AP42 Section: 11.1

Reference Number: 22

Title: Emission Of Volatile Organic Compounds From Drum Mix Asphalt Plants,

EPA-600/2-81-026,

U. S. Environmental Protection Agency, Cincinnati, OH,

February 1981.

EMISSION OF VOLATILE ORGANIC COMPOUNDS FROM DRUM-MIX ASPHALT PLANTS

By

Thomas W. Beggs, P.E.
JACA Corp.
Fort Washington, PA 19034

Contract No. 68-01-2585
Work Directive 3

Project Officer

Mark J. Stutsman
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, OH 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

DISCLAIMER

This report has been reviewed by the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report summarizes a research program that was carried out to determine the emissions of volatile organic compounds (VOCs) from a relatively new industrial process -- the drum-mix asphalt process. The results of this program can be used in the preparation of emission inventories and in the design of sampling equipment for similar studies. For further information on this subject, contact the Organic and Inorganic Chemicals and Products Branch of IERL.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

This research program was undertaken in order to develop a quantitative estimate of the emission of volatile organic compounds (VOCs) from drum-mix asphalt plants.

The study was carried out by field sampling of five drum-mix plants under a variety of operating conditions. Included in these plants was a plant that processed a mixture of recycled pavement and virgin aggregate, and a plant that employs a wet scrubber, which was tested both at the stack and also upstream of the scrubber to determine if wet scrubbing provides any significant VOC removal. The sampling method used was EPA Proposed Method 25, modified to filter out particulate emissions which would interfere with the laboratory determination of VOC concentration in the collected samples. In most cases, three simultaneous samples were taken for each set of operating conditions in order to calculate a mean and standard deviation for a statistical comparison of VOC emissions under different conditions.

Results are that VOC emission factors for drum-mix plants are on the order of 0.1 to 0.4 pounds of VOC (as carbon) per ton of asphalt concrete produced. VOC emissions appear to be independent of operating parameters, over the normal range of plant operation and within the limited scope of the statistical testing employed. It appears that a wet scrubber reduces VOC emissions somewhat but the reduction is difficult to quantify because of variation in the results.

The nationwide emission of VOCs from all drum-mix asphalt plants is estimated to be about 20,600 tons per year.

This report was submitted in fulfillment of Contract No. 68-01-2585, Work Directive 3, by JACA Corp., under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from November 28, 1979, to July 31, 1980, and work was completed as of September 30, 1980.

CONTENTS

Foreword iii
Abstract iv
Figures. vi
Tables vii
Acknowledgements viii

1. Introduction 1

   The Drum-Mix Asphalt Process. 1
   The Drum-Mix Recycle Process. 3
   Emissions from the Drum-Mix and the Drum-Mix Recycle Process 4

2. Conclusions. 5

3. Recommendations. 6

4. Objectives 7

   Quantitative Estimate 7
   Dependence on Operating Parameters. 7
   Nationwide Impact of VOC Emissions. 7

5. Procedure. 8

   Preparation of the Sampling Equipment 8
   Selection of Plants 9
   Sampling and Analysis 12
   Analysis of the Data. 13

6. Results. 14

7. Discussion 23

   Emission Factors - General. 23
   Emission Factor Dependence on Process Parameters. 23
   Efficacy of the Test Method 27

References 30
Appendices

A. EPA Method 25. 31
B. Sample Calculations. 67

FIGURES

Number		Page
1	Typical drum-mix process	2
2	Combined Method 5 and 25 sampling system	10
3	Modified filter assembly	11
4	Emissions and aggregate coating vs. asphalt injection point.	25

TABLES

Number		Page
1	VOC Emissions -- Plant "A"	15
1-A	Particulate Emissions -- Plant "A"	16
2	VOC Emissions -- Plant "B"	17
3	VOC Emissions -- Plant "C"	18
4	VOC Emissions -- Plant "D"	19
5	VOC Emissions -- Plant "E"	10
6	Summary of Individual VOC Test Runs.	21
7	Summary of VOC Test Results by Plant	22

ACKNOWLEDGMENTS

The cooperation of the officers, supervisors, and plant operators of numerous asphalt paving companies is gratefully acknowledged. Indeed this study could not have been completed without their cooperation and receptiveness.

Mr. Fred Kloiber performed the greater part of the effort of plant selection as a consultant to JACA Corp. on this project. He also provided liaison between the asphalt companies and JACA during the pretest period.

The field sampling and laboratory analysis was conducted by Pollution Control Science, Inc. (PCS), Miamisburg, Ohio, under a subcontract agreement. The majority of field sampling was performed by Messrs. Gary D. Hipple and Craig R. Jones under the supervision of JACA; the laboratory analysis was conducted by PCS, under the direction of Mr. Jerry L. Fair.

SECTION 1

INTRODUCTION

THE DRUM-MIX ASPHALT PROCESS

Although most existing asphalt concrete plants are still the batch type, the majority of new plants sold in the last few years have been the drum-mix type. The drum-mix process represents the state-of-the-art in the production of asphalt concrete. The process is a vast improvement over the asphalt batching process as it involves fewer items of equipment, it is simpler and more portable. Because the product mix is controlled at the feed end of the drum rather than at the discharge end, the process is more versatile than the conventional batching process, allowing rapid changes in production rate and mix temperature.

Figure 1 shows the basics of the drum-mix process. Sand and aggregate are metered out of several storage bins by variable speed conveyor belts and conveyed by a single belt to the dryer drum. The aggregate size gradation is determined by the intended use of the mix; base mix is designed for bearing loads and thus includes a large percentage of larger particles, while surface mix is designed for skid resistance and is usually a finer aggregate gradation. The aggregate is tumbled by flights as it travels down the length of the dryer in parallel flow with combustion gases from the burner. (Some drum-mixers operate in counterflow, with aggregate and combustion gases traveling in opposite directions; however, this arrangement is rare.) Asphalt is injected into the drum to coat the aggregate; the point of injection varies from plant to plant but is generally about halfway down the length of the dryer, protected from direct contact with the flame by not only distance but also a dense curtain of tumbling aggregate. Particulate-laden gas is directed from the dryer through a collection device and to the stack.

Inside the dryer drum four phenomena occur in the following order: bulk moisture removal; asphalt injection with partial coating; foaming, which completes the coating process; and rapid temperature rise of the mix. Upon entering the dryer, the aggregate is directly exposed to the burner flame; this heat vaporizes most of the moisture in the aggregate. As the aggregate continues down the length of the dryer out of direct contact with the flame, it reaches the point of asphalt injection. At this point the liquid asphalt is distributed by nozzles so that the aggregate is uniformly covered. In some plants, chemical additives are injected along with the asphalt to improve the spray distribution of the asphalt and its adhesion to the aggregate surface. After asphalt injection, the aggregate attains

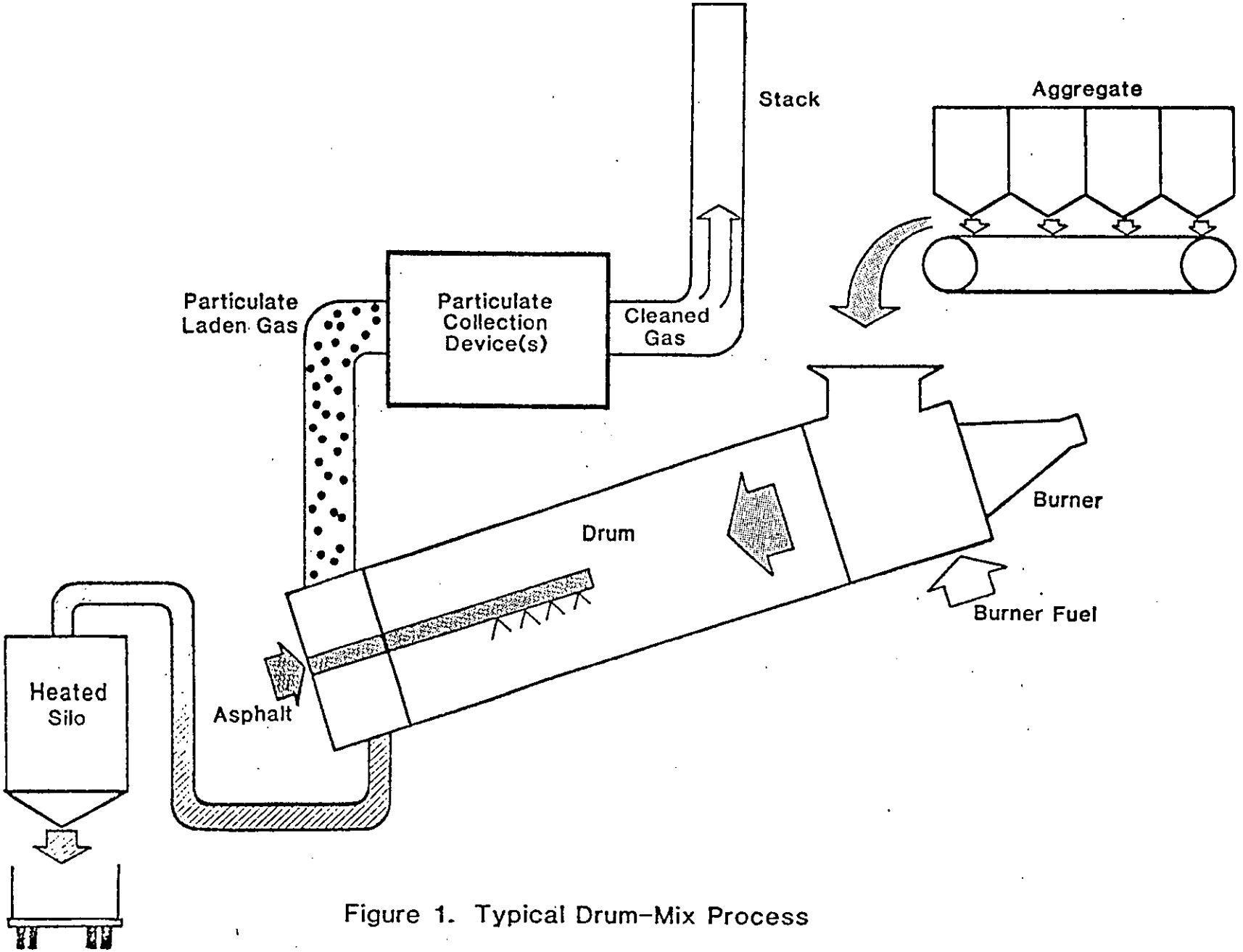

Figure 1. Typical Drum-Mix Process

a temperature high enough to vaporize moisture in the pores of the stone. As this water vapor reaches the surface, it escapes by foaming through the asphalt coating. This action is thought to increase the uniformity of asphalt coating. Near the discharge end of the drum, the dryer heat is absorbed in the aggregate itself since the bulk of the moisture has been vaporized. The total residence time of the aggregate in the dryer is five to seven minutes.

The product discharges from the drum at about 250 F to 285 F, and is conveyed to a storage silo for truck loadout. Because the final product is discharged continuously and because it must be kept hot or it will not remain workable, many plants employ heated storage silos to avoid plugging in the silo conveyors or the silo itself when the loading of trucks cannot keep pace with the production.

Referring to Figure 1, the simplicity of the drum-mix process, as compared to the conventional process, can be easily seen. The aggregate and asphalt are mixed in the same vessel in which the aggregate is dried and heated, namely the dryer drum, which obviates the need for the pugmill that is found in the conventional batch process. Also, the hot screens and weigh hoppers required in the batch process are not required in the drum-mix process due to careful control of the incoming aggregate blend by variable-speed conveyors.

THE DRUM-MIX RECYCLE PROCESS

Because asphalt is injected directly into the dryer in the drum-mix process, it is uniquely suited for the new, fast-developing technology of recycling asphalt pavement. In fact, many drum-mix plants are now sold with a "recycle kit", which allows the plant to be converted in order to process blends of virgin and recycled material sometime in the future.

In a recycling process, salvaged asphalt pavement (or base material) that has been crushed and screened is introduced into the dryer drum at a point somewhere downstream of the virgin aggregate inlet. The amount of recycled pavement that can be successfully processed has not yet been determined; eventually, as the technology is developed, the blends may approach 100 percent recycled material. Current blends generally range from about 20 percent to a maximum of 50 percent recycled material.

The advantages of the recycling process are obvious: a blend of recycled material and virgin aggregate is generally less expensive than 100 percent virgin aggregate; liquid asphalt requirements are less due to residual asphalt in the recycled material; and the recycled material requires less drying than the virgin aggregate. The chief disadvantage of recycling is the inability to meet opacity standards due to emissions of blue smoke -- an aerosol of submicron droplets of hydrocarbons volatalized from the asphalt and subsequently condensed before exiting out the stack. However, as discussed later, current recycle plant designs have reduced blue smoke emissions greatly by preventing direct contact between the flame and the liquid asphalt as it is injected.

EMISSIONS FROM THE DRUM-MIX AND THE DRUM-MIX RECYCLE PROCESS

As in the conventional asphalt batch process, the bulk of the particulate emissions are from the dryer in the drum-mix and drum-mix recycle processes. However, because the aggregate is coated with liquid asphalt as it dries, the level of uncontrolled particulate emissions from these processes is 1 to 2 orders of magnitude less than for the conventional process. For this reason, most drum-mix plants employ only a secondary particulate control device and do not require the primary cyclone that is found in most conventional plants; instead, a diverging dryer outlet plenum that functions as a settling chamber to remove large agglomerated particles is usually employed ahead of a venturi scrubber or fabric filter.

Emissions of organic compounds from drum-mix and drum-mix recycle processes can be either liquid (blue smoke) or gaseous (VOC). The former are actually particulate emissions; in an EPA Method 5 test, the liquid aerosol particles are trapped by the filter. These liquid organic emissions are less of a problem in the drum-mix process than in the drum-mix recycle process, largely due to the fact that the optimum asphalt injection point has been found after years of field testing and development by the plant manufacturers. Therefore, less volatilization of the liquid asphalt particles occurs and thus less recondensation of these particles as a liquid aerosol.

Control of liquid organic emissions in the drum-mix recycle process has necessarily been slower to develop since recycling is still largely an experimental technology. However, significant strides have been made in reducing these emissions, generally by employing one of the following methods: (1) introduction of recycled material at the center of the drum or even farther toward the discharge end, coupled with a flight design that causes a dense curtain of aggregate between the flame and the residual asphalt; (2) protection of the material from the flame by use of a heat shield; or (3) insulation of the recycled material from the combustion zone entirely by the drum-within-a-drum arrangement in which virgin material is dried and coated in the inner drum, recycled material is indirectly heated in the annular space surrounding the inner drum, and the materials are mixed at the discharge of the inner drum.

