ($): (Cell H33)

1.74 * total system costs* 1.25 [3rd quarter, 1990]

where,
1.74 factors installation for nonpackaged systems
25 percent covers manifolding

Direct Costs

Operating Labor ($): (Cell H35)

= 0.5 hours/shift*$15.64/hour*H51*H52

where:
$15.64/hr is operating labor rate;
H51 = shifts/day; and
H52 = days/year.

So, substituting the values for the example into this equation:

= 0.5*15.64*1*365

= $2,854/year

Supervisory Labor ($): (Cell H36)

= 1.15*H35

So, substituting the values from the example into this equation:

= 1.15 • $2,854/year

= $3,282/year

Maintanence Labor ($): (Cell H37)

= 0.5 hour/shift*$17.21/hour*H51*H52

where:
$17.21 = maintanence labor rate.

So, substituting the values from the example into the equation:

= 0.5*17.21*1*365

= $3,141/year

Maintanence Materials ($): (Cell H38)

= H37

= $3,141/year

Electric Compressor Motor, ($): (Cell H39)

Electricity requirements were based on the average tons of refrigeration required during a year and refrigeration temperature.

kw/Ton	T (°F)
1.3	40
2.2	20
4.7	-20
5.0	-50
11.7	-100

We used a regression line, where

$$T = -13.08\ (\text{kw/ton}) + 43.16$$

r^2 correlation to these data points = 0.955

The regression line was used to obtain (kw/ton).

So,

= ((($CE$6*1.8+32)-43.16)/-13.08)*H24*8,760*.059/0.85

where:
$.059 = Cost/kwh; and
0.85 = Efficiency of motor.

So, subsituting the correct values into the equation:

= (((-14.06*1.8+32)-43.16)/-13.08)*5.57*8,760*.059/0.85

= $9,449

Overhead, ($): (Cell H40)

= .6*sum(H35..H38)

where:
H35 - H38 = the costs of operating, supervisory, and maintanence labor and maintenance materials.

So, substituting the correct values into the example equation:

= $7,451/year

Capital Recovery, ($): (Cell H41)

Assume 15-year life, 10 percent interest

= .1315*H33

= $82,227

General Administrative, Taxes, Insurance, ($): (Cell H42)

= .04*H33

= $25,012

Total Annualized Cost, ($): (Cell H43)

The total annualized cost is the sum of all the direct costs.

= $136,558/yr

Mg/yr Controlled: (Cell H44)

= (M14*0.454/1000)*J6

= (100,000*0.454*1,000)*0.9

= 40.86 Mg/yr

Cost Effectiveness ($/Mg): (Cell H45)

= H43/H44

= 136,558/40.86

= $3,342/Mg

Calculation of Time Variation: (Cell M17)

= M17*998.97*293*(1/60)*(1/8,760)*(1/$BZ$11)/H11/(H6*760)

So, substituting the correct values into the equation:

= 100,000*998.97*293/60/8,760/58/.3037/(1,000*760)

= 0.00415

CONDENSER MODEL SPREADSHEET

CONDENSER MODEL

PARAMETERS:

Flowrate, (scfm):	1,000
Flowrate, (acfm):	1,000
Temperature, (Deg C):	25
Pressure, (mmHg):	760
Duration, (min):	60
VOC, (vol %):	30.37%
VOC, (ppmv):	303,733

CALCULATIONS:

Non-condensable Volume Percent, (%):	69.63%
Emissions, (lbs/event):	2,702
Condenser Exit Flowrate(variable), (ft3/min)	631
Condenser Exit Volume Percent, (%):	4.18%
Constant Properites Exit, (lbs VOC/event):	270.26
Condenser Control Efficiency, (%)	90%
Condenser Heat Load, (BTU/event)	544,613
Concenser Heat Load During Non Events, (BTU/event)	64,461
Concenser Heat Load (tons), (12,000 BTU/hr)	5.57
Delta T	32.43
QCOOL, (lb/hr):	1,112
Refrigeration Unit Cost (DIFF TEMP), ($)	$229,996

COSTS:

Total System Costs (1.25*Unit Cost), ($)	$287,495
Total Capital Investment (TCI) ($)	$625,302
DIRECT COSTS:	
Operating Labor ($):	$2,854
Supervisory Labor, ($):	$3,282
Maintanence Labor, ($):	$3,141
Maintanence Materials, ($):	$3,141
Electric Compressor Motor, ($):	$9,449
Overhead, ($)	$7,451
Capital Recovery, ($):	$82,227
General Administrative, Taxes, Insurance, ($):	$25,012
TOTAL ANNUALIZED COST, ($):	$136,558
Mg/yr CONTROLLED	40.86
COST EFFECTIVENESS, ($/Mg):	$3,342

TIME FACTORS

events/shift:	0.13292
shifts/day	1
days/year	365
% of time	0.00554
DURATION	0.00115

Required Condenser Control Efficiency, (%):
90%

Partial Pressure at Exit Stream, (mmHg):
31.7677

Condenser Exit Temperature, (C):	(F)
-14.06	6.68

Mass Emissions, (lb/yr):	100,000
Time Variation:	0.00415
Energy, (BTU/Mg):	1.43E+07

```
     \n

  40  {if contemp>=40}/ECFORM1~H27~{Q
  30  {if contemp>=30}/ECFORM2~H27~{Q
  20  {if contemp>=20}/ECFORM3~H27~{Q
  10  {if contemp>=10}/ECFORM4~H27~{Q
   0  {if contemp>=0}/ECFORM5~H27~{Q
 -10  {if contemp>=-10}/ECFORM6~H27~{
 -20  {if contemp>=-20}/ECFORM7~H27~{
 -30  {if contemp>=-30}/ECFORM8~H27~{
 -40  {if contemp>=-40}/ECFORM9~H27~{
 -50  {if contemp>=-50}/ECULA1~H27~{Q
 -60  {if contemp>=-60}/ECULA2~H27~{Q
 -70  {if contemp>=-70}/ECULA3~H27~{Q
-100  /ECULA4~H27~{QUIT}
```

40	88761.408
30	108830.25
20	136720.46
10	185707.54
0	229996.2
-10	313283.3
-20	419556.95
-30	272901.59
-40	333127.02
-50	400116.58
60	427829.12
70	521811.96
100	1002973.9

```
A1  [W16] [F2] 'CONDENSER MODEL
A4  [W16] [F2] 'PARAMETERS
J5  [W15] 'Required Condenser Control Efficiency, (%)
A6  [W16] 'Flowrate, (scfm)
H6  (,0) [W14] 1000
J6  (P0) [W15] 0.9
A7  [W16] 'Flowrate, (acfm)
H7  (,0) [W14] (H8+273)*SCFM/298
A8  [W16] 'Temperature, (Deg C)
H8  (,0) [W14] 25
J8  [W15] 'Partial Pressure at Exit Stream, (mmHg)
A9  [W16] 'Pressure, (mmHg)
H9  (,0) [W14] 760
J9  (F4) [W15] 760*(H11*(1-J6))/(1-H11*J6)
A10  [W16] 'Duration, (min)
H10  (,0) [W14] 60
A11  [W16] 'VOC, (vol %)
H11  (P2) [W14] 10^($BW$11-($BX$11/(H8+$BY$11)))/H9
J11  [W15] 'Condenser Exit Temperature, (C)
M11  [W16] "(F)
A12  [W16] 'VOC, (ppmv)
H12  (,0) [W14] +H11*1000000
J12  (F2) [W15] (($BX$11/($BW$11-@LOG(J9))-$BY$11))
M12  (F2) [W16] 1.8*J12+32
A14  [W16] [F2] 'CALCULATIONS
J14  [W15] 'Mass Emissions, (lb/yr)
M14  (,0) [W16] 100000
A16  [W16] 'Non-condensable Volume Percent, (%)
H16  (P2) [W14] 1-H11
A17  [W16] 'Emissions, (lbs/event)
H17  (,0) [W14] +H11*H10*FLOW*H9/(998.97*(H8+273))*$BZ$11
J17  [W15] 'Time Variation
M17  (F5) [W16] +E*998.97*293*(1/60)*(1/8760)*(1/$BZ$11)/H11/(FLOW*760)
A18  [W16] 'Condenser Exit Flowrate(variable), (ft3/min):
H18  (,0) [W14] +FLOW*H16*(((1.8*$CE$6)+32)+460)/(((1.8*H8)+32)+460)*H9/$CH$6/(1-H19)
A19  [W16] 'Condenser Exit Volume Percent, (%):
H19  (P2) [W14] 10^($BW$11-($BX$11/($CE$6+$BY$11)))/$CH$6
J19  [W15] 'Energy, (BTU/Mg)
M19  (S2) [W16] ((H22*8760*M17)+(H23*8760*(1-M17)))/H44
A20  [W16] 'Constant Properites Exit, (lbs VOC/event):
H20  (,2) [W14] +H19*H18*$CH$6*$BZ$11/(998.97*$CE$6)*H10
A21  [W16] 'Condenser Control Efficiency, (%)
H21  (P0) [W14] @IF(((H17-H20)/H17)<0,0,(H17-H20)/H17)
```

```
A22: [W16] 'Condenser Heat Load, (BTU/event)
H22: (,0) [W14] (((+H17-H20)*($CB$11+$CA$11*(H8-$CE$6)*1.8)+(H20*$CA$11*(H8-$CE$6)*1.8)+(H18*(1-H19)*H10/(998.97*($CE$6+273))*29*H10)*$CA$20*(H8-$CE$6)*1.8))
A23: [W16] 'Condenser Heat Load During Non-Events, (BTU/event)
H23: (,0) [W14] 0.1*H22
A24: [W16] 'Condenser Heat Load (tons), (12,000 BTU/hr):
H24: (,2) [W14] @IF(((+H22/H10*60*8760*M17)+(H23/H10*60*8760*(1-M17)))/8760/12000<0,0,((H22/H10*60*8760*M17)+(H23/H10*60*8760*(1-M17)))/8760/12000)
A25: [W16] 'Delta T:
H25: (,2) [W14] ((H8-($CE$6+5.7))-($CE$6-($CE$6-8.3)))/@LN((H8-($CE$6+5.7))/($CE$6-($CE$6-8.3)))*1.8
K25: [W10] \0
A26: [W16] 'QCOOL, (lb/hr):
H26: (,0) [W14] +H24*12000/(0.65*13.9*1.8)
A27: [W16] 'Refrigeration Unit Cost (DIFF TEMP), ($):
H27: (C0) [W14] (4013*($H$22/$H$10*60/12000)+14427)
J27: (F0) [W15] 40
K27: [W10] '{if contemp>=40}/ECFORM1~H27~{QUIT}
J28: (F0) [W15] 30
K28: [W10] '{if contemp>=30}/ECFORM2~H27~{QUIT}
J29: (F0) [W15] 20
K29: [W10] '{if contemp>=20}/ECFORM3~H27~{QUIT}
A30: [W16] [F2] 'COSTS:
J30: (F0) [W15] 10
K30: [W10] '{if contemp>=10}/ECFORM4~H27~{QUIT}
J31: (F0) [W15] 0
K31: [W10] '{if contemp>=0}/ECFORM5~H27~{QUIT}
A32: [W16] 'Total System Costs (1.25*Unit Cost), ($)
H32: (C0) [W14] 1.25*H27
J32: (F0) [W15] -10
K32: [W10] '{if contemp>=-10}/ECFORM6~H27~{QUIT}
A33: [W16] 'Total Capital Investment (TCI) ($):
H33: (C0) [W14] 1.74*H32*1.25
J33: (F0) [W15] -20
K33: [W10] '{if contemp>=-20}/ECFORM7~H27~{QUIT}
A34: [W16] 'DIRECT COSTS:
J34: (F0) [W15] -30
K34: [W10] '{if contemp>=-30}/ECFORM8~H27~{QUIT}
A35: [W16] 'Operating Labor ($):
H35: (C0) [W14] 0.5*15.64*H51*H52
J35: (F0) [W15] -40
K35: [W10] '{if contemp>=-40}/ECFORM9~H27~{QUIT}
A36: [W16] 'Supervisory Labor, ($)
H36: (C0) [W14] 1.15*H35
J36: (F0) [W15] -50
K36: [W10] '{if contemp>=-50}/ECFLAT~H27~{QUIT}
```

```
A37 [W16] 'Maintanence Labor, ($)
H37 (C0) [W14] 0.5*17.21*H51*H52
J37 (F0) [W15] -60
K37 [W10] '{if contemp>=-60}/ECULA2~H27~{QUIT}
A38 [W16] 'Maintanence Materials, ($):
H38 (C0) [W14] +H37
J38 (F0) [W15] -70
K38 [W10] '{if contemp>=-70}/ECULA3~H27~{QUIT}
A39 [W16] 'Electric Compressor Motor, ($):
H39 (C0) [W14] ((($CF$6*1.8+32)-43.16)/-13.08)*H24*8760*0.059/0.85
J39 (F0) [W15] -100
K39 [W10] '/ECULA4~H27~{QUIT}
A40 [W16] 'Overhead, ($):
H40 (C0) [W14] 0.6*@SUM(H35..H38)
A41 [W16] 'Capital Recovery, ($):
H41 (C0) [W14] 0.1315*H33
A42 [W16] 'General Administrative, Taxes, Insurance, ($)
H42 (C0) [W14] 0.04*H33
A43 [W16] 'TOTAL ANNUALIZED COST, ($)
H43 (C0) [W14] @SUM(H35..H42)
J43 (F0) [W15] 40
K43 [W10] (1451*($H$22/$H$10*60/12000)+10817)
A44 [W16] 'Mg/yr CONTROLLED:
H44 [W14] +F*0.454/1000*J6
J44: (F0) [W15] 30
K44 [W10] (1820*($H$22/$H$10*60/12000)+11064)
A45: [W16] 'COST EFFECTIVENESS, ($/Mg):
H45 (C0) [W14] @IF(M17>1,"",@IF(H51>1,"",H43/H44))
J45: (F0) [W15] 20
K45 [W10] (2340*($H$22/$H$10*60/12000)+11021)
J46 (F0) [W15] 10
K46 [W10] (3197*($H$22/$H$10*60/12000)+13972)
J47 (F0) [W15] 0
K47 [W10] (4013*($H$22/$H$10*60/12000)+14427)
A48 [W16] 'TIME FACTORS:
J48 (F0) [W15] -10
K48 [W10] (5582*($H$22/$H$10*60/12000)+13431)
J49 (F0) [W15] -20
K49 [W10] (7560*($H$22/$H$10*60/12000)+13451)
A50 [W16] 'events/shift
H50 (F5) [W14] 32*H54
J50 (F0) [W15] -30
K50 [W10] (4334*($H$22/$H$10*60/12000)+40089)
```

```
A51: [W16] 'shifts/day
H51: [W14] @IF(M17<=0.66,(@IF(M17<=0.33,1,2)),3)
J51: (F0) [W15] -40
K51: [W10] (5459*($H$22/$H$10*60/12000)+40082)
A52: [W16] 'days/year:
H52: [W14] 365
J52: (F0) [W15] -50
K52: [W10] (6704*($H$22/$H$10*60/12000)+39993)
A53: [W16] '% of time:
H53: (F5) [W14] +H10/60*H50*H51*H52/8760
J53: (F0) [W15] -60
K53: [W10] (7152*($H$22/$H$10*60/12000)+43640)
A54: [W16] 'DURATION:
H54: (F5) [W14] +M17
J54: (F0) [W15] -70
K54: [W10] (8938*($H$22/$H$10*60/12000)+41713)
J55: (F0) [W15] -100
K55: [W10] (17798*($H$22/$H$10*60/12000)+46906)
```

```
A67: 'Operator, ($):
F67: (C0) [W15] 0.5*15.64*F17*F18
A68: 'Supervisory Labor, ($):
F68: (C0) [W15] 0.15*F67
A69: 'Maintanence Labor, ($):
F69: (C0) [W15] 0.5*17.21*F17*F18
A70: 'Materials, ($):
F70: (C0) [W15] 1*F69
A72: 'Utilities:
A73: 'Natural Gas, ($):
F73: (C0) [W15] +F42/1000*3.3
G73: '($3.3/1000SCF)
A74: 'Electricity, ($):
F74: (C0) [W15] 0.000117*F41*29/0.6*0.059*8760
G74: '($.059/kwh)
I74: '** CHANGE DELTP FOR DIFF ENERGY RECO **
A75: 'Btu:
F75: (,0) [W15] ((F73*1000/3.3*892)+(F74/0.059*3412.1))
A76: 'Total Diect Cost, ($):
F76: (C0) [W15] 1*@SUM(F67..F74)
A78: 'Indirect Annual Costs:
A79: 'Overhead, ($):
F79: (C0) [W15] 0.6*(F67+F68+F69+F70)
A80: 'Administrative, ($):
F80: (C0) [W15] 0.02*F62
A81: 'Property Tax, ($):
F81: (C0) [W15] 0.01*F62
A82: 'Insurance, ($):
F82: (C0) [W15] 0.01*F62
A83: 'Capital Recovery, ($):
F83: (C0) [W15] 0.16275*F62
A85: 'Total Annualized Cost, ($):
F85: (C0) [W15] 1*@SUM(F76..F83)
```

CAPITAL COST CALCULATIONS:

Direct Costs	
Equipment Cost (Recouperative Incin.), ($):	$106,677
Auxiliary Equipment (Ductwork, Stack), ($):	$16,101
Auxiliary Collection Fan, ($):	$2,701
Instrumentation, ($):	$12,548
Sales Tax, ($):	$3,764
Freight, ($):	$6,274
TOTAL PURCHASED EQUIP COST ($):	$148,066
Direct Installation Costs, ($):	$44,420
Indirect Costs, ($):	$45,900
Total Capital Investment (TCI), ($):	$185,082

ANNUALIZED COST CALCULATIONS:

Operating Labor:			
Operator, ($):	$2,854		
Supervisory Labor, ($):	$428		
Maintanence Labor, ($):	$3,141		
Materials, ($):	$3,141		
Utilities:			
Natural Gas, ($):	$1,928	($3.3/1000SCF)	
Electricity, ($):	$339	($.059/kwh)	** CHANGE DELTP FOR DIFF ENERGY RECO **
Btu:	540,759,189		
Total Dicet Cost, ($):	$11,831		
Indirect Annual Costs:			
Overhead, ($):	$5,738		
Administrative, ($):	$3,702		
Property Tax, ($):	$1,851		
Insurance, ($):	$1,851		
Capital Recovery, ($):	$30,122		
Total Annualized Cost, ($):	$55,095		

THERMAL INCINERATOR MODEL

PARAMETERS:

Flowrate, (scfm):	100
Waste Gas VOC Concentration, (ppmv):	10,000
Heating Value of VOC's, (Btu/scf):	2,000
Energy Recovery, (%):	70
Incinerator Operating Temperature, (F):	1,600
Waste Gas Temperature, (F):	70
Preheater Temperature, (F):	
Molecular Weight of VOC:	64.50
Molecular Weight of Gas:	29.36
Duration, (min):	0.60
Events/Shift:	8
Shifts/Day:	1
Days/Year:	365
Time Variation:	0.28401
Length of Collection Main, (ft):	300
Number of Manifolded Sources:	10

VOC's Controlled, (Mg/yr):	11.12
Cost Effectiveness, ($/Mg):	$4,953
Mass Emissions, (lb/yr):	25,000
Time Variation:	0.2840
Energy, (Btu/Mg):	48,616,308

Step 1: Calculate Total Waste Gas Flow

Oxygen (O2) Content of Waste Gas, (volume %):	20.79
Dilution Air Required for Combustion, (scfm):	0.00
Dilution Air for Safety, (scfm):	14.29
Total Gas Flowrate, (scfm):	114.29

Step 2: Heat Content of Waste Gas, (Btu/scf):	17.50
Step 3: Calculate Gas Temp. Exit Preheater, (F):	1,141.00
Step 4: Calculate Auxiliary Fuel Required, (scfm): for events	0.00
Step 5: Calculate total Gas Flow, (scfm): for events	114.29
Calculate Maximum Auxiliary Gas Flow, (scfm):	1.55
Calculate Maximum Total Gas Flow, (scfm):	115.84
Calculated Annual Gas Flow, (scfy):	584,282

CALCULATIONS

ANTOINE'S EQ COEFFICIENTS

VOC	A	B	C	MW	Cp	hv
Acetone	7.117	1210.595	229.664	58.08	0.3004	220.127
NITROGEN					0.24	

CONDENSER EXIT TEMPERATURE (C)	(K)	COMPRESSOR P
-14.0644	258.9356	760

```
BV1: 'CALCULATIONS
CE2: 'CONDENSER
CH2: 'COMPRESSOR PRESSURE
CE3: 'EXIT
CF3: 'TEMPERATURE
BV5: 'ANTOINE'S EQ COEFFICIENTS
CE5: ^(C)
CF5: ^(K)
CE6: +J12
CF6: +$CE$6+273
CH6: 760
BV8: 'VOC
BW8: 'A
BX8: 'B
BY8: 'C
BZ8: 'MW
CA8: 'Cp
CB8: 'hv
BV11: 'Acetone
BW11: 7.117
BX11: 1210.595
BY11: 229.664
BZ11: 58.08
CA11: 0.3004
CB11: 220.127
BV20: 'NITROGEN
CA20: 0.24
```

Thermal Incineration Model Calculations

The calculations below can be cross-referenced with the example thermal incinerator model spreadsheet, which is included as an attachment to this set of calculations.

1. The information necessary to calculate incinerator costs for any given situation is listed under "Parameters" in the spreadsheet. This data is also listed below:

Example Inputs			Cell I.D.
100	1.	Flowrate, (scfm);	F6
10,000	2.	Waste Gas VOC Concentration;	F7
2,000	3.	Heating Value of VOC's, (Btu/scf);	F8
70	4.	Energy Recovery, (%);	F9
1,600	5.	Incinerator Operating Temperature, (°F);	F10
70	6.	Waste Gas Temperature, (°F);	F11
	7.	Preheater Temperature, (°F);	F12
64.5	8.	Molecular Weight of VOC;	F13
.6	9.	Duration, (min);	F14
8	10.	Number of events per shift;	F15
1	11.	Number of shifts per day;	F16
365	12.	Number of days per year; and	F17
25,000	13.	Mass Emissions, (lb/yr).	F18

There are also several fields in the "Parameters" section which do not contain information that must be input for each given case. They are:

a. Molecular Weight of Gas: (Cell F14)

This value is calculated from the input VOC concentration and the molecular weight of the VOC as below:

$$MW_{gas} = \frac{[\text{VOC Conc (ppmv)}]}{1 \times 10^6}] \times MW_{VOC}] + \frac{[(1-\text{VOC Conc (ppmv)})] \times (29)}{1 \times 10^6}$$

The formula contained in the example thermal incinerator model is:

`F7/1,000,000*F13+(1-F7/1,000,000)*29`

So, substituting the coreect values into the equation:

= 10,000/1,000,000*64.5+(1-10,000/1,000,000)*29

= 29.36 lb/lbmole

b. Time Variation: (Cell J15)

This field is used to calculate the fraction of time that the event occurs over a year (continuous maximum of 8,760 hours). In other words, if the event lasts 0.6 minutes and occurs 8 times a shift, 3 shifts per day, 365 days per year, the time variation equals 1 percent.

c. Length of Collection Main and Number of Manifolded Sources: (Cells F20, F21)

These fields were inserted to cost out the collection main. Because we have no specific situation, we assumed the collection main would be 300 feet in length and have 10 takeoffs (sources). These values remained constant during our analysis, although real data could be input for any given situation.

2. Calculations

The calculations done by the spreadsheet are presented below:

Step 1: Calculate Total Waste Gas Flow

a. O_2 Content of Waste Gas, (volume %), (Cell F25)

This equation assumes that the waste gas is composed of air and VOC's. Air contains 21% oxygen, on average. Therefore, O_2 content can be expressed as:

$(1 - \text{VOC conc}/1 \times 10^6) * 0.21 * 100$

b. Dilution Air Required for Combustion, (scfm): (Cell F26)

The OAQPS Control Cost Manual states that there must be at least 20 percent O_2 in the waste gas for combustion to occur (p. 3-24). An average of 3.96 moles of O_2/mole of VOC was found to be an acceptable ratio to express 20 percent O_2.

c. Dilution Air Required for Safety, (scfm): (Cell F27)

According to the OAQPS Cost Manual, p. 3-26, safety codes require that the maximum VOC concentration in the waste gas stream not exceed 25 percent of the lower explosive limit of the organic compound when a preheater is used. We assumed that a reasonable LEL value for common compounds was about 3.5 percent, or 35,000 ppmv streams; 25 percent of 3.5 percent corresponds to a value of 8,750 ppmv.

This LEL value was derived from the following data:

Compound	LEL (ppmv)
Acetone	26,000
Benzene	14,000
Ethanol	33,000
Ethlene	28,000
Ethylene	28,000
H_2	40,000
H_{25}	43,000
Methane	50,000
Methanol	67,000
Propylene	24,000

Average = 35,000 ppmv
0.25 (35,000) = 8,750

Therefore, additional air must be added to the waste gas to dilute the waste gas VOC concentration to 8,750.

This formula for calculation of dilution air was derived in the following way:

$$\frac{\left[\frac{\text{VOC conc (ppmv)}}{1 \times 10^6}\right][\text{flowrate}]}{\left[\begin{matrix}\text{waste gas} \\ \text{flowrate}\end{matrix} + \begin{matrix}\text{dilution} \\ \text{combustion air}\end{matrix} + \begin{matrix}\text{dilution} \\ \text{safety air}\end{matrix}\right]} = 8{,}750/1 \times 10^6$$

By cancelling and manipulation, this formula reduces to:

$$\begin{matrix}\text{Dilution} \\ \text{safety} \\ \text{air}\end{matrix} = \frac{(\text{Flowrate})(\text{PPMVOC}) - 8{,}750 \bullet (\text{Flowrate}) - 8{,}750 \ast \begin{pmatrix}\text{Dilution} \\ \text{combustion} \\ \text{air}\end{pmatrix}}{8{,}750}$$

d. Calculate Total Gas Flow, (scfm): (Cell F28)

This field calculates the total amount of gas flowing into the incinerator during the emission event, the total gas is composed of:

Input flow (waste gas) + dilution air for combustion +

dilution air for safety

Step 2: Calculate Heat Content of the Waste Gas, (Btu/scf): (Cell F32)

The formula for this field is:

$$\frac{\left[\frac{\text{VOC}}{1 \times 10^{6}}\right]\left[\begin{array}{c}\text{Initial}\\\text{Flowrate}\end{array}\right]}{\text{Total Gas Flow}} * \text{VOC heat content (Btu/scf)}$$

$$= \text{Btu/scf}$$

Step 3: Calculate Gas Temperature Exit Preheater, (F): (Cell F34)

From the OAQPS Cost Manual, the preheater temperature is related to the fractional energy recovery and the incinerator operating temperature and waste gas inlet temperature by the following equation:

$$\text{Energy Recovery} = \frac{T_{wo} - T_{wi}}{T_{fi} - T_{wi}}$$

where, T_{wo} = Gas preheater exit temperature

T_{wi} = Waste gas inlet temperature

T_{fi} = Incinerator operating temperature

This equation is manipulated to

$$\frac{\text{Energy Recovery}}{100} * (T_{fi} - T_{wi}) + T_{wi} = T_{wo}$$

in the spreadsheet.

Step 4: Calculate Auxiliary Fuel Required, (scfm): (Cell F36)

The equation for auxiliary fuel is presented on pages 3-32 of the OAQPS Cost Manual. It is:

$$\frac{[\rho_{af}\, Q_{af} = \rho_{wo}\, Q_{wo}\, [Cp_{m}\ \text{air}\ (1.1\ T_{fi} - T_{wo} - 0.1\ T_{ref}) - (-\Delta hc_{wo})]}{(-\Delta h_{caf}) - 1.1Cp_{m}\ \text{air}\ (T_{fi} - T_{ref})}$$

where: ρ_{af} = density of methane, 0.0408 lb/ft^3 @ 77°F, 1 atm

Q_{af} = natural gas flowrate, scfm

$\rho_{wo} = \rho_{wi}$ = density of the waste gas, @ 77°F, 1 atm
(0.0739 lb/scf @ 77°F, 1 atm)

$Cp_{m\ air}$ = mean heat capacity of air

Assume 0.255 BTU/lb°F (the mean heat capacity of air between 77°F and 1,375°F)

$T_{ref} = T_{af}$ = temp. ambient
(Temp. auxiliary fuel) = 77°F

$-\Delta h_{cwo}$ = heat content of the waste stream, BTU/lb

$-\Delta h_{caf}$ = heat content of natural gas, 886 BTU/lb
(21,502 BTU/lb)

Step 5: Total Gas Flow = Total Waste Gas Flow + Auxiliary Fuel, (scfm): (Cell F38)

Maximum Auxiliary Gas Flow

This field considers the amount of auxiliary fuel necessary to keep the incinerator working in the absence of a VOC emission stream. In other words, during the period of time when there is not an emission event in the incinerator. This equation is similar to the one used above, except that - Δhcwo is 0.

The maximum total gas flow equals the amount of necessary auxiliary fuel when there is no VOC plus the total amount of waste gas from Step 1 (d).

The calculated annual gas flow, in standard cubic feet per year (SCFY) is the amount of natural gas that is required in the incinerator in a year, considering the weighted average of the gas flow during emission events and without emission events.

Capital Cost Calculations

Equipment Costs. (Based on p. 3-44 of the OAQPS Cost Manual) Equipment costs for recuperative incinerators depend on the total gas flow through the incinerator to some power multiplied by a constant. For 70 percent heat recovery, the equation is:

$$EC = 21,342\ Q_{tot}^{0.2500}$$

The minimum flow through the incinerator was assumed to be 500 scfm. The equipment cost was multiplied by cost indices of (357.5/340.1) to correct equipment costs to October 1990, dollars.

Auxiliary Equipment (duct work, stack). The costs for auxiliary equipment were originally taken from an article in the May 1990, Chemical Engineering and assuming 1/8 inch carbon steel and 24 inch diameter with two elbows per 100 feet; and one elbow per source. We assumed that there would be 10 sources manifolded to a 300 foot collection main. The cost was adjusted on indices of (357.5/352.4).

Auxiliary Collection Fan

The auxiliary collection fan is sized on a minimum gas flowrate of 500 scfm. The equation is:

$$\$ = 79.1239 \bullet [\text{Total gas flow from Step 1 (d)}]^{0.5612} * (357.5/342.5)$$

(based on the 1988 Richardson Cost Manual)

Instrumentation	10 percent of purchased and auxiliary equipment
Sales tax	3 percent of purchased and auxiliary equipment
Freight	5 percent of purchased and auxiliary equipment

Total purchased equipment - sum of the above factors
Direct costs - 30 percent of total purchased equipment
Indirect costs - 31 percent of total purchased equipment

Total Capital Investment. If the maximum total gas flow is less than 20,000 scfm, then the installation costs are 25 percent of the purchased equipment costs. If not, then the installation costs are 61 percent of the purchased equipment costs (from p. 3-51 of the OAQPS Cost Manual).

Annualized Costs

Operator: \$15.64/hr x 0.5 hr/shift x shifts/day x day/year

(Assume that 3 shifts/day, 365 days/year)

Supervisor: 15 percent of operator

Maintenance: \$17.21/hr x 0.5 hr/shift x shifts/day x day/year

Material: 100 percent of maintenance

Natural gas: Yearly natural gas usage (scfy) x $\frac{\$3.3}{1{,}000 \text{ scf}}$

Electricity:
From pages 3-55 of the OAQPS Cost Manual

$$\text{Power}_{\text{fan}} = \frac{1.17 \times 10^{-4}\, Q_{tot} \Delta P}{E}$$

Where:

Q_{tot} = maximum gas flow
ΔP = pressure drop, in H_2O (Assume 29 in H_2O; 19 inches for the preheater and 10 inches for ducting)
E = efficiency
P = power, in KW
$.059/kwh → electricity cost

Total Direct Costs:

Sum of labor, materials, natural gas, electricity

Indirect: Overhead: 60 percent of labor and materials
Administrative: 2 percent of total capital investment (TCI)
Prop Tax: 1 percent of total capital investment (TCI)
Insurance: 1 percent of total capital investment (TCI)

Capital Recovery Factor:
10 percent, 10-year life .16275 (TCI)

THERMAL INCINERATOR MODEL SPREADHSEET

```
A1: [F2] 'THERMAL INCINERATOR MODEL
A4: [F2] 'PARAMETERS:
G5: '
J5: [W13] 'VOC's Controlled, (Mg/yr):
A6: 'Flowrate, (scfm):
F6: (,0) [W15] 100
J6: (F2) [W13] 0.98*MF*0.454/1000
A7: 'Waste Gas VOC Concentration, (ppmv):
F7: (,0) [W15] 10000
A8: 'Heating Value of VOC's, (Btu/scf):
F8: (,0) [W15] 2000
J8: [W13] 'Cost Effectiveness, ($/Mg):
A9: 'Energy Recovery, (%):
F9: (,0) [W15] 70
J9: (C0) [W13] @IF(J15>1,"",@IF(F17>1,"",F85/J6))
A10: 'Incinerator Operating Temperature, (F):
F10: (,0) [W15] 1600
A11: 'Waste Gas Temperature, (F):
F11: (,0) [W15] 70
J11: [W13] 'Mass Emissions, (lb/yr):
A12: 'Preheater Temperature, (F):
J12: (,0) [W13] 25000
A13: 'Molecular Weight of VOC:
F13: (F2) [W15] 64.5
A14: 'Molecular Weight of Gas:
F14: (F2) [W15] +F7/1000000*F13+(1-F7/1000000)*29
J14: [W13] 'Time Variation:
A15: 'Duration, (min):
F15: (F2) [W15] 0.6
J15: (F4) [W13] +MF*(998.97*293)*(1/60)*(1/8760)*(1/F13)/(F7/1000000)/(FLOW*760)
A16: 'Events/Shift:
F16: (,0) [W15] 8
A17: 'Shifts/Day:
F17: (,0) [W15] @IF(F19<=0.66,(@IF(F19<=0.33,1,2)),3)
J17: [W13] 'Energy, (Btu/Mg):
A18: 'Days/Year:
F18: (,0) [W15] 365
J18: (,0) [W13] +F75/J6
A19: 'Time Variation:
F19: (F5) [W15] +J15
A20: 'Length of Collection Main, (ft):
F20: (,0) [W15] 300
A21: 'Number of Manifolded Sources:
F21: (,0) [W15] 10
A23: 'Step 1: Calculate Total Waste Gas Flow
A25: 'Oxygen (O2) Content of Waste Gas, (volume %):
```

```
A26: 'Dilution Air Required for Combustion, (scfm):
F26: (,2) [W15] @IF((F25/100*FLOW/392)<(3.96*F7/1000000*FLOW/392),((3.96*F7/1000000*FLOW/392)-(F25/100*FLOW/392))*392/0.21,0)
A27: 'Dilution Air for Safety, (scfm):
F27: (,2) [W15] @IF((F7*FLOW)/(FLOW+F26)<8750,0,(FLOW*F7-8750*FLOW-8750*F26)/8750)
A28: 'Total Gas Flowrate, (scfm):
F28: (,2) [W15] +$FLOW+$F$26+$F$27
A32: 'Step 2: Heat Content of Waste Gas, (Btu/scf):
F32: (,2) [W15] +F7/1000000*FLOW/F28*F8
A34: 'Step 3: Calculate Gas Temp. Exit Preheater, (F):
F34: (,2) [W15] +F9/100*(F10-F11)+F11
A36: 'Step 4: Calculate Auxiliary Fuel Required, (scfm):
F36: (,2) [W15] @IF(1.8*F28*(0.255*(1.1*F10-F34-0.1*77)-(F32*379/F14))/(21081-1.1*0.255*(F10-77))<0,0,1.8*F28*(0.255*(1.1*F10-F34-0.1*77)-(F32*379/F14))/(21081-1.1*0.255
A37: '       for events
A38: 'Step 5: Calculate total Gas Flow, (scfm):
F38: (,2) [W15] +$F$36+$F$28
A39: '       for events
A40: 'Calculate Maximum Auxiliary Gas Flow, (scfm):
F40: (,2) [W15] @IF(1.8*F28*(0.255*(1.1*F10-F34-0.1*77)-(0*379/F18))/(21081-1.1*0.255*(F10-77))<0,0,1.8*F28*(0.255*(1.1*F10-F34-0.1*77)-(0*379/F14))/(21081-1.1*0.255*(F10
A41: 'Calculate Maximum Total Gas Flow, (scfm):
F41: (,2) [W15] +F40+F28
A42: 'Calculated Annual Gas Flow, (scfy):
F42: (,0) [W15] (+F40*(1-F19)+F36*F19)*60*8760
A45: |::
A47: [F2] 'CAPITAL COST CALCULATIONS:
A49: 'Direct Costs
A50: 'Equipment Cost (Recouperative Incin.), ($):
F50: (C0) [W15] @IF(F41<500,(21342*((500)^(0.25))*(359.5/340.1)),(21242*((F41)^(0.25))*(359.5/340.1)))
A51: 'Auxiliary Equipment (Ductwork, Stack), ($):
F51: (C0) [W15] (((210*24^0.839)+(2*4.52*24^1.43))*(F20/100)+(F21*4.52*24^1.43))*(357.5/352.4)
A52: 'Auxiliary Collection Fan, ($):
F52: (C0) [W15] @IF(F28<500,(79.1239*500^0.5612)*(357.5/342.5),(79.1239*F28^0.5612)*(357.5/342.5))
A53: 'Instrumentation, ($):
F53: (C0) [W15] 0.1*(F50+F51+F52)
A54: 'Sales Tax, ($):
F54: (C0) [W15] 0.03*(F50+F51+F52)
A55: 'Freight, ($):
F55: (C0) [W15] 0.05*(F50+F51+F52)
A57: 'TOTAL PURCHASED EQUIP COST ($):
F57: (C0) [W15] 1*@SUM(F50..F55)
A59: 'Direct Installation Costs, ($):
F59: (C0) [W15] 0.3*F57
A60: 'Indirect Costs, ($):
F60: (C0) [W15] 0.31*F57
A62: 'Total Capital Investment (TCI), ($):
F62: (C0) [W15] @IF(+F41<20000,1.25*F57,1*@SUM(F57..F60))
A64: [F2] 'ANNUALIZED COST CALCULATIONS:
A66: 'Operating Labor:
```

APPENDIX E.

