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GRI-93/0337

GATC INTERIM REPORT

on

GUIDELINES FOR MEASURING EMISSIONS FROM VENTED GAS APPLIANCES
VOLUME I: SAMPLING AND ANALYSIS FUNDAMENTALS

to

Gas Appliance Technology Center

GAS RESEARCH INSTITUTE
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AUGUST 1993

by

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GRI Contracts 5086-241-1219 and 5092-281-2494

RESEARCH SUMMARY

Title: Guidelines for Measuring Emissions from Vented Gas Appliances Volume I: Sampling and Analysis Fundamentals

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Objective: To provide guidelines and recommendations for manufacturers and agencies to measure the levels of CO, NO, and NO_2 and hydrocarbons in the exhaust gas from vented gas appliances.

Report Period: Interim Report, May 1991 to August 1993

Technical Perspective: The literature offers many approaches to sampling and analysis techniques for emission measurements and reported emission values that may differ by orders of magnitude for similar appliances. One approach to resolving these discrepancies is to establish a scientifically sound, proven methodology for analysts to follow. This approach has been successful, and consistent measurements have been made by different laboratories.

This report offers suggestions for all the main elements of an emission test. Sources of error are identified and methods for minimizing their impacts are incorporated to improve the reliability of emission measurements. This report, Volume I, is divided into three major sections: appliance emissions testing, sampling and analysis, and documentation and reporting. Volume II, a series of reports, recommends methods of sampling emissions from specific types of appliances. Volume II.1 (GRI-93/0338), the first of the series on specific appliances, focuses on domestic storage water heaters.

Results: The report presents background information on several factors likely to influence emission testing results, including appliance operational history, operational sequence, measurement timing, sampling location, the actual sampling and analysis system, and ambient conditions. Key components of the sampling system and several on-line gas analyzers used for emissions testing of gas-fired appliances are also provided. The last section of the report details the proper procedures for collecting and analyzing gas samples, and documenting and reporting the results.

Technical Approach: These guidelines represent work in progress. The best available information to date was obtained from a literature survey of data on the emissions measurement process. Critical input was also obtained from experts in area of sampling methodology. Until these recommendations have been subjected to confirmation and verification of accuracy by a round-robin test program, they must be considered "interim" guidelines. Additional work is needed to quantify the effects of the influential factors.

Project Implications: This report is intended to provide technical input to manufacturors of appliances, as well as agencies responsible for defining the measurement protocols associated with regulations and standards. These users may find the information in this report helpful in establishing protocols and improving the accuracy, repeatability, and reliability of the measurements made.

