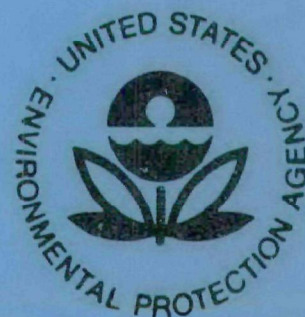


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**EVALUATION OF ODOR
MEASUREMENT TECHNIQUES:
VOLUME I - ANIMAL RENDERING
INDUSTRY**



Office of Research and Development
U.S. Environmental Protection Agency
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**EVALUATION OF ODOR
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VOLUME I
ANIMAL RENDERING
INDUSTRY**

by

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ABSTRACT

This report presents the results of investigations conducted by TRC - THE RESEARCH CORPORATION of New England to establish the performance requirements for odor emission measurements for rendering plant process emissions, based on a dilution-to-threshold ratio technique. The study was conducted between November 1, 1972, and May 15, 1973, under EPA contract No. 68-02-0662. An in-situ dynamic dilution system, referred to subsequently as the ISDD technique, was used as the reference or referee method. In this method the odorous emissions were continuously vented directly from the sample point to an eight-member olfactory panel by means of a dynamic dilution system installed in an on-site mobile odor laboratory.

An identical system, installed in TRC's Wethersfield laboratories, was used for off-site dynamic dilution measurements, hereinafter referred to as the OSDD method. The EPA modification of the ASTM 1391-57 syringe dilution technique was also evaluated. This is referred to in the report as the off-site static dilution (OSSD). By comparing the deviations between the OSSD and ISDD results, we attempted to determine the causes of the variations of the various methods.

Field tests were carried out at a rendering plant in Tewksbury, Massachusetts. In this plant, all process emissions are vented into a two-stage scrubbing system before release to the atmosphere. Total air flow through the scrubber is 100,000 SCFM. Samples were collected at the scrubber outlet, scrubber inlet, and in the cooker non-condensable line to provide a wide range of odor levels for testing the applicability of the various dilution techniques, and sampling methods.

The effects of sampling factors, such as pre-conditioning of containers, container materials, storage time (aging) of samples, surface-to-volume ratio of containers and humidity of emitted gases, on the validity of odor measurements were evaluated. In addition, the effects of panel selection and training procedures, number of panelists and dilution method and calculation procedures on the accuracy and reproducibility of rendering process odor measurements were determined. Finally, correlations between chemical measurements of rendering process emissions and dynamic odor unit levels were developed.

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SECTION I

CONCLUSIONS

The data developed by using the in-situ dynamic dilution method (ISDD) as a reference standard, both in the laboratory and at an operating rendering plant, substantiate the following conclusions. These conclusions have been grouped into four categories.

SAMPLING

- (1) Lack of pre-conditioning of sample containers for off-site odor measurement has the greatest impact of any sampling parameter on the validity of the odor measurements.
- (2) The magnitude of the error caused by not pre-conditioning sample containers may be as large as a factor of 2 less than the true odor unit value.
- (3) Aging (storage) of samples prior to presentation to the sample to an odor panel can result in odor unit values significantly lower than the true value, depending on the container material. Within 24 hours the magnitude of this error can be as great as 60 per cent with Saran bags.
- (4) There is considerable difference in the effect of sample container materials on the validity of off-site odor measurements of rendering process emissions.
- (5) Pre-conditioned Mylar, Tedlar (and Teflon) and Polyethylene containers all will maintain rendering process emission sample integrity for 24 hours after which there is a rapid decrease in odor level. Stainless steel has similar adsorption characteristics but is difficult to pre-condition.
- (6) Saran will maintain acceptable sample integrity for periods up to two hours, after which there is a rapid loss in odor unit level of stored samples. Many Saran containers also leak excessively.
- (7) Glass containers, primarily because of their large surface-to-volume ratio, have the greatest effect on the validity of off-site odor measurement results for rendering emissions. With no pre-conditioning of containers the magnitude of the error with glass can be an order of magnitude low. With pre-conditioned glass containers, the magnitude of the error may be as much a factor of two higher than the true value.
- (8) Condensation of moist rendering process emissions in the sample container can result in an odor unit measurement low by as much as 30 per cent, except in glass containers.

Condensation in gas sampling tubes may result in an error as much as a factor of two high, especially at low dynamic odor unit levels (e.g., 200 odor units).

ODOR PANEL SELECTION, SIZE AND TRAINING

- (1) Selection of panelists according to their ability to detect and discriminate between standard odorants, does not indicate their response to rendering process odorants or their suitability as odor panelists for rendering process measurements.
- (2) Panelists' unfamiliarity with the odor quality to be measured can result in median panel responses low by a factor of two from the true odor unit value.
- (3) Lack of training of the odor panelists with the specific dilution-to-threshold ratio technique to be used, can cause results low by as much as a factor of two.
- (4) Fewer than 8 panelists can be used to provide responses similar to those of an eight-member panel provided the panelists are properly selected according to their measured day-to-day variability and olfactory acuity for the odorants to be measured:

COMPARISON OF DILUTION-TO-THRESHOLD TECHNIQUES

- (1) Off-site dynamic dilution (OSDD) methods yield results within 10 per cent of the reference ISDD values, provided that suitable pre-conditioned containers are used and the evaluation is made within 24 hours.
- (2) The reproducibility of the dynamic dilution systems used, within 95 per cent confidence limits, is \pm 18 per cent.
- (3) The portable dynamic dilution system developed by IITRI for the National Renderers Association yielded results within 50 per cent of the ISDD reference values in the range between 100 and 1500 dynamic odor units. Each single measurement was within the 95 per cent confidence limits of the ISDD measurement.
- (4) At low odor levels, e.g., 200 dynamic odor units, the syringe dilution method (OSSD) yields results lower than the ISDD reference value by as much as a factor of 6 with actual rendering plant emissions. On synthetic mixtures of chemicals contained in rendering process emissions, this variation can be as much as a factor of 15 low.
- (5) At higher odor levels, e.g., 1000 dynamic odor units, the syringe dilution method yields values a factor of two lower than ISDD reference values with actual plant emissions.

- (6) Discrepancy between ISDD reference values and syringe dilution (OSSD) values results principally from two factors:
- a. adsorption of rendering odorants on the walls of the glass sampling containers and the syringes involved. Variations in the transfer technique in preparing the final dilution can produce a four-fold variation in the measurement results.
 - b. dilution with air in presentation of the sample to the panelist. The reference ISDD systems provides for an excess flow of 5 liters per minute, at least 3 times the measured average inhalation rate of our panelists of 1.4 liters per minute.

CORRELATION OF CHEMICAL AND ODOR MEASUREMENTS

- (1) The correlation coefficient obtained between total sulfur measurements, as ppm SO₂, and dynamic odor units was 0.91. For the combined infrared methyl disulfide and butyric acid measurement the correlation coefficient was 0.87. Thus, either measurement reflects about 80 per cent of the variance of the rendering odor which should be sufficient to permit development of instrumental monitoring of odorous emissions from rendering processes. The 0.91 correlation coefficient is higher than previously reported correlations of a single component of complex emissions and odor levels.¹

SECTION II

RECOMMENDATIONS

Following the format we used for presenting our conclusions, our recommendations are also grouped into four categories.

SAMPLING

- (1) Sample containers for off-site odor measurements by dilution-to threshold methods must be pre-conditioned by partially inflating or filling the container, with the emission to be measured, holding for 30 to 60 seconds, expelling this sample, and refilling.
- (2) Samples for off-site odor measurements must be evaluated within 24 hours for accurate results.
- (3) Mylar, Tedlar, and thick-walled Polyethylene (23 mils) containers are all suitable for off-site odor measurements of rendering plant emissions. Saran may also be used if samples are evaluated within two hours. Glass containers are not recommended.
- (4) Pre-dilution of emissions with pure, dry air should be used during sampling to prevent condensation.

ODOR PANEL SELECTION, SIZE, AND TRAINING

- (1) Potential panelists should be screened and accepted according to their ability to detect the odorants to be measured. For rendering plant measurements, the screening materials should be methyl disulfide and butyric acid.
- (2) Panelists should be trained, so that they are thoroughly familiar with the mechanics of the dilution-to-threshold method to be used before any measurements are made for the record.
- (3) An eight-member panel and three replicate samples should be used for maximum reliability of results. If a 95% confidence limit variation of ± 18 per cent from the mean for any single measurement is acceptable, less than 8 panelists can be used with a single sample.

USE OF DILUTION-TO-THRESHOLD

- (1) Dynamic dilution techniques are recommended for off-site odor level measurements of rendering process emissions.
- (2) If syringe dilution techniques are used, the sample should be collected in a pre-conditioned Mylar, Tedlar or Polyethylene container of at least 15-liter volume. Transfer of sample

from syringe to syringe should be done so as to minimize exposure of sample to glass. A correction factor should be used to convert the syringe results to the equivalent dynamic odor value.

CORRELATION OF CHEMICAL AND ODOR MEASUREMENTS

- (1) Additional simultaneous sampling of odor emissions and total sulfur content should be done at a variety of rendering plants, and during summertime conditions, to determine the applicability of the correlation established in the reported study.

SECTION III

INTRODUCTION

Odor measurements require, obviously, the sensory act of smelling. The particular perceptual attribute of odor that meets the dual criteria of being both measurable and applicable to evaluation of odorous process emissions is odor pervasiveness or odor potential. It is the ability of an odorant to maintain a perceivable odor intensity upon dilution with odor-free air.

Under EPA Contract 68-02-0662, TRC - THE RESEARCH CORPORATION of New England is conducting a study whose primary objective is to establish the performance requirements for dilution-to-threshold ratio odor measurements for various industry categories. This report presents the results of both laboratory and field investigations of the factors influencing the application of dilution-to-threshold odor measurements to the emissions from animal rendering processes. This study of the animal rendering industry was conducted by TRC in the period between November 1, 1972 and June 1, 1973.

A secondary objective of the study was to investigate and develop, if possible, correlations between chemical or physical measures of rendering process emissions and the odor threshold dilution ratios measured simultaneously. If a satisfactory correlation is established then it will be possible to use objective, instrumental methods for monitoring odorous emissions from typical rendering processes. The need for continual use of subjective odor panels, used in the dilution-to-threshold measurement techniques would thereby be eliminated.

SECTION IV

EXPERIMENTAL APPROACH

There are four general methods of adapting the dilution-to-threshold ratio principle to odor measurement.

CATEGORIES OF DILUTION-TO-THRESHOLD MEASUREMENT TECHNIQUES

- (1) In-situ dynamic dilution (ISDD) -- direct diversion of part of the odorous emissions, or ambient air, to the odor panelists on a continuous basis^{1,2,5}
- (2) In-situ static dilution (ISSD) -- direct diversion of discrete samples of odorous emissions or ambient air, to odor panelists housed in a static mixing chamber
- (3) Off-site dynamic dilution (OSDD) -- collection of discrete samples of odorous samples in suitable containers, transport to the odor panel, presentation to the panelists on a continuous basis^{3,4}
- (4) Off-site static dilution (OSSD) -- same as 3 for collection and transport, presentation to panelists in discrete parcels (e.g., syringe dilution)⁶

Of these four methods, the in-situ dynamic dilution (ISDD) method intrinsically has the least number of variables affecting the validity of the odor measurements, since it eliminated the need for storage and/or transport of discrete samples of the odorous emissions. The ISSD technique, therefore, was used in our studies as the reference method for comparing various dilution-to-threshold ratio measurement techniques and for evaluating the effects of specific parameters relative to sampling, storage and presentation of odorous emissions from various industrial processes.

IV-1 SELECTION OF ODOR MEASUREMENT PARAMETERS FOR DETAILED STUDY

In order to form a common basis for establishing equivalency of results of odor measurements obtained by various techniques, potentially significant parameters were defined, taking all procedural steps of the odor measurement process into account. The selected parameters are listed in Table 1. Variables and performance requirements which apply to the individual parameters are also shown in this table. Procedures used to evaluate these factors and partial results obtained to date are summarized in the following sections.

A combination of both laboratory and field investigations were used to evaluate the relative effect of each of the seven parameters on

TABLE 1

EPA ODOR STUDY APPROACH (applied to each industry)

Measurement Parameter	Method	Application	Variables	Performance Requirements
1. Sampling Point Selection	Locate point of emission	All situations	Uniform comp'n traverse; time stability of comp'n.	Representativeness of sample must be insured by selecting a sampling point where complete mixing is insured.
2. Sample Transport	Extraction probe in stack and pump system	All situations	Materials of probe; sampling time	Maintain sample integrity; no addition of contaminant; no removal of reaction of odorants by material. Continue sampling long enough to even out fluctuations.
3. Sample Collection	Container	Dynamic off-site; Static off-site	Time of storage; materials for storage; environmental conditions; sample volume; sample humidity	Maintain sample integrity with no loss or change of composition with storage. Adequate volume for proposed dilution.
4. Panelist (detector)	Odor detection (Yes-No)	All situations	Motivation; sex; ability to follow directions; smoking habits	Responsive subject to odor under test
5. Panel Composition	Average population by statistical treatment	All situations	Number of panelists; threshold response of individual subjects	Must represent average population in terms of geometric deviation
6. Sample Presentation	Known dilution	All situations	Number and spacing of dilutions (Velocity of stream) rel. vol. flow rate of inhalation to incoming stream; exposure interval	Ascending conc., beginning with subthreshold dil.; geometric progression (4x); sample volume or flow rate \geq inhal'n. vol. or flow rate
7. Data Evaluation	Statistical evaluation	All situations	Number on panel; Number of dil. ratios	50% response value and geometric deviation

the validity of odor measurements by dilution-to-threshold ratio.

IV-2 LABORATORY INVESTIGATIONS

Prior to any field work, we conducted laboratory investigations on measurement parameters associated with items 3 through 7 on Table 1. Specifically, we investigated the following factors in TRC's odor laboratory:

- (1) Panel selection and training methods
- (2) Factors affecting the performance of individual panelists
 - (a) age
 - (b) sex
 - (c) smoking habits
 - (d) time of day, rest periods and meals
- (3) Panel composition
 - (a) number of panelists
 - (b) individual sensitivity
- (4) Order of presentation of dilutions
- (5) Data evaluation and calculation procedures
- (6) Comparison of dilution techniques
 - (a) dynamic (off-site)
 - (b) static (syringe dilution)
- (7) Absorption characteristics of container materials

IV-3 FIELD INVESTIGATIONS

The field experimental program was designed to evaluate the effects of factors associated with collecting representative samples of odorous emissions, and maintaining the integrity of the sample prior to presentation to the odor panel. (Items 1 through 3 on Table 1). The specific factors investigated in the field program were:

- (1) Sampling location
 - (a) physical conditions, e.g., temperature, moisture
 - (b) relative odor level
- (2) Sample humidity
- (3) Pre-conditioning of sample container
- (4) Sample container material

- (a) handling
- (b) mechanical reliability
- (c) affinity for odorants

(5) Sample container size and shape

(6) Aging of samples (storage time)

In addition, simultaneous measurement of odor levels and concentration of selected chemicals was done in the field program.

SECTION V

FACILITIES AND EQUIPMENT

V-1 TRC ODOR LABORATORY - DYNAMIC DILUTION SYSTEM

The basic principle underlying the TRC odor laboratory is that of dilution of samples of odorous air with pure air by a dynamic dilution technique, and presenting the resulting near-threshold concentrations of odor samples simultaneously to a panel of trained judges. The panelists are located in a well-ventilated odor-free room. The panelists are separated by partitions. The room is kept under a slight positive pressure, the air being continuously purified by two stages of activated charcoal filtration. During a typical odor measurement session, the panelists are periodically asked to smell and determine whether they can detect an odor (i.e., any odor different from "background") in the diluted sample which is being presented to them through individual glass funnel ports (5 LPM flow per port). They indicate their individual responses by means of two-way electrical switches, throwing the switch into either the "yes" or the "no" position. Their responses appear on an indicator light panel which is out of their sight, and remote from the laboratory.

The dynamic dilution apparatus used to prepare the diluted samples for presentation to the panelists is schematically shown in Figure 1. Dilutions of odorous air samples are accomplished out of sight of the panelists, using a system of calibrated rotameters, as shown. Two stages of dilution are used at dilution ratios of 1000 and higher. At dilution ratios below 1000, one dilution stage is employed. Pre-determined rotameter settings, corresponding to dilution ratios in the 10 to 1,500,000 range are given in Table 2.

All components with which odor samples come into contact are made of inert, odor-free materials such as glass and Teflon. Valves and fittings are made of stainless steel. The preferred method of injecting the odor sample into the dilution system is by aspiration, the dilution air stream providing the necessary motive force. When circumstances dictate, however, sample injection is accomplished by means of a metal bellows pump.

V-2 MOBILE ODOR MEASUREMENT LABORATORY - IN-SITU DYNAMIC DILUTION

A mobile odor measurement laboratory is being used for all field odor measurements by the ISDD method. An unfurnished 27-foot recreational motor vehicle was converted into a mobile field laboratory. The dynamic dilution system used in TRC's Odor Research Laboratory (schematically shown in Figure 1) was duplicated for field use and installed in the mobile laboratory. By using this approach, the initial screening of odor panel candidates in the laboratory, all laboratory studies and the final evaluation of actual odorants in the field were done with identical equipment and methods.

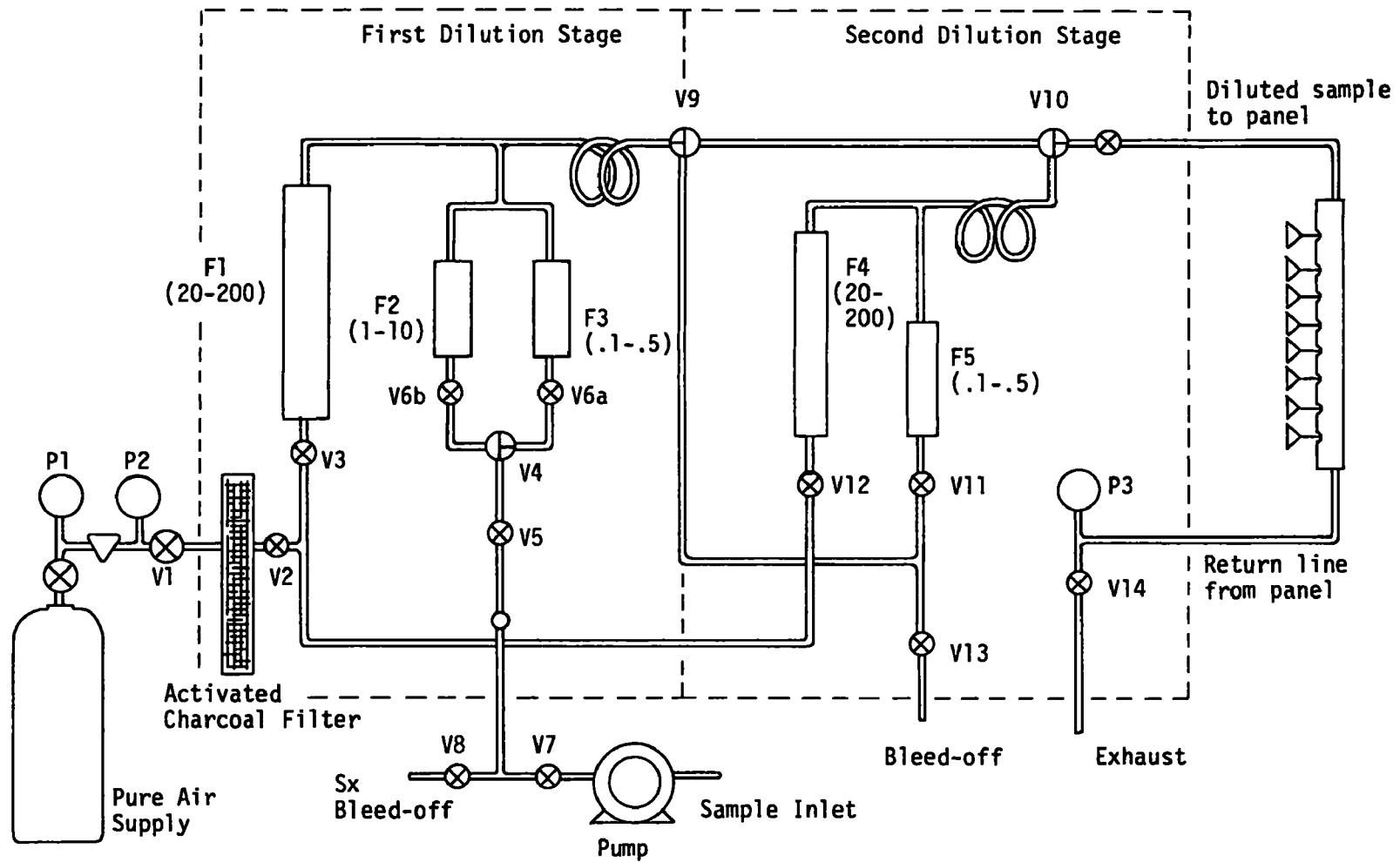


Fig. 1 Schematic of TRC Dynamic Dilution Odor Measurement System.

