APPENDIX B-1

VACUUM METHOD

From

"Test Plan for Control of Fugitive Emissions
from the
Synthetic Organic Chemical Manufacturing Industry"

Prepared for U.S. Environmental Protection Agency
by
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The screening process gives a rough estimate of the leak rate from a source, but more rigorous procedures are required to accurately determine the mass emission rate. Several procedures have been used successfully in previous sampling efforts, and each has advantages in certain situations. The final decision as to which method will be used primarily will not be made until the process selection is finalized. The first step in any of these methods, however, is source enclosure.

5.3.1 Source Enclosure

To accurately measure the leak rate from any given fitting, it is necessary to isolate that fitting from the ambient air. This is accomplished by an enclosure (or tent) of Mylar plastic (polyethylene terephthalate) formed around the leak source. The thickness of the Mylar can range from 1.5-15 mil depending on the type of source being bagged. Radian has found that Mylar is well suited to this function as it does not absorb significant amounts of hydrocarbons, it is very tough, and it has a high melting point (250°C). A typical tent is shown in Figure 5-1.

The enclosures should be kept as small as practical. This has several beneficial effects.

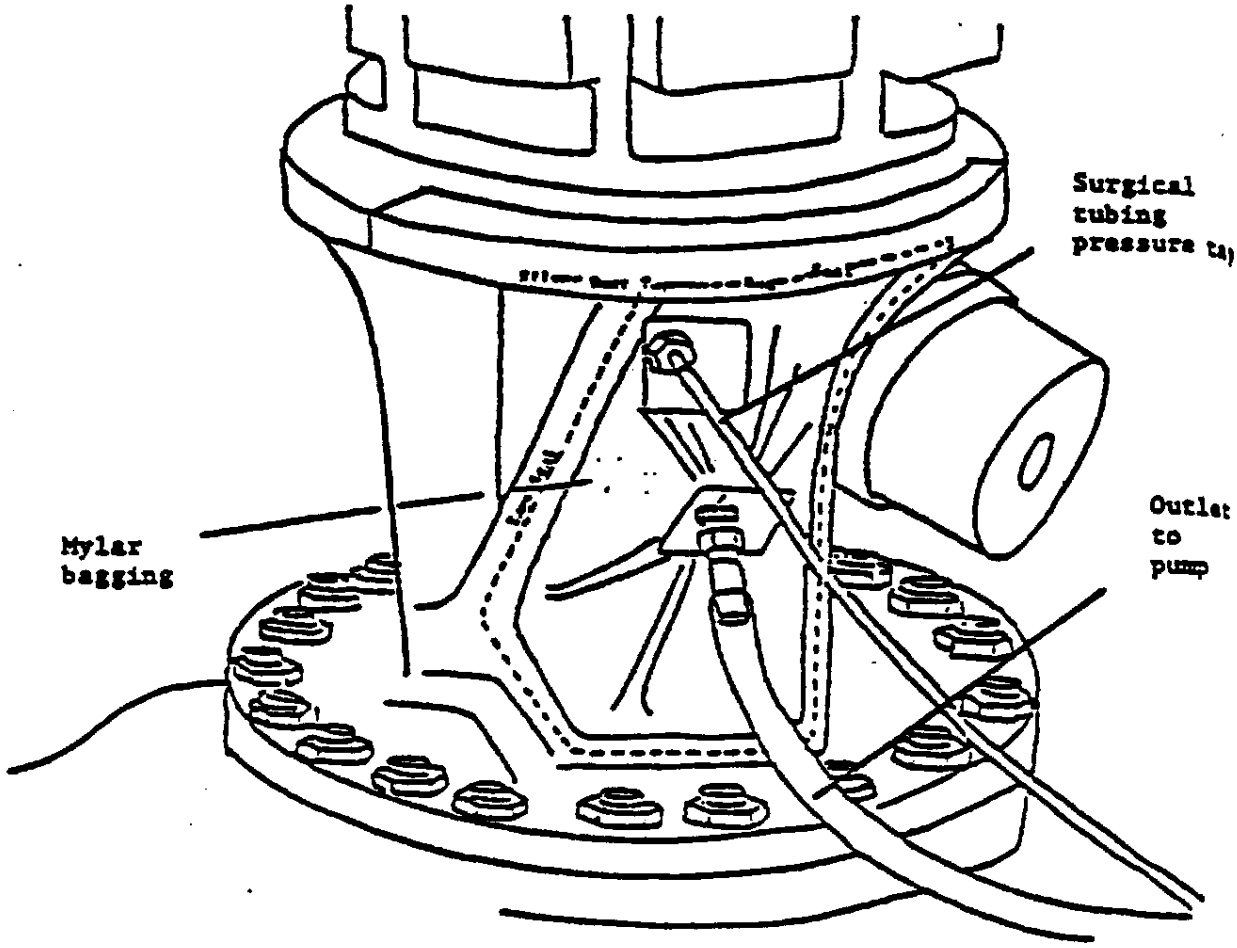

Figure 5-1. Tent construction around the seal area of a vertical pump.

