

TRIAL BURNS: METHODS PERSPECTIVE*

LARRY D. JOHNSON

Source Methods Standardization Branch, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711 (U.S.A.)

Summary

This paper addresses the status and technology of several of the key stack sampling and analysis methods required for conducting a trial burn test of a hazardous waste incinerator. The methods upon which most of the discussion is focused are EPA Method 0010, EPA Method 0030, and the new Multiple Metals Train. These methods have been shown to be reliable when used by knowledgeable and experienced personnel. They are definitely more technically sophisticated, and the equipment requires more skill and care than the simpler devices employed in the early days of emission testing. The state of the art is continuing to change rapidly, and more detailed procedures are becoming available.

Introduction

During a trial burn, a number of measurements must be made to adequately define the performance of the incinerator. In addition to measurements of the flue gas for particulate matter, HCl, and selected organics, measurements also must be made of the incinerator operating temperature, stack gas volume flow, waste feed rate, concentration of selected organics in the waste fed, and many other important parameters. Thus many continuous and manual measurement methods are used.

A relatively small, but important segment of this trial burn sampling and analysis universe is addressed in the current paper. The sampling and analysis procedures receiving the most attention until recently have been those for organic compounds. The knowledge base and availability of detailed procedures is still expanding. Recently, concerns about metals emissions have prompted further research into sampling technology in that area. Accordingly, the principal sampling and related analytical methods discussed are Method 0010, Method 0030, and the new Multiple Metals Train, under the US Resource Conservation and Recovery Act.

*Paper presented at the First Annual GCHSRC Symposium on Hazardous Waste Incineration: Current Practices and Future Directions, Lamar University, Beaumont, TX, February 23-24, 1989.

Sampling and analysis methods

The official measurement methods manual for sources regulated under the Resource Conservation and Recovery Act is usually referred to as SW-846 [1]. Method 0010 in that manual describes a sampling train often known as the Modified Method 5 Train (MM5) or Semi-VOST (Semivolatile Organic Sampling Train) Method. This sampling train is illustrated in Fig. 1. Method 0010 apparatus includes a glass- or quartz-lined probe, glass fiber or quartz filter, and a cooling section followed by a sorbent cartridge, containing XAD-2 resin. It is important that the sorbent module be placed vertically so the gas and condensed liquid flow downward through it. Condensate is collected and should be analyzed as a quality control check, even for materials efficiently stripped by the resin. Method 0010 is effective for a variety of organic compounds having boiling points exceeding 100°C and is almost always the method of choice for compounds boiling above 140°C . Compounds boiling in the 100°C to 140°C range may be sampled with Method 0010, but special care is required because of the potential for breakthrough during sampling and for volatility-related