MODEL PLANTS
AND
MODEL EMISSION STREAM CALCULATIONS

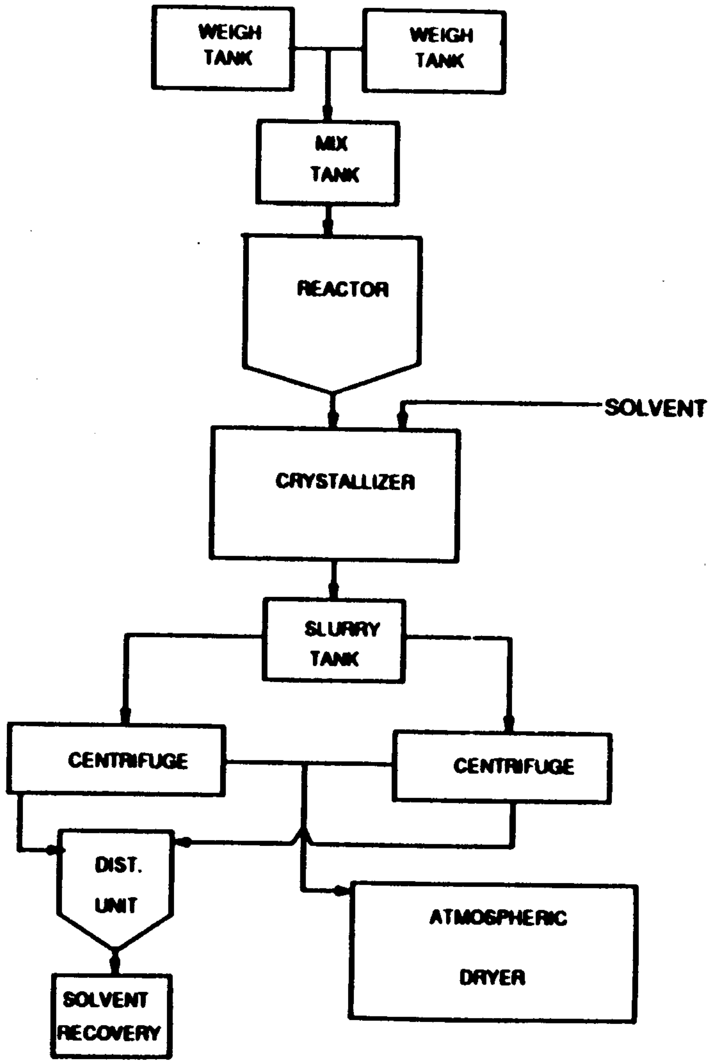


Figure E-1. Model batch process for solvent reaction with atmospheric dryer

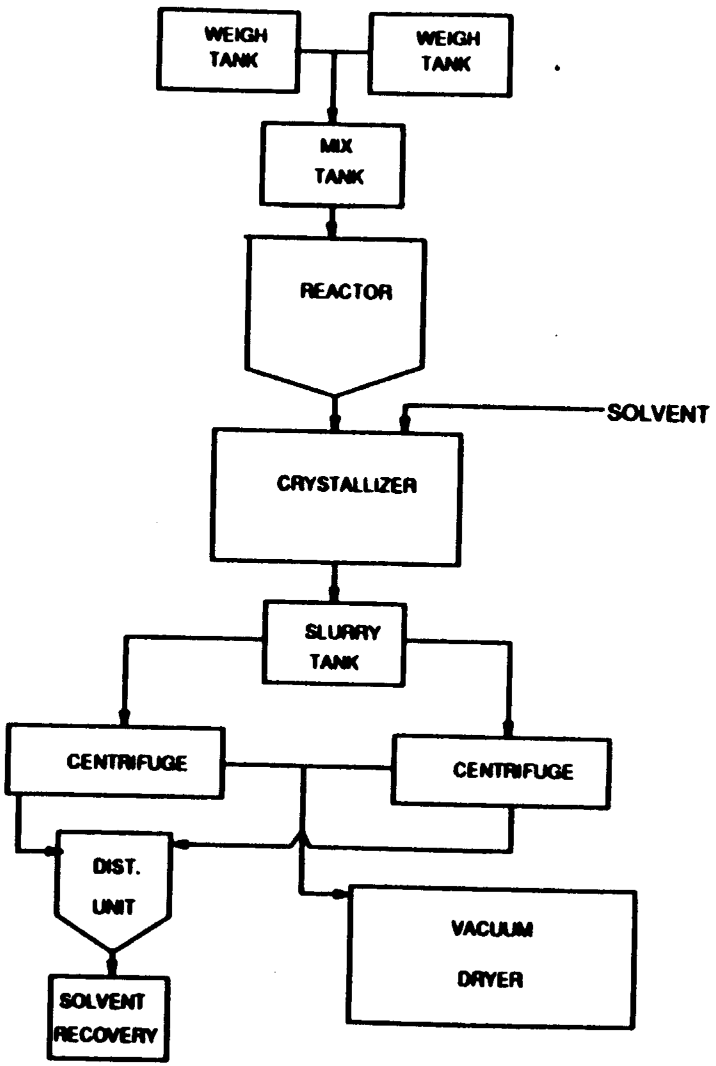


Figure E-2. Model batch process for solvent reaction with vacuum dryer

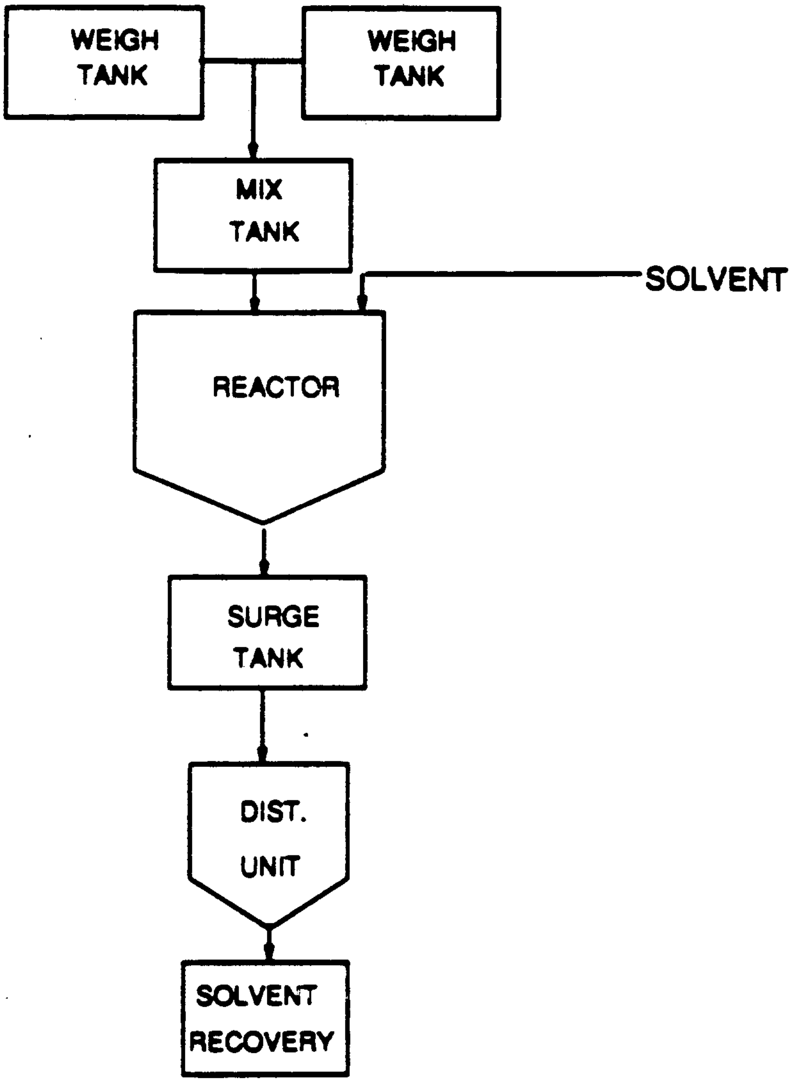


Figure E-3. Model batch process for liquid reaction

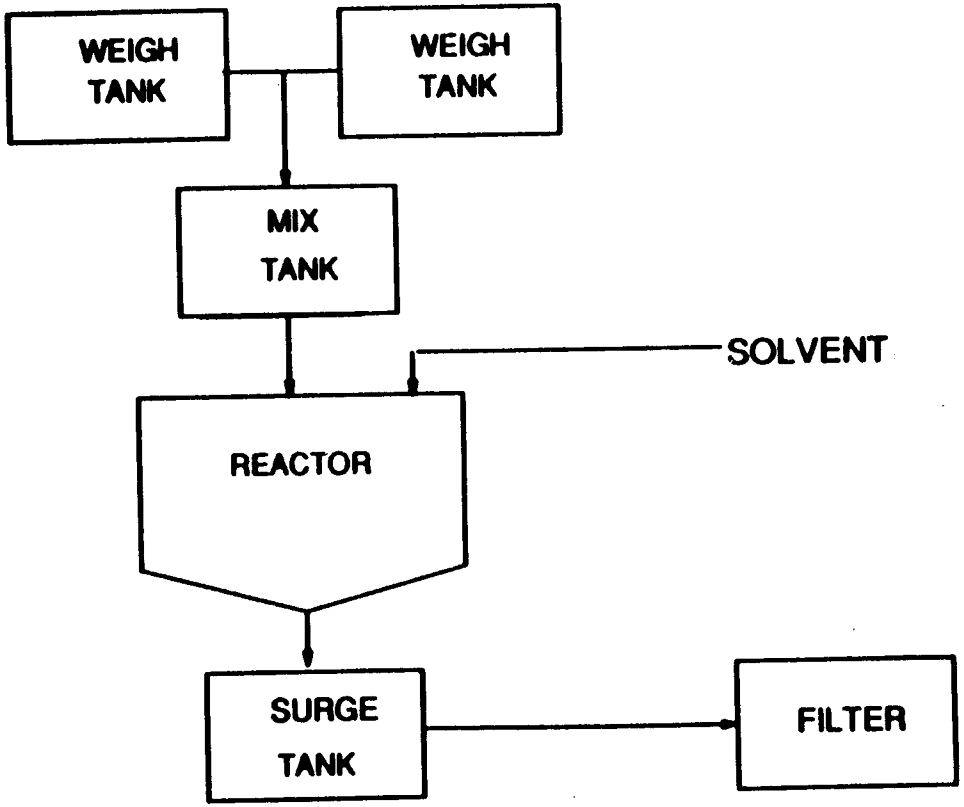


Figure E-4. Model batch process for formulation

TABLE E-1. EMISSION STREAM CHARACTERISTICS FOR SOLVENT REACTION MODEL PROCESS WITH ATMOSPHERIC DRYER

# of unit ops per model batch	Calculation for 1 unit operation	Emission Stream VOC	Flow Rate (acfm)	Temp (Deg C)	Duration (min)	VOC (vol %)	Emissions lb/event	Emissions lbs/batch (Note 1)	NO CONTROL Mass Flux lbs/batch	CPC (Note 2) Mass Flux lbs/batch
9.25	Displacement (2000-gallon vessel)	LOW VOLATILITY	18	20	15	0.6%	0.29	2.64	2.64	2.64
		MODERATE VOLATILITY	18	20	15	12.6%	2.82	26.08	26.08	7.82
		HIGH VOLATILITY	18	20	15	57.9%	30.02	277.66	277.66	30.54
	TOTAL DISPLACEMENT EMISSIONS (lbs-batch/year)	LOW VOLATILITY							727.02	727.02
		MODERATE VOLATILITY							7172.28	2151.68
		HIGH VOLATILITY							76355.65	8399.12
	REACTORS									
1	Charging w/purge	LOW VOLATILITY	30	20	15	0.1%	0.12	0.12	0.12	0.12
		MODERATE VOLATILITY	30	20	15	3.1%	1.17	1.17	1.17	1.17
		HIGH VOLATILITY	30	20	15	14.5%	12.51	12.51	12.51	5.63
1	Heat-up w/purge	LOW VOLATILITY	30	20 to 30	5		0.1	0.10	0.10	0.10
		MODERATE VOLATILITY	30	20 to 30	5		0.52	0.52	0.52	0.52
		HIGH VOLATILITY	30	20 to 30	5		5.13	5.13	5.13	1.85
1	Reaction w/purge	LOW VOLATILITY	150	37	3	0.5%	0.39	0.39	0.39	0.39
		MODERATE VOLATILITY	150	37	3	7.5%	2.65	2.65	2.65	1.35
		HIGH VOLATILITY	150	37	3	27.2%	22.19	22.19	22.19	5.33
1	Empty Reactor Purging	LOW VOLATILITY	100	20	1	0.1%	0.06	0.06	0.06	0.06
		MODERATE VOLATILITY	100	20	1	2.7%	0.5	0.50	0.50	0.32
		HIGH VOLATILITY	100	20	1	12.8%	1.5	1.50	1.50	1.26
	TOTAL REACTOR EMISSIONS (lbs-batch/year)	LOW VOLATILITY							184.08	184.08
		MODERATE VOLATILITY							1332.65	925.91
		HIGH VOLATILITY							11365.50	3866.79

TABLE E-1. (continued)

# of unit ops per model batch	Calculation for 1 unit operation	Emission Stream VOC	Flow Rate (acfm)	Temp. (Deg C)	Duration (min)	VOC (vol %)	Emissions lb/event	Emissions lbs/batch (Note 1)	NO CONTROL Mass Flux lbs/batch	CPC (Note 2) Mass Flux lbs/batch
	CENTRIFUGES									
2	Loading/spinning w/inerting	LOW VOLATILITY	3	20	30	0.1%	0.02	0.05	0.05	0.05
		MODERATE VOLATILITY	3	20	30	3.1%	0.23	0.47	0.47	0.47
		HIGH VOLATILITY	3	20	30	14.5%	2.50	5.00	5.00	2.25
2	Cake cutting/unloading w/purge -- 3 min	LOW VOLATILITY	20	20	3	0.1%	0.02	0.03	0.03	0.03
		MODERATE VOLATILITY	20	20	3	3.1%	0.16	0.31	0.31	0.31
		HIGH VOLATILITY	20	20	3	14.5%	1.67	3.34	3.34	1.50
	TOTAL CENTRIFUGE EMISSIONS (lbs-batch/year)	LOW VOLATILITY							21.83	21.83
		MODERATE VOLATILITY							215.38	215.38
		HIGH VOLATILITY							2292.96	1031.83
	DRYERS									
	Tray Dryer									
1	Convective - start of cycle	LOW VOLATILITY	6000	65	60	0.3%	200	200.00	200.00	20.00
		MODERATE VOLATILITY	6000	65	60	0.8%	200	200.00	200.00	20.00
		HIGH VOLATILITY	6000	65	60	0.3%	200	200.00	200.00	20.00
1	Convective - middle of cycle	LOW VOLATILITY	6000	65	240	0.1%	180	180.00	180.00	18.00
		MODERATE VOLATILITY	6000	65	240	0.2%	180	180.00	180.00	18.00
		HIGH VOLATILITY	6000	65	240	0.1%	180	180.00	180.00	18.00
1	Convective - end of cycle	LOW VOLATILITY	6000	65	60	0.0%	20	20.00	20.00	2.00
		MODERATE VOLATILITY	6000	65	60	0.0%	20	20.00	20.00	2.00
		HIGH VOLATILITY	6000	65	60	0.1%	20	20.00	20.00	2.00
	TOTAL DRYER EMISSIONS (lbs-batch/year)	LOW VOLATILITY							110000	11000
		MODERATE VOLATILITY							110000	11000
		HIGH VOLATILITY							110000	11000

TABLE E-1. (continued)

# of unit ops per model batch	Calculation for 1 unit operation	Emission Stream VOC	Flow Rate (acfm)	Temp. (Deg C)	Duration (min)	VOC (vol %)	Emissions lb/event	Emissions lbs/batch (Note 1)	NO CONTROL Mass Flux lbs/batch	CPC (Note 2) Mass Flux lbs/batch
	BATCH DISTILLATION (Note 11)									
1	Atmos. op'n - Startup Step 1	LOW VOLATILITY	1.4		5	0.7%	0.01	0.01	0.01	0.01
	Atmos. op'n - Startup Step 2	LOW VOLATILITY	12.6	25	60	0.7%	0.52	0.52	0.52	0.52
1	Atmos. op'n - Startup Step 1	MODERATE VOLATILITY	5.5		5	14.5%	0.33	0.33	0.33	0.09
	Atmos. op'n - Startup Step 2	MODERATE VOLATILITY	14.4	25	45	16.8%	5.96	5.96	5.96	2.03
1	Atmos. op'n - Startup Step 1	HIGH VOLATILTIY	28.9		5	60.0%	16.4	16.40	16.40	1.80
	Atmos. op'n - Startup Step 2	HIGH VOLATILTIY	39.9	25	30	72.8%	164.6	164.60	164.60	14.81
	TOTAL DISTILLATION EMISSIONS (lbs-batch/year)	LOW VOLATILITY							145.75	145.75
		MODERATE VOLATILITY							1729.75	580.855
		HIGH VOLATILITY							49775	4569.95

Note 1:
Assume 1 event/batch
Note 2:
CPC = CURRENT PHARMACEUTICAL CONTROL

TABLE E-2. EMISSION STREAM CHARACTERISTICS FOR SOLVENT REACTION MODEL PROCESS WITH VACUUM DRYER

# of unit ops per model batch	Calculation for 1 unit operation	Emission Stream VOC	Flow Rate (acfm)	Temp. (Deg C)	Pressure (mm Hg)	Duration (min)	VOC (vol %)	Emissions lb/event	Emissions lbs/batch (Note 1)	NO CONTROL Mass Flux lbs/batch	CPC (Note 2) Mass Flux lbs/batch
9.25	Displacement	LOW VOLATILITY	18	20	760	15	0.6%	0.29	2.64	2.64	2.64
	(2000-gallon vessel)	MODERATE VOLATILITY	18	20	760	15	12.6%	2.82	26.08	26.08	7.82
		HIGH VOLATILITY	18	20	760	15	57.9%	30.02	277.66	277.66	30.54
	TOTAL DISPLACEMENT EMISSIONS	LOW VOLATILITY								727.02	727.02
	(lbs-batch/year)	MODERATE VOLATILITY								7172.28	2151.68
		HIGH VOLATILITY								76355.65	8399.12
	REACTORS										
1	Charging w/purge	LOW VOLATILITY	30	20	760	15	0.1%	0.12	0.12	0.12	0.12
		MODERATE VOLATILITY	30	20	760	15	3.1%	1.17	1.17	1.17	1.17
		HIGH VOLATILITY	30	20	760	15	14.5%	12.51	12.51	12.51	5.63
1	Heat-up w/purge	LOW VOLATILITY	30	20 to 30	760	5		0.1	0.10	0.10	0.10
		MODERATE VOLATILITY	30	20 to 30	760	5		0.52	0.52	0.52	0.52
		HIGH VOLATILITY	30	20 to 30	760	5		5.13	5.13	5.13	1.85
1	Reaction w/purge	LOW VOLATILITY	150	37	760	3	0.5%	0.39	0.39	0.39	0.39
		MODERATE VOLATILITY	150	37	760	3	7.5%	2.65	2.65	2.65	1.35
		HIGH VOLATILITY	150	37	760	3	27.2%	22.19	22.19	22.19	5.33
1	Empty Reactor Purging	LOW VOLATILITY	100	20	760	1	0.1%	0.06	0.06	0.06	0.06
		MODERATE VOLATILITY	100	20	760	1	2.7%	0.5	0.50	0.50	0.32
		HIGH VOLATILITY	100	20	760	1	12.8%	1.5	1.50	1.50	1.26
	TOTAL REACTOR EMISSIONS	LOW VOLATILITY								184.08	184.08
	(lbs-batch/year)	MODERATE VOLATILITY								1332.65	925.91
		HIGH VOLATILITY								11365.50	3866.79

TABLE E-2. (continued)

# of unit ops per model batch	Calculation for 1 unit operation	Emission Stream VOC	Flow Rate (acfm)	Temp. (Deg C)	Pressure (mm Hg)	Duration (min)	VOC (vol %)	Emissions lb/event	Emissions lbs/batch (Note 1)	NO CONTROL Mass Flux lbs/batch	CTC (Note 2) Mass Flux lbs/batch
	CENTRIFUGES										
2	Loading/spinning w/inerting	LOW VOLATILITY	3	20	760	30	0.1%	0.02	0.05	0.05	0.05
		MODERATE VOLATILITY	3	20	760	30	3.1%	0.23	0.47	0.47	0.47
		HIGH VOLATILITY	3	20	760	30	14.5%	2.50	5.00	5.00	2.25
2	Cake cutting/unloading w/purge -- 3 min	LOW VOLATILITY	20	20	760	3	0.1%	0.02	0.03	0.03	0.03
		MODERATE VOLATILITY	20	20	760	3	3.1%	0.16	0.31	0.31	0.31
		HIGH VOLATILITY	20	20	760	3	14.5%	1.67	3.34	3.34	1.50
	TOTAL CENTRIFUGE EMISSIONS (lbs-batch/year)	LOW VOLATILITY								21.83	21.83
		MODERATE VOLATILITY								215.38	215.38
		HIGH VOLATILITY								2292.96	1031.83
	DRYERS										
	Tray Dryer										
1	Vacuum Op'n - start of cycle	LOW VOLATILITY	15	50	150	360		72	72.00	72.00	7.20
		MODERATE VOLATILITY	15	50	150	360		72	72.00	72.00	7.20
		HIGH VOLATILITY	15	50	150	360		72	72.00	72.00	7.20
1	Vacuum Op'n - middle of cycle	LOW VOLATILITY	12	50	82	480		133	133.00	133.00	13.30
		MODERATE VOLATILITY	12	50	82	480		133	133.00	133.00	13.30
		HIGH VOLATILITY	12	50	82	480		133	133.00	133.00	13.30
1	Vacuum Op'n - end of cycle	LOW VOLATILITY	12	50	23	360		10	10.00	10.00	1.00
		MODERATE VOLATILITY	12	50	23	360		10	10.00	10.00	1.00
		HIGH VOLATILITY	12	50	23	360		10	10.00	10.00	1.00
	TOTAL DRYER EMISSIONS (lbs-batch/year)	LOW VOLATILITY								59125	5912.5
		MODERATE VOLATILITY								59125	5912.5
		HIGH VOLATILITY								59125	5912.5

TABLE E-2. (continued)

# of unit ops per model batch	Calculation for 1 unit operation	Emission Stream VOC	Flow Rate (acfm)	Temp. (Deg C)	Pressure (mm Hg)	Duration (min)	VOC (vol %)	Emissions lb/event	Emissions lbs/batch (Note 1)	NO CONTROL Mass Flux lbs/batch	CPC (Note 2) Mass Flux lbs/batch
	BATCH DISTILLATION										
1	Atmos. op'n - Startup Step 1	LOW VOLATILITY	1.4		760	5	0.7%	0.01	0.01	0.01	0.01
	Atmos. op'n - Startup Step 2	LOW VOLATILITY	12.6	25	760	60	0.7%	0.52	0.52	0.52	0.52
1	Atmos. op'n - Startup Step 1	MODERATE VOLATILITY	5.5		760	5	14.5%	0.33	0.33	0.33	0.09
	Atmos. op'n - Startup Step 2	MODERATE VOLATILITY	14.4	25	760	45	16.8%	5.96	5.96	5.96	2.03
1	Atmos. op'n - Startup Step 1	HIGH VOLATILTIY	28.9		760	5	60.0%	16.4	16.40	16.40	1.80
	Atmos. op'n - Startup Step 2	HIGH VOLATILTIY	39.9	25	760	30	72.8%	164.6	164.60	164.60	14.81
	TOTAL DISTILLATION EMISSIONS	LOW VOLATILITY								145.75	145.75
	(lbs-batch/year)	MODERATE VOLATILITY								1729.75	580.855
		HIGH VOLATILITY								4977.5	4569.95

Note 1:
Assume 1 event/batch
Note 2:
CPC = CURRENT PHARMACEUTICAL CONTROL

TABLE E-3. EMISSION STREAM CHARACTERISTICS FOR LIQUID REACTION MODEL PLANT

# of unit ops per model batch	Calculation for 1 unit operation	Emission Stream VOC	Flow Rate (acfm)	Temp. (Deg C)	Duration (min)	VOC (vol %)	Emissions lb/event	Emissions lbs/batch (Note 1)	NO CONTROL Mass Flux lbs/batch	CPC (Note 2) Mass Flux lbs/batch
6.25	Displacement (2000-gallon vessel)	LOW VOLATILITY	18	20	15	0.6%	0.29	1.79	1.79	1.79
		MODERATE VOLATILITY	18	20	15	12.6%	2.82	17.62	17.62	5.29
		HIGH VOLATILITY	18	20	15	57.9%	30.02	187.61	187.61	20.64
	TOTAL DISPLACEMENT EMISSIONS (lbs-batch/year)	LOW VOLATILITY							491.23	491.23
		MODERATE VOLATILITY							4846.14	1453.84
		HIGH VOLATILITY							51591.65	5675.08
	REACTORS									
1	Charging w/purge	LOW VOLATILITY	30	20	15	0.1%	0.12	0.12	0.12	0.12
		MODERATE VOLATILITY	30	20	15	3.1%	1.17	1.17	1.17	1.17
		HIGH VOLATILITY	30	20	15	14.5%	12.51	12.51	12.51	5.63
1	Heat-up w/purge	LOW VOLATILITY	30	20 to 30	5		0.1	0.10	0.10	0.10
		MODERATE VOLATILITY	30	20 to 30	5		0.52	0.52	0.52	0.52
		HIGH VOLATILITY	30	20 to 30	5		5.13	5.13	5.13	1.85
1	Reaction w/purge	LOW VOLATILITY	150	37	3	0.5%	0.39	0.39	0.39	0.39
		MODERATE VOLATILITY	150	37	3	7.5%	2.65	2.65	2.65	1.35
		HIGH VOLATILITY	150	37	3	27.2%	22.19	22.19	22.19	5.33
1	Empty Reactor Purging	LOW VOLATILITY	100	20	1	0.1%	0.06	0.06	0.06	0.06
		MODERATE VOLATILITY	100	20	1	2.7%	0.5	0.50	0.50	0.32
		HIGH VOLATILITY	100	20	1	12.8%	1.5	1.50	1.50	1.26
	TOTAL REACTOR EMISSIONS (lbs-batch/year)	LOW VOLATILITY							184.08	184.08
		MODERATE VOLATILITY							1332.65	925.91
		HIGH VOLATILITY							11365.50	3866.79

TABLE E-3. (continued)

# of unit ops per model batch	Calculation for 1 unit operation	Emission Stream VOC	Flow Rate (acfm)	Temp. (Deg C)	Duration (min)	VOC (vol %)	Emissions lb/event	Emissions lbs/batch (Note 1)	NO CONTROL Mass Flux lbs/batch	CPC (Note 2) Mass Flux lbs/batch
	BATCH DISTILLATION (Note 11)									
1	Atmos. op'n - Startup Step 1	LOW VOLATILITY	1.4		5	0.7%	0.01	0.01	0.01	0.01
	Atmos. op'n - Startup Step 2	LOW VOLATILITY	12.6	25	60	0.7%	0.52	0.52	0.52	0.52
1	Atmos. op'n - Startup Step 1	MODERATE VOLATILITY	5.5		5	14.5%	0.33	0.33	0.33	0.09
	Atmos. op'n - Startup Step 2	MODERATE VOLATILITY	14.4	25	45	16.8%	5.96	5.96	5.96	2.03
1	Atmos. op'n - Startup Step 1	HIGH VOLATILTIY	28.9		5	60.0%	16.4	16.40	16.40	1.80
	Atmos. op'n - Startup Step 2	HIGH VOLATILTIY	39.9	25	30	72.8%	164.6	164.60	164.60	14.81
	TOTAL DISTILLATION EMISSIONS (lbs-batch/year)	LOW VOLATILITY							145.75	145.75
		MODERATE VOLATILITY							1729.75	580.855
		HIGH VOLATILITY							49775	4569.95

Note 1:
Assume 1 event/batch
Note 2:
CPC = CURRENT PHARMACEUTICAL CONTROL

TABLE E-4. EMISSION STREAM CHARACTERISTICS FOR FORMULATOR MODEL PLANT

# of unit ops per model batch	Calculation for 1 unit operation	Emission Stream VOC	Flow Rate (acfm)	Temp. (Deg C)	Duration (min)	VOC (vol %)	Emissions lb/event	Emissions lbs/batch (Note 1)	NO CONTROL Mass Flux lbs/batch
4.5	Displacement	LOW VOLATILITY	18	20	15	0.6%	0.29	1.29	1.29
	(2000-gallon vessel)	MODERATE VOLATILITY	18	20	15	12.6%	2.82	12.69	12.69
		HIGH VOLATILITY	18	20	15	57.9%	30.02	135.08	135.08
	TOTAL DISPLACEMENT EMISSIONS	LOW VOLATILITY							353.69
	(lbs-batch/year)	MODERATE VOLATILITY							3489.22
		HIGH VOLATILITY							37145.99
	REACTORS								
1	Charging w/purge	LOW VOLATILITY	30	20	15	0.1%	0.12	0.12	0.12
		MODERATE VOLATILITY	30	20	15	3.1%	1.17	1.17	1.17
		HIGH VOLATILITY	30	20	15	14.5%	12.51	12.51	12.51
1	Heat-up w/purge	LOW VOLATILITY	30	20 to 30	5		0.1	0.10	0.10
		MODERATE VOLATILITY	30	20 to 30	5		0.52	0.52	0.52
		HIGH VOLATILITY	30	20 to 30	5		5.13	5.13	5.13
1	Reaction w/purge	LOW VOLATILITY	150	37	3	0.5%	0.39	0.39	0.39
		MODERATE VOLATILITY	150	37	3	7.5%	2.65	2.65	2.65
		HIGH VOLATILITY	150	37	3	27.2%	22.19	22.19	22.19
1	Empty Reactor Purging	LOW VOLATILITY	100	20	1	0.1%	0.06	0.06	0.06
		MODERATE VOLATILITY	100	20	1	2.7%	0.5	0.50	0.50
		HIGH VOLATILITY	100	20	1	12.8%	1.5	1.50	1.50
	TOTAL REACTOR EMISSIONS	LOW VOLATILITY							184.08
	(lbs-batch/year)	MODERATE VOLATILITY							1332.65
		HIGH VOLATILITY							11365.50

Note 1:
Assume 1 event/batch

TABLE E-5. ASSUMPTIONS FOR SOLVENT REACTION MODEL PLANT WITH ATMOSPHERIC DRYER

Basis:

A. Equipment required for each solvent reaction model batch process

1 reactor @ 2,000 gallons
2 weigh tanks @ 1,000 gallons
1 mix tank @ 2,000 gallons
1 crystallizer @ 3,000 gallons
1 slurry tank @ 3,000 gallons
2 centrifuges @ 200 ft^3 each
1 distillation unit @ 2,000 gallons
1 solvent recovery tank @ 1,500 gallons
1 atmospheric dryer @ 300 ft^3

B. Operation

Small plant has 3 "model batch process"
Medium plant has 10 "model batch processes"
Large plant has 30 "model batch processes"

Each batch is run 1 X per day
Plant operates 275 days per year

C. Chemistry

For calculations:

	vapor pressure equivalent to:
Low volatility solvent	n-butanol
Moderate volatility solvent	methanol
High volatility solvent	ether

TABLE E-6. ASSUMPTIONS FOR SOLVENT REACTION MODEL PLANT WITH VACUUM DRYER

Basis:

A. Equipment required for each solvent reaction model batch process

1 reactor @ 2,000 gallons
2 weigh tanks @ 1,000 gallons
1 mix tank @ 2,000 gallons
1 crystallizer @ 3,000 gallons
1 slurry tank @ 3,000 gallons
2 centrifuges @ 200 ft^3 each
1 distillation unit @ 2,000 gallons
1 solvent recovery tank @ 1,500 gallons
1 vacuum tray dryer @ 300 ft^3

B. Operation

Small plant has 3 "model batch process"
Medium plant has 10 "model batch processes"
Large plant has 30 "model batch processes"

Each batch is run 1 X per day
Plant operates 275 days per year

C. Chemistry

For calculations:

	vapor pressure equivalent to:
Low volatility solvent	n-butanol
Moderate volatility solvent	methanol
High volatility solvent	ether

TABLE E-7. ASSUMPTIONS FOR LIQUID REACTION MODEL PLANT

Basis:

A. Equipment required for each solvent reaction model batch process

1 reactor @ 2,000 gallons
2 weigh tanks @ 1,000 gallons
1 mix tank @ 2,000 gallons
1 surge tank @ 3,000 gallons
1 distillation unit @ 2,000 gallons
1 solvent recovery tank @ 1,500 gallons

B. Operation

Small plant has 3 "model batch process"
Medium plant has 10 "model batch processes"
Large plant has 30 "model batch processes"

Each batch is run 1 X per day
Plant operates 275 days per year

C. Chemistry

For calculations:

	vapor pressure equivalent to:
Low volatility solvent	n-butanol
Moderate volatility solvent	methanol
High volatility solvent	ether

TABLE E-8. ASSUMPTIONS FOR FORMULATION MODEL PLANT

Basis:

A. Equipment required for each fomulation model batch process

1 reactor @ 2,000 gallons
2 weigh tanks @ 1,000 gallons
1 mix tank @ 2,000 gallons
1 surge tank @ 3,000 gallons
1 closed in-line process filter (no emissions)

B. Operation

Small plant has 3 "model batch process"
Medium plant has 10 "model batch processes"
Large plant has 30 "model batch processes"

Each batch is run 1 X per day
Plant operates 275 days per year

C. Chemistry

For calculations:

	vapor pressure equivalent to:
Low volatility solvent	n-butanol
Moderate volatility solvent	methanol
High volatility solvent	ether

TABLE E-9. EMISSIONS FROM SOLVENT REACTION MODEL PLANT WITH ATMOSPHERIC DRYER

MODEL PLANT EMISSIONS(lbs/yr)

	SMALL/NC	SMALL/CPC
LOW VOLATILITY	333,236	36,236
MODERATE VOLATILITY	361,350	44,621
HIGH VOLATILITY	749,367	86,603

	MEDIUM/NC	MEDIUM/CPC
LOW VOLATILITY	1,109,676	120,666
MODERATE VOLATILITY	1,203,296	148,590
HIGH VOLATILITY	2,495,393	288,388

	LARGE/NC	LARGE/CPC
LOW VOLATILITY	3,332,360	362,360
MODERATE VOLATILITY	3,613,502	446,215
HIGH VOLATILITY	7,493,673	866,031

MODEL PLANT EMISSIONS(tons/yr)

	SMALL/NC	SMALL/CPC
LOW VOLATILITY	166.62	18.12
MODERATE VOLATILITY	180.68	22.31
HIGH VOLATILITY	374.68	43.30

	MEDIUM/NC	MEDIUM/CPC
LOW VOLATILITY	554.84	60.33
MODERATE VOLATILITY	601.65	74.29
HIGH VOLATILITY	1247.70	144.19

	LARGE/NC	LARGE/CPC
LOW VOLATILITY	1666.18	181.18
MODERATE VOLATILITY	1806.75	223.11
HIGH VOLATILITY	3746.84	433.02

NC = No Control
CPC = Current Pharmaceutical Control

1. For surface condensers on sources emitting:
   - -25C for VP>300mmHg
   - -15C for 150<VP<300mmHg
   - -0C for 77.5<VP<150mmHg
   - 10C for 52<VP<77.5mmHg
   - 25C for 26<VP<52mmHg
2. Air dryers emitting over 330 lbs/day controlled to 90%
3. Air dryers emitting <330 lbs/day only allowed to emit 33 lbs/day

TABLE E-10. EMISSIONS FROM SOLVENT REACTION MODEL PLANT WITH VACUUM DRYER

MODEL PLANT EMISSIONS(lbs/yr)

	SMALL/NC	SMALL/CPC
LOW VOLATILITY	180,611	20,974
MODERATE VOLATILITY	208,725	29,359
HIGH VOLATILITY	596,742	71,341

	MEDIUM/NC	MEDIUM/CPC
LOW VOLATILITY	601,435	69,842
MODERATE VOLATILITY	695,055	97,765
HIGH VOLATILITY	1,987,152	237,564

	LARGE/NC	LARGE/CPC
LOW VOLATILITY	1,806,110	209,735
MODERATE VOLATILITY	2,087,252	293,590
HIGH VOLATILITY	5,967,423	713,406

MODEL PLANT EMISSIONS(tons/yr)

	SMALL/NC	SMALL/CPC
LOW VOLATILITY	90.31	10.49
MODERATE VOLATILITY	104.36	14.68
HIGH VOLATILITY	298.37	35.67

	MEDIUM/NC	MEDIUM/CPC
LOW VOLATILITY	300.72	34.92
MODERATE VOLATILITY	347.53	48.88
HIGH VOLATILITY	993.58	118.78

	LARGE/NC	LARGE/CPC
LOW VOLATILITY	903.06	104.87
MODERATE VOLATILITY	1043.63	146.79
HIGH VOLATILITY	2983.71	356.70

NC = No Control
CPC = Current Pharmaceutical Control

1. For surface condensers on sources emitting:
   - -25C for VP>300mmHg
   - -15C for 150<VP<300mmHg
   - -0C for 77.5<VP<150mmHg
   - 10C for 52<VP<77.5mmHg
   - 25C for 26<VP<52mmHg
2. Air dryers emitting over 330 lbs/day controlled to 90%
3. Air dryers emitting <330 lbs/day only allowed to emit 33 lbs/day

TABLE E-11. EMISSIONS FROM LIQUID REACTION MODEL PLANT

MODEL PLANT EMISSIONS(lbs/yr)

	SMALL/NC	SMALL/CPC
LOW VOLATILITY	2,463	2,463
MODERATE VOLATILITY	23,726	8,882
HIGH VOLATILITY	338,196	42,335

	MEDIUM/NC	MEDIUM/CPC
LOW VOLATILITY	8,202	8,202
MODERATE VOLATILITY	79,006	29,576
HIGH VOLATILITY	1,126,194	140,977

	LARGE/NC	LARGE/CPC
LOW VOLATILITY	24,632	24,632
MODERATE VOLATILITY	237,256	88,818
HIGH VOLATILITY	3,381,965	423,355

MODEL PLANT EMISSIONS(tons/yr)

	SMALL/NC	SMALL/CPC
LOW VOLATILITY	1.23	1.23
MODERATE VOLATILITY	11.86	4.44
HIGH VOLATILITY	169.10	21.17

	MEDIUM/NC	MEDIUM/CPC
LOW VOLATILITY	4.10	4.10
MODERATE VOLATILITY	39.50	14.79
HIGH VOLATILITY	563.10	70.49

	LARGE/NC	LARGE/CPC
LOW VOLATILITY	12.32	12.32
MODERATE VOLATILITY	118.63	44.41
HIGH VOLATILITY	1690.98	211.68

NC = No Control
CPC = Current Pharmaceutical Control

1. For surface condensers on sources emitting:
   - -25C for VP>300mmHg
   - -15C for 150<VP<300mmHg
   - -0C for 77.5<VP<150mmHg
   - 10C for 52<VP<77.5mmHg
   - 25C for 26<VP<52mmHg
2. Air dryers emitting over 330 lbs/day controlled to 90%
3. Air dryers emitting <330 lbs/day only allowed to emit 33 lbs/day

TABLE E-12. EMISSIONS FROM FORMULATION MODEL PLANT

MODEL PLANT EMISSIONS(lbs/yr)

	SMALL/NC
LOW VOLATILITY	1,613
MODERATE VOLATILITY	14,466
HIGH VOLATILITY	145,534

	MEDIUM/NC
LOW VOLATILITY	5,372
MODERATE VOLATILITY	48,170
HIGH VOLATILITY	484,630

	LARGE/NC
LOW VOLATILITY	16,133
MODERATE VOLATILITY	144,656
HIGH VOLATILITY	1,455,345

MODEL PLANT EMISSIONS(tons/yr)

	SMALL/NC
LOW VOLATILITY	0.81
MODERATE VOLATILITY	7.23
HIGH VOLATILITY	72.77

	MEDIUM/NC
LOW VOLATILITY	2.69
MODERATE VOLATILITY	24.09
HIGH VOLATILITY	242.31

	LARGE/NC
LOW VOLATILITY	8.07
MODERATE VOLATILITY	72.33
HIGH VOLATILITY	727.67

NC = No Control

Model Emission Stream Calculations

OPERATION REFERENCE 2.1.1

Reactors

2.1.1.2.1 Charging without purge

Assume reactor volume of 500 gallons (350 gallons to fill)

Filling occurs at 20°C (Room Temperature)

Flowrate

$$\frac{350\ \text{gal}}{} \left| \frac{\text{ft}^3}{7.48\ \text{gal}} \right| \frac{}{15\ \text{min}} = 3.12\ \text{ft}^3/\text{min}$$

A. Low volatility (n-Butanol)

% VOC

4.4 mmHg/760 mmHg = 0.0058 = 0.6%

Total lb VOC, event

$$\frac{(4.4\ \text{mmHg})(3.12\ \text{ft}^3/\text{min})}{\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\ (293\text{K})}\ (74\ \text{lb/lbmol})(15\ \text{min/event})$$

= 0.05 lb/event

B. Medium volatility (methanol)

% VOC

92 mmHg/760 mmHg = 0.121 = 12.0%

Total lb VOC, event

$$\frac{(92\ \text{mmHg})(3.12\ \text{ft}^3\ /\text{min})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)\ (293\text{K})}\ (32\ \text{lb/lbmol})(15\ \text{min/event})$$

= 0.5 lb/event

C. High volatility (ether)

% VOC

442 mmHg/760 mmHg = 0.582 = 58.0%

Total lb VOC, event

$$\frac{(442\ \text{mmHg})(3.12\ \text{ft}^3/\text{min})}{\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\ (293\text{K})}\ (74\ \text{lb/lbmol})(15\ \text{min/event})$$

$= 5$ lb/event

2.1.2.2.1 Charging with purge

flow rate out of reactor = purge rate

A. Low volatility (n-Butanol)

% VOC

4.4 mmHg/760 mmHg = 0.0058 = 0.6%

Assume 10% of saturation

(0.10)(0.6) = 0.06%

Total lb VOC, event

$$\frac{(760\ \text{mmHg})(0.0006)(30\ \text{ft}^3/\text{min})}{\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\ (293\text{K})}\ (74\ \text{lb/lbmol})(15\ \text{min})$$

$= 0.05$ lb/event

B. Medium volatility (methanol)

% VOC

92 mmHg/760 mmHg = 0.121 = 12.0%

Assume 10% of saturation

(0.10)(12.0) = 1.2%

Total lb VOC, event

$$\frac{(760\ \text{mmHg})(0.012)(30\ \text{ft}^3/\text{min})}{\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\ (293\text{K})}\ (32\ \text{lb/lbmol})(15\ \text{min})$$

$= 0.45$ lb/event

C. High volatility (ether)

% VOC

442 mmHg/760 mmHg = 0.582 = 58.0%

Assume 10% of saturation

(0.1)(58.6) = 5.8%

Total lb VOC, event

$$\frac{(760\ \text{mmHg})(0.058)(30\ \text{ft}^3/\text{min})}{\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}(293\text{K})}(74\ \text{lb/lbmol})(15\ \text{min})$$

= 5.0 lb/event

2.1.1.2.2 Heatup without purge

Assume reactor volume is 500 gallons. (Headspace is 150 gallons)

A. Low volatility (n-Butanol)

Flow rate, Emissions

VP of n-butanol @ 30 percent = 17.8 mmHg

$$\Delta n = \frac{(150\ \text{gal})\frac{\text{ft}^3}{7.48\ \text{gal}}}{\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}}\Bigg)\Bigg(\frac{(760-4.4)\ \text{mmHg}}{(273+20)\text{K}} - \frac{(760-17.8)\ \text{mmHg}}{(273+30)\text{K}}\Bigg)$$

Δn = 0.0026 lbmoles gas displaced

$$\frac{0.0026\ \text{lbmole gas displaced}}{}\bigg|\frac{379\ \text{ft}^3}{\text{lbmol}} = 1\ \text{ft}^3\ \text{displaced}$$

1 ft^3/5 min = 0.2 ft^3/min displaced (average flow rate)

$$n_t = \frac{\left(\frac{4.4}{760-4.4}\right)\text{mmHg} + \left(\frac{17.8}{760-17.8}\right)\text{mmHg}}{2}\left(\begin{array}{l}0.0026\ \text{lbmoles}\\ \text{gas displaced}\end{array}\right)$$

n_t = 0.000039 lbmoles n-Butanol (MW = 74 lb/lbmol)

(0.000039 lbmol n-butanol)(74 lb/lbmol)

n_t = 0.003 lb n-Butanol

B. Medium volatility (methanol)

Flow rate, Emissions

VP of methanol @ 30°C = 165 mmHg

$$\left(\frac{(150\ \text{gal})\left(\frac{\text{ft}^3}{7.48\ \text{gal}}\right)}{\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}}\right)\left(\frac{(760-92)\ \text{mmHg}}{(273+20)\text{K}}-\frac{(760-165)\ \text{mmHg}}{(273+30)\text{K}}\right)$$

Δn = 0.00634 lbmoles gas displaced

$$\frac{0.00634\ \text{lbmoles}}{}\left|\frac{379\ \text{ft}^3}{\text{lbmol}}\right|\frac{}{5\ \text{min}} = 0.48\ \text{ft}^3/\text{min}$$

$$n_t = \frac{\left(\frac{92}{760-92}\right)\text{mmHg} + \left(\frac{165}{760-165}\right)\text{mmHg}}{2}$$

n_t = (0.0013 lbmol methanol)(32 lb/lbmol)

n_t = 0.0013 lbmoles methanol (MW = 32 lb/lbmol)

n_t = 0.04 lb methanol

C. High volatility (ether)

Flowrate, Emissions

VP of ether @ 30°C = 661 mmHg

$$\Delta n = \left(\frac{(150\ \text{gal})\left(\frac{\text{ft}^3}{7.48\ \text{gal}}\right)}{\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}}\right)\left(\frac{(760-442)\text{mmHg}}{(273+20)\text{K}}-\frac{(760-661)\text{mmHg}}{(273+30)\text{K}}\right)$$

Δn = 0.0152 lbmoles gas displaced

$$\Delta n_t = \frac{\left(\frac{442}{760 - 442}\right) \text{mmHg} + \left(\frac{661}{760 - 661}\right) \text{mmHg}}{2} \left[\begin{array}{l}0.0152 \text{ lbmoles} \\ \text{gas displaced}\end{array}\right]$$

n_t = 0.0613 lbmoles ether (MW = 74 lb/lbmol)

(0.0613 lbmol ether)(74 lb/lbmol)

n_t = 4.5 lb ether

2.1.1.2.2 Heatup with purge

Assume flow rate = 30 acfm and 10% of saturation

- Temperature increases from 20 to 30°C

A. Low volatility (n-Butanol)

$$\frac{(0.10)(30 \text{ acfm})(4.4 \text{ mmHg})}{\left(\frac{998.97 \text{ mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})} = 0.000045 \text{ lbmol/min (initial)}$$

$$\frac{(0.10)(30 \text{ acfm})(17.8 \text{ mmHg})}{\left(\frac{998.97 \text{ mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(303\text{K})} = 0.000176 \text{ lbmol/min (final)}$$

Calculate average

$$\frac{(0.000045 + 0.000176) \text{ lbmol/min}}{2}$$

= 0.00011 lbmol/min n-butanol (MW = 74 lb/lbmol)

$$\frac{0.00011 \text{ lbmol n-butanol}}{\text{min}} \left| \frac{74 \text{ lb}}{\text{lbmol}} \right.$$

= (0.008 lb/min)(5 min) = 0.04 lb n-butanol

B. Medium volatility (methanol)

$$\frac{(0.10)(30\ \text{acfm})(92\ \text{mmHg})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})} = 0.000943\ \text{lbmol/min (initial)}$$

$$\frac{(0.10)(30\ \text{acfm})(165\ \text{mmHg})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(303\text{K})} = 0.00164\ \text{lbmol/min (final)}$$

Calculate average

$$\frac{(0.000943 + 0.00164)\ \text{lbmol/min}}{2}$$

$= 0.0013$ lbmol/min methanol (MW = 74 lb/lbmol)

$$\frac{0.0013\ \text{lbmol methanol}}{\text{min}} \left| \frac{74\ \text{lb}}{\text{lbmol}} \right.$$

= (0.04 lb/min)(5 min) = 0.2 lb methanol

C. High volatility (ether)

$$\frac{(0.10)(30\ \text{acfm})(442\ \text{mmHg})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})} = 0.0045\ \text{lbmol/min (initial)}$$

$$\frac{(0.10)(30\ \text{acfm})(661\ \text{mmHg})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(303\text{K})} = 0.0066\ \text{lbmol/min (final)}$$

Calculate average

$$\frac{(0.0045 + 0.0066)\ \text{lbmol/min}}{2}$$

$= 0.00555$ lbmol/min ether (MW = 74 lb/lbmol)

$$\frac{0.00555\ \text{lbmol ether}}{\text{min}} \left| \frac{74\ \text{lb}}{\text{lbmol}} \right.$$

= (0.411 lb/min)(5 min) = 2 lb ether

2.1.1.2.2 Reaction with purge

This event actually is the purging of a reactor prior to charging (or sampling).