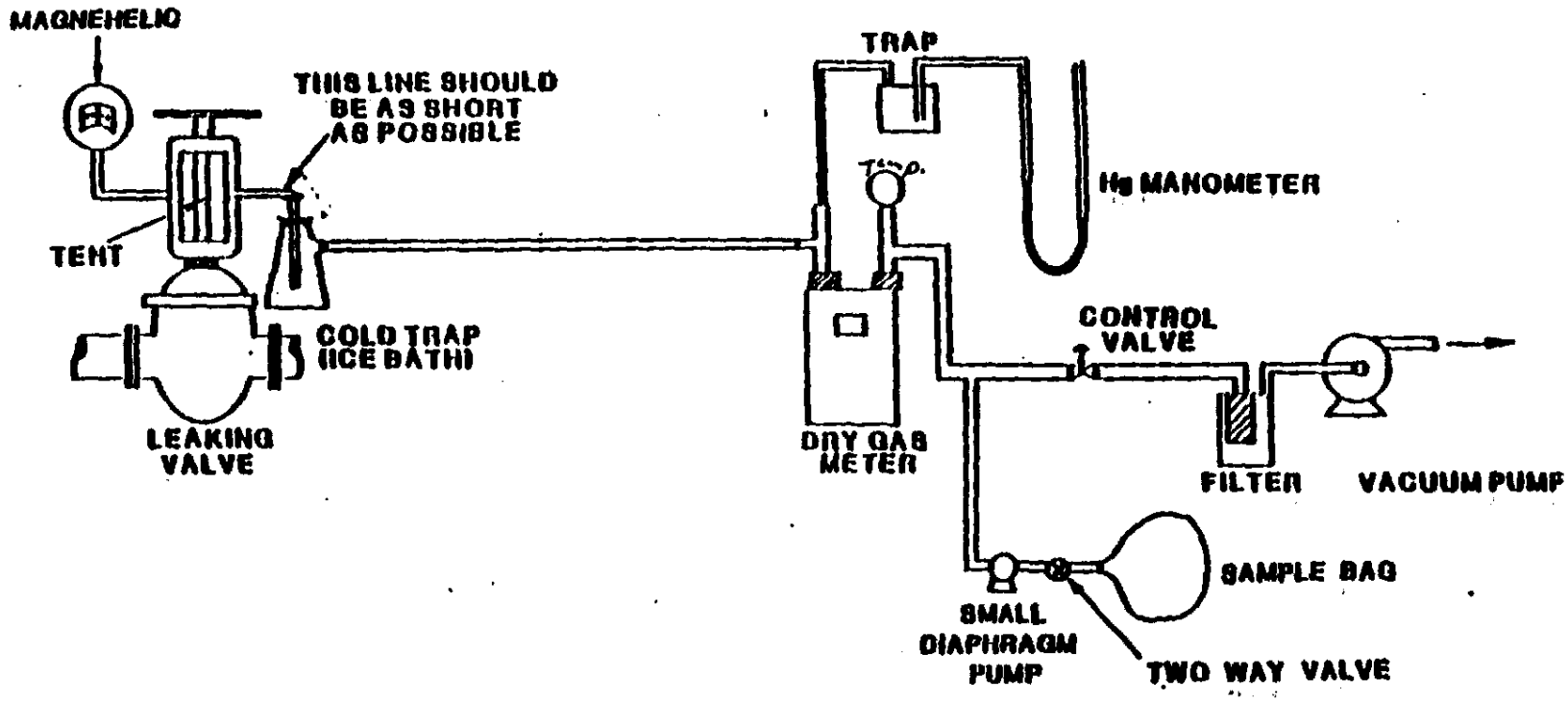

Figure 5-2. Sampling train for baggable sources of hydrocarbon emissions using a diaphragm sampling pump.