TABLE 2

SCHEDULE OF ROTAMETER SETTINGS

DILUTION RATIO	ROTAMETER SETTINGS				
	First Dilution Stage			Second Dilution Stage	
	F1	F2	F3	F4	F5
1,500,000	125	-	0.10	120	0.10
1,000,000	100	-	0.10	100	0.10
750,000	100	-	0.10	75	0.10
500,000	100	-	0.10	50	0.10
375,000	75	-	0.10	50	0.10
225,000	45	-	0.10	50	0.10
175,000	35	-	0.10	50	0.10
100,000	40	-	0.20	50	0.10
66,700	40	-	0.20	50	0.15
50,000	40	-	0.20	50	0.20
33,330	40	-	0.20	50	0.30
25,000	50	-	0.20	50	0.50
20,000	50	-	0.25	50	0.50
16,000	40	-	0.25	50	0.50
10,000	50	-	0.50	50	0.50
8,000	40	-	0.50	50	0.50
5,600	25	-	0.45	50	0.50
4,000	40	1.0	-	50	0.50
2,800	40	1.5	-	50	0.50
2,000	40	2.1	-	50	0.50
1,400	40	3.0	-	50	0.50
1,000	40	4.45	-	50	0.50
600	60	-	0.10	-	-
400	50	-	0.125	-	-
280	50	-	0.18	-	-
200	50	-	0.25	-	-
140	50	-	0.35	-	-
100	50	-	0.50	-	-
70	35	-	0.50	-	-
50	50	1.0	-	-	-
34	50	1.5	-	-	-
26	50	2.0	-	-	-
17.5	50	3.0	-	-	-
13.5	50	4.0	-	-	-
10	45	5.0	-	-	-

The vehicle came equipped with an air conditioning system and generator. Activated charcoal filters were installed in the air conditioning system to treat both the 85 per cent recirculated air and the 15 per cent make-up, ensuring a continuous supply of odor-free air to the panelists. The entire van is kept under positive pressure. Thus, the eight panelists are not exposed to the background odorants in the vicinity of the odor source under test at any time, either en route to the site or during the field tests. The generator provides 115 V AC current used to power the odor sampling and ISDD systems along with the chemical instrumentation during the field tests.

The selection of the mobile field testing system was based on a consideration of the requirements for the field lab:

- (1) Seating for 6 to 8 panelists
- (2) Air purification and ventilation system
- (3) Sample metering and dilution system
- (4) Sample presentation apparatus (isolated from assembly area)
- (5) Room to move back and forth between seats and point of presentation
- (6) Room for chemical analysis apparatus
- (7) Electric power supply (115 V AC)

V-3 ODOR SAMPLING SYSTEM

The dynamic sampling system used in our field tests to provide a continuous stream of odor sample consists of a heated glass/Teflon probe, a calibrated dynamic pre-dilution device shown in Figure 2, two alternate sources of pure air, a sample-bag filling port, and a stainless steel bellows-type booster pump connected to a 150-foot long 3/8-in. ID sample transmission line (clear, odor-free PVC) for transferring a continuous stream of odorous gas sample to the mobile odor laboratory.

The probe requires heating only if the ambient temperature is below the dew point of the gas being samples. When heating the probe, a temperature of 10 to 20°F above the gas temperature is maintained at the outer surface of the Teflon probe, as measured by a thermocouple located near the downstream end of the probe.

To prevent dry particulate matter from entering the sampling system, clean, dry, odor-free glass wool is packed loosely into the expanded inlet of the probe. This step is not taken, however, when the sample contains entrained mist, since the resulting wet glass wool is likely to be detrimental to the odor integrity of the sample.

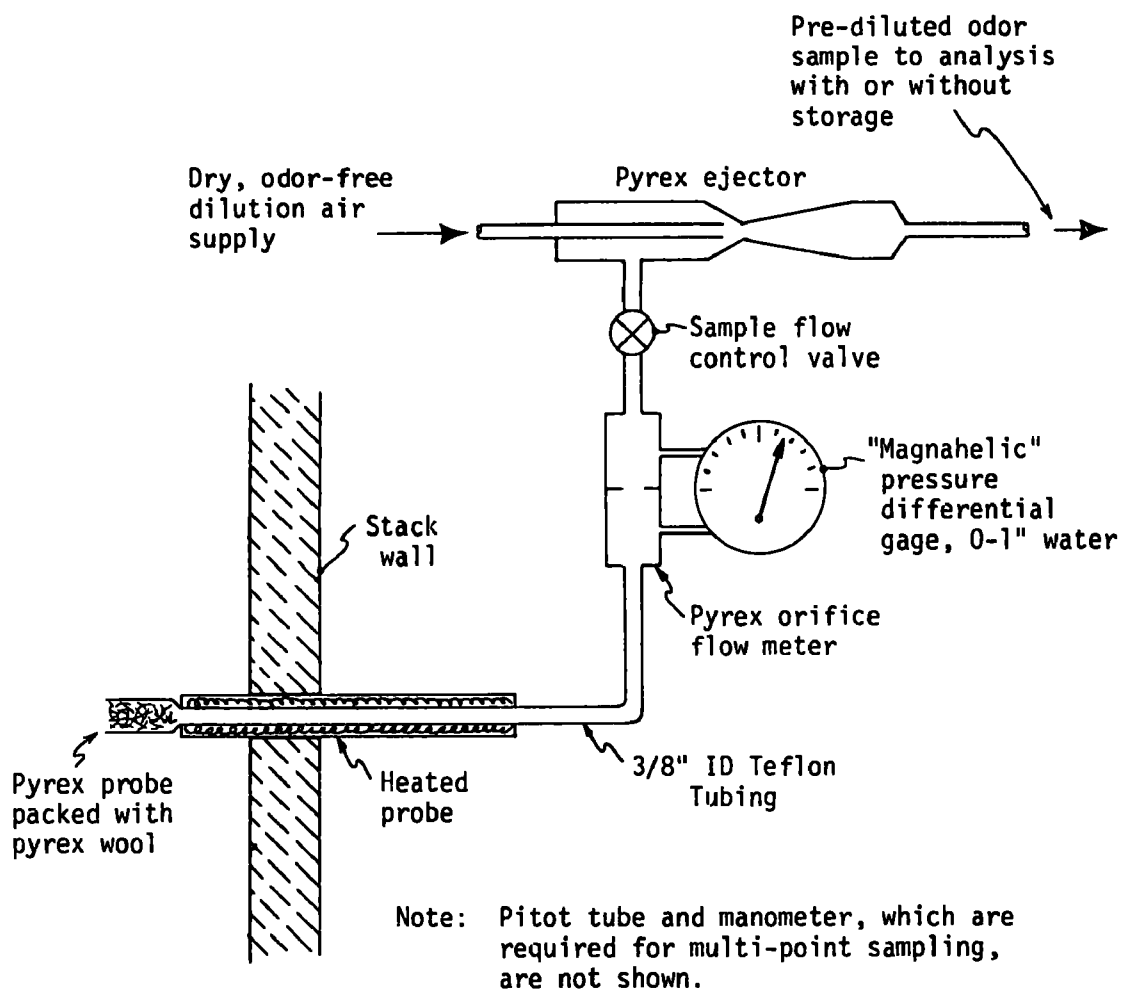


Fig. 2 Odor sampling probe and pre-dilution device.

The purpose of the pre-dilution device is to lower the dew point of the gas sample to below the ambient temperature and hence to prevent condensation of moisture in the sampling containers and in the sample transmission line. Accurate (within 4 per cent) adjustment of the pre-dilution ratio D_f using the two calibrated flowmeters, is possible within the range of 2:1 to 10:1. Dry, odor-free air can be supplied either from compressed-air cylinders or from the ambient atmosphere via an air pump. In the latter case, however, a one-liter cartridge packed with coarse (6-12 mesh) granular desiccant followed by another one-liter cartridge packed with coarse (6-12 mesh) activated carbon is used.

The heart of the pre-dilution device is the glass aspirator which serves the triple purpose of providing the motive force for extracting a sample from the source, acting as a mixing chamber, and cooling the sample (if hot) before collecting into containers or transmitting to the mobile laboratory through the heat-sensitive PVC line.

Necessity of pre-dilution of the sample gas or the minimum amount of dilution required to prevent condensation is determined by the following criteria.

The pre-dilution factor, D_f , is calculated using equation 1.

$$D_f = \frac{B_{WO}}{B_{wa}} \quad \text{equation 1}$$

where,

D_f = pre-dilution factor, dimensionless (ratio of the volume of the final pre-diluted sample gas to the volume of the undiluted stack gas)

B_{WO} = proportion by volume of water vapor in the stack gas

B_{wa} = proportion by volume of water vapor present in saturated air at the ambient temperature

If D_f is equal to or less than one, stack gas pre-dilution is not required.

If D_f is greater than one, pre-dilution of the stack gas is necessary.

Pre-dilution air and sample flow rates are adjusted using Table 3. Note that the combined (pre-diluted sample) flow rate is about 40 SCFH (20 LPM). This flow is maintained for at least five minutes to bring the sampling system to dynamic odor equilibrium, before any samples are taken or before any ISDD odor measurements are made. Equilibration of the sampling system is required regardless of whether pre-dilution is used.

TABLE 3

PRE-DILUTION FLOW RATES

Pre-Dilution Ratio, D_f	Dilution Air Flow, SCFH	Sample Flow, SCFH	Combined Flow, SCFH
2	20	20	40
3	30	15	45
4	30	10	40
6	35	7	42
8	35	5	40
10	36	4	40

When no pre-dilution is used, the same sampling rate of 40 SCFH is maintained. If it is desired to collect a given size sample over a specified sampling period, a separately metered portion of the main sample stream can be diverted into the sample container. Sample containers must be clean, undamaged, odor-free, and completely empty. Flexible bags (provided with tightly sealable inlet tubes) are filled at a point just downstream from the booster pump simply by connecting the sample stream (pre-diluted, if necessary) to the bag inlet tube. The positive pressure in the sample line is more than sufficient to inflate the bags with sample and a control valve is recommended for regulating the rate of filling of the bag.

V-3.1 Batch (Static) Sampling Systems

A "grab-sample" method of filling bags with odor samples without pre-dilution is to place the empty bags inside a sampling assembly shown in Figure 3. This device is essentially an airtight rigid container large enough to hold the bag when inflated. The bag's inlet port is connected to a bulkhead fitting passing through the tight-fitting lid of the assembly. Sample is drawn into the bag via the probe and the ball valve by evacuating the rigid container with the vacuum pump. As soon as the bag has expanded without stretching (as seen through the transparent cover) the valve is closed, the pump is disconnected, the lid is removed and the filled bag detached, capped, and labeled.

Rigid containers, such as glass tubes and stainless steel bombs (both furnished with inlet as well as outlet ports and valves) can be filled with undiluted sample either by purging the sample through them to displace the air originally occupying them (at least ten displacements of volume used), or by first evacuating the containers (to below 0.1 psia pressure) and then allowing the sample to slowly fill the vacuum. Both methods were evaluated under field conditions at a rendering plant.

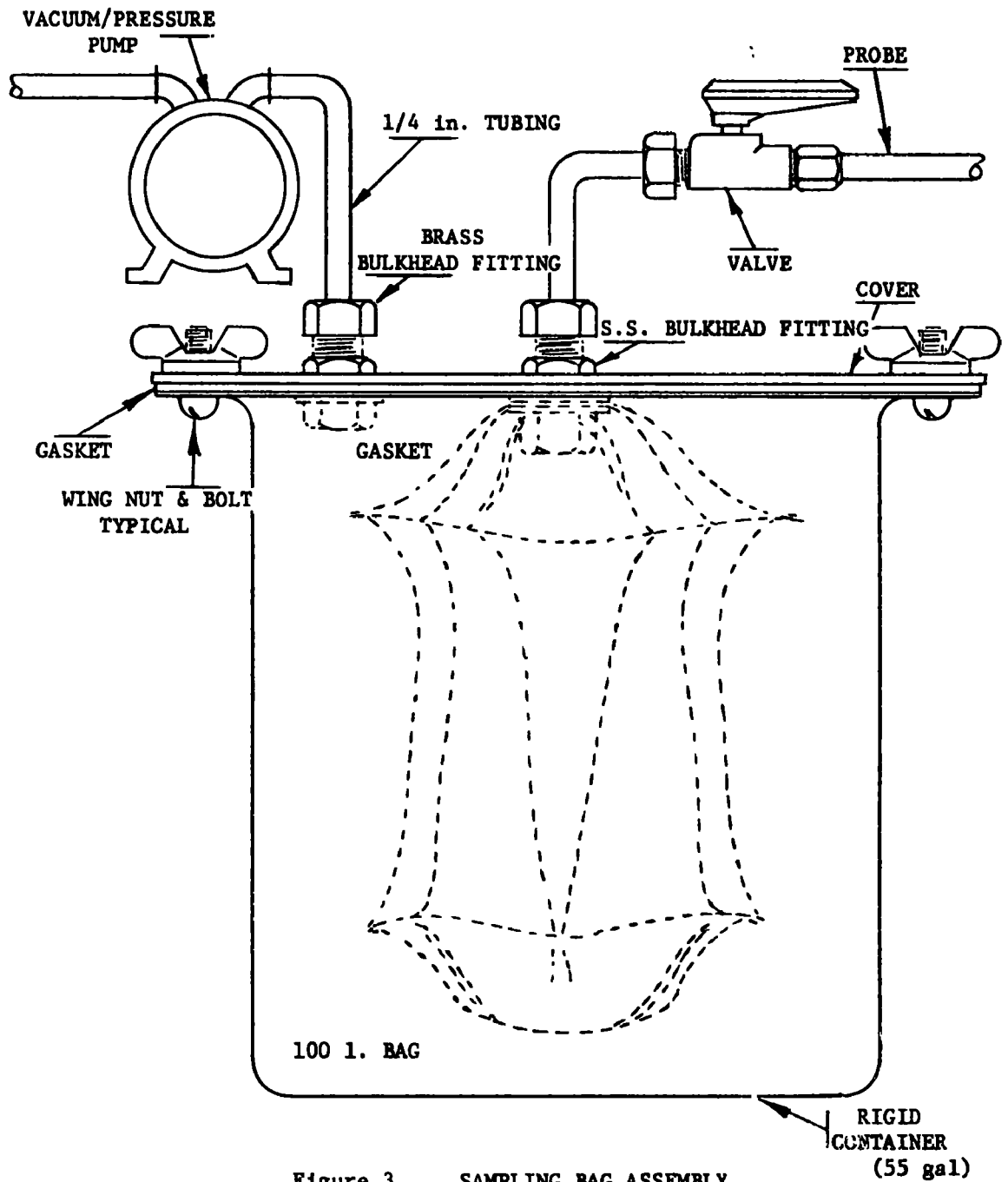


Figure 3 SAMPLING BAG ASSEMBLY

SECTION VI

METHODS AND CORRELATIONS

LABORATORY INVESTIGATIONS

VI-1 ODOR PANEL SELECTION

Efforts to recruit independent panelists were directed toward mature, motivated individuals who had few restrictions (if any) as to availability during usual working hours. There were no requirements regarding age, sex, educational level beyond 8th grade, and work experience. Interested individuals responding to local newspaper, bulletin board, or radio announcements were explained the nature and circumstances of panel participation, clearly pointing out that they were to be tested first for ability to detect odors (triangle tests) and their ability to follow instructions. They were made aware that several sessions of training would be involved after which participation would be on an irregular basis, as requested from time to time with at least 24 hours advance notice. Smoking, eating, coffee breaks, use of scented substances such as perfumes were not allowed, starting one hour before scheduled participation until the session was over. Sessions ran up to four hours, with frequent rest periods. One or two sessions were scheduled on any one day. Compensation was purposely modest but somewhat over minimum wage guidelines. On days when two sessions were scheduled, lunch was provided for the panelists.

VI-1.1 Screening Test

The candidate is seated next to a clean, empty table or bench in an odor-free room. He is first asked to fill in Part A of the Triangle Test Form, Table 4. He is then presented with a set of three 300-ml Erlenmeyer flasks, each containing 100 ml of liquid. Two of the flasks contain pure solvent and the third one contains an odorous substance in solution. The candidate is asked to sniff (inhale slowly through the nose for short periods) by holding his nose close to the mouth of one flask at a time, in any order he pleases, and pick out the one flask which he judges to contain an odor different from any background odor which he may or may not perceive in the other two flasks. The first set for practice includes one flask containing a 500 ppm (.05% by weight) solution of methyl salicylate (oil of wintergreen) in water* while the other two flasks have pure water. Questions are invited on the procedure. It is pointed out that in case of doubt a guess must be made; i.e., a choice is mandatory.

Some 40 candidates were then given triangle tests with aqueous solutions

*Freshly made up by adding one drop of reagent grade methyl salicylate to 100 ml of pure water at room temperature and thoroughly mixing to dissolve.

of butyric acid, pyridine, furfural and eucalyptus. To be considered for further training, candidates had to be able to detect 10 ppm of butyric acid, 100 ppm of pyridine, 10 ppm of furfural, and 100 ppm of eucalyptus oil, and also to follow instructions and to show interest.

Twenty-four of the initial candidates passed this screening test. Triangle tests using methyl salicylate and vanillin⁷, as specified in the EPA modification of ASTM 1391-57 syringe dilution procedure (Appendix A) and also solutions of methyl disulfide and butyric acid in benzyl benzoate were administered to 16 of these accepted candidates. These latter compounds were shown to be representative of rendering odors.⁸

The triangle screening test, using both vanillin and methyl salicylate solutions together, as specified by the EPA version of ASTM method D 1391-57 (Appendix A), was tried but was abandoned for the following reasons:

- a. Results were highly unreproducible from one triangle test to another. Rankings of panelists changed drastically, in random manner, from trial to trial.
- b. The olfactory sense of the panelists was quickly fatigued by the higher initial concentrations of the two odorants used.
- c. The individual's ability to make a selection based on distinguishing between two different "pleasant" odors was found to have no direct bearing on his ability to detect an entirely different malodor, (Tables 5A and 5B).
- d. Panelists have complained about eye and throat irritation (probably caused by benzyl benzoate vapor). In their attempt to distinguish between two different odors, panelists were inclined to inhale solution vapors for prolonged periods.

Subsequent triangle test sets for scoring purposes were presented according to the compositions specified in Table 6, in the order listed. Responses for these tests were recorded by the candidate in Part B of the Triangle Test Form (Table 4). Sets numbered 1 through 7 contained solutions of butyric acid in benzyl benzoate, in increasing concentrations. Sets 8 through 14 contain solutions of methyl disulfide in benzyl benzoate.

A five minute period was allowed between sets 7 and 8.

The triangle tests were scored in the candidates presence. He was informed of the results and was asked to fill in Part C of the Triangle Test Form. He was made aware that his score is considered along with every other candidates' scores on a statistical scale, every time a group of panelists is called into session. There were always more qualified panelists available than the number needed at an odor measurement session. Combined scores of 7 or higher qualified a candidate for rendering odor work, provided he was also able

TABLE 4

TRIANGLE TEST FORM

PART A (Please complete now)

Panelist Name: _____ Address: _____
Date: _____ City or Town: _____
Time: _____ State & Zip Code _____
Telephone Number: _____

PART B (Please fill in your response as instructed)

<u>Set No.</u>	<u>Response*</u>	<u>Set No.</u>	<u>Response*</u>
1.	_____	8.	_____
2.	_____	9.	_____
3.	_____	10.	_____
4.	_____	11.	_____
5.	_____	12.	_____
6.	_____	13.	_____
7.	_____	14.	_____

*Write down number of flask containing the odorous solution.

Test Results: 1 through 7 score = _____; 8 through 14 score = _____.
Combined score = _____.