Little is known about the amount of gaseous organic (VOC) emissions generated by these processes; much less about how to control them if they are significant. Intuitively, it can be expected that VOC emissions from the dryer in a drum-mix or drum-mix recycle process are greater than VOC emissions from the dryer in a conventional asphalt batch process, due to the heating of a petroleum-based product (liquid asphalt) in a closed space. However, there are no known field data to support this speculation. Therefore this study has been undertaken with the general objectives of gathering data to support or refute this speculation and attempting to develop a quantitative estimate of these emissions. In addition, it is intended that the VOC removal efficiency of a wet scrubber can be determined in the course of the study.

SECTION 2

CONCLUSIONS

As a result of this study, VOC emission factors for the drum-mix asphalt process are established to be in the range of 0.1 to 0.4 pounds carbon per ton. Within the limits of the procedures used and the narrow ranges of process parameters found in most plants, no real dependence of VOC emission factors was detected for parameters such as mix temperature, percentage of recycled material, production rate, and type of fuel. A high-energy wet scrubber (venturi) is capable of reducing VOC emissions, but the reductions achievable varied widely so that a separate emission factor range was not established for plants with wet scrubbers.

The nationwide impact of VOC emissions from drum-mix asphalt plants is estimated to be approximately 20,600 tons per year.

The procedure of EPA Proposed Method 25, as modified to filter out particulate, performed well in the field. However, additional modifications were necessary to sample under the high particulate loading experienced upstream of a particulate control device.

SECTION 3

RECOMMENDATIONS

The repeatability of the test method employed in this study should be improved by careful investigation of the possible causes of inaccuracies and analysis of the causes to determine the magnitude of error (if any) that can be attributed to each. Possible causes to be investigated would include contamination of sampling equipment, in-leakage of ambient air, and interferences such as carbon dioxide dissolved in the moisture collected in the sampling train. Proposed measures to reduce or remove the causes that are found to be major should be field tested.

The method of sampling under high particulate loading should be continually improved. The modified filter assembly, while simpler to employ than a combined Method 5 and Method 25 train, does not provide for retention of a large volume of particles such as may be encountered when sampling upstream of a particulate control device. A filtering device should be developed that is capable of retaining several times the volume of particles that can be retained by a Method 5 glass fiber filter without severely decreasing the sampling flowrate. This device might be an improved filter or perhaps an improved version of the thimble employed in this study.

SECTION 4

OBJECTIVES

The objectives of this study were as follows:

- To develop a quantitative estimate of the emissions of VOCs from the drum-mix and drum-mix recycle asphalt processes;
- To establish the dependence (if any) of VOC emissions on process operating parameters;
- To conduct simultaneous particulate and VOC testing on one plant;
- To evaluate the efficacy of the test method.

QUANTITATIVE ESTIMATE

By gathering data on VOC emissions from several different plants -- representing various plant manufacturers, types and temperatures of mix, production rates, and asphalt injection points -- an emission factor range can be established. This emission factor range will be useful in estimating the air quality impacts of VOC emissions from drum-mix and drum-mix recycle asphalt plants.

DEPENDENCE ON OPERATING PARAMETERS

If it can be established that VOC emissions are dependent on one or more process parameters, these emissions could then be minimized.

NATIONWIDE IMPACT OF VOC EMISSIONS

The emission factor range can be used to estimate total nationwide VOC emissions from drum-mix asphalt plants. A comparison of this total emissions estimate with estimates of emissions from other VOC sources will place emissions from this source in perspective.

SECTION 5

PROCEDURE

This study was carried out in the following four overlapping stages:

- Preparation of the Sampling Equipment
- Selection of Plants
- Sampling and Analysis
- Analysis of the Data.

PREPARATION OF THE SAMPLING EQUIPMENT

The test method chosen for measuring VOC emissions from the drum-mix asphalt process was EPA Proposed Method 25, "Determination of Total Gaseous Nonmethane Organic Emissions as Carbon: Manual Sampling and Analysis Procedures" (sometimes referred to as the "TGNMO" procedure). The principle of this procedure is to anisokinetically draw a sample of stack gas through a stainless steel probe and condensate trap and into an evacuated cylinder. Heavy VOCs condense in the trap, which is packed in dry ice; light VOCs remain gaseous and are collected in the tank. Both trap and tank are subsequently analyzed for total carbon by a laboratory procedure in which all nonmethane organic compounds are oxidized to carbon dioxide, reduced to methane, and then measured by a flame ionization detector (FID). (For more detail, consult the Method itself, in Appendix A.)

The exhaust gas from the drum-mix asphalt process contains solid particulates, organic liquid aerosols, and VOCs. However, the proposed method does not provide for a filter to remove the solid particulates and the organic liquid aerosols. For this purpose, Method 25 was modified by the addition of a heated filter, in addition to the heated probe to prevent condensation.

Since the number of aerosol particles condensing will increase with decreasing temperature, it is necessary to hold the temperature of the filter constant at the temperature used in EPA Method 5 for particulate sampling, that is, 248 $\pm$ 25 F. In this way, any material that would be particulate by definition in a Method 5 test would be prevented from entering the VOC sampling equipment. The material passing through the filter is collected as condensed or gaseous VOCs.

One of the objectives of the study was to conduct simultaneous VOC and particulate sampling. For this purpose a combined train was used in which the VOC sampling train begins as a slip-stream, taken off the Method 5 train downstream of the heated filter (Figure 2). This combination method required isokinetic sampling at preselected traverse points representing equal areas of stack cross-section, as in sampling by Method 5 alone. The addition of the VOC train does not appreciably affect the isokinetic factor of the Method 5 test since the sampling rate of the VOC train is two orders of magnitude less than the sampling rate normally employed in Method 5.

To perform VOC samping only, a combined train is not necessary. A modified filter assembly can be used instead, consisting of a filter and holder enclosed in a box which can be maintained (along with the probe) at the desired temperature by means of an electrical-resistance heater such as that used in Method 5 (Figure 3). After solid and liquid particulates are removed by the filter, the gas passes into the VOC sampling train.

As a result of several days of field testing, much can be learned about the application of the test method to drum-mix asphalt plants, including the following: the effectiveness of the modification that was made to the sampling train to filter out organic particulate; the repeatability of sampling; and the general precision of the method, as determined by the analysis of simultaneously-collected samples.

SELECTION OF PLANTS

There are over 4,500 asphalt concrete plants in the U.S., of which probably 10 to 15 percent are drum-mix plants (Reference 2). With such a large number to choose from, finding a number of plants to test is simple; however, if these plants were randomly selected, the result would be plants scattered throughout the country, possibly involving extensive travel and shipping of sampling equipment. Alternatively, some criteria can be used to narrow the field geographically.

The criterion that was selected is that candidate plants must be within reasonable (12 hours or less) driving distance of the sampling and analytical laboratory of Pollution Control Science, Inc. (PCS) in Miamisburg, Ohio (near Dayton). This categorization provides a grouping of plants that is small enough to handle but still covers a large enough area to provide a wide range of aggregates, mixes, fuels, and so on. A large side benefit of this categorization is that the cost per plant of sampling is low because both air travel by the sampling personnel and air shipment of sample containers back to the laboratory are avoided.

The next phase of plant selection was conducted primarily by a JACA consultant who is thoroughly familiar with the asphalt industry through current consulting work as well as a previous association with the National Asphalt Pavement Association. The consultant developed a list of candidate plants primarily by contacting personnel of state asphalt assocations for suggested companies and then confirming the willingness of company officials

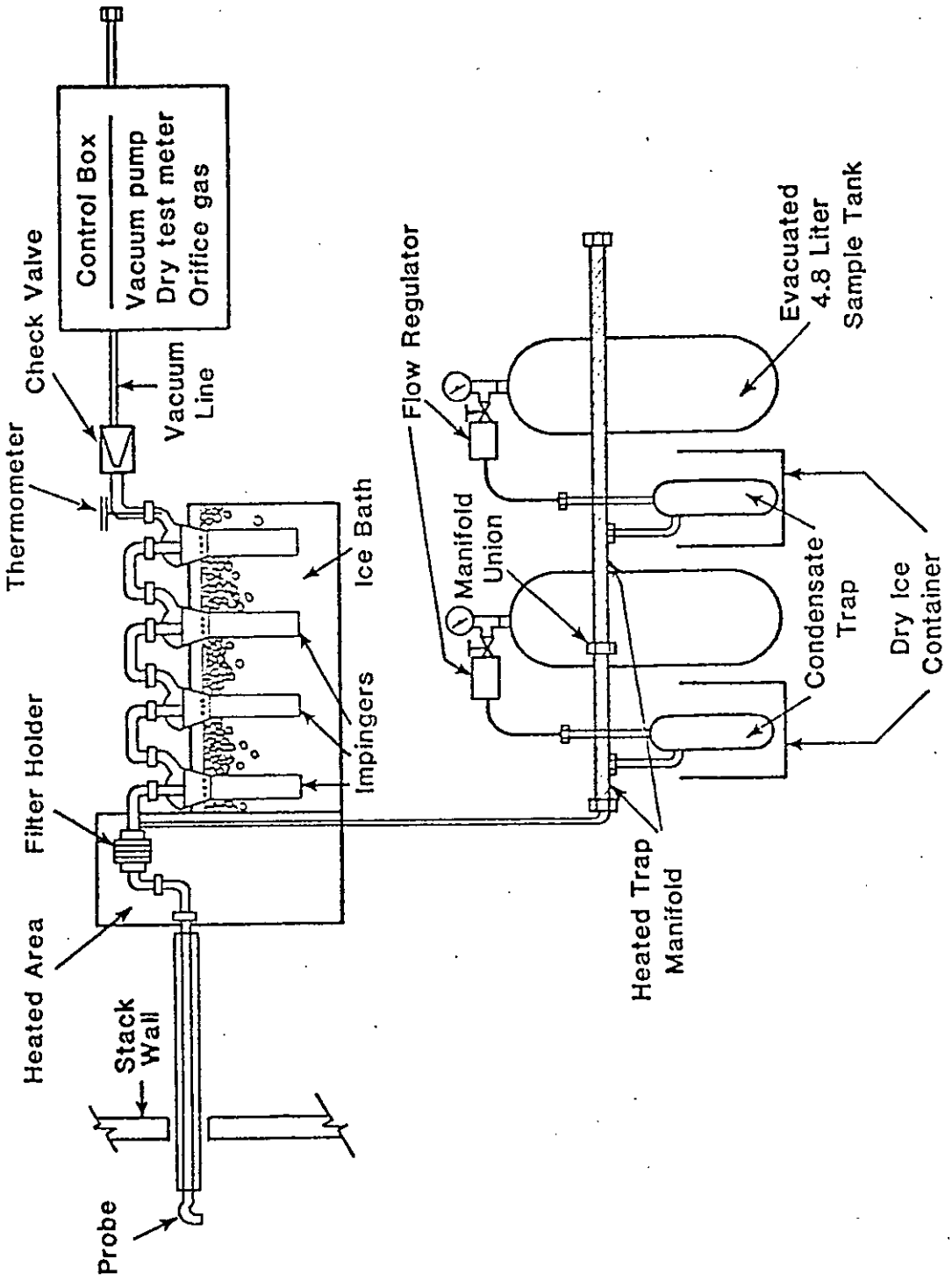

Figure 2. Combined Method 5 and 25 Sampling System

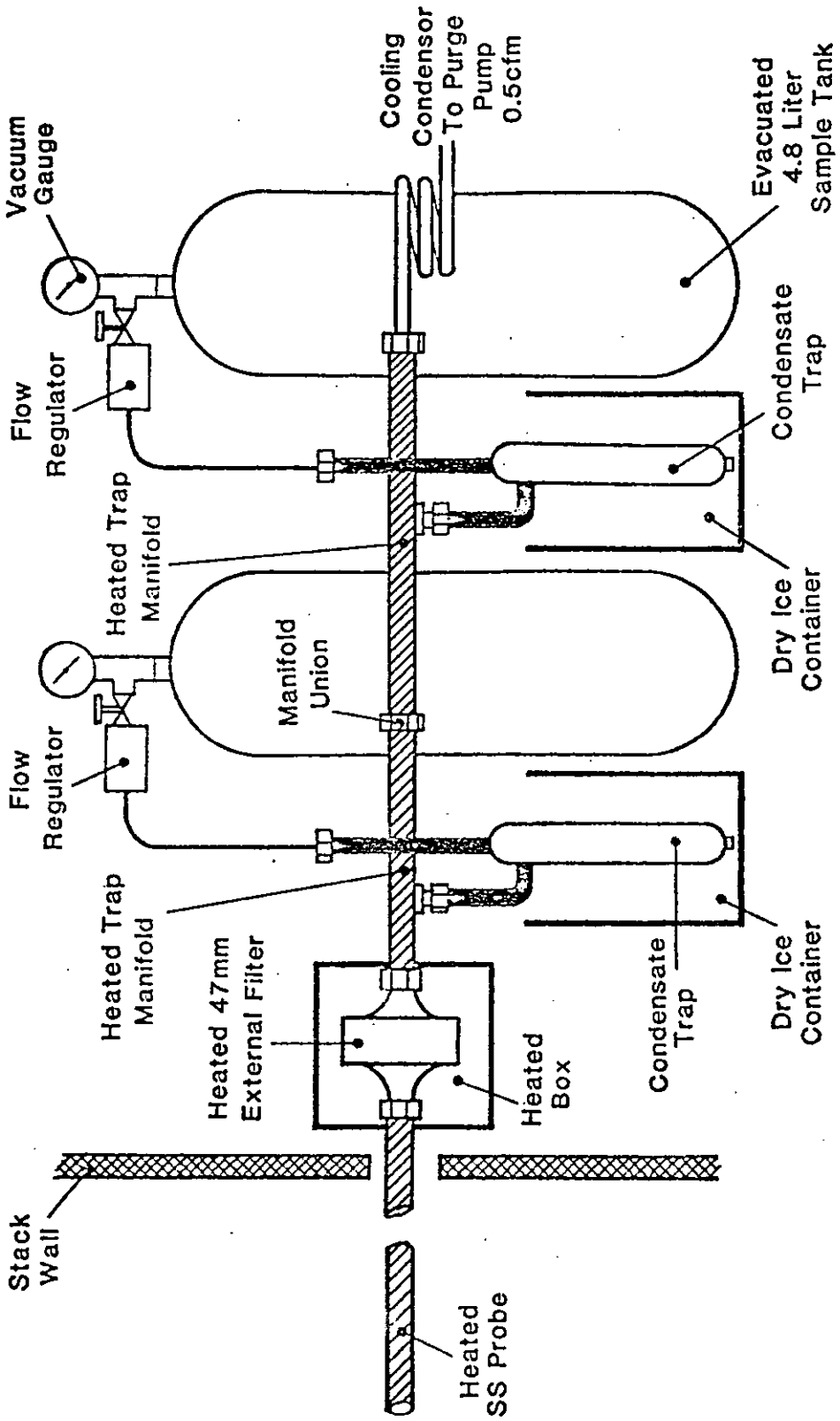

Figure 3. Modified Filter Assembly

to participate in the program. The majority of the plants on this list were located in Ohio, Indiana, and Kentucky, and represented a cross-section of plant manufacturers.