Assume temperature = 310K and 10% of saturation

A. Low volatility (n-Butanol)

VP n-butanol @ 310K = 16 mmHg

$$\frac{(0.10)(150\ \text{acfm})(16\ \text{mmHg})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(310\text{K})} = 0.00077\ \text{lbmol/min}$$

= 0.00077 lbmol/min n-butanol (MW = 74 lb/lbmol)

$$\frac{0.00077\ \text{lbmol n-butanol}}{\text{min}}\,\Big|\,\frac{74\ \text{lb}}{\text{lbmol}}$$

= (0.057 lb/min) (3 min) = 0.17 lb n-butanol

B. Medium volatility (methanol)

VP methanol at 310K = 229 mmHg

$$\frac{(0.10)(150\ \text{acfm})(229\ \text{mmHg})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(310\text{K})} = 0.011\ \text{lbmol/min}$$

= 0.011 lbmol/min methanol (MW = 32 lb/lbmol)

$$\frac{0.011\ \text{lbmol methanol}}{\text{min}}\,\Big|\,\frac{32\ \text{lb}}{\text{lbmol}}$$

= (0.355 lb/min) (3 min) = 1.1 lb methanol

C. High volatility (ether)

VP ether at 310K = 760 mmHg

$$\frac{(0.10)(150\ \text{acfm})(760\ \text{mmHg})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(310\text{K})} = 0.0368\ \text{lbmol/min (initial)}$$

= 0.0368 lbmol/min ether (MW = 74 lb/lbmol)

$$\left.\frac{0.0368 \text{ lbmol ether}}{\text{min}}\right|\frac{74 \text{ lb}}{\text{lbmol}}$$

$$= (2.72 \text{ lb/min})(3 \text{ min}) = 8.2 \text{ lb ether}$$

2.1.1.2.3 Reactor vacuum transfer

Vacuum transfer would typically occur when transferring the contents of a 55 gallon drum to a reactor. The emissions would result from displacing air saturated with VOC's out of the reactor prior to drawing in new product.

Air displaced: assume 500 gallon reactor

A. Low volatility (n-butanol)

Initial air

$$\frac{(760 \text{ mmHg})(500 \text{ gal}/7.48 \text{ gal/ft}^3)}{\left(\frac{998.97 \text{ mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})} = 0.1735 \text{ lbmol}$$

Final air

$$\frac{(100 \text{ mmHg})(500 \text{ gal}/7.48 \text{ gal/ft}^3)}{\left(\frac{998.97 \text{ mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})} = 0.0228 \text{ lbmol}$$

0.1735 lbmol - 0.0228 lbmol = 0.1507 lbmol

Flow rate

$$\left.\frac{0.1507 \text{ lbmol}}{10 \text{ min}}\right|\frac{379 \text{ ft}^3}{\text{lbmol}} = 5.7 \text{ ft}^3\text{/min}$$

VOC emissions

A. Low volatility (n-butanol)

VP @ 20°C = 4.4 mmHg

Assume saturation; vol% ranges from 0.6 to 4.4

Total VOC emissions based on average vol%

(0.6 + 4.4)/2 = 2.5 vol%

(0.1512 lbmol)(0.025)(74 lb/lbmol) = 0.3 lb n-butanol

B. Medium volatility (methanol)

VP @ 20°C = 92 mmHg

92 mmHg/760 mmHg = 12.1 vol%

92 mmHg/100 mmHg = 92 vol%

Total VOC emissions based on average vol%

(12.1 + 92)/2 = 52.1 vol%

(0.1512 lbmol)(0.52)(32 lb/lbmol) = 2.5 lb methanol

C. High volatility (diethyl ether)

VP @ 20°C = 442 mmHg

442 mmHg/760 mmHg = 58.2%

Assume 100 vol% at 100 mmHg

(58.2 + 100)/2 = 79.1 vol%

(0.1512 lbmol)(0.791)(74 lb/lbmol) = 8.9 lb ether

2.1.1.2.3 <u>Pressure transfer</u>

Pressure transfers often consist of "blowing" lines to rid them of solvent. Assuming a typical situation involves 30 ft of 3.5 inch flexible line containing 1% residual solvent, the amount of solvent evaporated from each line is:

$$\pi \left(\frac{\frac{3.5\ \text{in}}{12\ \text{in./ft}}}{2}\right)^2 (30\ \text{ft}) = 2\ \text{ft}^3\ \text{material}$$

$(2\ \text{ft}^3)(0.01) = 0.02\ \text{ft}^3$ in liquid form

A. Low volatility (n-butanol)

VP @ 20°C = 4.4 mmHg

Specific gravity = 0.81

$$(0.10)\left(\frac{150\ \text{ft}^3}{\text{min}}\right)\left(\frac{4.4\ \text{mmHg}}{760\ \text{mmHg}}\right)(\text{min}) =$$

$$\frac{0.02\ \text{ft}^3\left(\frac{62.4\ \text{lb}}{\text{ft}^3}\right)(0.81)\left(\frac{\text{lbmol}}{74\ \text{lb}}\right)\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})}{760\ \text{mmHg}}$$

$0.087 \times \text{min} = 5.26\ \text{ft}^3$ gas
x = 60 minutes (assuming 10% saturation of the stream)

B. Medium volatility (methanol)

VP @ 20°C = 92 mmHg

Specific gravity = 0.792

$$(0.10)\left(\frac{150\ \mathrm{ft}^3}{\mathrm{min}}\right)\left(\frac{92\ \mathrm{mmHg}}{760\ \mathrm{mmHg}}\right)(\mathrm{min}) = \frac{0.02\ \mathrm{ft}^3\left(\frac{62.4\ \mathrm{lb}}{(\mathrm{ft}^3)}\right)(0.792)\left(\frac{\mathrm{lbmol}}{32\ \mathrm{lb}}\right)\left(\frac{998.97\ \mathrm{mmHg}\cdot\mathrm{ft}^3}{\mathrm{lbmol}\cdot\mathrm{K}}\right)(293\mathrm{K})}{760\ \mathrm{mmHg}}$$

$1.82\ \mathrm{x\ min} = 11.9\ \mathrm{ft}^3$ gas

$x = 6.5$ minutes

C. High volatility (diethyl ether)

VP @ 20°C = 442 mmHg

Specific gravity = 0.8

$$(0.10)\left(\frac{150\ \mathrm{ft}^3}{\mathrm{min}}\right)\left(\frac{442\ \mathrm{mmHg}}{760\ \mathrm{mmHg}}\right)(\mathrm{min}) = \frac{0.02\ \mathrm{ft}^3\left(\frac{62.4\ \mathrm{lb}}{\mathrm{ft}^3}\right)(0.8)\left(\frac{\mathrm{lbmol}}{74\ \mathrm{lb}}\right)\left(\frac{998.97\ \mathrm{mmHg}\cdot\mathrm{ft}^3}{\mathrm{lbmol}\cdot\mathrm{K}}\right)(293\mathrm{K})}{760\ \mathrm{mmHg}}$$

$8.72\ \mathrm{x\ min} = 5.2\ \mathrm{ft}^3$ gas

$x = 0.596$ minutes

2.1.1.2.3 Empty reactor purging

A. Low volatility (n-butanol)

$$C_{\mathrm{low}_i} = \frac{(4.4\ \mathrm{mmHg})(74\ \mathrm{lb/lbmol})}{\left(\frac{998.97\ \mathrm{mmHg}\cdot\mathrm{ft}^3}{\mathrm{lbmol}\cdot\mathrm{K}}\right)(293\mathrm{K})}$$

$= 0.0011\ \mathrm{lb/ft}^3$

Standard industry practice (Chapter 3)

$(500\ \mathrm{gal})(\mathrm{ft}^3/7.48\ \mathrm{gal}) = 67\ \mathrm{ft}^3$

$100\ \mathrm{ft}^3/67\ \mathrm{ft}^3 = 1.5$ vessel volume changes

$$(C_f/C_i)^{1.5} = (0.37)^{1.5} = 0.22$$

$$(0.0011\ \text{lb/ft}^3)(0.22) = 0.000242\ \text{lb/ft}^3$$

$$\text{Emissions} = 67\ \text{ft}^3\ (0.0011\ \text{lb/ft}^3 - 0.000242\ \text{lb/ft}^3) = 0.057\ \text{lb}$$

B. Medium volatility (methanol)

$$\frac{(92\ \text{mmHg})(32\ \text{lb/lbmol})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})} = 0.0101\ \text{lb/ft}^3$$

$$\text{Emissions} = 67\ \text{ft}^3[0.0101\ \text{lb/ft}^3 - 0.22(0.0101\ \text{lb/ft}^3)]$$

$$= 0.53\ \text{lb}$$

C. High volatility (diethyl ether)

$$\frac{(442\ \text{mmHg})(74\ \text{lb/lbmol})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})} = 0.1118\ \text{lb/ft}^3$$

$$\text{Emissions} = 67\ \text{ft}^3[0.1118\ \text{lb/ft}^3 - (0.22)(0.1118\ \text{lb/ft}^3)]$$

$$= 5.84\ \text{lb}$$

<u>Exhaust composition</u>

A. Low volatility (n-butanol)

$$\frac{\left(\frac{0.000242\ \text{lb butanol}}{\text{ft}^3\ \text{air}}\right)\left(\frac{\text{lbmol}}{74\ \text{lb}}\right)\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})}{760\ \text{mmHg}} = 0.00126$$

B. Medium volatility (methanol)

$$\frac{\left(\frac{0.00222\ \text{lb methanol}}{\text{ft}^3\ \text{air}}\right)\left(\frac{\text{lbmol}}{32\ \text{lb}}\right)\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})}{760\ \text{mmHg}} = 0.027$$

C. High volatility (diethyl ether)

$$\frac{\left(\frac{0.0246\ \text{lb diethyl ether}}{\text{ft}^3\ \text{air}}\right)\left(\frac{\text{lbmol}}{74\ \text{lb}}\right)\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})}{760\ \text{mmHg}} = 0.128$$

2.1.2.1 Depressurization of a nutsche filter

See example C-14. Assume volume of filter is 1,000 gallons. A total of 0.403 moles of gas are emitted from the filter in a 40 minute period. For simplicity, we have to assume that the flowrate is constant over the duration of the filtration, although we know it will decrease with decreasing pressure.

Midpoint of pressure range = 1,665 mmHg

$$\frac{(0.403\ \text{lbmol})\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{(\text{lbmol}\cdot\text{K})}\right)(300\text{K})}{1{,}665\ \text{mmHg}\cdot 40\ \text{min}} = 1.8\ \text{ft}\ /\text{min}^3$$

The range is from 1.2 to 4.0 ft^3/min

A. Low volatility (n-butanol)

VP @ 27°C = 6.5 mmHg

(0.403 lbmol)(6.5 mmHg/2,570 mmHg)(74 lb/lbmol) = 0.08 lb

B. Medium volatility (methanol)

(0.403 lbmol)(143 mmHg/2,570 mmHg)(32 lb/lbmol) = 0.72 lb

C. High volatility (diethyl ether)

(0.403 lbmol)(596 mmHg/2,570 mmHg)(74 lb/lbmol) = 6.92 lb

2.1.2.1 Filtercake purging

Assume 25% of saturation

N_2 stream at 293K

A. Low volatility (n-butanol)

$$\frac{(0.25)(4.4\ \text{mmHg})(100\ \text{ft}^3/\text{min})(30\ \text{min})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})} = 0.0113\ \text{lbmol}\ (0.8\ \text{lb})$$

B. Medium volatility (methanol)

$$\frac{(0.25)(92\ \text{mmHg})(100\ \text{ft}^3/\text{min})(30\ \text{min})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})} = 0.236\ \text{lbmol}\ (7.5\ \text{lb})$$

C. High volatility (diethyl ether)

$$\frac{(0.25)(442\ \text{mmHg})(100\ \text{ft}^3/\text{min})(30\ \text{min})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{(\text{lbmol}\cdot\text{K})}\right)(293\text{K})} = 1.13\ \text{lbmol}\ (83.8\ \text{lb})$$

2.1.2.2 <u>Heated filtercake purging</u>

A. Low volatility (n-butanol)

VP @ 100°C = 390 mmHg

Assume 25% saturation

$$\frac{(0.25)\left(\frac{390\ \text{mmHg}}{760\ \text{mmHg}}\right)(760\ \text{mmHg})(100\ \text{ft}^3/\text{min})(30\ \text{min})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{(\text{lbmol}\cdot\text{K})}\right)(373\text{K})} = 0.8\ \text{lbmol}$$

B. Medium volatility (methanol)

VP @ 100°C > 760 mmHg

$$\frac{(0.25)(760\ \text{mmHg})(100\ \text{ft}^3/\text{min})(30\ \text{min})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(373\text{K})} = 1.53\ \text{lbmol}$$

C. High volatility (diethyl ether)

$$\frac{(0.25)(760\ \text{mmHg})(100\ \text{ft}^3/\text{min})(30\ \text{min})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(373\text{K})} = 1.53\ \text{lbmol}$$

2.1.2.3 <u>Centrifuge loading/spinning</u>

Same as filtercake purging - but smaller flow rate

flowrate = 3 acfm

duration = 30 minutes

Exhaust composition

A. Low volatility (n-butanol)

$$\frac{(0.25)(3\ \text{ft}^3/\text{min})(4.4\ \text{mmHg})(30\ \text{min})(74\ \text{lb}/\text{lbmol}}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})} = 0.025\ \text{lb}$$

B. Medium volatility (methanol)

$$\frac{(0.25)(3\ \text{ft}^3/\text{min})(92\ \text{mmHg})(30\ \text{min})(32\ \text{lb/lbmol})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})} = 0.226\ \text{lb}$$

C. High volatility (diethyl ether)

$$\frac{(0.25)(3\ \text{ft}^3/\text{min})(442\ \text{mmHg})(74\ \text{lb/lbmol})(30\ \text{min})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{(\text{lbmol}\cdot\text{K})}\right)(293\text{K})} = 2.51\ \text{lb}$$

Filtercake cutting/unloading with purge

Same as centrifuge loading/spinning - but larger flow rate

flow rate = 20 ft^3/min

duration = 30 minutes

A. Low volatility (n-butanol)

$$\frac{(0.25)(20\ \text{ft}^3/\text{min})(4.4\ \text{mmHg})(30\ \text{min})(74\ \text{lb/lbmol})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})} = 0.167\ \text{lb}$$

B. Medium volatility (methanol)

$$\frac{(0.25)(20\ \text{ft}^3/\text{min})(92\ \text{mmHg})(30\ \text{min})(32\ \text{lb/lbmol})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})} = 1.51\ \text{lb}$$

C. High volatility (diethyl ether)

$$\frac{(0.25)(20\ \text{ft}^3/\text{min})(442\ \text{mmHg})(74\ \text{lb/lbmol})(30\ \text{min})}{\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\text{K})} = 16.8\ \text{lb}$$

2.1.3 Vacuum drying - Blender Dryer

The emission stream characteristics for this unit operation are based on data that was reported from industry. A total of 160 lb of MeOH over the entire cycle (6 hours) was reported to be emitted. We assume that 100 lb was emitted over the first 2 hours, 50 over the next 3 hrs, and 10 in the last hour. Because the vapor pressure of MeOH and acetone exceeded the minimum operating pressure in the dryer (50 mm) at 40°C, the solvent was assumed to be boiling off the product the entire time.

This calculation is consistent with Example 6 of Chapter 3.

The average emission rate over the drying cycle is:

160 lb/6 hr = 26.7 lb/hr

Assuming the initial (max) emission rate is twice the average, then 53 lb/hr should be emitted over the initial drying period, which is consistent with 100 lb over the first 2 hours.

TRAY Dryer

Again, the solvents were effectively "boiling off" the product because of the low dryer operating pressure. Pressure was reported to be in the range of 150 mmHg to 20 mmHg. The cycle time for this dryer is 36 hours.

$$\frac{\text{215 lb total}}{\text{36 hours}} = \text{6 lb/hr}$$

We assumed twice this rate for the initial 6 hours, or (6)(2)(6) = 72 lb

The emissions over the remainder of the cycle are: 143 lb. We assumed that the last 6 hours of the cycle only contributed to 10 lb, and therefore emissions over the middle of the cycle are 143 - 10 = 133 lb over 24 hours.

Convective Dryers

TRAY Dryer

The documentation for this model emission stream comes from p. 75 of Environmental Progress Magazine, May 1990, in which 180 kg of solvent must be evaporated over the course of an entire drying cycle. Assuming 50 percent of the total material evaporated during the cycle comes off in the first hour, the hourly emission rate is 90 kg (200 lb/hr) during the first hour. Assuming the last hour of the drying cycle tubes care of 5 percent of the total solvent, or 9 kg (20 lb/hr), then the middle part of the cycle, which lasts four hours emits 180 kg - 90 - 9 = 81 kg (180 lb) or 45 lb/hr.

The volume percentage of VOC in the exit gas was calculated for all cases of volatility according to the difference in molecular weights of the low, moderate, and high volatility materials.

$$\frac{(\text{200 lb/hr})\left(\frac{\text{lbmol}}{\text{74 lb}}\right)\left(\frac{\text{998.97 mmHg ft}^3}{\text{lbmol K}}\right)(\text{338 K})}{\text{760 mmHg}}$$

$$= 1{,}200\ \text{ft}^3/\text{hr}\left(\frac{\text{hr}}{\text{60 min}}\right) = 20\ \text{ft}^3/\text{min}$$

% vol = (20)/6000 = 0.3%

Rotary Dryer

Reported solvent exhaust rate was 15.5 lb/cycle. Flow rate was 1.8 acfm.

We assume 90 percent emitted over the first 6 hours (which is 1/4 of the cycle). We assume 9 percent of the emissions were emitted over the next 12 hours, and that the remaining 1 percent was evaporated over the last 6 hours of the cycle.

Calculation of Vol %:

(15.5 lb)(0.90) = 14 lb

(14 lb)/(6 hr) = 2.3 lb/hr

$$\frac{(2.3\ \text{lb/hr})\left(\frac{\text{lbmol}}{32\ \text{lb}}\right)\left(\frac{998.97\ \text{mmHg}\cdot\text{ft}^3}{\text{lbmol}\cdot\text{K}}\right)(293\ \text{K})}{760\ \text{mmHg}} = 27.9\ \text{ft}^3/\text{hr or } 0.46\ \text{ft}^3/\text{min}$$

$$\frac{0.46\ \text{ft}^3/\text{min}}{1.8\ \text{ft}^3/\text{min}} = 25.8\%$$

VACUUM SYSTEMS

Vacuum pump - liquid ring type

Event: Vacuum system (reactor or crystallizer or solvent-removal batch still, etc.) where single VOC is being evaporated, condensed, and some vapors pulled from the system via the air in-leakage. Our example is toluene boiling at 74 mmHg (45°C)

Assumption: Stream will be saturated in the VOC - either from the process, or if not, from the intimate contact of n/c gas with the seal fluid in the vacuum pump

Basis for noncondensable gas flow - Appendix C - Example 9

in-leakage estimates of 9.7 scfm

If toluene is the seal fluid/process fluid

Temp at discharge of pump is 25° - cooler on seal fluid

VP toluene = 28.4 mmHg

Discharge of vac. pump is to atmosphere at 760 mmHg

$$\text{moles of air} = \frac{9.7}{359\ \text{ft}^3/\text{lbmol}} \times \frac{273}{298} = 0.02475\ \text{moles air/min}$$

$$Y_{VOC} = \frac{28.4}{760} = 0.03737 \qquad \text{MW toluene} = 92$$

$$\frac{\text{lb}}{\text{hr}} = 0.02475\ \frac{\text{moles}}{\text{min}} \times \frac{60\ \text{min}}{\text{hr}} \times 0.03737 \times \frac{92\ \text{lb}}{\text{mol}} = 5.1\ \text{lb/hr}$$

Steam-jet

Assume noncondensable gas in-leakage is saturated at 45°C with toluene

In-leakage = 44.6 lb/hr (9.7 scfm)

Using

$$S_E = MW_{VOL}\ \frac{La}{29}\left(\frac{P_{sys}}{P_{sys} - P_s} - 1\right)$$

$$= 92 \times \frac{44.6}{29}\left(\frac{760}{760 - 74} - 1\right)$$

$$= 15.26\ \text{lb/hr}$$

Composition of uncontrolled emission stream must have motive steam included

From Perry's (4th) pg. 6-31   Using 100 psi steam

$$\frac{P_{oa}}{P_{ob}} = \frac{760}{74} = 10.3$$

$$\frac{P_{oa}}{P_{ob}} = 0.0143$$

entrainment - roughly

$$\frac{0.06}{1} = \frac{W_b}{W_a}$$

0.06 lb air/lb steam

In example problem 10, Appendix C, air at 9.7 scfm is equivalent to 44.6 lb/hr

∴ steam required 1/0.06 x 44.6 = 743 lb/hr (if single stage)

wt. fr.			mw	moles	mole fractions
92.54	H_2O	743 lb	18.02	41.23	0.9603
1.90	Tol	15.26	92	0.1659	0.00386
5.56	Air	44.06	29	1.5379	0.03582
		802.86		42.9338	0.99998

<u>Batch distillation</u> - atmospheric - heat up to boiling point

Solvent	BP	VP @ 25°C
n-butanol	117°-118°	5.6 mmHg
Methanol	64.7°C	128 mmHg
Ethyl ether	34.6°C	553 mmHg

Suppose we heat up a distillation kettle to boiling point - in theory - all the air will be expelled - and will pass through the primary condenser. Initially, the material will be saturated at starting temperature of 20°C.

When heated up to 25° and above - the primary condenser will cause condensation and discharge gas stream will be saturated at 25°C.

Emissions from the heatup of the kettle and during the actual kettle distillation are calculated as follows:

Assume Batch still is 4 ft diameter x 30 ft high

volume = 377 ft^3

Using the heatup formula from Chapter 3, (for butanol)

$$\Delta n = \left(\frac{377}{998.9}\right)\left[\left(\frac{760 - 4.4}{273 + 20}\right) - \left(\frac{760 - 5.6}{273 + 25}\right)\right]$$

$$2.57884 \quad - \quad 2.53154$$

= 0.3774 x 0.047296

= 0.01785 moles total noncondensable gas emitted during heatup

$${}^{\wedge}S = \frac{\dfrac{4.4}{760 - 4.4} + \dfrac{5.6}{760 - 5.6}}{2} \times 0.01785 \times 71.2 = 0.0081 \text{ lb during heatup}$$

For MeOH use 92 and 128 mm 2.27986 - 2.1208 → 0.06003 total moles gas expelled during heatup

For ether use 442 and 553 1.08532 - 0.69463 → 0.1474 total moles gas expelled during heatup

At 25° → BP all the remaining noncondensable (n/c's) are vented at saturation level

Volume of system 377 ft^3 = 0.9790 moles

Butanol

0.9790 - 0.01785 discharged during heatup

= 0.9611 x 392 = 377 acf

at 25° VP = 5.6

Y = 5.6/760 = 0.007368

Pounds butanol discharged = 0.9611 x 0.007368 x 74.12

= 0.525 + 0.0088 = 0.534 lb (total pounds discharged)

Methanol

at 25° VP = 128

Y = 128/760 = 0.1684

Ratio of VOC to nc = 128/(760 - 128) = 0.2025

Moles of VOC discharged = moles of n/c x ratio

Moles noncendensable = 0.9790 - 0.060 moles discharged during heatup = 0.919 x ratio

= 0.919 x 0.2025

= 0.186 moles

0.186 x 32 = 5.96 lb (+0.327 lb during heatup)

Gas flow during 2nd step of process (during distillation):

0.919 + 0.186 moles = 1.105 moles

At 25°C → 433 acf + 30 min = 14.4 acfm

Ether

at 25° VP = 553   Y = 553/760 = 0.728

Ratio of VOC to NC: 553/(760 - 553) = 2.671

NC flow: 0.979 - 0.1474 = 0.8316

Moles of VOC discharged = moles of NC x ratio

= 0.8316 x 2.671

= 2.221 moles

x 74.12 (mw) = 164.6 lb

Gas flow: 0.8316 + 2.221 = 3.053 moles

3.053 x 392 = acf/30 min = 39.89 acfm during 2nd step of process

<u>Summary</u>

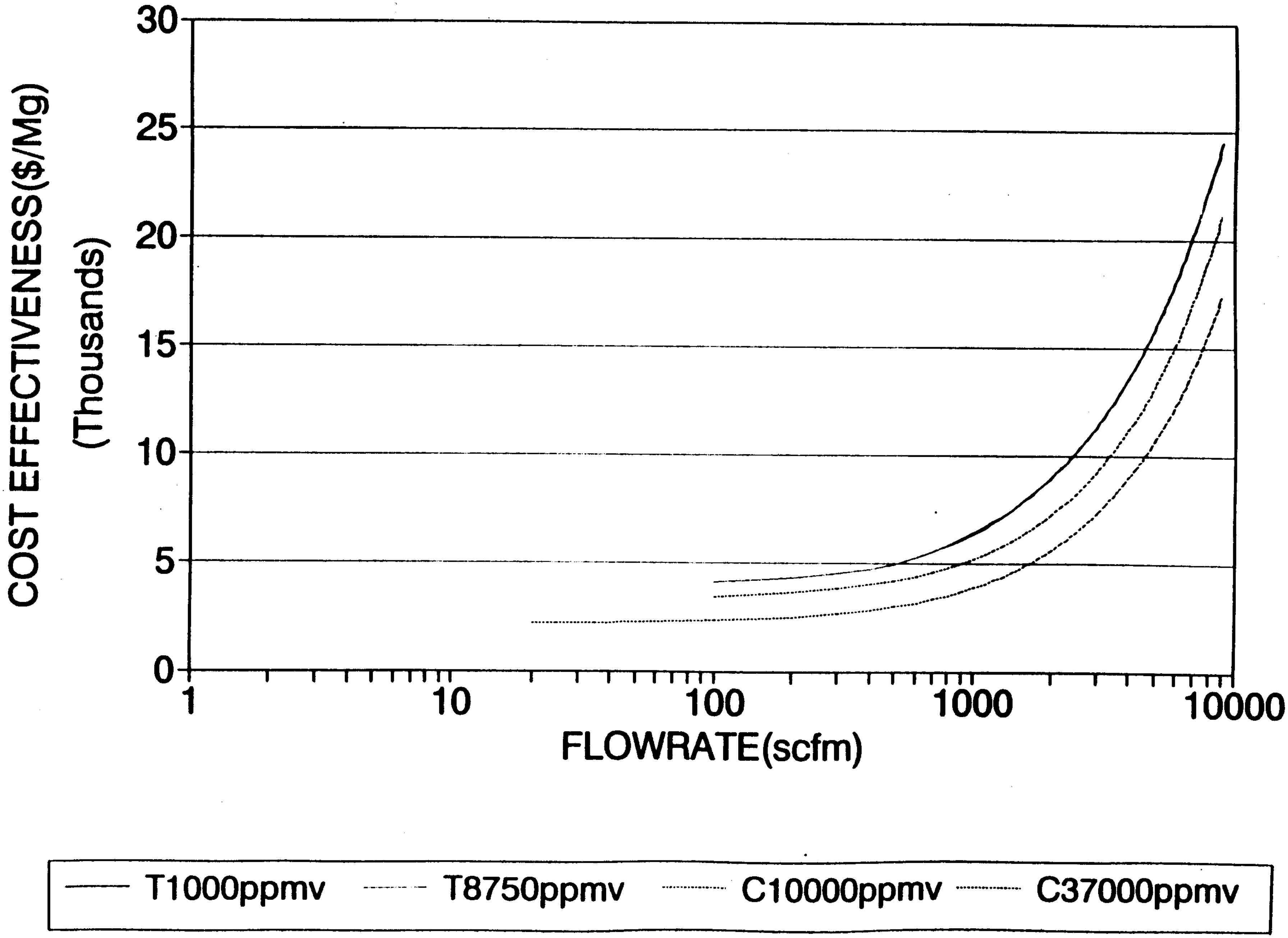
	Flow rate	Temp	Pross	Dur	VOC	N/C	lb/ event
Butanol							
Heatup 20-25 25->BP	1.4	20-25	760	5	0.66	99.34	0.01
N/C venting	12.6	25	760	60	0.74	99.26	0.52
MeOH							
Heat	5.5	20-25	760	5	14.5	85.5	0.33
Vent	14.4	25	760	45	16.8	83.2	5.96
Ether							
Heat	28.9	20-25	760	5	60	40	16.4
Vent	39.9	25	760	30	72.8	27.2	164.6

APPENDIX F.