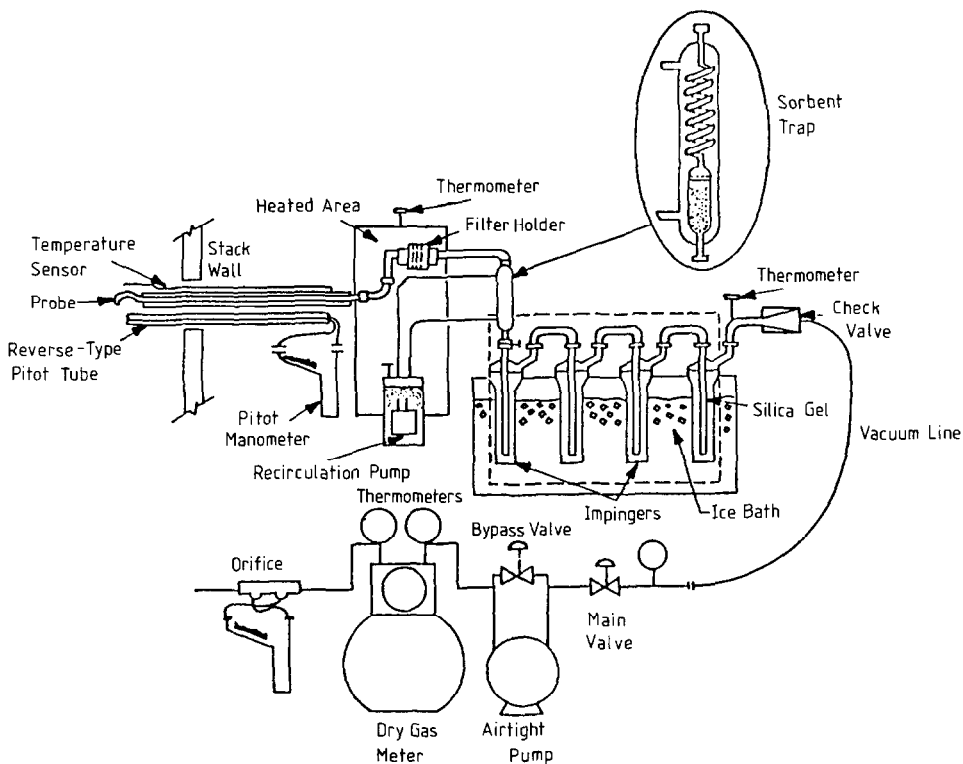


Fig. 1. Modified Method 5 train.

loss during extraction and preparation for analysis. The laboratory and field evaluation study for Method 0010 illustrated the need for adding surrogate compounds to obtain recovery efficiency information for each analysis [2].

The MM5 train has been successfully used for a number of years, and although field validation has been completed for only a few compounds, behavior of a number of other compounds can be inferred from behavior of these few along with laboratory-generated information about sorbent-compound interactions, sampling train component performance, solvent extraction efficiency, etc.

The organic compounds are recovered by solvent extraction of the train component subsamples, usually with dichloromethane. Some difficult-to-recover compounds may require special solvents such as benzene, toluene, or certain others. Incinerator flue-gas samples are usually complex enough that gas chromatography-mass spectroscopy (GC-MS) is required for its analysis. In some exceptional cases, gas chromatography with detection by techniques such as flame ionization or electron capture may be acceptable or even preferable.

For organic compounds boiling between 30°C and 100°C, the usual sampling choice is Method 0030, also known as the Volatile Organic Sampling Train (VOST) Method. This method may be readily used for many compounds with boiling points up to 130°C and, with some technical modifications and difficulty, for compounds with boiling points up to 145°C. Likewise, the train has been used for compounds with boiling points as low as -27°C, but with extraordinary precautions. Figure 2 illustrates the Method 0030 VOST setup. A glass wool filter in the probe removes particulate material, and the entire train is made of glass or inert plastic materials. The gas stream is cooled just before

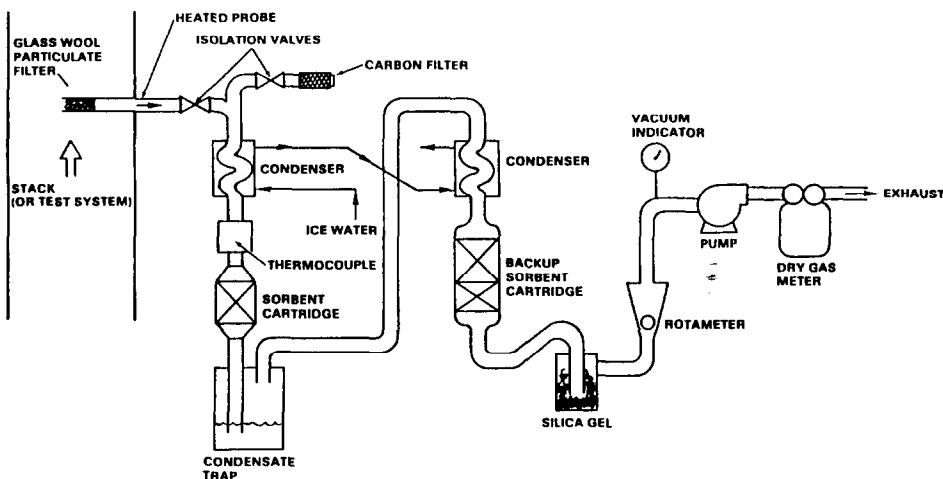


Fig. 2. Volatile organic sampling train (VOST).

reaching the first sorbent cartridge, which contains Tenax. The second sorbent tube contains Tenax backed up with charcoal.