PART C

Personal Data: Age (if under 18): _____ Occupation: _____
Best time to reach for making future appointments _____
Indicate times not available _____
Do you smoke? _____ Do you have frequent colds or sinus trouble? _____
Present condition of health _____
Person to contact in case of emergency: Name: _____
Address: _____
Telephone: _____

Interviewer's remarks:

TABLE 5A

ODOR PANELIST CLASSIFICATION BY THREE SEPARATE TRIANGLE TESTS INTO TWO PANEL GROUPS:

- I. MEDIAN GROUP (2nd and 3rd quartiles)
- II. EXTREMES GROUP (1st and 4th quartiles)

(Scores determined as stated in Tables 6 and 7. Ranking is in order of decreasing score. In cases of equal scores, the individual with the highest total number of correct answers (including correct guesses) ranks first. E.g., revised score for example given at bottom of Table 2 would be 4.)

CLASSIFICATION OF INDIVIDUAL PANELISTS

Triangle Test Used	High Extreme 1st Quartile	Median Group 2nd 3rd	Low Extreme 4th Quartile
A. Vanillin and Methyl Salicylate (ASTM Method D1391-57)	BC LD MT CS	CE EG NB RM RB MS MB DC	CR MD JK LR
B. Butyric Acid	LR MD CE BC	JK MT MB DC LD RM EG CS	RB MS CR NB
C. Methyl Disulfide	BC LR JK LD	EG DC RM CS MS MB MD MT	CE CR NB RB

TABLE 5B

ACCEPTANCE OF INDIVIDUALS BY THREE TRIANGLE TEST METHODS

Panelist's Initials	Method A Vanillin/Meth. Salicylate	Method B Butyric Acid	Method C Meth. Disulfide
RB ^a	✓		
MB*	✓	✓	✓
NB ^a	✓		
BC			
DC*	✓	✓	✓
LD		✓	
MD			✓
CE ^a	✓		
EG*	✓	✓	✓
JK		✓	
RM*	✓	✓	✓
CR			
LR			
CS		✓	✓
MS ^a	✓		✓
MT		✓	✓

* Panelists thus marked (4 out of 16) were accepted by all three triangle test methods.

^a Would not be acceptable for rendering odor study.

TABLE 6

COMPOSITION AND SCORE VALUES OF TRIANGLE TEST SOLUTIONS USED
TO SELECT PANELISTS FOR THE MEASUREMENT OF RENDERING PLANT ODORS

Set Number	Solvent	Odorant	Odorant Concentration, ppm (wt.)	Score Value
1	Benzyl Benzoate	Butyric Acid	0.15	7
2	"	"	0.31	6
3	"	"	0.62	5
4	"	"	1.25	4
5	"	"	2.50	3
6	"	"	5.00	2
7	"	"	10.00	1
8	Benzyl Benzoate	Methyl Disulfide	0.31	7
9	"	"	0.62	6
10	"	"	1.25	5
11	"	"	2.50	4
12	"	"	5.00	3
13	"	"	10.00	2
14	"	"	20.00	1

- Notes: a. Each triangle set contains one solution of the specified odorant (i.e., the "odd sample") and two pure solvent samples.
- b. Score value corresponds to the lowest concentration correctly identified, with all higher concentrations also correctly identified.

to follow instructions precisely and showed interest and motivation for this type of activity.

VI-2 ODOR PANEL TRAINING

Individuals who qualified on the basis of the triangle screening tests and other acceptance criteria were scheduled in groups of 6 to 8 for training.

First Training Session Agenda (3 hours - A.M.)

1. General orientation, including a tour of the odor measurement facilities and statement of the general principle of odor measurement by the dilution to odor threshold techniques (static and dynamic).
2. Triangle testing. The same series of butyric acid and methyl disulfide previously administered during the screening test was repeated by each individual. Consistency of individual responses was checked, although an increase in score can be expected for the majority of the panelists. Records of individuals' scores were kept (see Table 7, for example, where the first number in each column refers to butyric acid and the second to methyl disulfide).
3. Syringe dilution (OSSD) method demonstration and practice, using a mixture of methyl disulfide vapor, butyric acid vapor and pure air. The procedure for generating this "standard rendering mixture" is given in Appendix B. This method of odor measurement is described in detail in Appendix A.
4. Dynamic dilution (OSDD) method demonstration and practice. The same "standard rendering mixture" is used as for the previously demonstrated syringe method.
5. Question and answer period. Procedural details are explained and help is provided for those experiencing difficulties in responding to odor stimuli using the two techniques.

Second Training Session Agenda (3 hours - A.M., another day)

1. Triangle testing, same as first session. A continuing record on each individual was maintained.
2. Syringe dilution technique practice with the "standard rendering mixture" used during the first session. A comparison with the results from the first session was made.
3. Dynamic dilution technique practice with the "standard". A comparison with the results from the first session was made.

TABLE 7

RENDERING ODOR SENSITIVITY RANKING OF PANELISTS

Initials of Qualified Panelists	Combined Triangle Test Scores				
	Test 1	Test 2	Test 3	Average	Ranking
MB *	6 + 5 = 11	6 + 5 = 11	5 + 4 = 9	10.3	3
BC	5 + 5 = 10	6 + 5 = 11	5 + 4 = 9	10.0	4
DC *	3 + 3 = 6	5 + 4 = 9	4 + 3 = 7	7.3	12
MD	5 + 3 = 8	6 + 4 = 10	4 + 3 = 7	8.3	9
CE *	5 + 1 = 6	6 + 3 = 9	4 + 2 = 6	7.0	13-14
EG *	4 + 4 = 8	5 + 6 = 11	5 + 5 = 10	9.7	5
JK *	4 + 4 = 8	6 + 5 = 11	5 + 4 = 9	9.3	6-7
RM *	6 + 6 = 12	7 + 6 = 13	4 + 5 = 9	11.3	1
CR *	5 + 3 = 8	5 + 2 = 7	5 + 1 = 6	7.0	13-14
LR	4 + 5 = 9	7 + 6 = 13	4 + 5 = 9	10.7	2
CS	4 + 4 = 8	5 + 5 = 10	5 + 5 = 10	9.3	6-7
KS *	3 + 5 = 8	6 + 3 = 9	6 + 4 = 10	9.0	8
MS	2 + 4 = 6	4 + 5 = 9	3 + 5 = 8	7.7	11
MT	4 + 3 = 7	5 + 4 = 9	5 + 3 = 8	8.0	10
Averages	4.3 + 3.9 = 8.2	5.6 + 4.5 = 10.1	4.6 + 3.8 = 8.4	8.9	-

* Persons selected for rendering field trip. This group of panelists has a combined average triangle test score of 8.9 (same as average of all qualified panelists).

Third Training Session Agenda (2 hours, P.M., same day as second session)

Repeat three items on second session's agenda, compare results and discuss training program just completed in preparation for odor measurements on actual rendering plant emission samples. Present such a sample to the trained panel at this final session if available, using the dynamic dilution (OSDD) method.

VI-3 EVALUATION OF ODOR PANEL RESPONSE DATA (STATIC AND DYNAMIC METHODS)

An example of odor response data as recorded is shown in Table 8. Those positive responses which are in parentheses are considered "false" indications because they are either responses to pure background air (not shown) or are followed by negative responses to lower dilution factors. These false positive responses must be recognized as negative responses before proceeding with the calculation of the cumulative percentage positive responses at or above specified dilution ratios.

Next, observe the solid-line plot of dilution factors vs. corresponding cumulative percentages of positive responses on 3-cycle logarithmic probability paper as shown in Figure 4. A solid straight line was fitted easily through the data points by eye without resorting to the least square method. The odor concentration value of 860 odor units can be read from the graph, which by definition is the dilution factor corresponding to 50 per cent positive response.

Had the corrections to the raw data not been made as explained above, the dashed line in Figure 4 would have resulted, yielding a positively biased value of 1220 odor units.

VI-3.1 Criteria for Acceptance of Odor Measurement Results

Sometimes, whether due to panel fatigue, or malfunctioning equipment, widely scattered data were obtained especially at the higher dilution ratios. When this situation was evident, the odor measurement procedure was repeated after corrective action had been taken. In doubtful cases we applied the following test to the plotted data:

- a. Graphically determine s_g , the geometric standard deviation of the response data. This is simply D_{16}/D_{50} .
- b. For a measurement made by a dynamic dilution method, if s_g is 2.0 or less, accept D_{50} as the odor concentration.
- c. For a measurement made by a static dilution (syringe) method, accept D_{50} as the odor concentration only if s_g is 2.8 or less.

VI-4 NUMBER OF PANELISTS ON ODOR PANEL

Repeated (9 times) laboratory odor measurements were conducted, using our "standard rendering mixture", with eight panel members, over a two-day period. Individual responses, however, were statistically

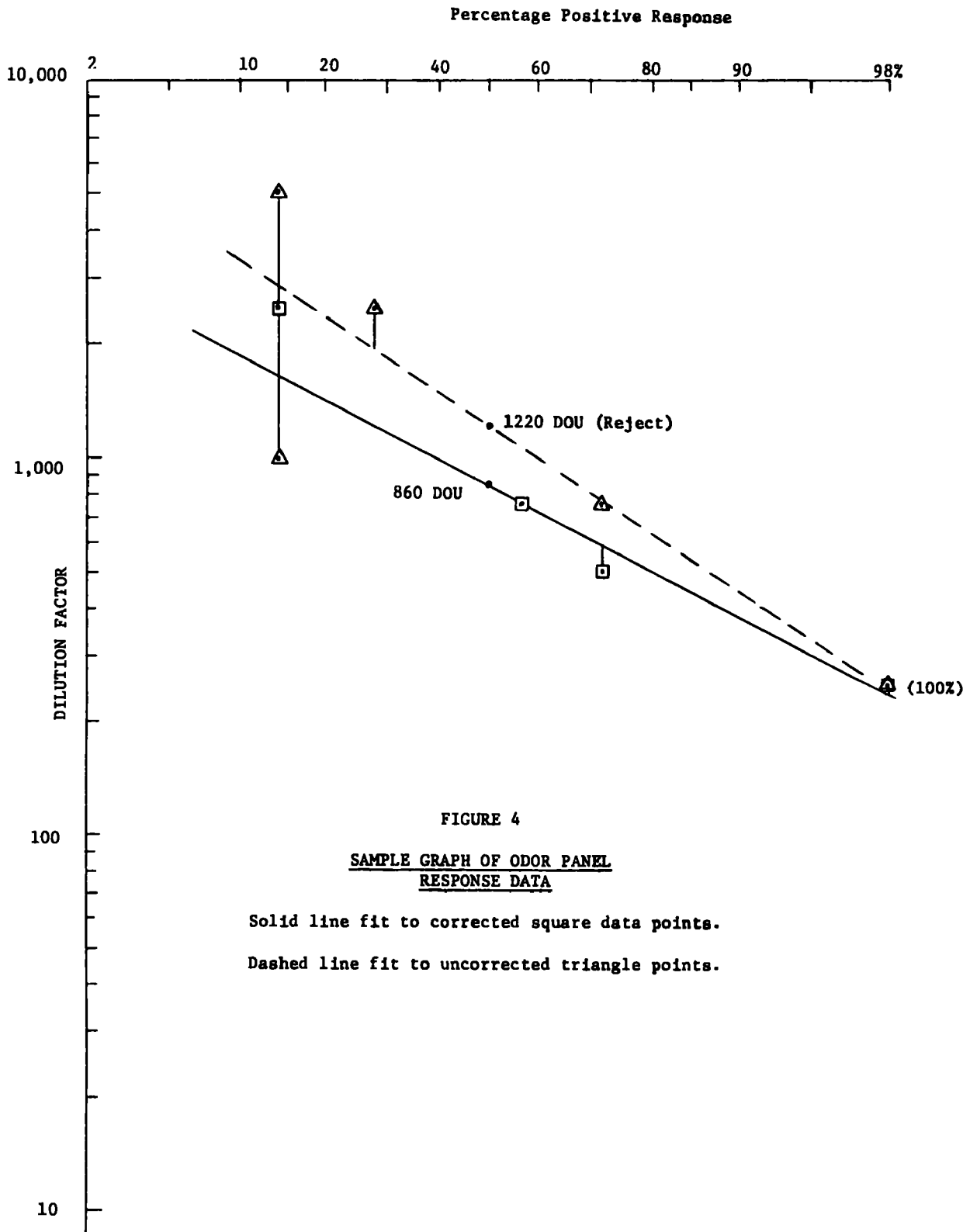
TABLE 8

DATA SHEET FOR ODOR MEASUREMENT BY DYNAMIC DILUTION METHOD

Sample Identification: Scrubber Inlet Gas in 75-l. Tedlar bagDate of Analysis: 3/30/73 Time: from 3:20 PM to 3:27 PMPreliminary Dilution Factor, $D_f = 1$ (no pre-dilution)

Sample Age: 164 hours

Panelists' Initials	Sample Dilutions & Panelist Responses							
	D_p	5000	2500	1000	750	500	250	
	$D_p \times D_f$	5000	2500	1000	750	500	250	
1. E.G.		-	(+)	-	+	+	+	
2. C.R.		-	+	+	+	+	+	
3. C.E.		-	-	-	+	+	+	
4. M.B.		(+)	-	-	-	+	+	
5. J.K.		-	-	-	(+)	-	+	
6. K.S.		-	-	-	-	-	+	
7. D.C.		-	-	-	+	+	+	
8. VACANT								
% Positive Response		0	14	14	57	72	100	
		(14)	(28)	(14)	(72)	(72)	(100)	J.W.
					Analyst			



analyzed in groups ranging from a single panelist up to eight panelists, in terms of the coefficient of variation. The coefficient of variation (C.V.) is given by the expression:

$$(C.V.) = \frac{100S}{D_{50}}$$

where S is the standard deviation based on nine odor concentration values and D_{50} is the average (of 9) odor concentration (i.e., the dilution ratio corresponding to 50% positive response).

VI-5 ORDER OF PRESENTATION OF DILUTIONS DURING ODOR MEASUREMENT, INCLUDING PURE AIR BACKGROUND

Odor samples were presented to the panel starting at the highest dilution ratio (lowest odor concentration) first, followed by a succession of gradually decreasing dilution ratios until at least 75% of the panel has responded positively. Reversal of the order of presentation was also tried, with the usual 1-minute interval between presentations, but the odor measurement results were significantly lower (30 to 50 per cent) in the latter case.

In order to monitor the panel (for alertness) and the measurement equipment (for possible contamination), frequent presentations (at least one in three) of pure background air were made in randomized order. The fact that background air was being presented was announced to the panel at the beginning of a new series of presentations (new sample).

VI-6 EVALUATION OF MATERIALS

A series of laboratory tests was also conducted using pure odorants including butyric acid, methyl disulfide and quinoline - identified by Snow and Reilich of IITRI⁸ as components of rendering plant emissions - to determine adsorption characteristics when exposed at low concentrations to various container materials.

The materials selected for evaluation were Saran, Mylar, Polyethylene, and Stainless Steel.

Actual concentrations of odorants not determined. Odor samples were generated by bubbling pure air (2 LPM) through two 200-ml batches of 0.05 wt.% solutions of pure odorant in benzyl benzoate, using two bubblers in series.

ISDD odor measurements were made at the time of sample generation (and container filling), using a six-member odor panel.

OSDD odor measurements on stored samples in specific containers were conducted the following day using the same six-member odor panel.

None of the containers were pre-conditioned with odor sample.

VI-7 REPRODUCIBILITY OF DYNAMIC AND STATIC DILUTION METHODS

The reproducibility of both the dynamic dilution technique and the syringe method was evaluated in the laboratory. A synthetic rendering mixture comprised of vapors of butyric acid, methyl disulfide, quinoline and valeraldehyde in air, was prepared and stored in 100-liter Tedlar bags. Three replicate evaluations of this mixture were done by dynamic dilution on the same day with the same panel, two in the morning and one in the afternoon. On the same day, and with the identical mixture and odor panel, four replications of the syringe method were conducted.

The geometric standard deviation, and the confidence limits of the means were determined for each method, as shown in Table 9.

The effect of the technique employed in making the final dilutions by the syringe method was also investigated. The test odorant in this case was air saturated with vapors from a 0.05 per cent solution of benzyl benzoate. The sample syringe was pre-conditioned in all trials. The results are shown in Table 10.

VI-8 EVALUATION OF POTENTIAL ANALYTICAL METHODS FOR ODOR CORRELATION

To accomplish the second objective of this program, we reviewed available data on the composition of rendering odorants. Snow and Reilich⁸ had reported on extensive evaluations of rendering odorant identification. From their studies, we selected carboxylic acids, measured as butyric acid, and sulfide concentrations as good potential chemical indicators of the odor level in rendering emissions. Laboratory studies of "standard rendering odor mixtures", containing various vapor mixtures of butyric acid and methyl disulfide were made. As a matter of interest, mixtures of these two components have an odor quality (characteristic smell) identical with general rendering plant odors. Our panelists were unable to identify which bags had scrubber inlet samples brought back from the field trip and which contained the synthetic mixture.

A single-beam infrared analyzer (Wilks Scientific MIRAN) with a 20-meter cell was used on synthetic mixtures, "live" field streams and the samples returned to TRC's laboratories in various containers. Carboxylic acid, as ppm butyric, was monitored at a wavelength of 3.5 microns. Sulfides, as ppm methyl disulfide, were monitored at 10.5 microns. We also attempted to monitor amines at 14.2 microns. A Meloy Total Sulfur Analyzer was also used to measure total sulfur content, as ppm SO₂, of the container samples as returned from the field.

A number of other compounds were investigated for possible correlation analysis by means of infrared absorption. These included valeraldehyde, quinoline, hydrogen sulfide, and pyridine. All of these had to be eliminated, however, either because their primary absorption bands were in the region corresponding to absorption by water or carbon dioxide, or because of insufficient sensitivity at typical concentrations from controlled sources.

TABLE 9
REPRODUCIBILITY OF ODOR MEASUREMENT

(Test Date: April 17, 1973)

A. SYRINGE METHOD

<u>Run No.</u>	<u>Time</u>	<u>Odor Units, D₅₀</u>
1	10:35 to 10:50	345
2	10:55 to 11:10	310
3	14:20 to 14:35	400
4	14:50 to 15:05	360
Sum of odor units		= 1415
Arithmetic mean of odor units, D ₅₀		= 354
Variance of odor units, v		= 1040
Standard deviation of odor units, s		= $\sqrt{1040} = 32$
Coefficient of variation		= $100S/\overline{D}_{50} = 9.1\%$
95% confidence limits of individual determinations		= $D_{50} \pm 18\%$

B. DYNAMIC DILUTION METHOD

<u>Run No.</u>	<u>Time</u>	<u>Odor Units, D₅₀</u>
1	09:40 to 09:55	4600
2	10:10 to 10:25	5000
3	13:50 to 14:05	4000
Sum of odor units		= 13,500
Arithmetic mean of odor units, D ₅₀		= 4540
Variance of odor		= 169,000
Standard deviation of odor units,		= $\sqrt{169,000} = 411$
Coefficient of variation		= $100S/\overline{D}_{50} = 9.1\%$
95% confidence limits of individual determinations		= $D_{50} \pm 18\%$

TABLE 10

EFFECT OF METHOD OF PREPARING SYRINGE SAMPLES FOR PRESENTATION - OSSD METHOD

Sample analyzed: Air saturated with vapors from 0.05% solution of butyric acid in benzyl benzoate

Method A - Minimum exposure to glass syringe surface with pre-conditioning of sample syringe

<u>Transfer Sample Volume, ml</u>	<u>Sample Syringe Size, ml</u>	<u>Intermediate Dilution Factor(s) in 100-ml Transfer Syringe(s)</u>	<u>Final Dilution in 100-ml Panelists Syringes</u>	<u>Per Cent Positive Panel Response</u>	<u>Result Odor Units</u>
1.00	2	100	1000	25	
1.33	2	75	750	37	
2.00	2	50	500	67	610 o.u. by Method A
4.00	10	25	250	87	
6.67	10	15	150	100	

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Method B - Use of 100-ml sampling syringe (pre-conditioned) and two 100-ml transfer syringes

10.0	100	10 & 100 (2 stages)	1000	0	
13.3	100	7.5 & 75 (2 stages)	750	0	
20.0	100	5 & 50 (2 stages)	500	12-1/2	
10.0	100	10 & 25 (2 stages)	250	25	145 o.u. by Method B
10.0	100	10 & 15 (2 stages)	150	50	
10.0	100	10 (1 stage only)	100	63	
20.0	100	5 (1 stage only)	50	87-1/2	

Chlorine demand observations of synthetic mixtures were also made. We contacted 100-liter portions of synthetic mixtures with standardized hypochlorite solutions, and determined residual chlorine, as an indicator of net chlorine demand. This approach had to be dropped, because so-called pure dilution air, used as "blank" caused drops in residual chlorine nearly as large as the standard mixtures.

