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STANDARDIZATION OF METHOD 11 AT A PETROLEUM REFINERY: Volume II

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Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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STANDARDIZATION OF METHOD 11
AT A PETROLEUM REFINERY

VOLUME II

by

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FOREWORD

Midwest Research Institute (MRI) under Task 6 of EPA Contract No. 68-02-1908, conducted in-house work toward the standardization of Method 11 (Federal Register, Vol. 39, pp. 9321-9323, March 8, 1974) as applied to the analysis of H_2S in petroleum refinery fuel gases. The results of this in-house work are given in Volume I of this report.

Further work on the method was done under Task 8 of EPA Contract No. 68-02-1908. This continuation of efforts was a collaborative test to evaluate the accuracy and precision of the modified Method 11. The results of the collaborative test are given in this report. The collaborators' data sheets are in Volume III.

Approved for:

MIDWEST RESEARCH INSTITUTE

L. J. Shannon, Director
Environmental and Materials
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April 4, 1977

ABSTRACT

A collaborative test was run of the revised Method 11 procedure that was developed and is reported in Volume I of this report. Ten collaborators were selected from a total of 24 interested organizations. Part of the screening process was to require each potential collaborator to analyze a set of liquid samples in accordance with the procedure.

A test manifold was constructed which could generate controlled, simulated refinery fuel gas streams using spiked natural gas. The major constituent of the stream was methane (~ 80%) with smaller amounts (in decreasing order) of ethane, propylene, nitrogen, propane, methyl mercaptan, ethyl mercaptan, sulfur dioxide, isobutane and n-butane present in addition to H_2S. Carbonyl sulfide was also used for one test.

During February 22 to 27, 1976, a total of 16 runs of three different H_2S levels were made, as well as a series of standard samples analyses. MRI then made a statistical analysis of the collaborators' results. Without mercaptans present (standard cylinder gas mixtures of H_2S in methane), results averaged 4% low with a standard deviation of 2% for any single collaborator and a standard deviation between collaborators of 4%. With mercaptans present at a total concentration equivalent to 120 mg/dscm of H_2S, precision was unaffected but the results varied from 2% low to 14% high at respective H_2S concentrations of 400 and 100 mg/dscm. The tentative procedure was found to be adequately written for those knowledgeable of sampling and analysis techniques.

This report was submitted in fulfillment of Task 8 of Contract No. 68-02-1098 by Midwest Research Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from November 1, 1975 to December 31, 1976, and work was completed as of December 31, 1976.

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ACKNOWLEDGMENTS

Task 8 was conducted under the technical management of Mr. Paul C. Constant, Jr., Head, Environmental Measurements Section of MRI's Environmental and Materials Sciences Division, who is the program manager. Dr. George Scheil was task leader. He was assisted by Messrs. John LaShelle, Bruce DaRos, Thomas Merrifield, and Michael Sharp of MRI. Texas Analytical Control, Inc., of Houston, Texas, provided the solid-state H_2S monitor used during the collaborative test.

SECTION 1

INTRODUCTION

This report covers the tests and evaluations conducted by Midwest Research Institute (MRI) of proposed methods to replace the present Method 11 procedure (Federal Register, Vol. 39, pp. 9321-9323, March 8, 1974). The testing is being done for the Environmental Protection Agency (EPA) under Contract No. 68-02-1098, "Standardization of Stationary Source Emission Measurement Methods." This report covers Tasks 6 and 8 of the contract. The first task covered the search for a method which is free of the mercaptan interference, its evaluation, and field testing of the final method. The work done on Task 6 is in Volume I of this report. Task 8 included a collaborative test of the proposed, new Method 11 and is covered in this volume (II) of the report.

A collaborative test is a procedure in which a group of persons from different laboratories conduct sampling and analysis under identical conditions using the same method. It provides information on the variability of method results between laboratories as well as the reproducibility of a single analyst's results. A properly designed collaborative test should demonstrate the reliability of the method being tested under typical, realistic sampling and analysis conditions.

Task 8 began in December 1975 with the selection of collaborators. A total of 24 organizations received a Request for Proposal (RFP) which outlined the duties of each collaborator. As a part of the selection process each potential collaborator was required to analyze a set of liquid samples of pure cadmium sulfide suspended in absorbing solution. After eliminating those who made serious analytical errors or who failed to meet the requirements of the RFP, the 10 lowest bidders were accepted as collaborators. Construction and testing of the sampling manifold for the test proceeded concurrently with the collaborator selection. The collaborative test took place during February 22 to 27, 1976, at MRI's Deramus Field Station in Grandview, Missouri. As part of the test each collaborator was required to analyze a series of synthetic liquid samples, a set of three reference cylinder gases and to sample simulated fuel gases from a sampling manifold. After allowing the collaborators to check their results and report changes, the results were statistically analyzed by MRI.

The following sections of this report cover the selection of collaborators, a description of the sampling system used in the collaborative test, the experimental design of the test, a discussion of the collaborative test, the collaborators' analysis results, a statistical analysis of the test results and finally the general conclusions and recommendations from the study.

Volume III of this report contains only copies of the original collaborator data sheets.

SECTION 2

CONCLUSIONS

The major conclusions that can be drawn from the results of this collaborative test are:

1. The "Tentative Method for the Determination of Hydrogen Sulfide Emissions from Stationary Sources," as shown in Appendix A of this report, is adequately written for those knowledgeable of sampling and analysis techniques.

2. If the tentative procedure is followed by people knowledgeable of the sampling and analysis techniques given therein, then in the absence of mercaptans the results will be on the average 4% low, ± 4%,* over the range 100 to 400 mg/dscm. If a set of such people, each sampling independently, follow the method, then results will be on the average 4% low, ± 8%.*

3. When methyl and ethyl mercaptans are present in addition to H_2S at a total level of 150 ppm, the results vary from 2% low at an H_2S concentration of 400 mg/dscm to 14% high at an H_2S concentration of 100 mg/dscm. The presence of mercaptans has no significant effect on precision.

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* Precision is for the 95% confidence limit (2 σ).

SECTION 3

RECOMMENDATIONS

Based upon the conclusions that have been drawn from the results of this collaborative test, it is recommended that the tentative method be used as written as a replacement for the original Method 11 with the addition of the information given in Conclusion 3.

SECTION 4

SELECTION OF COLLABORATORS

To select participants for the collaborative test, MRI sent letters to more than 60 organizations. Those organizations that expressed interest in the test then received an RFP and a set of synthetic liquid samples. The samples had to be titrated according to the proposed method and the results were used in selecting competent collaborators.

Twenty-one organizations responded in the affirmative to the letter seeking interested organizations. Three additional organizations were added to the list, giving a total of 24. A copy of the proposed RFP was submitted to the project officer for approval. After making the suggested changes, the RFP was sent to the 24 organizations on December 22, 1975. A copy of the RFP is included in Appendix A.

The samples shipped to the potential collaborators contained 1 to 28 mg of cadmium sulfide suspended in 45 ml of absorbing solution (equivalent to 25 to 700 mg/dscm assuming a 10 liter sample volume).

The synthetic samples were tested before shipment. When the samples were analyzed by the normal procedure, low recovery efficiencies were found--approximately 60%. However, by making two simple changes in the analysis procedure, 100% recovery could be obtained. First, the samples had to be uniformly suspended since otherwise numerous unreacted particles could be seen in the flask after titration. Vigorous shaking by hand prior to sample recovery was only partially successful, but placing the sample bottles in an ultrasonic bath for 10 min broke up all the particles. The second change was that 30 sec of vigorous shaking was needed after the acidified iodine had been added to the sample in the iodine flask. Since 30 sec of shaking was one of the noncritical variables checked in the ruggedness test, making these changes for the liquid samples should not affect the experimental design.

To check the stability of the liquid samples, one set was prepared and analyzed after standing at room temperature for 1- and 2-week intervals. A second set was placed outdoors and analyzed in the same way. After 1 week, no change in value could be measured. After 2 weeks, recoveries of 103 to 105% were obtained. The higher values were found in the outdoor samples which were frozen solid when brought indoors for analysis. None of the frozen samples were broken or otherwise damaged. Therefore, it was assumed that the samples would survive shipment and would give predictable values if analyzed within 2 weeks of preparation.

Most of the liquid samples were shipped on December 31, except for three sets sent after New Year's Day since three companies requested delayed shipments due to vacations. The shipments contained instructions for the modified analysis (see Appendix A) and each organization was required to report the results of any four of the six samples shipped. This allowed for losses in handling or for practice purposes.

A total of 22 organizations responded to MRI's RFP for the collaborative test.

One collaborator withdrew before evaluation and one submitted incomplete data. Of the 20 remaining collaborators, five failed to execute the method without gross errors.

After these five were eliminated, the remaining 15 collaborators were rank-ordered via their mean square errors* (see Table 1). It is not the purpose of collaborator selection to construct an optimum group, but rather to construct a representative group of collaborators for the field test. For this reason, the only collaborators eliminated from Table 1 were C11 and C13, because these two are outliers (Dixon-Massey test, $r_{22} = 0.517$, $\alpha < 0.10$).

Ten of the remaining 13 collaborators were selected purely on the basis of cost. These are identified in Table 1 by a line under their number. The 10 collaborators are:

The Research Corporation of New England
125 Silas Deane Highway
Wethersfield, Connecticut 06109

Monsanto Research Corporation
Dayton Laboratory
1515 Nicholas Road
Dayton, Ohio 45418

---

* The mean square error (MSE) is a standard statistical descriptor of "total uncertainty," namely, MSE = (bias) 2 + (variance).

TABLE 1. COLLABORATOR MEAN SQUARE ERRORS

Collaborator	MSE (% of true value)
2	7.4
5	8.1
6	9.2
8	9.4
12	9.6
18	10.6
19	11.2
21	11.2
1	12.5
3	12.6
16	14.1
17	16.0
14	19.0
11	26.0
13	27.1

Clayton Environmental Consultants
25711 Southfield Road
Southfield, Michigan 48075

York Research Corporation
One Research Drive
Stanford, Connecticut 06906

Washington State University
College of Engineering
Pullman, Washington 99163

California Department of Health
Health and Welfare Agency
Air and Industrial Hygiene Laboratory
2151 Berkeley Way
Berkeley, California 94704

Interpoll, Inc.
1996 West County Road C
St. Paul, Minnesota 55113

Roy F. Weston, Inc.
Weston Way
Westchester, Pennsylvania 19380

Research Triangle Institute
P.O. Box 12194
Research Triangle Park, North Carolina 27709

Ecology Audits
11061 Shady Trail
Dallas, Texas 75229

SECTION 5

HYDROGEN SULFIDE SAMPLING SYSTEM

The system shown in Figure 1 was used to generate known levels of H_2S in natural gas while also controlling the levels of the interferences and other compounds normally found in refinery fuel gas streams. The test assembly was constructed at MRI's Deramus Field Station in Grandview, Missouri. The test facility provided ample room and electrical power for the test and included a large exhaust hood over the sampling manifold to avoid buildup of noxious fumes.

The equipment specifications for the sampling system are as follows:

1. Gas regulator - A standard natural gas regulator was used to drop the 10 psig main gas supply pressure down to a stable 5 psig pressure for the system.

2. Dry gas meter - A Singer Model AL-425 dry gas meter measured the natural gas flow rate. The meter had a large observation index for greater reading accuracy. The meter was calibrated against a Precision Scientific 1 ft^3/rev. wet test meter.

3. Thermometer - The gas stream thermometer was a 0 to 50°C bimetallic thermometer mounted in the gas meter outlet with the entire stem in the gas flow.

4. Precision pressure gauge - Stainless steel 0 to 15 psig, Matheson Gas Products No. 63-5615, 0.25% accuracy, readable to 0.05 psig (2.5 mm Hg). Checked against a mercury manometer at working pressure.

5. Gases, regulators - All gases and regulators were obtained from Matheson Gas Products except for nitrogen which was prepurified grade, Union Carbide. Shutoff valves were those supplied with the regulators and lecture bottle controls.

6. Filters - Stainless steel, 7 μm pores, Type 4FR, Nupro Company. The filters prevented particulates from reaching the rotameters.

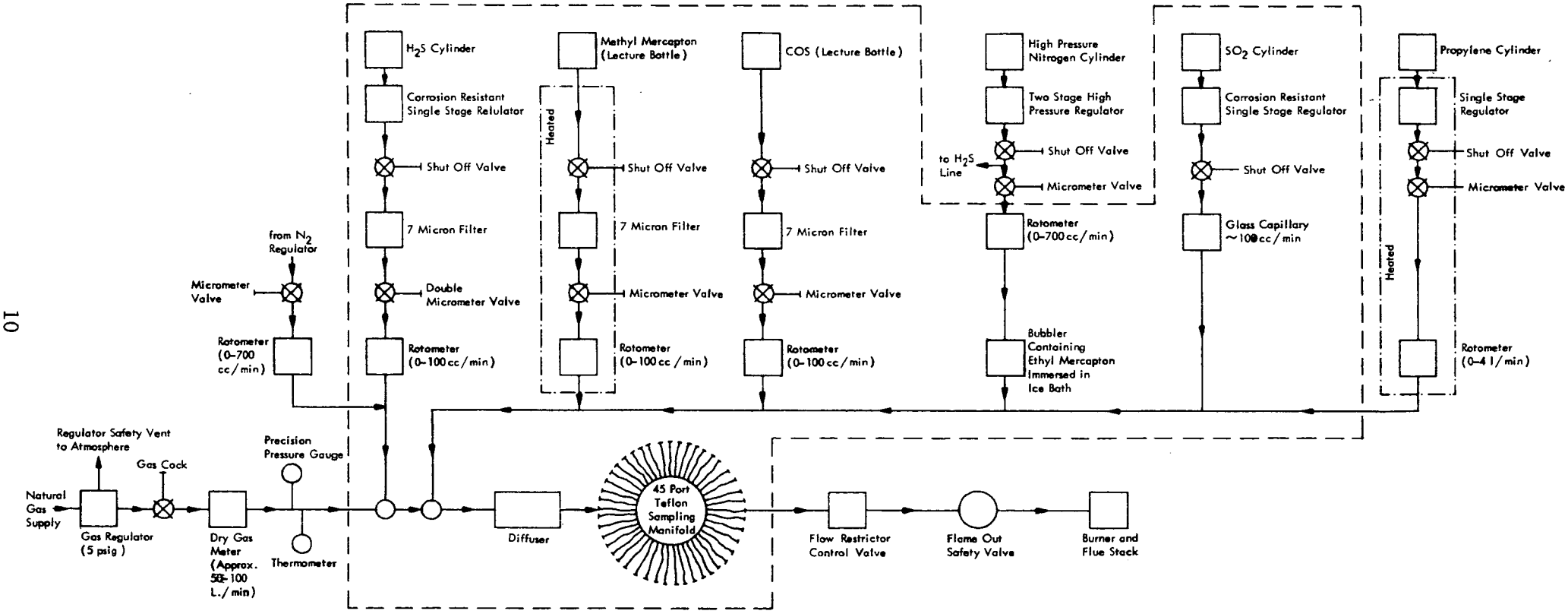


Figure 1 - Block Diagram of H_2S Sampling System

7. Rotameters - Supplied by Matheson Gas Products with stainless steel housing. Nitrogen rotameters use 602 tubes, propylene uses a 603 tube, H_2S uses a 601 tube, and methyl mercaptan and carbonyl sulfide each use a 610 tube with a micrometer valve built into the housing.

8. Micrometer valves - All are standard Whitey valves, except that for H_2S which is a Nupro SS-2MGD double micrometer valve for very low flow rates.

9. Glass capillary - The SO_2 for flow control was a short section of dropping mercury electrode capillary.

10. Ethyl mercaptan bubbler - The bubbler used to saturate the N_2 carrier with ethyl mercaptan was a 200 mm glass vacuum trap with side arm outlet. In operation the trap was filled with mercaptan outdoors, capped and brought inside and connected to the system. The rate of mercaptan addition was calculated from the partial pressure assuming a temperature of 2°C in an ice bath:

$$\log 10\ P\ (\text{mm Hg}) = 6.95206 - \frac{1{,}084.53}{231.4 + (^\circ C)}$$ 1/

Figures 2 and 3 show the gas spiking assembly mounted in the fume hood.

11. Diffuser - The diffuser was the same as that used at the laboratory test facility (Figure 4) except that the end plates were replaced with stainless steel plates with O-ring seals and 1 in. O.D. stainless steel tubes welded to the end plates. This change was necessary to eliminate leaks in the assembly. The inlet tube to the diffuser was drilled and tapped for 1/4 in. NPT (National Pipe Thread) to accept the lines from the gas measuring system.

12. Sampling manifold - The sampling manifold is shown in Figure 5. To obtain gastight seals in the manifold, the original end plates were removed and O-ring sealed stainless steel plates with tubing similar to those used for the diffuser were installed. An additional O-ring was used between the two Teflon subassemblies, and the ports were drilled out to accept 1/8 in. Teflon tubing which was expoxied in place for all ports. Stainless steel Swaglok caps were used to seal off the ends of all unused ports. The diffuser and sampling manifold were connected by a 2 m equilibration section of 3 cm O.D. Teflon pipe.

1/ Lange, Handbook of Chemistry, 10th ed., p. 1429 (1961).