- the time required to reach equilibrium is kept to a minimum,
- the time required to construct the enclosure is minimized,
- a more effective seal results from the reduced seal area, and
- condensation of heavy hydrocarbons inside the enclosure is minimized or prevented due to reduced residence time and decreased surface area available for heat transfer.

5.3.2 Vacuum Method

In the past, the method preferred for sampling leaks from baggable sources has been the dilution or vacuum method. The sampling train used in this method is shown in Figure 5-2.

The train is mounted on a portable cart, which can be easily pushed around the unit from source to source. The major equipment items in the sampling train are the vacuum pump used to draw air through the system, and the dry gas meter used to measure the flow rate of gas through the train.

The vacuum pump is a 4.8 CFM Teflon-ring piston type equipped with a ¾ horsepower air-driven motor. Low pressure air (~100 psig) is available at or near most process units. The dry gas meter is a Rockwell Modal 1755 Test Gas Meter with a Number 83 Test Index. Other equipment in the train includes Whitey valves, copper and stainless steel tubing, Teflon hose, 100 cc glass airtight syringe, thermometers, mercury and water manometers, a cold trap, and an air-driven diaphragm sampling pump. The leak source is shown as a valve in Figure 5-2. However, the same sampling train can be used for all baggable source sampling with the vacuum technique. The size and shape of the leak source enclosure (tent) is adjusted to fit each particular source shape and operating condition. When the full sampling train is connected to a source, the vacuum pump is able to maintain a maximum flow rate of approximately 2½ cubic feet per minute.

The tent is connected by means of the bulkhead fitting and Teflon hose to the sample train. A separate line is connected from the tent to a magnahelic. This allows continuous monitoring of the pressure inside of the tent. If a significant vacuum exists inside the tent when air is being pulled through, a hole is made in the opposite side of the tent from the outlet to the sampling train. This allows air to enter the tent more easily and thus reduces the vacuum in the enclosure. In practice, it has been found that only a very slight vacuum (0.1 in. H_2O) is present in the tent during most of the sampling, even in the absence of a hole through the tent wall. Sufficient air enters around the seals to prevent the development of a significant vacuum in the tent.

Sample bags will be used to collect gas samples and transport them to the mobile laboratory for analysis. Several types of bags were tested by Radian in the laboratory and in the field. Most of them, including Calibrated Instrument Company's five-layer "snout" bags, were found to adsorb hydrocarbons, making them unsuitable for use. Bags of 2 mil Mylar and Tedlar plastic have been constructed and found to be satisfactory. A drawing of a typical sample bag is shown in Figure 5-3.

A cold bath is placed in the system to condense water and heavy organics, thus preventing condensation in downstream lines and equipment. The cold trap is simply a 500 ml flask in an ice bath. It should be placed as close as possible to the tent. This ice bath was found to be very effective in preventing condensation in the remainder of the sampling train and in the gas sample bag. Any organic condensate that collects in the cold trap will be measured for later use in calculating total leak rates. The use of such a cold trap is critical; without it, order of magnitude errors are possible.