GRI Project Managers
Bob Hemphill and Rod Rinholm
Appliances

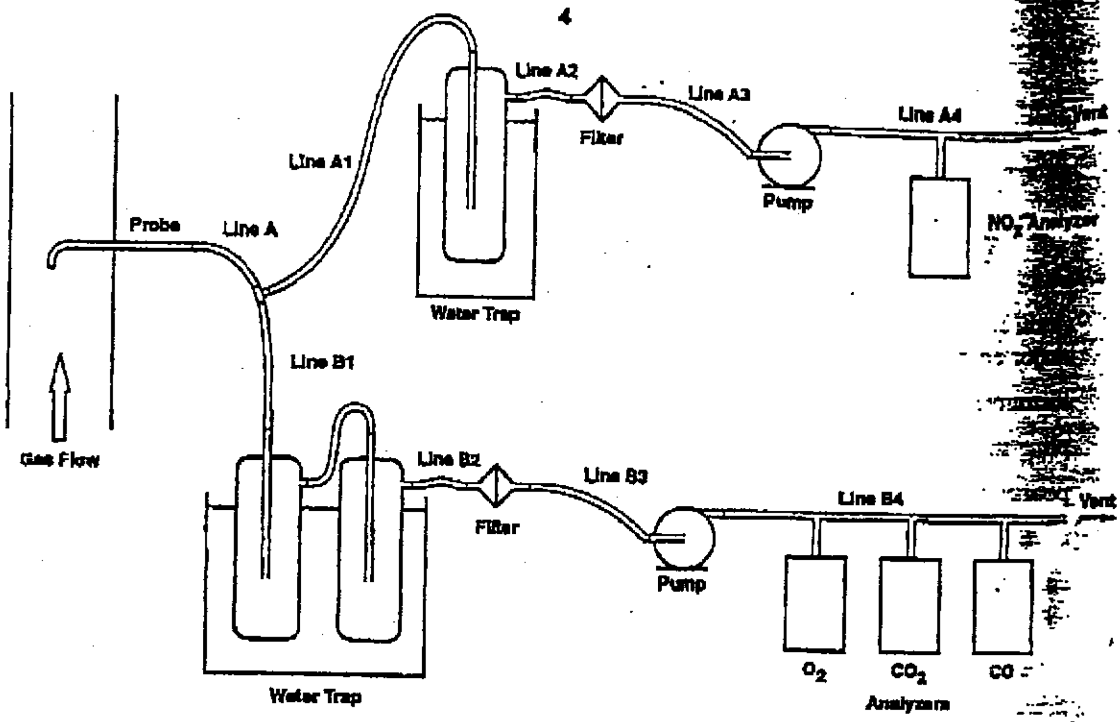

Figure I-1a. System using water traps

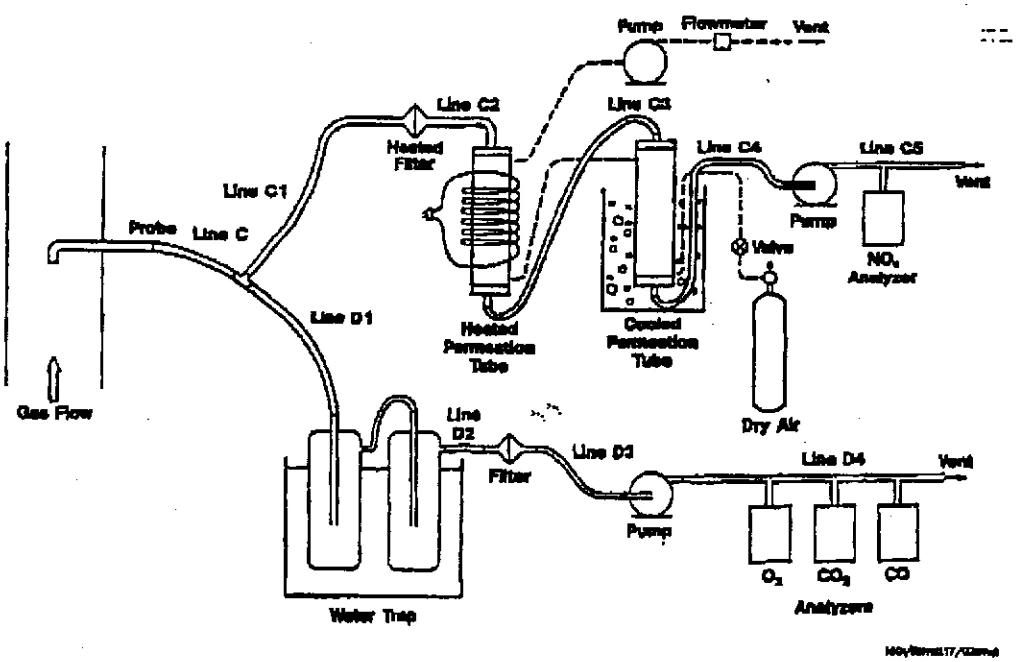

Figure I-1b. System using permeation tubes

Figure I-1. Major components of appliance sampling systems cold-trap system (Waters and DeWerth, 1979). Laboratory tests at Battelle, where the dry-ice trap catch was analyzed for nitrate and nitrite, showed 4 to 8 percent of the NO_2 in the gas sample was retained in the trap. If the NO_2 constituted 25 percent of the total NO_x, this NO_2 retention would represent about 1 to 2 percent of the total NO_x, about the accuracy of the analyzers. It is expected that refrigerated-ethanol traps would produce similar results. However, there are refrigerated condenser systems that incorporate water removal via a drain; these may have a lesser effect on NO_2 measurements.

If the entire sample required for all gas analyzers is passed through the dry-ice or refrigerated-ethanol trap, the sample line can become plugged by ice flakes, necessitating frequent cleaning to keep the lines open. An alternate is to pass only the gas sample for the NO_x analyzer through a dry-ice trap and to pass the gas for other analyzers through an ice-water trap, as shown in Figure I-1. However, even at the reduced flow rate, the A.G.A. Laboratories reports plugging by ice flakes in refrigerated ethanol traps (Waters and DeWerth, 1979).