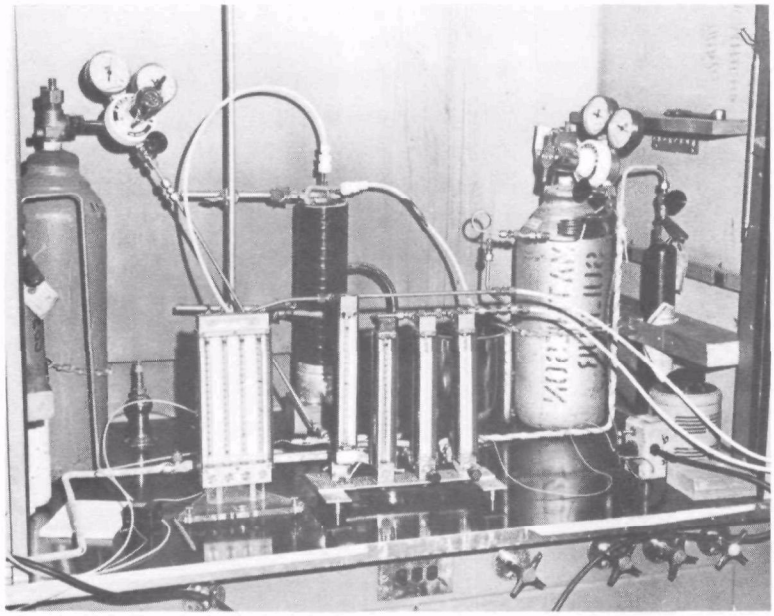


Figure 2 - Close-up View of the Spike Gas Cylinders and Metering Equipment

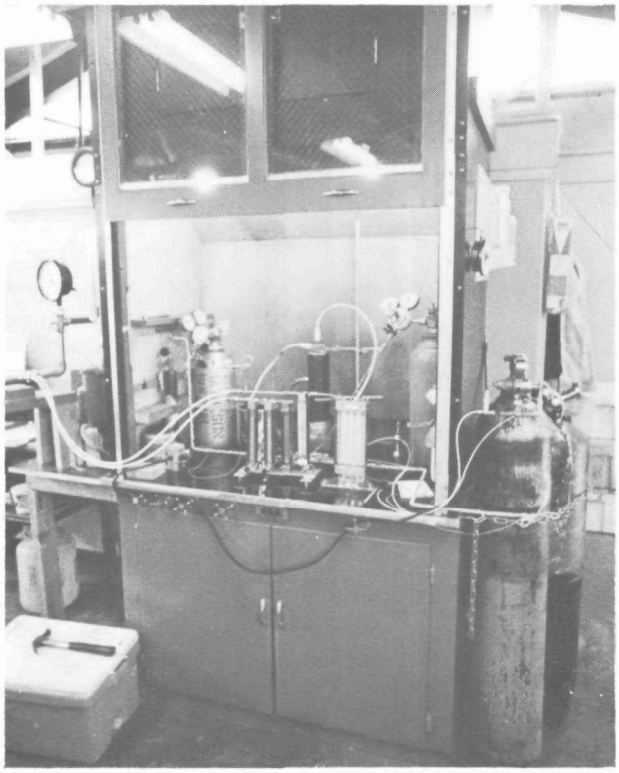


Figure 3 - View of the Spike Gas Assembly

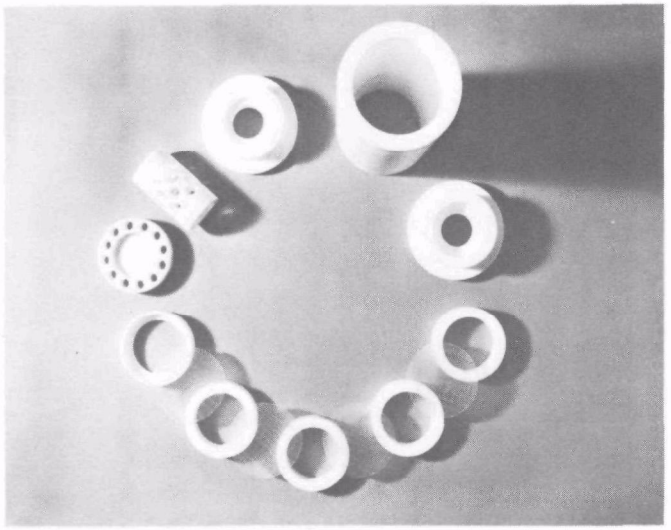


Photo 1 - Top View Diffuser Components: Housing, End Sections, Spiraler Tube, Teflon Screens, Retaining Rings.

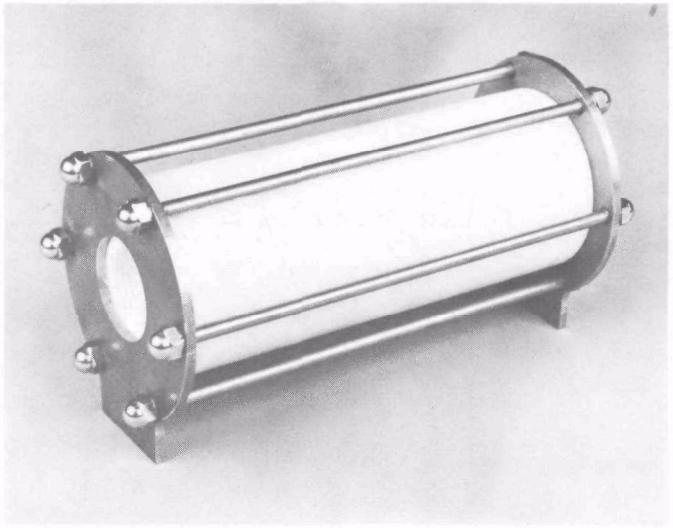
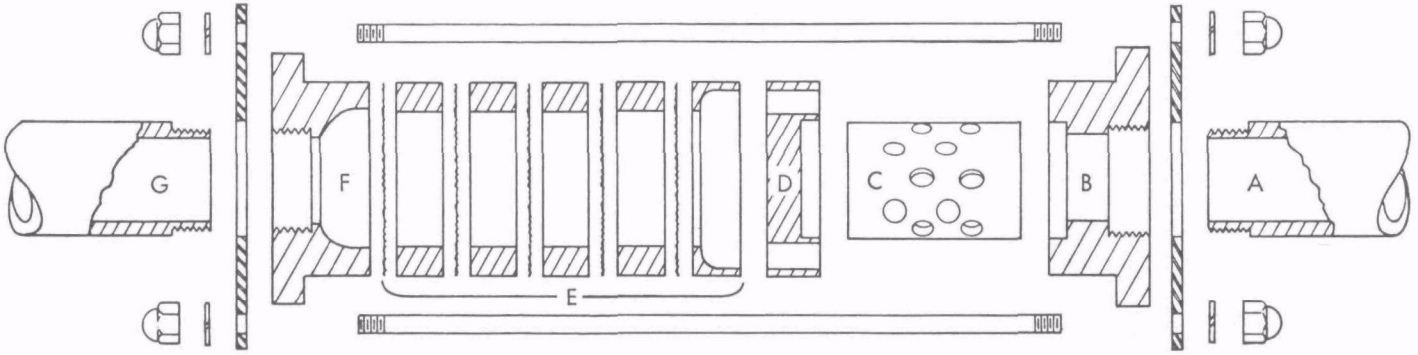


Photo 2 - External View of Diffuser.



Exploded cross section of all-Teflon diffuser with inlet (A), end section (B), spiraler tube with angled holes (C), prescreen block with holes (D), five sets of fine mesh Teflon screen and retaining blocks (E), end section (F), exit (G) and diffuser housing (H). Double cross-hatched end plates are stainless steel.

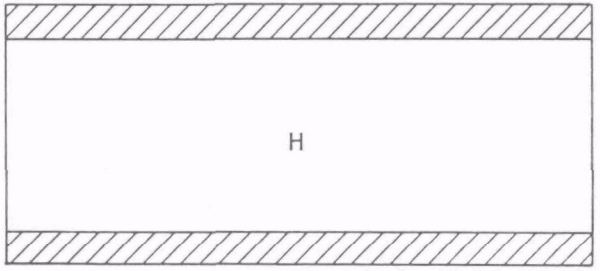


Figure 4 - Schematic Drawing and Photographs of the Diffuser

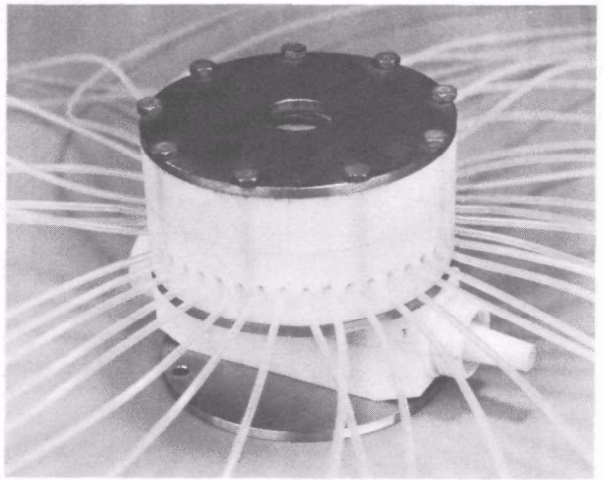


Photo 1 - Sampling Manifold External View. The bottom section was not used for this test and the end plates were modified as described in the text.

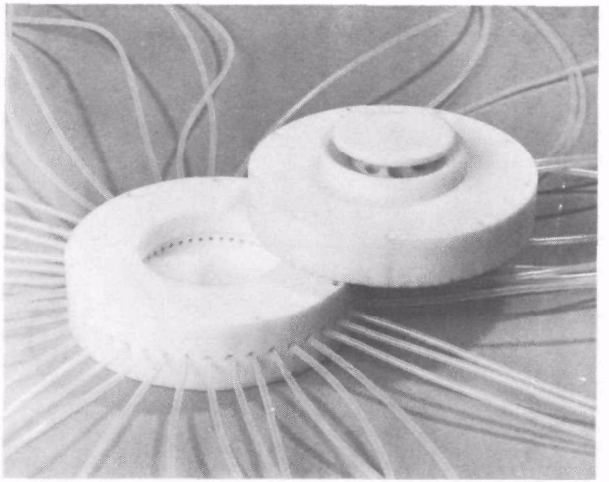
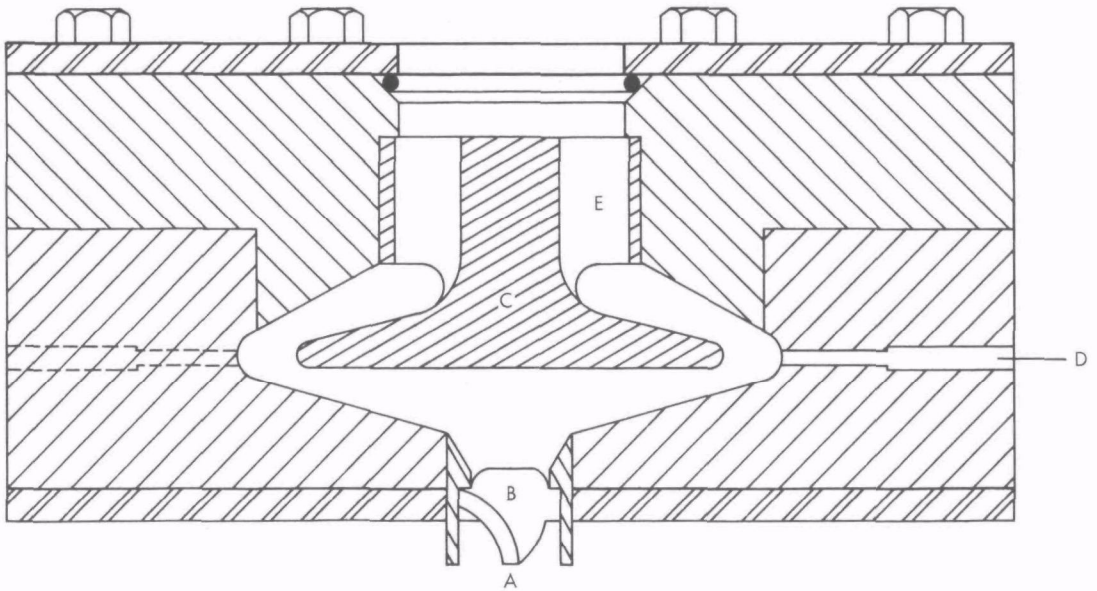


Photo 2 - Internal View (Right Component is Inverted in this Photo).



Cross section of all-TFE Teflon manifold with inlet (A), mixing impeller (B), main chamber flow spreader (C), exits to collaborator ports (D), channel to exhaust manifold (E), double cross-hatched assembly plates at top and bottom are stainless steel.

Figure 5 - Schematic Drawing and Photographs of the Sampling Manifold

13. Control valve - A 1/2 in. NPT multiturn valve was used to control the gas flow rate. Since the burner had a regulator to drop pressure to about 10 cm water pressure and with little flow resistance between the manifold and the main supply regulator, this valve provided the primary flow restriction in the system. Thus, the sampling manifold remained very near the 5 psig supply pressure.

14. A Cox 250,000 Btu natural gas burner was installed outside the building with a 30 cm diameter stack approximately 4 m tall (see Figure 6). The burner orifice was increased to the maximum and a 1/4 in. tube was run to the center at the flame to augment the gas flow. A pressure sensor with alarm was connected to the burner such that if a flame-out occurred shutting down the burner, then the alarm would sound.

All gas cylinders except for nitrogen and propylene were installed in an exhaust hood together with the controls and rotameters. Two short sections of stainless steel tubing connected the metered gases to the diffuser inlet tubing.

The sampling manifold was mounted on a 3 m diameter circular table with the sampling ports fastened at the edge of a raised, center platform. An exhaust hood was then suspended directly above the manifold. The lower edge of the hood had a fringed rubber curtain which extended below the sampling ports yet allowed access to the ports when necessary. The sampling table and hood are shown in Figure 7.

The test manifold can supply H_2S levels of 50 to 500 mg/dscm for up to 30 separate devices. A total of 20 liters/min can be withdrawn from the manifold at a pressure of 5 psig without upsetting the system.

The entire system was leak tested above normal working pressure. Several of the ports in the sampling manifold leaked and were plugged from the inside of the manifold. Each remaining port was then tested for flow restrictions by measuring the maximum flow through each line. About 30 of the 45 ports passed both checks and these 30 ports were used for the collaborative test.

A solid-state H_2S monitor was then used to check each port for consistent H_2S levels. The spike assembly was set for approximately 300 mg/dscm of H_2S. All ports showed identical H_2S levels $\pm$ 5%. With the sampling system set to 151 mg/dscm of H_2S, duplicate sample trains gave 135 and 136 mg/dscm of H_2S. At 288 mg/dscm, duplicate trains gave 328 and 292 mg/dscm; at 387 mg/dscm duplicate trains gave 405 and 414 mg/dscm.

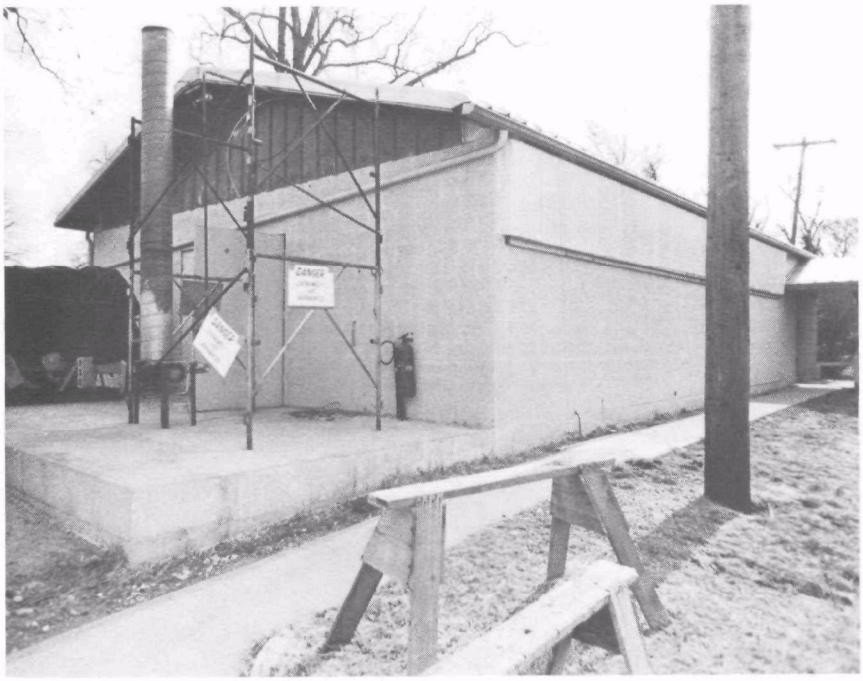


Figure 6 - Burner Assembly for Combustion of Excess Gas

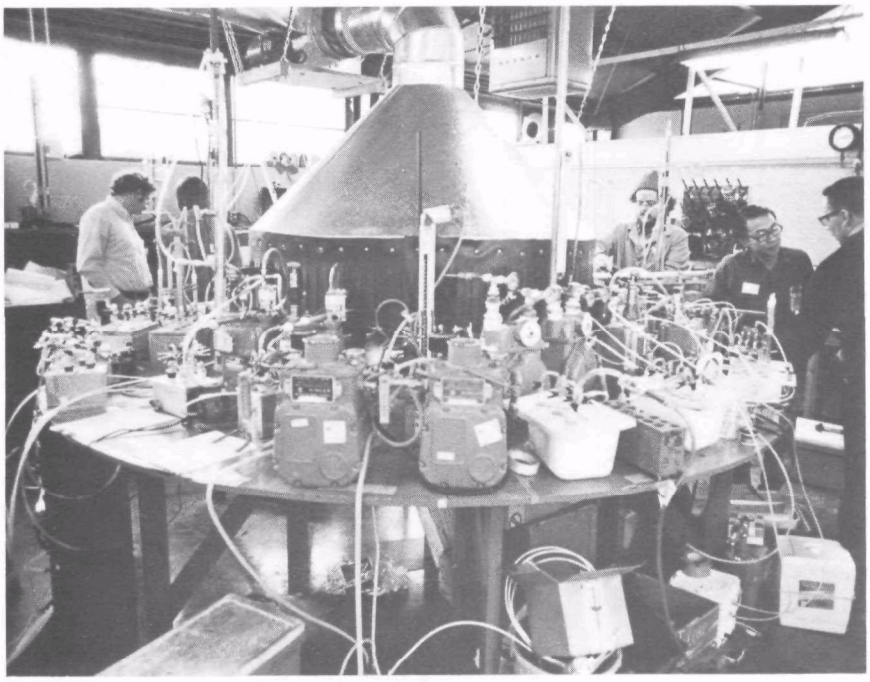


Figure 7 - Sampling Table and Exhaust Hood

SECTION 6

EXPERIMENTAL DESIGN

GENERAL CONSIDERATIONS

The major considerations that entered into the experimental design of the collaborative test were:

Analysis Method

All collaborators shall follow the revised cadmium sulfate procedure, copies of which were provided with the RFP's for the test. MRI would check equipment specifications, make calibration checks on all dry gas meters, and any other checks necessary to ensure that the procedure was being followed.

Location of Test

The test will take place at MRI's field station which is located approximately 15 miles south of MRI in a suburban area of Kansas City.

Sampling Time

All sampling times shall be 15 min. For the reference gases, no special order of analyses is required. For the 3 days of sampling from the test manifold, all collaborators shall sample simultaneously. Duplicate trains will be used for all sampling.

Number of Collaborators

In making all preparations for the test, it was assumed that 10 qualified collaborators would participate in the test.

Test Levels

There would be three challenge levels. Each test manifold level would comprise H_2S, natural gas and possible interferences. The three levels of challenge would be 100, 200, and 400 mg/m^3 of H_2S.

Standard Samples

There would be two types of standard samples given to each collaborator at the field site: eight liquid samples (two each at Levels 1, 2 and 3, one sample near zero, and one blank) and six gas samples (two each at Levels 1, 2 and 3). One set of standard samples would be given to each collaborator before the 3-day test starts to be analyzed on-site. A similar set would be given to each collaborator after completion of the 3-day test to be analyzed on-site.