The sampling train was designed to use six pairs of sorbent tubes sequentially, each operating for 20 min at 1 L/min. The first set of tubes is analyzed as a range finder. If an adequate amount of the compound of interest is found, then the samples in the other five sets of tubes can be analyzed in an identical manner. If the first analysis detects no compound of interest, the remaining five sets of tubes are desorbed and collected onto a single Tenax tube. Analysis of that tube gives an effective detection limit relative to stack concentrations five times as low as that for the single-set analysis.

In application of the VOST method to trial burns, it has seldom been necessary to utilize the lowest limits of detection, and it has not been unusual to operate the train at 0.5 L/min for three or four 20-min intervals. This equipment should be useful in several operation modes, as long as excessive volumes of gas are not pulled through a single tube, causing compounds with low boiling points to break through the sorbent.

The status of Method 0030 is similar to that of Method 0010, even though the former is a much more recently developed sampling train. Method 0030 has been used successfully for a number of compounds, and field precision and accuracy data has been generated for several representative compounds [3-5]. For trial burn purposes, the train is almost always used for collecting organic materials for which adequate evaluation data has been obtained. Audit gas cylinders containing a variety of these compounds have been prepared and are available from EPA [6,7].

The analytical finish for samples collected by Method 0030 is Method 5040. This procedure consists of heat desorption of the sorbent tubes, purge and trap through a water trap, and GC-MS analysis. The water trap is necessary because of high water loading in the sorbent cartridges. A new alternate method employing capillary GC column technology has been written, and is under review for inclusion in SW-847.

Although most trial burns employ one of the techniques previously discussed, unusual situations may require the use of other methods.

Plastic sampling bags are deceptively simple in appearance and very easy to misuse. Nonetheless, with proper precautions and sufficient knowledge of the bag-sample interactions for the compounds of interest, good results can be obtained with them. Sampling bags should not be chosen in preference to Method 0030 when both are applicable, but when Method 0030 is limited for some reason, such as high sample concentration or very low boiling point.

Method 0020, usually known as the Source Assessment Sampling System, has been used very little for incineration trial burns, but is available as a research tool when large amounts of sample are required.

Specialized methods for such compounds as formaldehyde require a separate sampling train. When none of the more routinely sampled principal organic