MASS EMISSIONS CURVES

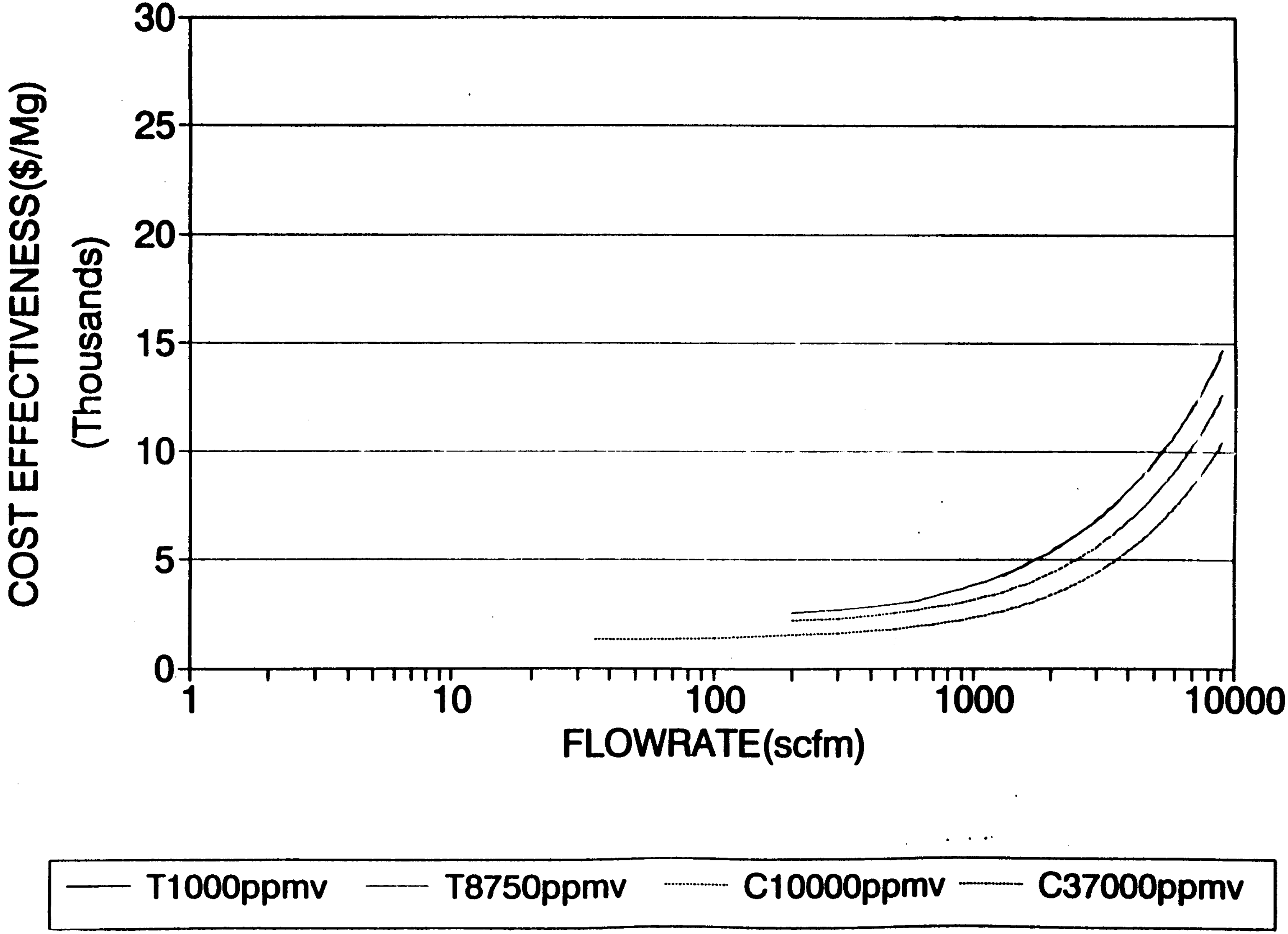
Annual Mass Emission Total=30,000lb/yr

Low Vol.(Toluene); Cond. Crtl. Eff.=90%



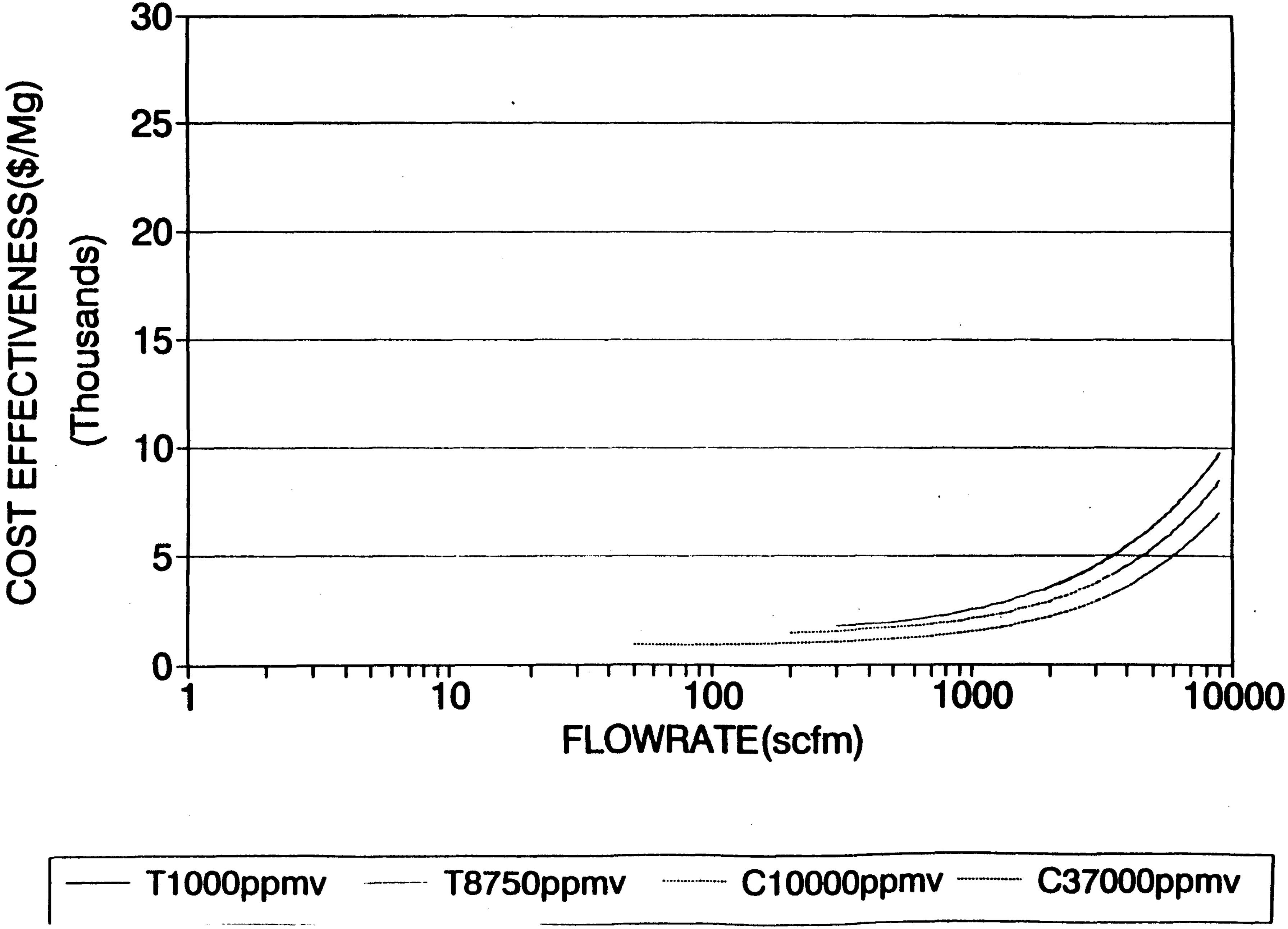
Annual Mass Emission Total=50,000lb/yr

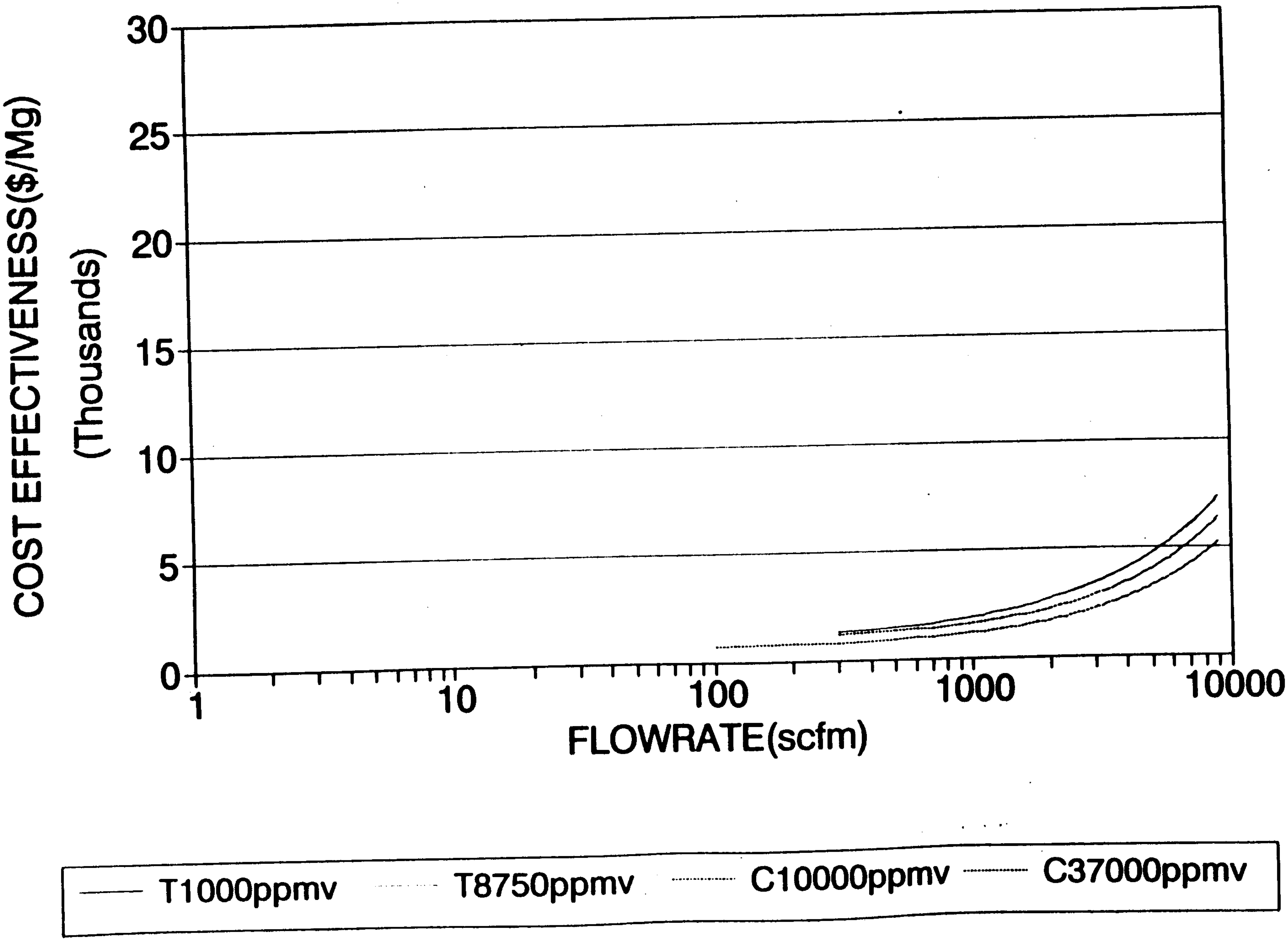
Low Vol.(Toluene); Cond. Crtl. Eff.=90%



Annual Mass Emission Total=75,000lb/yr

Low Vol.(Toluene); Cond. Crtl. Eff.=90%

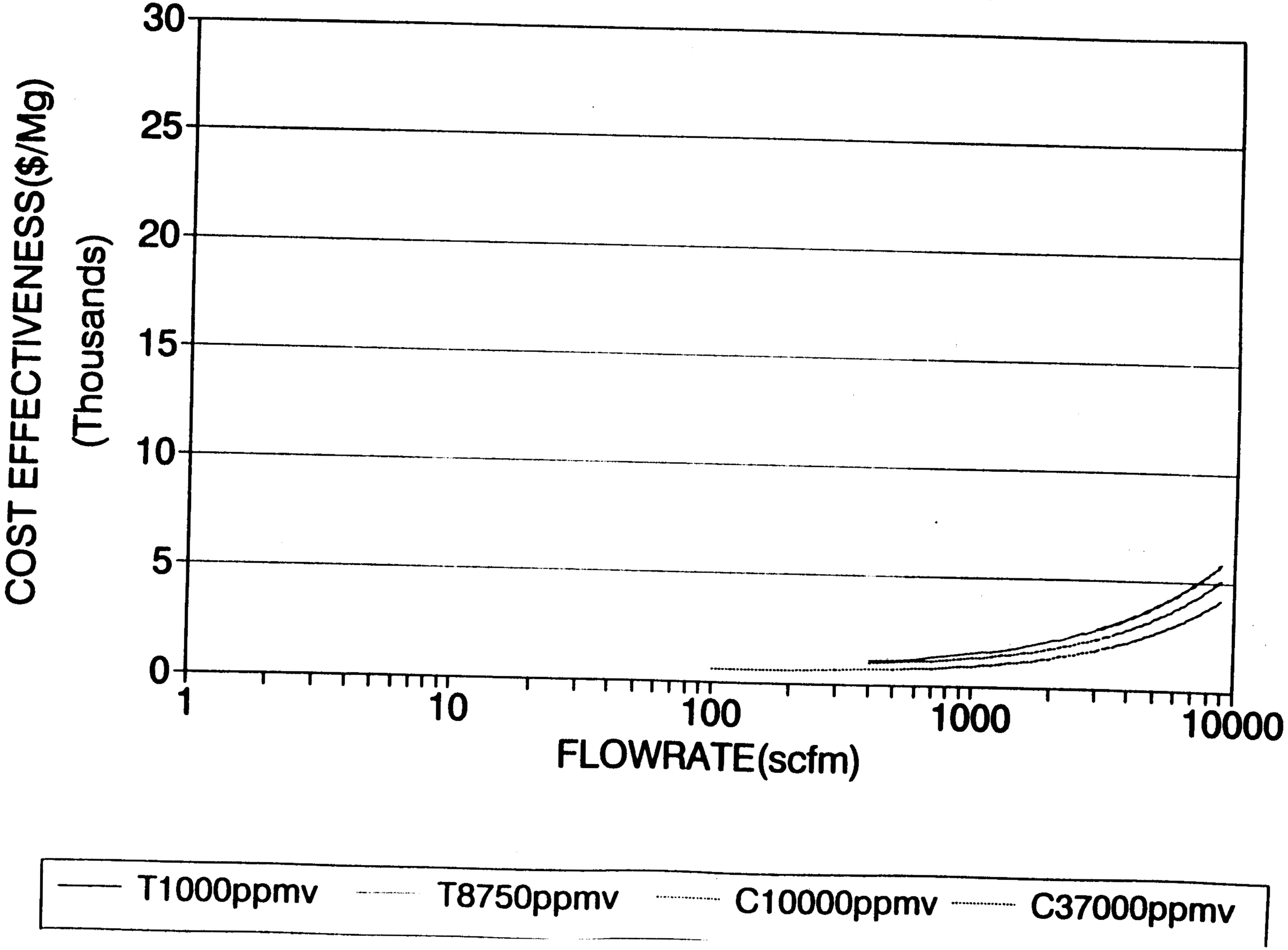


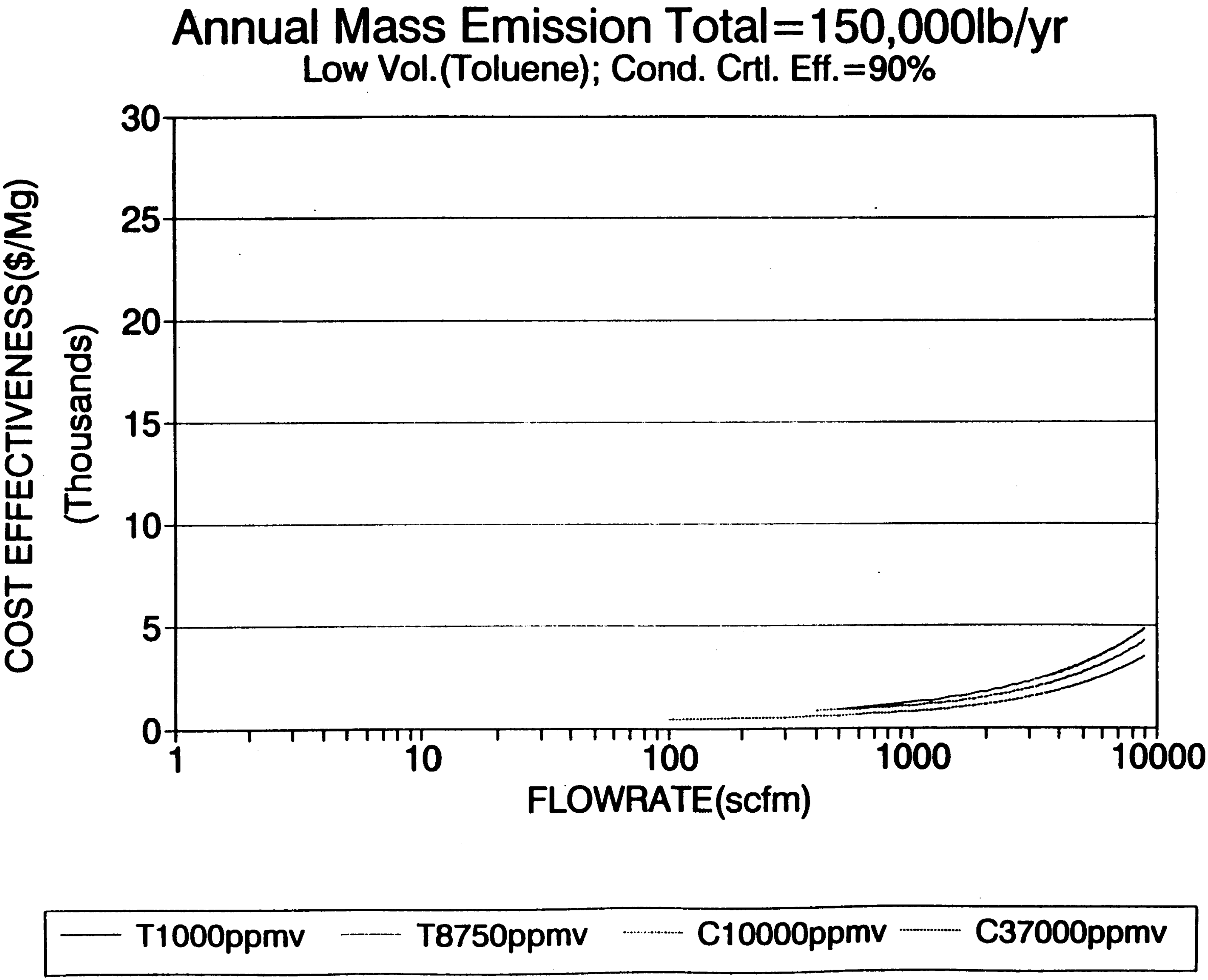


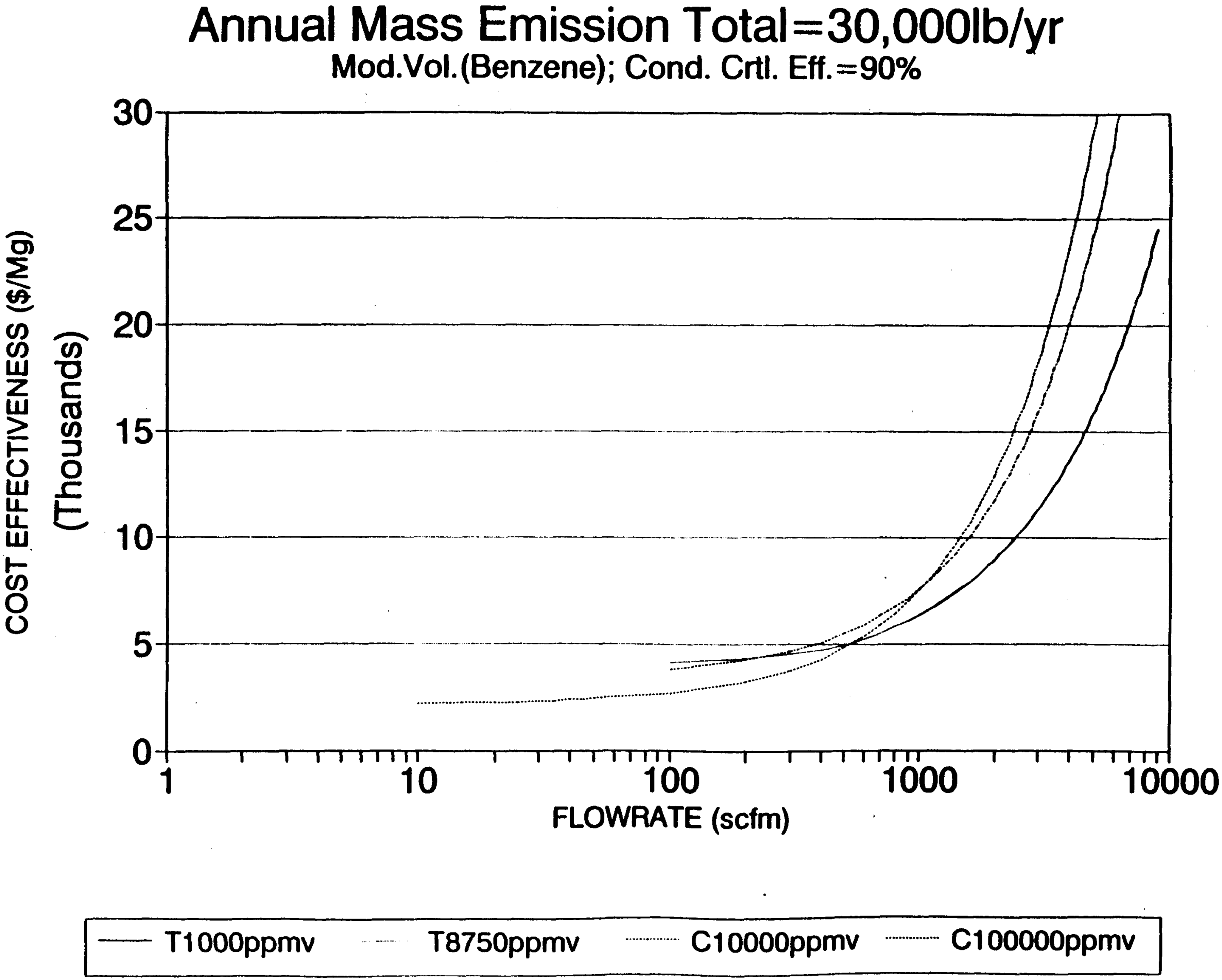
Annual Mass Emission Total=100,000lb/yr
Low Vol.(Toluene); Cond. Crtl. Eff.=90%

Annual Mass Emission Total=125,000lb/yr

Low Vol.(Toluene); Cond. Crtl. Eff.=90%

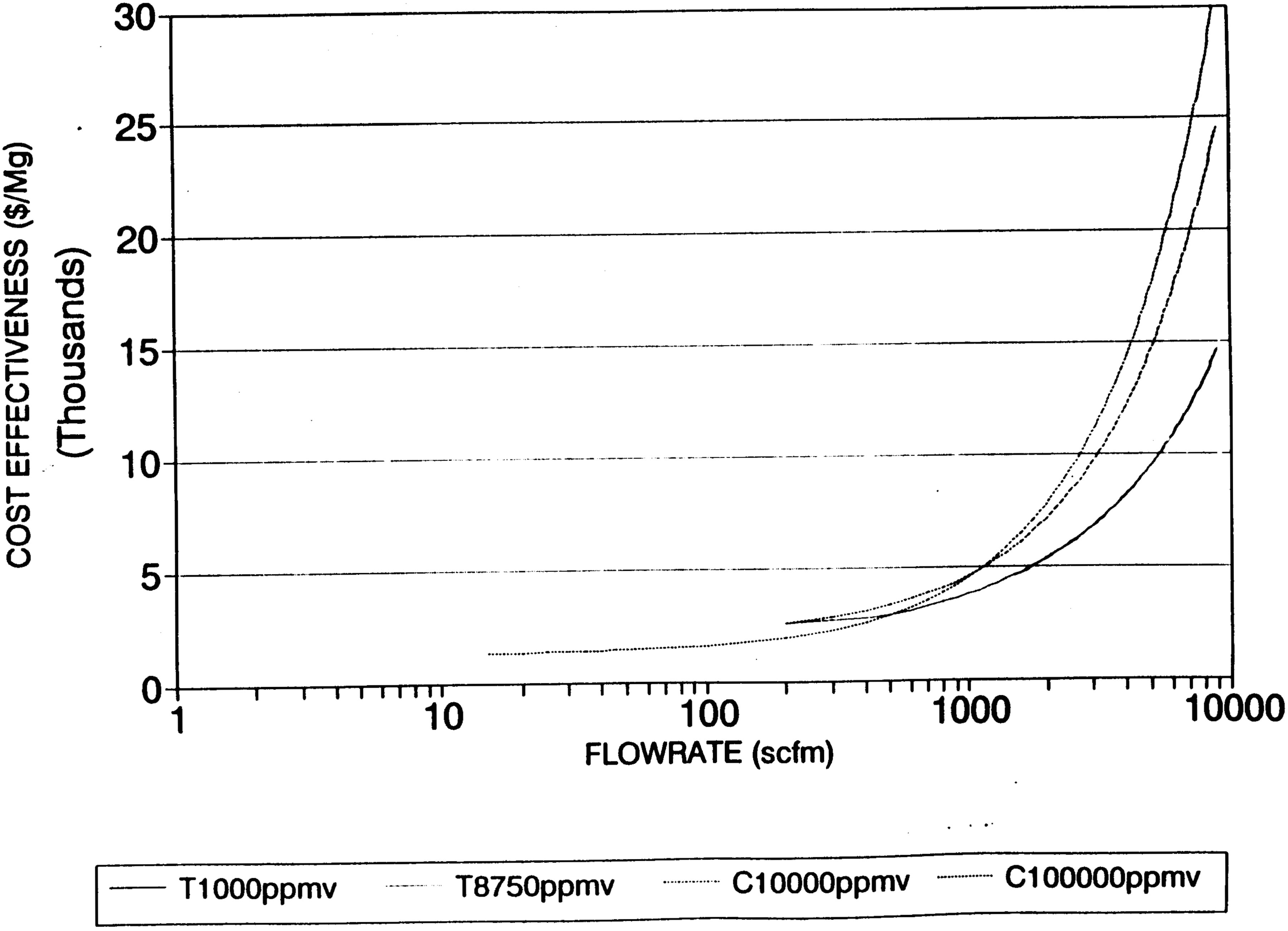



Annual Mass Emission Total=150,000lb/yr
Low Vol.(Toluene); Cond. Crtl. Eff.=90%
COST EFFECTIVENESS($/Mg)
(Thousands)
30
25
20
15
10
5
0
1
10
100
1000
10000
FLOWRATE(scfm)
T1000ppmv
T8750ppmv
C10000ppmv
C37000ppmv


Annual Mass Emission Total=30,000lb/yr
Mod.Vol.(Benzene); Cond. Crtl. Eff.=90%
COST EFFECTIVENESS ($/Mg)
(Thousands)
30
25
20
15
10
5
0
1
10
100
1000
10000
FLOWRATE (scfm)
T1000ppmv
T8750ppmv
C10000ppmv
C100000ppmv

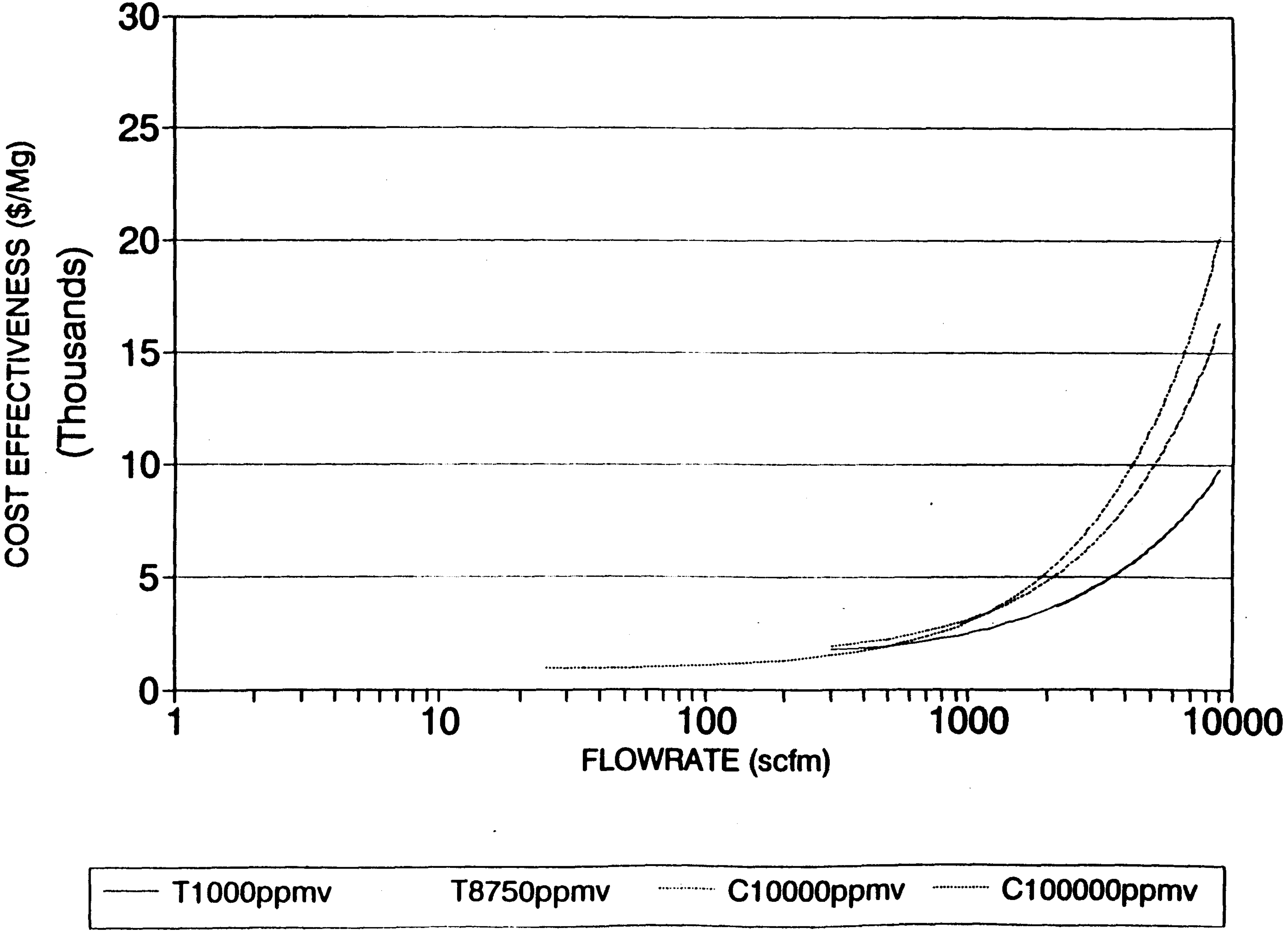
Annual Mass Emission Total=50,000lb/yr

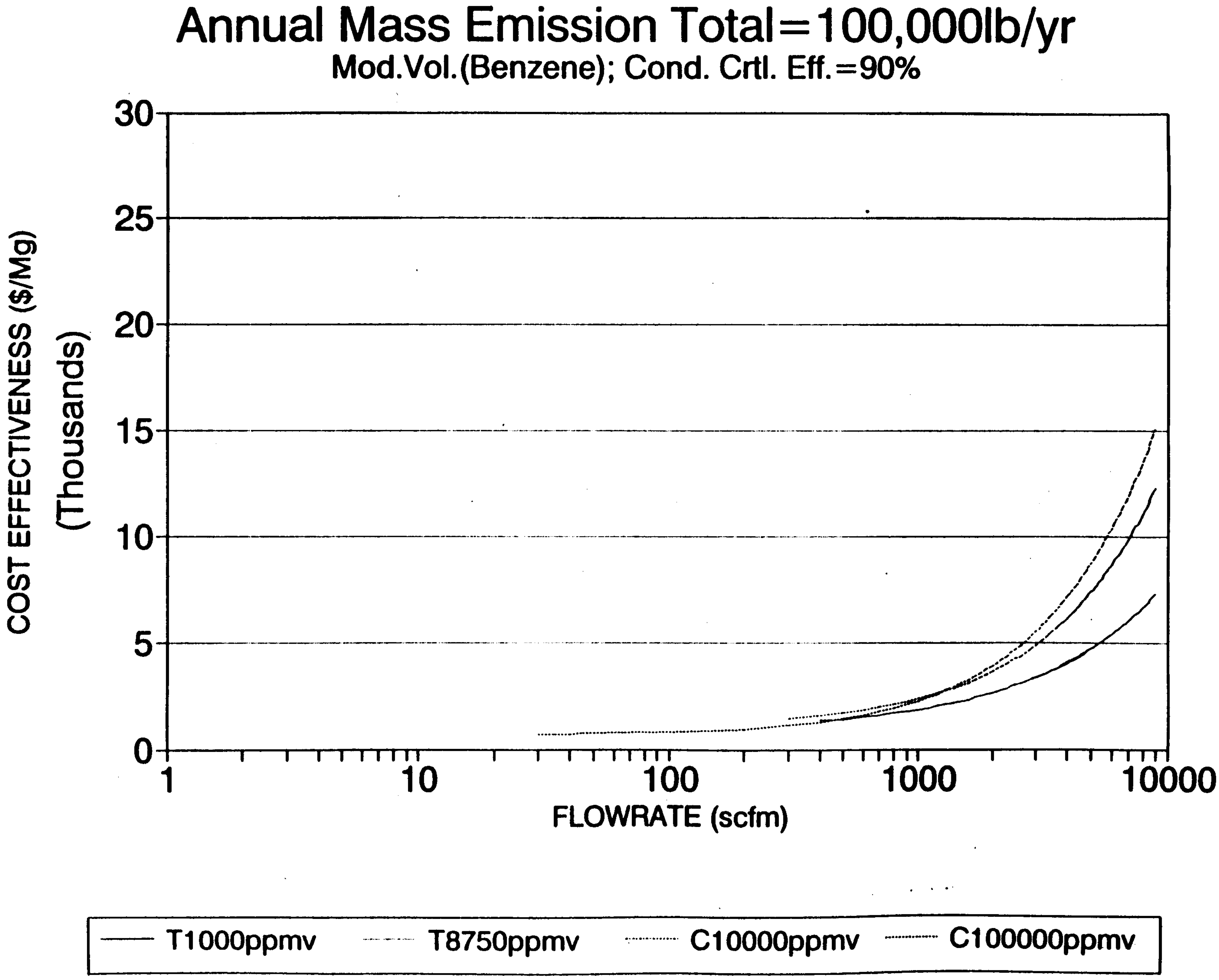
Mod.Vol.(Benzene); Cond. Crtl. Eff.=90%



Annual Mass Emission Total=75,000lb/yr

Mod.Vol.(Benzene); Cond. Crtl. Eff.=90%




Annual Mass Emission Total=100,000lb/yr
Mod.Vol.(Benzene); Cond. Crtl. Eff.=90%
COST EFFECTIVENESS ($/Mg)
(Thousands)
30
25
20
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100
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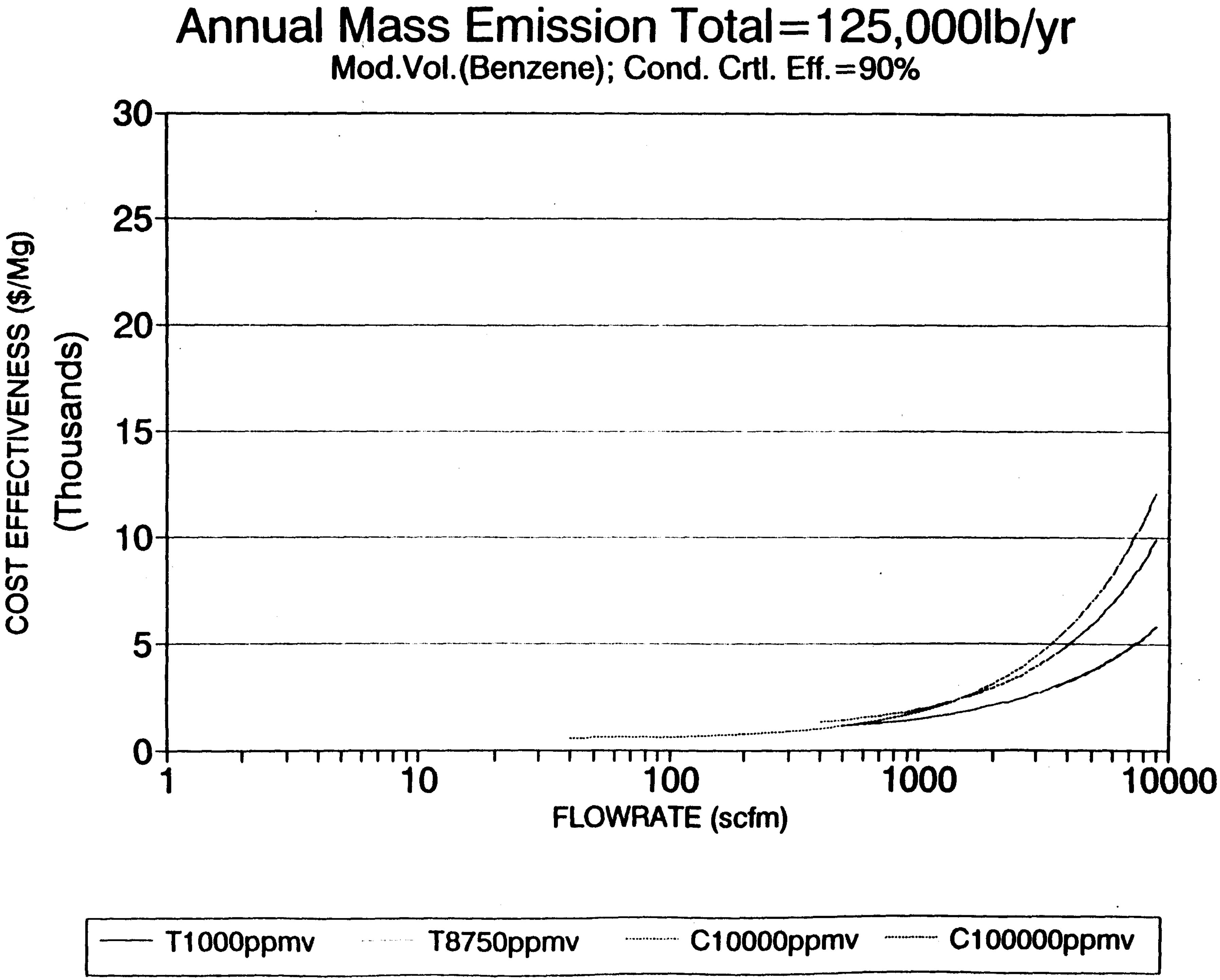
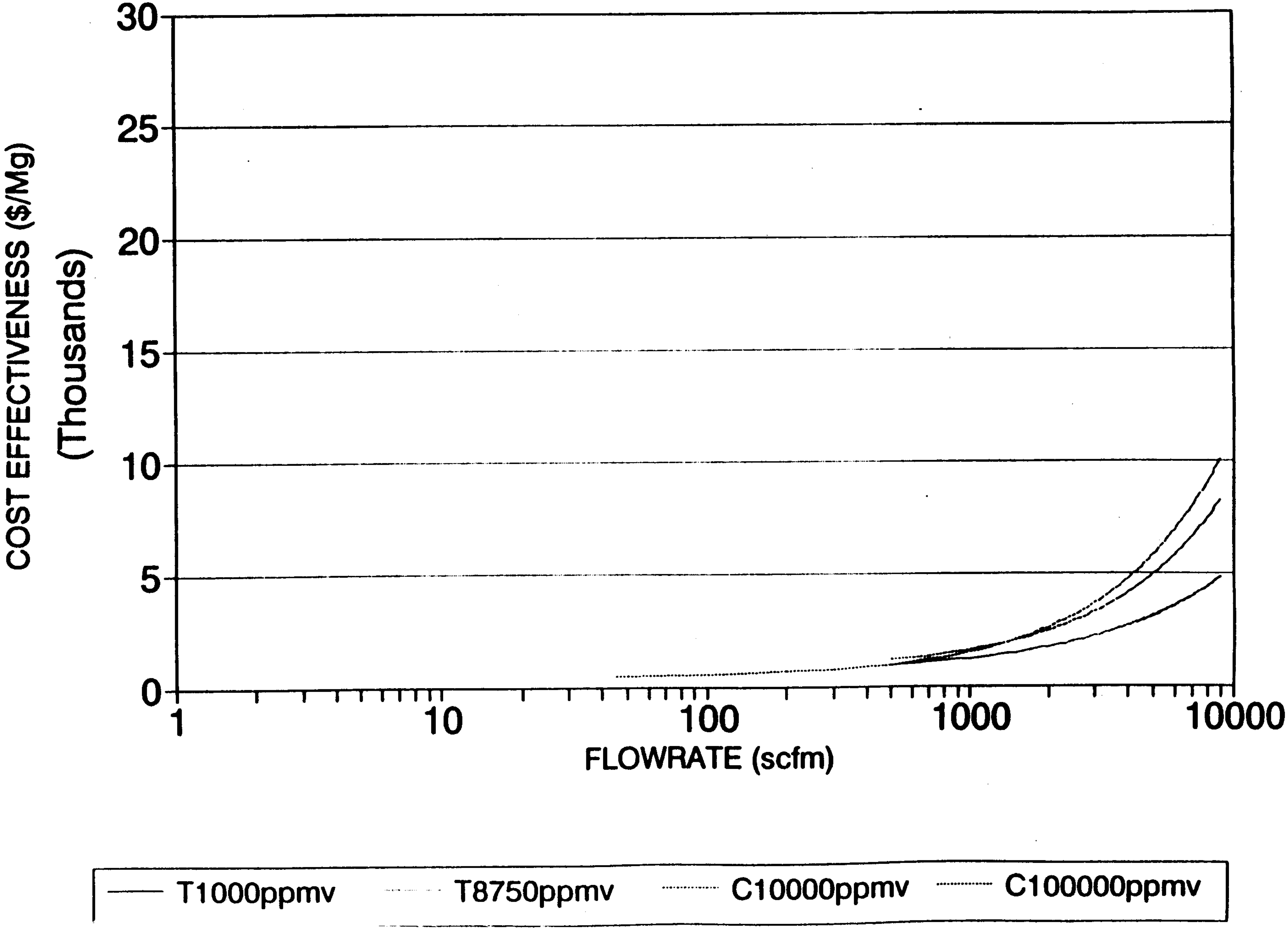
10000
FLOWRATE (scfm)
T1000ppmv
T8750ppmv
C10000ppmv
C100000ppmv



Annual Mass Emission Total=125,000lb/yr
Mod.Vol.(Benzene); Cond. Crtl. Eff.=90%

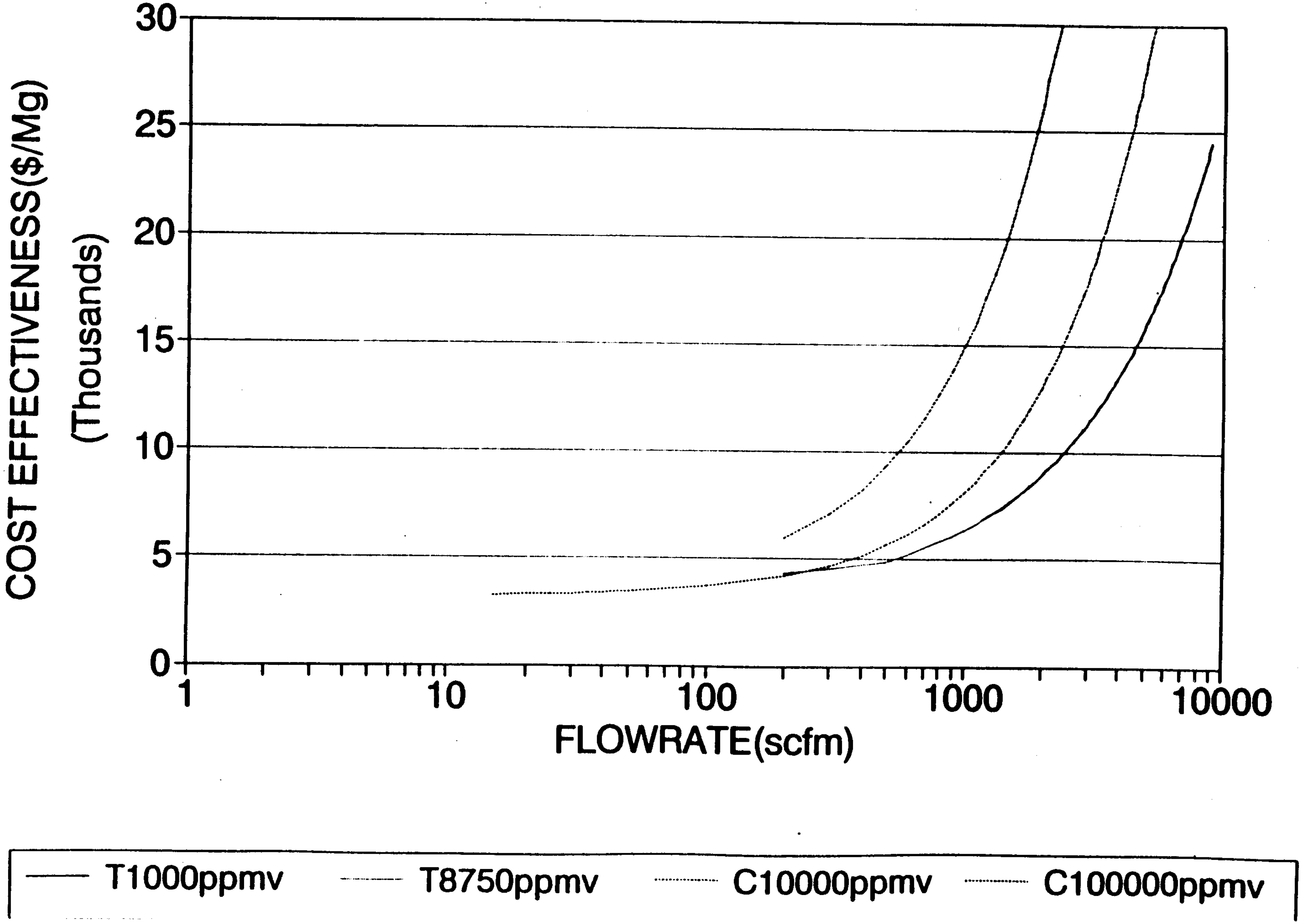
Annual Mass Emission Total=150,000lb/yr

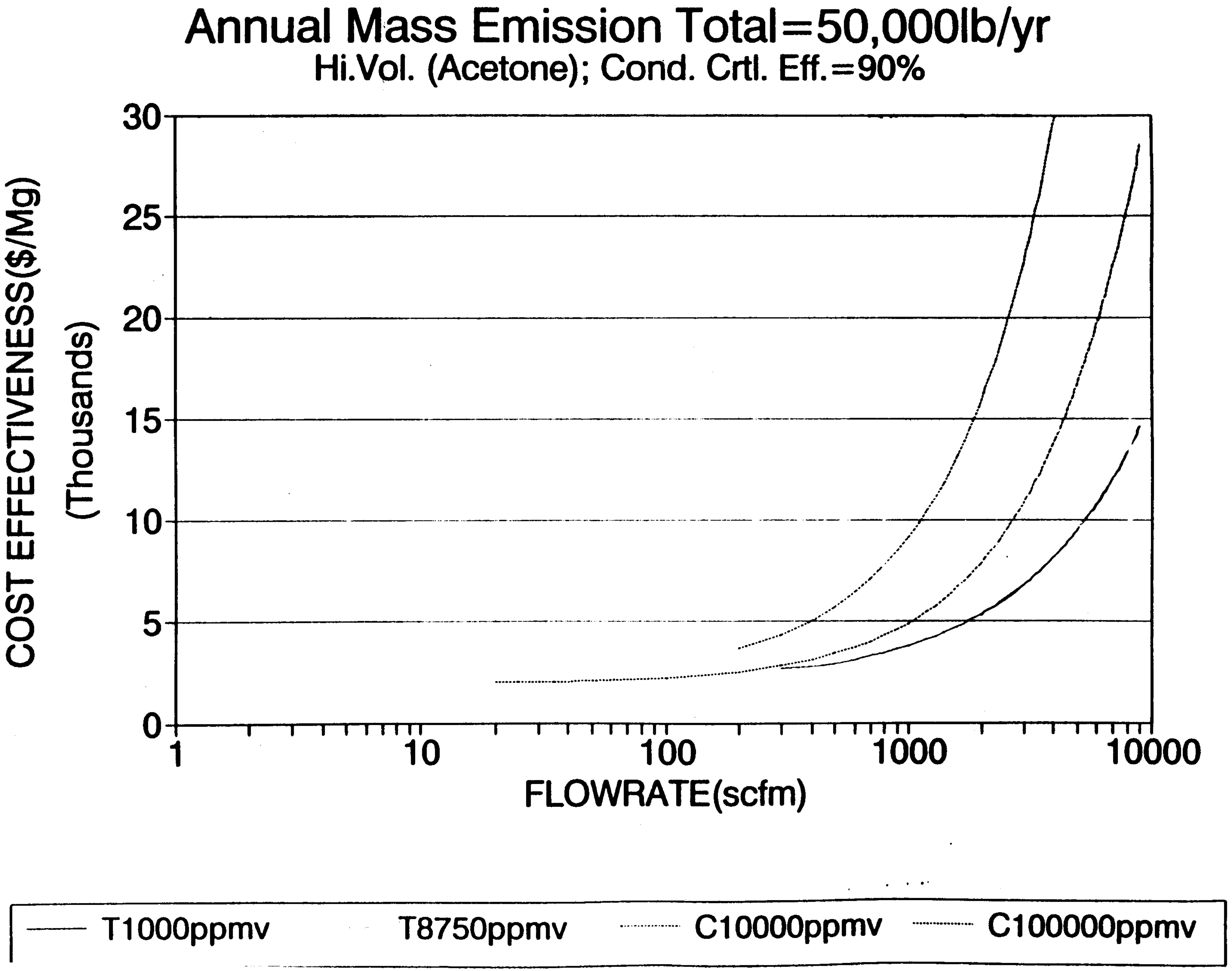
Mod.Vol.(Benzene); Cond. Crtl. Eff.=90%



Annual Mass Emission Total=30,000lb/yr

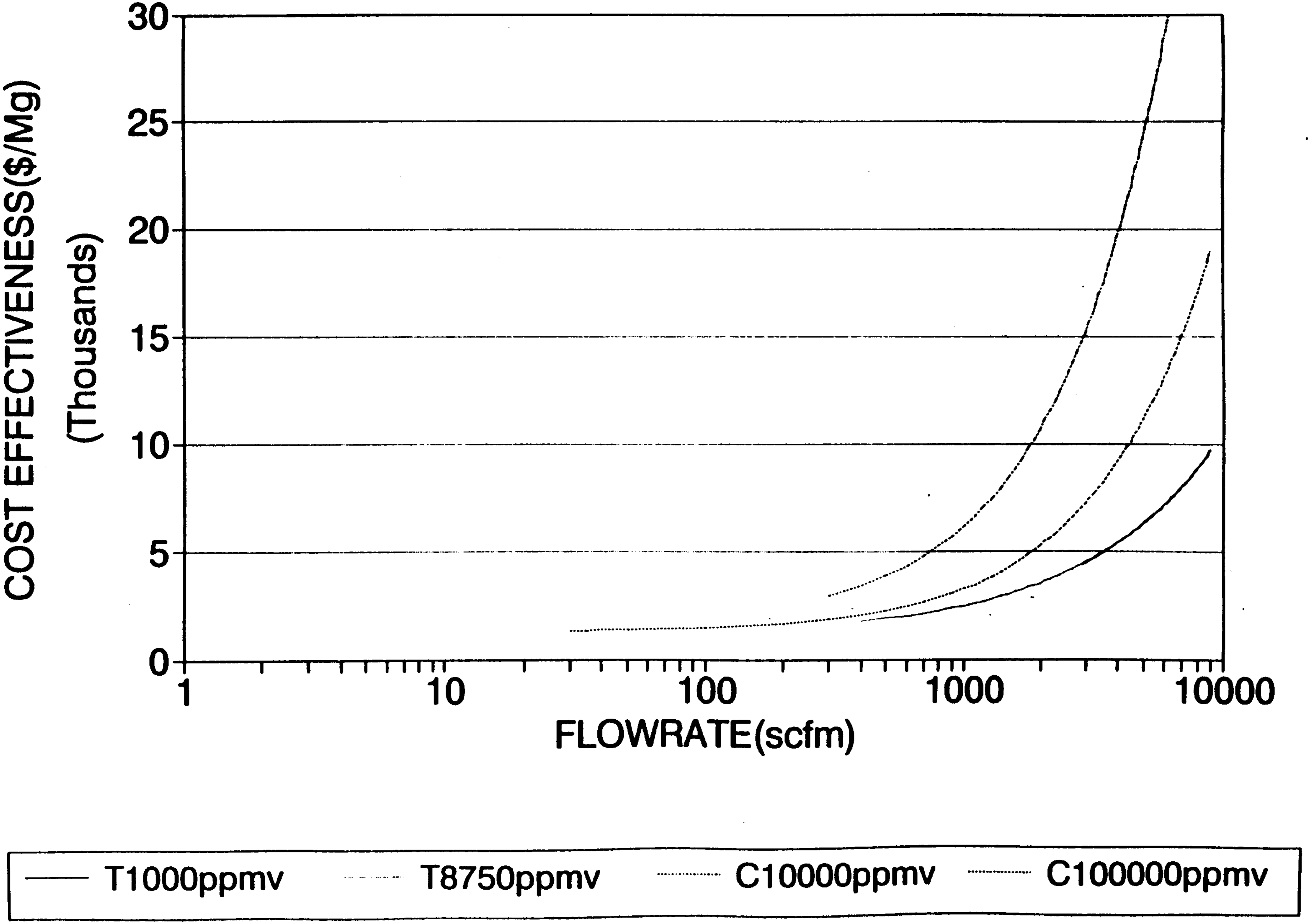
Hi.Vol. (Acetone); Cond. Crtl. Eff.=90%




Annual Mass Emission Total=50,000lb/yr
Hi.Vol. (Acetone); Cond. Crtl. Eff.=90%
COST EFFECTIVENESS($/Mg)
(Thousands)
30
25
20
15
10
5
0
1
10
100
1000
10000
FLOWRATE(scfm)
T1000ppmv
T8750ppmv
C10000ppmv
C100000ppmv