Test Schedule

The field work would be executed as follows:

Day	Activity
Sunday	Collaborators travel to Kansas City. Site will be available to collaborators Sunday afternoon for unpacking equipment, set up, etc.
Monday	Orientation. Equipment set up. Calibration of collaborator's equipment. Analysis of standard samples.
Tuesday	Sampling at Level 1. Analysis of samples.
Wednesday	Sampling at Level 2. Analysis of samples.
Thursday	Sampling at Level 3. Analysis of samples.
Friday	Analysis of second set of liquid and gas samples. Packing of equipment. Turn in of field test data and results of analysis.
Saturday	Complete packing and return home.

Every effort would be made to have the collaborators ship their equipment and materials so that the equipment and material would arrive at MRI a week prior to Day 1 of the field test. If the collaborator is driving and is bringing his equipment with him, this advance delivery would not be necessary.

MRI would assist the collaborators with the shipment of their equipment back to their home organization to expedite site-clearing operations.

True Value of H_2S

A set of three cylinders of H_2S in methane would provide the standard gas samples. Each cylinder would be carefully analyzed by the supplier before shipment and again upon return of the cylinders after the test. MRI would also check the reported levels prior to the test using the proposed test method.

The liquid standard samples were prepared by suspending accurately weighed amounts of pure cadmium sulfide in the absorbing reagent. A random selection of the samples were analyzed by MRI prior to the test.

The primary calibration of the H_2S levels in the manifold was the calculated dilution factor of pure H_2S added to the natural gas stream. The H_2S rotameter was calibrated with H_2S at different pressures using a soap film bubblemeter. The natural gas flow was measured with a dry gas meter calibrated against a wet test meter. The pressure and temperature were also measured during operation which allowed the H_2S spike level to be calculated using the gas laws and empirically measured rotameter temperature and pressure corrections. Further checks were made using a potentiometric titration with standard silver nitrate and flame photometric gas chromatography analyses. A commercial solid-state H_2S sensor was also used to monitor the integrity of the spike but was not used as a primary calibration method.

Simulation of a Typical Refinery Fuel Gas Stream in the Test Manifold

Refinery fuel gas streams can vary widely in composition. However, they normally consist of hydrogen, methane, and/or natural gas with smaller amounts of H_2S, SO_2, mercaptans, C_3-C_4 unsaturates, COS, amines used in scrubbers and water present in varying proportions. For this test commercial natural gas was used as the primary constituent. The natural gas in Kansas City normally is methane with < 5% ethane, and small amounts of nitrogen, argon, and higher hydrocarbons. Constant amounts of propylene (~ 4%), SO_2 (~ 50 ppm), methyl mercaptan (~ 100 ppm) and ethyl mercaptan (~ 50 ppm) were added during all tests to generate a stream which would be more difficult to analyze than the majority of real samples.

FORMAL DESIGN

The H_2S collaborative test can be considered as furnishing three data sets:

1. Analysis of known liquid samples to estimate purely analytical errors.

2. Analysis of known calibration gas samples (without interferences) to estimate sampling and analysis errors.

3. Analysis of known field samples with realistic interferences present in the gas stream.

In all cases, three H_2S levels of approximately 100, 200, and 400 mg/dscm will be used. In addition, blanks and very low level samples will be included in the liquid samples. At all times all 10 collaborators will be observing the same stream so that direct estimates of accuracy and precision are possible.

The three analyses of variance models are presented in Tables 2 through 4.

TABLE 2. ANALYSIS OF VARIANCE MODEL FOR LIQUID SAMPLES

$X_{ijk} = \mu + C_i + L_{ij} + CL_{ij} + e_{(ij)K}$, where

μ = overall mean response,

Ci = i^{th} collaborator (i = 1, ..., 10),

L_j = j^{th} H_2S level (j = 1, ..., 5 including a blank level),

CL_{ij} = collaborator-level interaction,

$e_{(ij)k}$ = k^{th} error in ij^{th} cell (k = 1,2 replicates for each cell)*,

X_{ijk} = ijk^{th} response, i.e., ijk^{th} difference between observed H_2S and true value.

Source	d.f.	EMS
Collaborator (C)	9	$\sigma_e^2 + 8\ \sigma_c^2$
Level (L)	4	$\sigma_e^2 + 2\ \sigma_{CL}^2 + 20\ \sigma_L^2$
C x L	27	$\sigma_e^2 + 2\ \sigma_{CL}^2$
Error (e)	40	σ_e^2

* The first replicate before and the second replicate after the field test.

TABLE 3. ANALYSIS OF VARIANCE FOR CALIBRATION GAS SAMPLES

$X_{ijkl} = \mu + C_i + L_j + CL_{ij} + T_{k(i)} + LT_{jk(k)} + e_{(ijk)l}$, where

μ = overall mean response,

C_i = i^{th} collaborator (i = 1, ..., 10),

L_j = j^{th} H_2S level (j = 1, ..., 3),

CL_{ij} = collaborator-level interaction,

$T_{k(i)}$ = k^{th} train within i^{th} collaborator (k = 1, 2 trains per collaborator),

$LT_{jk(i)}$ = level-train interaction,

$e_{(ijk)l}$ = l^{th} error in ijk^{th} cell (l = 1, 2 replicates per cell),

X_{ijkl} = $ijkl^{th}$ response, i.e., $ijkl^{th}$ difference between observed H_2S and true value.

Source	d.f.	EMS
Collaborator (C)	9	$\sigma_e^2 + 6\ \sigma_T^2 + 12\ \sigma_C^2$
Level (L)	2	$\sigma_e^2 + 4\ \sigma_{CL}^2 + 2\ \sigma_{LT}^2 + 40\ \sigma_L^2$
C x L	18	$\sigma_e^2 + 2\ \sigma_{LT}^2 + 4\ \sigma_{CL}^2$
Train (T)	10	$\sigma_e^2 + 6\ \sigma_T^2$
L x T	20	$\sigma_e^2 + 2\ \sigma_{LT}^2$
Error (e)	60	σ_e^2

TABLE 4. ANALYSIS OF VARIANCE FOR FIELD SAMPLES

$X_{ijkl} = \mu + C_i + L_j + CL_{ij} + T_{k(i)} + LT_{jk(i)} + e_{(ijk)l}$, where

μ = overall mean response,

C_i = i^{th} collaborator ($i = 1, \ldots, 10$),

L_j = j^{th} H_2S level ($j = 1, \ldots, 3$),

CL_{ij} = collaborator-level interaction,

$T_{k(i)}$ = k^{th} train within i^{th} collaborator ($k = 1$, 2 trains per collaborator),

$LT_{jk(i)}$ = level-train interaction,

$e_{(ijk)l}$ = l^{th} error in ijk^{th} cell ($l = 1, \ldots, 5$ replicates per cell)

X_{ijkl} = $ijkl^{th}$ response, i.e., $ijkl^{th}$ difference between observed H_2S and true value.

Source	d.f.	EMS
Collaborator (C)	9	$\sigma_e^2 + 15\ \sigma_T^2 + 30\ \sigma_C^2$
Level (L)	2	$\sigma_e^2 + 10\ \sigma_{CL}^2 + 5\ \sigma_{LT}^2 + 100\ \sigma_L^2$
C x L	18	$\sigma_e^2 + 5\ \sigma_{LT}^2 + 10\ \sigma_{CL}^2$
Train (T)	10	$\sigma_e^2 + 15\ \sigma_T^2$
L x T	20	$\sigma_e^2 + 5\ \sigma_{LT}^2$
Error (e)	240	σ_e^2

SECTION 7

COLLABORATIVE TEST

The collaborative test was conducted at MRI's Deramus Field Station on February 22 through 27, 1976. Instructions for the test were sent to the collaborators prior to the test (see Appendix B). A log of the test is given in Table 5. Photographs taken during the tests are shown in Figures 8, 9, and 10. Figure 11 is a group photo of the test participants.

Most of the collaborators arrived at the site on February 22 to set up their equipment. All collaborators were present by 0800 on February 23 and following the orientation meeting proceeded to analyze the three gas cylinders and a set of five liquid samples. The liquid samples included one blank and one very low level CdS sample in addition to the three levels of ~ 100, 200, and 400 mg/dscm assuming a 10-liter sample volume. Except for the two collaborators who did not come on Sunday to set up, everyone finished by 5 p.m. The dry gas meters of half the collaborators were checked on February 23 and the remaining meters were checked by MRI against a 3 liter/revolution wet test meter on February 24. Five runs at a level of ~ 200 mg/dscm H_2S were made on February 24. Five runs at ~ 400 mg/dscm were made on February 25 and six runs at a level of 100 mg/dscm were made on February 26. On all 3 days a constant interference level was maintained of ~ 3% propylene, 100 ppm methyl mercaptan, 50 ppm ethyl mercaptan and 50 ppm SO_2. For the sixth run on February 26, 100 ppm carbonyl sulfide was also added. All collaborators finished testing by 5 p.m. on all 3 days of manifold testing. On February 27, a second set of liquid samples was analyzed and the three cylinders retested. All results were submitted and equipment packed by 3 p.m. on February 27.

No significant deviations from the proposed method were observed during the test, although several collaborators did have varying degrees of difficulty in getting the sampling trains to operate properly. It was discovered during troubleshooting that some trains can require more than 25 cm of water pressure to simply overcome the water column resistance of the impingers. Increasing the test pressure should eliminate this problem. Several procedural errors were noted in the test log. Most of the errors were obvious and probably caused by lack of familiarity with the method, which was unavoidable since even the original Method 11 procedure has been used infrequently.

TABLE 5. COLLABORATIVE TEST LOG

Date	Test	Comments
2-23	Dry test meter calibrations check	Meters for six of the collaborators were tested
2-23	Standard samples	Some collaborators had trouble making connections to the reference gas cylinders. A few bottlenecks occurred when more collaborators wanted to sample a cylinder than there were ports available. The liquid samples were issued with no problems. A few samples were spoiled during analysis and replacements were issued. Several problems passing leak checks. One train backed up during sampling.
2-24	Level A Run 1	Start at 0905, stop at 0920, System stable. Two collaborators (3,7) discovered leaks during the test-only one (3) was serious. Collaborator 8 pulled cadmium solution into the peroxide on both trains.
2-24	Level A Run 2	Start at 1005, Stop at 1020, System stable. Collaborator 8 again pulled over the cadmium solution. Collaborator 7 had a brief leak.
2-24	Level A Run 3	Start at 1105, stop at 1120, System stable. Collaborator 6 forgot the charcoal filters during purge.
2-24	Level A Run 4	Start at 1345, stop at 1400, System stable. Collaborator 6 had a leak in one train for about 1 min. Collaborator 3 had a flow loss in one train.
2-24	Level A Run 5	Start at 1445, stop at 1500, System stable.
2-24	Dry test meter calibration check	Meters for the remaining four collaborators were checked.
2-25	Absorbing solution pH test	pH's were between 2.80 and 3.10.

TABLE 5 (Concluded)

Date	Test	Comments
2-25	Level B Run 1	Start at 0905, stop at 0920, System stable. Collaborator 8 backed up both trains.
2-25	Level B Run 2	Start at 1015, stop at 1030, System stable.
2-25	Level B Run 3	Start at 1115, stop at 1130, System stable.
2-25	Level B Run 4	Start at 1345, stop at 1400, System stable.
2-25	Level B Run 5	Start at 1440, stop at 1455, System stable.
2-26	Level C Run 1	Start at 0855, stop at 0910, propylene and methyl mercaptan showed some drift.
2-26	Level C Run 2	Start at 0950, stop at 1005, System stable Collaborator 9 lost one sample--wrong impinger order.
2-26	Level C Run 3	Start at 1040, stop at 1055, System stable.
2-26	Level C Run 4	Start at 1315, stop at 1330, System stable.
2-26	Level C Run 5	Start at 1410, stop at 1425, methyl mercaptan varying, H_2S reading rose briefly.
2-26	Level C Run 6	Start at 1505, stop at 1520, carbonyl sulfide on at ~ 80 ppm. Methyl mercaptan, carbonyl sulfide, H_2S, and ethyl mercaptan drifted 10 to 20% during test.
2-27	Standard samples	No problems reported.

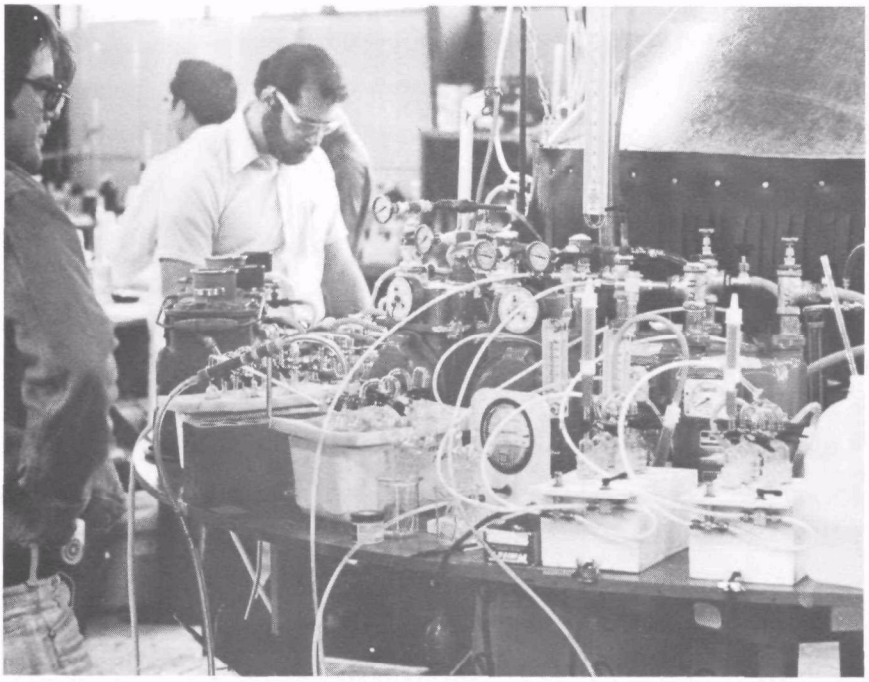


Figure 8 - Collaborators Sampling Trains

Figure 9 - Collaborators Analyzing Samples

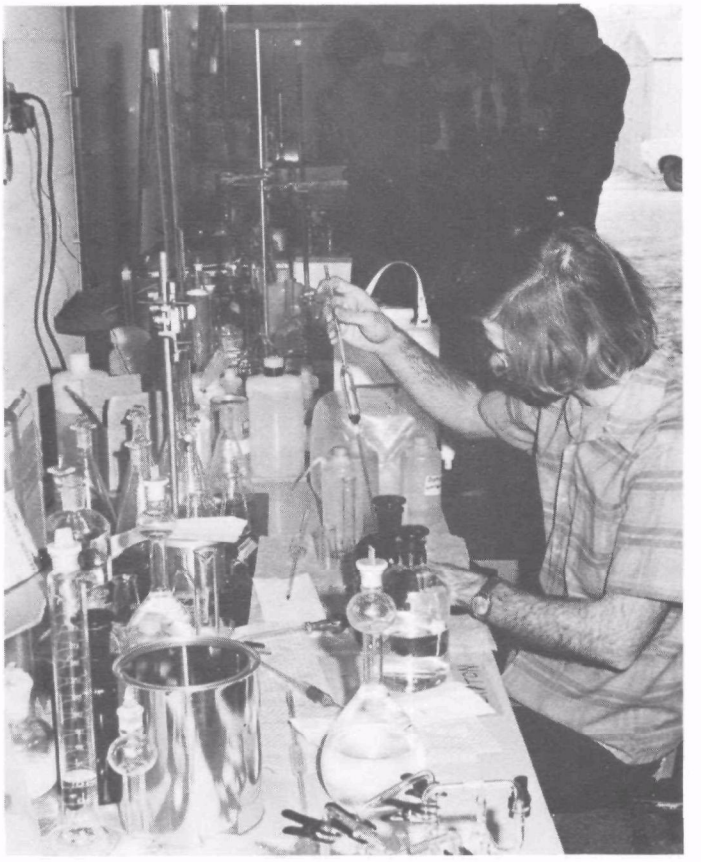


Figure 10 - Collaborator Analyzing Test Samples

Figure 11 - Participating Collaborators and Midwest Research Institute Staff, Hydrogen Sulfide Collaborative Test, February 23 through 27, 1976, MRI Field Station, Grandview, Missouri

Left to right, standing: David Henry, Ecology Audits; Kent Shoemaker, Clayton Environmental Consultants; Mark Childers, Ecology Audits; Paul C. Constant, Midwest Research Institute; Larry Hackworth, Research Triangle Institute; Dave Harsch, Washington State University; Denny Wagoner, Research Triangle Institute; Lee Bamesberger, Washington State University; Robert Epstein, York Research Corporation; Windle McDonald, Monsanto Research Corporation; Harold Hubbard, Midwest Research Institute; Lewis Cash, Monsanto Research Corporation; Bruce DaRos, Midwest Research Institute; Barry Jackson, Roy F. Weston; George Scheil, Midwest Research Institute; Rodney Midgett, EPA, Quality Assurance Branch; and John LaShelle, Midwest Research Institute.

Left to right, kneeling: Harilal Patel, Interpoll; Perry Lonnes, Interpoll; James Fries, California Department of Health; Emil DeVera, California Department of Health; Victor Hansen, Clayton Environmental Consultants; Michael Carey, Roy F. Weston; Nicola Grappone, The Research Corporation of New England.

Not pictured: Sam Cha, The Research Corporation of New England; and Michael Horowitz, York Research Corporation.

All collaborator data for the test was recorded in duplicate on the data forms shown in Figures 12 and 13. One copy of the data was submitted before leaving the test site and the second copy was retained by the collaborators. After returning to their home laboratories, the collaborators checked their results and reported any errors or changes to MRI.

MIDWEST RESEARCH INSTITUTE
DATA SHEET
HYDROGEN SULFIDE - CADMIUM SULFATE METHOD
SAMPLING

Collaborator_____ Date _____
Run No._____ Sampled by_____
Sampling Train No._____ Port No._____

INITIAL READINGS		FINAL READINGS	
Dry Gas Meter	_____	_____	Dry Gas Meter
Meter Temp. °C	_____	_____	Meter Temp. °C
Time	_____	_____	Time
Rotameter	_____	_____	Rotameter

Type Ball Used: Glass Steel (Circle)

Sampling Flow Rate _____ℓ/min

Barometric Pressure mm Hg_____ Meter Correction Factor*_____

Measured Gas Meter Vol. (Vs) _____ℓ At Standard Cond. (V_{STD})_____ℓ

REMARKS:

ANALYSIS

Analyzed by_____ Burette: (.01 N Thiosulfate)
Final RDG. _____ml
Time at I_2 Addition_____ Initial RDG. _____ml
Volume of Thio (V_T)_____ml
Time at Titration_____

Volume of Iodine Added to Sample_____

Normalities: .01 N Iodine_____ .01 N Thiosulfate_____

Blank: .01 N Thiosulfate

Volume_____ml

Volume of Iodine Added to Blank_____

H_2S Concentration_____
mg/DSCM

REMARKS:

*$\frac{Vs}{Vm}$ where Vs is the true gas volume and Vm is the gas volume indicated by the gas meter.