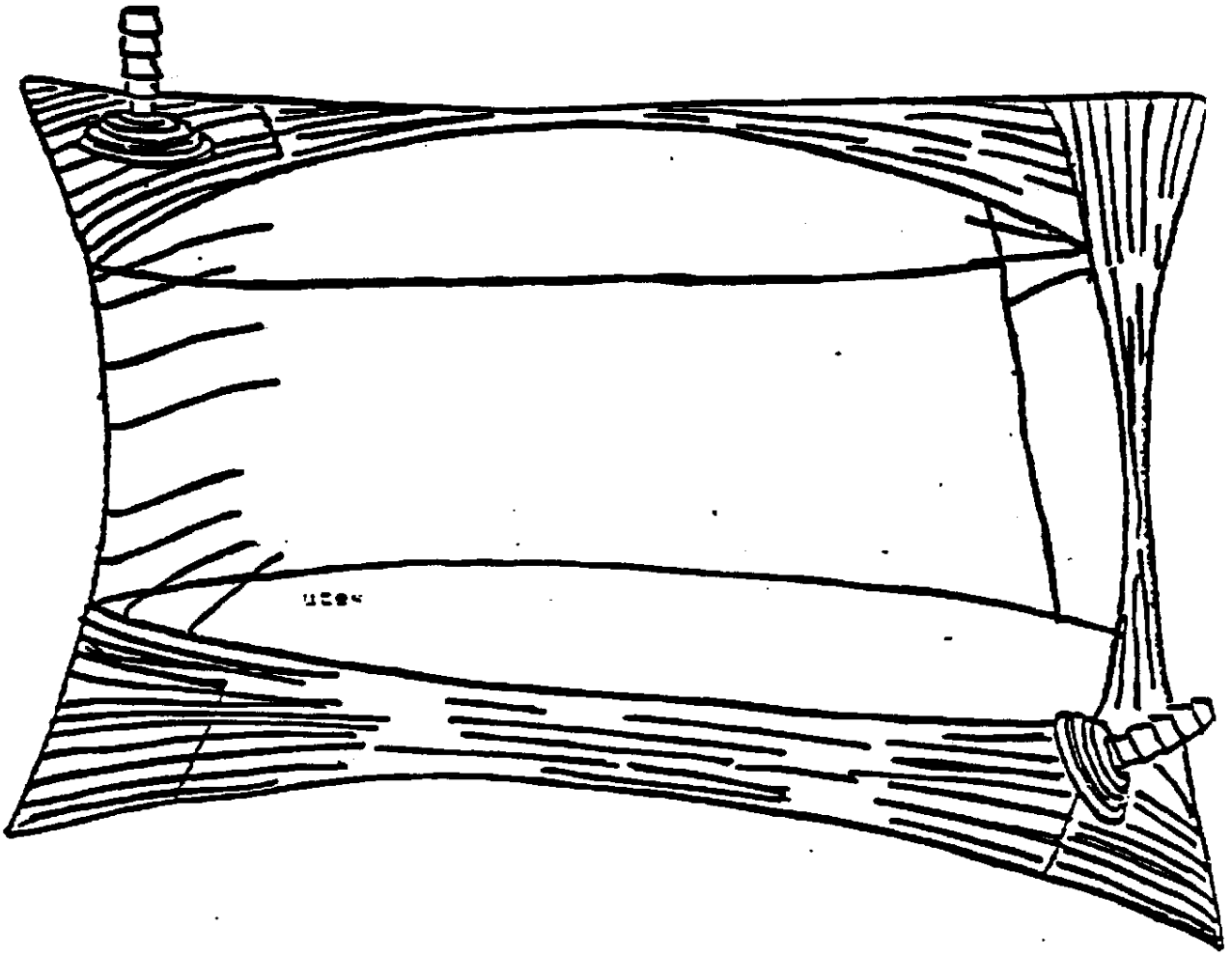

Figure 5-3. Mylar plastic sample bag.

The sampling procedure is accomplished in the following steps:

- obtain screening value with the OVA,
- enclose the fitting in a tight Mylar shroud,
- connect the sampling train to the "tent,"
- immerse the cold trap in an ice bath,
- note the initial reading of the dry gas meter,
- start the vacuum pump and a stopwatch simultaneously,
- record the temperature and pressure at the dry gas meter,
- observe the VOC concentration at the vacuum pump exhaust with the OVA,
- record the temperature, pressure, dry gas meter reading, outlet VOC concentration and elapsed time every 2 to 5 minutes,
- when the outlet VOC concentration stabilizes, the system is at equilibrium and a gas sample bag is filled from the discharge of the Teflon-lined diaphragm pump,
- another bag is filled with ambient air near the tent area to detect the background VOC concentration,*
- a final set of readings is taken and the vacuum pump stopped,
- the cold trap is removed, sealed, and transported to the laboratory along with the two bag samples and the data sheet,
- remove tent,
- rescreen source with the OVA.

All of the above data and any pertinent comments are recorded in a permanent laboratory notebook as well as on the individual data sheet.

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*This bag sample may be omitted in favor of the OVA reading if the background VOC concentration is less than 5 percent of the lower limit of the screening range (i.e., <50 ppm for the 1000 to 10,000 ppm class).

The flow rate through the system can be varied by throttling the flow with a control valve immediately upstream of the vacuum pump. As the flow rate is decreased, the concentration of hydrocarbon increases in the gas flowing through the sampling system. This allows considerable flexibility in avoiding operations with an explosive mixture of hydrocarbon in the air. If an explosive mixture is present, the flow rate may either be adjusted upward (to the maximum pump capacity) or downward. The hydrocarbon concentration in the gas stream can be raised above the upper explosive limit in many cases by reducing the flow rate. Conversely, increasing the flow rate can reduce the hydrocarbon concentration below the lower explosive limit.