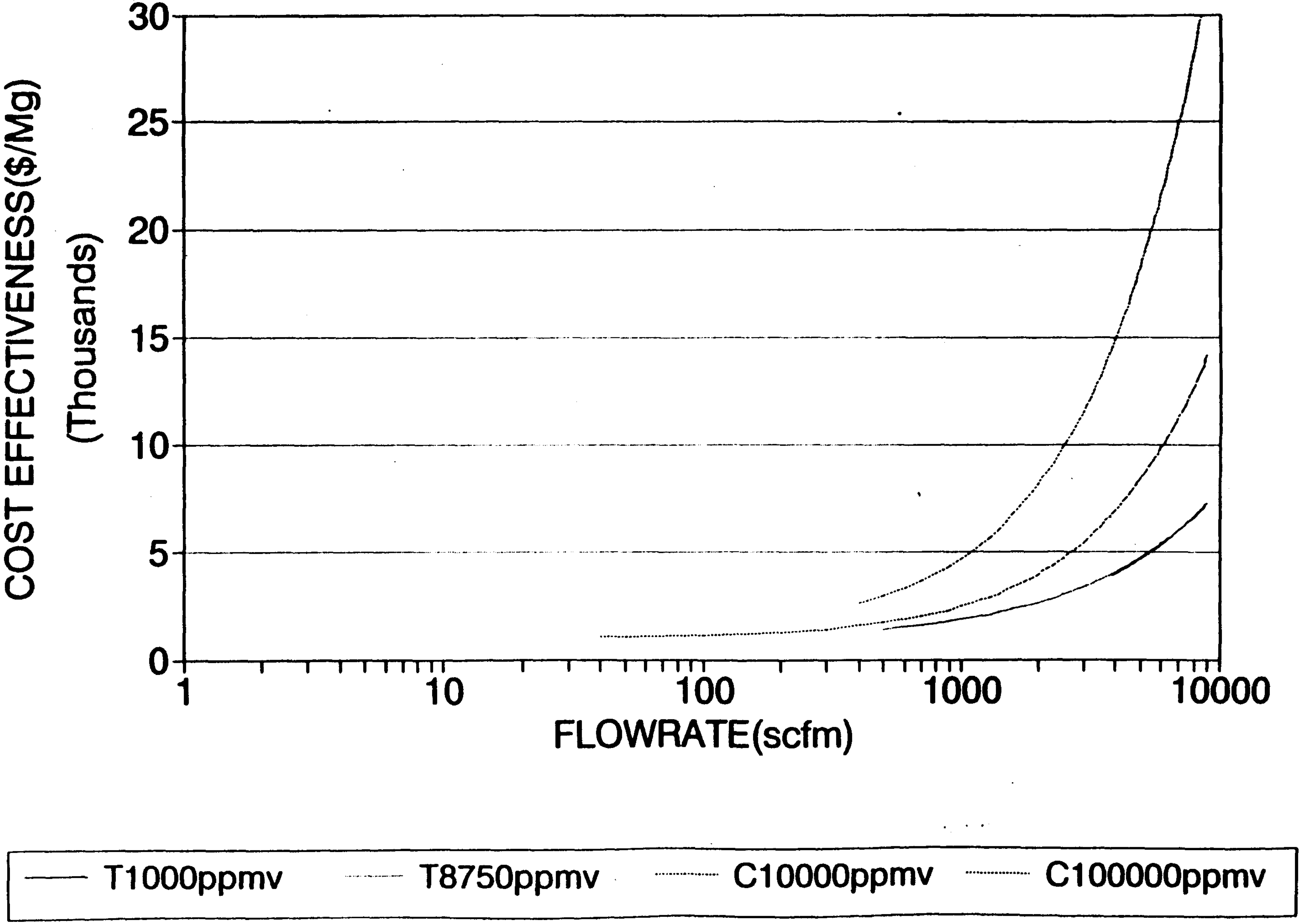
Annual Mass Emission Total=75,000lb/yr

Hi.Vol. (Acetone); Cond. Crtl. Eff.=90%



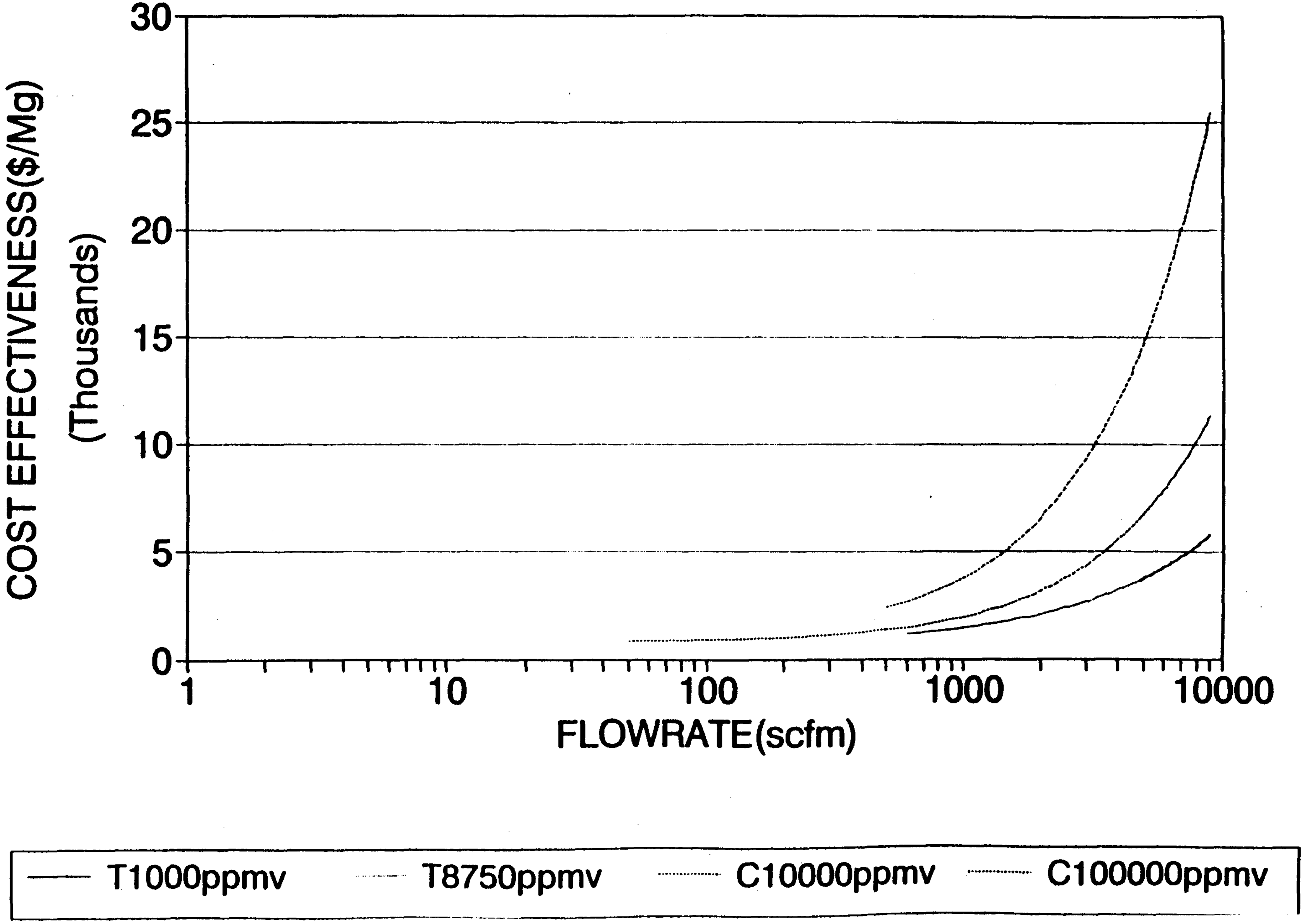
Annual Mass Emission Total=100,000lb/yr

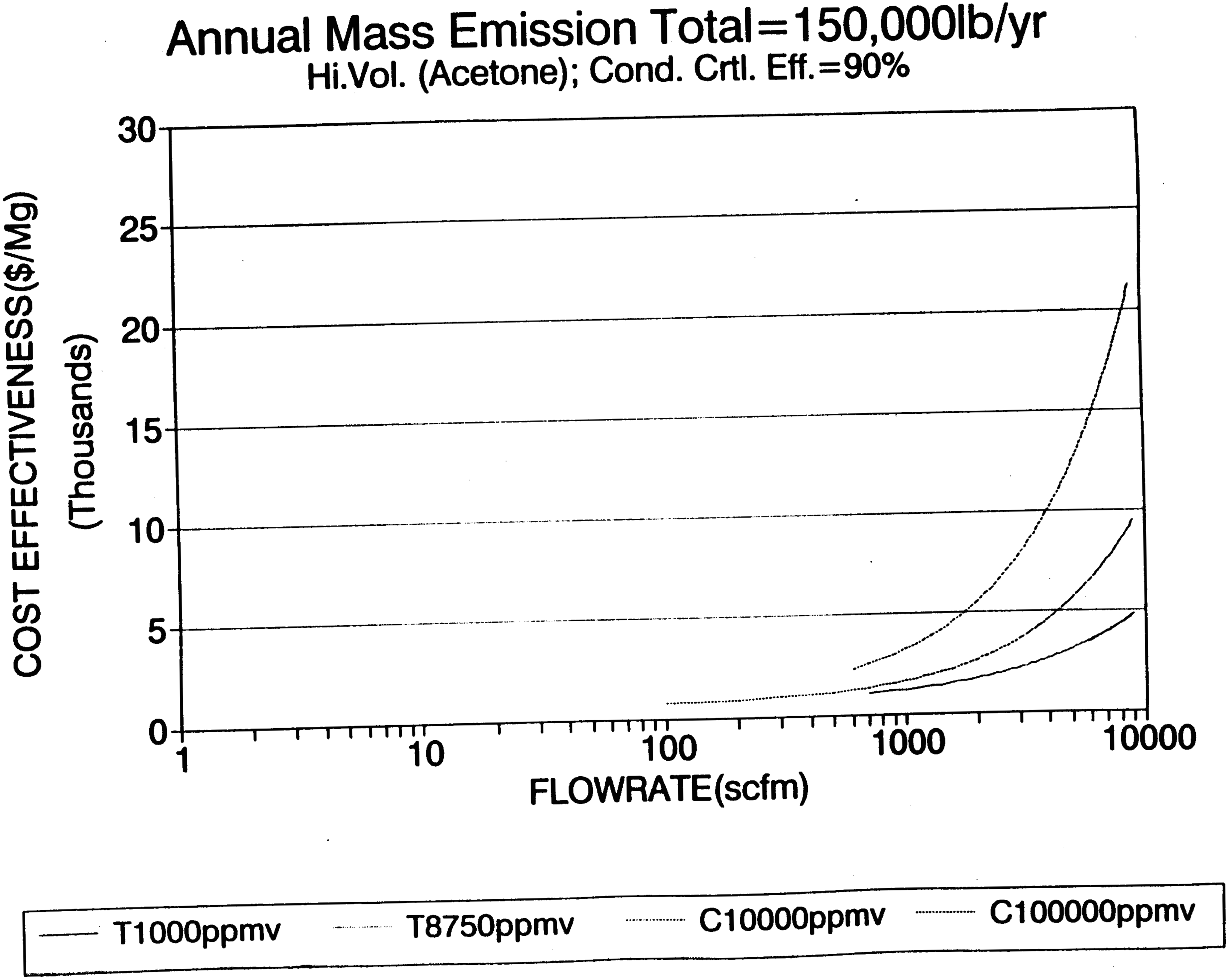
Hi.Vol. (Acetone); Cond. Crtl. Eff.=90%



Annual Mass Emission Total=125,000lb/yr

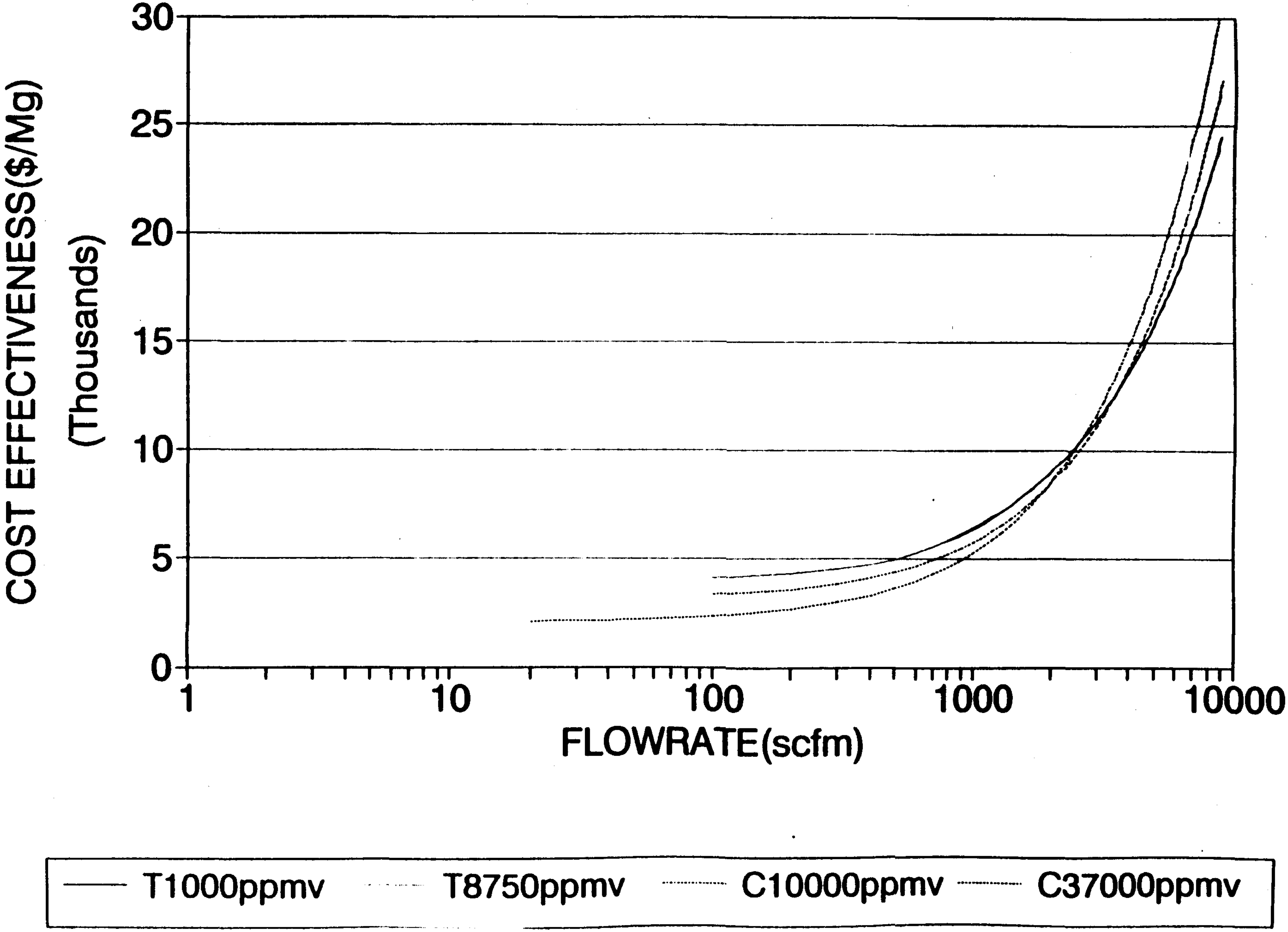
Hi.Vol. (Acetone); Cond. Crtl. Eff.=90%

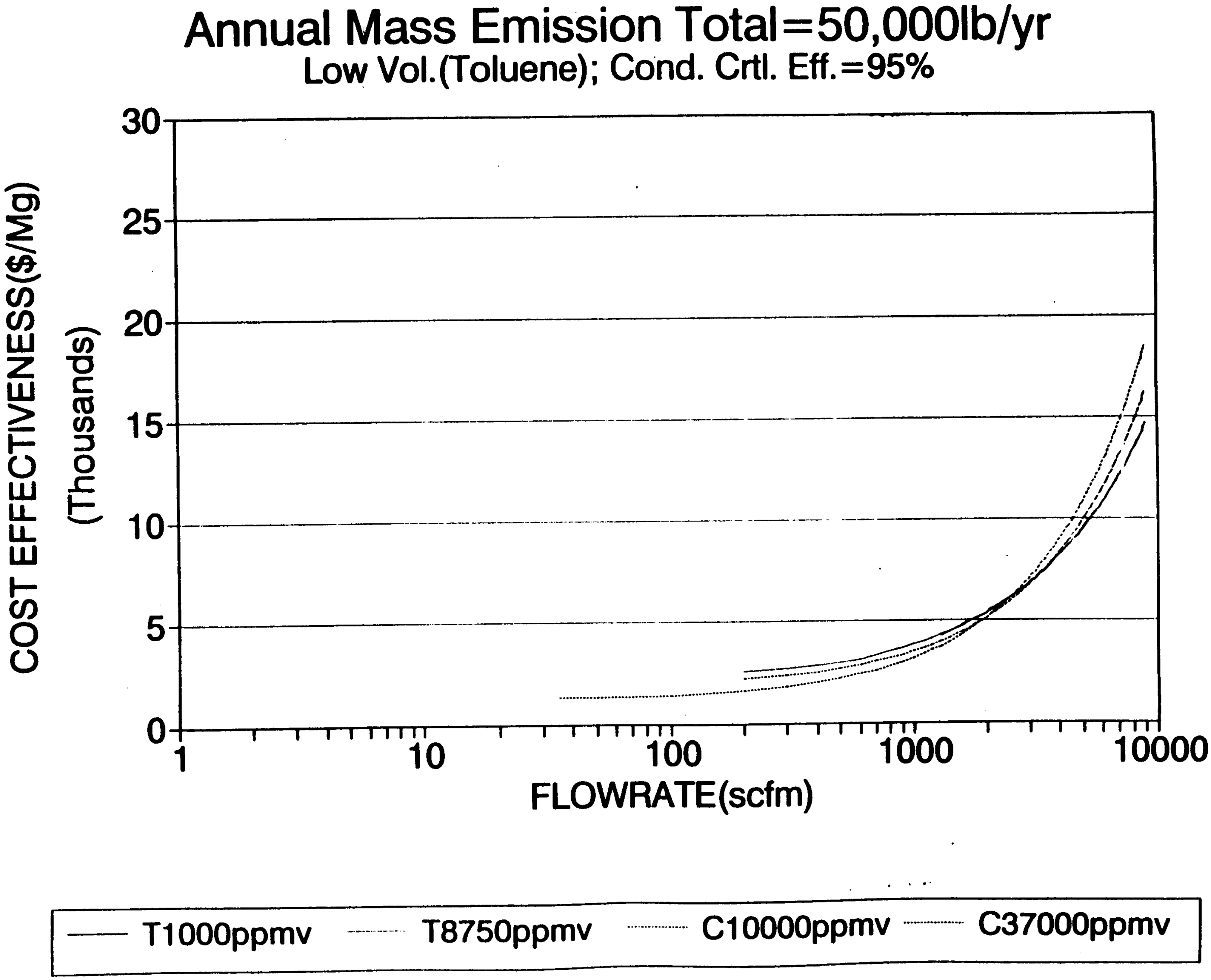



Annual Mass Emission Total=150,000lb/yr
Hi.Vol. (Acetone); Cond. Crtl. Eff.=90%
COST EFFECTIVENESS($/Mg)
(Thousands)
30
25
20
15
10
5
0
1
10
100
1000
10000
FLOWRATE(scfm)
T1000ppmv
T8750ppmv
C10000ppmv
C100000ppmv

Annual Mass Emission Total=30,000lb/yr

Low Vol.(Toluene); Cond. Crtl. Eff.=95%




Annual Mass Emission Total=50,000lb/yr
Low Vol.(Toluene); Cond. Crtl. Eff.=95%
COST EFFECTIVENESS($/Mg)
(Thousands)
30
25
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0
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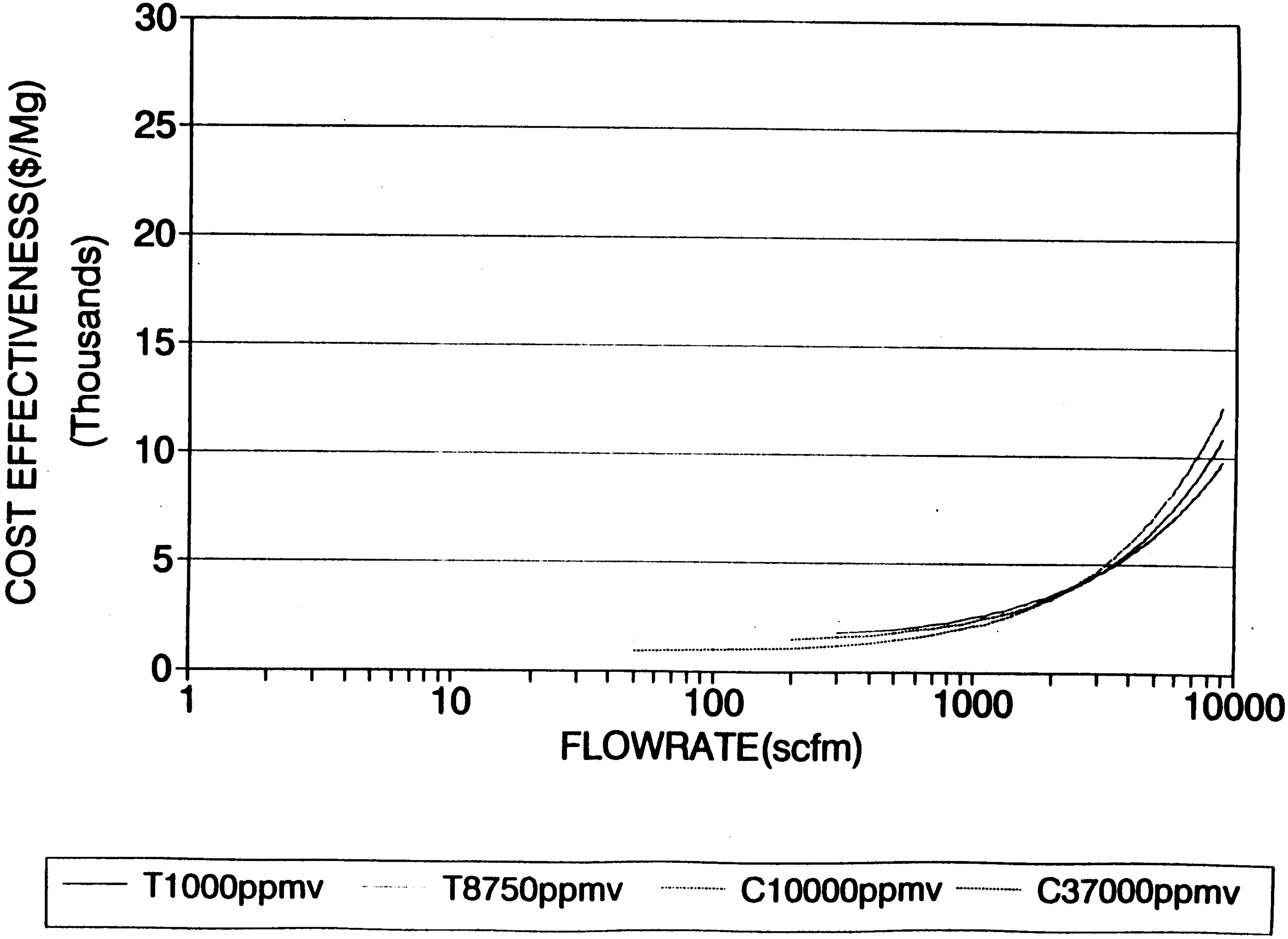
100
1000
10000
FLOWRATE(scfm)
T1000ppmv
T8750ppmv
C10000ppmv
C37000ppmv