Figure 12 - Sampling and Analysis Data Sheet

MIDWEST RESEARCH INSTITUTE
DATA SHEET
HYDROGEN SULFIDE - CADMIUM SULFATE METHOD
STANDARDIZATIONS

Collaborator_____ Analyzed by_____ Date_____

0.1 N Sodium Thiosulfate

Weight of $K_2Cr_2O_7$ _____g

Volume of $K_2Cr_2O_7$ Solution_____ml

Final Buret Reading	_____	_____	_____	_____	_____
Initial Buret Reading	_____	_____	_____	_____	_____
Volume of 0.1 N Thio	_____	_____	_____	_____	_____

Sodium Thiosulfate Volume (V_T) _____ml

Normality_____(N_T)

0.01 Iodine Volume of Iodine _____

Final Buret Reading	_____	_____	_____	_____	_____
Initial Buret Reading	_____	_____	_____	_____	_____
Volume of .01 N Thio	_____	_____	_____	_____	_____

Thiosulfate Volume (V_I) _____ml

Normality _____(N_I)

Blanks

Time at I_2 Addition	_____	_____	_____	_____	_____
Time at Titration	_____	_____	_____	_____	_____
Final Buret Reading	_____	_____	_____	_____	_____
Initial Buret Reading	_____	_____	_____	_____	_____
Volume of .01 N Thio	_____	_____	_____	_____	_____

Volume of Thiosulfate_____ml (V_T)

REMARKS:

Figure 13 - Data Sheet for Standardizations

SECTION VIII

RESULTS OF ANALYSES

The collaborators' results are summarized in Tables 6 and 7. Copies of the original data sheets are in Volume III of this report. The results of MRI's measurements of the H_2S levels during the manifold tests are summarized in Table 8.

The liquid samples were prepared by weighing portions of 99% pure cadmium sulfide to the nearest 10 μg. Each sample was then stored dry until the collaborative test. Shortly before issuing each set of samples, MRI added 45 ml of absorbing solution to each sample and the samples were mixed for at least 10 min in an ultrasonic bath. The collaborators were instructed to assume a sample volume of 10 liters in the calculations. The true value for each sample was calculated thus:

$$H_2S \text{ concentration (mg/dscm)} = \frac{34.1 \cdot (\text{sample wt}) \cdot 100}{144.5}$$

where sample weight is expressed as milligrams of CdS

The H_2S standard gases were prepared using research grade methane. Each cylinder was analyzed by the supplier using a flame photometric procedure before shipment and again after the collaborative test. MRI also checked the cylinders before the collaborative test using the cadmium sulfide train and using the potentiometric method. Both methods agreed within ± 5% of the reported values. The reported H_2S concentrations measured in parts per million were converted to milligrams per dry standard cubic meter by multiplying by 1.429. Cylinder 1 was analyzed as 75 ppm initially and 69 ppm following the test. Cylinder 2 was reported as 250 and 240 ppm and Cylinder 3 was reported as 130 and 127 ppm. The average of the two analyses was taken as being the true value.

TABLE 6. H_2S CONCENTRATION (mg/dscm) DETERMINED BY COLLABORATORS FOR STANDARD LIQUID AND CYLINDER SAMPLES

Standard samples	Collaborators 1 MRI	1 Coll	2 MRI	2 Coll	3 MRI	3 Coll	4 MRI	4 Coll	5 MRI	5 Coll	6 MRI	6 Coll	7 MRI	7 Coll	8 MRI	8 Coll	9 MRI	9 Coll	10 MRI	10 Coll
Test No. 1	0	6.5	0	< 8(0)	357	333	2.83	1.2	179	179.1	0	3	0	4.62	3.7	11.9	99	103.61	0	5.78
	133	132.7	4	10.0	113	98.4	0	0.9	4.5	9.5	138	43	2.8	9.74	171	149.6	243	237.85	4.5	11.73
	175	174.2	204	198.6	2	-4.8	341	316.6	379	370.7	231	224	98	96.92	123	110.5	348	339.95	104	105.4
	421	416.7	100	100.6	0	-4.8	127	110.3	0	6.1	4.5	14	256	251.62	381	331.5	4	8.54	257	248.2
	4.7	25.6[a]	377	363.8	182	174	224	208.8	131	134.3	460	433	358	343.92	0	5.1	0	9.37	387	374.3
Cylinders																				
Test No. 1																				
Cyl. 1	157.7		116.0		88.9		93.07		90.8		93		92.94		100.1		87.31		100.9	
(103 mg/DSCM)	118.9		117.1		82.8		90.39		92.3		93		89.92		100.6		87.87		90.6	
Cyl. 2	364.1		366.3		331		334.9		330.2		342		343.93		232.5[a]		297.08		329.0	
(350 mg/DSCM)	377.4		354.7		333		335.7		323.6		339		332.37		257.2[a]		314.77		332.5	
Cyl. 3	204.5		193.3		171.0		181.7		172.1		177		228.92		176.9		166.5		177.7	
(184 mg/DSCM)	199.5		197.3		168.0		179.5		173.6		179		227.16		172.4		168.41		170.1	
Standard Samples	MRI	Coll	MRI	Coll	MRI	Coll	MRI	Coll	MRI	Coll	MRI	Coll	MRI	Coll	MRI	Coll	MRI	Coll	MRI	Coll
Test No. 2	0	-11.6	470	442.9	0	0	450	427.6	232	220	174	178	2.59	0.43	136.0	113.1	370	368.72	196	191.9
	110	110.4	242	230.0	2.83	6.8	98.1	91.9	121	122.1	448	415	0	-2	396	333.3	97	121.74	397	370.4
	340	328.9	106	111.0	139	132	192	175.6	334	320.4	131	126	137	126.06	2.1	4.19	189	201.27	133	132.8
	251	245.8	4.01	8.8	187	175	0	0.3	0	2.71	0	7	218	199.57	0	2.69	3.5	17.08	2.4	10.2
	2.36	1.7	0	< 8(0)	367	339	3.06	0.5	4.25	3.22	3.06	5	408	381.61	238	208.5	0	13.73	0	8.5
Cylinders																				
Test No. 2																				
Cyl. 1	117.3		101.3		94.9		93.4		88.8		95		100.85		83.8		111.13		95.47	
(103 mg/DSCM)	107.2		97.4		94.3		91.0		89.4		95		102.06		90.30		106.78		94.14	
Cyl. 2	329.8		309.4		328		333.2		317.4		338		355.67		284.3		312.50		330.9	
(350 mg/DSCM)	346.8		305.6		338		333.9		318.6		334		335.06		286.4		312.84		333.9	
Cyl. 3	192.4		186.8		175		179.7		170.1		180		189.34		155.8		173.92		184.5	
(184 mg/DSCM)	190.1		184.3		183		178.1		169.7		174		182.83		153.2		174.70		180.1	

a/ Error during sampling or analysis. Sample deleted.

TABLE 7. H_2S CONCENTRATION (mg/dscm) DETERMINED BY COLLABORATORS AT TEST LEVELS A, B, C

Level	Run[a]	H_2S present	Collaborators 1	2	3	4	5	6	7	8	9	10
	1a	180	187.9	271.0	217	184.2	181.7	180	191.83	122.2[b]	170.79	219.1
	1b		199.2	277.9	246[b]	181.0	181.7	182	179.72	144.5[b]	176.43	221.5
	2a	180	191.9	210.0	174	182.8	177.3	174	180.34	114.2[b]	164.02	205.8
	2b		203.9	214.2	177	176.0	173.8	177	173.29	150.1[b]	172.82	205.6
A	3a	188	215.1	221.9	194	196.6	190.3	195	175.55	144.4	183.88	224.6
	3b		208.2	204.1	194	193.2	189.3	196	187.19	157.4	188.94	216.3
	4a	191	213.8	212.2	195	198.4	193.7	197	230.466	164.7	183.91	193.6
	4b		216.0	203.8	236[b]	197.6	195.9	199	190.750	204.8	186.81	217.7
	5a	192	223.2	211.1	197	200.7	194.2	200	202.66	167.0	184.25	224.3
	5b		218.5	214.1	-	202.4	194.7	204	196.13	220.8	191.05	227.1
	1a	342	375.3	356.3	338	334.8	328.4	337	347.99	312.6[b]	315.15	364.3
	1b		333.7	351.2	346	333.3	327.7	339	337.70	-	321.98	369.9
	2a	380	406.7	399.0	376	375.0	364.8	375	439.55	331.6	290.51	392.6
	2b		407.7	340.3	364	374.0	362.1	386	417.51	314.5	354.18	401.1
B	3a	378	384.2	392.2	369	379.7	365.3	377	439.61	366.3	342.31	388.6
	3b		395.1	388.4	373	373.5	361.0	376	426.05	356.3	354.03	394.1
	4a	426	447.7	420.4	399	395.1	386.1	402	416.55	416.9	372.88	411.2
	4b		432.8	446.6	393	402.2	383.7	405	408.72	393.2	384.65	409.4
	5a	426	434.2	436.4	397	404.1	382.4	400	424.32	378.5	384.43	420.8
	5b		415.5	427.2	403	399.4	390.0	405	422.01	371.7	375.27	417.3
	1a	100	109.3	114.0	111	115.99	108.6	113	118.61	110.8	109.61	182.66
	1b		108.5	116.7	112	113.7	109.4	113	116.34	110.6	115.31	144.4
	2a	100	107.4	118.2	114	114.3	111.1	113	119.86	102.4	71.35	144.9
	2b		105.0	117.7	113	111.6	111.8	112	112.98	103.0	50.19[b]	143.05
C	3a	99	115.3	121.7	113	111.1	109.5	111	117.73	99.4	102.20	142.9
	3b		110.9	122.2	112	110.7	109.4	119	113.48	100.4	115.13	143.8
	4a	97	127.0	123.3	110	112.0	110.6	114	118.95	109.7	114.48	138.9
	4b		123.9	114.4	114	111.9	110.4	115	115.22	109.9	118.31	143.9
	5a	102	128.4	120.4	113	116.9	115.5	114	128.71	113.7	123.08	150.3
	5b		127.6	118.6	116	115.4	115.6	113	116.74	107.9	118.03	146.1
	6a	100	123.1	117.9	117	111.5	113.5	120	120.76	106.6	121.52	151.1
	6b		122.6	121.3	117	112.8	112.5	116	112.99	105.8	125.24	129.0

a/ Each collaborator ran two trains simultaneously each run.
b/ Error during sampling or analysis. Sample deleted.

TABLE 8. DATA SUMMARY OF MRI MEASUREMENTS AT THE H_2S MEASURE CONCENTRATION DURING THE MANIFOLD TEST

		Potentiometric titrations			Dilution factor calculations							
Level	Run	1 Vol. titrant (ml)	2 Gas vol. sampled (l) at 760 mm, 21°C	3 H_2S measured (mg/dscm)	4 H_2S Flow rate (ml/min)	5 Gas Pres. (mm Hg)	6 H_2S flow rate at manifold (ml/min)	7 Total flow rate/min at manifold conditions	8 H_2S conc. (ppm)	9 H_2S conc. (mg/m^3)	10 Avg. potentiometric result (mg/dscm)	11 Final avg. (mg/dscm)
A	1a	11.7	16.19	188	20.25	994	18.73	150.0	124.9	178	182	180
	1b	11.3	16.80	175								
	2a	12.0	16.19	193	19.98	992	18.49	150.9	122.5	175	184	180
	2b	11.3	16.80	175								
	3a	14.0	18.89	193	21.06	991	19.53	153.4	127.3	182	193	188
	3b	14.5	19.60	193								
	4a	17.8	18.86	246	21.18	988	19.71	151.3	130.3	186	196	191
	4b	14.7	19.57	196								
	5a	14.5	18.86	200	21.37	990	19.82	150.6	131.6	188	196	192
	5b	14.4	19.57	192								
B	1a	18.7	18.94	348	38.67	989	35.89	151.4	237.1	339	344	342
	1b	18.9	19.65	339								
	2a	20.8	18.75	391	42.82	988	39.82	151.2	263.4	376	385	380
	2b	20.9	19.45	379								
	3a	17.5	16.12	383	42.20	986	39.26	151.3	259.5	371	386	378
	3b	18.4	16.73	388								
	4a	20.3	17.84	401	50.85	991	47.40	148.6	319.0	456	396	426
	4b	20.1	18.06	392								
	5a	21.5	18.74	405	50.61	989	47.11	149.3	315.5	451	400	426
	5b	21.8	19.45	395								
C	1a	12.3	19.17	98	11.30	998	10.43	148.2	70.4	101	98	100
	1b	12.8	19.96	98								
	2a	12.8	19.12	102	11.34	996	10.49	148.6	70.6	101	100	100
	2b	12.7	19.84	98								
	3a	12.7	19.07	102	11.38	996	10.53	156.0	67.5	96	102	99
	3b	13.3	19.79	103								
	4a	12.5	19.04	100	11.38	997	10.63	151.5	70.2	100	94	97
	4b	11.5	19.76	89								
	5a	12.6	18.89	102	11.34	996	10.57	149.6	70.7	101	102	102
	5b	13.2	19.60	103								
	6a	12.3	18.89	99	11.05	995	10.29	148.1	69.5	99	100	100
	6b	13.0	19.60	101								

The methods used to determine the H_2S content of the manifold stream showed a consistent 15% spread in the H_2S measured. The gas chromatography results are the lowest of the three. H_2S is apparently irreversibly absorbed by reactive surfaces with the chromatograph since rapid, repeated injections show increasing peak heights until a plateau is reached. If the injections are then made with longer delay times, the peaks decrease in height. Therefore, the gas chromatography results were not used in determining the true H_2S levels.

The potentiometric titrations of H_2S (and mercaptans) gave a change in potential much lower than expected. However, duplicate samples agree within $\pm$ 5% and runs made with the standard gas cylinders showed 100% collection efficiencies.

The gas dilution measurements showed excellent stability, and initially agreed with the GC analyses. After measuring the flow of H_2S at ambient and at 5 lb pressure MRI showed that the published equation for rotameter pressure corrections is in error for the rotameter used in the test. Using the empirical corrections, the dilution factors were in reasonable agreement with the potentiometric titrations, and both were in agreement with the predicted mercaptan interferences. The average of the potentiometric and dilution results was used as the true value for each run.

SECTION IX

STATISTICAL ANALYSIS OF COLLABORATORS' RESULTS

The H_2S collaborative test data consist of three sets of results: (a) standards data, (b) the actual field data, and (c) liquid standards data. These sets were analyzed individually and results for each block will be presented. A summary description of all results will be presented last.

(DRY) STANDARDS DATA

Each collaborator produced two replicate determinations for three test cylinders (103, 350, and 184 mg/dscm), and this procedure was repeated at the end of the week. Thus, the data set is described by the 10 x 3 x 2 x 2 factorial model:

$$X_{ijkl} = \mu + C_i + L_j + CL_{ij} + T_k + CT_{ik} + LT_{jk} + CLT_{ijk} + e_{(ijk)l}$$

where μ = overall mean response

$C_i = i^{th}$ collaborator ($i = 1, \ldots, 10$) (random factor)

$L_j = j^{th}$ test level ($j = 1,2,3$) (fixed factor)

$T_k = k^{th}$ test ($k = 1,2$) (fixed factor)

CL_{ij} = collaborator-level interaction, etc.

$e_{(ijk)l} = e^{th}$ residual in ijk^{th} cell ($l = 1,2$ everywhere)

$X_{ijkl} = ijkl^{th}$ response where a response is a bias, i.e., collaborator reading - true value (mg/dscm).

Five observations were deleted as outliers from the data set; two due to mechanical failure (C7-L3-T1); and three as statistical outliers (Dixon-Massey outlier test, C8-L2-T1 and the first value of C1-L1-T1).*

* $\sqrt{22} = 0.744$ ($p < 0.005$), and $\sqrt{11} = 0.421$ ($p < 0.10$).

Before performing an analysis of variance of the data set, the cell ranges were compared to the H_2S levels as a check on the homeoscedastic assumption of analyses of variance. It was found that the average cell range ($\bar{R}$) was proportional to the H_2S level ($\bar{R}$ = 2.9, 3.5, 7.7 versus L = 103, 184, 350); i.e., σ_e is proportional to the H_2S level (rather than constant).

Therefore a log transformation was applied to the data; in particular $Z_{ijkl} = \ln(100 + X_{ijkl})$. The analysis of variance was then performed and the results are shown in Table 9.

TABLE 9. ANALYSIS OF VARIANCE OF H_2S STANDARDS DATA

Source	dF	SS	MS	F
Collaborator (C)	9	1.2059	0.1340	40.64, $p < 0.01$
Level (L)	2	0.7699	0.3849	12.00, $p < 0.01$
Test (T)	1	0.0886	0.0886	0.90, NS
CL	18	0.5772	0.0321	9.73, $p < 0.01$
LT	2	0.2009	0.1005	5.49, $p < 0.05$
CT	9	0.8869	0.0985	29.89, $p < 0.01$
CLT	16	0.2995	0.0187	5.68, $p < 0.01$
Error (e)	57	0.1879	0.0033	

As can be seen from Table 9, all effects except Test are statistically significant. Such a high number of significant effects is the usual result when the replicate is a duplicate measurement only rather than a genuine recreation of the same experimental conditions.

The primary results of interest from the analysis are the estimates of components of variance (see Table 10) and, in particular, the components σ_e^2 and σ_C^2 (or their square roots). Note that, due to the log transformation of the data, σ_e, etc., are theoretically constant percentages of the H_2S level; i.e., a constant coefficient of variation (σ/μ) exists in the data. The observed CV's in the data set for replicate readings were 2.50, 1.69, and 1.95% (versus theoretically constant 2.16%), so this idealization does not seem unrealistic.

In other words, from Table 10 we have:

- A collaborator produces readings with a standard deviation = 2.16% of the H_2S level being measured.
- The standard deviation of (mean) collaborator determinations of an H_2S level is 3.93% of that H_2S level.

TABLE 10. COMPONENTS OF VARIANCE, H_2S STANDARDS DATA

Source	EMS	σ^2 (Z-Scale)	CV (%)
C	$\sigma^2_e + 12\ \sigma^2_C$	0.010891	3.93
L	$\sigma^2_e + 4\ \sigma^2_{CL} + 40\ \sigma^2_L$	0.008822	
T	$\sigma^2_e + 6\ \sigma^2_{CT} + 60\ \sigma^2_T$	"0"	
CL	$\sigma^2_e + 4\ \sigma^2_{CL}$	0.007192	
LT	$\sigma^2_e + 2\ \sigma^2_{CLT} + 20\ \sigma^2_{LT}$	0.004087	
CT	$\sigma^2_e + 6\ \sigma^2_{CT}$	0.015875	
CLT	$\sigma^2_e + 2\ \sigma^2_{CLT}$	0.007712	
e	σ^2_e	0.003297	2.16

- The "total" standard deviation of a set of collaborators reading an H_2S level is $\sqrt{\sigma^2_e + \sigma^2_C} = 4.48\%$ of that H_2S level.