APPENDIX B-2

BLOW THROUGH METHOD

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BLOW-THROUGH TENTING OF COMPONENTS LEAKING VOC

Tenting refers to measuring the mass leak rate from a piece of equipment (i.e., a valve or pump) by enclosing it in an envelope of flexible sheet material (Figure 1). For instance, industrial grade aluminum foil can be wrapped around the valve yoke and the ends taped on the bonnet and stem or yoke. If the valve temperature is too high for duct tape, aluminum foil strips can be compressed around the bonnet area with a rope noose.

Blow-through refers to blowing nitrogen through the tent to create a constant VOC (volatile organic compound) concentration inside the tent. Nitrogen is metered into the tent through one or two polyvinyl chloride tubes. The temperature and oxygen concentrations are measured inside the tent with a platinum-RTD thermocouple and an oxygen/combustible gas monitor. The flow of nitrogen is monitored in a gas rotameter calibrated to nitrogen. The nitrogen passes through activated charcoal and drierite to remove any organics and moisture. The pressure in the tent should never exceed 1 psig.

Gas samples from the tent can be collected with a portable sampling pump and transported to a lab for chemical speciation and concentration measurement. Alternately, direct field measurements can be used to determine emission rate. This approach, as discussed below for an organic vapor analyzer (OVA) instrument, has not been generally recognized by regulatory agencies.

At least two OVA measurements are made inside the tent. Each measurement should be made at two or more different nitrogen flow rates to increase accuracy. (The OVA must be attached to a dilution probe and calibrated to nitrogen-diluted gases to allow its use in the nitrogen atmosphere in the tent.) The OVA readings are converted to emission rates of VOC via knowledge of the flow rates of the stream passing through the component.

The oxygen concentration is also measured to determine the total gas flow rate through the tent. However, oxygen concentration is also used to rate the quality of the tent, and except in a few extremely difficult situations, VOC concentrations are not measured until the oxygen concentration in the tent is reduced below 5%.

Air can replace nitrogen as a dilution gas if the hydrocarbon concentration is not expected to be high enough to cause an explosive atmosphere inside the tent. However, calculations based on air tent data must assume a nominal tent leakage rate, i.e., extra flow, through the tent due to air entering the tent that is not metered through the tubing.

Safety has been a key factor in the development of this procedure. In one company, over 400 valves have been tented with this technique without incident. Nitrogen is used as a dilution gas instead of air to prevent an explosive atmosphere within the tent. All of the instruments used are battery-operated, approved for Class I, Division I use.

Listed below is a step-by-step procedure for tenting a pump. Valve tenting is similar.

Pump Tenting Procedure

1. From the unit operator, determine the composition of the material in the pump (in weight or volume %), and the operating conditions of the pump.

2. Screen the pump by placing a Tygon nozzle on the end of the organic vapor analyzer, holding the end of the nozzle within 1 centimeter of the seal flange/shaft intersection, and recording the highest concentration seen on the OVA readout.

3. Cut a tent from appropriate material, such as heavy gauge aluminum foil, that will easily fit over the pump shaft housing.

4. Plug any holes in the pump base plate with an appropriate material.

5. Connect tubing from the nearest low pressure nitrogen station to a rotameter stand, which includes a regulator, dessicant, activated charcoal, and a rotameter in series.

6. Run tubing from the rotameter outlet to a "Y" that splits the nitrogen flow into two pieces of tubing. Insert the tubes into openings located on either side of the tent.

7. Turn on nitrogen at the utilities station and regulate it at the rotameter to approximately 40 liters/minute.

8. Wrap aluminum foil around the pump shaft housing after the nitrogen is flowing so that there is no avenue for air to enter the tent-enclosed volume. Cut-outs may be necessary for auxiliary piping, e.g., oil mist systems.

9. Secure the tent to the pump with an appropriate material such as duct tape, wire, and/or rope.

10. Put a third hole in the tent roughly equidistant from the two nitrogen feed holes.

11. Measure the oxygen concentration in the tent by inserting the lead from an O_2 meter into the third hole. Adjust the tent (add additional tape, foil, rope, etc.) until the O_2 concentration is less than 5%.

12. Measure the temperature in the tent with a platinum-RTD thermocouple.

13. Calibrate the OVA to methane or hexane at a known concentration in nitrogen using the OVA dilution probe. Remember to correct for the dilution.

14. Check the VOC concentration at several points in the tent with the OVA to insure that the tent contents are at steady state.