Next JACA contacted the companies identified above to confirm that: (1) the plant has properly-operating particulate control equipment (baghouse or scrubber); (2) the operating schedule is conducive to two or more days of testing; and (3) the amount of pretest preparation required is minimal. If all these requirements were met, a pretest inspection was arranged.

During the pretest inspection, the access to the stack was investigated. In ideal cases, testing ports were available in the correct location and quantity so that a proper velocity traverse could be done from a convenient platform or the top of the baghouse. In other cases, arrangements were made to: install new or alternate ports; provide better access, such as a temporary scaffold; or employ a crane and basket for difficult, high-elevation ports. During the inspection, it was possible to meet plant personnel face to face and answer their questions about the program as well as discuss testing arrangements such as variation of parameters. Normally after the inspection was completed, a tentative testing date was agreed upon.

As a result of discussion with company officials and pretest inspections, several plants were not ultimately selected for testing. Reasons for this included: scheduling difficulties; a desire to avoid testing several plants manufactured by the same vendor, especially identical plants; and a reluctance -- on the part of JACA and the asphalt company -- to undertake extensive plant modifications in order to be able to test. A few plants were added to the original candidate list, as necessary, to ensure that enough plants were tested to provide a good cross-section of plant manufacturers and plant variables.

SAMPLING AND ANALYSIS

Prior to testing at each plant, a rough schedule was worked out between JACA and the plant operator: in cases where some parameters were to be changed in the course of normal operations and independent of VOC testing, these were taken advantage of as much as possible; otherwise parameters that the plant operator felt were possible to vary were changed. In each case, plants were sampled during "normal" operations and during operations in which one parameter was varied at a time; in this way, it was possible to measure the effect of the parameter, if any, on VOC emissions.

For each test run, sampling was begun after steady-state operation had been achieved. When sampling included particulate measurement, the VOC train was connected as a slip-stream after the particulate filter and the probe was traversed in the stack according to EPA Method 5. For straight VOC testing, the probe to the heated filter box was placed in the stack near the center, and sampling was performed anisokinetically according to EPA Method 25. When testing under conditions of high particulate loading (upstream of a scrubber

in one plant), a pre-impactor was also employed along with other devices to keep particulate out of the VOC train. (See Discussion for more on this.) In most cases, three simultaneous VOC samples were obtained for each test run; each test run also included a velocity traverse and a Fyrite gas analysis for CO_2 and O_2 in the stack gas. Plant process parameters were monitored and recorded during each run.

At the completion of each test run, the sample tanks were packed away and the traps were sealed and packed in dry ice until analysis. Subsequent laboratory analysis of samples was done and the results were reported in terms of total carbon for the tank, the trap, and the total.

ANALYSIS OF THE DATA

All VOC values were converted to emission factors of pounds carbon per ton of asphalt produced by employing the measured stack gas velocity and recorded process parameters. For each test run the multiple VOC emission factors were averaged and the standard deviation was calculated. Statistical techniques were then used to compare results for parameter changes to determine if apparent differences were statistically significant.

SECTION 6

RESULTS

Tables 1 through 5 present the VOC emission factors for all test runs. (For illustration of converting ppm carbon to pounds carbon per ton, see sample calculations in Appendix B.) In addition, the tables show the primary data consisting of ppm carbon as measured for the trap, the tank, and the total. The concentration (ppm) of carbon in the trap is determined by oxidizing the organics to carbon dioxide which is collected quantitatively in an evacuated intermediate vessel. The concentration of carbon dioxide in this vessel is measured by flame ionization detection (FID) and related to the total volume of gas sampled by the tank. The concentration in the tank is determined by gas chromatography (GC) to separate out methane, carbon dioxide, and carbon monoxide, followed by oxidation of the non-methane organics to carbon dioxide, reduction to methane, and measurement by FID. (For more details, see Appendix A.) Table 1-A presents particulate emissions data for Plant "A", which was tested for both particulate and VOC.

Mean VOC emission factors and standard deviations for all test runs are presented in Table 6. Various combinations of these results are compared using a "Paired-T Test" to test for statistically significant differences in results attributable to process parameter changes. (For an example of how the Paired-T Test was employed, see Appendix B.)

In most cases, the statistical test indicates no dependency of VOC emissions on the operating parameters that were varied during the testing program. These results indicate that, for the relatively small number of samples per condition (normally three), and the necessarily narrow ranges of variation of the parameters, there is no statistical evidence to dispute the hypothesis that the emissions at each condition are essentially the same.

TABLE 1. VOC EMISSIONS -- DRUM-MIX PLANT "A"

Fuel: Diesel oil/natural gas
Asphalt Injection Point: 20 ft. from burner end/56% of drum length
Control Device: Baghouse

Plant Operating Parameters	Sample No.	Emissions as Total Carbon PPM, Trap	PPM, Tank	PPM, Total	lb/ hr	lb/ ton
350 tons/hr, 310° F Mix, Diesel	A-1-a[a]	781.6	141.2	922.8	59.01	0.17
	A-1-b[a]	891.1	187.4	1,078.5	68.87	0.20
	A-1-c[b]	659.8	141.4	801.2	51.20	0.15
350 tons/hr, 310° F Mix, Natural Gas	A-2-a[c]	1,997.0	175.8	2,172.8	112.97	0.32
	A-2-b[c]	1,378.4	121.2	1,499.6	77.99	0.22
	A-2-c[c]	636.4	85.6	722.0	37.59	0.11
375 tons/hr, 310° F Mix, Natural Gas	A-3-a[a]	1,251.9	175.9	1,427.8	73.79	0.20
	A-3-b[b]	1,751.4	283.4	2,034.8	105.14	0.28

[a]VOC samples collected from a combined Method 5 and 25 train.

[b]Single-point isokinetic sample taken separately.

[c]VOC samples collected with a heated filter manifold assembly.

TABLE 1-A. PARTICULATE EMISSIONS -- DRUM-MIX PLANT "A"

Fuel: Diesel oil/natural gas
Asphalt Injection Point: 20 ft. from burner end/56% of drum length
Control Device: Baghouse

Test Run No.	Stack Gas Flowrate, dscfm	Particulate Emissions lb/hr	Particulate Emissions lb/ton
A-1	34,169	61.4	0.18
A-2	27,970	72.2	0.21
A-3	27,550	93.6	0.25

TABLE 2. VOC EMISSIONS -- DRUM-MIX PLANT "B"

Fuel: Propane
Asphalt Injection Point: 24 ft. from burner end/70% of drum length
Control Device: Baghouse

Plant Operating Parameters	Sample No.	Emissions as Total Carbon PPM, Trap	PPM, Tank	PPM, Total	lb/ hr	lb/ ton
100 tons/hr, 320° F Surface Mix	B-1-a	213.3	48.1	261.4	3.69	0.037
	B-1-b	215.3	79.1	294.9	4.26	0.043
	B-1-c	243.9	65.0	308.9	4.26	0.043
150 tons/hr, 320° F Surface Mix	B-2-a	355.0	111.9	466.9	10.35	0.069
	B-2-b	244.8	77.4	322.3	7.20	0.048
	B-2-c	296.9	83.9	380.8	8.55	0.057
200 tons/hr, 320° F Base Mix	B-3-a	239.1	115.8	354.9	7.90	0.040
	B-3-b	279.5	105.3	384.8	8.34	0.042
	B-3-c	326.4	397.7	724.1	15.81	0.079
200 tons/hr, 330° F Base Mix	B-4-a	241.6	197.8	439.4	10.00	0.050
	B-4-b	187.5	360.0	547.5	12.27	0.061
	B-4-c	250.6	541.8	792.4	18.18	0.091
200 tons/hr, 310° F Base Mix	B-5-a	190.1	203.3	393.4	8.88	0.044
	B-5-b	328.3	1,169.1	1,497.4	33.30	0.167

TABLE 3. VOC EMISSIONS -- DRUM-MIX PLANT "C"

Fuel: No. 4 fuel oil
Asphalt Injection Point: 20 ft. from burner end/51% of drum length
Control Device: Baghouse

Plant Operating Parameters	Sample No.	Emissions as Total Carbon				
		PPM, Trap	PPM, Tank	PPM, Total	lb/ hr	lb/ ton
240 tons/hr, Surface/ Base	C-1-a	276.0	56.6	332.6	20.14	0.08
	C-1-b	379.8	50.7	430.5	24.88	0.10
	C-1-c	516.3	40.4	556.7	33.17	0.14
240 tons/hr, Surface	C-2-a	493.6	55.9	549.5	32.12	0.13
	C-2-b	363.9	35.1	399.0	23.79	0.10
	C-2-c	182.3	30.3	212.6	13.08	0.05
320 tons/hr, Base	C-3-a	226.6	53.3	279.9	19.65	0.06
	C-3-b	532.5	48.3	580.8	40.71	0.13
	C-3-c	414.8	89.5	504.3	19.65	0.06
260 tons/hr, Base	C-4-a	696.2	39.7	735.9	43.35	0.17
	C-4-b	221.4	55.3	276.7	16.40	0.06
	C-4-c	578.7	52.7	631.4	37.49	0.14

TABLE 4. VOC EMISSIONS -- DRUM-MIX PLANT "D"

Fuel: Natural gas
Asphalt Injection Point: 20 ft. from burner end/56% of drum length
Control Device: Baghouse
Note: Plant equipped for recycling; recycled material enters mid-drum.

Plant Operating Parameters	Sample No.	Emissions as Total Carbon				
		PPM, Trap	PPM, Tank	PPM, Total	lb/ hr	lb/ ton
250 tons/hr, Virgin Material	D-1-a	1576.7	135.7	1712.4	84.6	0.34
	D-1-b	3059.0	119.8	3178.8	158.3	0.63
	D-1-c	632.2	216.6	848.8	41.8	0.17
275 tons/hr, Virgin Material	D-2-a	2397.8	210.6	2608.4	104.4	0.38
	D-2-b	1527.3	87.8	1615.1	65.1	0.24
	D-2-c	786.5	73.9	860.5	34.6	0.12
250 tons/hr, 30% Recycle	D-3-a	1702.2	339.9	2042.1	99.6	0.40
	D-3-b	1959.0	399.3	2358.3	115.3	0.46
	D-3-c	2002.7	336.7	2339.4	114.3	0.46
200 tons/hr, 20% Recycle	D-4-a	619.6	183.7	803.3	38.1	0.19
	D-4-b	955.7	250.1	1205.8	57.2	0.29
	D-4-c	1511.2	189.8	1701.0	81.0	0.40
200 tons/hr, 35% Recycle	D-5-a	972.8	136.1	1109.0	53.7	0.27
	D-5-b	698.8	188.8	887.6	43.0	0.22
	D-5-c	1272.3	209.0	1481.3	72.2	0.36

TABLE 5. VOC EMISSIONS -- DRUM-MIX PLANT "E"

Fuel: No. 2 fuel oil
Asphalt Injection Point: 22 ft. from burner end/61% of drum length
Control Device: Venturi scrubber

Plant Operating Parameters	Sample No.	Emissions as Total Carbon PPM, Trap	PPM, Tank	PPM, Total	lb/ hr	lb/ ton
200 tons/hr	E-1-a*	838.5	81.2	919.7	40.75	0.20
	E-1-b*	749.9	106.4	856.3	35.04	0.18
	E-2-a	586.3	70.8	657.1	26.89	0.13
	E-2-b	574.9	34.7	609.6	24.45	0.12
	E-4-a	706.4	130.0	836.4	34.23	0.17
	E-4-b	474.8	84.4	559.2	22.82	0.11
200 tons/hr	E-3-a*	**	**	**	**	**
	E-3-b*	1132.3	152.2	1264.5	52.66	0.26
	E-6-a	866.4	89.1	955.5	39.50	0.20
	E-6-b	812.7	65.2	877.9	36.21	0.18
175 tons/hr	E-5-a*	2416.6	383.2	2799.8	103.25	0.59
	E-5-b*	1716.5	1020.8	2737.3	101.03	0.58
	E-8-a	701.1	132.3	833.4	30.97	0.18
	E-8-b	625.5	164.7	790.2	28.76	0.16
200 tons/hr	E-7-a*	721.0	90.2	811.2	33.02	0.16
	E-7-b*	598.3	153.1	751.4	30.61	0.15
	E-10-a	574.5	102.9	677.4	27.38	0.14
	E-10-b	687.9	125.9	813.8	33.02	0.16

*Taken upstream of the scrubber.
**Sample rejected due to possible contamination during handling.

TABLE 6. SUMMARY OF INDIVIDUAL VOC TEST RUNS

Test Run No.	Production tons/hr	Burner Fuel	Control Device	No. of Samples	VOC Emission Factors lb total carbon/ton	
					Mean	Standard Deviation
A-1	350	Diesel oil	Baghouse	3	0.17	0.02
A-2	350	Natural gas	Baghouse	3	0.22	0.10
A-3	375	Natural gas	Baghouse	2	0.24	0.06
B-1	100	Propane	Baghouse	3	0.041	0.003
B-2	150	Propane	Baghouse	3	0.058	0.010
B-3	200	Propane	Baghouse	3	0.054	0.022
B-4	200	Propane	Baghouse	3	0.067	0.021
B-5	200	Propane	Baghouse	2	0.106	0.087
C-1	240	No. 4 oil	Baghouse	3	0.11	0.03
C-2	240	No. 4 oil	Baghouse	3	0.09	0.03
C-3	320	No. 4 oil	Baghouse	3	0.08	0.04
C-4	260	No. 4 oil	Baghouse	3	0.12	0.06
D-1	250	Natural gas	Baghouse	3	0.38	0.15
D-2	275	Natural gas	Baghouse	3	0.25	0.13
D-3	250	Natural gas	Baghouse	3	0.44	0.03
D-4	200	Natural gas	Baghouse	3	0.29	0.10
D-5	200	Natural gas	Baghouse	3	0.28	0.07
E-1*	200	No. 2 oil	None*	2	0.19	0.01
E-3*	200	No. 2 oil	None*	1	0.26	-
E-5*	175	No. 2 oil	None*	2	0.58	0.01
E-7*	200	No. 2 oil	None*	2	0.16	0.01
E-2	200	No. 2 oil	Scrubber	2	0.12	0.01
E-4	200	No. 2 oil	Scrubber	2	0.14	0.04
E-6	200	No. 2 oil	Scrubber	2	0.19	0.01
E-8	175	No. 2 oil	Scrubber	2	0.17	0.01
E-10	200	No. 2 oil	Scrubber	2	0.15	0.01

*Upstream of venturi scrubber.