Of course, the uniform CV over the experimental H_2S range (100 to 350 mg/dscm) might not hold for other H_2S values.

The other result of primary interest is the bias exhibited by the method. These results,* along with the average mean square error (MSE) are shown in Table 11.

In general, the bias is ~ -5%; i.e., the H_2S method has a collection efficiency of about 0.952 on the standard cylinders. The individual bias curves are shown in Figure 14.

FIELD DATA

The field data are structurally similar to the standards data with three H_2S levels and 10 collaborators, but with five runs per level. Formally, the experimental design model is:

$$X_{ijkl} = \mu + C_i + L_j + CL_{ij} + R_k + CR_{ik} + LR_{jk} + CLR_{ijk} + e_{(ijk)l}$$

* The bias was estimated from actual results (not transformed but from the Z-scale).

TABLE 11. BIAS AND MSE, H_2S STANDARDS DATA

H_2S level	Bias (B) mg/dscm (%)	$\sqrt{MSE\ 1}$ a/	$\sqrt{MSE\ 2}$ b/
103 mg/dscm	-5.68 (-5.5)	5.91%	7.09%
184 mg/dscm	-6.20 (-3.4)	4.03%	5.62%
350 mg/dscm	-18.78 (-5.4)	5.82%	7.02%
Avg (212 mg/dscm)	-10.22 (-4.8)	5.26%	6.57%

a/ Within a collaborator.
b/ Between collaborators.

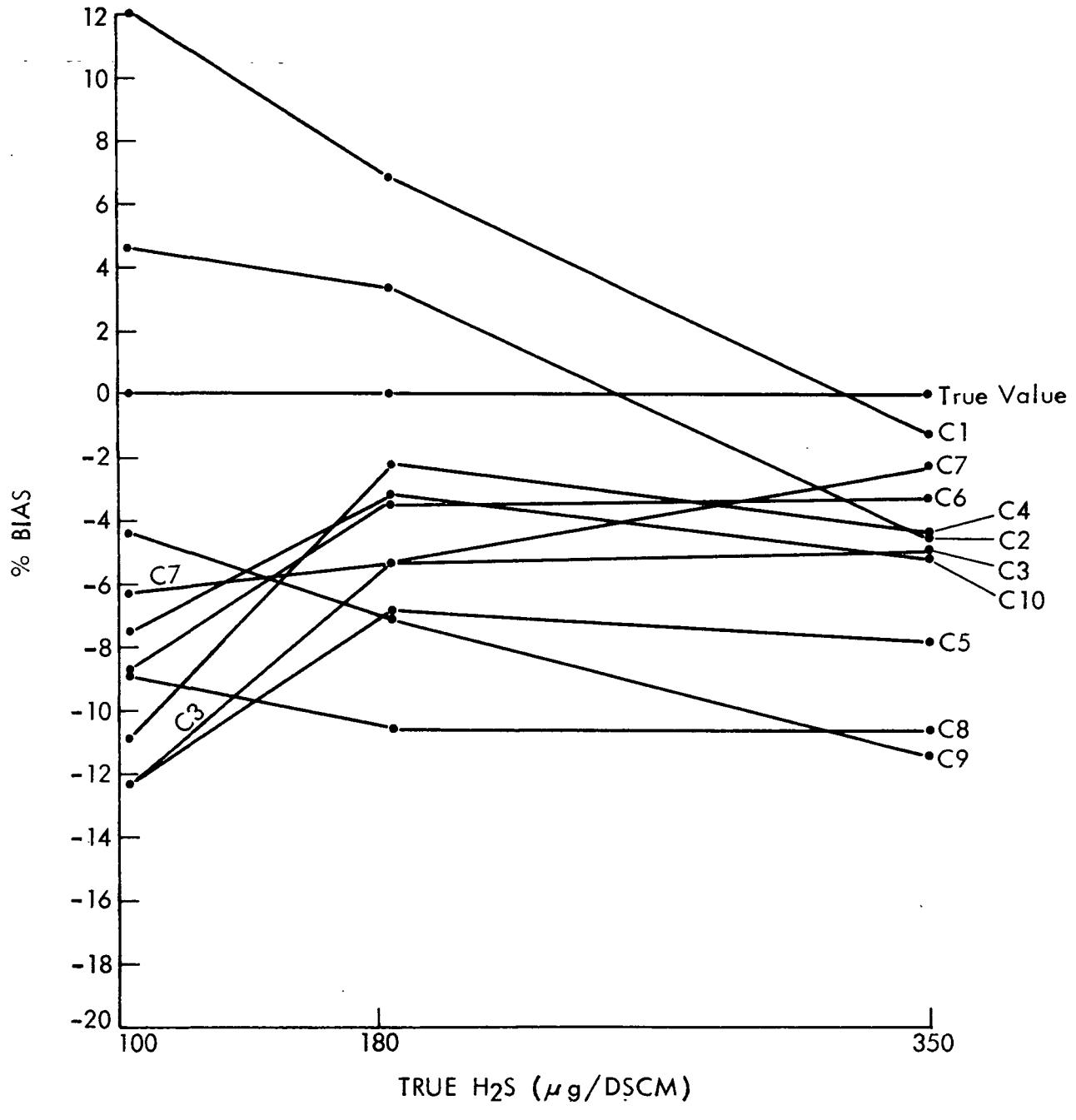


Figure 14 - Bias Results by Collaborator, H_2S Standards Data

The terms in (2) are the same as in (1) except that run (R) has replaced test (T), and there are five runs per H_2S level. As with the standards data, the cell ranges are proportional to the H_2S level, so that a log transformation was applied.*

In this data set all of C8's results at Level A and all of C10's results at Level C were discarded as outliers. Thirteen other values were also discarded. After these values were replaced by artificial readings, the analysis of variance was performed (Table 12) and components of variance estimated (Table 13). The individually observed σ_e's were 2.33, 2.41, and 2.09% of the H_2S level, respectively.

The σ_e, σ_C values from Table 13 are very similar to the corresponding estimates from Table 10; i.e., no deterioration in precision was observed between the standards and field results.

The biases in the field test are shown in Table 14 (individual bias curves are shown in Figure 15). The biases are different in the field than in the standards; namely, the field biases are about +2.6% on the average (although level dependent), whereas the standards biases were negative (-4.8% on the average).

LIQUID STANDARDS

Each collaborator also observed five standard liquid samples each during two tests. Unlike the other two data sets, however, in this block the H_2S level was not tightly controlled, so that each collaborator "saw" 10 unique H_2S values (of course the general H_2S span was similar for all collaborators).

Thus, instead of an analysis of variance, an analysis of covariance (with covariate = H_2S level) was performed.

No difference between tests was found ($f(1,96) < 1$), but in most other respects statistically significant influences were found:

- There was a significant collaborator effect; i.e., not all collaborators read the same H_2S value even after adjustment for the variability in levels ($F(9,89) = 7.22$, $p < 0.01$).

- One regression line does not describe the data as well as 10 individual regressions ($F(18,80) = 11.47$, $p < 0.01$).

---

* This time $Z = \log X$ was used where $X = H_2S$ reading (not bias). This was done for convenience only.

TABLE 12. ANALYSIS OF VARIANCE H_2S FIELD DATA

Source	df	SS	MS	F
Collaborator (C)	9	0.5511	0.0612	125.93, $p < 0.01$
Level (L)	2	72.2612	36.1306	4,152.94, $p < 0.01$
Run (R)	4	0.3589	0.0897	30.93, $p < 0.01$
CL	16	0.1399	0.0087	17.90, $p < 0.01$
CR	36	0.1037	0.0029	5.97, $p < 0.01$
LR	8	0.2449	0.0306	12.75, $p < 0.01$
CLR	61	0.1445	0.0024	4.94, $p < 0.01$
Error (e)	129	0.0627	0.000486	

TABLE 13. COMPONENTS OF VARIANCE, H_2S FIELD DATA

Source	EMS	σ^2 (Z-Scale)	CV (%)
C	$\sigma_e^2 + 30\ \sigma_C^2$	0.002025	4.50
L	$\sigma_e^2 + 100\ \sigma_L^2 + 10\ \sigma_{CL}^2$	0.3612	
CL	$\sigma_e^2 + 10\ \sigma_{CL}^2$	0.0008258	
CR	$\sigma_e^2 + 6\ \sigma_{CR}^2$	0.0003992	
CLR	$\sigma_e^2 + 2\ \sigma_{CLR}^2$	0.0009415	
R	$\sigma_e^2 + 60\ \sigma_R^2 + 6\ \sigma_{CR}^2$	0.001447	
LR	$\sigma_e^2 + 20\ \sigma_{LR}^2 + 2\ \sigma_{CLR}^2$	0.001410	
e	σ_e^2	0.000486	2.20

TABLE 14. BIAS AND MSE, H_2S FIELD DATA

H_2S Level	Bias (B) mg/dscm (%)	$\sqrt{MSE\ 1}$ a/	$\sqrt{MSE\ 2}$ b/
100 mg/dscm	+14 (+14.0)	14.2%	14.9%
186 mg/dscm	+10 (+5.4)	5.8%	7.4%
390 mg/dscm	-7 (-1.8)	2.8%	5.3%
Avg (225 mg/dscm)	+6 (+2.6)		

a/ Within a collaborator.
b/ Between collaborators.

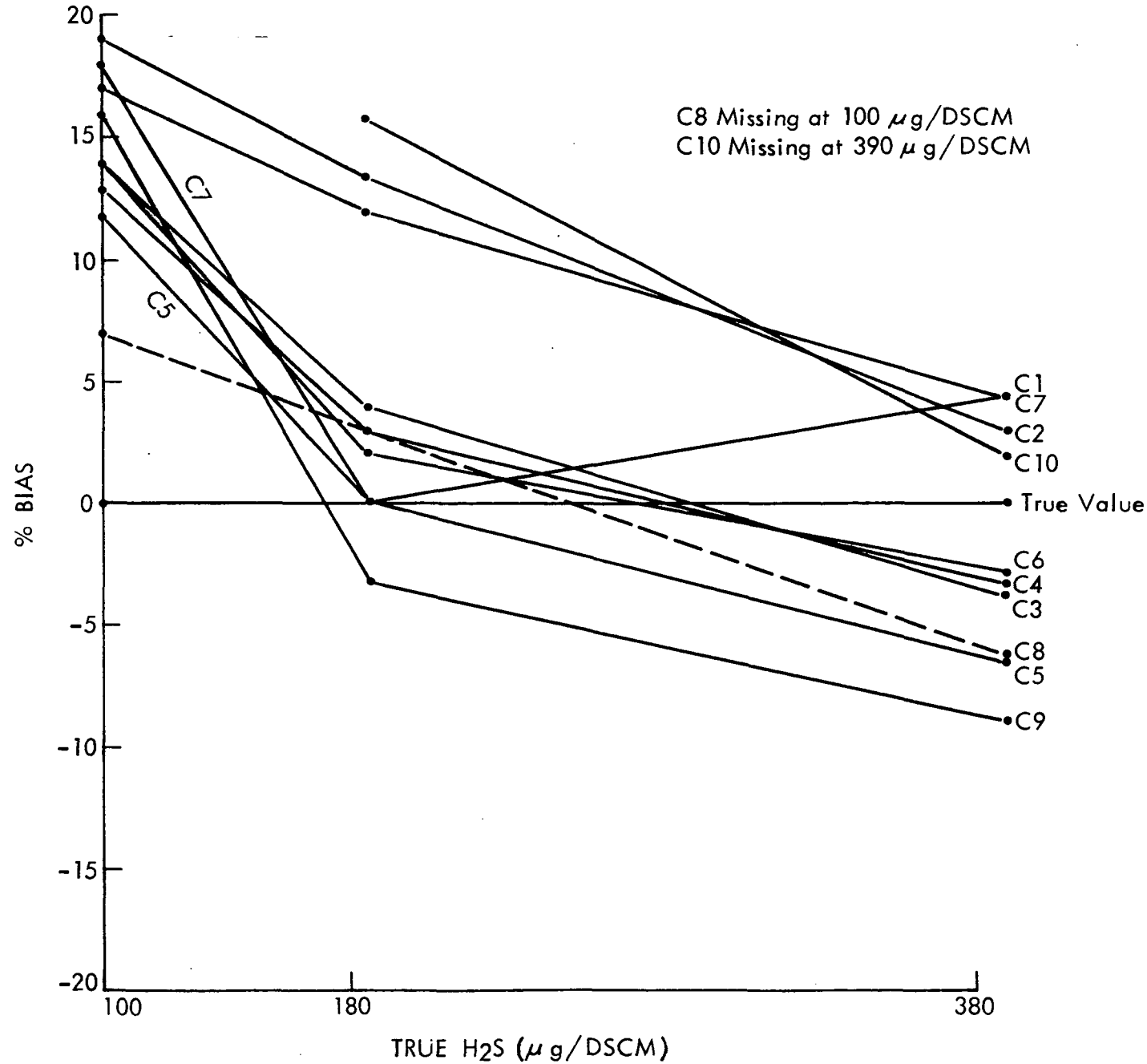


Figure 15 - Bias Results by Collaborator, H_2S Field Data

- Not all collaborator slopes are equal ($F(9,80) = 9.51$, $p < 0.01$).

- The regression on the means is not completely linear ($F(9,89) = 8.00$, $p < 0.01$).

The individual regression curves are described in Table 15, and illustrated in Figure 16. Note that the inequality of regression curve slopes is mostly due to one collaborator (C8). The average bias in the liquid standards data set is -3.75%, a value not very different from the dry standard result.

The standard deviation within a collaborator cannot be directly computed for this data set because a collaborator did not repeatedly observe a fixed H_2S value.

The standard error of the estimate from the AOCV is 3.83%, but this includes lack of fit. The collaborator standard deviation is $\sigma_C = 3.53\%$, a value comparable to the other such results.

SUMMARY

The primary results of all analyses are shown in Table 16. The precisions are good, and the biases in the standards data are also small and stable. However, the biases in the field data are H_2S level dependent, and are sizeable at the lower levels of H_2S.

TABLE 15. LIQUID STANDARD H_2S RESULTS BY COLLABORATOR

Collaborator	a (intercept)	b (slope)	r (correlation)
C1	-0.46	0.985	99.9% +
C2	-1.16	0.961	99.9% +
C3	-1.63	0.937	99.9% +
C4	-2.46	0.945	99.9% +
C5	4.12	0.958	99.9% +
C6	7.96	0.924	99.9% +
C7	1.69	0.944	99.9% +
C8	6.51	0.844	99.9% +
C9	12.97	0.955	99.9%
C10	8.14	0.930	99.9% +
All	3.91	0.936	99.6%

Note: Y (collaborator reading) = a + b X ("true value").

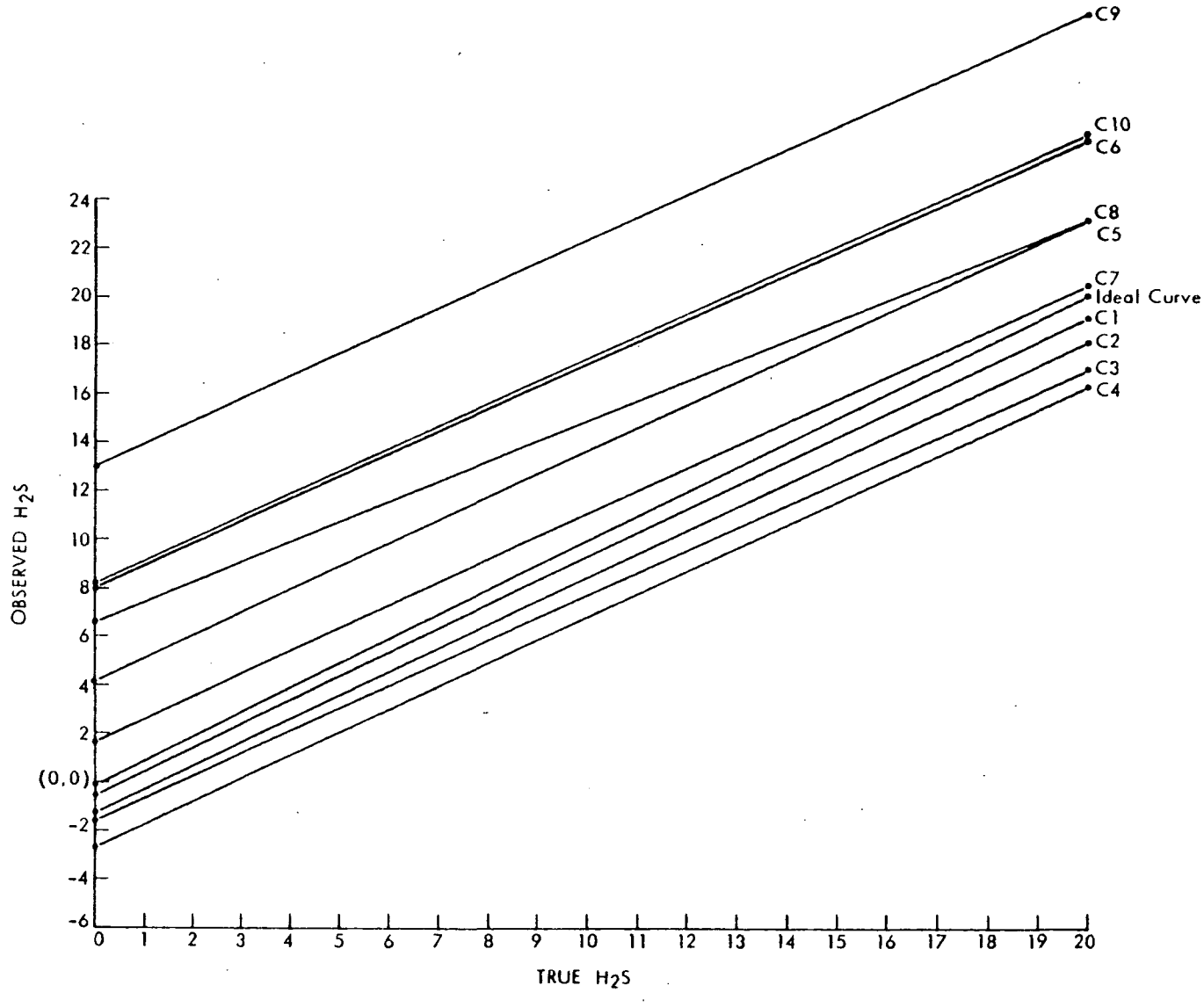


Figure 16 - Theoretical Calibration Curves, H_2S Liquid Samples

TABLE 16. SUMMARY OF ANALYSIS RESULTS

	Standards (%)	Field (%)	Liquid Standards (%)
σ_e	2.16	2.20	3.83[a/]
σ_C	3.93	4.50	3.53
$\sigma_T\sqrt{\sigma_e^2 + \sigma_C}$	4.48	5.01	5.21
B	-4.81	+2.67[b/]	-3.75

a/ But this includes lack of fit, and is not directly comparable to the other two values.

b/ But this bias is level dependent; the individual values are +14% (L = 100 mg/dscm), +5.4% (L = 186 mg/dscm), and -1.8% (L = 390 mg/dscm).