We attempted to correlate the oxidation reduction potential (ORP) of known dilute aqueous concentrations of pure odorants, such as butyric acid and pyridine. At concentrations corresponding to expected levels from rendering plant sources, there was no change in the measured potential.

FIELD METHODS

The purpose of the field program was to obtain data relative to the effects of the various factors identified in Section IV on the validity of odor measurements of emissions typical of a well-controlled rendering plant. Since the dilution system in the mobile odor laboratory is a duplicate of the system in TRC's Wethersfield laboratories, which was used for the off-site dynamic dilution measurements, variations in results of odor measurements attributable to sample container material, pre-conditioning of container, condensation, surface to volume ratio of container, and aging could be evaluated. The EPA modification of the ASTM 1391-57 syringe dilution technique, referred to as the OSSD method, was also evaluated. By comparing the deviations between the OSDD and OSSD results, we tried to determine the causes of the variations of the various methods.

Meetings were held with representatives of the National Renderers Association to explain the purpose of the field trip, and to enlist their aid in making arrangements with a suitable plant. The criteria established for selecting a test plant were:

- (1) raw material and process must be representative of the industry, and not a specialized system
- (2) emission control by means of best available technology must be installed and functioning, at least for cooker and hot-well emissions
- (3) access to emissions with a range of odor levels must be obtainable.

To meet these criteria, a plant in Tewksbury, Massachusetts was selected. This plant processes mostly shop scraps, meat and bones by means of the semi-continuous dry rendering process. All process emissions are vented into a two-stage scrubbing system before release to the atmosphere. The first stage is a dilute alkali spray chamber followed by a chlorinated water packed bed scrubber. Samples were collected at the scrubber inlet and outlet. Highly odorous samples were taken from the cooker non-condensable lines simply to provide a wide range of odor levels for

testing the applicability of the various odor dilution techniques.

Three sampling points were chosen:

- (a) Station 1 - scrubber outlet - this would provide a saturated emission at near ambient temperatures, and a low odor level.
- (b) Station 2 - scrubber inlet - all plant emissions are vented into a common plenum. At this point, total air flow is 100,000 SCFM, with relatively low humidity and moderate odor level.
- (c) Station 3 - condenser hot-well vapors - these are vented directly into the plenum. Saturated exhaust with a high odor level.

VI-9 PRELIMINARY FIELD TEST

Prior to the main field experimental program, a preliminary visit was made to the Tewksbury plant. Purpose of this visit was to prepare the sampling sites, and to check out the sampling and pre-dilution systems.

Samples were taken of the scrubber exhaust in 100-liter saran bags, in a 16-liter stainless steel tank, containing 8-liters of dry nitrogen, and in a 250-ml gas sampling tube. The saran bags were pre-conditioned prior to sampling.

We determined that 150 feet of sampling line would be required to connect the scrubber exhaust to the mobile odor laboratory. Accordingly, to evaluate the effect of this long transport line on odor levels, samples were taken directly at the scrubber outlet and at the end of a 1/2-inch diameter, flexible PVC tubing 150 feet in length. A stainless steel bellows pump was used to pump the pre-diluted samples through the line at a purge rate of 25-30 liters/min. Bottled, high pressure pure air was used for sample pre-dilution. All samples were evaluated by means of the EPA modified version of the syringe dilution method. The sampling locations and results are summarized below.

<u>Sampling Point</u>	<u>Container</u>	<u>Sample Size, liters</u>	<u>Pre-dilution Factor, D_c</u>	<u>Storage Time, Hr.</u>	<u>Odor Units</u>
<u>Pair 1</u>					
Scrubber outlet	Saran	100	4.0	15	200
Inlet to mobile lab	Saran	100	4.0	15	170
Scrubber outlet	Stainless Steel	16	2.0	16	150
Scrubber outlet	Glass	0.25	3.5	16	96
<u>Pair 2</u>					
Scrubber inlet	Saran	100	4.0	18	1700
Inlet to mobile lab	Saran	100	4.0	18	1300

From these tests, we concluded that the pre-dilution system performed satisfactorily and that the long sampling line metal bellows pump sampling system did not have an unacceptable effect on ISSD odor measurements.

VI-10 FIELD TEST

Following the preliminary test, a detailed test plan for the field trip was prepared. This is shown in Appendix C. Provisions were made to collect 25 stored samples in Saran, Mylar, and Polyethylene bags, in 16-liter stainless steel tanks, and in 250 ml gas sampling tubes.

Five direct in-situ measurements were made in the field, two on the scrubber outlet (Station 1), two on the scrubber inlet (Station 2), and one on the condenser hot-well vapor exhaust line. In addition, one of the bag samples was evaluated by the panel in the van, both by OSDD and OSSD techniques, to provide a reference for evaluating aging effects.

During the field test program, we also made provisions to compare another type of dynamic dilution system, with the TRC reference method. The National Renderers Association contracted with the Illinois Institute of Technology Research Institute (IITRI) to develop a portable dynamic dilution system for field use. This device was run in the field by Dr. A. Dravnieks of IITRI, inside the TRC mobile laboratory. Direct comparisons were obtained on two "live" samples, i.e., directly from the source to the van, and one bag sample. Additional comparisons on the bag samples, i.e., with the OSDD method, were made the following day.

SECTION VI

LABORATORY RESULTS

The results of our pre-field laboratory investigations are presented in the following sections. Results are grouped into four categories:

- (1) Screening and classification of panelists
- (2) Effects of training on panel response
- (3) Effects of individual panelist factors
- (4) Materials effects for standard rendering compounds

VII-1 SCREENING AND CLASSIFICATION OF PANELISTS

A tabulation of the individual panelists' responses for the triangle tests and for the two dilution-to-threshold techniques of odor measurement on "standard rendering mixtures" was made, as exemplified by Table 7 and Table 11. The data presented in Table 11 are also plotted in Figures 5 and 6 for graphically determining odor units. The following quantities were calculated:

- a. Ranking of individual panelists, based on average scores of three triangle tests, using both butyric acid and methyl disulfide. (See Table 7.)
- b. Geometric means of dilution factors corresponding to individuals' "standard rendering mixture" odor threshold concentrations, for both ISDD and OSSD methods (Tests 2 and 3 only in the example of Tables 7 and 11.)
- c. Individuals' specific response factor (calibration factor) for rendering odor, K_i , defined as the ratio of the dilution at the mean threshold concentration (i.e., the dilution at 50% positive panel response), D_{50} , to the individual's geometric mean dilution at his limit of odor perception, D_i :

$$K_i = \frac{D_{50}}{D_i} \qquad \text{equation 2}$$

K_i is the factor by which the dilution ratio corresponding to an individual panelist's first consistent positive response is multiplied to get a "one-man-panel" estimate of odor concentration. A 2 to 3-fold variation of K_i for the same individual has been noted on a day-to-day basis.¹ However, on any given day, an individual panelist's calibration factor is well within 50 per cent. Values of K_i for the ISDD and OSSD methods are different for the

TABLE 11

TYPICAL RESULTS FOR OLFACTORY CALIBRATION OF PANELISTS
USING "STANDARD RENDERING MIXTURE" DURING PANEL TRAINING

Initials of Qualified Panelists	Dilution ratios at individuals' odor threshold for "Standard Rendering Mixture"											
	Test 1		Test 2		Test 3		Geometric Mean		Response Factor, K_s		Ranking based on mean dilution factors	
	ISDD	OSSD	ISDD	OSSD	ISDD	OSSD	ISDD	OSSD	ISDD	OSSD	ISDD	OSSD
MB	4000	250	2000	500	2000	500	2000	500	0.90	0.48	3-5	2-3
BC	2000	100	4000	250	4000	250	4000	250	0.45	0.97	1	5-6
DC	400	50	1000	100	400	100	630	100	2.90	2.44	13	8-11
MD	1000	50	1000	100	1000	50	1000	71	1.81	3.41	8-12	12
CE	600	50	1000	100	1000	100	1000	100	1.81	2.44	8-12	8-11
EG	1000	100	2000	250	2000	250	2000	250	0.90	0.97	3-5	5-6
JK	1000	50	2000	100	1000	100	1410	100	1.28	2.44	6-7	8-11
RM	1000	250	2000	500	1000	250	1410	350	1.28	0.69	6-7	4
CR	400	10	600	50	400	50	490	50	3.70	4.85	14	13-14
LR	2000	500	4000	1000	2000	1000	2830	1000	0.64	0.24	2	1
CS	600	50	1000	250	1000	100	1000	160	1.81	1.51	8-12	7
KS	400	10	1000	100	1000	100	1000	100	1.81	2.44	8-12	8-11
MS	400	10	1000	50	1000	50	1000	50	1.81	4.85	8-12	13-14
MT	1000	250	2000	500	2000	500	2000	500	0.90	0.48	3-5	2-3
Dilution at 50% positive response	1080 DOU	97 SOU	2100 DOU	270 SOU	1560 DOU	220 SOU	1810 DOU	244 SOU				

Note: DOU signifies "dynamic odor units"; SOU signifies "static odor units" both determined by plotting on logarithmic probability graph paper as shown in Figure 5-1 and Figure 5-2.

same individual. (See Table 11 for typical values of K_1 .)

- d. Ranking of individual panelists, based on their average K_1 values, for both ISDD and OSSD methods. (See Table 11 for typical values of K_1 .)

Comparison of ranking by triangle tests (Table 7) and by K_1 values (Table 11) shows good agreement for all but two (RM & MT) of the 14 panelists listed. This discrepancy does not necessarily limit their value as panelists.

The panelists selected for the field trip are identified by an asterisk on Table 7. Note that the mean response for this 8-member panel was the same as that of the 14 trained panelists.

VII-1.1 Effect of Number of Panelists on Measurement Results

The effect of panel size was evaluated by conducting repeated (9 times) laboratory odor measurements, using the "standard rendering mixture" with eight panelists over a two-day period. Individual responses were statistically analyzed in groups ranging from a single panelist up to eight panelists.

Table 12 presents the results of our statistical analysis showing the relationship between number of panelists and the coefficient of variation (C.V.), given by the expression

$$(C.V.) = \frac{100S}{D_{50}}$$

where S is the geometric standard deviation based on nine odor concentration values and D_{50} is the average (of 9) odor concentrations (the dilution ratio corresponding to 50% positive response).

The data on Table 12 apply to single measurement values. With less than 8 panelists two or more replications should be made on each sample and the results averaged, in order to obtain the required accuracy at a specified statistical confidence level. The individual K_1 values, if accumulated over sufficient time and number of tests to lend statistical credence, could also be used to adjust values of less than 8 panel members to those of the full panel.

VII-2 EFFECTS OF TRAINING

The following situations on occasion interfered with the proper functioning of the odor panel. In each case, corrective action was taken:

- a. Certain individuals, by their personality, were distracting to others;
- b. Some inadvertently revealed their own responses to others;

TABLE 12
EFFECT OF NUMBER OF PANELISTS ON THE
REPRODUCIBILITY OF ODOR MEASUREMENT RESULTS

Number of Panelists Used	Coefficient of Variation, (C.V.), %	
	ISDD Method	OSSD Method
2	70 to 80	75 to 85
3	50	58
4	33	40
6	16	21
8	9	14

- c. Others could not resist the urge to compare results with their neighbors;
- d. Others were overly concerned about whether their performance was satisfactory or not;
- e. Some found it disturbing if they did not smell an odor most of the time. These individuals had a tendency to guess on the positive side, even to pure background air.

A few individuals had to be dropped from the panel for contributing to one or more of the situations just listed.

After their first training session, panelists generally performed satisfactorily using both dynamic and static methods. When a new, unfamiliar odor was first presented to a panel, the range of dilutions over which responses were given was relatively wide (2 orders of magnitude is common). On the next try, however, responses became narrowed to a range of just over one order of magnitude and at the same time close to double the former odor concentrations were obtained.

This effect is illustrated on Figures 5 and 6. On Figure 5, which applies to training on the dynamic dilution system, the odor unit value for one and the same sample with the same panelists doubled from the initial trial to the repeat test the next day. Also shown on this figure is the effect of lunch on panel sensitivity. Test 3 was conducted one hour after lunch, yet resulted in a 25 per cent drop in the panel response. We have found that approximately two hours is required after meals before odor panels perform at their maximum sensitivity level.

The data on Figure 6 apply to the syringe dilution technique. In this case there was a three-fold increase in panel response to the identical odorant sample from the initial exposure to the next. The potential for misleading results in the syringe technique by not cleaning syringes between presentations is also illustrated in this figure.

We conclude, therefore, that an odor panel must first be exposed to the type of odor they are asked to detect (not identify) before their responses are acceptable. A confounding factor with respect to the syringe method, however, is the effect of the technique employed by the panel administrator in preparing the final dilution. As shown in Table 10 this effect can be as great as a factor of 4 at relatively low odor levels.

VII-3 EFFECTS OF INDIVIDUAL PANELIST FACTORS

Preceding our field trip to the rendering plant, 24 qualified individuals (qualification based on a minimum triangle test score of 7 as described previously) were trained as panelists using both the dynamic and static dilution techniques. Fourteen of these people received further training involving exposure to a "standard rendering

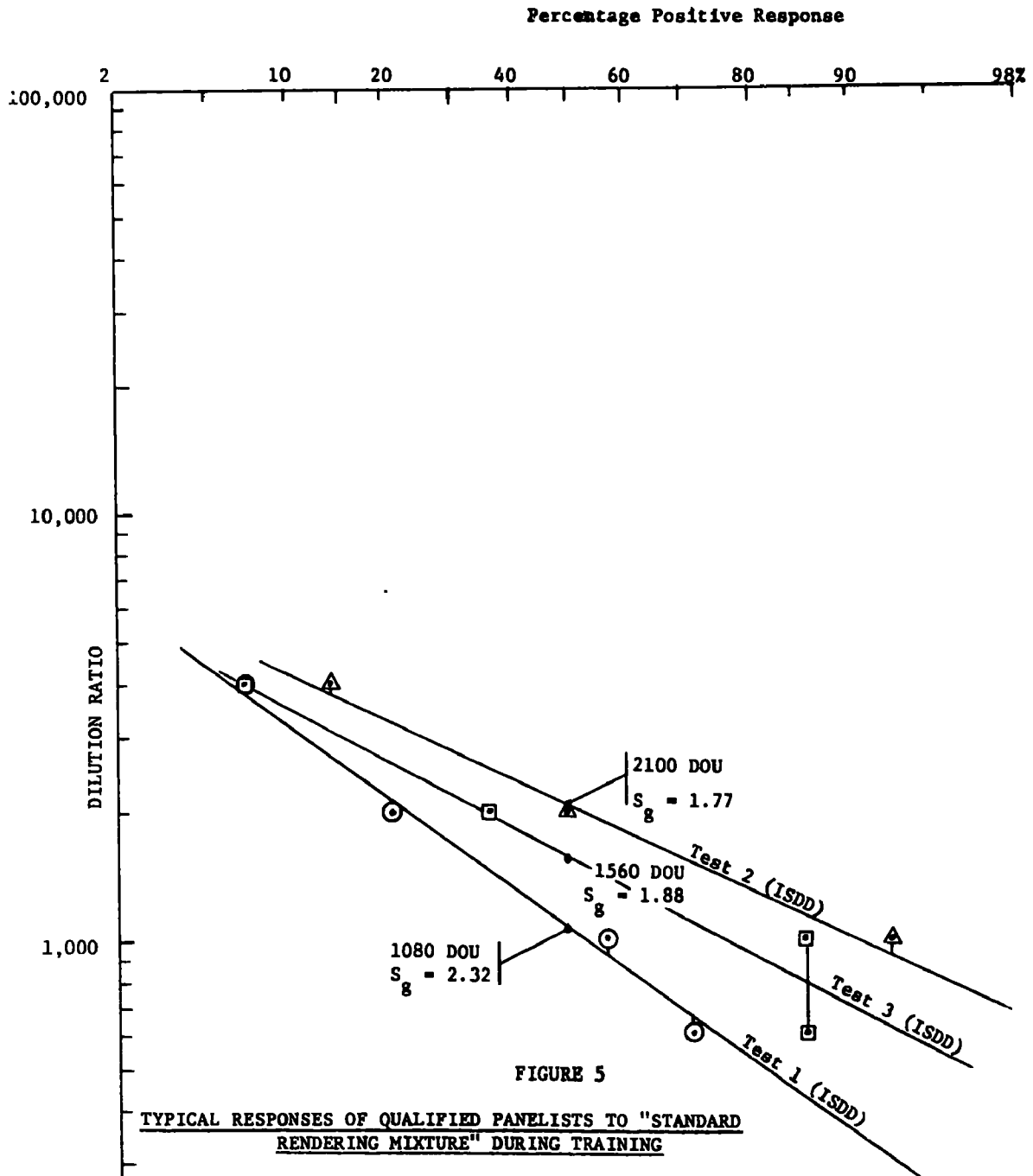


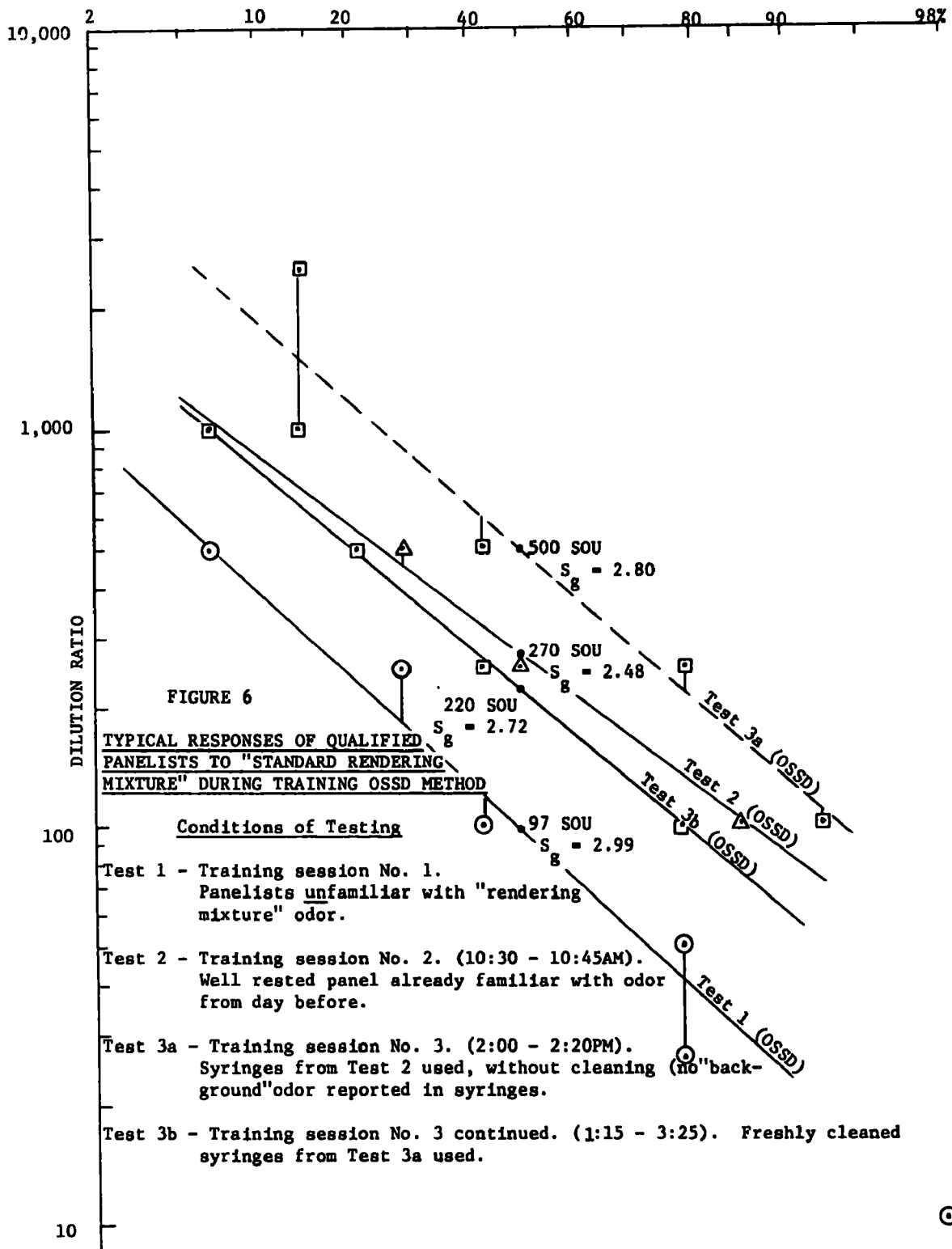
FIGURE 5

TYPICAL RESPONSES OF QUALIFIED PANELISTS TO "STANDARD RENDERING MIXTURE" DURING TRAINING

Conditions of Testing, using ISDD Method

- Test 1 - Training session No. 1. Untrained panelists but familiar with "rendering mixture" odor.
- Test 2 - Training session No. 2. (11:00 - 11:15AM). Well rested panel already familiar with odor from day before.
- Test 3 - Training session No. 3. (1:30 - 1:40PM). Same day as Test 2, following lunch. Note lower sensitivity and increased scatter of data points.