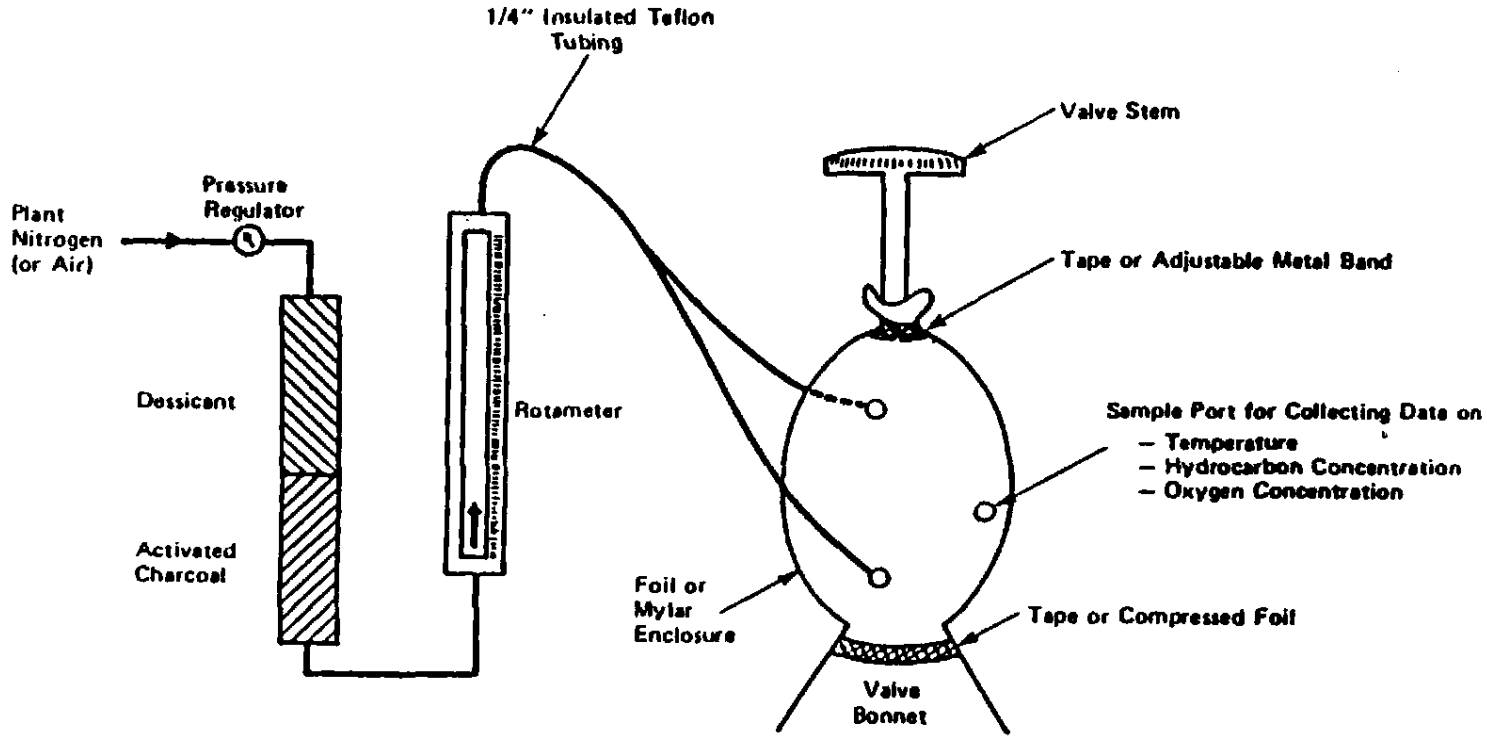
15. Measure the hydrocarbon VOC concentration in the tent with the OVA at three different nitrogen flow rates. Typically the flow rates will be 40, 30 and 20 liters/minute. However, the lowest rate may have to be at 5-10 liters/minute if there is no OVA response at the higher rates (i.e., the mass leak rate from the pump is very low). After each adjustment of the nitrogen flow, check the O_2 concentration to ensure it stays below 5%. Alternatively, collect samples in Tedlar or aluminized sample bags by drawing a sample out of the bag with a portable sampling pump.

16. Remove the tent and any plugs from the pump and collect any condensate on the inside of the tent in a plastic graduated cylinder. Record the amount collected and the elapsed time the tent was on the pump.

17. If there is liquid dripping from the seal area, collect the drips for a timed period to produce enough collected material for accurate volume measurement.