TABLE 7. SUMMARY OF VOC TEST RESULTS BY PLANT

Plant	Production tons/hr	Burner Fuel	Control Device	VOC Emission Factors, lb/ton No. of Samples	Mean	Standard Deviation
A	350-375	Diesel oil Natural gas	Baghouse	8	0.21	0.07
B	100-200	Propane	Baghouse	14	0.062	0.034
C	240-320	No. 4 fuel oil	Baghouse	12	0.13	0.05
D	200-275	Natural gas	Baghouse	15	0.41	0.17
E	175-200	No. 2 fuel oil	None*	7	0.36	0.22
			Venturi Scrubber	10	0.19	0.03

*Upstream of venturi scrubber.

SECTION 7

DISCUSSION

EMISSION FACTORS - GENERAL

A total of 67 VOC samples were collected in 26 test runs at five drum-mix asphalt plants in the course of this study. The samples represent a cross-section of three plant manufacturers, four fuels, both general mix types (surface and base), and cover a wide spectrum of production rates, mix temperatures, and types of stone (limestone and sandstone). The range of VOC emission factors is approximately 0.1 to 0.4 pounds of VOC (as carbon) per ton of product.

The emission factors are in terms of total carbon as determined by gas chromatography followed by flame ionization detection. The laboratory analysis reports only the mass of carbon in the sample and therefore does not distinguish the photochemical reactivity of the emissions.

EMISSION FACTOR DEPENDENCE ON PROCESS PARAMETERS

Many of the parameters that may have an effect on VOC emissions cannot be varied during the course of normal operation in a drum-mix plant. For example, the asphalt injection point, although variable over a narrow range, is rarely adjusted from the plant manufacturer's setting. The burner fuel may be limited by the type of burner, but is often determined by price and availability for burners capable of burning more than one fuel. However, one fuel is normally burned for days or weeks at a time and changeovers during a day would be rare.

Most other parameters are fixed by the specifications of the particular mix and set by the plant operator. These include aggregate composition, mix temperature, and percentage of recycled material, if used. Changes in these parameters during the production of the mix cannot normally be made for the purpose of sampling; variation of these parameters, however, can often be realized when product mixes are changed. The plant operator can usually vary the production rate for testing purposes if the storage capacity of silos and the availability of trucks permit.

Asphalt Injection Point

Although a minor adjustment of the injection point (a few feet in either direction) could be made, this would normally not be recommended by the plant equipment manufacturer. Each manufacturer apparently feels that the factory setting of the injection point represents the state-of-the-art as developed over years of monitoring operating units in the field; this point represents the optimum location which will provide for that particular drum diameter, length, flight design, rotational speed, the proper aggregate coating without generating blue smoke (and presumably VOC) emissions.

Figure 4 shows a highly idealized generalization of how three phenomena theoretically vary with the asphalt injection point. (Note that the graph is qualitative.) If the asphalt is injected close to the flame, VOC emissions will in general be high; in addition, aggregate coating will be thorough and therefore particulates generation will be minimal. However, if this arrangement were actually employed, the aggregate would be coated before the bulk of the moisture was driven off, resulting in a product that would not compact properly during paving, and excessive VOC emissions.

If the asphalt was injected at the discharge end of the drum, VOC emissions would be minimum, but generation of particulates would be maximum because the aggregate coating would be insufficient.

The ideal drum-mix design would then call for injection somewhere between these two extremes, where the optimum combination of aggregate coating with low particulate and VOC emissions occurs. Plant manufacturers and operators have found this optimum point by moving the design injection point as far from the flame as possible while still being able to ensure particulate compliance. To summarize, VOC emissions from drum-mix asphalt plants probably cannot be significantly further reduced by adjustment of the asphalt injection point without risking insufficient aggregate coating and without the possibility of jeopardizing particulate compliance.

The fixed injection point also represents an optimum location in terms of dryer drum operation. In most drum-mix plants, baghouse fines are pneumatically injected into the drum at the asphalt injection point. This design ensures that these fines are rapidly coated to provide a higher quality mix as well as to minimize the entrainment of these small particles. Any adjustment of the injection point would have to be coupled with a similar adjustment in the fines injection point. Ensuring that both injection points were precisely adjusted in relation to each other would be difficult.

A further problem in adjusting the injection point is that the product quality may be adversely affected by changing the configuration of the spray pattern. The liquid asphalt pipe enters the discharge end of the drum on a line which is not co-axial with the centerline of the drum as a result of the pipe being horizontal and the drum at a tilt of 5 to 10 degrees. Therefore a longitudinal adjustment of the asphalt pipe would move

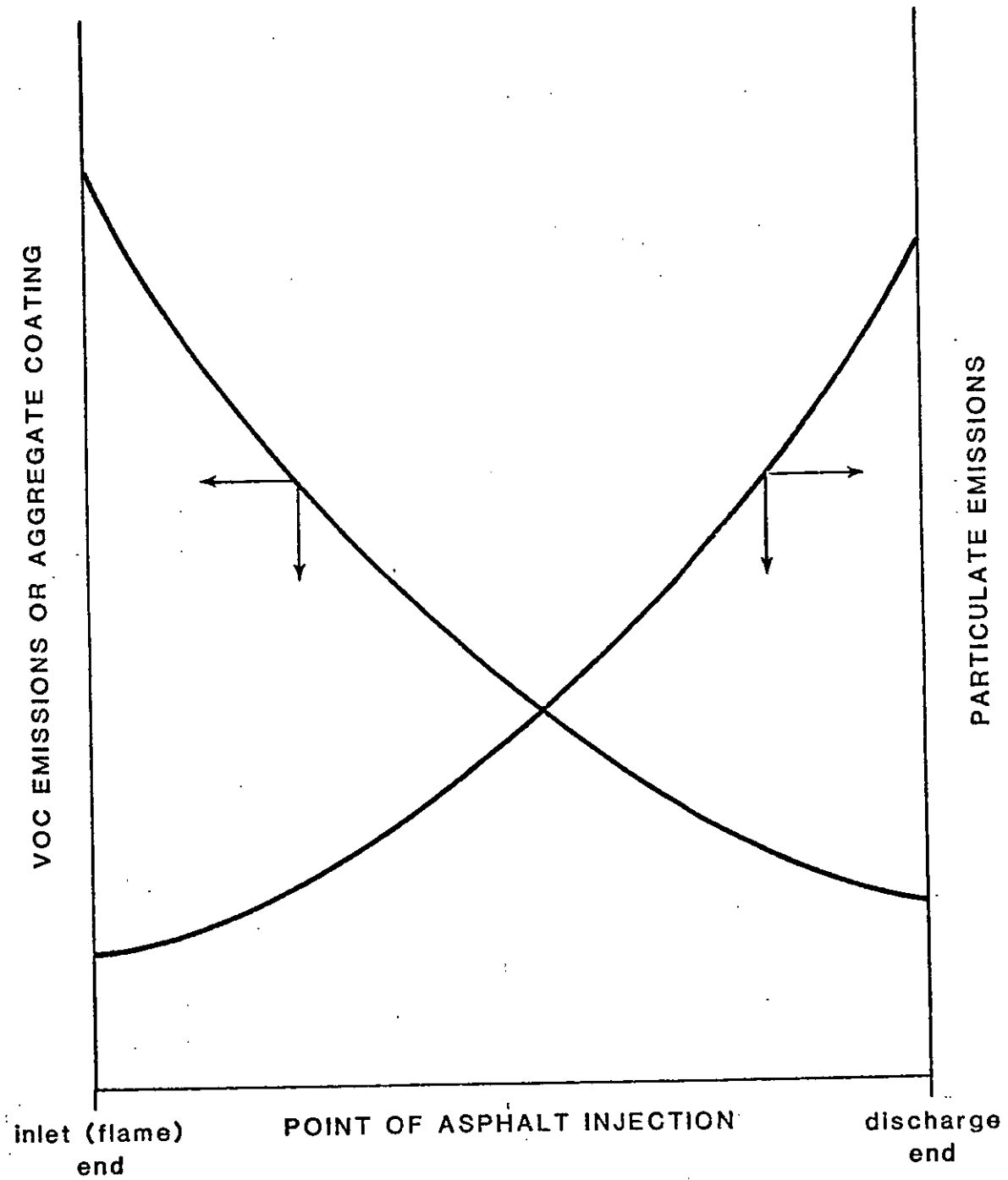

Figure 4. Emissions and aggregate coating vs. asphalt injection point in a drum-mix dryer. (Source: Information Series 65, National Asphalt Pavement Association.)

the sprays closer to or farther from the flights at the bottom of the dryer. If an extreme adjustment was attempted the spray nozzles could be broken off by the dryer flights.

For all of these reasons, none of the plant operators at the plants tested in this study were agreeable to adjusting the point of asphalt injection for the purpose of testing. The only variation available was from plant to plant; comparison of these results showed that the point of injection seemed to have little effect on VOC emissions, probably because although the points differed, each has an optimum for the particular drum design.

Mix Temperature

No dependency of VOC emission factors on mix temperature was demonstrated over the range of temperatures investigated. This range was narrow because the plant operator could not be asked to lower the mix temperature to a point where the specified minimum temperature could not be met at the jobsite (and thus risk rejection of the load). Conversely, an excessively high mix temperature would mean very high fuel costs as well as, perhaps, present some difficulties in paving because of the longer curing time.

Percent of Recycled Material

No dependency of VOC emission factors on percentage of recycled material was demonstrated over the range of percentages (0 to 35 percent) tested. This range was the "normal" operating range for the plant, although it is possible that higher percentages of recycled material will be tried in the future in order to determine the maximum percentage that will not generate blue smoke emissions. Presumably, if percentages are kept below this maximum, emission of VOCs will also be minimized.

Production Rate

Production rates were varied widely during the testing. The result was that, with one exception, VOC emission factors appeared to not be dependent on production rate. However, the one opposite result, coupled with the fact that several of the pairs tested were close to showing dependency, suggests that with a larger number of samples for each run, a mild dependency might have been established.

Fuel Type

No dependency of VOC emission factors on fuel type was demonstrated in the few cases where valid comparisons could be made. This result suggests

that some VOC emissions may be due to unburned fuel, but the relative amount of these emissions does not differ appreciably from one fuel to another, or that the difference is not quantifiable from the results.

VOC Reduction by Wet Scrubbing

There is a demonstrable reduction of VOC emissions by wet scrubbing. However, the reduction achieved varied considerably among the test runs (20 percent to 70 percent). Therefore it is difficult to establish a VOC removal efficiency for wet scrubbing in drum-mix asphalt plants. If further testing were done, consisting of several simultaneous samples taken under varying process conditions at several scrubber plants, the VOC emission reduction attainable by wet scrubbing could be established.

National Impact of VOC Emissions

In order to estimate the national impact of VOC emissions from drum-mix asphalt plants, the following must be known or estimated: the VOC emission factor in pounds per ton; the average production rate in tons per hour; the number of operating drum-mix plants; and the average number of operating hours per year. Using the midpoint of the range of emission factors found in this study and the following assumed parameters (Reference 2):

Average production rate	200 TPH
Number of drum-mix plants	700
Number of annual operating hours	1000

the impact of this source can be estimated. The result is on the order of 17,500 tons per year, total carbon basis.

The emission factors developed in this study were based on total organic carbon; if nationwide emissions from this source were to be compared to those from other sources, the emissions would first have to be converted to a total mass basis. Without complete knowledge of the chemical makeup of the emissions it is not possible to convert from one basis to the other. However, for emissions of this type, a ratio of carbon mass to total mass of VOC of 0.85 is commonly used. Applying this to the figure above yields a total mass VOC emission of 20,600 tons per year.

EFFICACY OF THE TEST METHOD

Generally speaking, the modified version of EPA Method 25 (heated filter manifold) was employed in a straightforward manner and yielded good results. The heated filter performed the function of removing liquid

particulates, as evidenced by discoloration of the filter catches. A filter catch not contaminated with oily particles would be expected to be white to brown and exhibit a characteristic cake-like appearance; the filter catches from this study, however, ranged from dark brown to black and would be more accurately described as mud-like than cake-like. It was not possible to ascertain the proportion of filtered material that was organic, nor the proportion that was liquid at the filtering temperature. The only difficult testing application was the high particulate loading upstream of the scrubber at Plant "E"; the only problem in data consistency was high variation in simultaneously collected samples.

Sampling With High Particulate Loading

In testing upstream of the scrubber, clogging of the particulate filter by coarse particles was anticipated because the test port was located at the dryer outlet plenum, approximately at the centerline of the drum. Accordingly, an Andersen 2000 pre-impactor (10 micron diameter separation) was placed on the end of the probe ahead of the heated filter for test run number E-1. Few coarse particles were encountered but the filter rapidly plugged up with very fine particles. This plugging reduced the sampling rate so severely that the filter had to be changed every 5 to 10 minutes. This made it impossible to sample simultaneously upstream of the scrubber and at the stack.

The next run (E-3) was tried with an "alundum" thimble (manufactured by Research Appliance Corporation) with fine (approximately 2 microns diameter) pores. The thimble was placed in the probe end of the train between the pre-impactor and the filter; the objective was to capture the fine particulates in the thimble rather than on the filter since the thimble is capable of holding a much larger volume of particles. The result of this attempt was that the high pressure drop through the thimble caused a sampling flowrate much lower than the sampling flowrate of the stack, again preventing exactly simultaneous sampling. The thimble had to be changed every 10 to 20 minutes, which represented an improvement over the filter-only arrangement, but still was not ideal. There was also some difficulty in properly seating the thimble to prevent leakage past it with subsequent clogging of the heated filter.

The final two pre-scrubber runs (E-5 and E-7) were done with a coarse thimble with pores of 20 microns in diameter. After minor seating problems were overcome this method worked rather well, although a thimble change was required during the run. However, sampling could be accomplished essentially simultaneously by the use of this method. Although the thimble was rated for 20 microns separation, visual inspection revealed that a significant amount of smaller particles was separated. The thimble reduced the filtering burden of the heated filter and prolonged continuous sampling.

Variation Among Simultaneous Samples

Many results for simultaneous samples show significant variation. While it is beyond the scope of this study to determine all the causes for this variation, a few of the possibilities can be briefly mentioned.

Contamination of sampling equipment (such as the trap and the tank) with organic matter is the factor most likely to have caused high results. In-leakage of ambient air to the sampling train could have caused low results by dilution of the collected samples.

There are a number of theories that could be proposed to account for more complex interferences in the results; chief among these would be dissolution of carbon dioxide in condensing moisture in the trap. In the laboratory analysis, the carbon dioxide would subsequently report to the FID as methane as if it were produced by the combustion of hydrocarbons. Further investigation of such theories will not be attempted here.

REFERENCES

1. _____, Update on Drum Mixers. Highway and Heavy Construction, 121(8): 48-51, 1978.

2. Personal communication, National Asphalt Pavement Association, Riverdale, Maryland.

APPENDIX A

*METHOD 25 - DETERMINATION OF TOTAL GASEOUS NONMETHANE ORGANIC EMISSIONS AS CARBON

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of volatile organic compounds (VOC) as total gaseous nonmethane organics (TGNMO) as carbon in source emissions. Organic particulate matter will interfere with the analysis and therefore, in some cases, an in-stack particulate filter is required. This method is not the only method that applies to the measurement of TGNMO. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular weight of the organics in the effluent stream, a totally automated semi-continuous nonmethane organic (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semi-continuously over an extended time period.

Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the

---

* The drum-mix asphalt sampling program of this report was conducted during May, June and July of 1980. The above Method 25 was promulgated by EPA on October 9, 1980.

detector responds predictably to the organic compounds in the stream. If present, methane will, of course, also be measured. In practice, the FID can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions under the following limited conditions: (1) where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentage of the compounds is known or can be determined, and the FID response to the compounds is known; (4) where a consistent mixture of compounds exists before and after emission control and only the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

1.2 Principle. An emission sample is withdrawn from the stack at a constant rate through a chilled condensate trap by means of an evacuated sample tank. TGNMO are determined by combining the analytical results obtained from independent analyses of the condensate trap and sample tank fractions. After sampling is completed, the organic contents of the condensate trap are oxidized to carbon dioxide (CO_2) which is quantitatively collected in an evacuated vessel; then a portion of the CO_2 is reduced to methane (CH_4) and measured by a FID. The organic content of the sample fraction collected in the sampling tank is measured by injecting a portion into a gas chromatographic (GC) column to achieve separation of the nonmethane organics from carbon monoxide (CO), CO_2 and CH_4; the nonmethane organics (NMO) are oxidized to CO_2, reduced to CH_4, and measured by a FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

2. Apparatus

The sampling system consists of a condensate trap, flow control system, and sample tank (Figure 1). The analytical system consists of two major sub-systems; an oxidation system for the recovery and conditioning of the condensate trap contents and a NMO analyzer. The NMO analyzer is a GC with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. (Figures 2 and 3 are schematics of a typical NMO analyzer.) The system for the recovery and conditioning of the organics captured in the condensate trap consists of a heat source, oxidation catalyst,

nondispersive infrared (NDIR) analyzer and an intermediate collection vessel (Figure 4 is a schematic of a typical system.) TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. NMO analyzers are available commercially or can be constructed from available components by a qualified instrument laboratory.

2.1 Sampling. The following equipment is required:

2.1.1 Probe. 3.2-mm OD (1/8-in.) stainless steel tubing.

2.1.2 Condensate Trap. Constructed of 316 stainless steel; construction details of a suitable trap are shown in Figure 5.

2.1.3 Flow Shut-off Valve. Stainless steel control valve for starting and stopping sample flow.

2.1.4 Flow Control System. Any system capable of maintaining the sampling rate to within $\pm$ 10 percent of the selected flow rate (50 to 100 cc/min range).

2.1.5 Vacuum Gauge. Gauge for monitoring the vacuum of the sample tank during leak checks and sampling.

2.1.6 Sample Tank. Stainless steel or aluminum tank with a volume of 4 to 8 liters, equipped with a stainless steel female quick connect for assembly to the sample train and analytical system.

2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0-900 mm range.

2.1.8 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2 Analysis. The following equipment is required:

2.2.1 Condensate Recovery and Conditioning Apparatus. An apparatus for recovering and catalytically oxidizing the condensate trap contents is required. Figure 4 is a schematic of such a system. The analyst must demonstrate prior to initial use that the analytical system is capable of proper oxidation and recovery, as specified in section 5.1. The condensate recovery and conditioning apparatus consists of the following major components.

2.2.1.1 Heat Source. A heat source sufficient to heat the condensate trap (including probe) to a temperature where the trap turns a "dull red" color. A system using both a propane torch and an electric muffle-type furnace is recommended.

2.2.1.2 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.1.2). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.1.3 Water Trap. Any leak proof moisture trap capable of removing moisture from the gas stream.

2.2.1.4 NDIR Detector. A detector capable of indicating CO_2 concentration in the zero to 1 percent range. This detector is required for monitoring the progress of combustion of the organic compounds from the condensate trap.

2.2.1.5 Pressure Regulator. Stainless steel needle valve required to maintain the trap conditioning system at a near constant pressure.

2.2.1.6 Intermediate Collection Vessel. Stainless steel or aluminum collection vessel equipped with a female quick connect.

Tanks with nominal volumes in the 1 to 4 liter range are recommended.

2.2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0-900 mm range.

2.2.1.8 Gas Purifiers. Gas purification systems sufficient to maintain CO_2 and organic impurities in the carrier gas and auxiliary oxygen at a level of less than 10 ppm (may not be required depending on quality of cylinder gases used).

2.2.2 NMO Analyzer. Semi-continuous GC/FID analyzer capable of: (1) separating CO, CO_2, and CH_4 from nonmethane organic compounds, (2) reducing the CO_2 to CH_4 and quantifying as CH_4, and (3) oxidizing the nonmethane organic compounds to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4. The analyst must demonstrate prior to initial use that the analyzer is capable of proper separation, oxidation, reduction, and measurement (section 5.2). The analyzer consists of the following major components:

2.2.2.1 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.1). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.2 Reduction Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.3). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.3 Separation Column(s). Gas chromatographic column(s) capable of separating CO, CO_2, and CH_4 from NMO compounds as demonstrated according to the procedures established in this method (section 5.2.5). Addendum I of this method lists a column found to be acceptable.

2.2.2.4 Sample Injection System. A GC sample injection valve fitted with a sample loop properly sized to interface with the NMO analyzer (1 cc loop recommended).

2.2.2.5 FID. A FID meeting the following specifications is required.

2.2.2.5.1 Linearity. A linear response (± 5%) over the operating range as demonstrated by the procedures established in section 5.2.2.

2.2.2.5.2 Range. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale for a full scale range of 10 to 50000 ppm CH_4.

2.2.2.6 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

2.2.3 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

2.2.4 Thermometer. Capable of measuring the laboratory temperature within 1°C.

2.2.5 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2.6 Syringe(2). 10 µl and 100 µl liquid injection syringes.

2.2.7 Liquid Sample Injection Unit. 316 SS U-tube fitted with a Teflon injection septum, see Figure 6.

3. Reagents

3.1 Sampling. Crushed dry ice is required during sampling.

3.2 Analysis.

3.2.1 NMO Analyzer. The following gases are needed:

3.2.1.1 Carrier Gas. Zero grade gas containing less than 1 ppm C. Addendum I of this method lists a carrier gas found to be acceptable.

3.2.1.2 Fuel Gas. Pure hydrogen, containing less than 1 ppm C.

3.2.1.3 Combustion Gas. Zero grade air or oxygen as required by the detector.

3.2.2 Condensate Recovery and Conditioning Apparatus.

3.2.2.1 Carrier Gas. Five percent O_2 in N_2, containing less than 1 ppm C.

3.2.2.2 Auxiliary Oxygen. Zero grade oxygen containing less than 1 ppm C.

3.2.2.3 Hexane. ACS grade, for liquid injection.

3.2.2.4 Toluene. ACS grade, for liquid injection.

3.3 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than $\pm$ 5 percent from its certified value). The date of gas cylinder preparation, certified organic concentration and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required.

3.3.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

3.3.2 Flame Ionization Detector Linearity and Nonmethane Organic Calibration Gases (3). Gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

3.3.3 Carbon Dioxide Calibration Gases (3). Gas mixture standards with nominal CO_2 concentrations of 50 ppm, 500 ppm, and 1 percent, in air. Note: total NMO less than 1 ppm required for 1 percent mixture.

3.3.4 NMO Analyzer System Check Calibration Gases (4).

3.3.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 2 percent CO_2, and 20 ppm C_3H_8, prepared in air.

3.3.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

3.3.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

3.3.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

4. Procedure

4.1 Sampling.

4.1.1 Sample Tank Evacuation and Leak Check. Either in the laboratory or in the field, evacuate the sample tank to 10 mm Hg absolute pressure or less (measured by a mercury U-tube manometer) then leak check the sample tank by isolating the tank from the vacuum pump and allowing the tank to sit for 10 minutes. The tank is acceptable if no change in tank vacuum is noted.

4.1.2 Sample Train Assembly. Just prior to assembly, measure the tank vacuum using a mercury U-tube manometer. Record this vacuum (P_{ti}), the ambient temperature (T_{ti}), and the barometric pressure (P_{bi}) at this time. Assuring that the flow shut-off valve is in the closed position, assemble the sampling system as shown in Figure 1. Immerse

the condensate trap body in dry ice to within 2.5 or 5 cm of the point where the inlet tube joins the trap body.

4.1.3 Pretest Leak Check. A pretest leak check is required. After the sampling train is assembled, record the tank vacuum as indicated by the vacuum gauge. Wait a minimum period of 10 minutes and recheck the indicated vacuum. If the vacuum has not changed, the portion of the sampling train behind the shut-off valve does not leak and is considered acceptable. To check the front portion of the sampling train, assure that the probe tip is tightly plugged and then open the sample train flow shut-off valve. Allow the sample train to sit for a minimum period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the pretest leak rate (cm/Hg per 10 minutes). At the completion of the leak check period, close the sample flow shut-off valve.

4.1.4 Sample Train Operation. Place the probe into the stack such that the probe is perpendicular to the direction of stack gas flow; locate the probe tip at a single preselected point. If a probe extension which will not be analyzed as part of the condensate trap is being used, assure that at least a 15 cm section of the probe which will be analyzed with the trap is in the stack effluent. For stacks having a negative static pressure, assure that the sample port is sufficiently sealed to prevent air in-leakage around the probe. Check the dry ice level and add ice if necessary. Record the clock time and sample tank gauge vacuum. To begin sampling, open the flow shut-off valve and adjust (if applicable) the control valve of the flow control system used in the sample train; maintain a constant flow rate ($\pm$ 10 percent) throughout the duration of the sampling period. Record the gauge vacuum and flowmeter

setting (if applicable) at 5-minute intervals. Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulation; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained due to reduced sample tank vacuum. When the sampling is completed, close the flow shut-off valve and record the final sample time and gauge vacuum readings. Note: If the sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After removing the probe from the stack, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train) and connect another sample tank to the sampling train. Prior to attaching the new tank to the sampling train, assure that the tank vacuum (measured on-site by the U-tube manometer) has been recorded on the data form and that the tank has been leak-checked (on-site). After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

4.1.5 Post Test Leak Check. A leak check is mandatory at the conclusion of each test run. After sampling is completed, remove the probe from the stack and plug the probe tip. Open the sample train flow shut-off valve and monitor the sample tank vacuum gauge for a period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the post test leak rate (cm Hg per 10 minutes). If the sampling train does not pass the post leak check, invalidate the run or use a procedure acceptable to the Administrator to adjust the data.

4.2 Sample Recovery. After the post test leak check is completed, disconnect the condensate trap at the flow metering system and tightly seal both ends of the condensate trap. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Remove the flow metering system from the sample tank. Attach the U-tube manometer to the tank (keep length of connecting line to a minimum) and record the final tank vacuum (P_t); record the tank temperature (T_t) and barometric pressure at this time. Disconnect the manometer from the tank. Assure that the test run number is properly identified on the condensate trap and the sample tank(s).

4.3 Condensate Recovery and Conditioning. Prepare the condensate recovery and conditioning apparatus by setting the carrier gas flow rate and heating the catalyst to its operating temperature. Prior to initial use of the condensate recovery and conditioning apparatus, a system performance test must be conducted according to the procedures established in section 5.1 of this method. After successful completion of the initial performance test, the system is routinely used for sample conditioning according to the following procedures:

4.3.1 System Blank and Catalyst Efficiency Check. Prior to and immediately following the conditioning of each set of sample traps, or on a daily basis (whichever occurs first) conduct the carrier gas blank test and catalyst efficiency test as specified in sections 5.1.1 and 5.1.2 of this method. Record the carrier gas initial and final blank values, B_{ti} and B_{tf}, respectively. If the criteria of the tests cannot be met, make the necessary repairs to the system before proceeding.

4.3.2 Condensate Trap Carbon Dioxide Purge and Sample Tank Pressurization. The first step in analysis is to purge the condensate trap of any CO_2 which it may contain and to simultaneously pressurize the sample tank. This is accomplished as follows: Obtain both the sample tank and condensate trap from the test run to be analyzed. Set up the condensate recovery and conditioning apparatus so that the carrier flow bypasses the condensate trap hook-up terminals, bypasses the oxidation catalyst, and is vented to the atmosphere. Next, attach the condensate trap to the apparatus and pack the trap in dry ice. Assure that the valves isolating the collection vessel connection from the atmospheric vent and the vacuum pump are closed and then attach the sample tank to the system as if it were the intermediate collection vessel. Record the tank vacuum on the laboratory data form. Assure that the NDIR analyzer indicates a zero output level and then switch the carrier flow through the condensate trap; immediately switch the carrier flow from vent to collect. The condensate trap recovery and conditioning apparatus should now be set up as indicated in Figure 8. Monitor the NDIR; when CO_2 is no longer being passed through the system, switch the carrier flow so that it once again bypasses the condensate trap. Continue in this manner until the gas sample tank is pressurized to a nominal gauge pressure of 800 mm Hg. At this time, isolate the tank, vent the carrier flow, and record the sample tank pressure (P_{tf}), barometric pressure (P_{bf}), and ambient temperature (T_{tf}). Remove the sample tank from the system.

4.3.3 Recovery of Condensate Trap Sample. Oxidation and collection of the sample in the condensate trap is now ready to begin.

From the step just completed in section 4.3.1.2 above, the system should be set up so that the carrier flow bypasses the condensate trap, bypasses the oxidation catalyst, and is vented to the atmosphere. Attach an evacuated intermediate collection vessel to the system and then switch the carrier so that it flows through the oxidation catalyst. Switch the carrier from vent to collect and open the valve to the collection vessel; remove the dry ice from the trap and then switch the carrier flow through the trap. The system should now be set up to operate as indicated in Figure 9. During oxidation of the condensate trap sample, monitor the NDIR to determine when all the sample has been removed and oxidized (indicated by return to baseline of NDIR analyzer output). Begin heating the condensate trap and probe with a propane torch. The trap should be heated to a temperature at which the trap glows a "dull red" (approximately 500°C). During the early part of the trap "burn out," adjust the carrier and auxiliary oxygen flow rates so that an excess of oxygen is being fed to the catalyst system. Gradually increase the flow of carrier gas through the trap. After the NDIR indicates that most of the organic matter has been purged, place the trap in a muffle furnace (500°C). Continue to heat the probe with a torch or some other procedure (e.g., electrical resistance heater). Continue this procedure for at least 5 minutes after the NDIR has returned to baseline. Remove the heat from the trap but continue the carrier flow until the intermediate collection vessel is pressurized to a gauge pressure of 800 mm Hg (nominal). When the vessel is pressurized, vent the carrier; measure and record the final intermediate collection vessel pressure

(P_f) as well as the barometric pressure (P_{bv}), ambient temperature (T_v), and collection vessel volume (V_v).