Percentage Positive Response



mixture" of butyric acid and methyl disulfide in air. Individual panelists' response factors*, K_i , were tabulated (See Table 11) based on duplicate analyses of "standard rendering mixtures" using both the static and the dynamic methods of odor measurement. These K_i values are useful in evaluating the effects of age, sex, smoking, and other personal characteristics of panelists on the response of a panel to a particular type of odor. One must however keep in mind, that up to three-fold day-to-day variations in individual panelists' K_i values have been found to occur in our study.

VII-3.1 Effect of Panelist's Age

Table 13 below shows the effect of age on a panelist's probable relative standing to that of a properly selected panel.

There is no clear evidence that age of a panelist has any significance with regard to his response during a dynamic dilution measurement relative to other panelists. However, our older panelists gave their first positive responses at lower dilutions (higher odor concentrations) than the younger panelists during a static (syringe dilution) odor analysis. Further experimentation is needed to come to any certain conclusion in this regard.

VII-3.2 Effect of Panelist's Sex on Response

Although a slightly higher sensitivity of male panelists is indicated by the results of Table 14, the difference is not significant at the 90% confidence level.

VII-3.3 Effect of Smoking of Panelist's Response

Smokers are clearly less sensitive to odors presented to them during rendering odor measurement sessions. It is assumed that panelists who are smokers abstain from smoking starting at least one hour before reporting for work until their work for the day is finished (See Table 15).

VII-4 MATERIALS EFFECTS FOR STANDARD RENDERING COMPOUNDS

To obtain preliminary data on potential adsorption of rendering odors by various materials, we exposed sample bags to representative odorants associated with rendering process emissions. Solutions of butyric acid, methyl disulfide, and quinoline in benzyl benzoate were prepared. Air was bubbled through each of these solutions and passed into the dynamic dilution system, making this an in-situ (ISDD) measurement. Simultaneously, with making the ISDD measurements, part of the odorant vapor stream was diverted to fill containers that had not been preconditioned. The samples in the containers were then evaluated, on the same day, by the dynamic dilution system (OSDD) and the same panel. The results are shown in Table 16.

Mylar, of 2 mils thickness, had the best overall performance. For quinoline, all materials performed equally showing a 10 to 30 per cent drop of odor level. Stainless steel, as expected, caused a sharp drop

TABLE 13

EFFECT OF PANELIST'S AGE ON RESPONSE

<u>Age Group, Yrs.</u>	<u>Number of Panelists in Study Group</u>	<u>Average Response Factor, K_1</u>	
		<u>Dynamic</u>	<u>Static</u>
14 to 24	7	1.4 \pm 0.3	1.5 \pm 0.3
25 to 49	3	2.1 \pm 0.6	2.3 \pm 0.7
50 and over	4	1.4 \pm 0.3	3.2 \pm 0.8

TABLE 14

EFFECT OF PANELIST'S SEX ON RESPONSE

<u>Sex Group</u>	<u>Number of Panelists in Study Group</u>	<u>Average Response Factor, K_1</u>	
		<u>Dynamic</u>	<u>Static</u>
Male	5	1.4 \pm 0.3	1.6 \pm 0.4
Female	9	1.7 \pm 0.3	2.3 \pm 0.4

TABLE 15

EFFECT OF SMOKING ON PANELIST'S RESPONSE

<u>Group</u>	<u>Number of Panelists in Study Group</u>	<u>Average Response Factor, K_1</u>	
		<u>Dynamic</u>	<u>Static</u>
Smokers	7	2.2 \pm 0.4	3.3 \pm 0.6
Non-Smokers	7	1.0 \pm 0.2	0.75 \pm 0.15

in odor level (50 per cent) with methyl disulfide. Saran also had a significant adsorption of this compound (20 per cent drop in odor). With the exception of Mylar, all materials caused a steep drop of about 50 per cent or more in odor in the butyric acid samples.

TABLE 16

ADSORPTION CHARACTERISTICS OF VARIOUS MATERIALS
EXPOSED TO REPRESENTATIVE RENDERING ODORANTS

Material	Container Size, l.	Odor Units					
		Butyric Acid		Methyl Disulfide		Quinoline	
		ISDD	OSDD	ISDD	OSDD	ISDD	OSDD
Saran	100	1,800	890	610	450	130	100
Mylar	100	2,000	1,400	550	530	110	80
Polyethylene	19	1,600	840	500	530	90	75
Stainless Steel	16	1,400	600	480	230	100	90

SECTION VIII

FIELD RESULTS

The results of our field investigations have been grouped into three categories:

- (1) sampling parameters
- (2) odor measurement technique and apparatus
- (3) chemical correlation

Each of these categories is discussed in detail in the following sections.

VIII-1 INVESTIGATION OF SAMPLING PARAMETERS

VIII-1.1 Sample Humidity

This effect was studied in the field by taking samples of scrubber exhaust gas, saturated with water vapor at 53°F, with and without the addition of dry bottled pre-dilution air. The ambient temperature was 35°F. A pre-dilution factor, D_f , of 4 was used. Odor samples were collected in 100-liter Saran bags, evaluated by the OSDD method using an eight-member odor panel. The results are tabulated in Table 17.

The higher odor concentration value corresponding to the pre-diluted sample is considered to be the more accurate. Condensation on the cold (35°F) surface of the container was noted while taking the undiluted sample. Apparently, some of the odorous materials condensed along with water. Just before odor analysis, the sample temperature was allowed to rise to 72°F (temperature of the odor laboratory). Although all the visible condensate had evaporated within the Saran bag, apparently some of the odorous substances had not, which would be the reason for the lower measured odor concentration of the undiluted sample.

VIII-1.2 Pre-conditioning of Sample Container

Pre-conditioning is simply the partial (30 to 50%) filling of the container with odor sample (pre-diluted if the final sample is to be pre-diluted) and expelling this sample completely before taking the final odor sample. The purpose of pre-conditioning is to equilibrate the container surfaces with odorants so that the odor of the final sample is not significantly affected by adsorption. As the results of Table 18 show, pre-conditioning of the 100-liter Saran bag used to collect the scrubber outlet sample (with pre-dilution) brought the results of the OSDD odor measurement close to the results obtained by the ISDD (reference) method. This was the case in spite of the fact that the ambient temperature during field testing was 20°F below the sample temperature of 58°F. Table 19 shows that the results of the scrubber measurements by the OSDD method agree (within 25%) with the ISDD (reference) method in only those two cases (Saran and Mylar bag samples) in which the bags were pre-conditioned.

TABLE 17

EFFECT OF SAMPLE HUMIDITY ON MEASURED ODOR

	Sample Humidity,* lbs H ₂ O/lb dry air	Dewpoint, °F	Dynamic Odor Units, per ft ³ of undiluted sample
Without pre-dilution	0.0092	53	220
With pre-dilution (D _f =4)	0.0030	25	310

* Measured psychrometrically.

TABLE 18

EFFECT OF PRE-CONDITIONING ON MEASURED ODOR

	Temperature, °F		Dynamic Odor Units	
	Scrubber Exhaust	Ambient	OSDD	ISDD
<u>Without</u> pre-conditioning	58	38	120	250
<u>With</u> pre-conditioning	58	38	280	250

Source: Scrubber Outlet

Sample Container: 100-liter Saran bag

TABLE 19

EFFECT OF SAMPLE CONTAINER MATERIAL AND PRE-CONDITIONING ON MEASURED ODOR

Container Material	Ease of Handling	Sample Retention	Pre-conditioned?	Dynamic Odor Units Measured	
				On stored sample (OSDD)	On live sample (ISDD) method
Saran (100-1 bag)	Needs protection from wind & sharp objects	Tears easily; leaks excessively	Yes	1200 (TRC)*	1200
Mylar (100-1. bag)	Needs protection from wind & sharp objects.	Sealed edges may crack under mechanical & temp. stress	Yes	1300 (TRC)	1050
Tedlar (75-1. bag)	Needs protection from wind & sharp objects.	Excellent	No	410 (TRC)	1400
Polyethylene 19-liter "cubitaier"	Very convenient to use.	Excellent	No	280 (TRC) 330 (IITRI)	1400
Stainless Steel evacuated (16-1. bomb)	Very convenient to use.	Excellent	No	490 (TRC)	1400
Glass, evacuated (0.25-1. tube)	Very convenient to use.	Breakage risk	120 o.u. by OSDD Method. Insufficient sample for OSDD Test (limited to OSDD Method).		1400

- Notes: (1) All samples were taken from scrubber inlet stream without pre-dilution.
 (2) Gusty winds prevailed at time of sampling.
 (3) Samples were serially collected over a 45-minute period during which time odor concentrations in the gas stream being sample may have changed significantly.
 (4) Bag thicknesses: Saran - two 1-mil layers bonded together (total thickness 2 mils); Tedlar and Mylar - 2 mils; Polyethylene - 23 mils.

*Where two values are reported, one (marked TRC) was obtained using TRC's dynamic dilution system, with yes or no response given by 8-member panel; the other value (marked IITRI) was obtained using the dynamic olfactometer developed by IITRI, with forced choice (1 out of 3) made by the same 8-member panel.

We have experimented in the field with small glass containers, to see whether representative rendering odor samples can be taken for OSSD measurements according to ASTM method D 1391-57. Pre-diluted ($D_f = 4$) scrubber exhaust samples were taken into 100-ml syringes and also into 250-ml gas sampling tubes. Pre-conditioning of the syringe was done by filling it with sample, holding for 30 seconds, then expelling the sample. The sampling tube (initially evacuated) was pre-conditioned by letting a sample fill the void space and holding the sample for 30 seconds before purging through the final sample for an additional 30 seconds (at a flow rate of 20 LPM), then closing both stopcocks to retain the final sample. The results of odor measurements are presented in Table 20 below.

The results indicate that pre-conditioning of glass containers has a proportionately greater effect on odor measurement results than in the case of other container materials. It may be that not only does physical adsorption of odorants take place on the glass surface but additional amounts of odorants may condense out on the cold (near freezing) glass surface as the odor sample is chilled by the thick glass walls. If indeed this is the case, pre-conditioning may greatly over-correct the odor content of the sample, especially when ambient temperatures are low.

It is clear from the results of both field and laboratory tests, that pre-conditioning is absolutely essential in order to provide a reasonably representative sample of a rendering plant emission.

VIII-1.3 Sample Container Material

The different sample container materials listed in Table 19 were evaluated with regard to the following characteristics:

- a. ease of handling during and after sampling;
- b. ability to physically retain the sample up to the time of odor measurement;
- c. affinity for odorants by adsorption, as determined by comparison of odor measurement results of stored samples with results of analyses by the ISDD (reference) method at the time of sample collection.

VIII-1.4 Sample Container Size and Shape

Having determined that odorants found in rendering plant emissions tend to adsorb on container surfaces, it can easily be concluded that the degree of odor removal from the sample by adsorption depends upon the surface area to which a given amount of sample is exposed. This conclusion is verified by the data in Table 21 which shows the effect of the size of the Saran bags on the measured odor (ASTM method).

With pre-conditioning, previously shown to be a requirement for collecting a representative odor sample, the sample in the smaller bag ($S/V = 10 \text{ ft}^{-1}$) had a measured odor concentration nearly twice

TABLE 20
ODOR SAMPLING CHARACTERISTICS OF
SMALL GLASS CONTAINERS

Sample Source: Scrubber Outlet
 Pre-dilution: $D_f = 4$

Container Type	100-ml syringe		250-ml gas tube	
Pre-conditioned?	No	Yes	No	Yes
Odor Units (ASTM)	48	270	80	640
Ambient temperature	34°F		34°F	

TABLE 21
EFFECT OF BAG SIZE ON MEASURED ODOR

Source: Scrubber Inlet. No pre-dilution.
Bag material: Saran

Bag Size	Bag Shape	Ratio of Surface to Volume, S/V	Odor Units			
			Without Pre-Cond.		With Pre-Cond.	
			OSDD	OSDD	OSDD	OSDD
5.5 l. = 0.2 ft ³	Square 12" x 12"	10 ft ² per ft ³	150	-	640	-
100 l. = 3.5 ft ³	rectangular 24" x 48"	4.5 ft ² per ft ³	210	750	330	1200

TABLE 22
SURFACE TO VOLUME RATIOS OF VARIOUS
SAMPLE CONTAINER SHAPES

Shape	Expression for S/V, ft ⁻¹	Dimensions for Stated S/V Values		
		S/V=2.5 ft ⁻¹	S/V=5 ft ⁻¹	S/V=10 ft ⁻¹
Sphere, with diameter, <u>D</u>	6/D	D = 2.4'	D = 1.2'	D = 0.6'
Cube, with edge, <u>ℓ</u>	6/ℓ	ℓ = 2.4'	ℓ = 1.2'	ℓ = 0.6'
Cylinder, with diameter, <u>D</u> and length, <u>L</u>	$\frac{4(L/D) + 2}{L}$	@L/D = 1.5'; L = 3.2'	@L/D = 1.5'; L = 1.6'	@L/D = 1.5'; L = 0.8'
Inflated square bag, with edge, <u>a</u> and average thickness of a/6	16/a	a = 6.4'	a = 3.2'	a = 1.6'

Note: All dimensions are in feet. To convert from ft²/ft³ = ft⁻¹ to cm²/liter, multiply by 32.8.

the concentration in the larger bag ($S/V = 4.5 \text{ ft}^{-1}$). The reverse was the case without pre-conditioning. These values are masked, however, by the effects of pre-conditioning, and the variability of the OSSD results with respect to OSDD.

The shape of a container, as well as its filled volume, determine S/V , the ratio of surface to volume. Table 22 lists the expressions for S/V for some of the common shapes encountered.

VIII-1.5 Sample Storage (Aging)

All samples collected at the rendering plant were immediately taken to the heated (65-70°F) mobile laboratory. To show the effect of aging on odor measurement results, two samples of scrubber inlet gas, stored in Saran and Tedlar bags, were analyzed by both the OSDD and the OSSD methods at the time intervals shown in Table 23.

A switch from the Saran bag sample to the Tedlar bag sample was necessitated by the loss of the sample from the former by leakage. The first OSSD value reported is in doubt because the assistant presenting the odor samples to the panelists in the clean air environment of the mobile laboratory was wearing clothes contaminated by rendering odors as noted by all of the panelists.

The results indicate a decrease of odor concentration with storage time. The rate of decrease appears to be less with the Tedlar bag sample. Approximately one half of the samples collected in Saran bags had leaked completely (bag flat) within 12 hours after collection. Accordingly, unless samples are to be evaluated immediately, we conclude that Saran bags are not suitable for rendering odor - or any other - measurements because of their lack of mechanical integrity.

VIII-2 ODOR MEASUREMENT TECHNIQUES AND APPARATUS

The dynamic dilution (ISDD or OSDD) method gives consistently higher values of odor concentration than the alternate static dilution (OSSD) technique. Table 24 contains comparative data from odor measurements on field samples, using the same panel. The relationship between the odor measurements by the two techniques as a function of odor concentration, is shown in Figure 7.

Carrier Corporation has come to the same general conclusion using the Hemeon Odormeter,⁴ a basically similar dynamic dilution odor measurement device as the one used in our investigation. Through their courtesy, we are presenting their correlation graph as Figure 8. The reason for the wider divergence found by them between the results of the two techniques is partly due to differences of interpretation of panelist response data with the Hemeon method (they determined odor concentration as the dilution factor corresponding to two out of three consistently positive responses, using only three panelists) and partly due to their different interpretation on the ASTM method (Mill's adaptation).³

TABLE 23

EFFECT OF SAMPLE AGING ON RENDERING ODOR MEASUREMENT RESULTS

Source: Scrubber inlet gas

Containers: 100-liter Saran and 75-liter Tedlar, both pre-conditioned

Odor units determined by ISDD reference method at time of sampling: 1400 odor units for Tedlar bag; 1200 odor units for Saran

Time elapsed since sampling, hours	Odor Units			
	OSDD(1)		OSDD(1)	
	Saran	Tedlar	Saran	Tedlar
1 to 2	1,200	--	260(?)	--
18 to 20	510	1,400	270	410
68 to 70	*	900	200	410
164 to 166	*	860	*	310
260 to 262	*	600	*	330

* Saran bag sample lost by leakage through bag.

TABLE 24

COMPARISON OF ODOR MEASUREMENT RESULTS OBTAINED
BY STATIC AND DYNAMIC TECHNIQUES

Sample Source	Odor Dilution Ratio, Odor Units per Ft ³		
	ISDD	OSDD Units	OSSD Units
Scrubber inlet	1,200	750	210
	1,400	1,200	330
	1,050	510	270
	1,400	1,400	610
	1,400	900	410
	1,200	860	310
	1,050	600	330
Scrubber outlet	250	260	75
	360	310	100
	250	250	55
	380	410	105
Cooker non-condensibles	12,000	11,500	10,000
	12,000	11,000	11,000
	9,600	9,600	8,000

RELATIONSHIP BETWEEN OS/DD AND OS/SD ODOR MEASUREMENT RESULTS.