APPENDIX A

COLLABORATOR SELECTION DOCUMENTS

REQUEST FOR PROPOSAL

1. Background

Midwest Research Institute (MRI) is under contract with the Environmental Protection Agency (EPA) to evaluate a modification of Method 11 - Determination of Hydrogen Sulfide Emissions From Stationary Sources in EPA's program for the Standardization of Method 11, which is a tentative method for determining the concentration of H_2S in fuel gas streams at petroleum refineries. This evaluation comprises three major phases: in-house laboratory evaluation, field collaborative test, and statistical analysis of the results of the collaborative tests.

MRI has completed the first phase and is now embarking on the second phase--a field collaborative test. This test will be held in the Kansas City, Missouri, area and will comprise ten collaborators sampling and analyzing strictly according to the modified Method 11. The collaborators' results will be analyzed by MRI.

2. Purpose

The purpose of this task is to provide EPA with data on the accuracy and precision of the modified Method 11. (A copy of the modified Method 11 forms Appendix A of this request for proposal.)

3. Statement of Work

A collaborative test program will be undertaken to achieve the purpose given in Section 2 of this RFP. MRI, as prime contractor, will

coordinate the testing. Each of the 10 collaborators participating in the test will participate according to the Collaborative Test Plan given in Section 4 of this RFP.

4. Collaborative Test Plan

4.1 Location of Test

The test will take place at MRI's field station which is located approximately 15 miles south of MRI in a suburban area of Kansas City. (See Appendix B.)

4.2 Date of Test

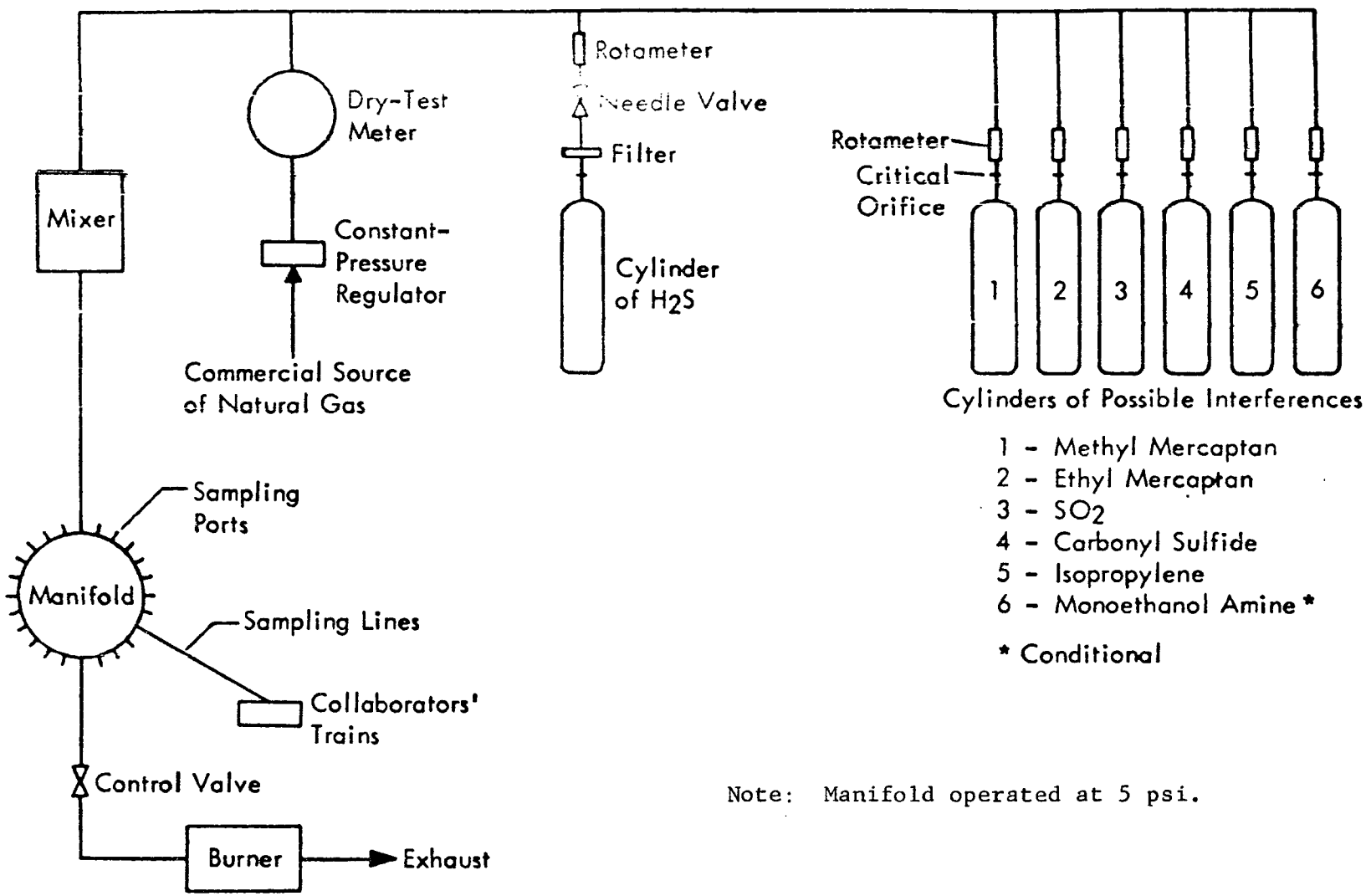
The test is planned for the week of February 22, 1976. See Section 4.6 of this RFP for test schedule.

4.3 Sampling System

Sampling by the collaborators will be done indoors using the sampling system shown diagrammatically in Figure A-1. Each collaborator will attach his sampling trains to the sampling ports of the manifold which will be operated at 5 psi (see Figure A-1). The ports are 1/8 in. Swagelok with nut and ferrule. The collaborator will need to furnish the appropriate matching connections for his trains to connect to his 1/4-in. O.D. Teflon sampling lines.

4.4 Number of Collaborators

There will be 10 different organizations, each of which will serve as an independent, unbiased qualified collaborator.



Note: Manifold operated at 5 psi.

Figure A-1 - Sampling System

4.5 Experimental Design

The collaborative test can be considered as furnishing three data sets:

(1) Analysis of known liquid samples to estimate purely analytical errors,

(2) Analysis of known calibration gas samples (without interferences) to estimate sampling and analysis errors,

(3) Analysis of known field samples with realistic interferences present in the gas stream.

In all cases, three H_2S levels will be used. In addition, blanks will be included in the liquid samples. At all times all 10 collaborators will be observing the same stream so that direct estimates of accuracy and precision are possible.

Each of the collaborators will sample from the sampling system with two trains simultaneously. Each collaborator's trains will be identical to the extent possible. This will provide each collaborator with replicate samples per run. Thus, a run will produce 20 samples.

There will be three challenge levels. Each level will comprise H_2S, natural gas and possible interferences.

There will be three sampling test days. Each day there will be a different challenge level. There will be at least 5 runs/test day.

In addition, there will be two types of standard samples given to each collaborator at the field site: eight liquid samples (two each at levels 1, 2 and 3 and one blank) and six gas samples (two each at levels 1, 2 and 3). One sample of each type and level, plus one liquid blank, will be given to each collaborator before the 3-day test starts--to be analyzed on-site. A similar set will be given to each collaborator after completion of the 3-day test, to be analyzed on-site.

4.6 Test Schedule

The field work will be executed as follows:

Day	Date	Activity
Sunday	February 22	Collaborators travel to Kansas City. Site will be available to collaborator Sunday afternoon for unpackaging equipment, set up, etc.
Monday	February 23	Orientation. Equipment set up. Check of calibration of collaborator's equipment. Analysis of standard samples.
Tuesday	February 24	Sampling at Level 1. Analysis of samples.
Wednesday	February 25	Sampling at Level 2. Analysis of samples.
Thursday	February 26	Sampling at Level 3. Analysis of samples.
Friday	February 27	Check of calibration of collaborator's equipment. Analysis of second set of standard samples. Packaging of equipment. Turn in of field test data and results of analysis.
Saturday	February 28	Complete packaging and return home.

A test day is an 8-hr work day (Monday through Friday) from 8:00 AM to 5:00 PM, with 1 hr off for lunch.

4.7 Collaborator Sampling and Analysis

Each collaborator will follow the modified Method 11 (see Appendix A) exactly. He will do his work entirely independent of any of the other collaborators. He will operate two trains simultaneously during a run. The analysis of all samples (see test schedule, Section 4.6 of this RFP) will be done at MRI's field station.

Each collaborator will need two people in the field. One will be the person who performs the sampling. The other will be the person who analyzes the samples. These jobs cannot be interchanged during any portion of the test.

MRI will supply each collaborator deionized water, a 15-a, 115-v, AC electrical service, analysis-bench space, and data forms. Also, a barometer, an analytical balance (1-mg sensitivity) and a pH meter will be part of MRI's test facilities available to collaborators.

Each collaborator shall calibrate each of his dry gas meters in strict accordance with the procedure given in the modified Method 11. The results of these calibrations shall be submitted to MRI at least 10 days before the field test commences. The calibrations of the collaborators dry gas test meters will be checked with MRI's wet test meter at the test site.

Each collaborator shall prepare the potassium dichromate standard at his home laboratory and standardize sodium thiosulfate at the field site.

Each collaborator will need to furnish a 1/8-in. O.D. Teflon tube to fit a 1/8-in. tube fitting (compression type). This is his connection to gas-cylinder set-ups where he will get his standard gas samples.

5. Collaborators

5.1 Qualifications

Each collaborator is required to provide MRI with its qualifications to do the required testing and analysis. These qualifications shall include:

(1) Capabilities and experience of personnel who will do the work;

(2) Equipment available for use on the project;

(3) Analysis of the standard liquid H_2S samples; and

(4) Related past and current programs of your company concerning sampling of stationary sources. Experience in the measurement of H_2S would be desirable.

5.2 Project Personnel

Each project person must be identified and his direct and unique qualifications given. This should include past sampling and analysis experience by Method 11--when and where this work was done.

Each person's function should be identified. The person who analyzes the standard samples that are included as a part of this request for proposal must also be the field analyst who will analyze test and standard samples at the test site. The person identified as the one who will be the operator of the H_2S sampling trains must be the one who performs this function at the collaborative test.

The project personnel will be considered to be "key personnel" and shall not be substituted by the collaborator after the proposal is received by MRI. Failure to provide the key personnel committed in the proposal shall make the collaborator nonresponsive and will be cause to terminate his subcontract.

5.3 Equipment

Each collaborator shall furnish all equipment and material as specified in Section 5 and 6 of the modified Method 11 procedure (with the exception of that specified in Section 4.7 of this RFP) necessary to (a) perform calibration of his equipment at his home laboratory before going to the field, and (b) perform the field sampling and analysis in the field according to the plan given in Section 4 of this RFP.

Each collaborator shall have in the field three sampling trains that meet the specifications given in modified Method 11. Two of these are for operating two trains simultaneously per run. The other is to serve as a backup. Also adequate chemicals, hardware, spare parts, etc., should be taken to the field. A sampling valve (needle valve or equivalent)

will be needed with each train for its connection to a port of the manifold in the sampling system (see Figure A-1).

The proposal shall identify the equipment and material that will be taken to the field for the collaborative test.

5.3 Standard Samples

Each request-for-proposal recipient will be sent standard liquid samples to be analyzed at his home laboratory by the analyst who will serve as the collaborative field-team analyst in Kansas City. The results of their analyses need to be part of the proposal submitted to MRI in response to this request for proposal.

These standard samples will be shipped to the collaborator one week after the request for proposal is mailed. This delay is to provide the respondee with time to acquire the necessary material to perform the analysis, since the samples must be analyzed immediately upon their arrival.

The cadmium absorbing solution must contain Antifoam B. All collaborators shall use the primary sample recovery method in the analysis of all samples. The acidified-iodine extraction of the impingers will not be used.

MRI will include a small amount of Antifoam B with the standard samples shipped to the collaborators. The collaborators must obtain their own Antifoam B for use in the field sampling.

5.4 Shipment of Equipment

Each collaborator should ship its field equipment and material to Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri, Attention: George Scheil, prepaid and in sufficient time so that it will arrive at MRI a week prior to Day 1 of the field test. If the collaborator is driving and is bringing his equipment with him, this advance delivery is not necessary. MRI should be apprised of the shipment method.

5.5 Lodging

The Ramada Inn shown on the figures of Appendix B is a recommended motel for collaborators. This motel, as shown in the figures, is 35 miles from the Kansas City International Airport and a few miles from MRI's field station where the test will take place.

6. Contractual Document

It is MRI's intent to issue each collaborator a cost-plus-fixed-fee type purchase order to authorize the work.

7. Insurance Coverage

Each collaborator assumes the risk of all injuries, including death resulting therefrom, to all persons including collaborators, employees, or any member of the public, and damage to and destruction of property by whomsoever owned resulting from the prosecution of any work or obligation undertaken or required by this project unless caused solely by the negligent acts or omissions of MRI, its employees, servants, and employees, from and against any and all liability arising therefrom,

including all expenses legal or otherwise, incurred by them in the investigation, defense, and settlement of any claim or suit.

Each collaborator shall secure before commencing and shall maintain during the performance of the work (a) Comprehensive General Liability Insurance with the minimum Bodily Injury Limits of $300,000 each occurrence and Property Damage Limits of $100,000 each occurrence; (b) Automobile Liability Insurance with minimum Bodily Injury Limits of $300,000 each occurrence and Property Damage Limits of $100,000 each occurrence; (c) Statutory Workmen's Compensation and Occupational Disease Disability Insurance; and (d) Employers' Liability Insurance with Limits at $25,000 each occurrence. Collaborators shall also furnish to MRI evidence of such insurance coverage in the form of Certificates of Insurance, together with evidence that the insurance carrier has assumed the Liability of the collaborator hereunder either by furnishing to MRI a properly executed "Assumption of Contractual Liability" endorsement or by Certificate of Contractual Liability Insurance. All Certificates of Insurance shall stipulate that MRI will be given 10 days' written notice prior to any change, substitution or cancellation prior to the normal expiration date.

TENTATIVE METHOD FOR THE DETERMINATION OF HYDROGEN SULFIDE EMISSIONS FROM STATIONARY SOURCES[a/]

a/ A tentative method is one which has been carefully drafted from available experimental information, review editorially within the Quality Assurance Branch, EMSL, and has undergone extensive laboratory evaluation. The method is still under investigation and, therefore, is subject to revision.

1.0 Principle and Applicability

1.1 Principle

Hydrogen sulfide (H_2S) is collected from a source in a series of midget impingers and absorbed in pH 3.0 cadmium sulfate solution to form cadmium sulfide (CdS). The latter compound is then measured iodometrically. An impinger containing hydrogen peroxide is included to remove SO_2 as an interfering species.

1.2 Applicability

This method is applicable for the determination of hydrogen sulfide emissions from stationary sources only when specified by the test procedures for determining compliance with the new source performance standards.

2.0 Range and Sensitivity

The limit of detection is approximately 8 mg/m^3 (6 ppm). The maximum of the range is 740 mg/m^3 (520 ppm).

3.0 Interferences

Any compound that reduces iodine or oxidizes iodide ion will interfere in this procedure, provided it is collected in the cadmium-sulfate impingers. Sulfur dioxide in concentrations of up to 0.1 mole percent is eliminated by the peroxide solution. Mercaptans coprecipitate with hydrogen sulfide. In the absence of H_2S, only traces of mercaptan are collected. A mercaptan concentration equal to that of the H_2S present yields results that are approximately 5% high. Carbon oxysulfide of 20% does not interfere. Certain carbonyl-containing compounds react with iodine and produce recurring endpoints. However, acetaldehyde and acetone at concentrations of 1 and 3%, respectively, do not interfere.

Entrained hydrogen peroxide produces a negative interference equivalent to 100% of that of an equimolar quantity of hydrogen sulfide. Avoid the ejection of hydrogen peroxide into the cadmium sulfate impingers.

4.0 Precision and Accuracy

Replicate analyses should not deviate by more than 5% relative standard deviation. The collection efficiency of hydrogen sulfide measurements has been established at 96 $\pm$ 2% of the absolute value based on known standards.

5.0 Apparatus

5.1 Sampling Train

5.1.1 Sampling line - Six to 7 mm (1/4 in.) Teflon* tubing to connect sampling train to sampling valve. Depending on sampling stream pressure, a pressure-reduction regulator may be required just prior to the Teflon sampling line.

If significant amounts of water or amine are present in the sample stream, a corrosion-resistant cold trap should be used immediately after the sample tap. The trap should not be operated below 0°C to avoid condensation of C_3 or C_4 hydrocarbons.

5.1.2 Impingers - Five midget impingers, each with 30 ml capacity. The internal diameter of the impinger tip must be 1.00 mm $\pm$ 0.05 mm. The impinger tip must be positioned 4 to 6 mm from the bottom of the impinger.

5.1.3 Glass or Teflon connecting tubing for the impingers.

5.1.4 Ice bath container - To maintain absorbing solution at a low temperature.

5.1.5 Silica gel drying tube - To protect pump and dry gas meter.

5.1.6 Sampling valve - Needle valve or equivalent to adjust gas flow rate. Stainless steel or other corrosion-resistant material.

5.1.7 Dry gas meter - Sufficiently accurate to measure sample volume to within 1% and calibrated with a wet test meter over the range of flow rates used in sampling. Gas volume for one dial revolution must not be more than 10 liters. The gas meter should have a gas petcock or equivalent on the outlet connector which can be closed during the leak test.