Moisture Removal Using Permeation Tubes. An alternate procedure for removing moisture from a gas sample stream is to pass the sample through permeation tubes designed to remove water vapor, as shown in Figure I-1b. In a permeation tube the gas sample is exposed to a proprietary surface that will pass water vapor when a moisture gradient is maintained across the surface (see Figure I-3a), but will not pass the other constituents in the gas sample. When dry air is supplied to the moisture-receiving side of the permeation tube, the moisture level in gas samples can be reduced to extremely low values. The moisture content of the gas sample at the outlet of the permeation tube is determined by tube design and size, moisture content of the moisture-receiving gas, and the temperature at the outlet end of the permeation tube.

Items of concern when using a permeation tube are:

- Supplying the dry gas that will receive the moisture
- Preventing condensation at the inlet end of the permeation tube
- Cooling the outlet end of the permeation tube to enable reaching low moisture levels in the gas sample.

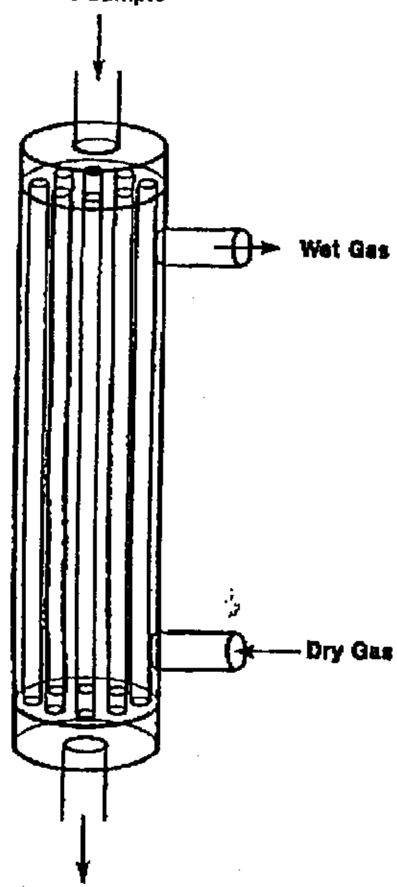

Figure I-3a. Permeation tube

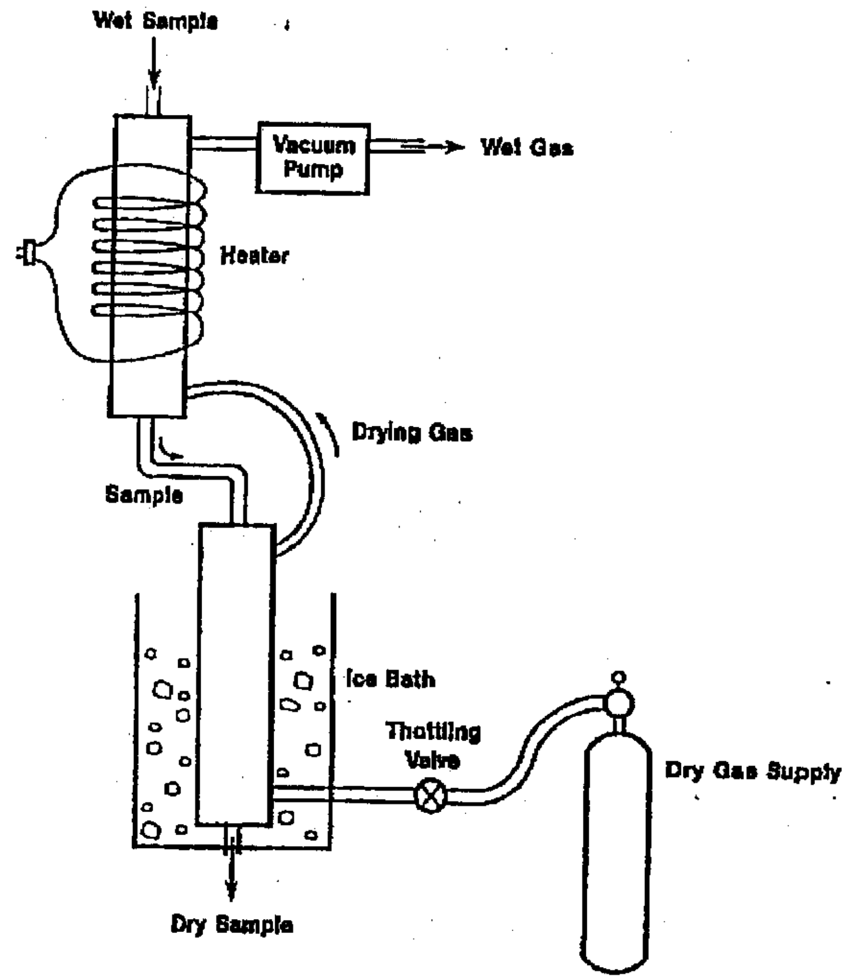

Figure I-3b. Permeation tube hookup

Figure I-3. Drying gas samples with permeation tubes

Battelle has conducted tests with a commercial permeation tube by introducing a gas sample that was saturated at 155 F (20-percent moisture) at a rate of 800 cc/min. These tests were conducted using a single 24-inch long, 50-tube permeation tube, using dry air at 0.5 atmospheres for moisture removal, and maintaining the upstream half of the permeation tube at about 170 F (using a heating tape). When the downstream end of the permeation tube was maintained at room temperature, moisture removal rates in excess of 90 percent were obtained. When the downstream end of the permeation tube was maintained at 32 F (by immersion in ice water), moisture removal rates in excess of 95 percent were obtained. Cooling the downstream end of the permeation tube to a lower temperature (e.g., by immersion in dry ice) would remove an even greater percentage of the moisture.

Because of the need to heat the upstream end of the permeation tube to prevent condensation) and to cool the downstream end (to achieve high levels of moisture reduction), the use of two separate 12-inch-long permeation tubes is recommended, as shown in Figure I-3b. This permits separating the heating and cooling functions. If two permeation tubes are used, the same drying gas can be used in both tubes by passing it in series through the downstream permeation tube and then the upstream tube.