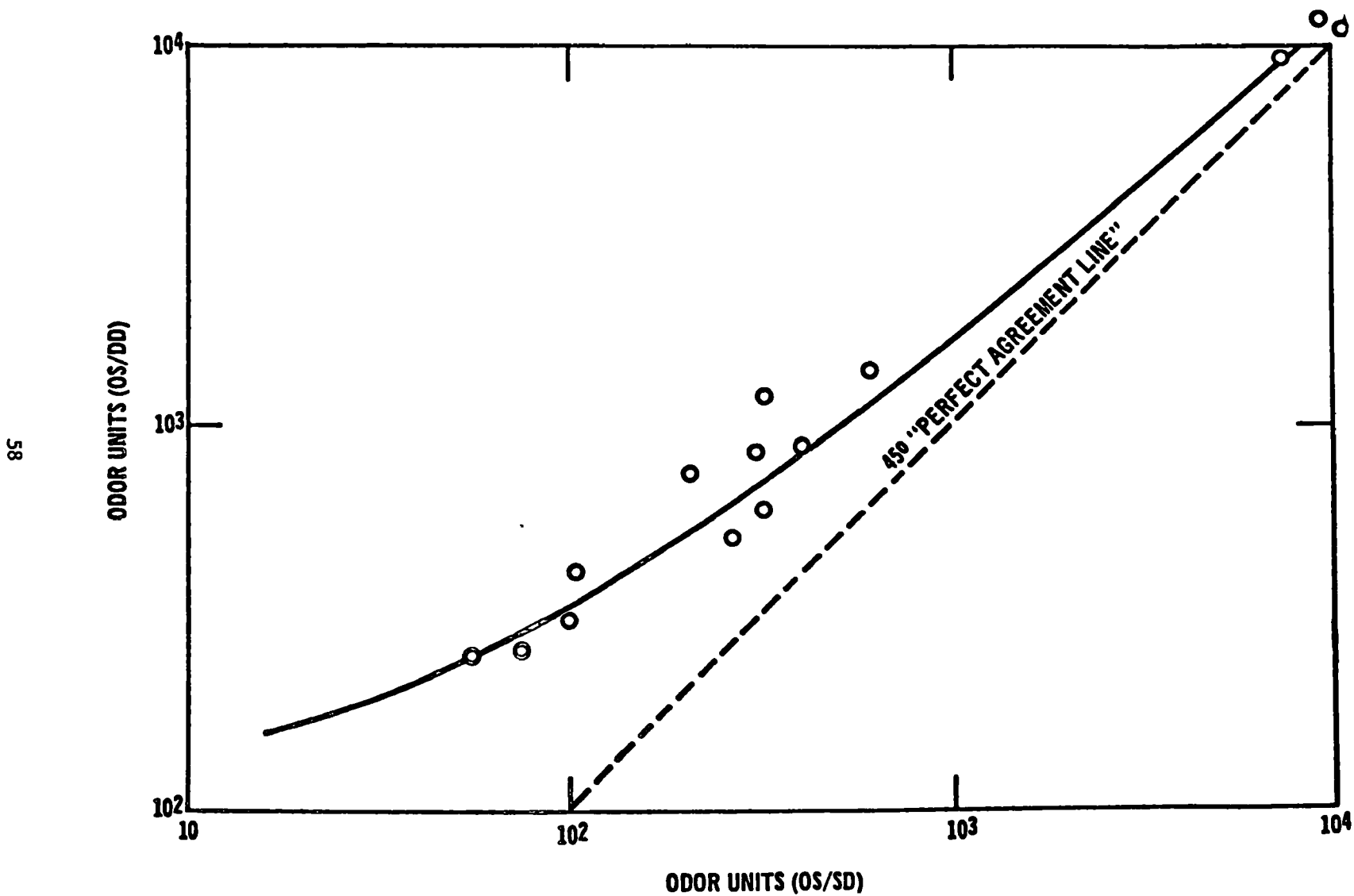


FIGURE 7

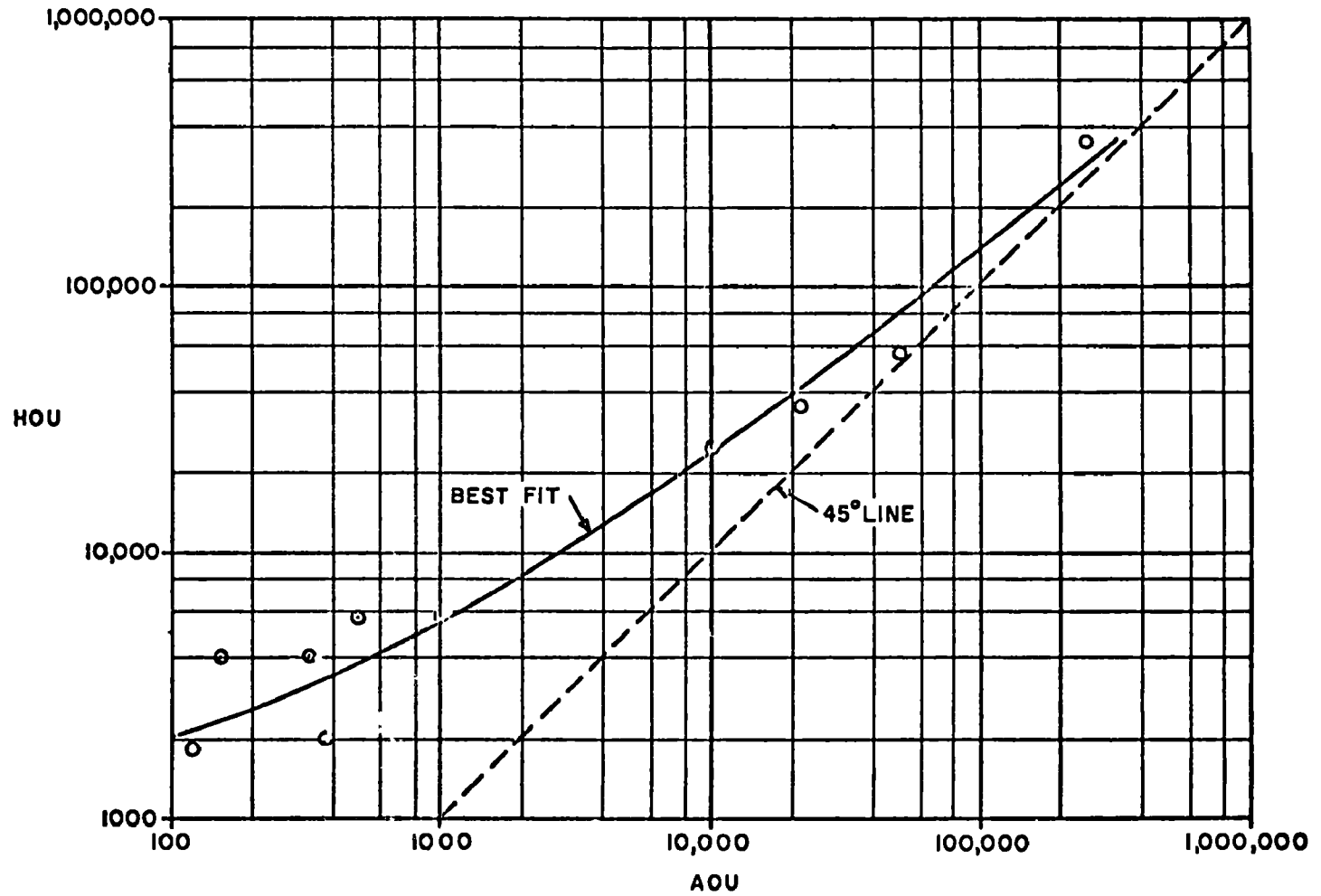


FIGURE 8
COMPARISON OF ODOR MEASUREMENT TECHNIQUES
ASTM ODOR UNITS PER CUBIC FOOT (AOU) vs
HEMEON ODOR UNITS PER CUBIC FOOT (HOU)

Courtesy of Carrier Corporation

Yet another dynamic dilution apparatus was evaluated in conjunction with our field tests. Dr. Andrew Dravnieks from the IIT Research Institute and Mr. William Prokop of the National Renderers Association have made odor measurements using their jointly developed dynamic Olfactometer with our panelists on five samples and two "live" streams which were also analyzed by our ISDD reference technique. Results of our comparative analyses are presented in Figure 9. Our two sets of dynamic odor measurements results agree within about 50 per cent. Two factors may have contributed to the divergence of the two sets of results: the difference in the manner of responding by the panelist (forced choice of one by the triangle method in the IITRI case - yes or no response in TRC); and the much lower flow rate of the diluted odor stream being presented to the panelist (0.5 l/min through small ports with the IITRI apparatus - 4 l/min through large ports with TRC system). The close agreement is still surprising, considering that we measured the rate of inhalation of panelists during odor sniffing to be in the range of 0.8 to 3 l/min. We did observe, however, that panelists automatically reduce their rate of inhalation to adjust to the lower rate of supply of odor sample.

VIII-3 INVESTIGATION OF INSTRUMENTAL MEASUREMENT TECHNIQUES FOR MEASURING ODORANTS IN RENDERING PLANT EMISSIONS

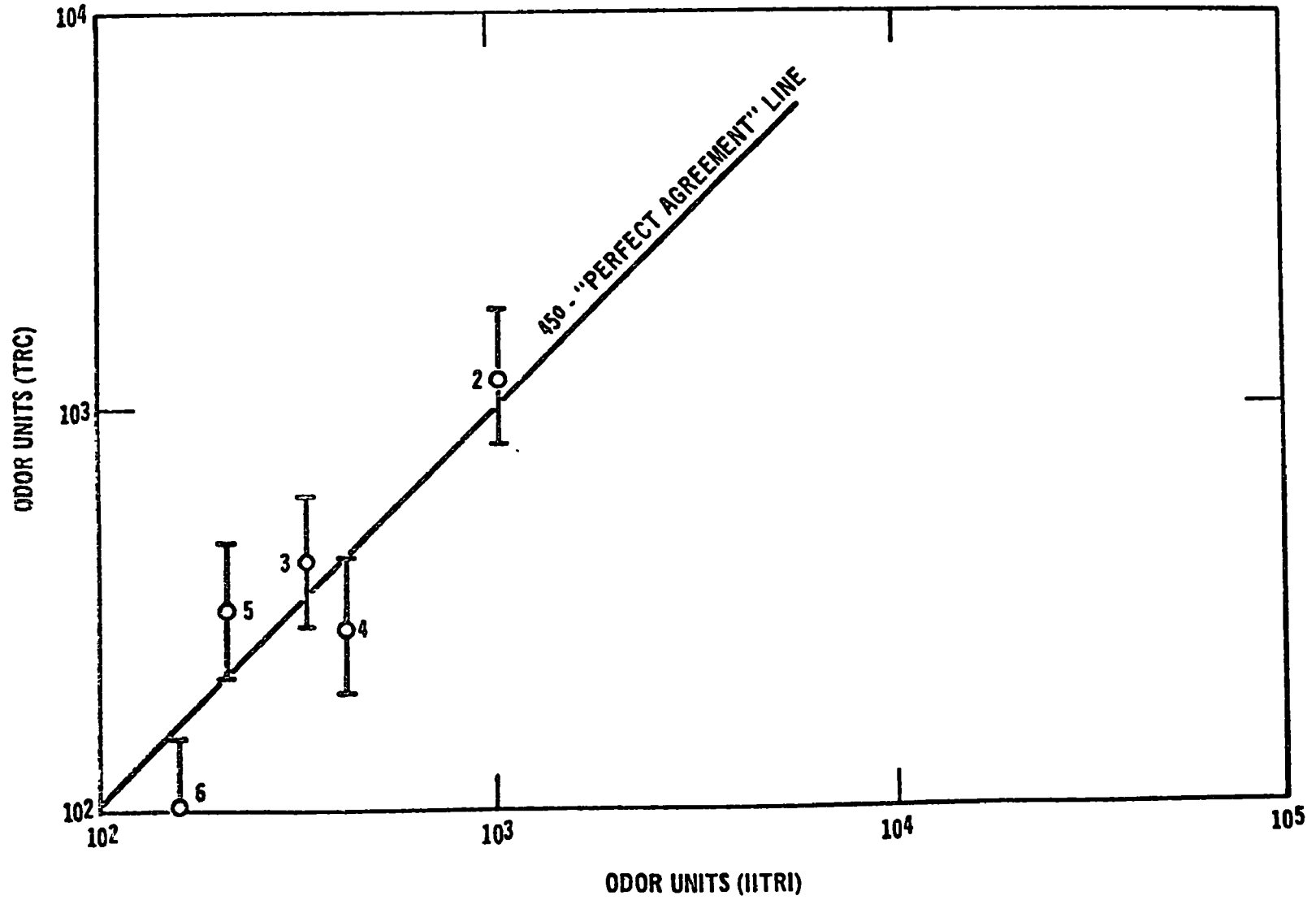
This task has as its objective the establishment of a correlation between odor levels and chemical or physical parameters. The ultimate objective of this would be to use a chemical or physical test to be used at the compliance level for odor testing. With this end in mind both chemical and odor measurements were made on-site as well as off-site. The odor measurements were made by both static and dynamic techniques.

A trip was made to the rendering plant on Friday, March 23, 1973. Infrared measurements at two wavelengths were made on samples which were simultaneously presented to the panel for odor analyses. Analysis for carboxylic acids (as butyric acid) at $\lambda = 3.35$ gave very strong signals. Sulfides, as methyl disulfide, was measured at 10.5μ in air. It was not possible to analyze for amines in air. The largest absorption peak (at 14.2μ) was overlapped by a strong CO_2 peak while the other peaks were of little value due to absorption of water vapor. These results were obtained using the Wilks Miran Infrared spectrophotometer with a 20-meter cell. Results are summarized in Table 25 and Figures 10 and 11.

Because of the fluctuation of odor level on "live" streams bag samples were also brought back for infrared spectrophotometric and other instrumental analyses. These 7 infrared analyses are summarized in Table 26 for dynamic dilution. Similar data for static dilution are given in Table 27.

The values given as ppm butyric acid and ppm methyl disulfide were obtained using the instrument reading and the calibration graphs obtained with the pure compounds. The values given in this report for IR active compounds calculated as either butyric acid or methyl disulfide depending on the wavelength used for the analysis.

COMPARISON OF ODOR UNITS OBTAINED BY DYNAMIC DILUTION



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ODOR UNITS (IITRI)

FIGURE 9

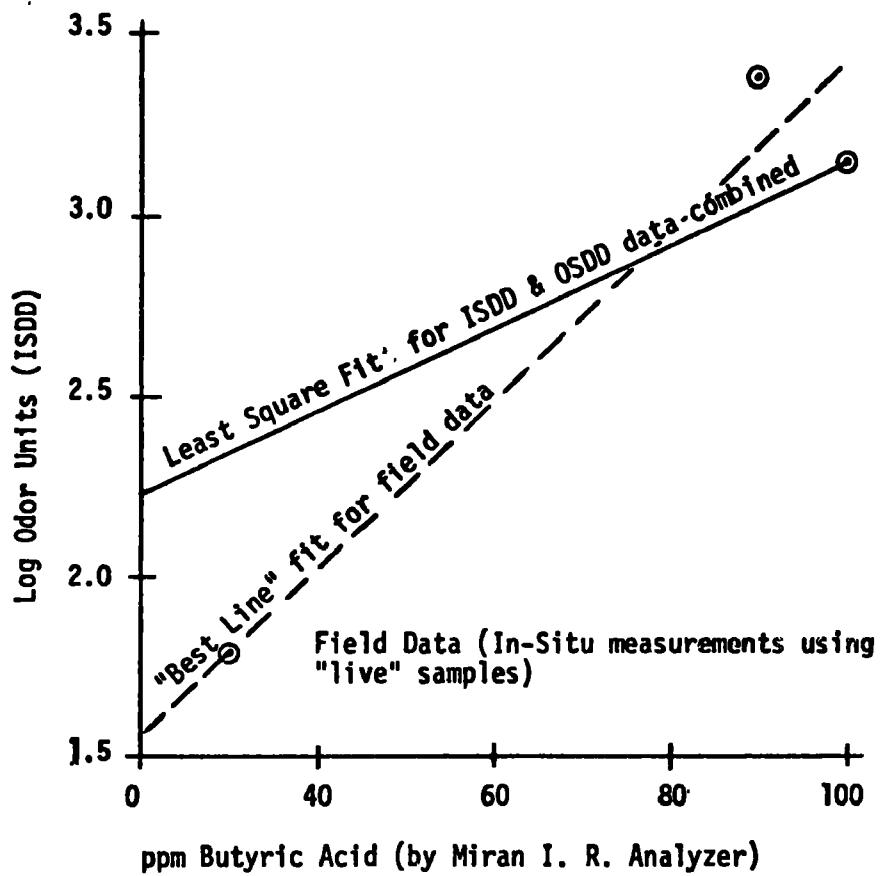


FIGURE 10

CORRELATION BETWEEN RENDERING ODOR UNITS (ISDD) AND BUTYRIC ACID CONCENTRATION

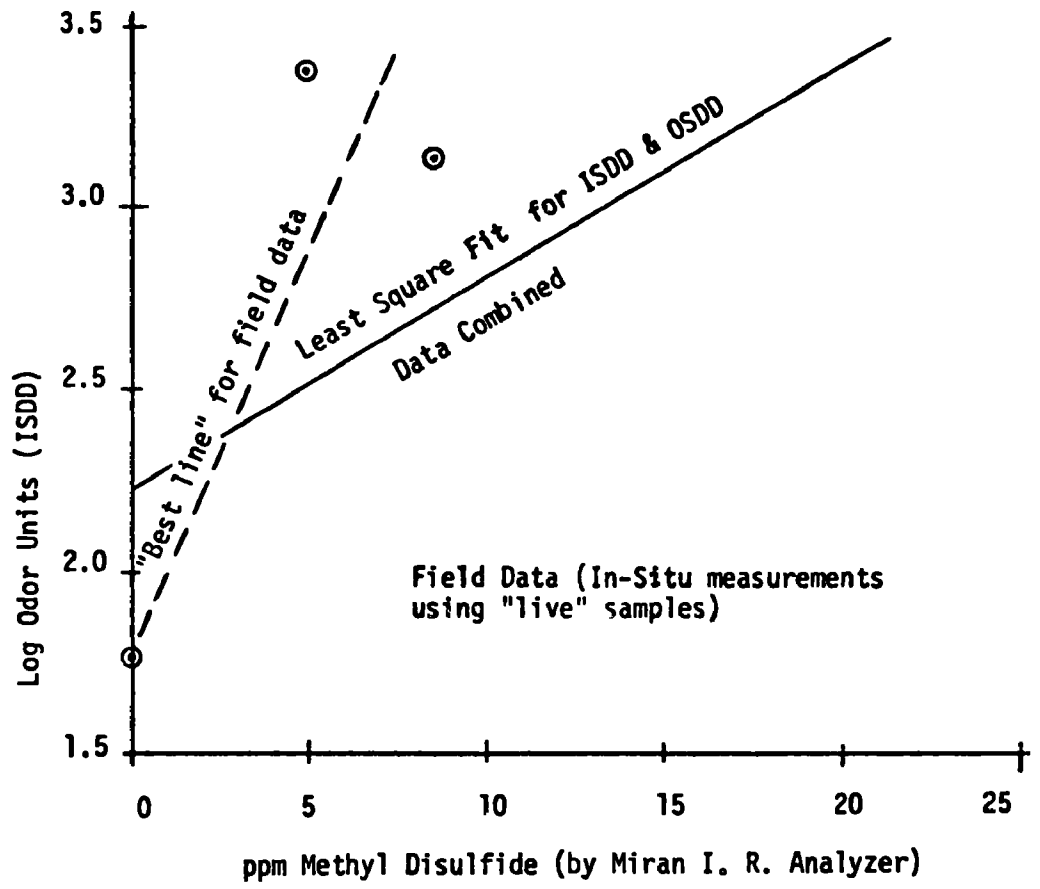


FIGURE 11

CORRELATION BETWEEN RENDERING ODOR UNITS (ISDD) AND METHYL DISULFIDE CONCENTRATION

TABLE 25
SUMMARY OF ON-SITE ODOR
AND CHEMICAL MEASUREMENTS

Source	On-Site Dynamic Dilution Odor Units	ppm Butyric Acid
I	62.5	10
II	1400	100
III	2400	90

Analyses for sulfur compounds yield the following results:

Source	Odor Units	ppm Methyl Disulfide
I	62.5	0
II	1400	8.5
III	2400	5

TABLE 26
 SUMMARY OF CORRELATION DATA BETWEEN
 DYNAMIC ODOR UNITS AND CHEMICAL MEASUREMENTS

Odor Units	Log Odor Units	ppm Butyric Acid	ppm Methyl Disulfide
62.5	1.795	10	0
65.0	1.813	2	5.0
208	2.318	2	5.0
410	2.613	100	8.5
860	2.935	8	7.0
1050	3.021	100	8.5
1200	3.079	100	8.5
1400	3.146	100	8.5
2400	3.380	90	5.0
2750	3.439	60	23.0
Average	2.753	61.2	7.9
Standard Deviation	0.599	48.1	5.9

TABLE 27
 SUMMARY OF CORRELATION DATA BETWEEN
 STATIC ODOR UNITS AND CHEMICAL MEASUREMENTS

Odor Units	Log Odor Units	ppm Butyric Acid	ppm Methyl Disulfide
23	1.362	2	5
260	2.415	8	7
900	2.954	8	7
2750	3.439	60	23
Average	2.542	19.5	10.5
Standard Deviation	0.891	27.1	8.4

In order to determine if there was, in fact, a correlation between the chemical data taken and the observed odor levels, all of the data taken were treated by the least squares method. When the log of the odor level was plotted versus the concentration of the odorant measured a straight line was obtained. As a test of the extent of correlation between the two variables, the correlation coefficient was calculated. The quantity Γ , called the coefficient of correlation, varies between 0 and ± 1 . The correlation between the butyric acid data and the log of the odor units was better than that of the methyl disulfide data. The combined correlation coefficient using both sets of data was found to be 0.87 indicating a fairly high degree of correlation. Equations were developed which relates the log of the odor level with the measured values for the concentrations of butyric acid and methyl disulfide, either single or combined:

$$\text{only methyl disulfide} \quad \log \text{ o.u.} = 2.24 + 0.06 (\text{ppm methyl disulfide})$$

$$\text{only butyric acid} \quad \log \text{ o.u.} = 2.24 + 0.009 (\text{ppm butyric acid})$$

The combined data obtained by the use of simultaneous equations is:

$$\log \text{ o.u.} = 1.68 + 0.007 (\text{ppm butyric acid}) + 0.09 (\text{ppm methyl disulfide})$$

The calculated correlation coefficients for these data are as follows:

$$\text{for butyric acid only} \quad \Gamma = 0.76$$

$$\text{for methyl disulfide only} \quad \Gamma = 0.64$$

These yield a calculated overall coefficient of correlation of = 0.87. These data are plotted and summarized in Figure 12.