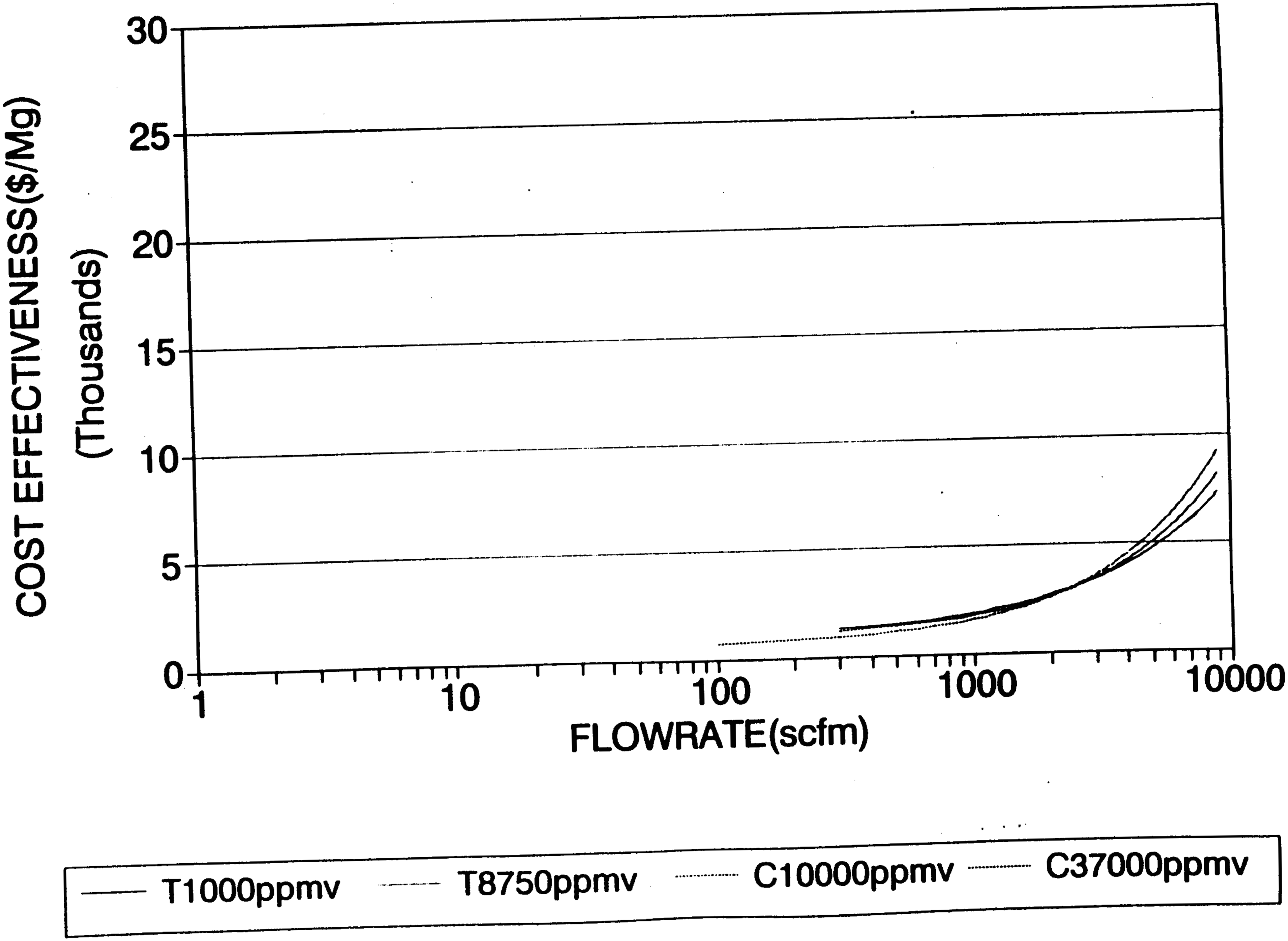
Annual Mass Emission Total=75,000lb/yr

Low Vol.(Toluene); Cond. Crtl. Eff.=95%

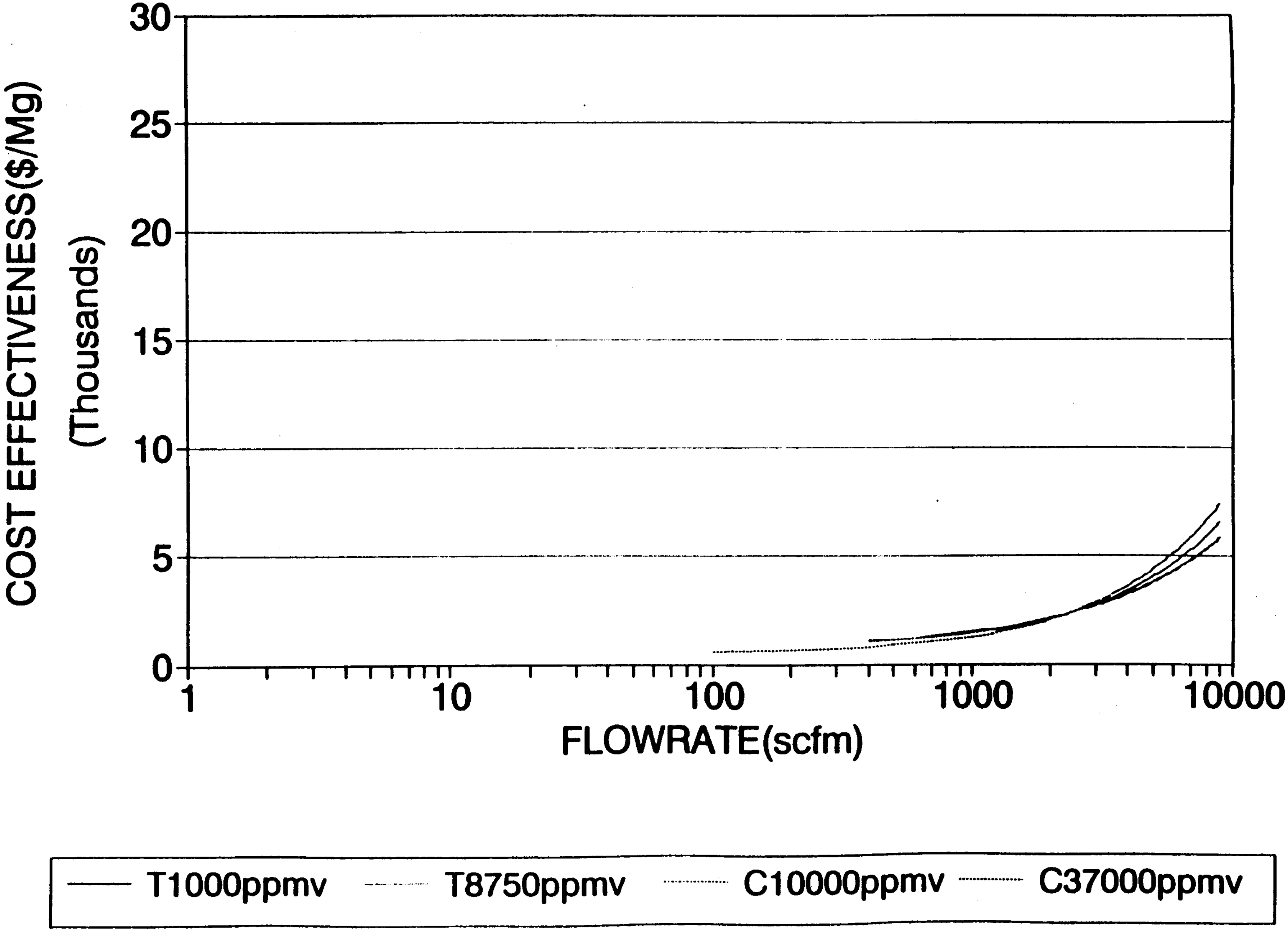


Annual Mass Emission Total=100,000lb/yr

Low Vol.(Toluene); Cond. Crtl. Eff.=95%

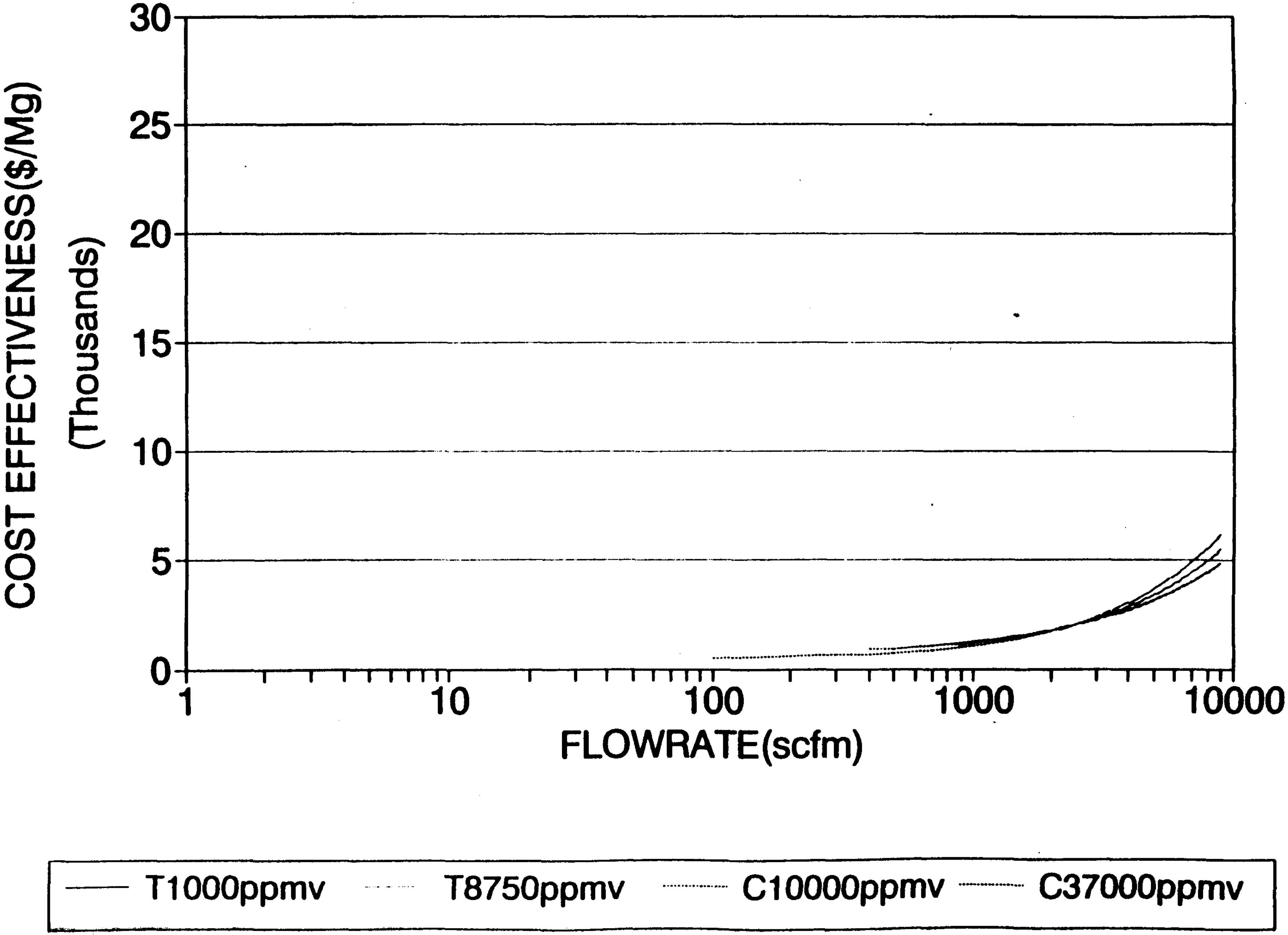


Annual Mass Emission Total=125,000lb/yr
Low Vol.(Toluene); Cond. Crtl. Eff.=95%



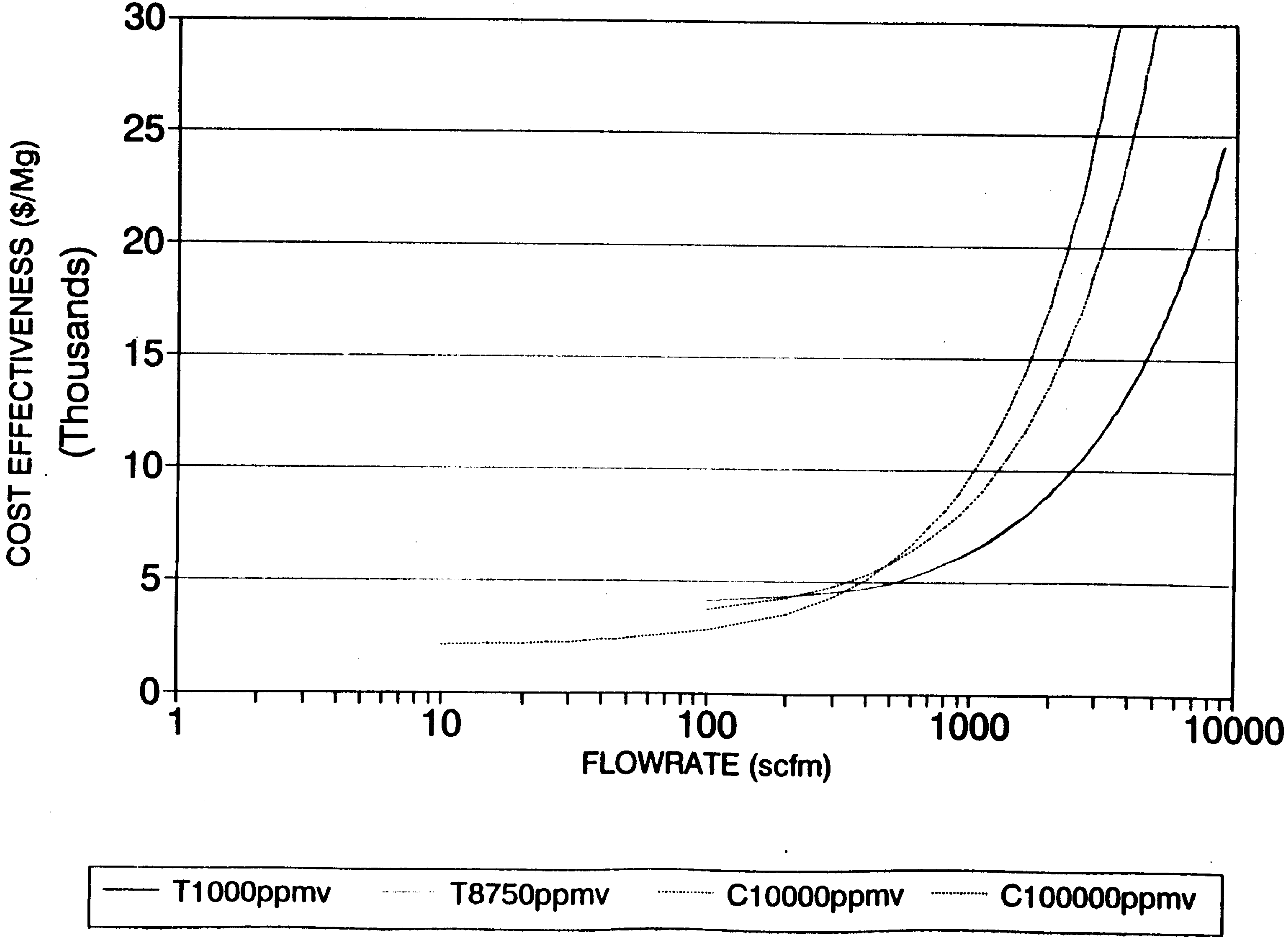
Annual Mass Emission Total=150,000lb/yr

Low Vol.(Toluene); Cond. Crtl. Eff.=95%



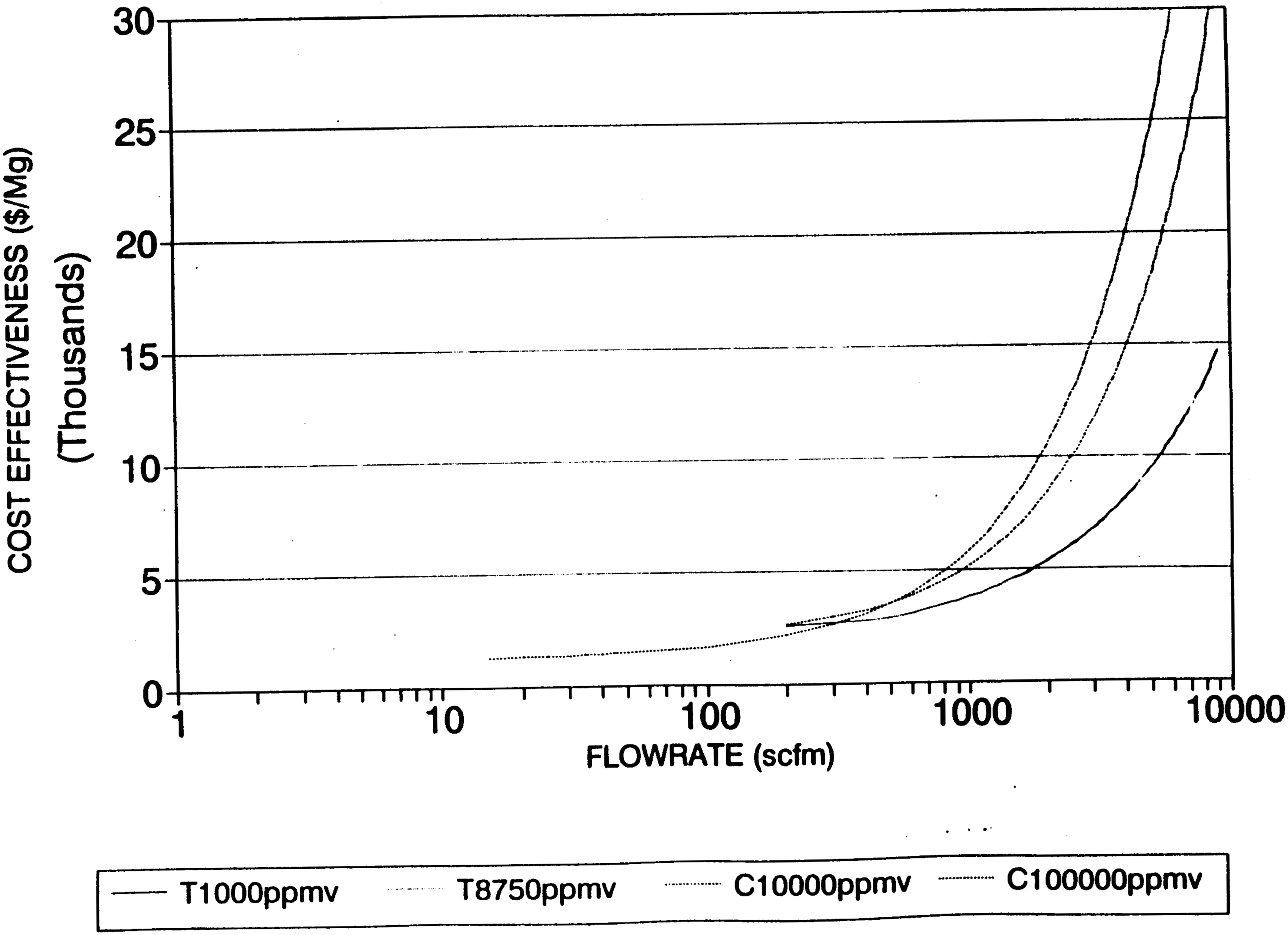
Annual Mass Emission Total=30,000lb/yr

Mod.Vol.(Benzene); Cond. Crtl. Eff.=95%



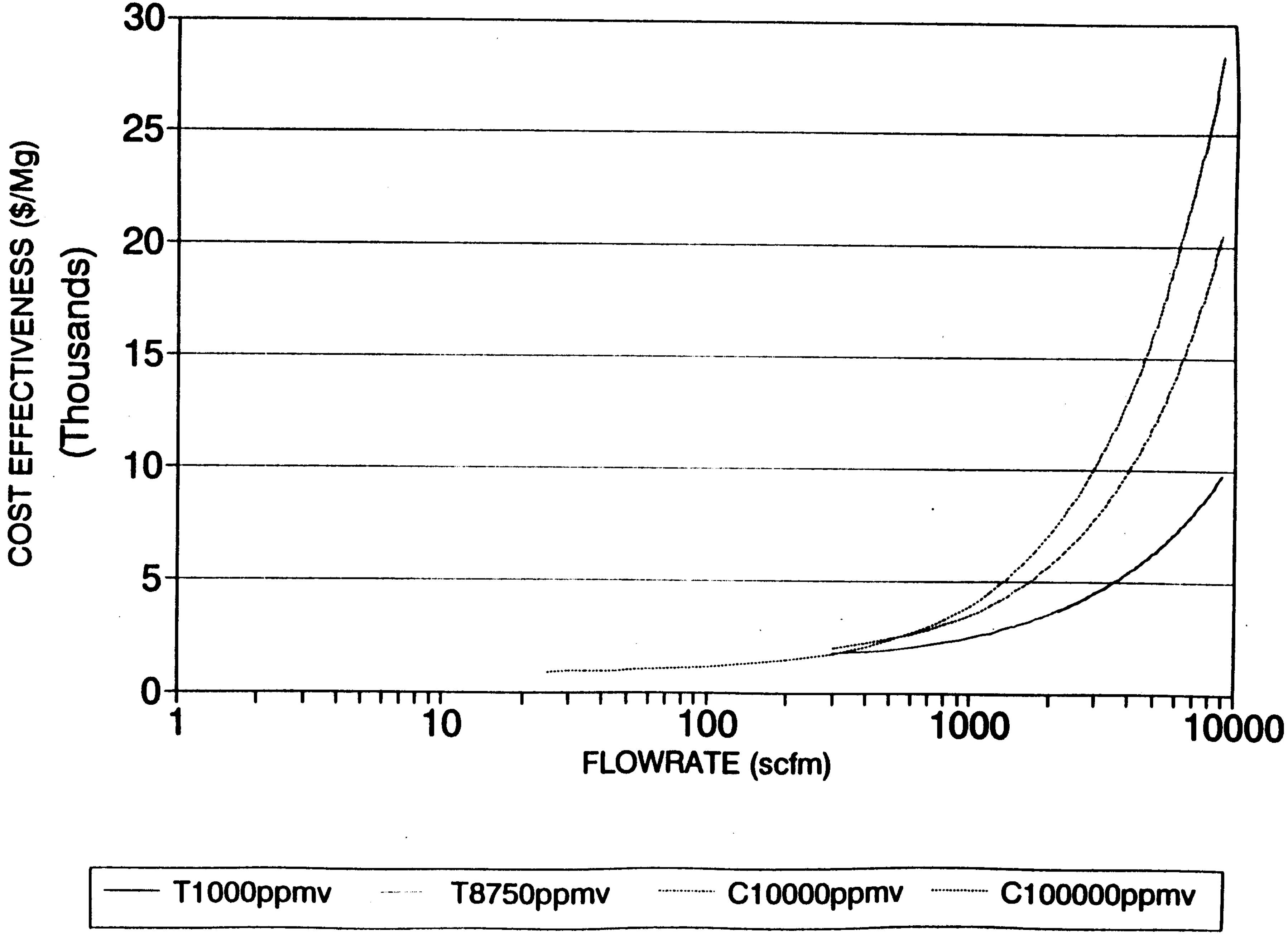
Annual Mass Emission Total=50,000lb/yr

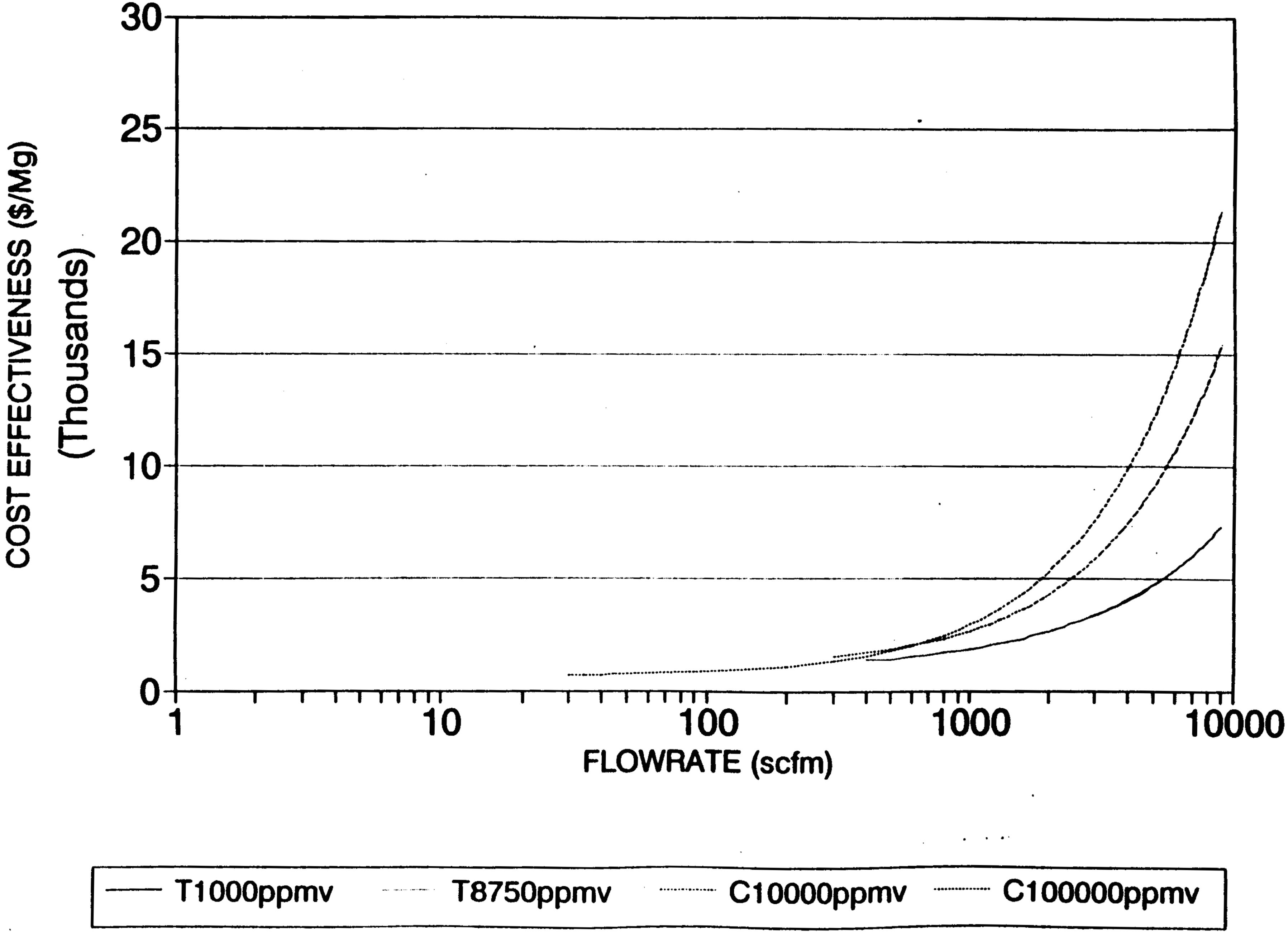
Mod.Vol.(Benzene); Cond. Crtl. Eff.=95%



Annual Mass Emission Total=75,000lb/yr

Mod.Vol.(Benzene); Cond. Crtl. Eff.=95%



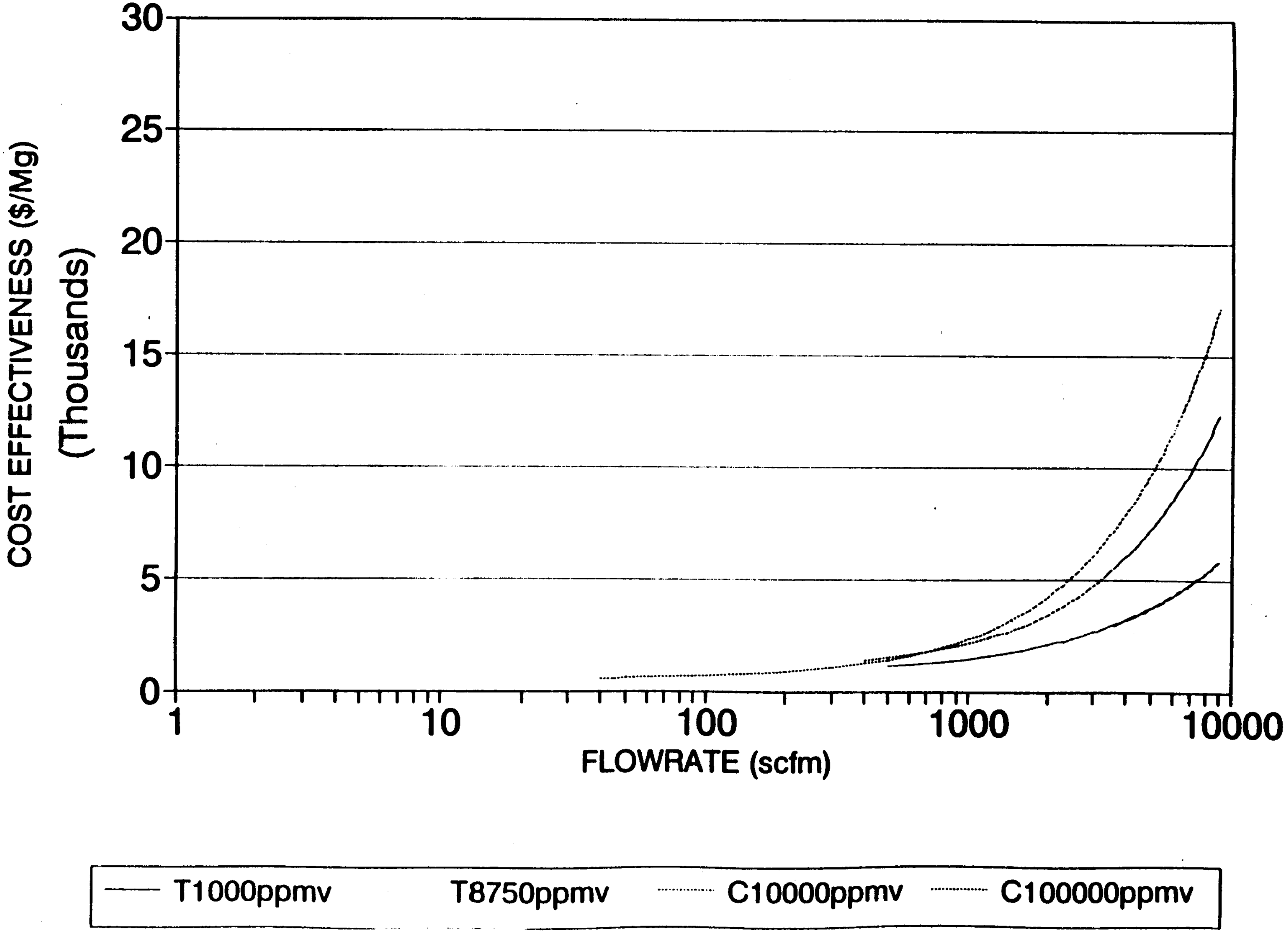


Annual Mass Emission Total=100,000lb/yr

Mod.Vol.(Benzene); Cond. Crtl. Eff.=95%

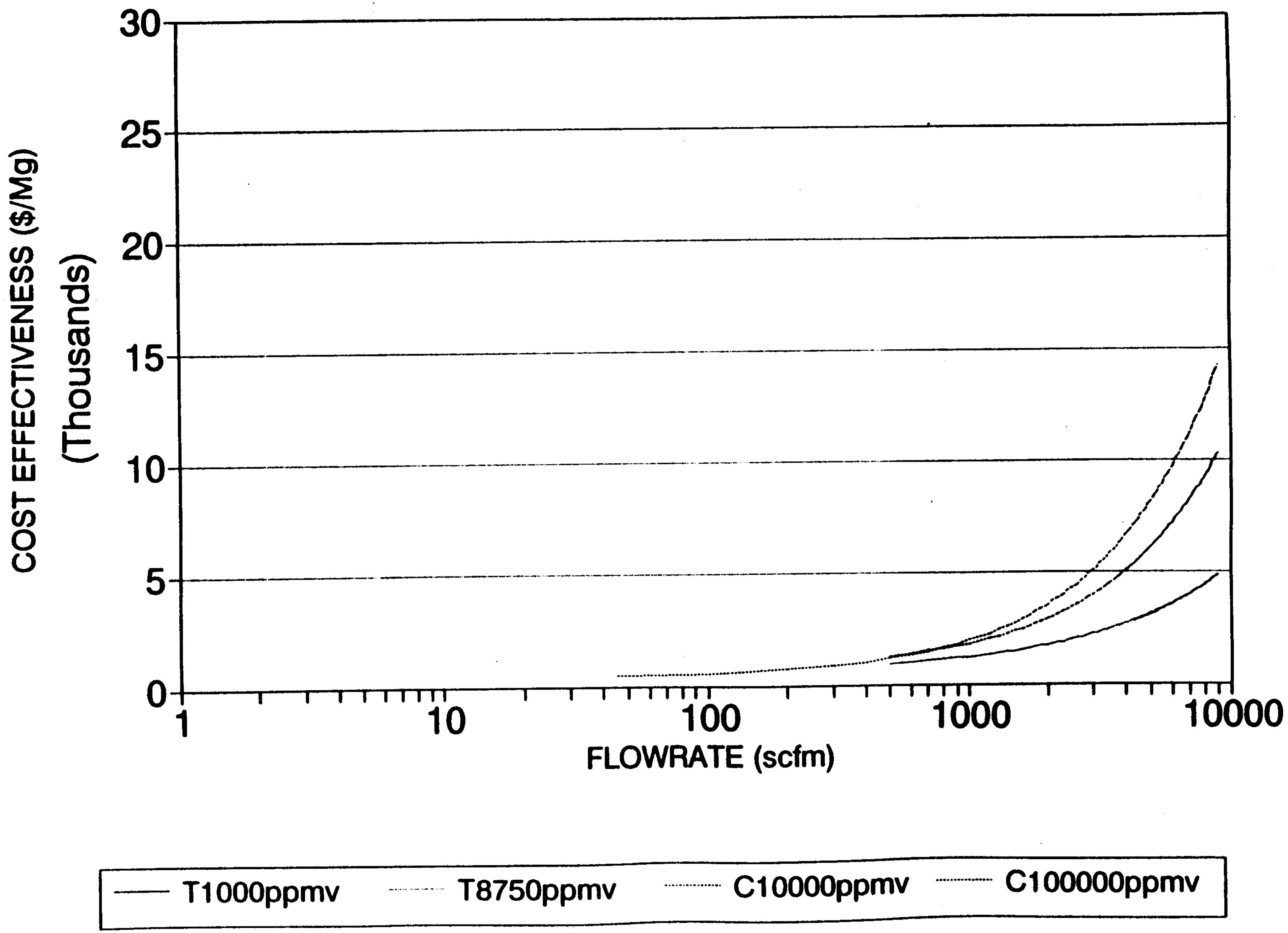
Annual Mass Emission Total=125,000lb/yr

Mod.Vol.(Benzene); Cond. Crtl. Eff.=95%



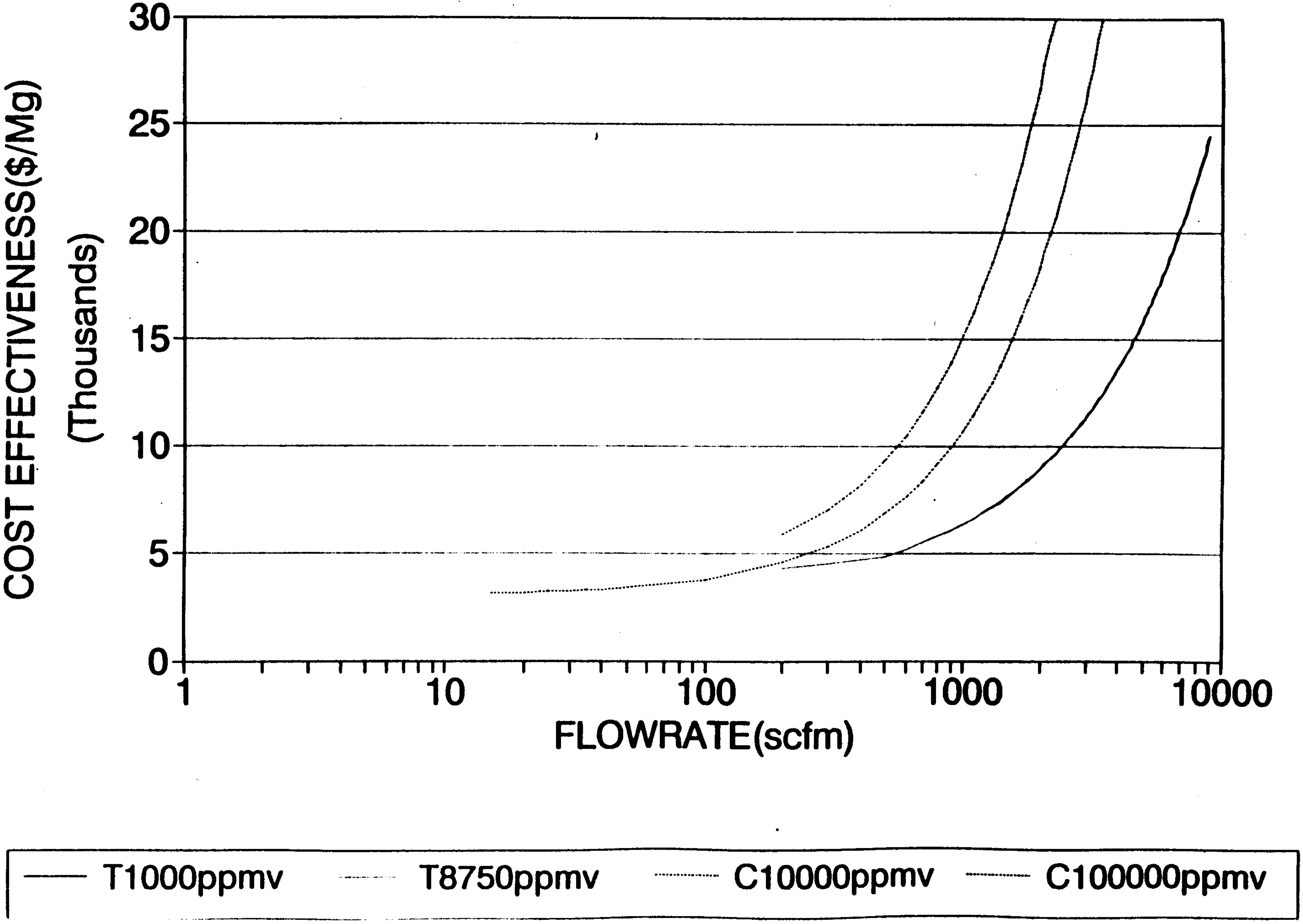
Annual Mass Emission Total=150,000lb/yr

Mod.Vol.(Benzene); Cond. Crtl. Eff.=95%



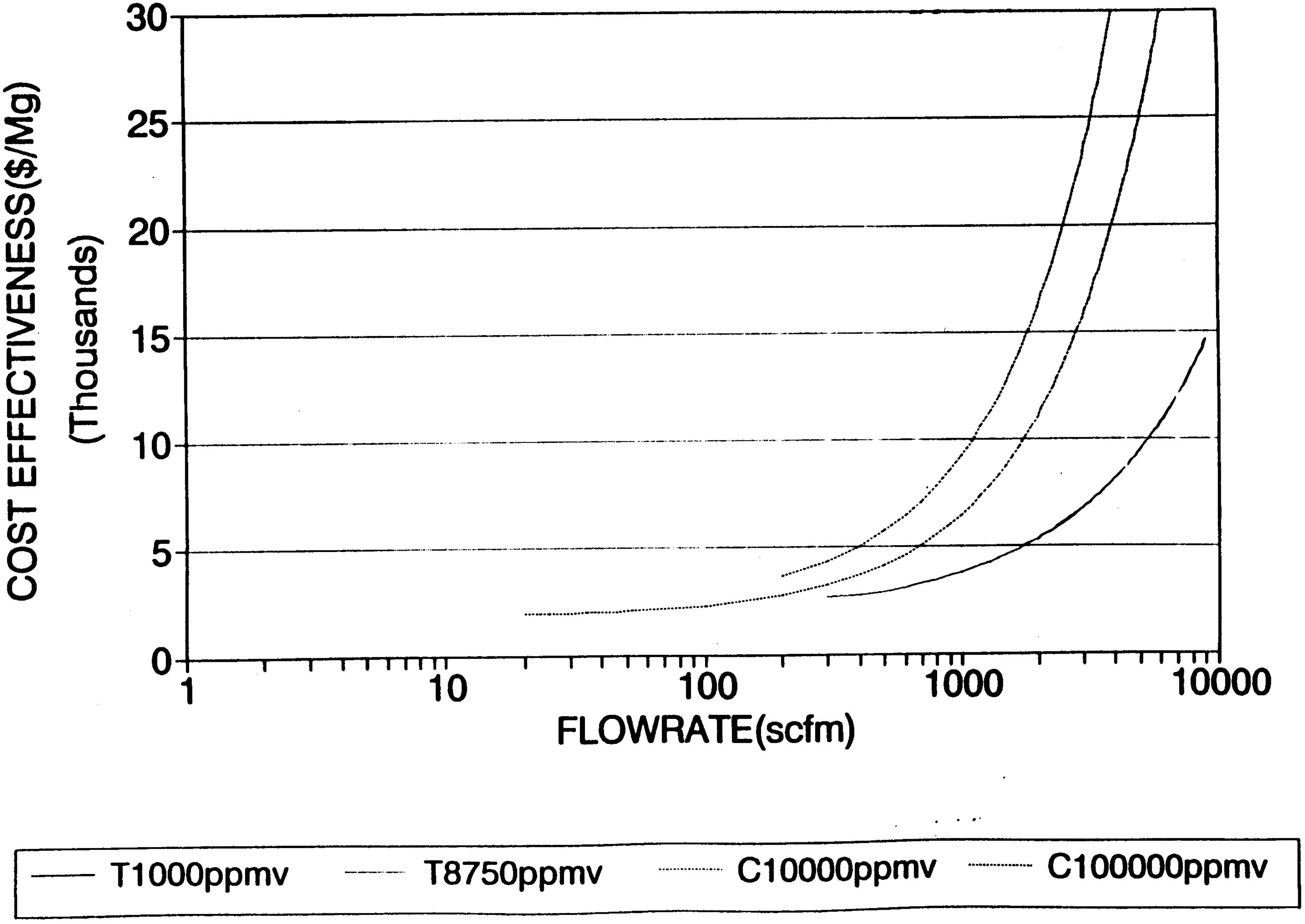
Annual Mass Emission Total=30,000lb/yr

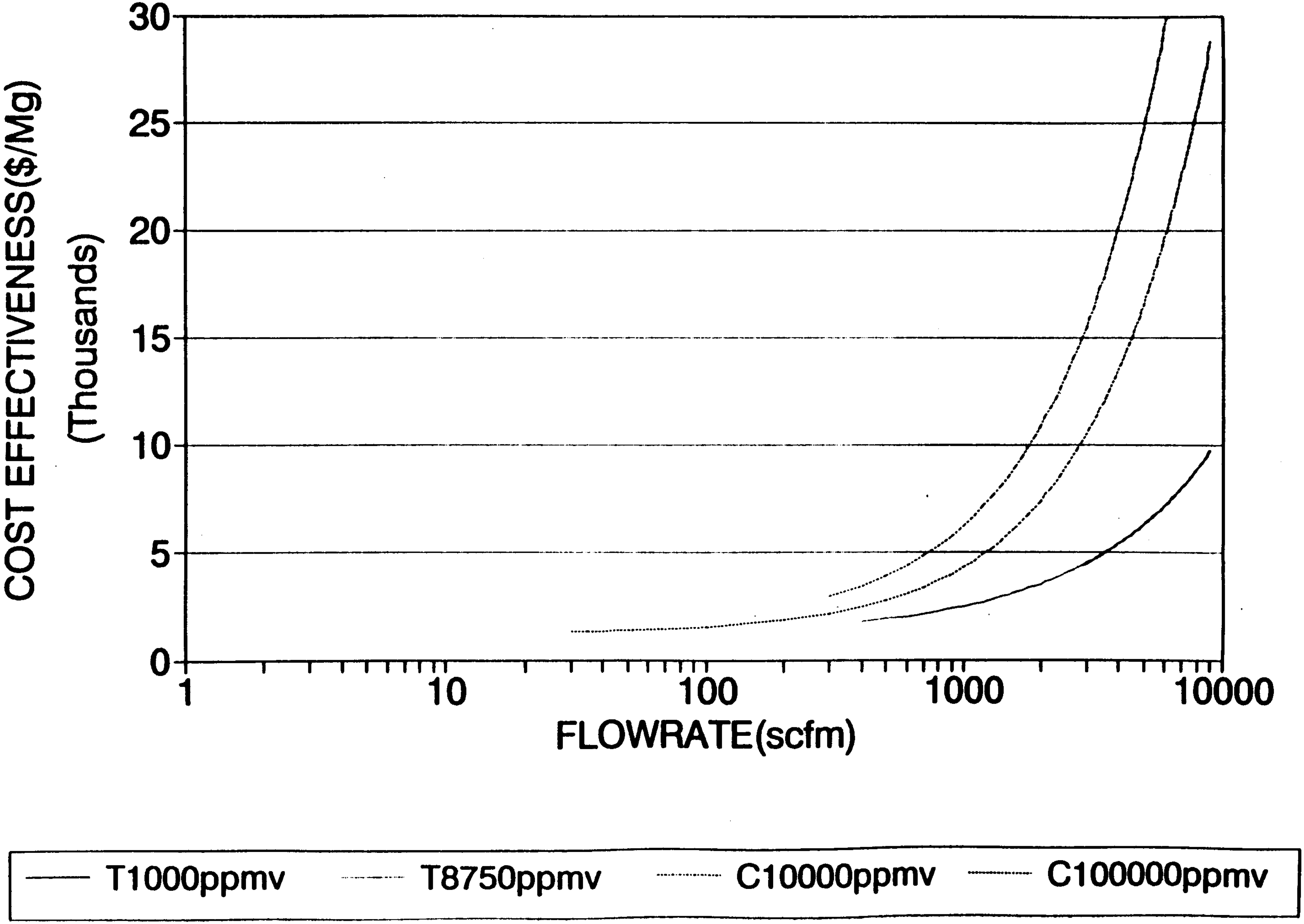
Hi.Vol. (Acetone); Cond. Crtl. Eff.=95%



Annual Mass Emission Total=50,000lb/yr

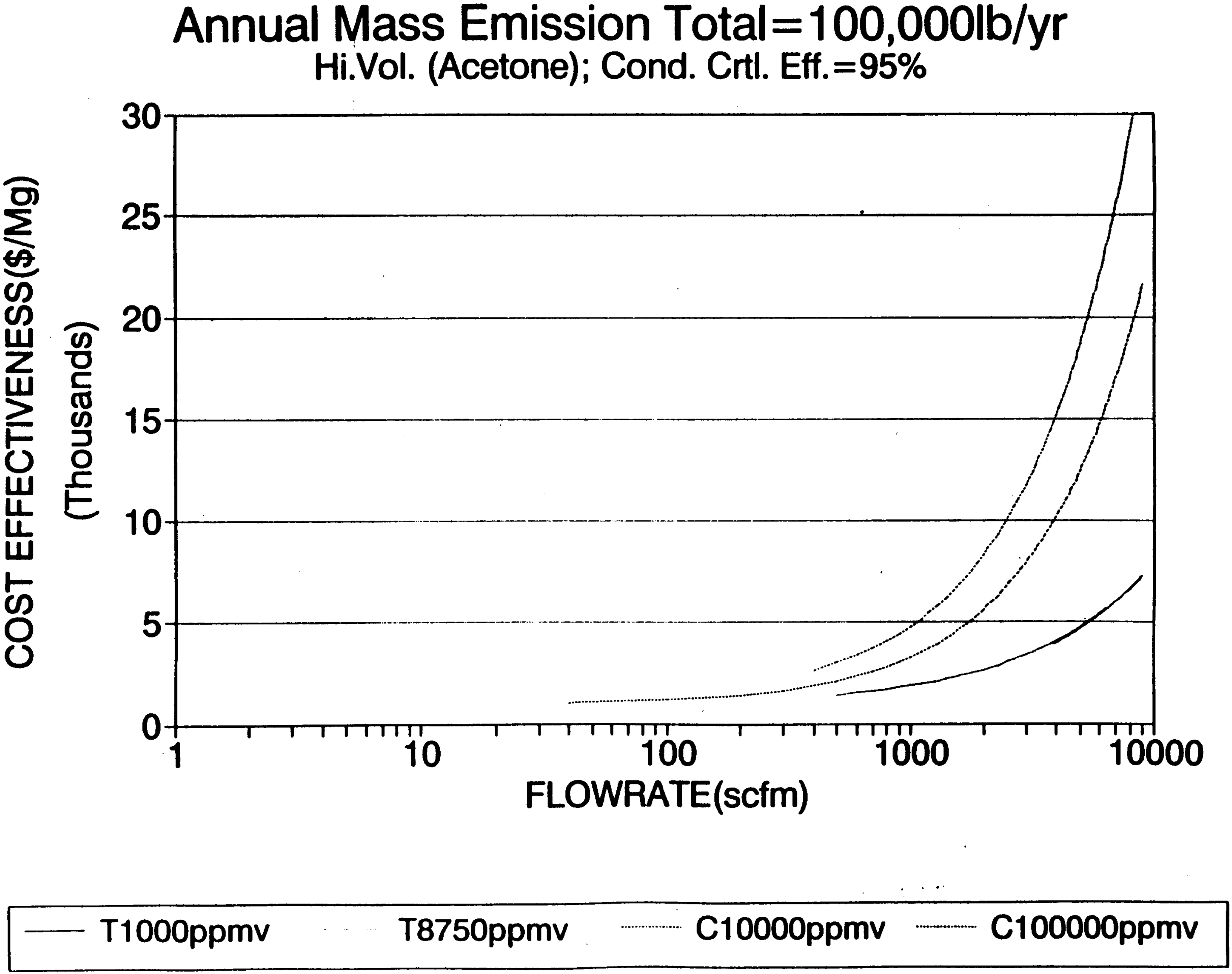
Hi.Vol. (Acetone); Cond. Crtl. Eff.=95%



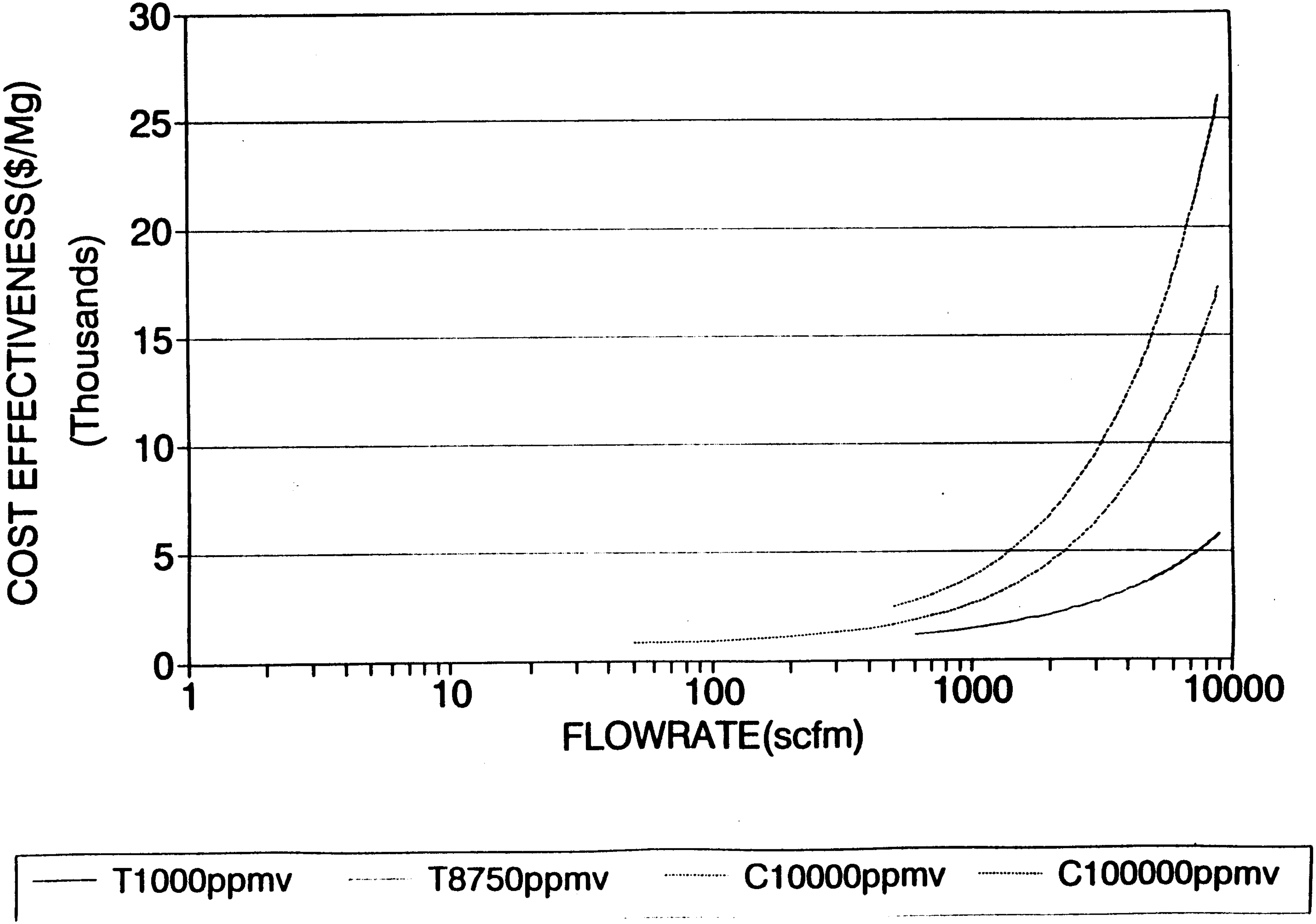


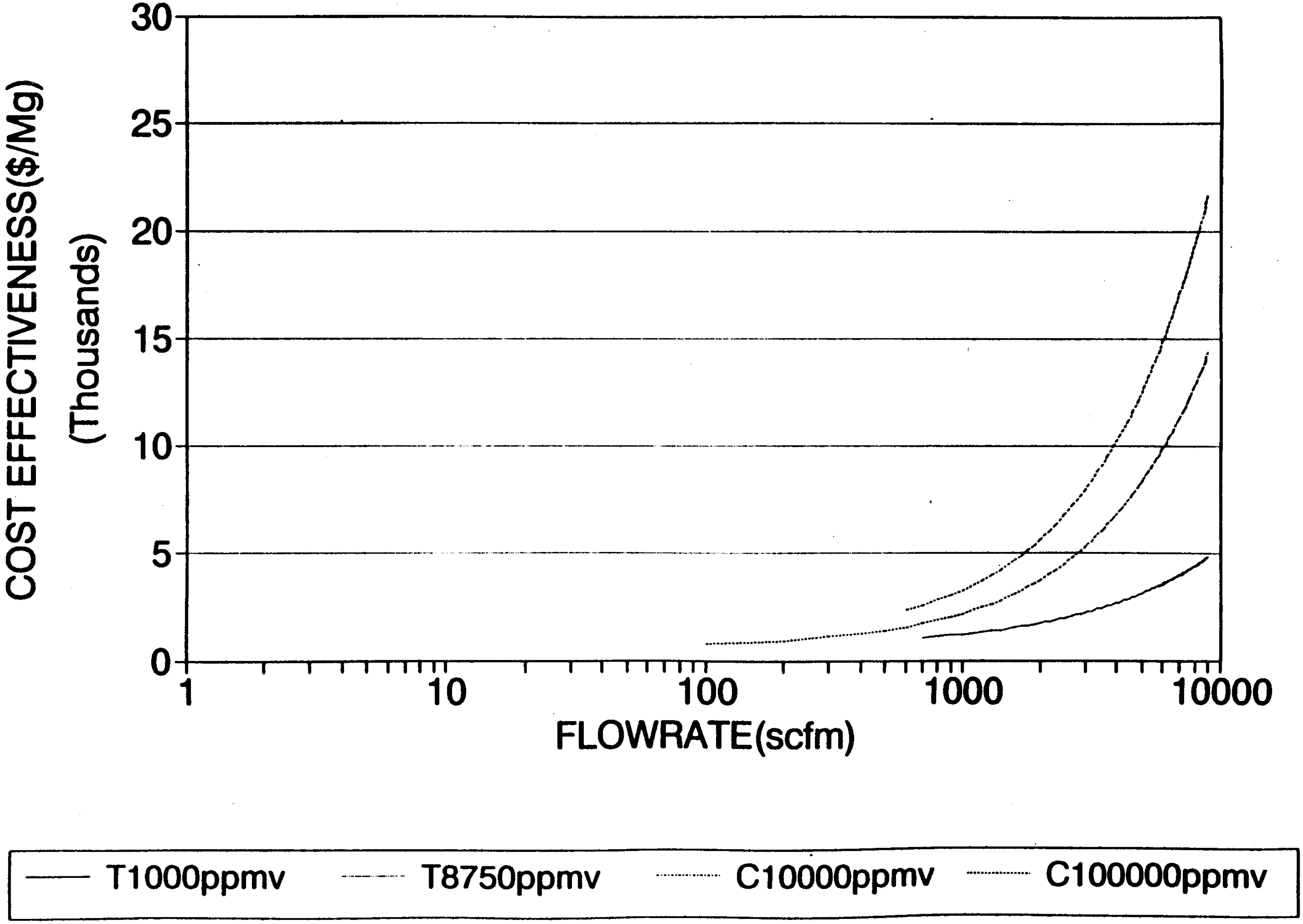
Annual Mass Emission Total=75,000lb/yr

Hi.Vol. (Acetone); Cond. Crtl. Eff.=95%


Annual Mass Emission Total=100,000lb/yr
Hi.Vol. (Acetone); Cond. Crtl. Eff.=95%
COST EFFECTIVENESS($/Mg)
(Thousands)
30
25
20
15
10
5
0
1
10
100
1000
10000
FLOWRATE(scfm)
T1000ppmv
T8750ppmv
C10000ppmv
C100000ppmv