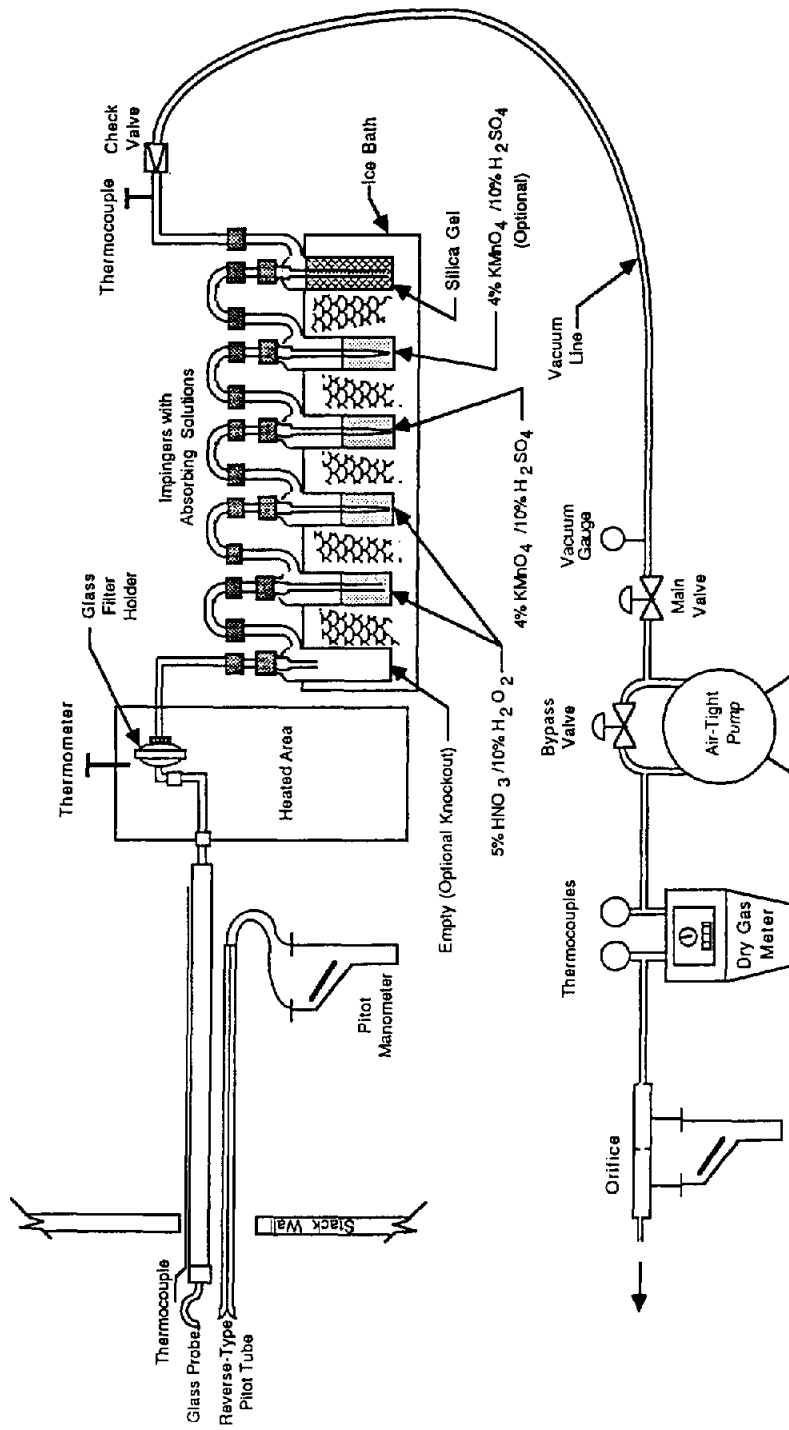


Fig. 3. Schematic of trace metals sampling train.

hazardous constituents has been appropriate for a trial burn, these specialized methods have been employed.

Recent concerns about emissions of potentially hazardous metals from incinerators and other waste combustion devices have resulted in the development and testing of a sampling train designed to collect a wide range of these metals. This train has been field tested and is being applied to hazardous waste incinerators, as well as municipal incinerators, sewage sludge incinerators, waste-firing boilers, and waste-firing industrial furnaces. Methods for the Multiple Metals Train are being written that will be reviewed and included in SW-846. Figure 3 shows the Multiple Metals Train. Like several of the other often used trains, it is a modification of the basic Method 5 train. The multiple metals train was designed to capture at least 16 metals including lead, zinc, phosphorus, chromium, copper, nickel, manganese, cadmium, selenium, arsenic, mercury, beryllium, thallium, silver, antimony, and barium. This train has been field tested at a municipal incinerator and a sewage sludge incinerator and has performed well [8-10].

The train has glass or quartz probe nozzles and probe, quartz fiber filter, and a series of impingers filled with oxidizing acid to capture any vapor-phase compounds containing metal. Other than mercury, vapor-phase metallic compounds are unusual, but must be provided for nonetheless.

Analysis of samples from the Multiple Metals Train is by inductively coupled plasma atomic emission spectroscopy or by atomic absorption spectroscopy. As in any application of these techniques, adequate digestion procedures to render the sample soluble are critical.

Hydrochloric acid emissions have usually been collected during trial burns by trapping in water or alkaline solution after a heated particulate filter. This has often been performed in conjunction with Method 5 sampling, but sometimes with a separate midget impinger train similar to that used for Method 6. Methods being drafted for inclusion in SW-846 will probably allow either train configuration, but will require a heated disc filter for reliable particulate removal. Analysis is best carried out by ion chromatography, because other methods are more interference prone.

For the reader interested in more details and further guidance, a number of sources of additional information are included in the references [11-17].

Conclusions

The methods discussed have been shown to be reliable when used by knowledgeable and experienced personnel. They are definitely more technical, and the equipment used requires more skill and care than the simpler devices employed in the early days of emissions testing, when only a few pollutants were determined. The state of the art is continuing to change rapidly, and more detailed procedures are becoming available.