The corresponding data obtained for static dilution measurements are shown in Table 27, and in the following equations:

$$\text{for butyric acid only} \quad \log \text{ o.u.} = 2.07 + 0.02 (\text{ppm butyric acid})$$

$$\text{for methyl disulfide only} \quad \log \text{ o.u.} = 1.70 + 0.08 (\text{pp. methyl disulfide})$$

The corresponding correlation coefficients are as follows:

$$\text{for butyric acid only} \quad \Gamma = 0.74$$

$$\text{for methyl disulfide only} \quad \Gamma = 0.75$$

Four bag samples brought back from the rendering plant were also analyzed by means of a Meloy Laboratories sulfur-hydrocarbon analyzer. The results of these analyses are presented in Table 28, and plotted in Figure 13.

When the values for ppm SO_2 were plotted versus the odor number (on semi-log paper) we found a correlation coefficient of 0.911 exists

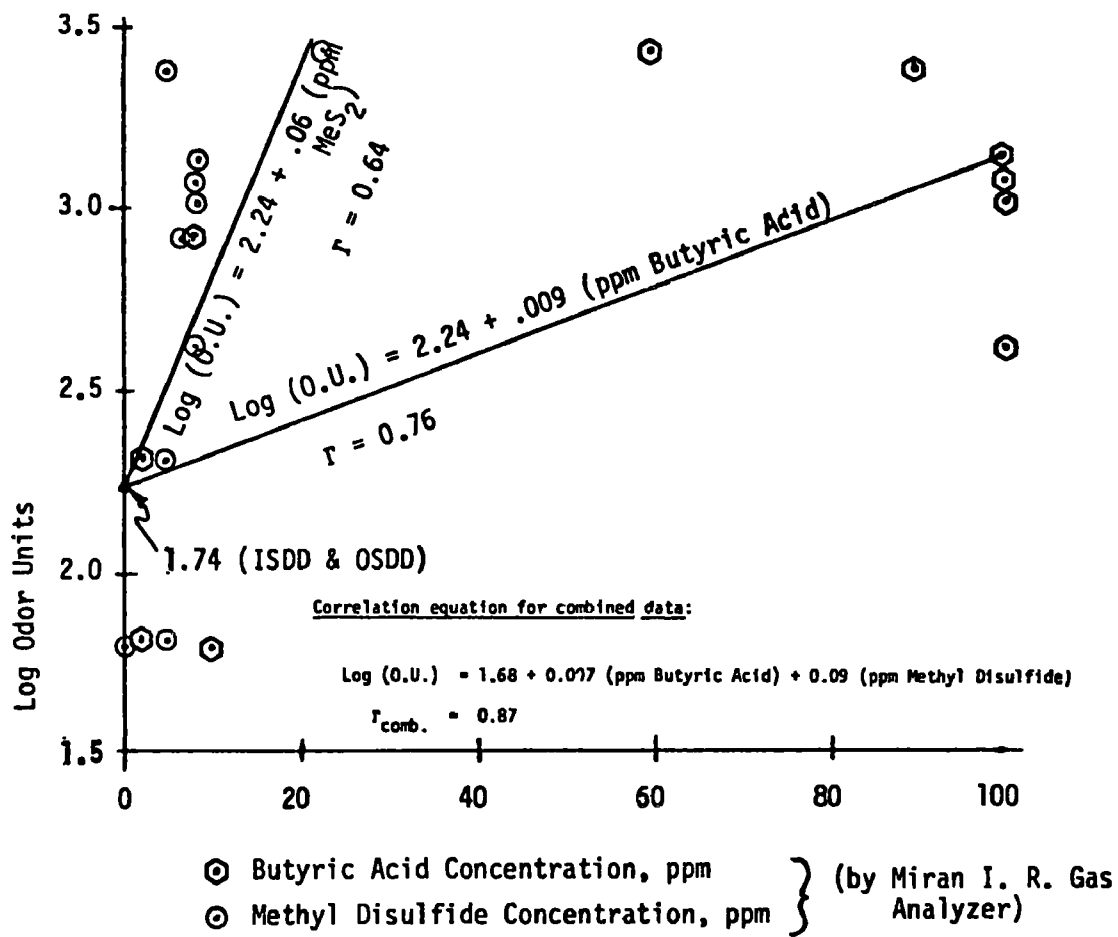


FIGURE 12

CORRELATION BETWEEN COMBINED FIELD AND OFF-SITE (ISDD AND OSDD) RENDERING ODOR UNITS AND ODORANT CONCENTRATION MEASUREMENTS

TABLE 28

DATA FOR CORRELATION OF ODOR UNITS WITH TOTAL SULFUR

Source	Bag #	ppm SO ₂	Odor Units	Log Odor Units
I	1-T-100A	0	260	2.415
II	2-T-100A	.067	860	2.935
II	2-T-100B	.146	1400	3.146
III	3-S-5A	.269	1975	3.297

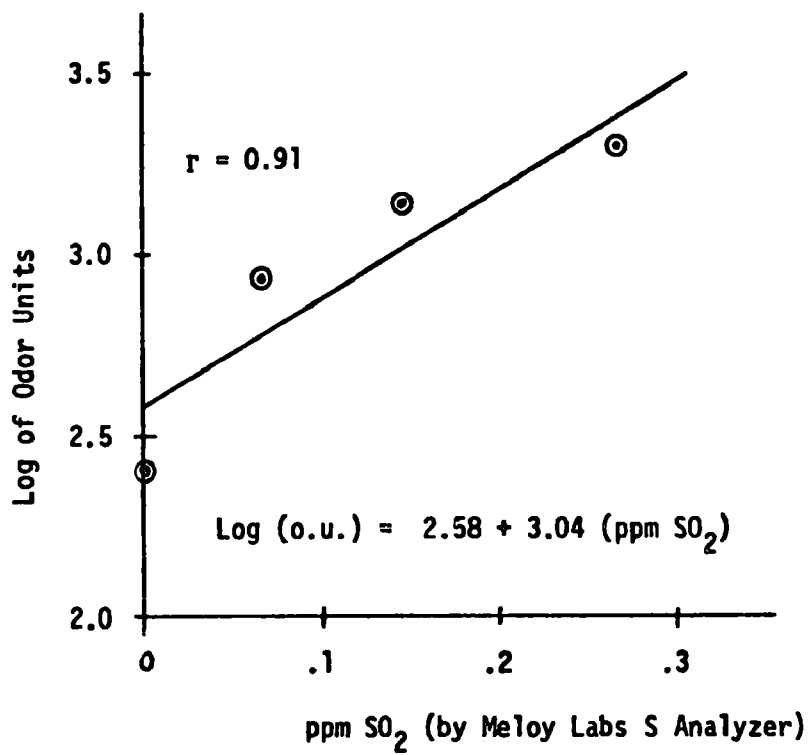


FIGURE 13

CORRELATION BETWEEN RENDERING ODOR UNITS
AND
TOTAL SULFUR (AS SO₂)

between the log of the odor units and the observed values for total sulfur, as ppm SO₂. The least squares line corresponding to the above data is:

$$\log \text{ o.u.} = 2.58 + 3.04 (\text{ppm SO}_2).$$

These data indicate that the variance in odor units (by dynamic dilution) related to the fluctuations in total sulfur is about 80 per cent, and slightly less for combined infrared absorption. This is certainly adequate to use total sulfur monitoring of rendering plant emissions for odor monitoring. As the constants in the regression equations show, neither correlation is applicable to dynamic odor unit values below approximately 300 dynamic odor units, equivalent to approximately 50 ASTM odor units.

SECTION IX

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SECTION X

APPENDICES

A.	Tentative Method for Syringe Dilution-to-Threshold Odor Measurements	73
B.	Procedure for Generating "Standard Rendering Mixture	100
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APPENDIX A

TENTATIVE METHOD FOR SYRINGE DILUTION-TO-THRESHOLD ODOR MEASUREMENTS

This modification of the ASTM 1391-57 syringe method is a tentative method only, developed specifically for the purposes of this contract. It is not a procedure recommended by the Environmental Protection Agency as a standard technique. However, because this was the procedure used for the off-site static dilution measurements (OSSD) in this study, the method is described in detail in this Appendix.

A-I PRINCIPLE AND APPLICABILITY

A-I.1 Principle

A grab sample of gas is extracted from the emission source to be measured and is diluted with odor-free air until a dilution is achieved in which the odor can barely be perceived. The ratio of the total volume of the diluted sample to the volume of original sample taken for dilution is a measure of the odor potential of the original sample. The technique is not intended to identify individual odor-causing materials or their concentrations, and does not take into account the character of an odor.

A-I.2 Applicability

This method is applicable for the determination of odorous emissions from stationary sources only when specified by the test procedures for determining compliance with the New Source Performance Standards.

A-II RANGE AND SENSITIVITY

A-II.1 Range

The lower limit of this method is that dilution factor (volume of the final diluted sample divided by the volume of the original undiluted sample contained therein) of odor which can just barely be perceived (odor threshold). The normal upper limit is a dilution factor of 100,000, although the range could be extended.

A-II.2 Sensitivity

The sensitivity depends upon the human olfactory sense and is subject to variations of this sense from person to person exposed to the same odorant; or in the same person exposed to various odorants.

A-III INTERFERENCES

A-III.1 Extraneous odors interfere in the test and all foreign odors must therefore be eliminated from the test environment. Hands and clothing of the observers and panelists, and any necessary equipment, must be clean and odor-free.

A-III.2 Colds and other physical conditions affecting the sense of smell will interfere with the panelists' perception of odors. Use of tobacco and gum or even eating can effect the sense of smell and shall not be indulged in for at least 30 minutes prior to the evaluation of odors. To avoid fatigue of the olfactory sense, the panelist shall carry out the odor test for no longer than fifteen minutes at a time, with a fifteen minute rest period between observations.

A-III.3 Some aromatic compounds desensitize the olfactory response and will cause erratic results. Longer rest periods between tests help alleviate this problem.

A-IV PRECISION AND ACCURACY

A-IV.1 The precision and accuracy of this method depends on the number, physical condition, experience and skill of the panelists. Consistent and reproducible results have been obtained with a panel of at least eight qualified observers. Any single panelist should be able to attain results that are reproducible within ± 50 per cent on any given day.

A-V APPARATUS

A-V.1 Sampling

A-V.1.1 Sampling Bag Assembly (Figure A-1)

- A-V.1.1.1 Rigid airtight container - Large enough to hold inflated bag.
- A-V.1.1.2 Cover - Constructed from 1/4 inch thick transparent plastic such as Plexiglas*, Lucite, Lexan, or equivalent.
- A-V.1.1.3 Cover gasket - Made from 1/16 inch thick rubber bonded to the cover or the rigid container.
- A-V.1.1.4 Bag - Shall be made from flexible FEP Teflon, heat sealed, about 10 by 12 inches.
- A-V.1.1.5 Bag attachment - Stainless steel bulkhead female connector, Swagelock Part No. 400-71-4-316, or equivalent.
- A-V.1.1.6 Vacuum pressure attachment - Brass bulkhead female connector, Swagelock Part No. 400-71-4, or equivalent.
- A-V.1.1.7 Attachment gaskets - Three Teflon, or equivalent, gaskets 1/16 inch thick, 7/16 inch inside diameter by 3/4 inch outside diameter.
- A-V.1.1.8 Pump - Vacuum/pressure pump, or equivalent, to alternately evacuate and pressurize the rigid container.
- A-V.1.1.9 Cover bolts - 1/4 inch diameter bolts with wing nuts, or equivalent, to permit ease of cover removal and replacement.
- A-V.1.1.10 Probe - 1/4 inch outside diameter Teflon tube of suitable length to enable access to the source, but not more than six feet long.
- A-V.1.1.11 Valve - 1/4 inch stainless steel ball valve, Whitey Part No. 4254-316, or equivalent.

*Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

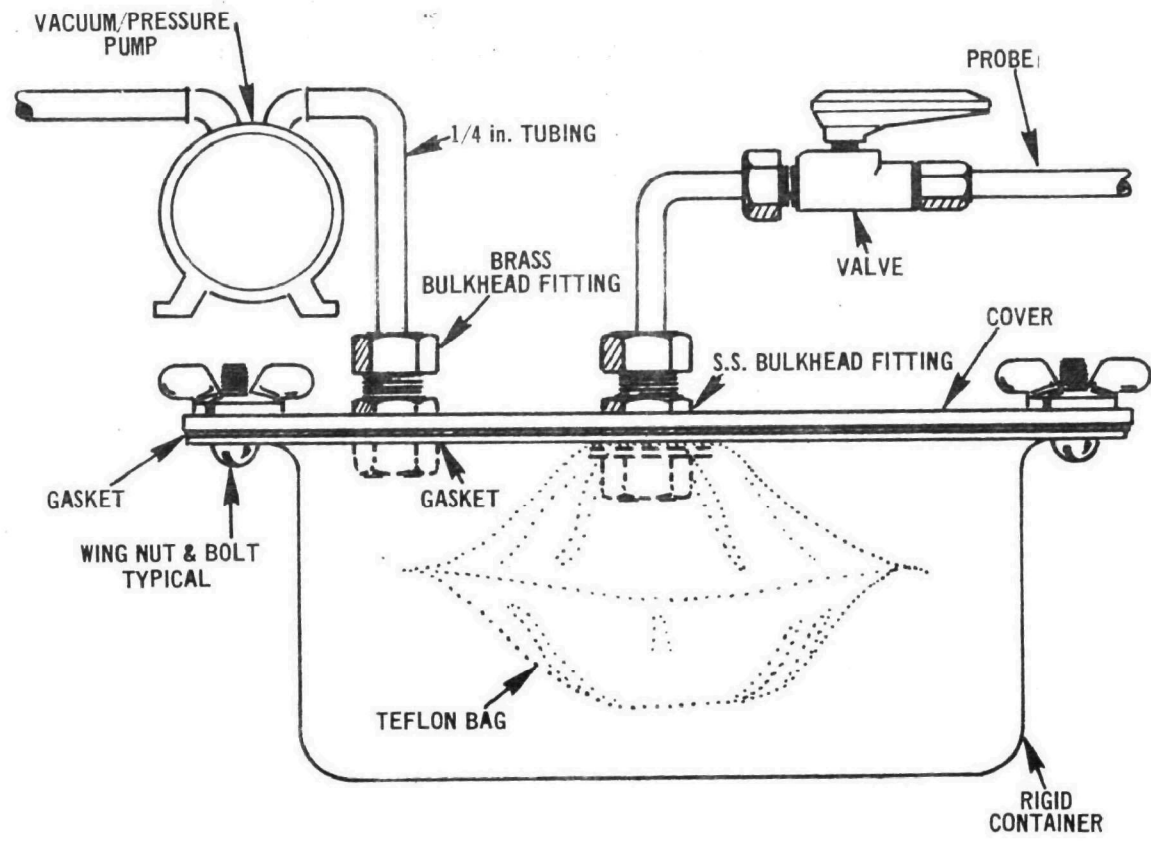


Figure A-1 Sampling bag assembly

A-V.1.1.12 Sample cap - A disc of 3/16 inch thick fluoroelastomer such as Viton A, or equivalent, to fit inside a 1/4 inch stainless steel tubing Swagelock nut, Part No. 402-1-316 or equivalent, which is used to seal off the bag attachment connector while permitting penetration and removal of a hypodermic syringe needle without leakage.

A-V.1.2 Dilution Sampling Assembly (Figure A-2)

A-V.1.2.1 Medical syringe - 10 ml Luer-type.

A-V.1.2.2 Sample tube - 250 ml glass tube with stopcocks at each end.

A-V.1.2.3 Glass capillary tube - 1 mm outside diameter, approximately 3 inches long.

A-V.1.2.4 Cork stopper, size 000.

A-V.1.2.5 Serum stopper, one.

A-V.1.2.6 Hypodermic needle, 18 gauge - two.

A-V.1.2.7 Heating tape.

A-V.1.2.8 Variable transformer.

A-V.2 Analysis

A-V.2.1 Odor-free and draft-free room - Maintained at comfortable temperature and humidity conditions. Large, well-ventilated, air-conditioned meeting rooms are often used.

A-V.2.2 Dilution syringes - Two or more 100 ml. Luer-type hypodermic syringes per panel member.

A-V.2.3 Transfer syringes - Two or more 2 ml Luer-type hypodermic syringes and one 100 ml Luer-type hypodermic syring.

A-V.2.4 Transfer needle - A fitting for connecting the transfer syringe with the dilution syringes, made from two standard 25 gauge hypodermic needles, 1-1/2 inches long (available from Becton-Dickinson and Company, Rutherford, New Jersey). The mating head of one needle is cut off at a point where its inside bore is equal to the outside diameter of the needle shaft. The mating head is slid over the other needle, with the mating opening toward the tip of the needle, and silver soldered in place (Figure A-3).

A-V.2.5 Syringe caps - One Luer syringe cap for each syringes

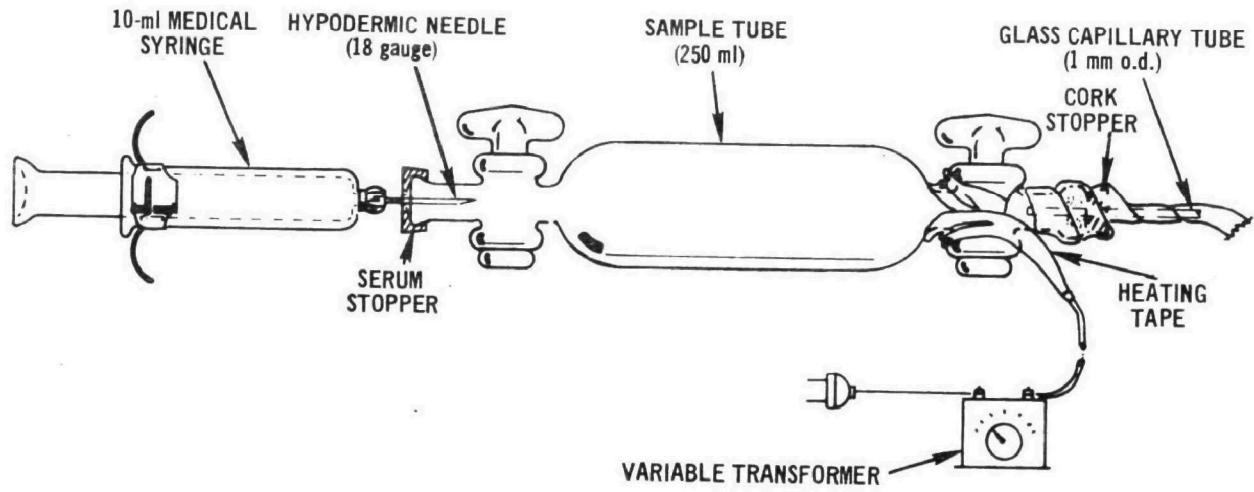


Figure A-2 Odor sampling equipment for dilution sampling

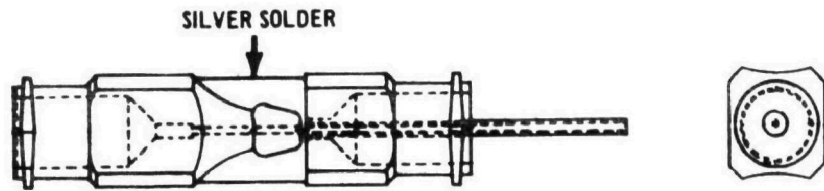


Figure A-3 Transfer needle

A-VI REAGENTS

A-VI.1 Odor-free air.

A-VI.2 Vanillin - 1.0 per cent in benzyl benzoate.

A-VI.3 Methyl Salicylate - 1.0 per cent solution in benzyl benzoate.

A-VII PROCEDURE

All syringes, transfer needles, sample bags or other equipment used in this procedure contacting the sample must be thoroughly washed with an unperfumed detergent, rinsed thoroughly in odor-free tap water or distilled water, and allowed to dry in the test room atmosphere for at least 15 minutes.

A-VII.1 Sampling

The stack gas sample shall be maintained at a temperature higher than its dewpoint at all times prior to analysis in order to prevent condensation of moisture in the sample. The sampled gas must be diluted with odor-free, dry air as specified in paragraph A-VII.1.2 if the gas sample cannot be maintained above its dewpoint temperature. Necessity of dilution of the sample gas or the minimum amount of dilution required to prevent condensation shall be determined by the following criteria:

Calculate the dilution factor, D_f , using equation A-1.

$$D_f = \frac{B_{wo}}{B_{wa}} \quad \text{Equation A-1}$$

where:

D_f = dilution factor, dimensionless, (ratio of the volume of the final diluted sample gas to the volume of the undiluted stack gas)

B_{wo} = proportion by volume of water vapor in stack gas

B_{wa} = proportion by volume of water vapor present in saturated air at the ambient temperature

If D_f is equal to or less than one, stack gas dilution is not required.