Annual Mass Emission Total=125,000lb/yr
Hi.Vol. (Acetone); Cond. Crtl. Eff.=95%



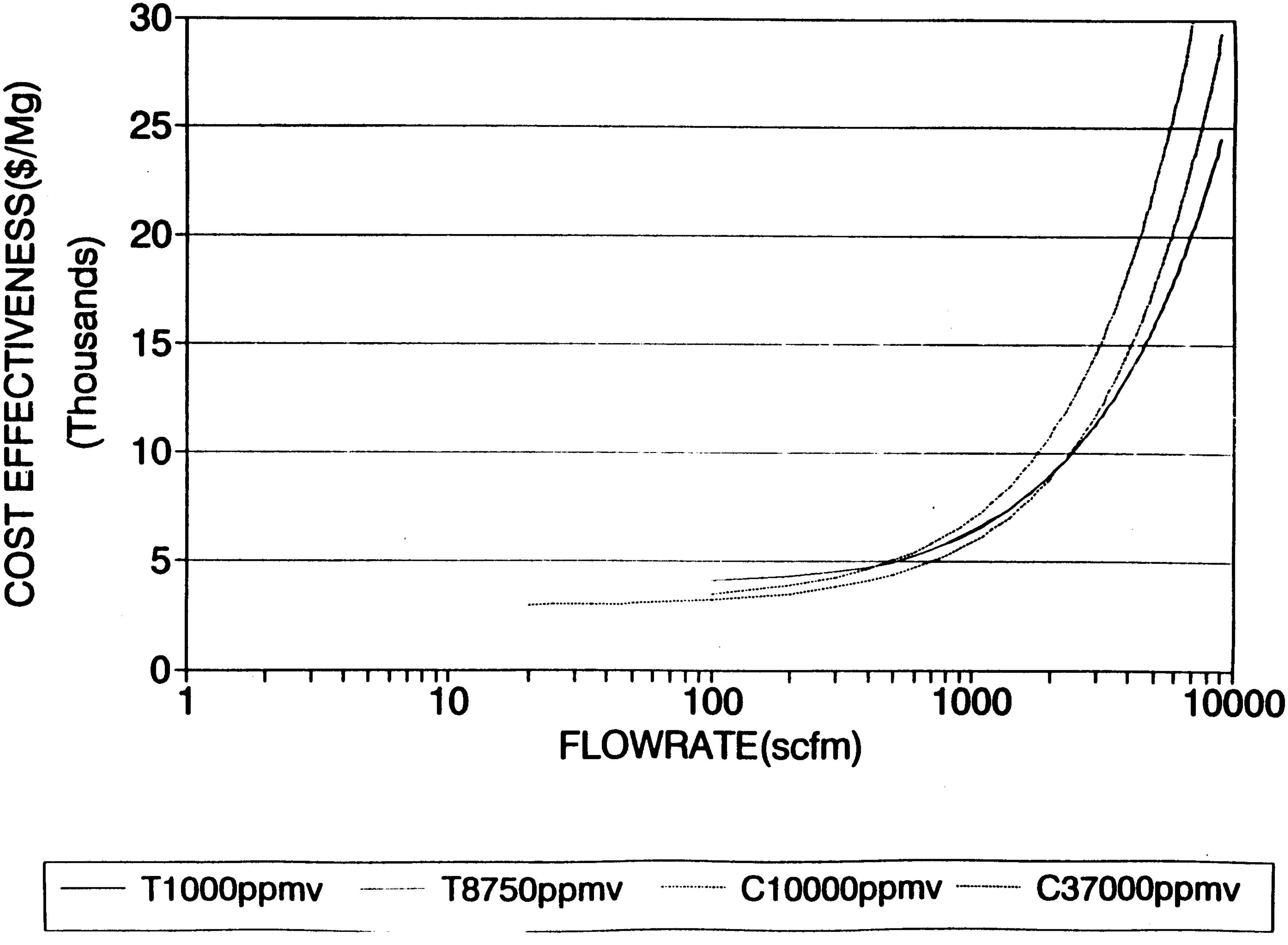


Annual Mass Emission Total=150,000lb/yr

Hi.Vol. (Acetone); Cond. Crtl. Eff.=95%

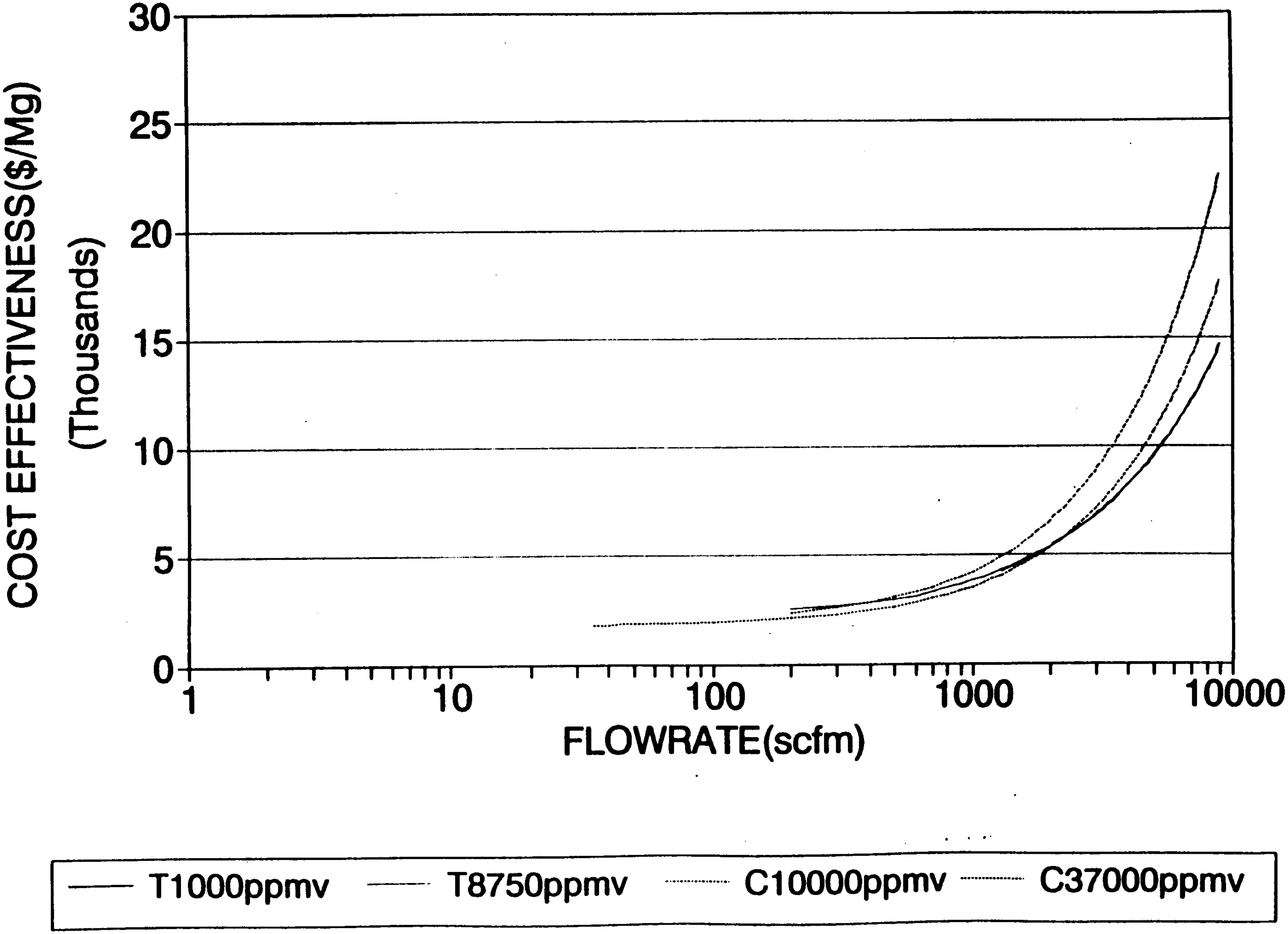
Annual Mass Emission Total=30,000lb/yr

Low Vol.(Toluene); Cond. Crtl. Eff.=98%



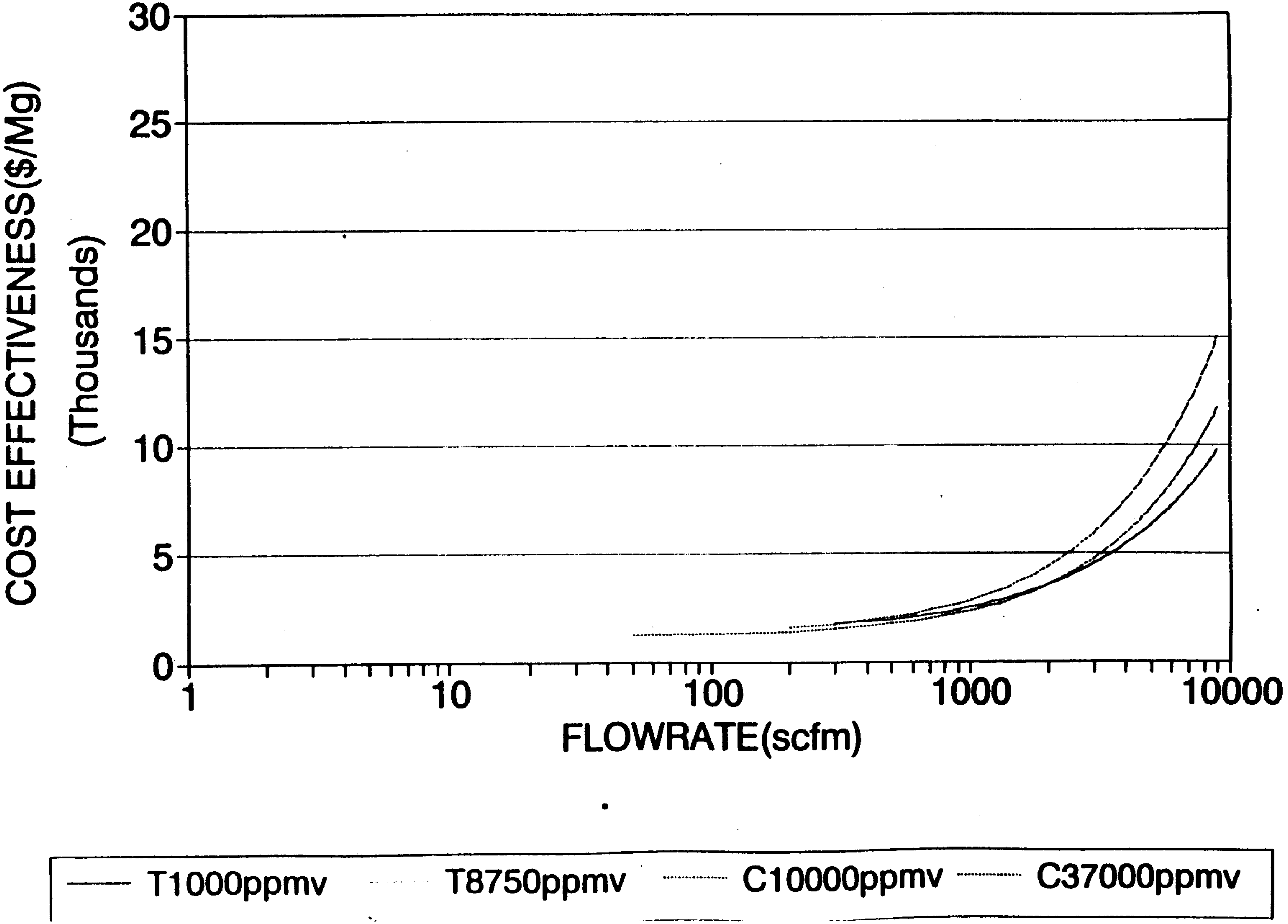
Annual Mass Emission Total=50,000lb/yr

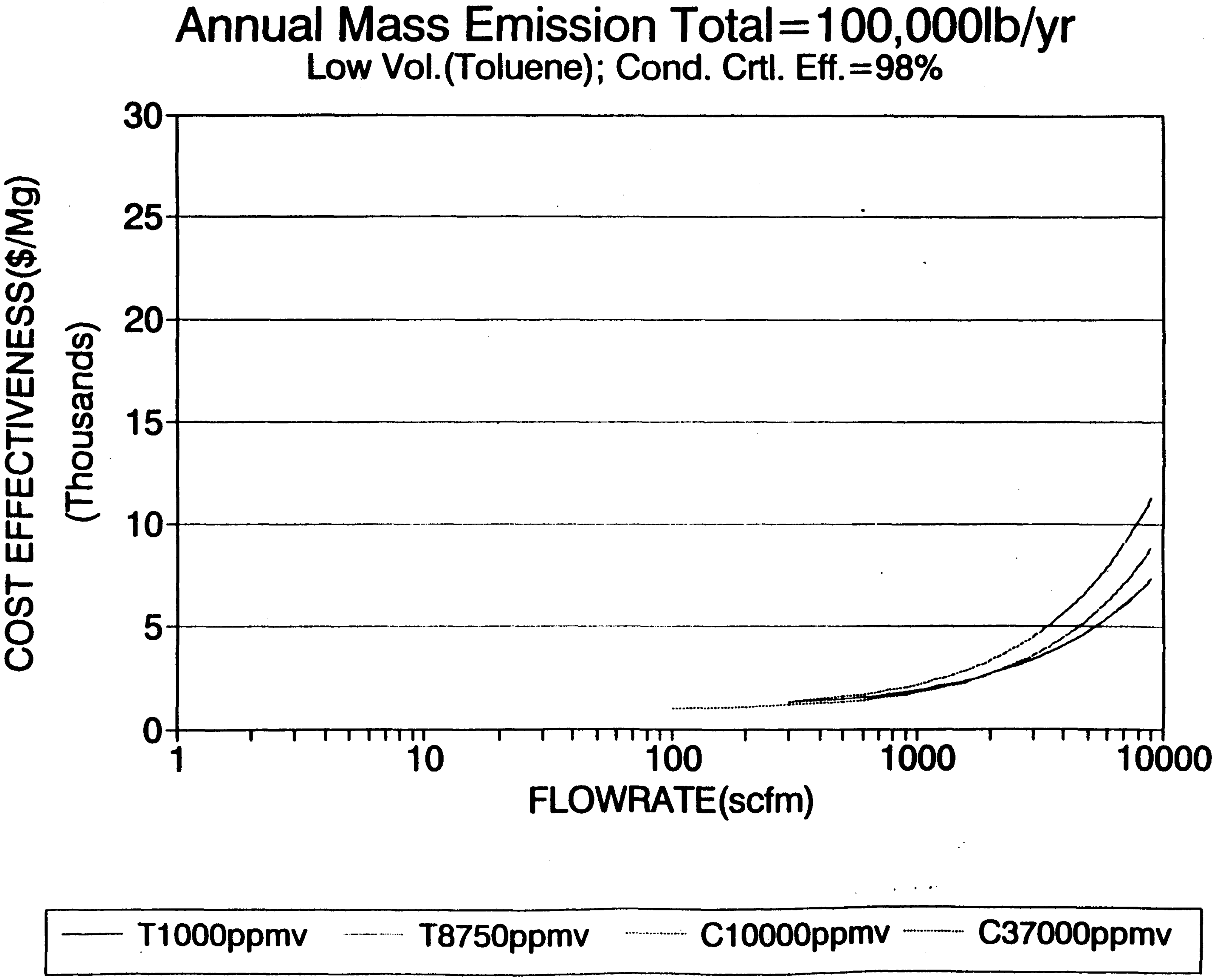
Low Vol.(Toluene); Cond. Crtl. Eff.=98%



Annual Mass Emission Total=75,000lb/yr

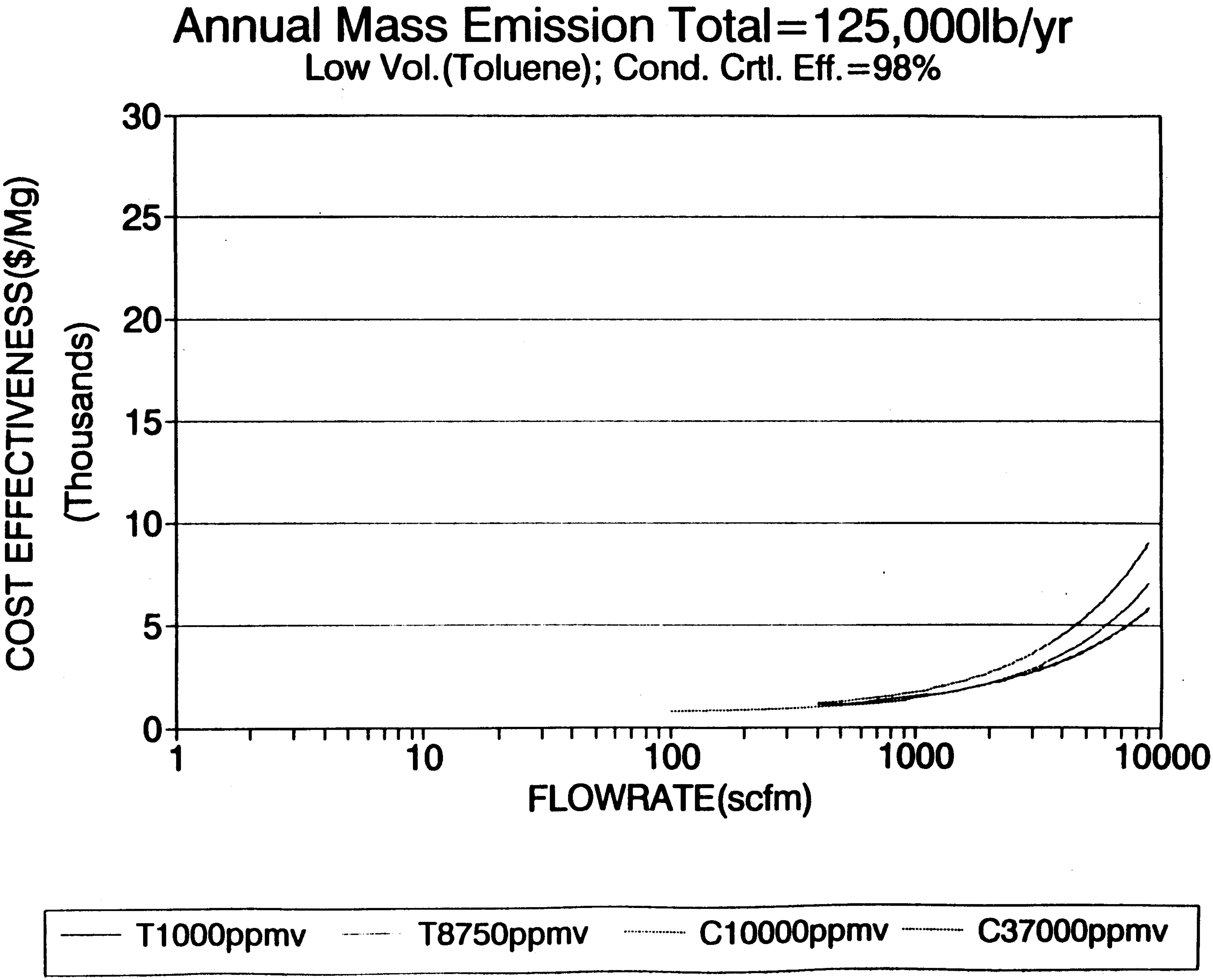
Low Vol.(Toluene); Cond. Crtl. Eff.=98%





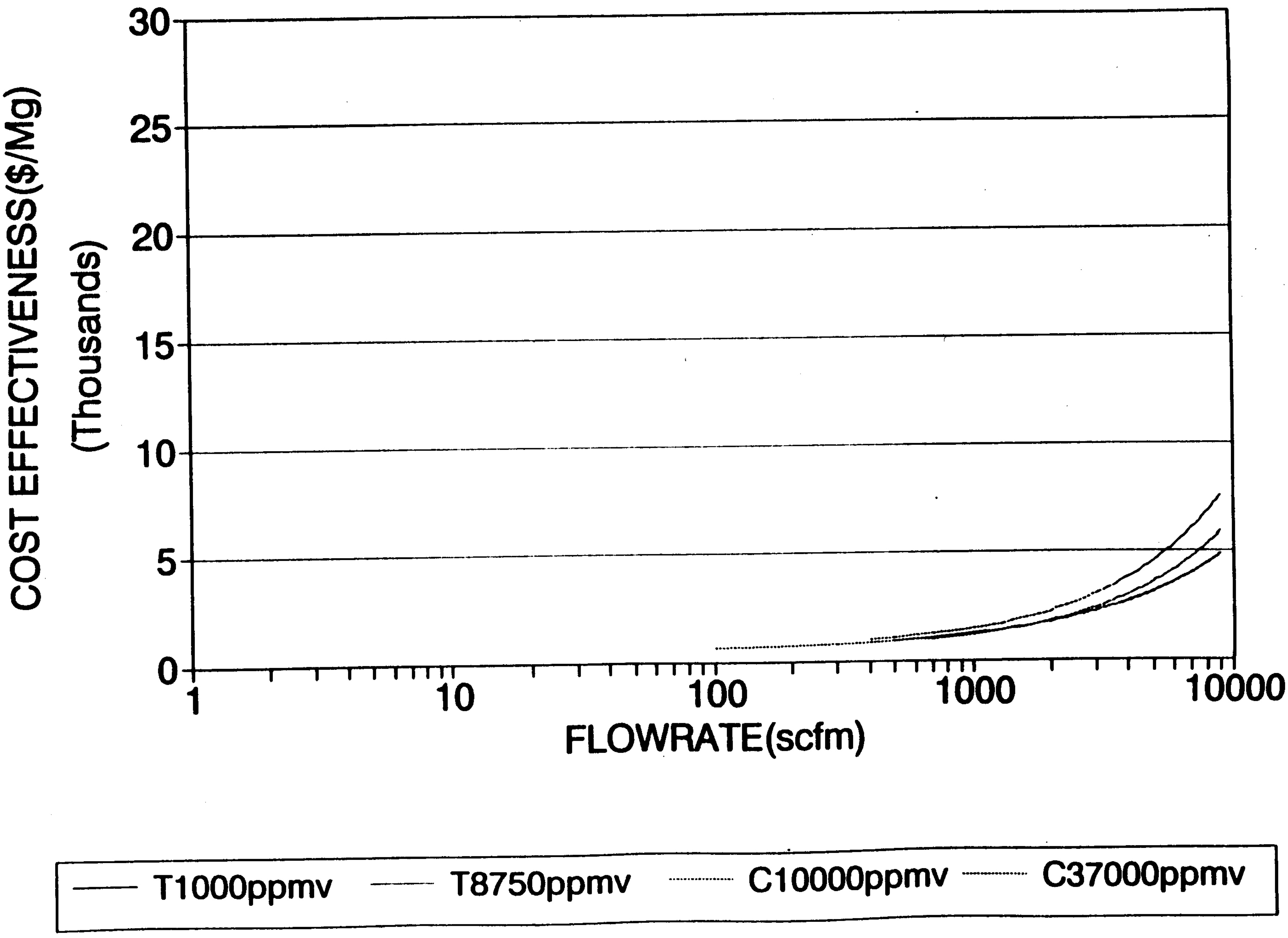
Annual Mass Emission Total=100,000lb/yr

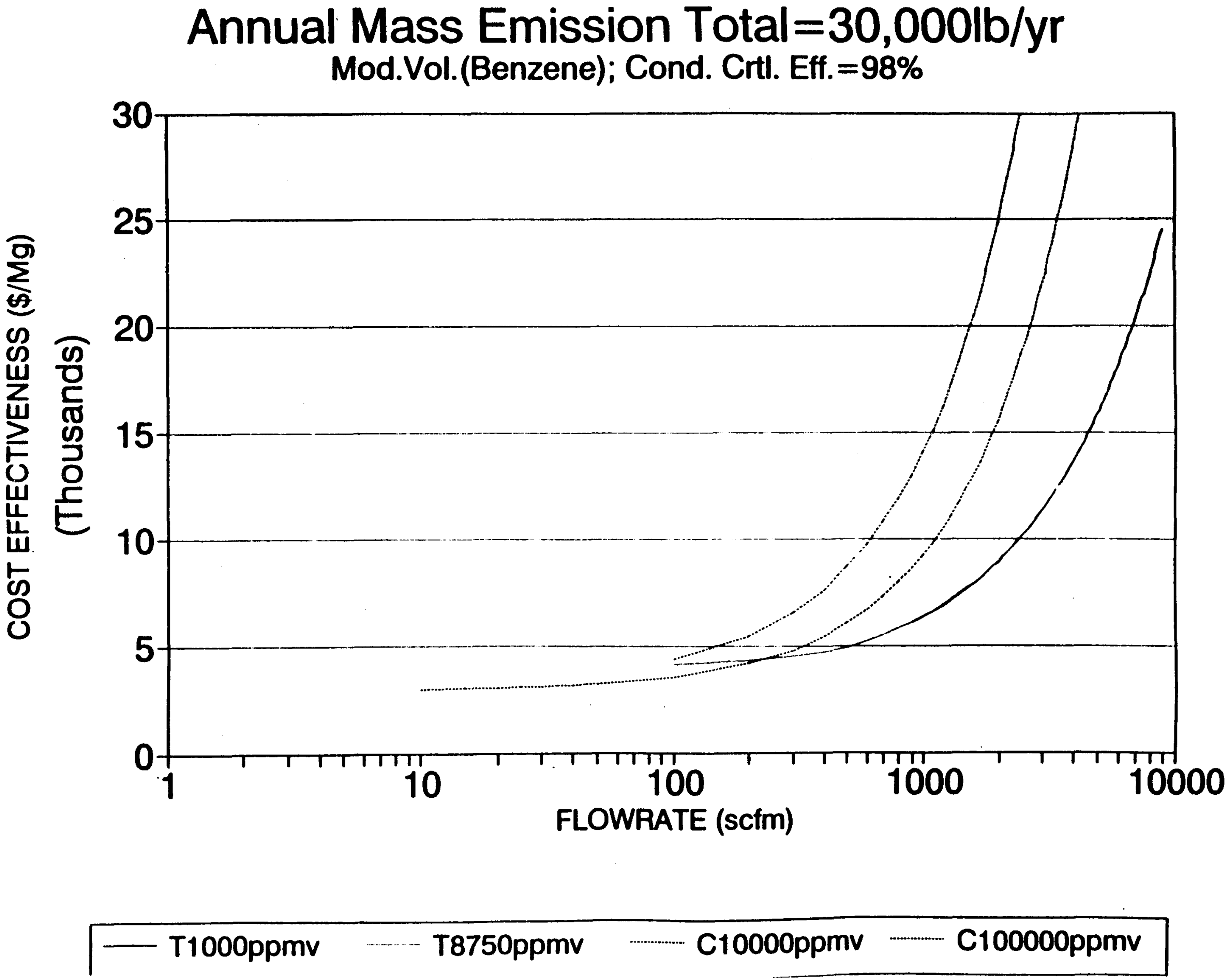
Low Vol.(Toluene); Cond. Crtl. Eff.=98%


Annual Mass Emission Total=125,000lb/yr
Low Vol.(Toluene); Cond. Crtl. Eff.=98%
COST EFFECTIVENESS($/Mg)
(Thousands)
0
5
10
15
20
25
30
1
10
100
1000
10000
FLOWRATE(scfm)
T1000ppmv
T8750ppmv
C10000ppmv
C37000ppmv

Annual Mass Emission Total=150,000lb/yr

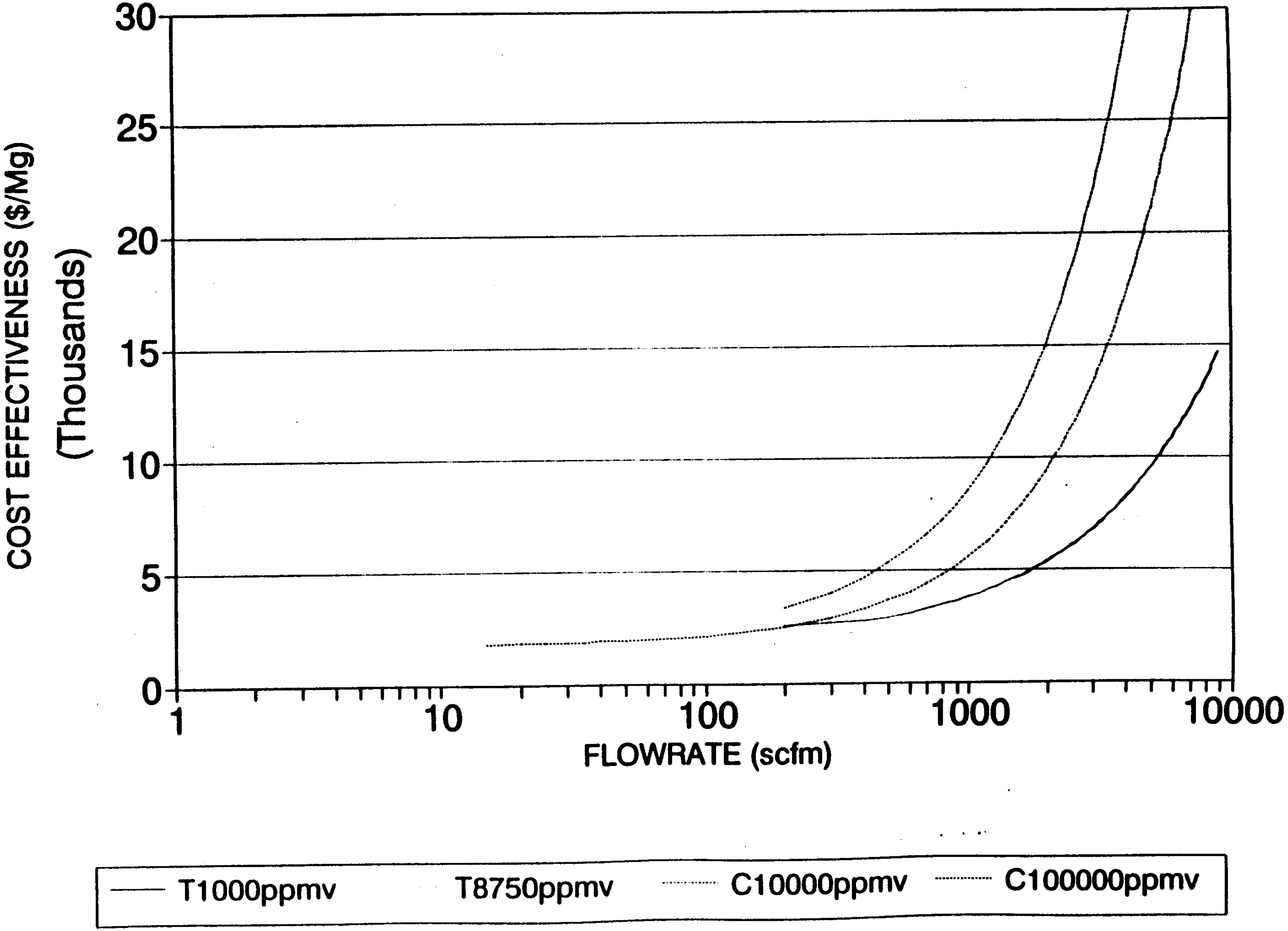
Low Vol.(Toluene); Cond. Crtl. Eff.=98%





Annual Mass Emission Total=30,000lb/yr

Mod.Vol.(Benzene); Cond. Crtl. Eff.=98%

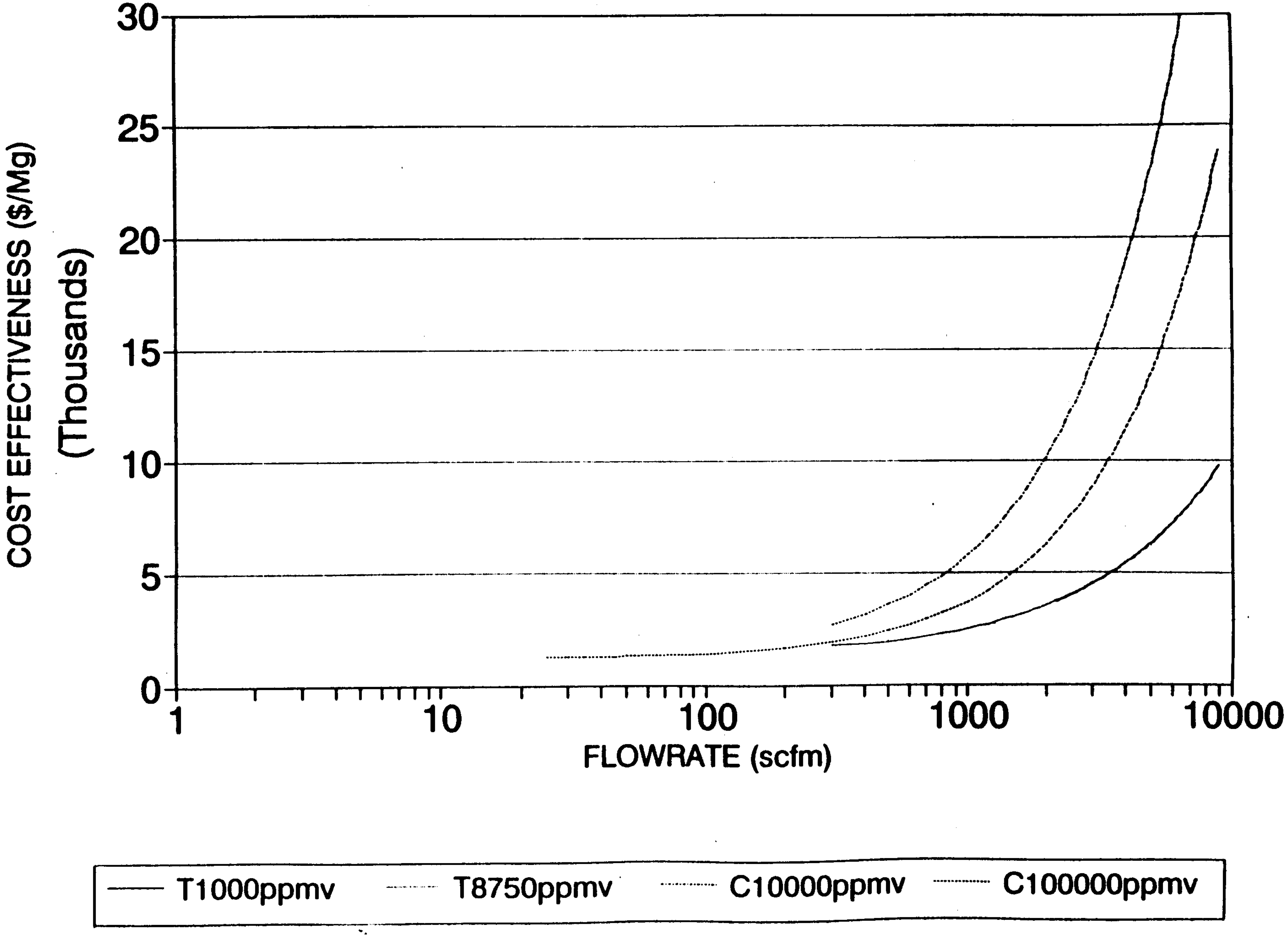


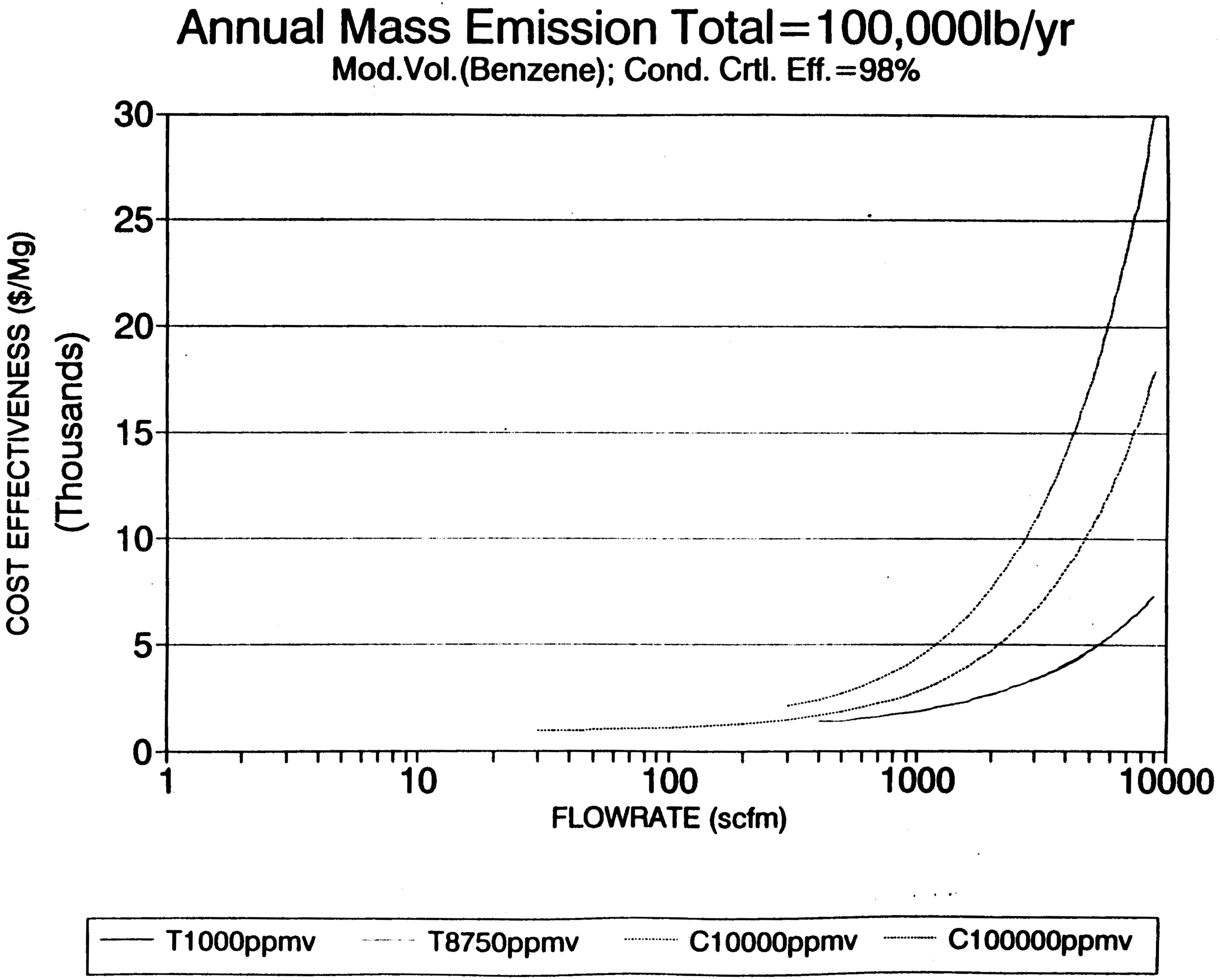
Annual Mass Emission Total=50,000lb/yr

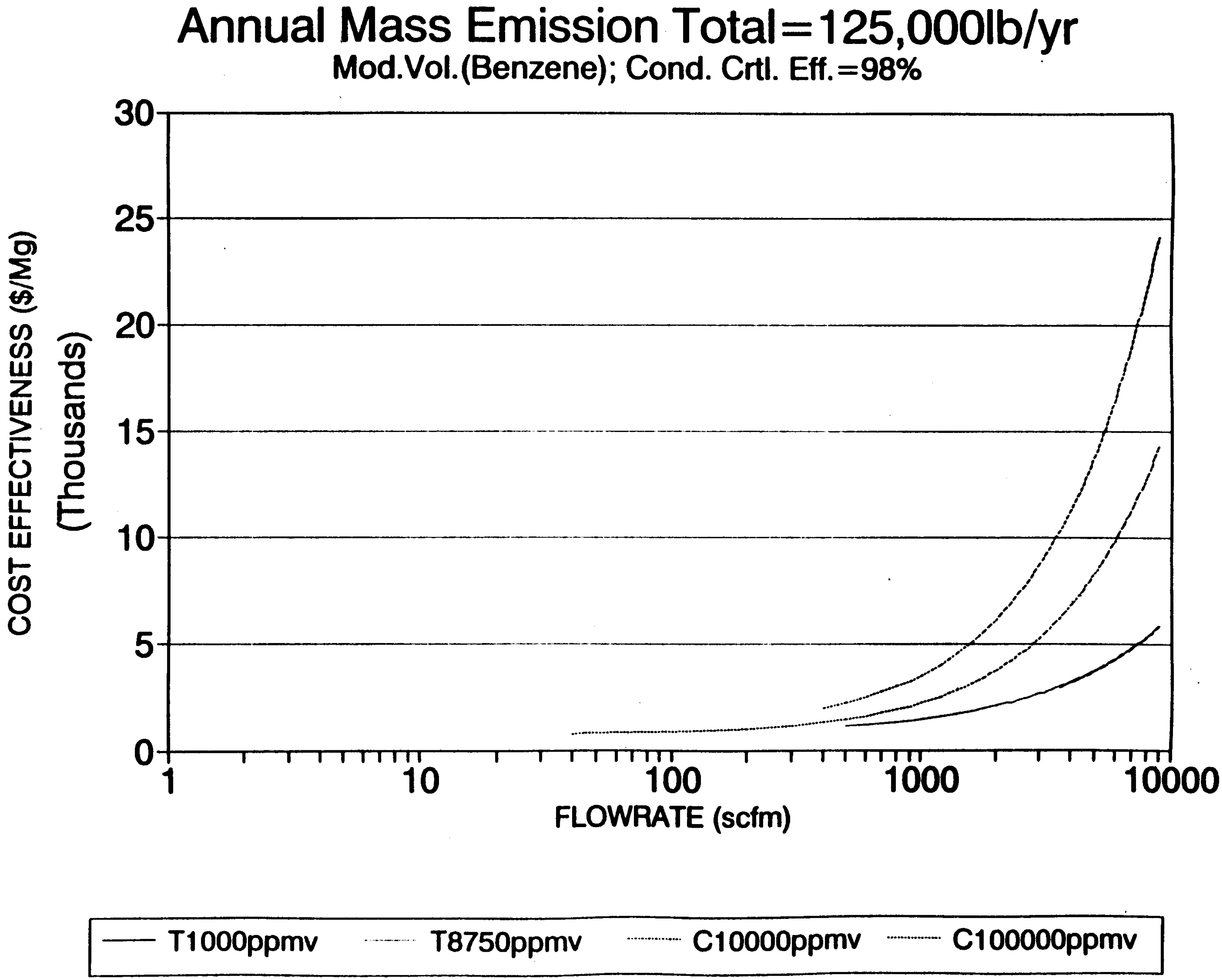
Mod.Vol.(Benzene); Cond. Crtl. Eff.=98%

Annual Mass Emission Total=75,000lb/yr

Mod.Vol.(Benzene); Cond. Crtl. Eff.=98%




Annual Mass Emission Total=100,000lb/yr
Mod.Vol.(Benzene); Cond. Crtl. Eff.=98%
COST EFFECTIVENESS ($/Mg)
(Thousands)
30
25
20
15
10
5
0
1
10
100
1000
10000
FLOWRATE (scfm)
T1000ppmv
T8750ppmv
C10000ppmv
C100000ppmv