5.1.8 Flow meter - Rotameter or equivalent, to measure a 0.5 to 2.0 liters/min (1 to 4 CFH) flow rate.

5.1.9 Graduated cylinder - 25 ml size.

5.1.10 Barometer - To measure atmospheric pressure to within $\pm$ 2.5 mm (0.1 in.) Hg.

5.1.11 U-Tube manometer - 0-30 cm. water column. For leak check procedure.

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

5.1.12 Rubber squeeze bulb - To pressurize train for leak check.

5.1.13 Tee, pinchclamp, and connecting tubing - For leak check.

5.1.14 Vacuum pump - Required for air purge.

5.1.15 Needle valve or orifice - To set air purge flow to 1 liter/min.

5.1.16 Tube packed with activated carbon - To filter air during purge.

5.1.17 Volumetric flask - One 1,000 ml.

5.1.18 Volumetric pipette - One 15 ml.

5.2 Sample Recovery

5.2.1 Sample container - Iodine flask, glass-stoppered; 500 ml size.

5.2.2 Pipette - 50 ml volumetric type.

5.2.3 Graduated cylinders - One each 25 and 250 ml.

5.2.4 Flasks - 125 ml, Erlenmeyer.

5.2.5 Wash bottle.

5.2.6 Volumetric flasks - Three 1,000 ml.

5.3 Analysis

5.3.1 Flask - 500 ml glass-stoppered iodine flask.

5.3.2 Burette - 50 ml.

5.3.3 Flask - 125 ml. Erlenmeyer.

5.3.4 Pipettes, volumetric - One 25 ml; two each 50 and 100 ml.

5.3.5 Volumetric flasks - One 1,000 ml; two 500 ml.

5.3.6 Graduated cylinders - One each 10 and 100 ml.

6.0 Reagents

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use best available grade.

6.1 Sampling

6.1.1 Cadmium sulfate absorbing solution - Dissolve 41.0 g of $3CdSO_4 \cdot 8\ H_2O$ and 15.0 ml of 0.1 M sulfuric acid in a 1-liter volumetric flask that contains approximately 3/4 liter of deionized distilled water. Dilute to volume with deionized water. Mix thoroughly. pH should be 3.0 $\pm$ 0.1. Add 10 drops of Dow-Corning Antifoam B.* Shake well before use. If Antifoam B is not used, the alternate acidified iodine extraction procedure must be used.

6.1.2 Hydrogen peroxide, 3% - Dilute 30% hydrogen peroxide to 3% as needed. Prepare fresh daily.

6.1.3 Water - Deionized, distilled, to conform to ASTM specifications D1193-72, Type 3.

6.2 Sample Recovery

6.2.1 Hydrochloric acid solution (HCl), 3 M - Add 240 ml of concentrated HCl (specific gravity 1.19) to 500 ml of deionized, distilled water in a 1-liter volumetric flask. Dilute to 1 liter with deionized water. Mix thoroughly.

6.2.2 Iodine solution, 0.1 N - Dissolve 24 g of potassium iodide (KI) in 30 ml of deionized, distilled water. Add 12.7 g of resublimed iodine (I_2) to the potassium iodide solution. Shake the mixture until the iodine is completely dissolved. If possible, let the solution stand overnight in the dark. Slowly dilute the solution to 1 liter with deionized, distilled water, with swirling. Filter the solution if it is cloudy. Store solution in a brown-glass reagent bottle.

6.2.3 Standard iodine solution, 0.01 N - Pipette 100.0 ml of the 0.1 N iodine solution into 1-liter volumetric flask and dilute to volume with dionized, distilled water. Standardize daily as in Section 8.1. This solution must be protected from light. Reagent bottles and flasks must be kept tightly stoppered.

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

6.3 Analysis

6.3.1 Sodium thiosulfate solution, standard 0.1 N - Dissolve 24.8 g of sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) or 15.8 g of anhydrous sodium thiosulfate ($Na_2S_2O_3$), in 1 liter of deionized, distilled water and add 0.01 g of anhydrous sodium carbonate (Na_2CO_3) and 0.4 ml of chloroform ($CHCl_3$) to stabilize. Mix thoroughly by shaking or by aerating with nitrogen for approximately 15 min and store in a glass-stoppered, reagent bottle. Standardize as in Section 8.2 below.

6.3.2 Sodium thiosulfate solution, standard 0.01 N - Pipette 50.0 ml of the standard 0.1 N thiosulfate solution into a volumetric flask and dilute to 500 ml with distilled water.

6.3.3 Starch indicator solution - Suspend 10 g of soluble starch in 100 ml of deionized, distilled water and add 15 g of potassium hydroxide (KOH) pellets. Stir until dissolved, dilute with 900 ml of deionized distilled water and let stand for 1 hour. Neutralize the alkali with concentrated hydrochloric acid, using an indicator paper similar to Alkacid test ribbon, then add 2 ml of glacial acetic acid as a preservative.
(Note 1: Test starch indicator solution for decomposition by titrating with 0.01 N iodine solution 4 ml of starch solution in 200 ml of distilled water that contains 1-g potassium iodide. If more than 4 drops of the 0.01 N iodine solution are required to obtain the blue color, a fresh solution must be prepared.)

7.0 Procedure

7.1 Sampling

7.1.1 Assemble the sampling train as shown in Figure A-2, connecting the five midget impingers in series. Place 15 ml of 3% hydrogen peroxide solution in the first impinger. Leave the second impinger empty. Place 15 ml of the cadmium sulfate absorbing solution in the third, fourth, and fifth impingers. Place the impinger assembly in an ice bath container and place crushed ice around the impingers. Add more ice during the run, if needed.

7.1.2 Connect the rubber bulb and manometer to first impinger, as shown in Figure A-1. Close the petcock on the dry gas meter outlet. Pressurize the train to 30-cm. water pressure with the bulb and close off tubing connected to rubber bulb. Train must hold a 30-cm. water pressure with not more than a 1 cm. drop in pressure in a 1-min interval. Stopcock grease is acceptable for sealing ground glass joints.

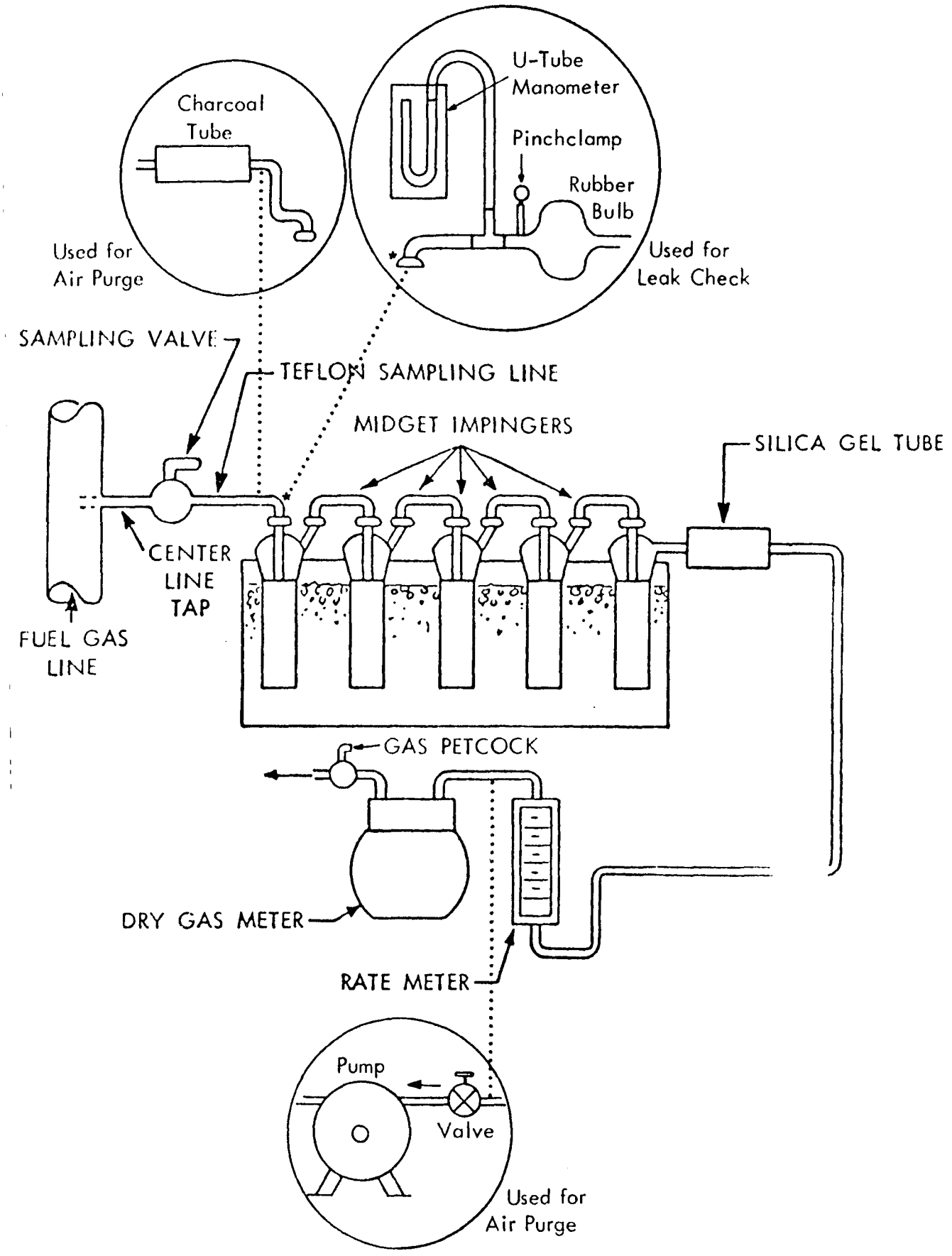


Figure A-2 - H_2S Sampling Train

7.1.3 Purge the connecting line between the sampling valve and the first impinger. Close valve and connect the sample line to the train. Open the petcock on the dry gas meter outlet. Record the initial reading on the dry gas meter.

7.1.4 Open the sampling valve and then adjust the valve to obtain a rate of approximately 1 liter/min. Maintain a constant flow rate during the test. Record the meter temperature.

7.1.5 Sample for at least 10 min. At the end of the sampling time, close the sampling valve and record the final volume and temperature readings.

7.1.6 Disconnect the impinger train from the sampling line. Connect the charcoal tube and the pump, as shown in Figure A-2. Purge the train with clean ambient air for 15 min to ensure that all H_2S is removed from the hydrogen peroxide. For sample recovery, cap the open ends and remove to a clean area that is away from sources of heat. The area should be well lighted, but not exposed to direct sunlight.

7.2 Sample Recovery

7.2.1 Discard the contents of the hydrogen peroxide impinger. Carefully rinse the contents of the third, fourth, and fifth impingers into a 500 ml iodine flask.

(Note 2: The impingers normally have only a thin film of cadmium sulfide remaining after a water rinse. If Antifoam B was not used or if significant quantities of yellow cadmium sulfide remain in the impingers, the alternate recovery procedure must be used.)

7.2.2 Pipette exactly 50 ml of 0.01 N iodine solution into a 125-ml Erlenmeyer flask. Add 10 ml of 3 M HCl to the solution. Quantitately rinse the acidified iodine into the iodine flask. Stopper the flask immediately and shake briefly.

7.2.2 (Alternate) Extract the remaining cadmium sulfide from the third, fourth, and fifth impingers using the acidified iodine solution. Immediately after pouring the acidified iodine into an impinger, stopper it and shake for a few moments, then transfer the liquid to the iodine flask. Do not transfer any rinse portion from one impinger to another; transfer it directly to the iodine flask. Once the acidified iodine solution has been poured into any glassware containing cadmium sulfide, the container must be tightly stoppered at all times except when adding more solution, and this must be done as quickly and carefully as possible. After adding any acidified iodine solution to the iodine flask, allow a few minutes for absorption of the H_2S before adding any further rinses. Repeat the iodine

extraction until all cadmium sulfide is removed from the impingers. Extract that part of the connecting glassware that contains visible cadmium sulfide.

Quantitatively rinse all of the iodine from the impingers, connectors, and the beaker into the iodine flask using deionized, distilled water. Stopper the flask and shake briefly.

7.2.3 Allow to stand about 30 min in the dark for absorption of the H_2S into the iodine, then complete the titration analysis as in Section 7.3.

(Note 3: CAUTION! Iodine evaporates from acidified iodine solutions. Samples to which acidified iodine have been added may not be stored, but must be analyzed in the time schedule stated above in 7.2.3.)

7.2.4 Prepare a blank by adding 45 ml of cadmium sulfate absorbing solution to an iodine flask. Pipette exactly 50 ml of 0.01 iodine solution into a 125-ml Erlenmeyer flask. Add 10 ml of 3 M HCl. Follow the same impinger extracting and quantitative rinsing procedure carried out in sample analysis. Stopper the flask, shake briefly, let stand 30 min in the dark, and titrate with the samples.

(Note 4: The blank must be handled by exactly the same procedure as that used for the samples.)

7.3 Analysis

(Note 5: Titration analyses should be conducted at the sample-cleanup area in order to prevent loss of iodine from the sample. Titration should never be made in direct sunlight.)

7.3.1 Using 0.01 N sodium thiosulfate solution, rapidly titrate samples in iodine flasks using gentle mixing, until solution is light yellow. Add 4 ml of starch indicator solution and continue titrating slowly until the blue color just disappears. Record V_t, the volume of sodium thiosulfate solution used (ml).

7.3.2 Titrate the blanks in the same manner as the samples. Run blanks each day until replicate values agree within 0.05 ml. Average the replicate titration values which agree within 0.05 ml.

8.0 Calibration and Standards

8.1 Standardize the 0.01 N iodine solution daily as follows: Pipette 25 ml of the iodine solution into a 125-ml Erlenmeyer flask. Add 2 ml of 3 M HCl. Titrate rapidly with standard 0.01 N thiosulfate solution until the solution is light yellow, using gentle mixing. Add four drops of starch

indicator solution and continue titrating slowly until the blue color just disappears. Record V_t, the volume of thiosulfate solution used (ml). Repeat until replicate values agree within 0.05 ml. Average the replicate titration values which agree within 0.05 ml and calculate the exact normality of the iodine solution using equation 9.1. Repeat the standardization daily.

8.2 Standardize the 0.1 N thiosulfate solution as follows: Oven-dry potassium dichromate ($K_2Cr_2O_7$) at 180 to 200°C. Weigh to the nearest milligram, two grams of potassium dichromate into a 500 ml volumetric flask, dissolve in deionized, distilled water and dilute to exactly 500 ml. In a 500-ml iodine flask, dissolve approximately 3 g of potassium iodide (KI) in 45 ml of deionized, distilled water, then add 10 ml of 3 M hydrochloric acid solution. Pipette 50 ml of the dichromate solution into this mixture. Gently swirl the solution once and allow it to stand in the dark for 5 min. Dilute the solution with 100 to 200 ml of deionized distilled water, washing down the sides of the flask with part of the water. Titrate with 0.1 N thiosulfate until the solution is light yellow. Add 4 ml of starch indicator and continue titrating slowly to a green end point. Record V_t, the volume of thiosulfate solution used (ml). Repeat until replicate analyses agree within 0.05 ml. Calculate the normality using eq. 9.2. Repeat the standardization each week.

9.0 Calculations

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off results only after the final calculation.

9.1 Normality of the Standard Iodine Solution.

$$N_I = \frac{N_T V_T}{V_I}$$

where:

N_I = normality of iodine, g-eq/liter;
V_I = volume of iodine used, ml;
N_T = normality of sodium thiosulfate, g-eq/liter; and
V_T = volume of sodium thiosulfate used, ml.

9.2 Normality of the Standard Thiosulfate Solution.

$$N_T = 2.04 \frac{W}{V_T}$$

where:

W = weight of $K_2Cr_2O_7$ used, g;
V_T = volume of $Na_2S_2O_3$ used, ml;
N_T = normality of standard thiosulfate solution, g-eq/liter; and
2.04 = conversion factor.

$$= \frac{(6 \text{ eq } I_2/\text{mole } K_2Cr_2O_7)\ (1{,}000 \text{ ml/liter})}{(294.2 \text{ g } K_2Cr_2O_7/\text{mole})\ (10 \text{ aliquot factor})}$$

9.3 Dry Gas Volume - Correct the sample volume measured by the dry gas meter to standard conditions (21°C) and 760 mm Hg.

$$V_{m_{std}} = V_m \left(\frac{T_{std}}{T_m}\right) \left(\frac{P_{bar}}{P_{std}}\right)$$

where:

$V_{m_{std}}$ = volume at standard conditions of gas sample through the dry gas meter, standard liters;
V_m = volume of gas sample through the dry gas meter (meter conditions), liters;
T_{std} = absolute temperature at standard conditions, 294 °K;
T_m = average dry gas meter temperature, °K;
P_{bar} = barometric pressure at the orifice meter, mm Hg; and
P_{std} = absolute pressure at standard conditions, 760 mm Hg.

9.4 Concentration of H_2S - Calculate the concentration of H_2S in the gas stream at standard conditions using equation:

$$C_{H_2S} = \frac{K[(V_I N_I - V_T N_T) \text{ sample} - (V_I N_I - V_T N_T) \text{ blank}]}{V_{m_{std}}}$$

where (metric units):

C_{H_2S} = concentration of H_2S at standard conditions, mg/dscm;
K = conversion factor = 17.0×10^3

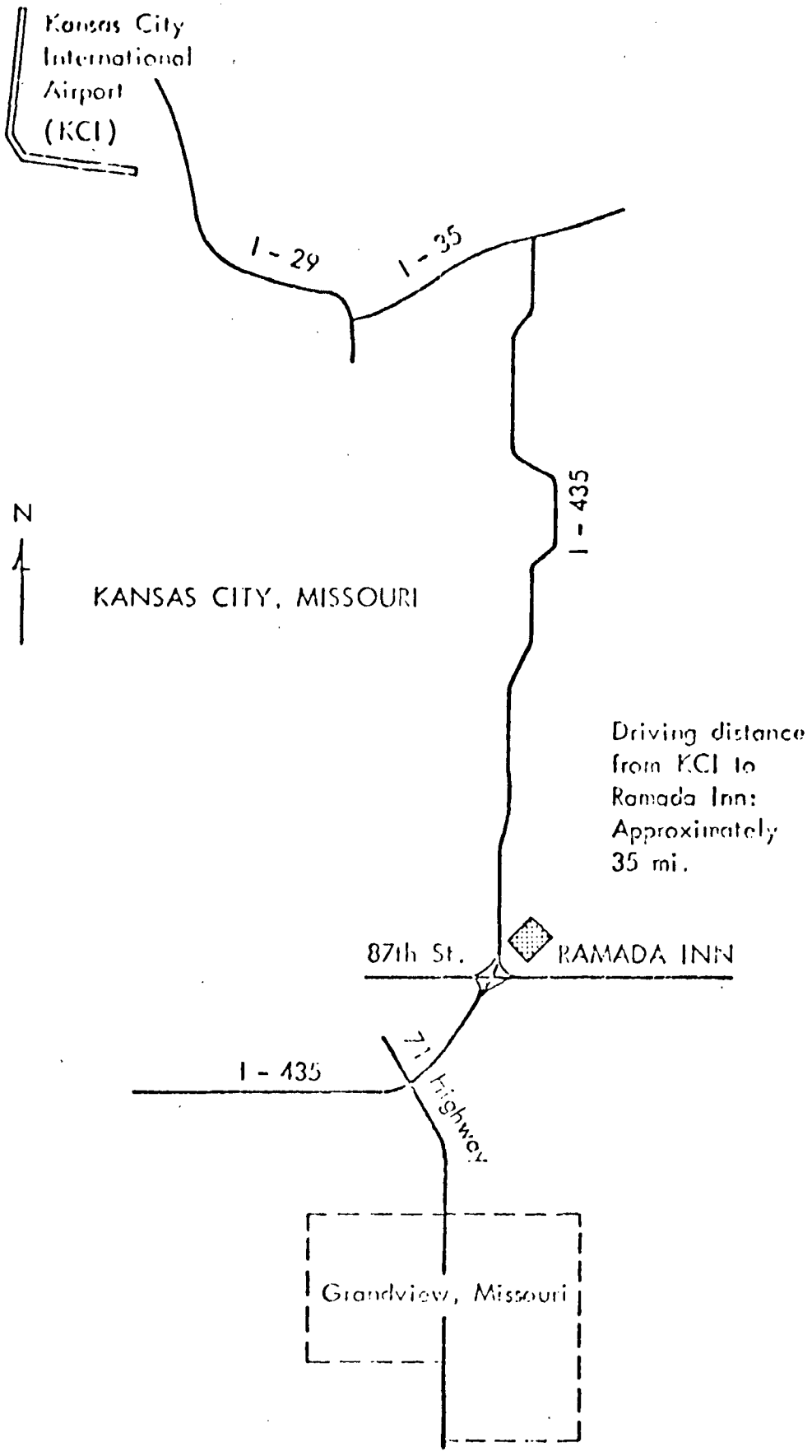
$$= \frac{(34.07 \text{ g/mole } H_2S)\ (1{,}000 \text{ liters/m}^3)\ (1{,}000 \text{ mg/g})}{(1{,}000 \text{ ml/liter})\ (2H_2S \text{ eq/mole})}$$

V_I = volume of standard iodine solution, ml;
N_I = normality of standard iodine solution, g-eq/liter;
V_T = volume of standard sodium thiosulfate solution, ml;
N_T = normality of standard sodium thiosulfate solution, g-eq/liter; and
$V_{m_{std}}$ = dry gas volume at standard conditions, liters.