If D_f is greater than one, dilution of the stack gas is necessary to a minimum dilution factor of one.

A-VII.1.1 **Sampling Without Simultaneous Stack Gas Dilution (Bag Method)** - Set up the equipment as shown in Figure A-1, making sure all connections are tight. Place the probe in the stack at a sampling point and purge the sampling line, including the valve, using a vacuum

pump or equivalent. Connect the purged line to the sampling bag assembly. Draw sample into the bag by evacuating the rigid container with the pump until the bag is expanded without stretching. Close the valve and remove the sample probe. Disconnect the vacuum pump and allow the container to come to atmospheric pressure. Remove the sample line and quickly close the sampling bag attachment with the sample cap and transport the assembly to the odor evaluation room.

A-VII.1.2 Sampling with Simultaneous Stack Gas Dilution

The following sampling techniques shall be used when stack gas dilution is necessary.

A-VII.1.2.1 Dilution with Positive Stack Pressure

Equipment used for dilution sampling is diagrammed in Figure A-2. Dilution air is first drawn through a cartridge charged with activated carbon and a suitable desiccant to fill the sample tube. The 1 millimeter outside diameter capillary tube used as a probe is inserted through a new, size 000, cork stopper with the aid of an 18-gauge hypodermic needle as a sleeve. The sample is obtained by placing the free end of the capillary into the stack gas stream and withdrawing the required 5 to 10 milliliters of air from the sample tube with the 10-millimeter syringe. The volume withdrawn is replaced by an equal volume of sample which enters through the capillary tube. The small diameter of the capillary minimizes diffusion across the tube. When equilibrium conditions are established, the other stopcock is closed and the final displacement of the medical syringe is noted.

A-VII.1.2.2 Dilution with Negative Stack Pressure

The sample shall be obtained with a heated probe and vacuum pump. The probe and pump shall be maintained at a temperature above the dewpoint of the stack gas. The pump shall be a leakless, Teflon-coated, diaphragm vacuum pump, Thomas Industries, Model Number 907-CA18, or equivalent. The sample shall be taken from the discharge of the pump as described in paragraph A-VII.1.2.1.

A-VII.2 Analysis

A-VII.2.1 Sample transfer - Dilution samples are prepared by an assistant out of sight of the panel and presented to the panelists in random order to prevent possible bias. Insert the transfer needle into the sample bag through the rubber disc in the sample cap, withdraw the desired volume, V_s , into the transfer syringe, then withdraw the needle from the bag.

A-VII.2.2 Sample dilution - The assistant makes up a sample preparation sheet identifying the dilution in each master transfer syringe. Insert the transfer needle tip into the dilution syringe, which has been partially filled with odor-free air. Inject the sample volume, V_s , into the syringe to the 100 ml mark with odor-free air from the test panel room. Cap the dilution syringe and let it stand for at least 15 seconds to allow mixing by diffusion. The diluted sample is then ready for odor evaluation.

Each panel member is furnished with one syringe to test all samples. The first dilution is usually planned such that a final dilution factor of 10 is made by the panelist in his syringe. Following each test, the panel member cleans out his syringe with room air until satisfied that he is back to a clean room air reference. Extra syringes should be available in case the panel member feels his syringe has become contaminated.

When it is necessary to dilute volumes of 2 ml or less, use the 2 ml transfer syringe. When diluting volumes of less than 0.2 ml, make an intermediate dilution with a factor of 10 using odor-free air and inject a portion of this intermediate dilution into the dilution syringe. Use the 100 ml transfer syringe for diluting volumes greater than 2 ml.

A-VII.2.3 Odor Evaluation - Prepare three or more samples having final dilution factors bracketing the estimated concentration (or as specified by the test procedure) in random order as described in paragraph A-VII.2.1. Members of the odor panel should uncap their syringe and (1) insert the tip of the syringe into one nostril or (2) hold the tip of the syringe near the nose. Each panel member should choose the method of smelling the sample which yields the most accurate and reproducible results for him, but as a general rule should suspend breathing for a few seconds and during this period expel the 100 ml diluted sample into the nostril or near the nose at a uniform rate over about 2-3 sec. The individual panelist should record on his worksheet, identifying the sample number, whether odor is perceived.

The assistant will calculate the odor concentration (see paragraph A-IX.1) and prepare one or more additional dilutions if desired to augment and expand the data.

The order of dilutions should be random, and at least one out of every four consecutive dilutions should be a "scramble" dilution in no way related to the fundamental trend. The "scramble" odor may range from no odor to considerably above the threshold concentration, and is used to assure that the panelist cannot anticipate what

the next concentration will be. In this way, he is forced to concentrate only on what he perceives for any given sample.

A-VIII CALIBRATION

The odor panel shall consist of at least eight persons. A group of at least twice the number of panelists required shall be screened to select neither the most nor the least sensitive individuals for panelists. The screening test consists of a "triangle" test in which two identical samples and one odd sample are presented to the prospective panelists in increasingly dilute concentrations. Each person is scored on his ability to distinguish the odd odorant from the two identical ones as dilution increases.

To conduct the screening test, prepare two identical solutions of 1.0 per cent vanillin in benzyl benzoate, and a solution of 1.0 per cent methyl salicylate in benzyl benzoate. Present these to the group in increasingly dilute concentrations until 75 per cent are unable to distinguish the odd odorant from the two identical ones. Panelists will be selected from those exhibiting average olfactory perception. The first 25 per cent (those who are first unable to distinguish the odd odorant) are not sensitive enough. The 25 per cent still able to distinguish the odd odorant are too sensitive.

A-IX CALCULATIONS

A-IX.1 Odor Concentration

A-IX.1.1 Definition

The odor responses of the panel are quantified by calculating the per cent of the panel members detecting odors at each dilution, as shown in Table A-1 for two samples (Runs 1 and 2). The ratio of the diluted volume to the original sample volume is termed the dilution factor. Odor responses are plotted against dilution factors to determine odor concentration.

Dilution response data follow a cumulative normal distribution curve. If plotted on rectilinear coordinates, these data produce an S-shaped curve. The points at the extremes of the curve would represent panelists who are the most and the least sensitive to the particular odors. The area in the middle of the curve would represent average panelist olfactory responses.

When dilution response data are plotted on logarithmic-probability coordinates, they tend to follow a straight line. This phenomenon is shown in Figure A-4, where typical test data for both samples (Runs 1 and 2) of Table A-1 are plotted. The data plot to a reasonably straight line. Maximum deviation from a straight line is principally a function of the number of panelists.

TABLE A-1

DATA FROM A TYPICAL DILUTION TEST

Run No.	Dilution Designation	Dilution Factor ^a	No. of Panel Members	No. Panel Members Detecting Odor	% of Panel Members Detecting Odor ^b
1	A	1,000	8	6	75
	B	2,500	8	4	50
	C	10,000	8	3	38
	D	5,000	8	2	25
2	A	2,500	8	5	63
	B	5,000	8	3	38
	C	10,000	8	1	13

^aThe dilution factor is the volume of the diluted sample evaluated by the panel members, divided by the volume of the original undiluted sample contained therein.

^bZero and 100 per cent responses are considered indeterminate.

The point at which the plotted line for each sample crosses the 50 per cent panel response line is the threshold concentration for that sample. The dilution factor at the threshold is the odor concentration for that sample, usually stated in terms of odor units per scf. The number of samples (runs) required are specified by the test procedure for determining compliance.

A-IX.1.2 Calculations

Summarize dilution test data for each sample as shown in Table A-1 and determine the odor concentration for each sample as described below.

A-IX.1.2.1 Graph the data for each sample on log-probability paper as shown in Figure A-4. The straight line best representing the data may be estimated visually in the field, but for the purposes of compliance the method of least squares shall be used to determine the best line fit.

A-IX.1.2.2 The point at which the line determined in paragraph A-IX.1.2.1 crosses the 50 per cent panel response line defines the odor concentration for that sample.

A-IX.2 Odor Emission Rate

Calculate the odor emission rate in odor units per minute for each run:

$$E = CVA \qquad \text{Equation A-2}$$

where:

E = Odor emission rate for each sample, odor units per minute.

C = Odor concentration for each sample, odor units per standard.

V = Velocity of stack or vent discharge for each sample, feet per minute at standard conditions.

A = Cross-sectional area of stack or vent, square feet.

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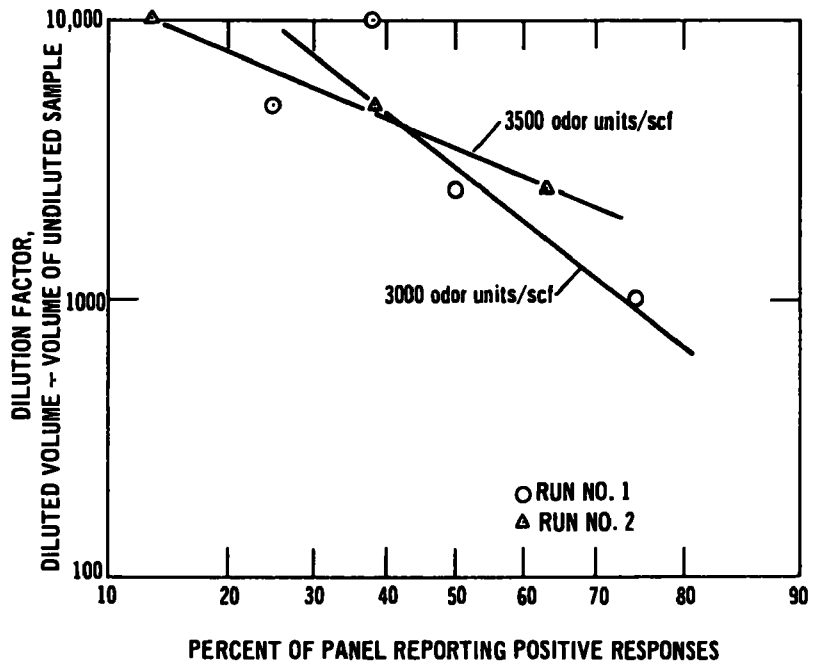


Figure A-4 Plot of dilution response data

APPENDIX B

Procedure for Generating "Standard Rendering Mixture"

Please refer to Figure B-1.

- a. Fill each of two impingers A and B (Greenberg-Smith type) with 200-ml of 0.05 wt.% butyric acid; also fill each of two impingers C and D with 0.05% methyl disulfide. The solvent for both solutions is benzyl benzoate. Place the four impingers into a constant-temperature water bath held at $70 \pm 2^{\circ}\text{F}$.
- b. Connect the four impingers and the two flowmeters (1-10 LPM range) to a small Teflon-lined vacuum pump.
- c. Allow at least two hours for solutions to come to equilibrium with air trapped inside the four impingers, at the water bath temperature of 70°F .
- d. With rotameter valves shut off, start vacuum pump.
- e. Slowly and simultaneously open the two rotameter valves and adjust both flow rates to 2.0 LPM.
- f. Use the air-vapor mixture, i.e., "Standard rendering mixture", leaving the pump for odor panel training and/or calibration.

Important: Up to a total volume of 100 liters of gaseous "standard rendering mixture" can be produced per charge of solution. Beyond 100 liters of gas volume, the odorant concentrations in solution change significantly (by about 5%), resulting in a similar decrease of odor concentration of the gas phase.

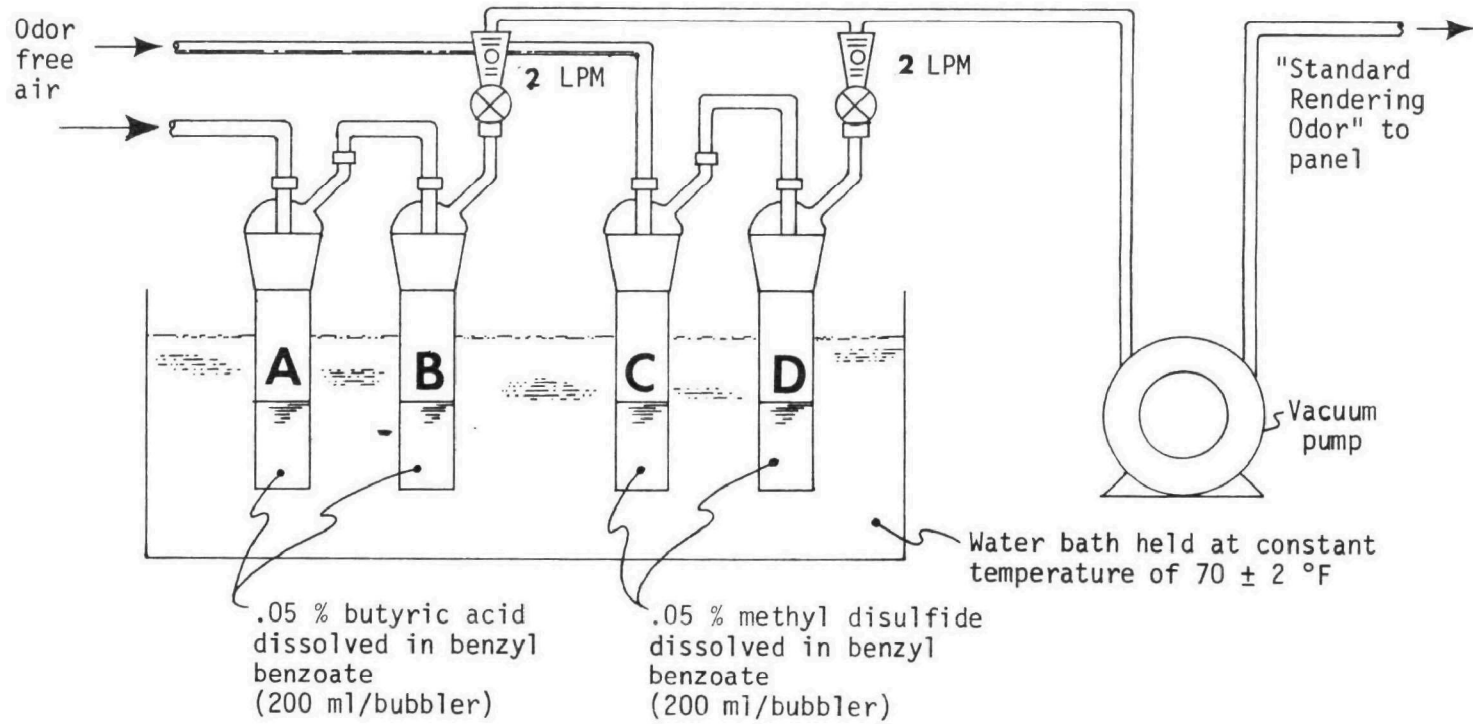


Fig. B-1 Schematic diagram of apparatus used to generate "Standard Rendering Odor".

APPENDIX C

<u>Plan</u>	<u>Item</u>	<u>Time</u>
1	Arrive at site, panel in van	12:00 noon
2	Deliver equipment to roof 3 predilution air cylinders pre-dilution system sampling line 2 vacuum pumps (metal bellows) drum sampler flashlite bags for Test 1 stainless steel tanks glass sampling tubes	12:00 to 12:45 P.M.
3	Connect tubing to van and pre-dilution system and pre-condition system (Station 1)	12:45 - 12:55
4	Precondition 2 mylar, 1 tedlar, 1 saran and 1 small (15 l) saran bags	12:55 - 1:05
5	Fill pre-conditioned saran bag (100 l) with pre-dilution system (downstream of 1st pump) identify bag as 1-s-100 A	1:05 - 1:10
6	Run in-situ dynamic dilution fill 100 l mylar bag simultaneously identify as 1-m-100 A get measurement on MIRAN on purge line dilution factors in mobile lab 1st 200:1 2nd 100:1 3rd 50:1 4th 25:1 5th 12:1 6th 6:1	1:10 - 1:25
7	Stop in-situ dynamic and fill 100 l tedlar mark it 1-t-100 A fill 1-ss-15 A 1-s-5 A 1-g-0.25 A stainless steel small saran glass syringe (disconnect pump and fill from pre-dilution)	1:25 - 1:30 1:30 - 1:35
8	Fill tedlar bag (100 l) designate as 1-t-100 B (pre-dilution downstream of pump)	1:35 - 1:40
9	Run in-situ dynamic dilution same dil. settings (adjust if necessary from 1st run but use factor of 2) fill saran (un-pre-conditioned) 1-su-100 B run MIRAN and absorption on purge	

Plan	Item	Time
10	Fill 100 l mylar bag (downstream of pump) mark 1-m-100 B	1:55 - 2:00
11	Move equipment on roof to point 2 (give panel break) except pre-dilution system. goes to Station 3	2:00 - 2:20
12	Pre-condition 3 saran, 2 tedlar, and 2 mylar and 1 small saran bag - no predilution down- stream of pump	2:20 - 2:30
13	Fill 100 l mylar bag - designate 2-m-100 A	2:35 - 2:40
14	Run in-situ dynamic system (factor of 2) purge sample line fill 100 l tedlar bag 2-t-100 A MIRAN reading on purge line	2:45 - 3:00
15	Fill 100 l saran bag (downstream of pump) connect IITRI device to sample purge line run IITRI study	3:00 - 3:15 3:00 - 3:10 3:10 - 3:30
16	Fill 100 l tedlar bag 2-t-100 B	3:30 - 3:35
17	Run in-situ dynamic dilution - run B fill 100 l mylar bag 2-m-100 B run MIRAN on purge	3:35 - 3:50
18	Fill 100 l saran bag downstream of pump 2-s-100 B fill 100 l saran upstream of pump with drum sampler 2-s-100 C	3:50 - 3:55 3:55 - 4:10
19	Take 2-s-100 B bag to van run dynamic dilution run static dilution run IITRI dilution on 2-s-100 B dynamic dilution first at site drive van to admin. bldg. panel break static test on 2-s-100 B IITRI on 2-s-100 B	4:00 - 5:30
20	Fill 2-ss-15 B 2-g-0.25 B 2-s-5 B stainless steel glass tube small saran	4:00 - 4:15
21	Move equipment to Station 3	4:15 - 5:15
22	Pre-condition 1 mylar, 1 tedlar, 2 saran bags and 1 small saran pre-diluted	5:15 - 5:30

<u>Plan</u>	<u>Item</u>	<u>Time</u>
23	Bring van back to site fill 100 l mylar bag 3-m-100 A (downstream of pump) predilution	5:30 - 5:35
24	Run in-situ dynamic fill 100 l saran bag 3-s-100 A MIRAN on purge line	5:35 - 5:50
25	Fill 100 l tedlar bag (downstream of pump) fill 3-ss-15 A 3-g-0.25 A 3-s-5 A stainless steel glass tube saran	5:50 - 5:55
26	Disconnect pre-dilution system fill 100 l saran bag directly from source through pump into bag	5:55 - 6:00
27	Remove equipment and pack and leave	6:00 - 6:30

TECHNICAL REPORT DATA
(Please read instructions on the reverse before completing)

1 REPORT NO. EPA-650/2-74-008-a		2	3 RECIPIENT'S ACCESSION NO.	
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15 SUPPLEMENTARY NOTES				
16 ABSTRACT <p>This report presents the results of investigations to establish the performance requirements for odor emission measurements for rendering plant process emissions, based on a dilution-to-threshold ratio technique. An in-situ dynamic dilution system, was used as the reference method. In this method the odorous emissions were continuously vented directly from the sample point to an eight-member olfactory panel by means of a dynamic dilution system installed in an on-site mobile odor laboratory. An identical system, installed in the laboratory, was used for off-site dynamic dilution measurements. The EPA modification of the ASTM 1391-57 syringe dilution technique was also evaluated.</p> <p>Field tests were carried out at a rendering plant in Tewksbury, Massachusetts. Samples were collected at the scrubber outlet, scrubber inlet and in the cooker non-condensable line.</p> <p>The effects of sampling factors, such as container materials, storage time (aging) of samples, etc., on the validity of odor measurements were evaluated. In addition, the effects of panel selection and training procedures, number of panelists, etc., on the accuracy and reproducibility of odor measurements were determined. Finally, correlations between chemical measurements and dynamic odor unit levels were developed.</p>				
17. KEY WORDS AND DOCUMENT ANALYSIS				
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Measurement techniques Odor Odor dilution ratio Animal Rendering Emission Measurement				
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