4.4 Analysis. Prior to putting the NMO analyzer into routine operation, an initial performance test must be conducted. Start the analyzer and perform all the necessary functions in order to put the analyzer in proper working order, then conduct the performance test according to the procedures established in section 5.2. Once the performance test has been successfully completed and the CO_2 and NMO calibration response factors determined, proceed with sample analysis as follows:

4.4.1 Daily operations and calibration checks. Prior to and immediately following the analysis of each set of samples or on a daily basis (whichever occurs first) conduct a calibration test according to the procedures established in section 5.3. If the criteria of the daily calibration test cannot be met, repeat the NMO analyzer performance test (section 5.2) before proceeding.

4.4.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample and then inject a preliminary sample in order to determine the appropriate FID attenuation. Inject triplicate samples from the intermediate collection vessel and record the values obtained for the condensible organics as CO_2 (C_{cm}).

4.4.3 Analysis of Sample Tank. Purge the sample loop with sample and inject a preliminary sample in order to determine the appropriate FID attenuation for monitoring the backflushed non-methane organics. Inject triplicate samples from the sample tank and record the values obtained for the nonmethane organics (C_{tm}).

5. Calibration and Operational Checks

Maintain a record of performance of each item.

5.1 Initial Performance Check of Condensate Recovery and Conditioning Apparatus.

5.1.1 Carrier Gas and Auxiliary Oxygen Blank. Set equal flow rates for both the carrier gas and auxiliary oxygen. With the trap switching valves in the bypass position and the catalyst in-line, fill an evacuated intermediate collection vessel with carrier gas. Analyze the collection vessel for CO_2; the carrier blank is acceptable if the CO_2 concentration is less than 10 ppm.

5.1.2 Catalyst Efficiency Check. Set up the condensate trap recovery system so that the carrier flow bypasses the trap inlet and is vented to the atmosphere at the system outlet. Assure that the valves isolating the collection system from the atmospheric vent and vacuum pump are closed and then attach an evacuated intermediate collection vessel to the system. Connect the methane standard gas cylinder (section 3.3.1) to the system's condensate trap connector (probe end, Figure 4). Adjust the system valving so that the standard gas cylinder acts as the carrier gas and adjust the flow rate to the rate normally used during trap sample recovery. Switch off the auxiliary oxygen flow and then switch from vent to collect in order to begin collecting a sample. Continue collecting a sample in a normal manner until the intermediate vessel is filled to a nominal gauge pressure of 300 mm Hg. Remove the intermediate vessel from the system and vent the carrier flow to the atmosphere. Switch the valving to return the system to its normal carrier gas and normal operating conditions.

Analyze the collection vessel for CO_2; the catalyst efficiency is acceptable if the CO_2 concentration is within $\pm$ 5 percent of the expected value.

5.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 6. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap and set the carrier gas and auxiliary oxygen flow rates to normal operating levels. Attach an evacuated intermediate collection vessel to the system and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see 5.1.3.1 to 5.1.3.4) via the injection septum. Heat the injection unit with a torch while monitoring the oxidation reaction on the NDIR. Continue the purge until the reaction is complete. Measure the final collection vessel pressure and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery using the equation in section 6.6.

The performance test is acceptable if the average percent recovery is 100 $\pm$ 10 percent with a relative standard deviation (section 6.7) of less than 5 percent for each set of triplicate injections as follows:

5.1.3.1 100 µl hexane.

5.1.3.2 10 µl hexane.

5.1.3.3 100 µl toluene.

5.1.3.4 10 µl toluene.

5.2 Initial NMO Analyzer Performance Test.

5.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (section 3.3.1). The oxidation catalyst operation is acceptable if no FID response is noted.

5.2.2 Analyzer Linearity Check and NMO Calibration. Operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 3.3. Make triplicate injections of each calibration gas and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within $\pm$ 5 percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than $\pm$ 5 percent. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{NMO}).

5.2.3 Reduction Catalyst Efficiency Check and CO_2 Calibration. An exact determination of the reduction catalyst efficiency is not required. Instead, proper catalyst operation is indirectly checked and continuously monitored by establishing a CO_2 response factor and comparing it to the NMO response factor. Operating both the oxidation and reduction catalysts make triplicate injections of each of the CO_2 calibration gases (section 3.3.3). Calculate the average response factor (area/ppm) for each calibration gas, as well as the overall mean of the

response factor values. The reduction catalyst operation is acceptable if the average response factor of each calibration gas is within ± 5 percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than ± 5 percent. Additionally, the CO_2 overall mean response factor must be within ± 10 percent of the NMO calibration response factor (RF_{NMO}) calculated in section 5.2.2. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{CO_2}).

5.2.4 NMO System Blank. For the high level CO_2 calibration gas (section 3.3.3) record the NMO value measured during the CO_2 calibration conducted in section 5.2.3. This value is the NMO blank value for the analyzer (B_a) and should be less than 10 ppm.

5.2.5 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 3.3.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within ± 12 percent of the expected value.

5.3 NMO Analyzer Daily Calibration.

5.3.1 NMO Blank and CO_2. Inject triplicate samples of the high level CO_2 calibration gas (section 3.3.3) and calculate the average response factor. The system operation is adequate if the calculated response factor is within ± 10 percent of the RF_{CO_2} calculated during the initial performance test (section 5.2.2). Use the daily response factor (DRF_{CO_2}) for analyzer calibration and the calculation of

measured CO_2 concentrations in the collection vessel samples. In addition, record the NMO blank value (B_a); this value should be less than 10 ppm.

5.3.2 NMO Calibration. Inject triplicate samples of the mixed propane calibration cylinder (section 3.3.4.1) and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within $\pm$ 10 percent of the RF_{NMO} calculated during the initial performance test (section 5.2.1). Use the daily response factor (DRF_{NMO}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

5.4 Sample Tank. The volume of the gas sampling tanks used must be determined. Prior to putting each tank in service, determine the tank volume by weighing the tanks empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

5.5 Intermediate Collection Vessel. The volume of the intermediate collection vessels used to collect CO_2 during the analysis of the condensate traps must be determined. Prior to putting each vessel into service, determine the volume by weighing the vessel empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

6. Calculations

Note: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge pressure.

6.1 Sample Volume. For each test run, calculate the gas volume sampled:

$$V_s = 0.386\ V\left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}\right)$$

6.2 Noncondensible Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C):

$$C_t = \left[\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}}\right]\left[\frac{1}{r}\sum_{j=1}^{r} C_{tm_j} - B_a\right]$$

6.3 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C):

$$C_c = 0.386\ \frac{V_v\ P_f}{V_s\ T_f}\left[\frac{1}{q}\sum_{k=1}^{q} C_{cm_k} - B_t\right]$$

6.4 Total Gaseous Nonmethane Organics (TGNMO). To determine the TGNMO concentration for each test run, use the following equation:

$$C = C_t + C_c$$

6.5 Total Gaseous Nonmethane Organics (TGNMO) Mass Concentration. To determine the TGNMO mass concentration as carbon for each test run, use the following equation:

$$M_c = 0.498\ C$$

6.6 Percent Recovery. To calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system use the following equation:

$$\text{percent recovery} = 1.6\ \frac{M}{L}\ \frac{V_v}{\rho}\ \frac{P_f}{T_f}\ \frac{C_{cm}}{N}$$

6.7 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{X}} \sqrt{\frac{\Sigma\ (x_i - \bar{x})^2}{n - 1}}$$

Where: B_a = Measured NMO blank value for NMO analyzer, ppm C

B_t = Measured CO_2 blank value for condensate recovery and conditioning system carrier gas, ppm CO_2.

C = Total gaseous nonmethane organic (TGNMO) concentration of the effluent, ppm C equivalent.

C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.

C_{cm} = Measured concentration (NMO analyzer) for the condensate trap (intermediate collection vessel), ppm CO_2.

C_t = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.

C_{tm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.

L = Volume of liquid injected, microliters.

M = Molecular weight of the liquid injected, g/g-mole.

M_c = Total gaseous non-methane organic (TGNMO) mass concentration of the effluent, mg C/dscm.

N = Carbon number of the liquid compound injected (N = 7 for toluene, N = 6 for hexane).

P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.

P_{ti} = Gas sample tank pressure prior to sampling, mm Hg absolute.

P_t = Gas sample tank pressure after sampling, but prior to pressurizing, mm Hg absolute.

P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.

T_f = Final temperature of intermediate collection vessel, °K.

T_{ti} = Sample tank temperature prior to sampling, °K.

T_t = Sample tank temperature at completion of sampling, °K.

T_{tf} = Sample tank temperature after pressurizing, °K.

V = Sample tank volume, cm.

V_y = Intermediate collection vessel volume, cm.

V_s = Gas volume sampled, dscm.

n = Number of data points.

q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 . . q).

r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . .r).

x_i = Individual measurements.

$\bar{X}$ = Mean value.

ρ = Density of liquid injected, g/cc.

7. Bibliography

7.1 Salo, Albert E., Samuel Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A comparison of Infrared with Flame Ionization Detectors. Paper No. 75-33.2. (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, MA. June 15-20, 1975.) 14 p.

7.2 Salo, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74-190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, CO. June 9-13, 1974.) 25 p.

METHOD 25

ADDENDUM I. SYSTEM COMPONENTS

In test Method 25 several important system components are not specified; instead minimum performance specifications are provided. The method is written in this manner to permit individual preference in choosing components, as well as, to encourage development and use of improved components. This addendum is added to the method in order to provide users with some specific information regarding components which have been found satisfactory for use with the method. This listing is given only for the purpose of providing information and does not constitute an endorsement of any product by the Environmental Protection Agency. This list is not meant to imply that other components not listed are not acceptable.

1. Condensate Recovery and Conditioning System Oxidation Catalyst. 3/8" OD X 14" inconel tubing packed with 8 inches of hopcalite* oxidizing catalyst and operated at 800°C in a tube furnace. Note: A this temperature, this catalyst must be purged with carrier gas at all times to prevent catalyst damage.

2. NMO Analyzer Oxidation Catalyst. 1/4" OD X 14" inconel tubing packed with 6 inches of hopcalite oxidizing catalyst and operated at 800°C in a tube furnace. (See note above.)

3. NMO Analyzer Reduction Catalyst. Reduction Catalyst Module; Byron Instruments, Raleigh, N.C.

---

* MSA registered trade mark.

4. Gas Chromatographic Separation Column. 1/8 inch OD stainless steel packed with 3 feet of 10 percent methyl silicone, Sp 2100 (or equivalent) on Supelcoport (or equivalent), 80/100 mesh, followed by 1.5 feet Porapak Q (or equivalent) 60/80 mesh. The inlet side is to the silicone. Condition the column for 24 hours at 200°C with 20 cc/min N_2 purge.

During analysis for the nonmethane organics the separation column is operated as follows: First, operate the column at -78°C (dry ice bath) to elute CO and CH_4. After the CH_4 peak operate the column at 0°C to elute CO_2. When the CO_2 is completely eluted, switch the carrier flow to backflush the column and simultaneously raise the column temperature to 100° C in order to elute all nonmethane organics (exact timings for column operation are determined from the calibration standard).

Note: The dry ice operating condition may be deleted if separation of CO and CH_4 is unimportant.

Note: Ethane and ethylene may or may not be measured using this column; whether or not ethane and ethylene are quantified will depend on the CO_2 concentration in the gas sample. When high levels of CO_2 are present, ethane and ethylene will elute under the tail of the CO_2 peak.

5. Carrier Gas. Zero grade nitrogen or helium or zero air.

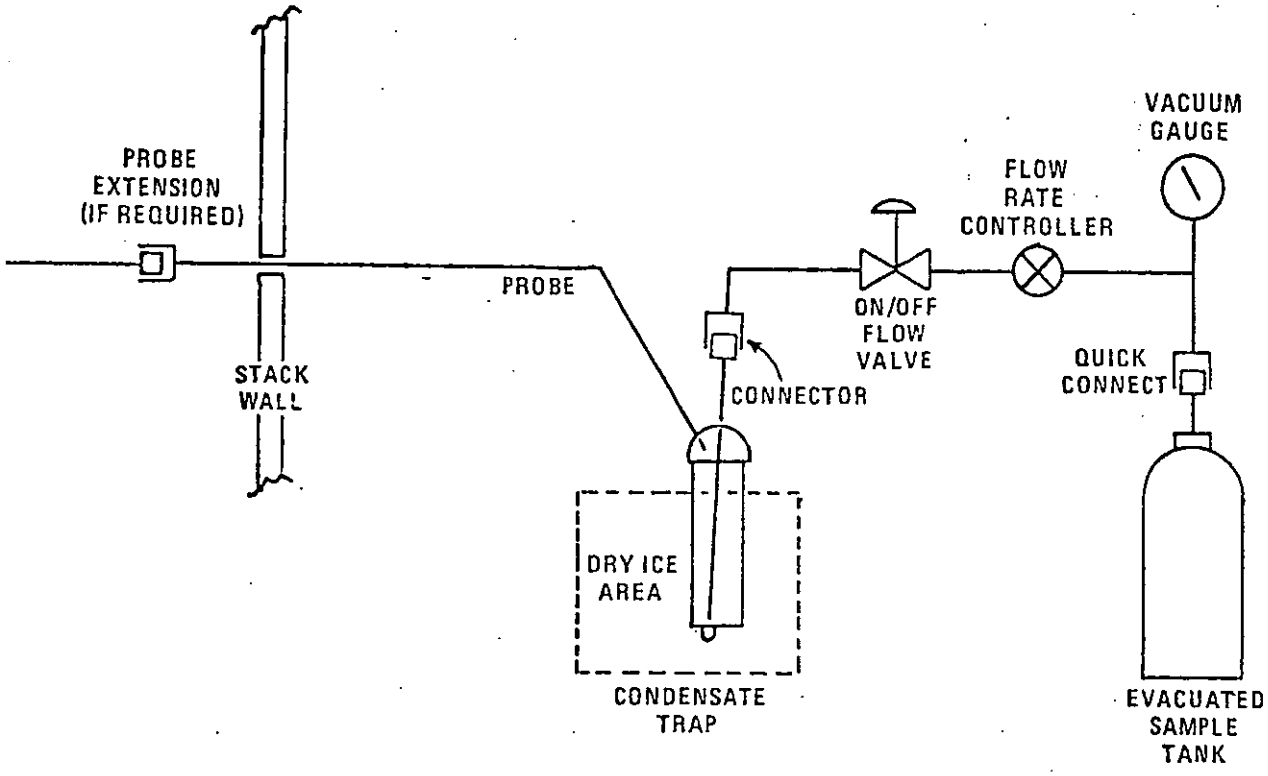

Figure 1. Sampling apparatus.