In tests conducted at Battelle, there was no evidence that the NO_2 concentration was affected by passing the sample through the permeation tube. The permeation tube tested by Battelle had a design capacity sufficient to treat the entire gas sample required by a set of gas analyzers for CO_2, O_2, CO, and NO_x. However, it was only tested at a flow rate sufficient to supply gas to the chemiluminescent NO_x analyzer. Using a permeation tube to remove the moisture from the entire gas sample would eliminate the need for ice traps to remove moisture from gas samples for the other analyzers. However, ice traps would still be necessary if it was desired to quantify the water vapor content of the gas being sampled.

__Dilution__. Another procedure for dealing with moisture in gas samples is to dilute the sample to the point that the water vapor concentration is not troublesome. Flue gas produced by the near-stoichiometric combustion of natural gas contains as much as 19 percent water vapor by volume (12.4 percent by weight). Reducing this to water vapor levels approximately equivalent to those obtainable using traps or permeation tubes (about a 95-percent reduction) requires a dilution of approximately 20 to 1.

When a gas sample is diluted to reduce the moisture concentration, the concentrations of all of the gases are reduced. Thus, one must consider the capability of gas analyzers for analyzing the reduced concentrations of the various gases. When purchasing new gas analyzers, it is possible to obtain instruments having the proper ranges for analyzing diluted gas samples. However, analyzers that were purchased to analyze undiluted gas samples may not be useful at the reduced concentrations of diluted gas samples. This is especially true for CO_2 and CO analyzers. Chemiluminescent NO_x analyzers usually are useful over a broad range of concentrations and offer no problems analyzing at the lower concentrations.

<u>Recommendation</u>. The current recommendation for the best moisture-control technique when making certification-level measurements for NO_x or NO_2 is to either

- Install and use a permeation-tube system for removing water vapor from the gas sample for the NO_x analyzer, and to use ice-water traps to remove water vapor from the gas sample for other analyzers
- Install and use a permeation-tube system for removing water vapor from the gas sample for all analyzers.

The need for cooling the downstream end of the permeation tube would depend upon the moisture removal required, which is a function of the excess air in the sample as discussed in Appendix A, Section A.4.

When certification-level measurements are not required, such as during preliminary evaluation tests, ice-water or dry-ice traps may be used. Dry-ice traps have less impact on NO_x data, but offer more operating problems, as discussed above. Of course, if a permeation tube system has been installed for certification-level measurements, there is no reason not to use it for all measurements.