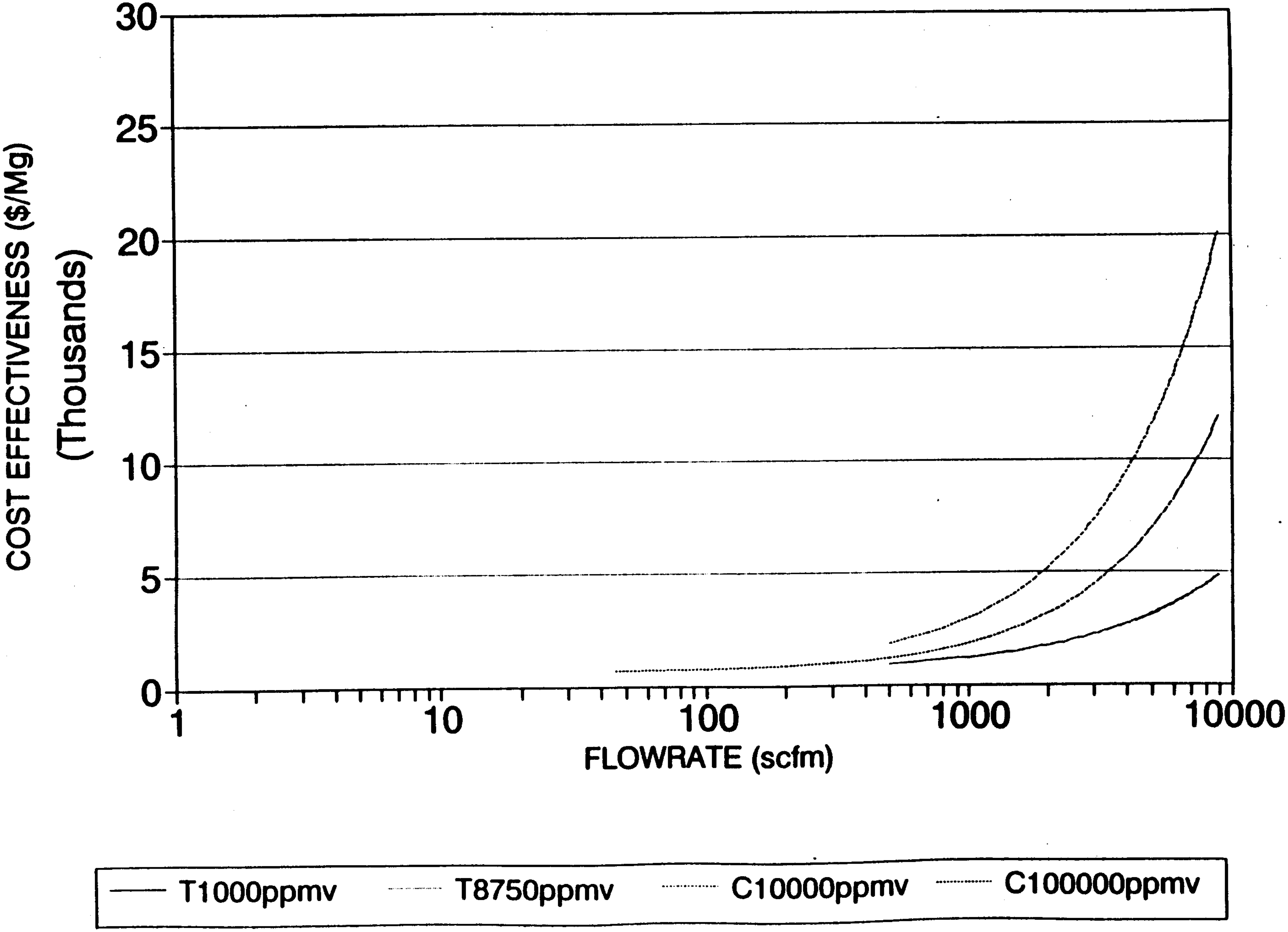


Annual Mass Emission Total=125,000lb/yr

Mod.Vol.(Benzene); Cond. Crtl. Eff.=98%

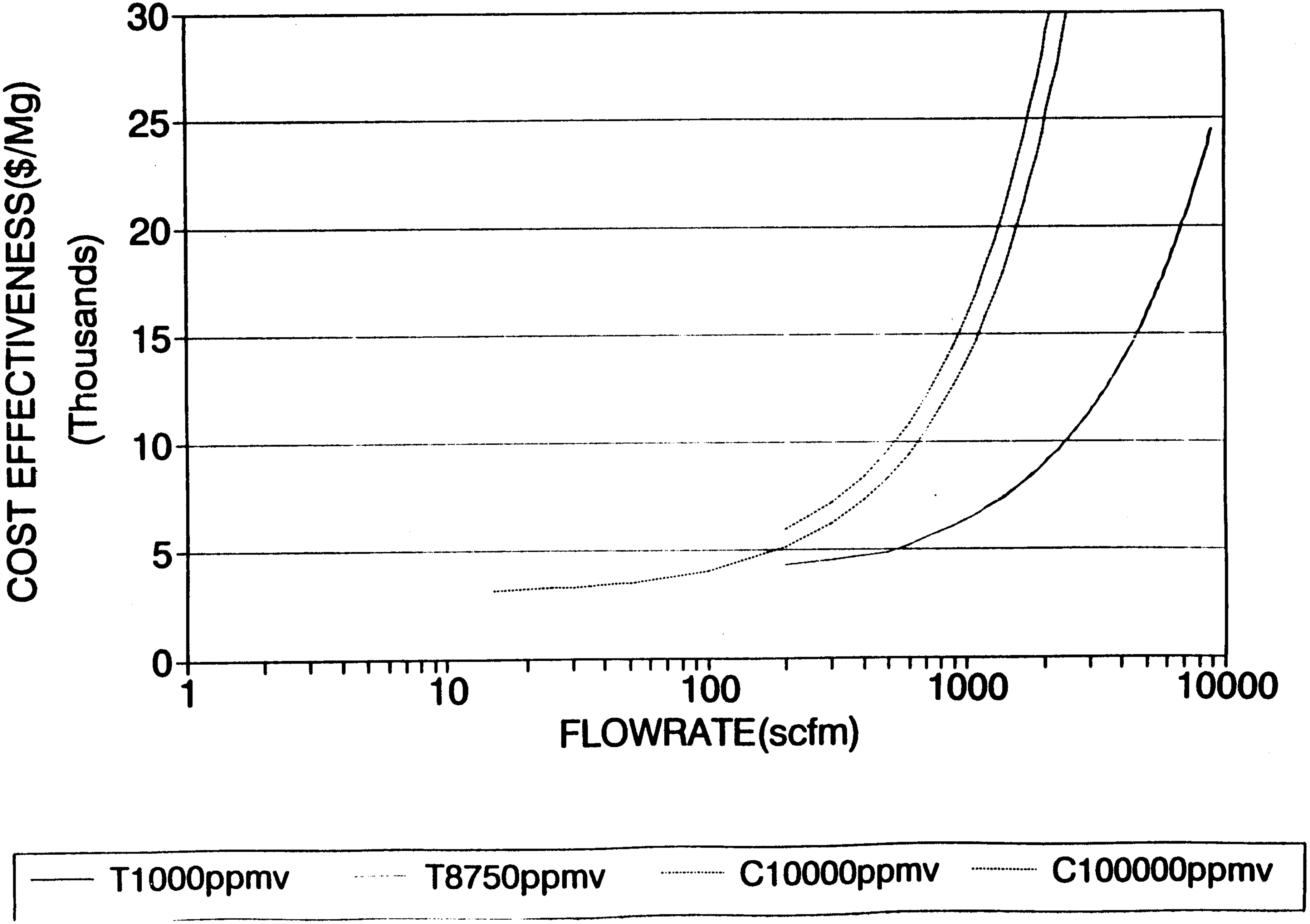
Annual Mass Emission Total=150,000lb/yr

Mod.Vol.(Benzene); Cond. Crtl. Eff.=98%



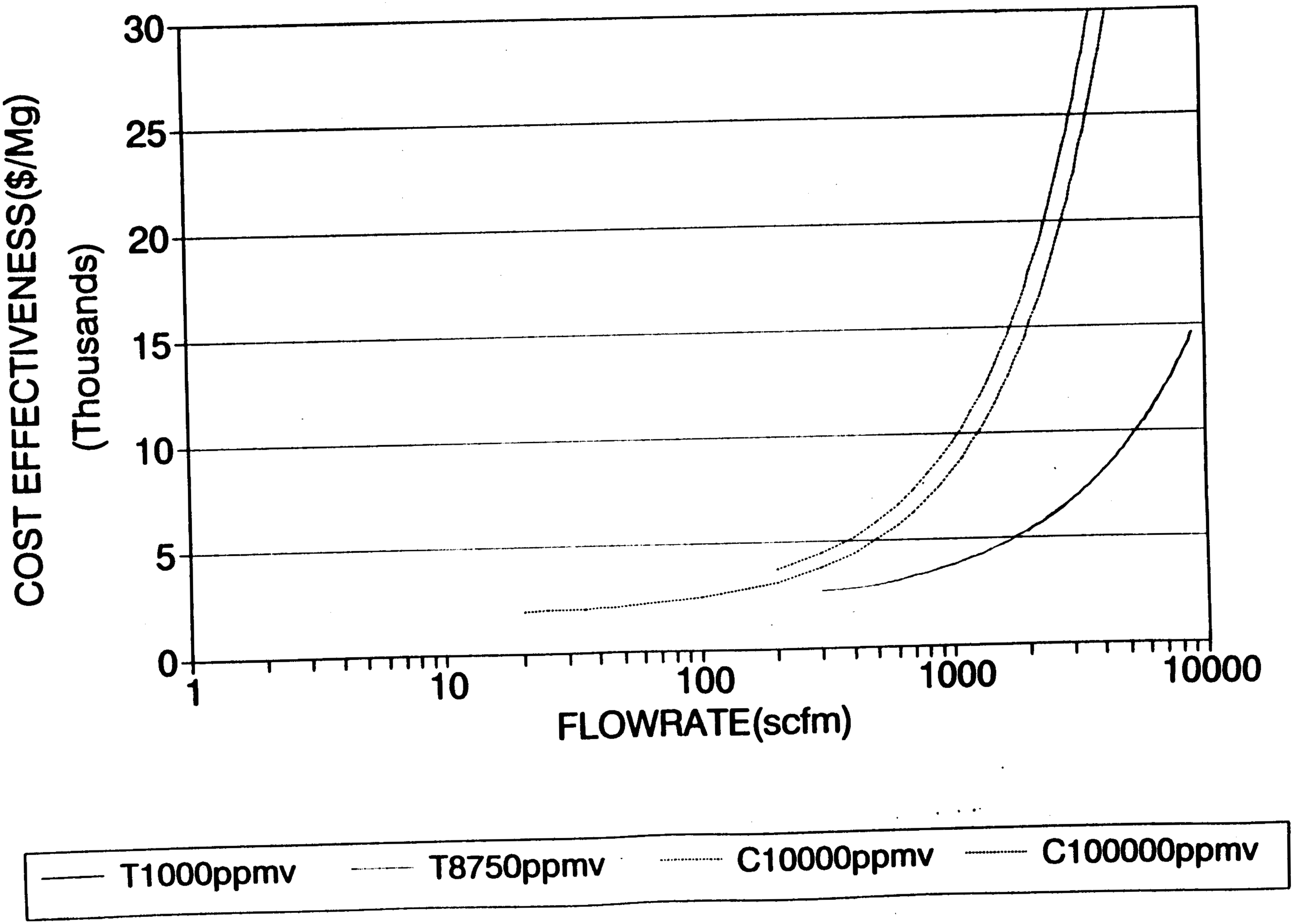
Annual Mass Emission Total=30,000lb/yr

Hi.Vol. (Acetone); Cond. Crtl. Eff.=98%



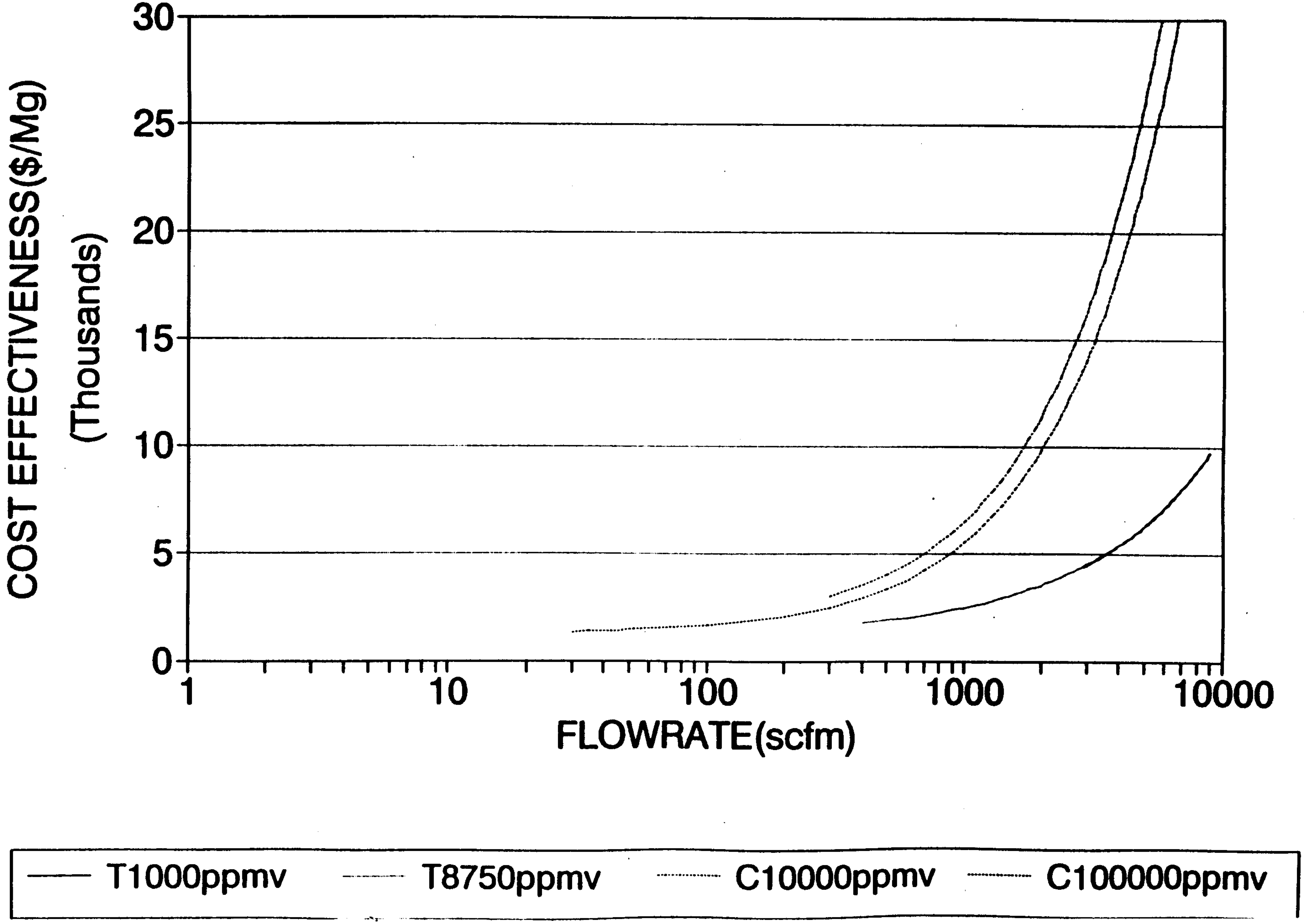
Annual Mass Emission Total=50,000lb/yr

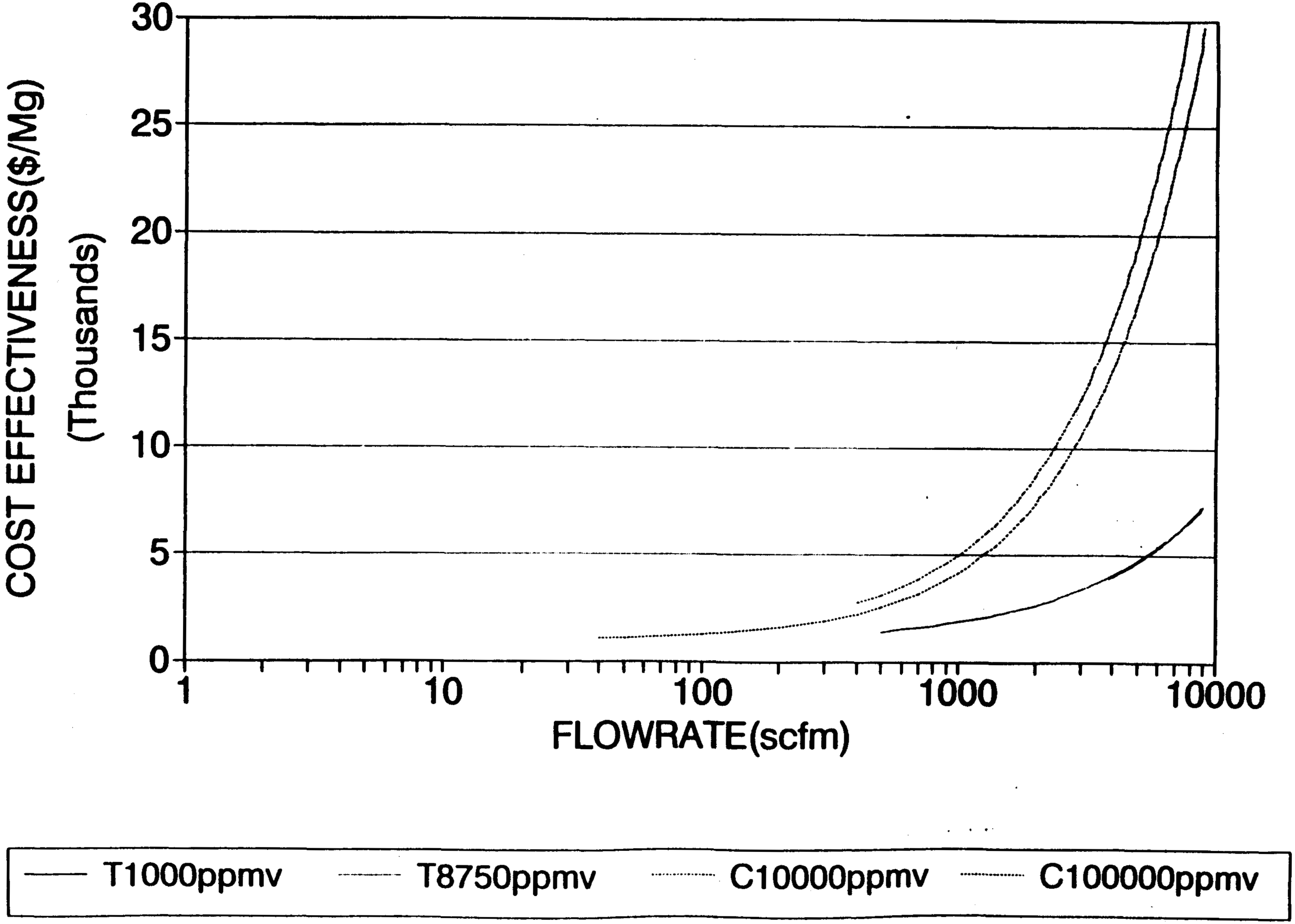
Hi.Vol. (Acetone); Cond. Crtl. Eff.=98%



Annual Mass Emission Total=75,000lb/yr

Hi.Vol. (Acetone); Cond. Crtl. Eff.=98%



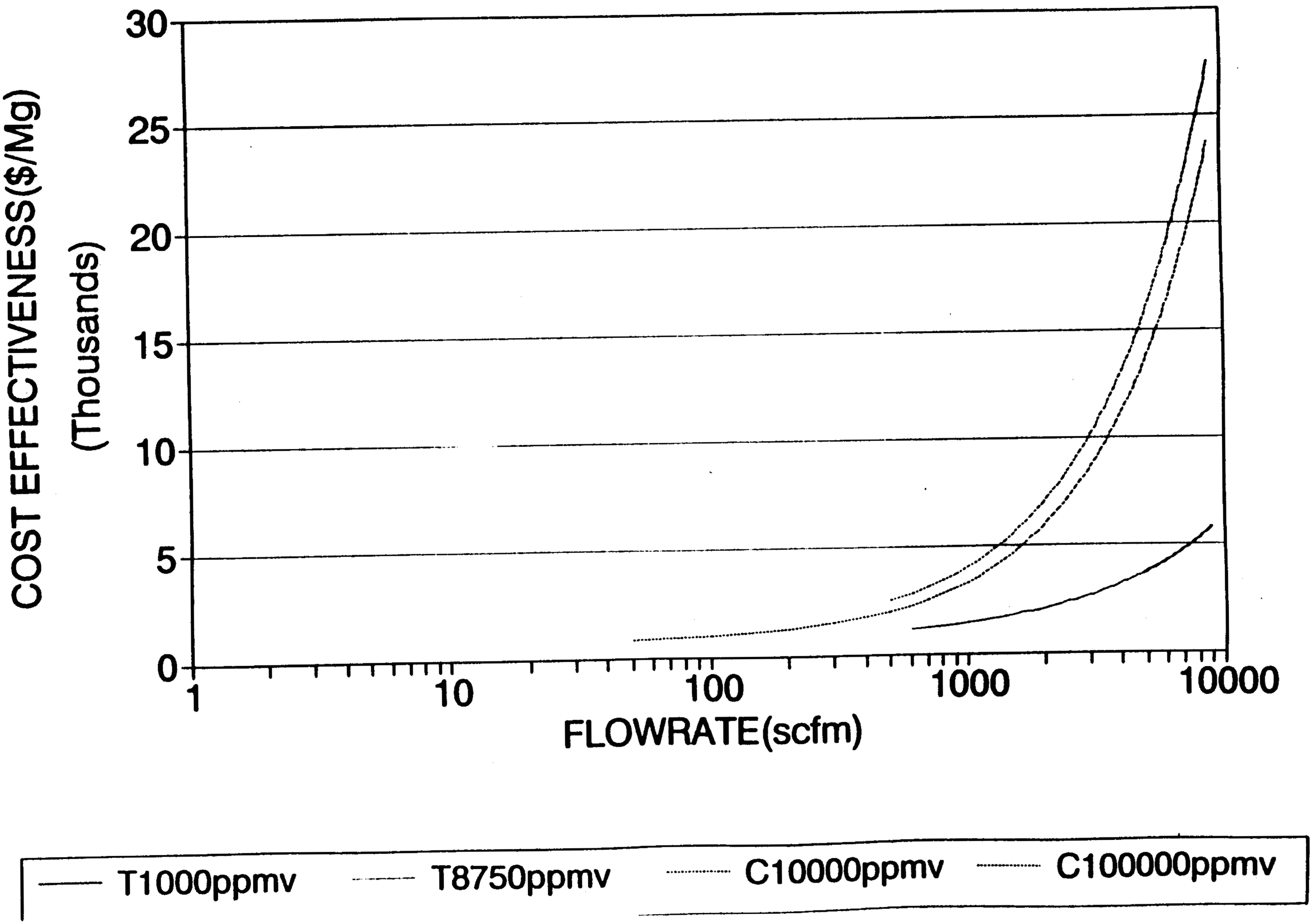


Annual Mass Emission Total=100,000lb/yr

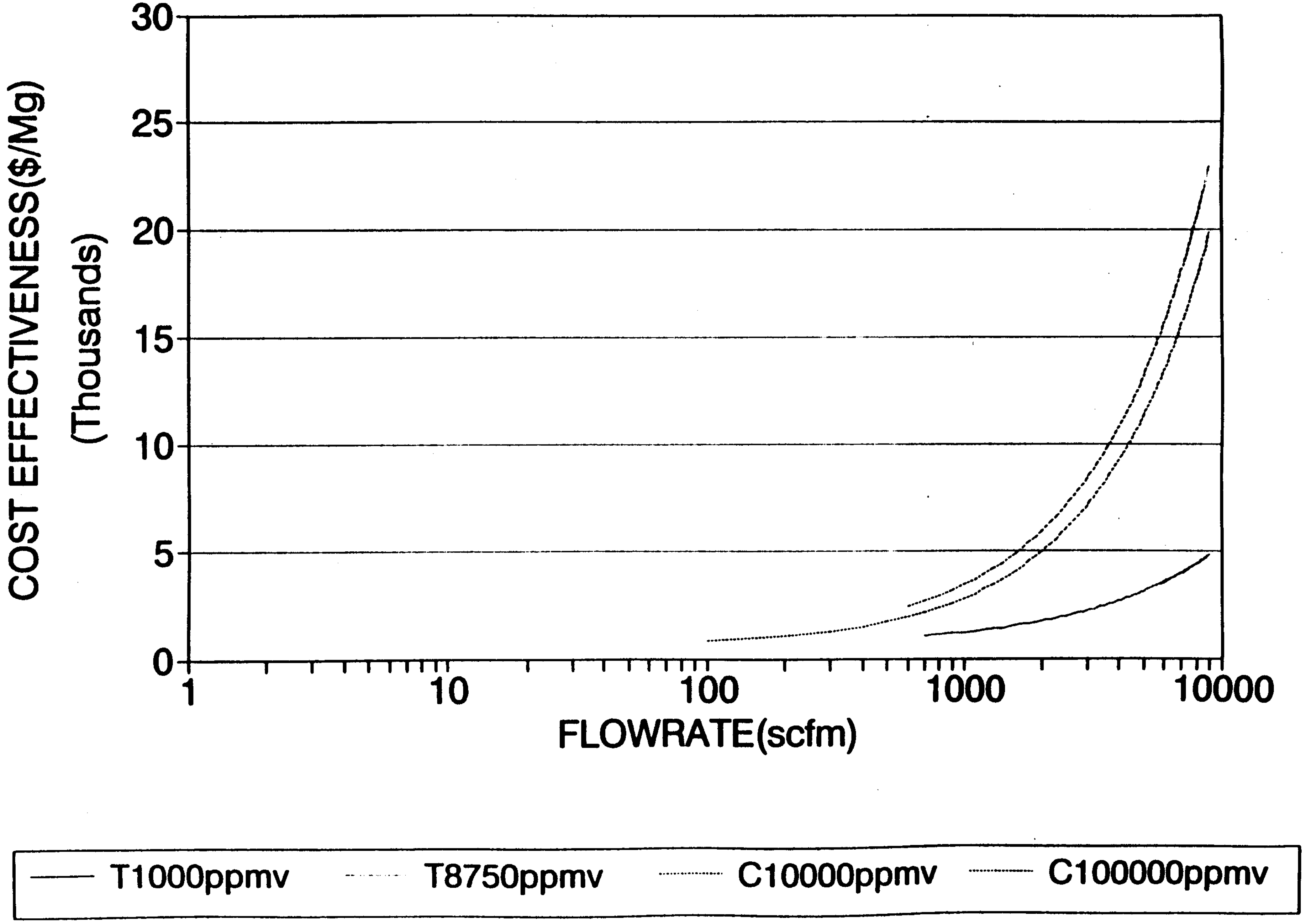
Hi.Vol. (Acetone); Cond. Crtl. Eff.=98%

Annual Mass Emission Total=125,000lb/yr

Hi.Vol. (Acetone); Cond. Crtl. Eff.=98%



Annual Mass Emission Total=150,000lb/yr
Hi.Vol. (Acetone); Cond. Crtl. Eff.=98%



APPENDIX G. BATCH PROCESSING EXAMPLE RULE

G.1 INTRODUCTION

This appendix presents an example rule limiting volatile organic compound emissions from batch processing operations. The example rule is for informational purposes only. The purpose of the example rule is to provide information on the factors that need to be considered in writing a rule to ensure that it is enforceable. The example rule is provided below. Sections include applicability, definitions, control requirements, performance testing, and recordkeeping/reporting requirements.

G.2 APPLICABILITY

(a) The provisions of this rule apply to process vents associated with batch processing operations. The scope of affected industries is limited to those industries in the following standard industrial classification (SIC) codes: 2821, 2833, 2834, 2861, 2865, 2869, 2879.

(b) Exemptions from the provisions of this rule except for the reporting and recordkeeping requirements listed in Section G.8 are as follows:

(1) Combined vents from a batch process train which have an annual mass emission total of 10,000 lb/yr or less.

(2) Single unit operations which have annual mass emissions of __X__ lb/yr or less.

G.3 DEFINITIONS

The agency responsible for developing a standard must define the terms that appear in the language for the standard. The source category of batch processes, for example, requires a definition of the term "batch" as it is used to describe the mode of operation of equipment and processes. Another term that will likely require defining is "vent". The feasibility analysis that has been described in Chapter 6 applies to any type of gaseous emission stream (continuous or batch) containing VOC's, as long as the flowrate and annual mass emission total requirements are met. Finally, the terms "flowrate" and "annual mass emissions" also should be defined clearly. Provided below is a listing of definitions for terms as they are used in this document.

Aggregated means the summation of all process vents containing VOC's within a process.

Annual mass emissions total means the sum of all emissions, evaluated before control, from a vent. Annual mass emissions may be calculated from an individual process vent or groups of process vents by using emission estimation equations contained in Chapter 3 of the Batch CTG and then multiplying by the expected duration and frequency of the emission or groups of emissions over the course of a year. For processes that have been permitted, the annual mass emissions total should be based on the permitted levels, whether they correspond to the maximum design production potential or to the actual annual production estimate.

Average flowrate is defined as the flowrate averaged over the amount of time that VOC's are emitted during an emission event. For the evaluation of average flowrate from an aggregate of sources, the average flowrate is the weighted average of the average flowrates of the emission events and their annual venting time, or:

$$\text{Average Flowrate} = \frac{\sum \text{(Average Flowrate per emission event)(annual duration of emission event)}}{\sum \text{(annual duration of emission events)}}$$

Batch refers to a discontinuous process involving the bulk movement of material through sequential manufacturing steps. Mass, temperature, concentration, and other properties of a system vary with time. Batch processes are typically characterized as "non-steady-state."

Batch cycle refers to a manufacturing event of an intermediate or product from start to finish in a batch process.

Batch cycle refers to a manufacturing event of an intermediate or product from start to finish in a batch process.

Batch process train means an equipment train that is used to produce a product or intermediate. A typical equipment train consists of equipment used for the synthesis, mixing, and purification of a material.

Control devices are air pollution abatement devices, not devices such as condensers operating under reflux conditions, which are required for processing.

Emissions before control means the emissions total prior to the application of a control device, or if no control device is used, the emission total. No credit for discharge of VOC's into wastewater should be considered when the wastewater is further handled or processed with the potential for VOC's to be emitted to the atmosphere.

Emission events can be defined as discrete venting episodes that may be associated with a single unit of operation. For example, a displacement of vapor resulting from the charging of a vessel with VOC will result in a discrete emission event that will last through the duration of the charge and will have an average flowrate equal to the rate of the charge. If the vessel is then heated, there will also be another discrete emission event resulting from the expulsion of expanded vessel vapor space. Both emission events may occur in the same vessel or unit operation.

Processes, for the purpose of determining RACT applicability, are defined as any equipment within a contiguous area that are connected together during the course of a year where connected is defined as a link between equipment, whether it is physical, such as a pipe, or whether it is next in a series of steps from which material is transferred from one unit operation to another.

Semi-continuous operations are conducted on a steady- state mode but only for finite durations during the course of a year. For example, a steady-state distillation operation that functions for 1 month would be considered semi-continuous.

Unit operations are defined as those discrete processing steps that occur within distinct equipment that are used to prepare reactants, facilitate reactions, separate and purify products, and recycle materials.

Vent means a point of emission from a unit operation. Typical process vents from batch processes include condenser vents, vacuum pumps, steam ejectors, and atmospheric vents from reactors and other process vessels. Vents also include relief valve discharges. Equipment exhaust systems that discharge from unit operations also would be considered process vents.

Volatility is defined by the following: low volatility materials are defined for this analysis as those which have a vapor pressure less than or equal to 75 mmHg at 20°C, moderate volatility materials have a vapor pressure greater than 75 and less than or equal to 150 mmHg at 20°C; and high volatility materials have a vapor pressure greater than 150 mmHg at 20°C. To evaluate VOC volatility for single unit operations that service numerous VOCs or for processes handling multiple VOCs, the weighted average volatility can be calculated simply from knowing the total amount of each VOC used in a year, and the individual component vapor pressure, as shown in the following equation:

$$\text{Weighted Average Volatility} = \frac{\sum_{i=1}^{n}\left[(\text{Vapor pressure of VOC component } i)\,\frac{(\text{mass of VOC component } i)}{(\text{molecular weight of VOC component } i)}\right]}{\sum_{i=1}^{n}\left[\frac{(\text{mass of VOC component } i)}{(\text{molecular weight of VOC component } i)}\right]}$$

G.4 CONTROL REQUIREMENTS

For individual process vents, or for vent streams in aggregate, within a batch process, having an actual average flow rate below the flow rate value calculated by the cutoff equations when annual mass emissions are input shall reduce emissions by X percent. The cutoff equations are specific to volatility. See page 6-18.

For aggregate streams within a process, the control requirements must be evaluated with the successive ranking scheme described on page 7-5 until control of a segment of unit operations is required or until all unit operations have been eliminated from the process pool.

G.5 (a) DETERMINATION OF UNCONTROLLED ANNUAL EMISSION TOTAL

Determination of the annual mass emissions total may be achieved by engineering estimates of the uncontrolled emissions from a process vent or group of process vents within a batch process train and multiplying by the potential or permitted number of batch cycles per year. Engineering estimates should follow the guidance provided in this document. Alternatively, if an emissions measurement is to be used to measure vent emissions, the measurement must conform with the requirements of measuring incoming mass flow rate of VOC's as described in G.6 (2) and (3) (i,ii).

G.5(b) DETERMINATION OF AVERAGE FLOW RATE

To obtain a value for average flowrate, the owners or operators may elect to measure the flow rates or to estimate the flow rates using emission estimation guidelines provided in Chapter 3. For existing manifolds, the average flow rate is often the flow that was assumed in the design. Regulators should be aware that oversized gas moving equipment used in manifolds may exempt many unit operations and batch processes from the cutoff requirements because the flowrates will exceed those described by the cutoff equations. Industry should have the burden of proving that the manifold flowrates are consistent with emission sources and not oversized. If measurements are to be used to estimate flow rates, the measurements must conform with the requirements of measuring incoming volumetric flow rate as described in G.6(b)(2).

G.6 PERFORMANCE TESTING

(a) For the purpose of demonstrating compliance with the control requirements of this rule, the process unit shall be run at full operating conditions and flow rates during any performance test.

(b) The following methods in 40 CFR 60, Appendix A, shall be used to comply with the percent reduction efficiency requirement listed in G.4.

(1) Method 1 or 1A, as appropriate, for selection of the sampling sites if the flow measuring device is a rotameter. No traverse is necessary when the flow measuring device is an ultrasonic probe. The control device inlet sampling site for determination of vent stream VOC composition reduction efficiency shall be prior to the control device and after the control device.

(2) Method 2, 2A, 2C, or 2D, as appropriate, for determination of gas stream volumetric flow rate flow measurements should be made continuously.

(3) Method 25A or Method 18, if applicable, to determine the concentration of VOC in the control device inlet and outlet.

(i) The sampling time for each run will be the entire length of the batch cycle in which readings will be taken continuously, if Method 25A is used, or as often as is possible using Method 18, with a maximum of 1-minute intervals between measurements throughout the batch cycle.

(ii) The emission rate of the process vent or inlet to the control device shall be determined by combining continuous concentration and flow rate measurements at simultaneous points throughout the batch cycle.

(iii) The mass rate of the control device outlet shall be obtained by combining continuous concentration and flow rate measurements at simultaneous points throughout the batch cycle.

(iv) The efficiency of the control device shall be determined by integrating the mass rates obtained in ii and iii, over the time of the batch cycle and dividing the difference in inlet and outlet mass flow totals by the inlet mass flow total.

G.7 MONITORING REQUIREMENTS

(a) The owner or operator of an affected facility that uses an incinerator to seek to comply with the VOC emission limit specified under G.4 shall install, calibrate, maintain, and operate according to manufacturer's specifications the following equipment.

(1) A temperature monitoring device equipped with a continuous recorder and having an accuracy of ± 0.5°C.

(i) Where an incinerator other than a catalytic incinerator is used, a temperature monitoring device shall be installed in the firebox.

(ii) Where a catalytic incinerator is used, temperature monitoring devices shall be installed in the gas stream immediately before and after the catalyst bed.

(b) The owner or operator of an affected facility that uses a flare to seek to comply with G.4 shall install, calibrate, maintain and operate according to manufacturer's specifications the following equipment:

(1) A heat sensing device, such as an ultra-violet beam sensor or thermocouple, at the pilot light to indicate continuous presence of a flame.

(c) The owner or operator of an affected facility that uses an absorber to comply with G.4 shall install, calibrate, maintain, and operate according to manufacturer's specifications the following equipment.

(1) A scrubbing liquid temperature monitoring device having an accuracy of ±1 percent of the temperature being monitored expressed in degrees Celsius or ±0.02 specific gravity unit, each equipped with a continuous recorder, or

(2) An organic monitoring device used to indicate the concentration level of organic compounds exiting the recovery device based on a detection principle such as infra-red photoionization, or thermal conductivity, each equipped with a continuous recorder.

(d) The owner or operator of an affected facility that uses a condenser or refrigeration system to comply with G.4 shall install, calibrate, maintain, and operate according to manufacturer's specifications the following equipment:

(1) A condenser exit temperature monitoring device equipped with a continuous recorder and having an accuracy of ±1 percent of the temperature being monitored expressed in degrees Celsius of ±0.5°C, whichever is greater, or

(2) An organic monitoring device used to indicate the concentration level of organic compounds exiting the recovery

device based on a detection principle such as infra-red, photoionization, or thermal conductivity, each equipped with a continuous recorder.

(e) The owner or operator of an affected facility that uses a carbon adsorber to comply with G.4 shall install, calibrate, maintain, and operate according to manufacturers specifications the following equipment:

(1) An integrating steam flow monitoring device having an accuracy of ±10 percent, and a carbon bed temperature monitoring device having an accuracy of ±1 percent of the temperature being monitored expressed in degrees Celsius or ±0.5°C, whichever is greater, both equipped with a continuous recorder, or

(2) An organic monitoring device used to indicate the concentration level of organic compounds exiting the recovery device based on a detection principle such as infra-red, photoionization, or thermal conductivity, each equipped with a continuous recorder.

G.8 REPORTING/RECORDKEEPING REQUIREMENTS

(a) Each batch processing operation subject to this rule shall keep records for a minimum of two years of the following emission stream parameters for each process vent contained in the batch process:

(1) The annual mass emission total, and documentation verifying these values; if emission estimation equations are used, the documentation shall be the calculations coupled with the expected or permitted (if available) number of emission events per year. If the annual mass emission total is obtained from measurement in accordance with G.6, this data should be available.

(2) The average flow rate in scfm and documentation verifying these values;

(b) Each batch processing operation subject to this rule shall keep records of the following parameters required to be measured during a performance test required under G.4, and required to be monitored under G.6.

(1) Where an owner or operator subject to the provisions of this subpart seeks to demonstrate compliance with G.4 through use of either a thermal or catalytic incinerator:

(i) The average firebox temperature of the incinerator (or the average temperature upstream and downstream of the catalyst bed for a catalytic incinerator), measured continuously and averaged over the same time period of the performance testing, and

(2) Where an owner or operator subject to the provisions of this subpart seeks to demonstrate compliance with G.4 through use of a smokeless flare, flare design, (i.e., steam-assisted, air-assisted or nonassisted), all visible emission readings, heat content determinations, flow rate measurements, and exit velocity determinations made during the performance test, continuous records of the flare pilot flame monitoring, and records of all periods of operations during which the pilot flame is absent.

(3) Where an owner or operator subject to the provisions of this subpart seeks to demonstrate compliance with G.4:

(i) Where an absorber is the final control device, the exit specific gravity (or alternative parameter which is a measure of the degree of absorbing liquid saturation, if approved by the Agency), and average exit temperature of the absorbing liquid, measured continuously and averaged over the same time period of the performance testing (both measured while the vent stream is routed normally), or

(ii) Where a condenser is the control device, the average exit (product side) temperature measured continuously and averaged over the same time period of the performance testing while the vent stream is routed normally, or

(iii) Where a carbon adsorber is the control device, the total steam mass flow measured continuously and averaged over the same time period of the performance test (full carbon bed cycle), temperature of the carbon bed after regeneration (and within 15 minutes of completion of any cooling cycle(s), and duration of the carbon bed steaming cycle (all measured while the vent stream is routed normally), or

(iv) As an alternative to D.7(b)(4)(i), (b)(4)(ii) or (b)(4)(iii), the concentration level or reading indicated by the organic monitoring device at the outlet of the absorber, condenser, or carbon adsorber, measured continuously and averaged over the same time period of the performance testing while the vent stream is routed normally.