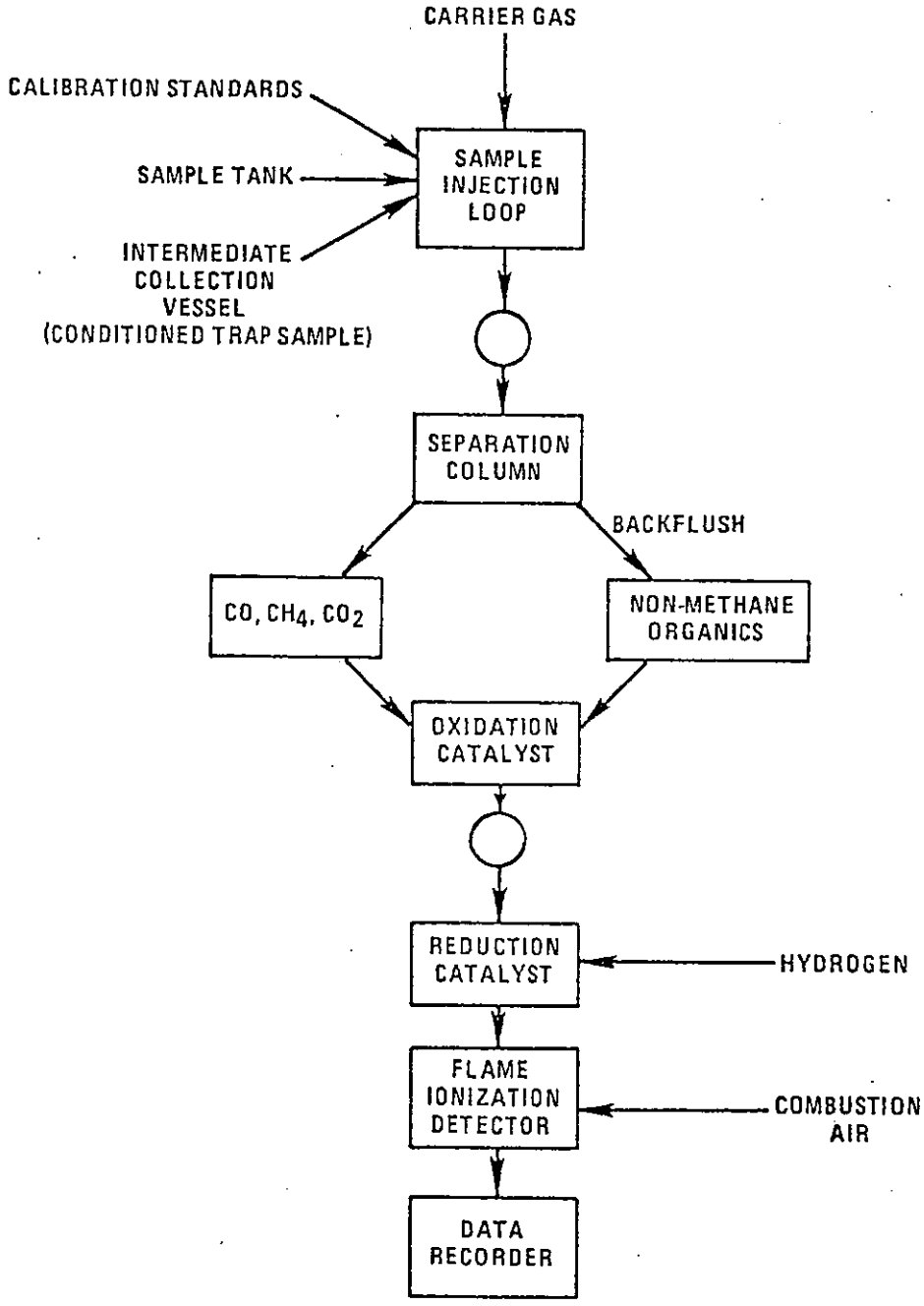

Figure 2. Simplified schematic of non-methane organic (NMO) analyzer.

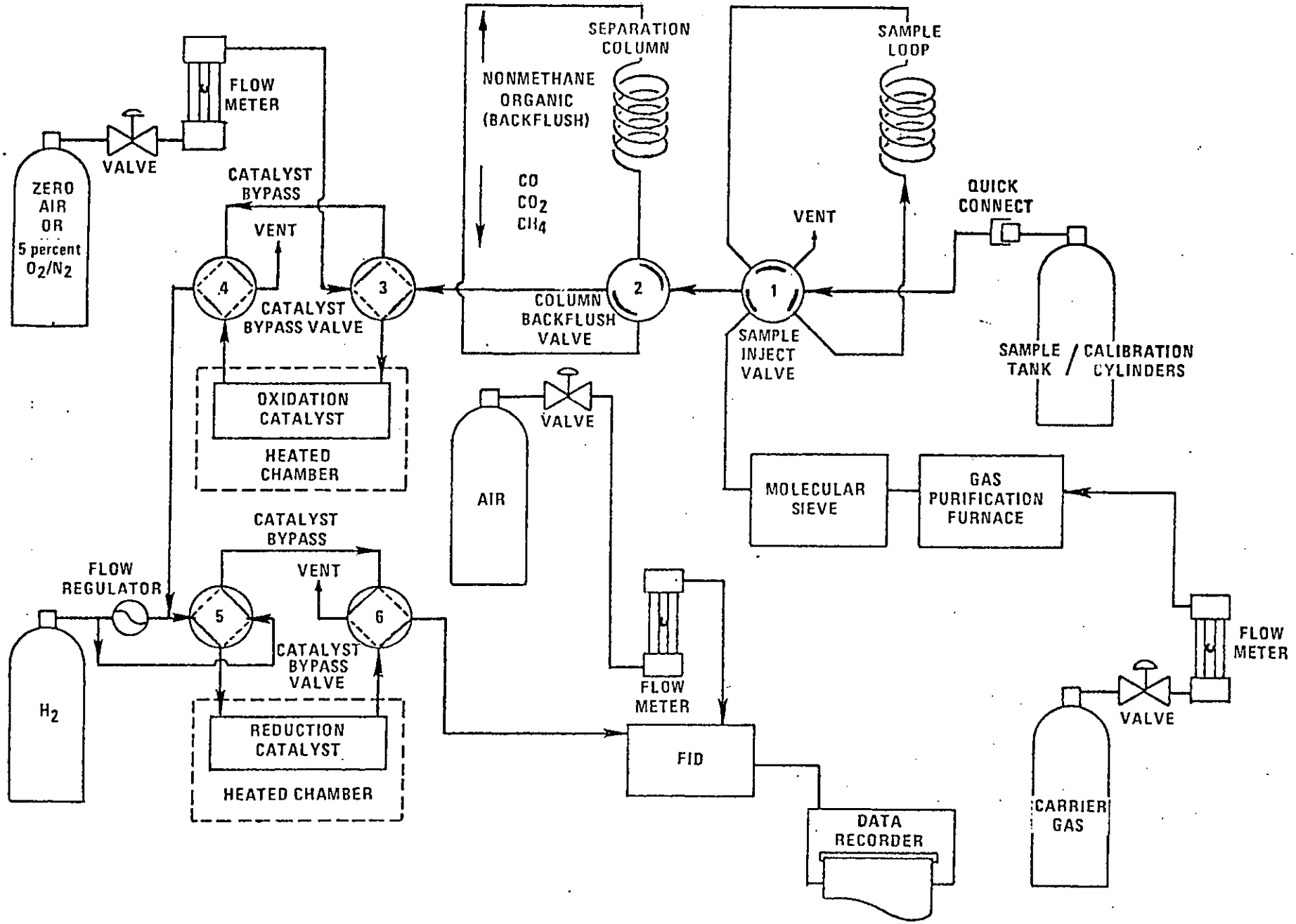

Figure 3. Nonmethane organic (NMO) analyzer.

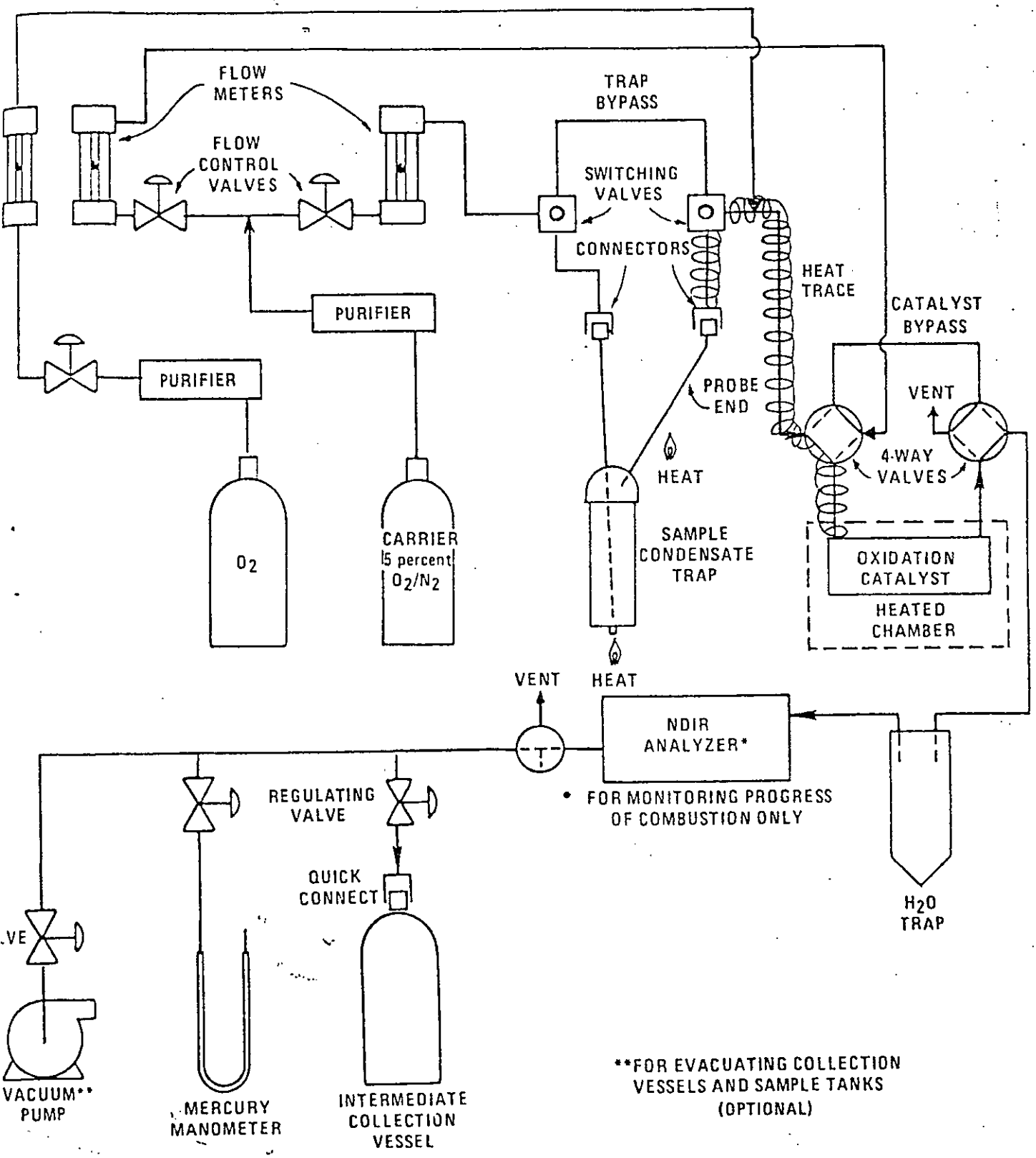

Figure 4. Condensate recovery and conditioning apparatus.

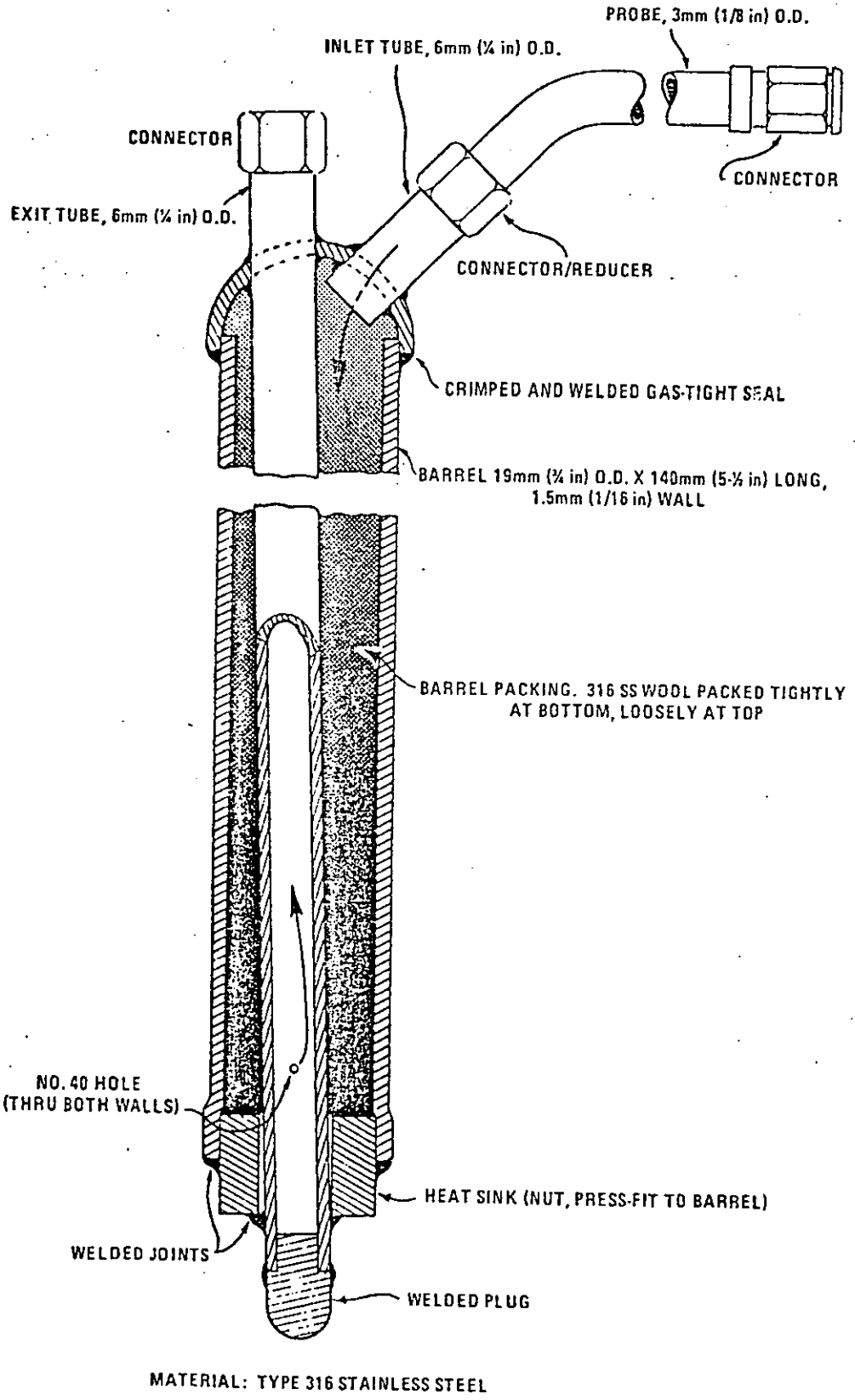

Figure 5. Condensate trap[2].