Figure 1

EQUIPMENT REQUIRED FOR TENTING VALVES



*Not To Scale

APPENDIX B-3

MULTICOMPONET EMISSION TESTING
TO VALIDATE DATA SETS

MULTICOMPONENT EMISSION TESTING

TO VALIDATE DATA SETS

EFFECTIVENESS OF FUGITIVE EMISSION CONTROLS

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The emission of specific hazardous pollutants to the workplace pose both workplace and exworkplace concerns. Understanding the control effectiveness of various fugitive emission control devices leads to use of effective engineering control practices and to acceptable personnel exposure levels. Verification of the emission rates from various fugitive emission sources for specific chemicals is a key to effective controls. A method for checking the fugitive emission rates from an operating plant will be presented along with validation results.

INTRODUCTION

The quantification of fugitive emissions is an increasingly important task as more is learned about the acute and chronic toxicity of various chemicals. The issue of workplace exposure and chronic exposure of those that live near chemical process units has become a key to operation of facilities handling hazardous or toxic chemicals. Where the initial work on fugitive emissions by the EPA for petroleum refineries centered on the issue of ozone formation, today the issue of concern is the impact of toxic chemicals on people.

In the mid 1970's the EPA worked to characterize emissions from fugitive sources (eg., flanges, valve stems, pumps, compressors, sampling systems and open ended lines) in terms of total hydrocarbon as measured by flame ionization, infrared and ultraviolet light detector devices held close to the source. While the concentration was not a direct measure of leakage rate it provided a rapid method of identifying sources that were the most probable sources of high volatile organic chemical (VOC) leakage rates. In fact correlations were defined which related concentration at the source to emission rate and as long as the methodology was applied to identical processing facilities (ie., other refineries) the methodology was reproducible.

In the late 1970's the EPA worked to apply the protocols developed in refineries to SOCMI (synthetic organic chemical manufacturing industries) facilities. The premise of their endeavors was:

"A LEAK IS A LEAK."

In some plants, those handling highly volatile low toxicity organics (eg., ethane, propane, ethylene, propylene etc) operating large scale equipment the results were found to be similar to refinery fugitive emission rates. This provided confirmation for the EPA that the petroleum refinery fugitive emission data base could be applied to SOCMI facilities. Unfortunately in selectively examining the data base the EPA ignored a substantial amount of data that illustrated that SOCMI facilities were different than refineries and that fugitive emissions in the chemical industry are not represented by the refinery data base. The reasons for differences noted in fugitive emissions rates and leak frequency were the type and size of equipment used in SOCMI plants and the fact that many SOCMI facilities handle highly toxic chemicals and must control emissions to protect workers and those that live near the production facilities. The EPA did adopt the lower leak frequency results found in the the chemical industry units but failed to acknowledge the lower emission rates defined in the same studies.

The issues the EPA failed to assess were the impact of the volatility of the chemicals being processed and the size and design of the equipment. A good example of this limited

picture of fugitive emission leak sources was the omission of agitator seal leakage rates. The petroleum refining industry uses few if any agitators and this class of equipment was ignored by the EPA. However, agitators are used extensively in the chemical industry and have been identified in several studies as a key source of fugitive emission losses. This is illustrated by SOCMI facilities efforts to control workplace exposure through special vent designs and the use of only double mechanical seals with flush fluid to limit fugitive losses to the workplace. It has been found that single mechanical seals on agitators are not appropriate because of inadequate heat removal and frequent seal failure.

Over the years a number of researchers have worked to quantify losses for a variety of valve and seal designs and the work has been published widely. A summary of the literature fugitive emission rates and those from the EPA may be found in the a paper published in the Annals of Occupational Hygiene (Schroy, 1986)

DISCUSSION

In an effort to understand when to use the widely varied fugitive emission factors Monsanto found it necessary to validate the fugitive emission factors for its widely diverse chemical processes. The validation work was also necessary to help understand the differences between organic chemical leakage and emissions of inorganic gases (e.g., HCl, HF, H2S, etc). Since the emission rates published by the EPA and most other researchers dealt with organics there is no clear answer for dealing with compressed acid gases or solutions of inorganic and or organic chemicals.

Fugitive Emissions

A comparison of fugitive emission rate factors taken from EPA publications and general literature is given in Table 1. As discussed above, EPA did not address all services (gas, liquid and heavy liquid), for all potential leak sources but data are available for these sources from literature. The impact of equipment size can also be derived from literature. The EPA's definition of light liquid (ie. any organic with a vapor pressure at 25 deg. C of greater than or equal to 2.2 mm Hg) also has led to classification of a lot of heavy liquids as light liquids.