Acknowledgements

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency peer review and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

References

- 1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846 Manual, 3rd ed. Document No. 955-001-0000001. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC, November 1986.
- 2 J.H. Margeson, J.E. Knoll, M.R. Midgett, D.E. Wagoner, J. Rice and J.B. Homolya, An evaluation of the semi-VOST method for determining emissions from hazardous waste incinerators, *J. Air Pollut. Control Assoc.*, 37 (9) (1987) 1067.
- 3 R.G. Fuerst, T.J. Logan, M.R. Midgett and J. Prohaska, Validation studies of the protocol for the volatile organic sampling train, *J. Air Pollut. Control Assoc.*, 37 (4) (1987) 388.
- 4 G.A. Jungclaus, P.G. Gorman, G. Vaughn, G.W. Scheil, F.J. Bergman, L.D. Johnson and D. Friedman, Development of a volatile organic sampling train (VOST), presented at Ninth Annual Research Symposium on Land Disposal, Incineration, and Treatment of Hazardous Waste, Ft. Mitchell, KY, May 1983. In Proceedings, EPA-600/9-84-015, PB84-234525, July 1985.
- 5 E.V. Robb, J.F. McGaughey, A.L. Sykes and D.E. Wagoner, Recovery of principal organic hazardous constituents and products of incomplete combustion from a volatile organic sampling train, EPA-600/7-86-025, PB86-219003, U.S. Environmental Protection Agency, July 1986.
- 6 R.K.M. Jayanty, J.A. Sokash, W.F. Gutknecht, C.E. Decker and D.J. von Lehmden, Quality assurance for principal organic hazardous constituents (POHC) measurements during hazardous waste trial burn tests, *J. Air Pollut. Control Assoc.*, 35 (2) (1985) 143.
- 7 R.K.M. Jayanty, S.W. Cooper, C.E. Decker and D.J. von Lehmden, Evaluation of parts-per-billion organic cylinder gases for use as audits during hazardous waste trial burn tests, *J. Air Pollut. Control Assoc.*, 35 (11) (1985) 1195.
- 8 N.F. Cole, D.E. Wagoner, C.R. Blackley, J.B. Homolya, T.E. Ward, T.J. Logan and M.R. Midgett, Laboratory evaluation of a test method for measuring emissions of selected toxic metals from the incineration of hazardous materials, Proceedings of the 1988 EPA/APCA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1988. APCA Publication VIP-10, Pittsburgh, PA, 1988, p. 441.
- 9 G.D. Osmond, W. Kelly, T.E. Ward, T.J. Logan and M.R. Midgett, Field test evaluation of a methodology for measuring emissions of selected toxic metals from stationary sources, Proceedings of the 1988 EPA/APCA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1988. APCA Publication VIP-10, Pittsburgh, PA, 1988, p. 497.
- 10 T.E. Ward, M.R. Midgett, G.D. Rives, N.F. Cole and D.E.L. Wagoner, Evaluation of methodology for measurement of toxic metals in incinerator stack emissions, Presented at 81st Annual Meeting of the Air Pollution Control Association, Dallas, TX, June 1988.
- 11 L.D. Johnson, Detecting waste combustion emissions, *Environ. Sci. Technol.*, 20 (1986) 223.
- 12 L.D. Johnson and R.G. Merrill, Stack sampling for organic emissions, *Toxicol. Environ. Chem.*, 6 (1983) 109.

- 13 J.C. Harris, D.J. Larsen, C.E. Rechsteiner and K.E. Thrun, Sampling and analysis methods for hazardous waste combustion, EPA-600/8-84-002, PB84-155845, February 1984.
- 14 E.M. Hansen, Protocol for the collection and analysis of volatile POHCs using VOST, EPA-600/8-84-007, PB84-170042, March 1984.
- 15 L.M. Schlickerieder, J.W. Adams and K.E. Thrun, Modified method 5 train and source assessment sampling system operators manual, EPA-600/8-85-003. PB85-169878, February 1985.
- 16 L.D. Johnson and R.H. James, Sampling and analysis of hazardous wastes in: H.M. Freeman (Ed.), Standard Handbook for Hazardous Waste Treatment and Disposal, McGraw-Hill, New York, NY, 1988.
- 17 U.S. EPA Handbook, Hazardous Waste Incinerator Guidance Series, Vol. 3: Hazardous Waste Incinerator Measurement Guidance Manual, Draft under EPA Review, 1989.