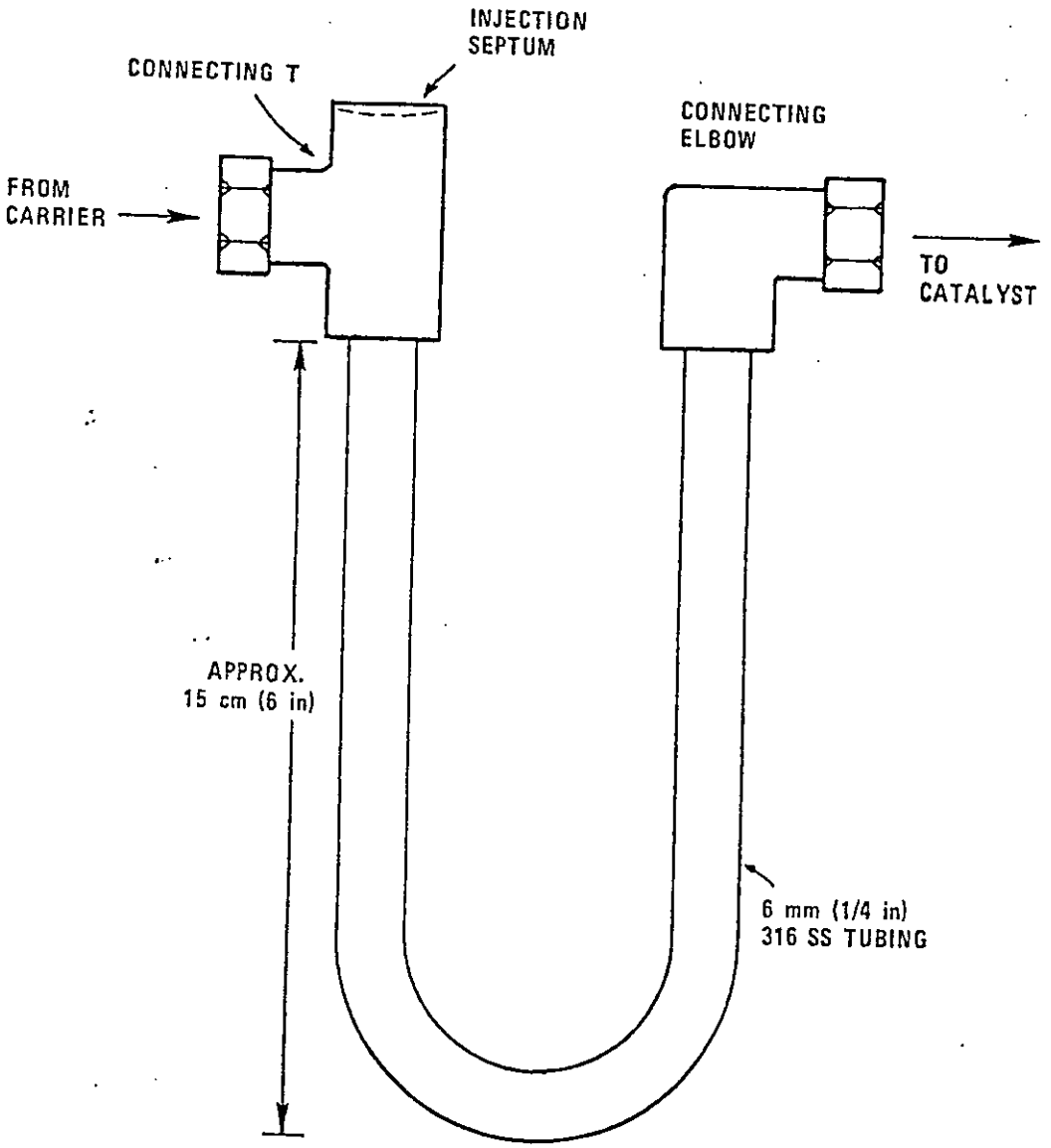

Figure 6. Liquid sample injection unit.

VOLATILE ORGANIC CARBON

FACILITY _____ SAMPLE LOCATION _____

LOCATION _____ OPERATOR _____

DATE _____ RUN NUMBER _____

TANK NUMBER _____ TRAP NUMBER _____ SAMPLE ID NUMBER _____

	TANK VACUUM, mm Hg	cm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)		(GAUGE)		
POST TEST (MANOMETER)		(GAUGE)		

LEAK RATE _____ cm Hg / 10 min

PRETEST _____

POST TEST _____

TIME CLOCK/SAMPLE	GAUGE VACUUM, cm Hg	FLOWMETER SETTING	COMMENTS

Figure 7. Example Field Data Form.

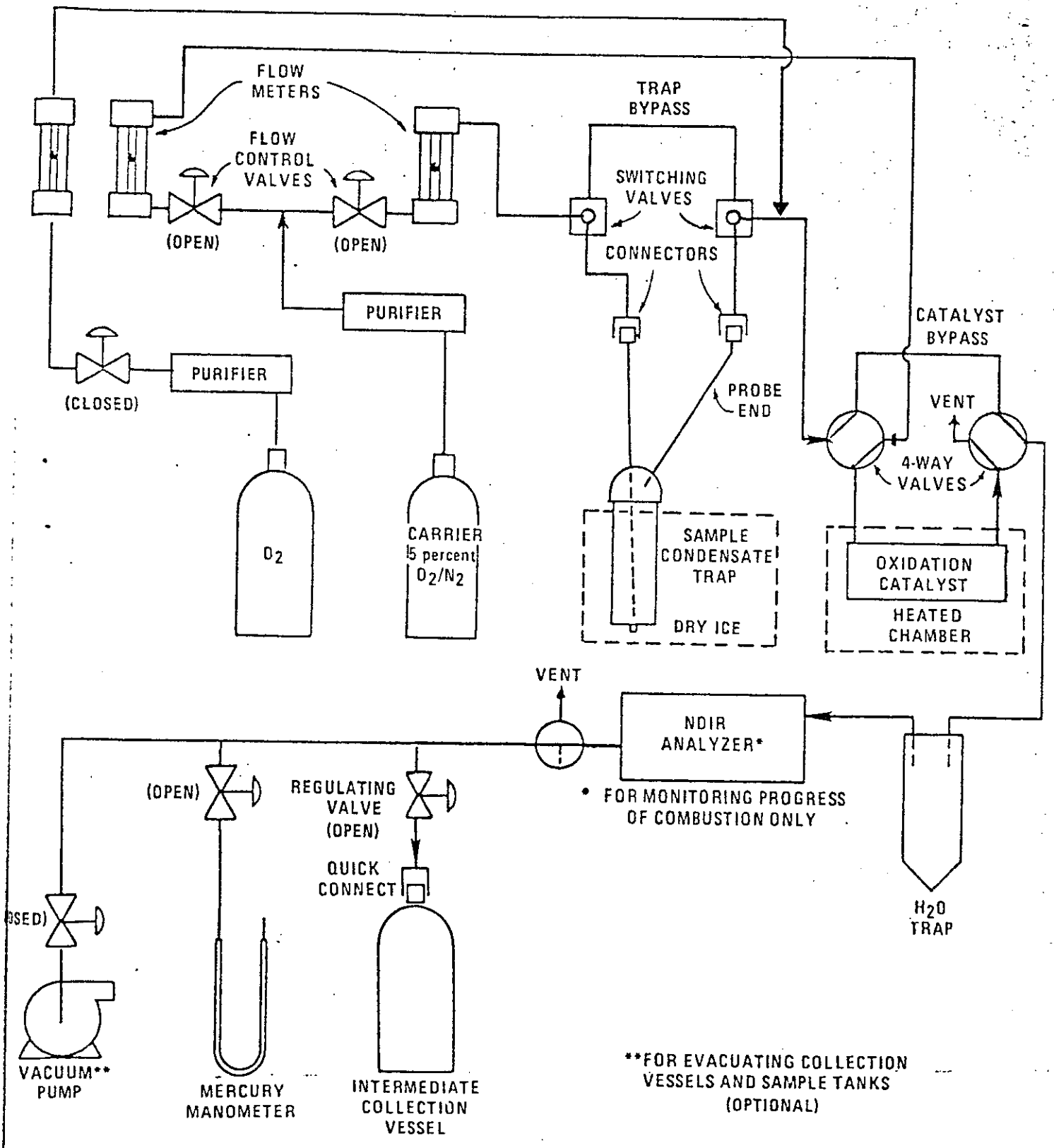

Figure 8. Condensate recovery and conditioning apparatus, carbon dioxide purge.

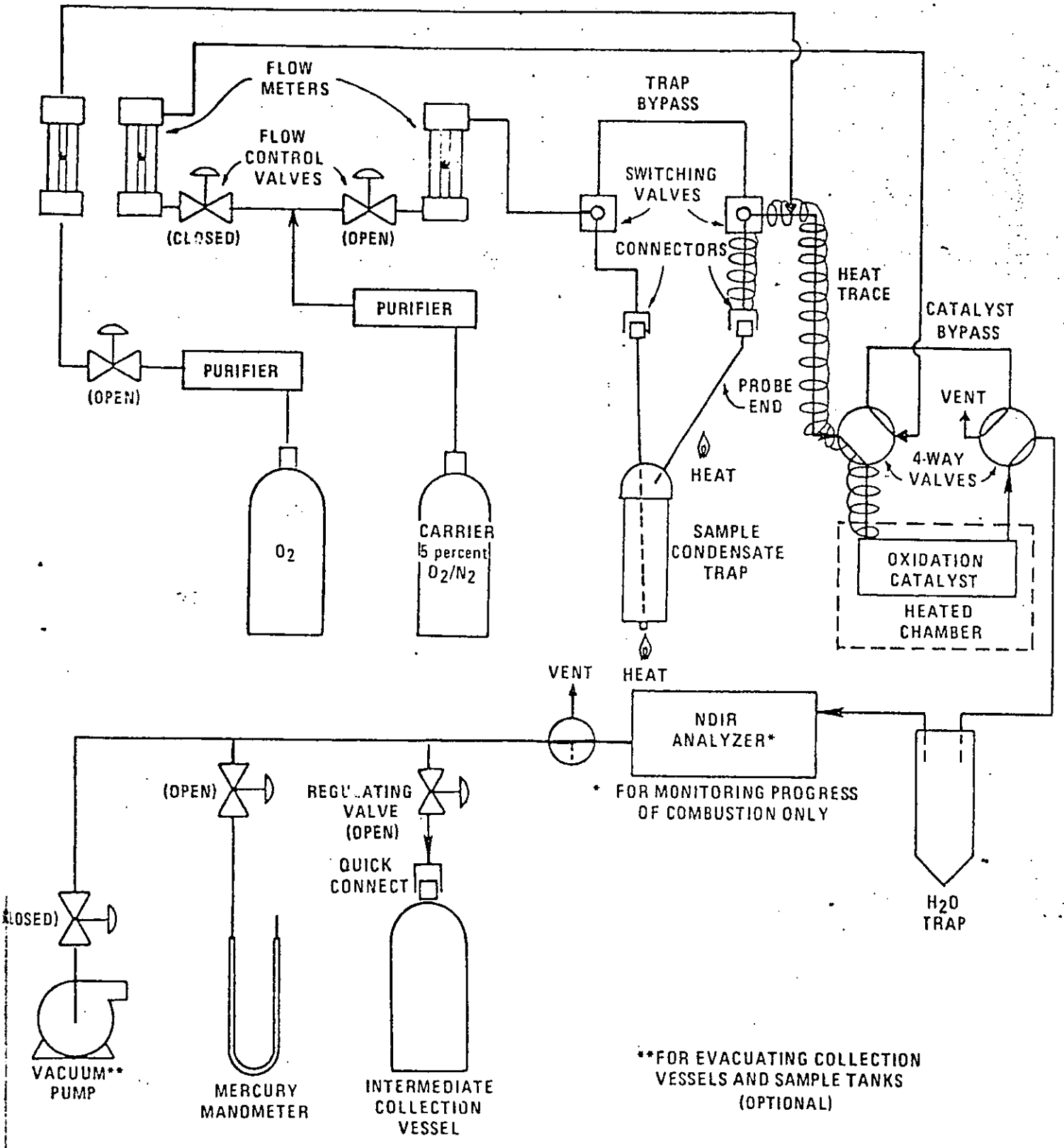

Figure 9. Condensate recovery and conditioning apparatus, collection of trap organics.

APPENDIX B

SAMPLE CALCULATIONS

1. Conversion of ppm carbon to pounds carbon per ton

Data: 922.8 ppm carbon in sample
34,172 dry std cubic feet per minute stack gas flowrate
350 tons per hour production rate

Constants: molecular weight of carbon = 12.01
standard molar gas volume = 386 $ft.^3$ (@ 70° F)

$$\frac{922.8 \text{ lb mole carbon}}{10^6 \text{ lb mole gas}} \times \frac{12.01 \text{ lb carbon}}{\text{lb mole carbon}} \times \frac{\text{lb mole gas}}{386 \text{ std ft}^3 \text{ gas}} \times \frac{34{,}172 \text{ std ft}^3 \text{ gas}}{\text{min}}$$

$$\times \frac{60 \text{ min}}{\text{hr}} = 59 \frac{\text{lb carbon}}{\text{hr}}$$

$$\frac{59 \text{ lb carbon}}{\text{hr}} \times \frac{\text{hr}}{350 \text{ tons}} = 0.17 \frac{\text{lb carbon}}{\text{ton}}$$

2. Paired T-Test

Data:

	Condition 1	Condition 2
mean, $\bar{x}$	$\bar{x}_1 = 0.17$	$\bar{x}_2 = 0.22$
std dev., S	$S_1 = 0.02$	$S_2 = 0.10$
no. of pts., n	$n_1 = 3$	$n_2 = 3$

Degrees of freedom = $(n_1 - 1) + (n_2 - 1) = (3-1) + (3-1) = 4$

For 95 percent confidence that there is no statistically significant difference, the calculated value of t must be inside the interval of - t (table) to + t (table)

t (table) = 2.776 (for four degrees of freedom)

$$s = \left[\frac{s_1^2 + s_2^2}{2}\right]^{1/2} = \left[\frac{(0.02)^2 \times (0.10)^2}{2}\right]^{1/2} = 0.072$$

$$t = \frac{x_2 - x_1}{s\left[\frac{2}{n_1}\right]^{1/2}} = \frac{0.22 - 0.17}{0.072\left[\frac{2}{3}\right]^{1/2}} = 0.85$$

The calculated t is <u>inside</u> the interval from -2.776 to + 2.776.

The hypothesis that there is no difference holds and the parameter dependency is <u>not</u> demonstrated.