The EPA's conservative approach to defining emission rate from sealing devices (eg., using very high emission rates from the petroleum refining industry for chemical industry facilities) may be appropriate when dealing with ozone but it leads to high estimates when characterizing control device effectiveness. This means that application of monitoring and maintenance standards will result in prediction of larger reductions and bigger improvements in ozone than are possible. The failure to achieve predicted ozone levels in the ambient air is one sign of the fallacy of this approach. For hazardous chemicals this use of

overly conservative emission rates will lead to over prediction of excess chronic impacts around chemical plants where they are used or produced.

The performance standards imposed by OSHA were based on the need to control toxic impacts in the workplace but are viewed by EPA as a lax control approach. This regulatory dichotomy results in duplication of standards for industry from the two agencies and redundant efforts by the agencies to further restrict the type of equipment that can be used. The truth lies somewhere between OSHA's and EPA's view of an industrial facility. The emissions from engineering controls in SOCMI facilities during normal operations is below the level defined by the EPA. The actual level depends on the type of chemicals used, the process conditions, the equipment sizes, and the type of products. The ambient concentration in and around a process unit are not totally a function of emissions from sealing devices during normal operations, as viewed by OSHA in their latest regulatory action on benzene. Upset conditions, routine maintenance (ie. equipment and instruments) and routine process monitoring actions (eg tank gauging) lead to emissions which result in a background ambient level in the workplace. These operations may in fact, be excluded from performance standards with personnel permitted to use respiratory protection. But in most cases EPA forgets that personnel not directly involved in the exempted operation may also be impacted.

At present, the fugitive emission control practices in vinyl chloride, acrylonitrile and benzene facilities maximize available engineering controls. Sophisticated sampling devices, use of ball valves, use of mechanically sealed pumps and minimizing use of open equipment all lead to low emissions to the workplace and low ambient VOC concentrations. The State of Illinois EPA, in their latest fugitive emission regulation, recognized the impact of OSHA control actions on fugitive emissions. They exempted any operation which uses ball valves, mechanically sealed pumps, etc. from the maintenance and monitoring standards established in accordance with EPA recommendations.

The losses from potential leak sources given in Tables 2 to 5 were calculated using EPA emission rate data for several Monsanto facilities. These calculations were then compared to levels found in the exhaust from workplace ventilation systems and a set of emission factors assembled from literature (Schroy, 1981 and Schroy, 1986). While these mass emission comparisons were only possible for enclosed production facilities, the significant deviation demonstrates that the EPA emission rates are not realistic when toxic chemicals are being processed. Similar comparisons have been made for outside production facilities, which incorporate area monitors, with similar findings. It should be pointed out that the comparisons given in Tables 2 to 5 do not represent a few hours or days

of data. They, in fact, represent years of workplace monitoring records and employed exposure monitoring records.

In response to any proposed regulatory action, OSHA or EPA driven, or any internally requirement to quantify fugitive emissions it is suggested that emission estimates be determined as follows:

1. using EPA SOCMI factors,

2. using a fugitive emission summary of literature results, and

3. monitoring exhaust gas concentrations in building exhausts along with exhaust gas flow rates and calculating mass losses for your specific building.

Both the EPA SOCMI emission factors and a summary of fugitive emission factors from literature are given in Table 1. The three estimates can be compared and the most appropriate calculated values (method 1 or 2) can be selected. The most appropriate estimated values would be those which matched most closely to the mass emission found through method 3.

It is suggested that for the initial estimates from the literature, values be made assuming good maintenance practices. If the values for the SOCMI estimates are high and the good maintenance estimates are low, select some fraction of good maintenance (eg., 0.9, 0.8, 0.7 etc.) for all components. The fraction of good maintenance is appropriate when the estimate of losses match the measured value for the facilities. For example, the Plant 4 figures represent 90% of good maintenance.

Summaries of comparisons made at four plants are given in Tables 2 and 3. The five production areas tested all had emissions significantly below the estimates based on EPA's SOCMI factors. Two cases, Tables 4 and 5, are given as examples of how the estimates are made.

If poor maintenance practices were the rule in SOCMI facilities, the fugitive emissions would be a significant loss, and it is likely OSHA exposure criteria may be exceeded. But, as has been demonstrated at most Monsanto facilities, OSHA criteria are being met and fugitive emissions are significantly below EPA forecasts.