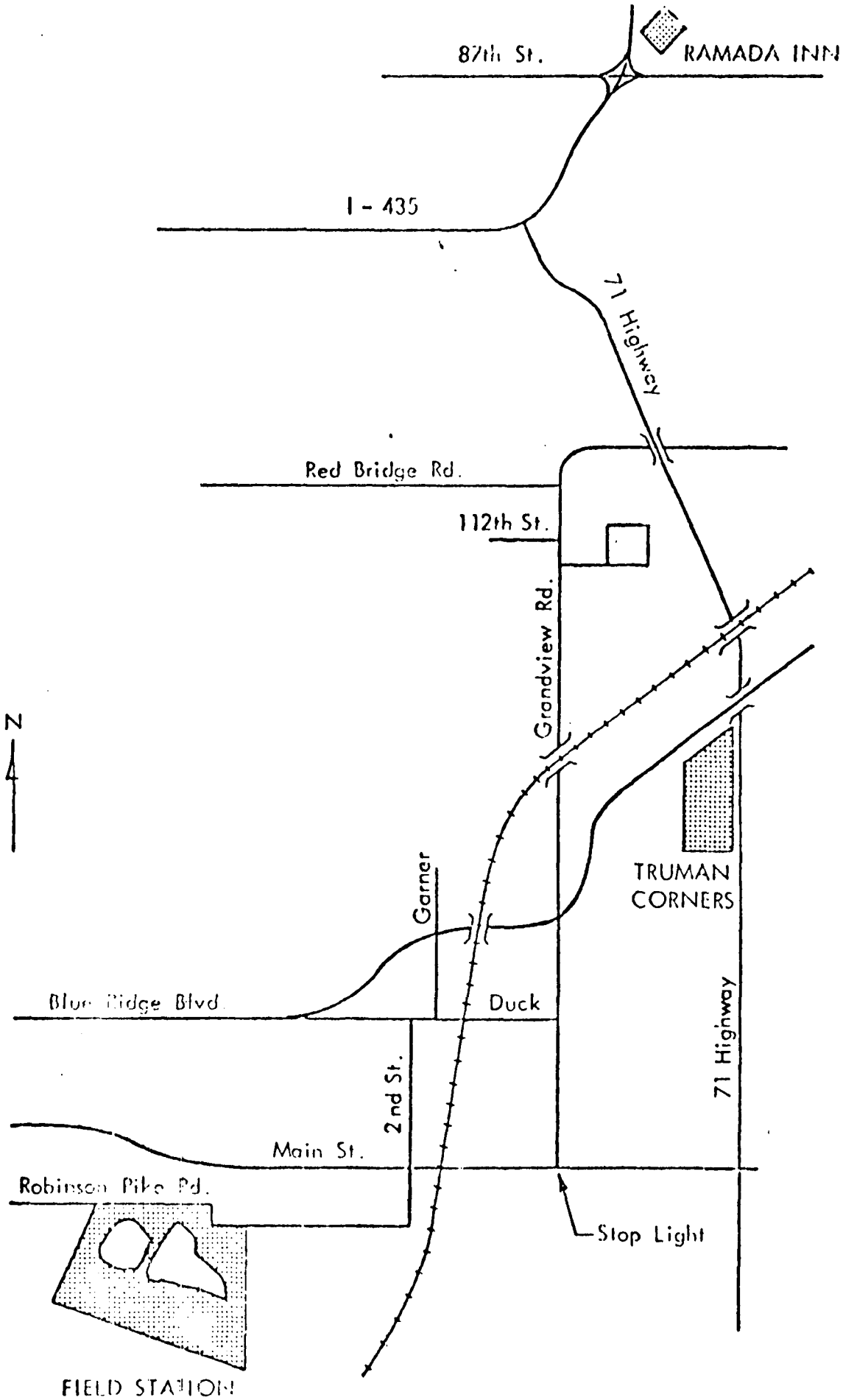
10.0 Stability

The absorbing solution is stable for at least 1 month. Sample recovery and analysis should begin within 1 hour of sampling to minimize oxidation of the acidified cadmium sulfide. Once iodine has been added to the sample, the remainder of the analysis procedure must be completed according to Sections 7.2.2, 7.2.3, and 7.3.

MAPS



Map -- Kansas City International Airport to Ramada Inn



Map: Ramada Inn to Field Station

INSTRUCTIONS FOR SAMPLE ANALYSIS

These test samples are similar to the liquid standard samples which will be used during the collaborative test. Temperature changes from -20 to +30°C do not adversely affect the samples. Over a 2-week period, the samples show only slight changes in value. Please complete the sample analyses within 2 weeks of the shipping date (December 29).

The sample analysis results and the standardization data must be recorded on the data sheets provided and the data sheets returned to MRI with your proposal. Report the results of <u>any four</u> of the six samples. Be sure to record the sample numbers on the proper data sheets in the remarks section. Report the analysis results as mg/dscm. Assume that the sampling data for each sample was as indicated on the data sheets.

A vial containing Antifoam B is included with the samples since this is not a commonly available item.

Please complete the standardizations data before analyzing the samples. Each sample should be treated as if it was the contents of an impinger train. The samples are suspended in the normal absorbing solution and the sample volume is identical to the total amount used in the sampling train (3 x 15 ml = 45 ml).

The synthetic samples are less reactive than the freshly precipitated cadmium sulfide obtained by Method 11. To obtain accurate results it is necessary to maintain the precipitate as a finely divided suspension.

To completely suspend the sample for analysis, the following changes must be made in the analysis. First, shake each sample thoroughly. Then place the samples in an ultrasonic bath for at least 10 min before sample recovery. After removing each sample from the ultrasonic, shake briefly, and proceed with the sample recovery steps without delay. Rinse the contents of the bottle into an iodine flask in the normal manner and, after adding the acidified iodine to the flask, stopper the flask and shake vigorously for 30 sec. If the ultrasonic bath is not used, if the sample recovery is not done immediately after removal from the ultrasonic, or if the sample/acidified iodine mixture is not shaken vigorously for 30 sec, recoveries will be low and erratic. The remainder of the sample analysis is the same as for a normal sample.

MIDWEST RESEARCH INSTITUTE
DATA SHEET
HYDROGEN SULFIDE - CADMIUM SULFATE METHOD
SAMPLING

Collaborator_____ Date _____
Run No._____ Sampled by_____
Sampling Train No._____ Port No._____

INITIAL READINGS		FINAL READINGS	
Dry Gas Meter	218.63	234.89	Dry Gas Meter
Meter Temp. °C	18°	18°	Meter Temp. °C
Time	1315	1330	Time
Rotameter	86	87	Rotameter

Type Ball Used: (Glass) Steel (Circle)

Sampling Flow Rate 1.0 ℓ/min

Barometric Pressure mm Hg 740 Meter Correction Factor* 0.98

Measured Gas Meter Vol. (Vs) ____ℓ At Standard Cond. (V_{MSTD})_____ℓ

REMARKS:

ANALYSIS

Analyzed by_____ Burette: (.01 N Thiosulfate)
Final RDG. _____ml
Time at I_2 Addition_____ Initial RDG. _____ml
Volume of Thio (V_T)_____ml
Time at Titration_____

Volume of Iodine Added to Sample_____

Normalities: .01 N Iodine_____ .01 N Thiosulfate_____

Blank: .01 N Thiosulfate

Volume_____ml

Volume of Iodine Added to Blank_____

H_2S Concentration_____
mg/DSCM

REMARKS:

*$\frac{Vs}{Vm}$ where Vs is the true gas volume and Vm is the gas volume indicated by the gas meter.

MIDWEST RESEARCH INSTITUTE
DATA SHEET
HYDROGEN SULFIDE - CADMIUM SULFATE METHOD
STANDARDIZATIONS

Collaborator_____ Analyzed by_____ Date_____

0.1 N Sodium Thiosulfate

Weight of $K_2Cr_2O_7$ _____g

Volume of $K_2Cr_2O_7$ Solution_____ml

Final Buret Reading	_____	_____	_____	_____	_____
Initial Buret Reading	_____	_____	_____	_____	_____
Volume of 0.1 N Thio	_____	_____	_____	_____	_____

Sodium Thiosulfate Volume (V_T) _____ml

Normality_____(N_T)

0.01 Iodine Volume of Iodine _____

Final Buret Reading	_____	_____	_____	_____	_____
Initial Buret Reading	_____	_____	_____	_____	_____
Volume of .01 N Thio	_____	_____	_____	_____	_____

Thiosulfate Volume (V_I) _____ml

Normality _____(N_I)

Blanks

Time at I_2 Addition	_____	_____	_____	_____	_____
Time at Titration	_____	_____	_____	_____	_____
Final Buret Reading	_____	_____	_____	_____	_____
Initial Buret Reading	_____	_____	_____	_____	_____
Volume of .01 N Thio	_____	_____	_____	_____	_____

Volume of Thiosulfate_____ml (V_T)

REMARKS:

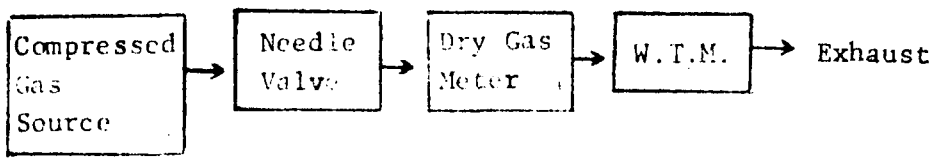
APPENDIX B

INSTRUCTIONS TO THE COLLABORATORS

INSTRUCTION TO COLLABORATORS

A number of details with regard to the collaborative test have not been mentioned or have surfaced in conversations with various prospective collaborators. The following comments should cover most questions that you may have with regard to the test.

1. Calibration data for the 3 dry gas meters (including spare unit) must be submitted to MRI 10 days prior to the test date, i.e., by February 13. Calibration must be done by wet test meter or spirometer (bell prover). Data must include specifications on the wet test meter (or spirometer) and a simple block diagram showing the gas flow path in the components of the test assembly. For example, the normal configuration using a wet test meter is:



Calibration can be done with air, nitrogen or natural gas. The data must include all pertinent pressures, temperatures, etc. necessary to calculate the meter correction factor, a sample calculation, and the final correction factors reported to 1 part per thousand.

2. The test manifold is mounted on a round table approximately 12 ft in diameter. The port assembly is mounted on a small elevated platform in the center of the table. An exhaust hood is suspended above the platform with a flexible rubber skirt which extends below the ports. Each

collaborator will be assigned a sector on the table approximately 3 ft along the circumference of the table. Both sampling trains must fit within this area (an equivalent space is available under the table). Exhaust gases from the trains should be vented to the exhaust hood. The 110 VAC power is available at the table and at a number of other locations in the building. Please note that the pumps are to be used only during the air purge. During the actual sampling the pressure head of the manifold (~ 4 to 5 psig) forces the gas through the trains. Upon arrival at the site you will be assigned two sample ports which will be used throughout the test. Each manifold port terminates at 1/8 in. swagelock nut w/ferrules. Cap plugs seal off any unused ports.

3. Space for sample recovery, titrations, etc., will be provided at a number of benches and tables in the room. Each collaborator will have at least 6 ft of bench/table space in addition to the sampling table area. The building has only one sink. All solution wastes must be dumped into waste buckets which MRI will provide. Deionized water is provided at a large reservoir with spigot. Each collaborator should bring a poly-pac or similar water bottle to avoid the creation of a traffic jam at the deionized water tap.

4. Since up to 25 people will be working in an area approximately 30 x 60 ft, large, cumbersome pieces of equipment should not be used. For example, anyone bringing the Rockwell meters used in RAC consoles should dismount the meter and bring only the essential components. Every effort

must be made during the test to plan ahead and work as rapidly and efficiently as possible. Monday will be the critical day because it is the first and due to the large number of tasks to be completed.

5. The specifications on impinger tip diameter and spacing must be adhered to for the 3 $CdSO_4$ impingers. If you can keep these impingers properly identified, peroxide and dry impingers need not meet the precise specifications. The specification on impinger tip diameter is not a misprint. The ruggedness test showed that this is a critical factor in collection efficiency. Most commercially available impingers will meet the specifications. The entire test will go much faster if you can bring enough spare impingers so that two sets of impingers can be prepared while another two sets are sampling and being purged.

6. The liquid samples which each collaborator will analyze on Monday and Friday are similar to those sent by mail. The samples used during the test will be freshly prepared and agitated in an ultrasonic by MRI before issuing them so that you may proceed immediately with the analysis after receiving them. All the liquid samples must be analyzed against a blank using your own absorbing solution.

7. Safety glasses must be worn at all times in the test building. No food or beverages are allowed in the building and smoking is also prohibited. A guest house is immediately adjacent to the test building where none of the above regulations apply. A drinking fountain, coffee, etc., will be available in the guest house.

8. Ice is available from a number of sources in the vicinity.

9. Anyone who wishes may come to the test facility on Sunday afternoon to unpack, assemble equipment, etc. However, no sample analyses can be done until Monday. The grounds of the MRI field station are normally kept locked except 8 AM through 5 PM weekdays. However someone will be on duty at the site from 12 noon until 6 PM on Sunday and from 7 AM until the completion of all work each weekday. Someone will also be available on Saturday, the 28th if needed. The test facility phone number is 761-1272.

10. All collaborators are to be present at the test site at 8 AM on Monday for a brief orientation meeting. The MRI field station location is shown on the map attached to the RFP. The test facility and guest house are the buildings nearest the main gate.

11. Data forms for standardizations and sample results will be provided by MRI. Each data form consists of two data sheets stapled together with carbon paper between them. Since no report is required of the sample results, the data sheets are to be a complete and original record of all data. One copy of all data for the day must be submitted to the MRI test supervisor before leaving the site each evening. Each collaborator will complete all necessary calculations for computing the final results. The second copy is to be retained by the collaborator. MRI requests that each collaborator check their data sheets and calculations after returning home and report any errors or amendments within 3 weeks of the completion of the test. We invite any comments on the test or the method from the participants.

12. On Monday, the 23rd, each collaborator must analyze a set of liquid samples, run at least one simultaneous pair of samples from each of the three reference gas cylinders and have the dry gas meters checked against MRI's wet test meter. MRI personnel will assist in the meter checks. On each of the next three days each collaborator will make at least five simultaneous, paired runs from the test manifold. On Friday another set of liquid samples will be analyzed and the reference gas cylinder sampling also repeated. After completing all required tests the collaborators may pack their equipment either Friday or Saturday. No testing is scheduled for Saturday.

13. Each reference gas cylinder will have a pressure regulator and enough sampling connections to allow up to 3 collaborators to sample each gas simultaneously. Each collaborator must provide a 1/8 in. O.D. Teflon tube to fit the compression fittings of the sampling connections.

14. All solution standardizations must be done on-site. However, the potassium dichromate standard should be dried and weighed at the home laboratory. The weighed portions may be shipped dry in sealed vials or in solution form. The other solutions may be shipped preweighed and dry or as stock solutions. Each collaborator is responsible for bringing enough reagents for the entire test schedule. In the event of loss or damage of the reagents, MRI will provide enough reagents to complete the test. MRI will also have a limited number of spare components for emergency use only. Each collaborator is expected to bring sufficient spare parts to cover breakage or malfunctions. This must include 3 complete sampling trains.

15. Any equipment which is shipped prepaid to MRI in advance of the test will be delivered to the test site. Please notify George Scheil or Paul Constant if you intend to ship equipment to the site and give shipping date, number of boxes and shipping firm so that MRI can check in the shipments and begin tracing any lost shipments. Any equipment shipped should arrive at MRI 1 week prior to the test. The MRI phone number is (816) 561-0202.

16. Each sampling period will be 15 min long. All sampling and analysis must conform to the method. All cadmium sulfate absorbing solution must contain Antifoam B and the impingers will be rinsed with water only-no $HCl-I_2$ extraction will be used during sample recovery.

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16. ABSTRACT

A collaborative test was run of the revised Method 11 procedures that was developed in Volume I. Ten collaborators were selected from a total of 24 interested organizations. Part of the screening process was to require each potential collaborator to analyze a set of liquid samples in accordance with the procedure. A test manifold was constructed which could simulate typical refinery fuel gas streams. During February 22 to 27, 1976, a total of 16 runs at three different H_2S levels were made, as well as a series of standard sample analyses. MRI then made a statistical analysis of the collaborators' results. Without mercaptans present, results averaged 4 percent low with a standard deviation of 2 percent for any single collaborator and a standard deviation between collaborators of 4 percent. With mercaptans present at 150 ppm, precision was unaffected but the results varied from 2 percent low to 14 percent high at H_2S concentrations of 400 and 100 mg/dscm. The tentative procedure was found to be adequately written for those knowledgeable of sampling and analysis techniques.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air pollution Gases Hydrogen sulfide Measuring Petroleum refineries Tests	Collaborative testing Methods standardization Methods evaluation Stationary sources	13B

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