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Project Summary

Field Validation of EPA Reference Method 23

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The accuracy and precision of EPA Reference Method 23 for use in the field was evaluated at a trichloroethylene degreasing facility and an ethylene dichloride manufacturing facility. The method consists of a procedure for obtaining an integrated sample followed by gas chromatographic analysis. This study identified a number of conditions, such as sunlight and sample volume, that may affect the performance of the method in the field. Results obtained in the presence and absence of these conditions were compared. The most significant variable was the use of Tedlar (E. I. Dupont de Nemours & Company, Inc.) polyvinyl bags versus mylar polyvinyl bags as sampling containers, a choice left open in the method as originally defined.

A paired sampling technique was employed to obtain identical chemical samples from two sampling trains operating simultaneously. Certain results fell outside the range of acceptable precision, due to the use of mylar bags and to rigid sample containers that were prone to leakage. The method was modified to specify that only Tedlar bags be used for sampling; to incorporate an on-site technique for early leak detection; and to discontinue procedures for moisture removal. With these modifications, EPA Reference Method 23 was fully validated as acceptable for field use.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

On June 11, 1980, under Section III of the Clean Air Act, the U.S. Environmental Protection Agency (EPA) proposed standards limiting the emission of chlorinated hydrocarbons from solvent degreasers, after determining that these substances presented a potential risk to public health and welfare. A national emission standard was proposed which included a method for measuring chlorinated hydrocarbons, designated EPA Reference Method 23. The Quality Assurance Division of the Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina has a program to evaluate and standardize such EPA source test methods.

Method 23 for the Determination of Halogenated Organics from Stationary Sources specifies integrated bag samples of a stack gas containing one or more halogenated organic compounds, which are subjected to gas chromatographic (GC) analysis using a flame ionization detector. The method is applicable to the measurement of halogenated organics such as carbon tetrachloride, ethylene dichloride (EDC), perchloroethylene, trichloroethylene (TCE), methylene chloride, methyl chloroform, and trichlorotrifluoroethane in stack gases from specified processes. The method is not applicable to particulate matter containing organics.

The goal in this evaluation was to test the accuracy of the Reference Method 23 apparatus and procedures. In this study EDC and TCE were measured by varying the field conditions of sunlight, sample volume, storage temperature and storage time before analysis. Perhaps the most significant variable being tested concerned the use of polyvinyl bags as sampling containers. The option of using either

Tedlar or aluminized mylar bags was left open in the Method as originally written. At the high concentrations encountered in source sampling, major problems result from sample contamination due to prior use of the bags. Although in the past experience of this laboratory Tedlar bags have been able to preserve sample concentrations better than mylar, for this evaluation program we wished to establish definitive results.

A potential difficulty with Tedlar bags is their capacity to retain "memory traces" of EDC, which, under conditions of simulated sunlight, results in contamination peaks. In order to avoid this problem, new bags were used for each experiment. More positive results were reported recently, in which Tedlar bags were successfully employed under laboratory conditions for a number of halogenated hydrocarbon gas mixtures.

Paired sampling trains were used to test the utility of Tedlar and mylar bags for preserving field samples and to vary the conditions mentioned above. Results obtained under strict adherence to Method 23 were compared to those where different parameters were varied, using both Tedlar and mylar bags. The concentration figures were then verified with the use of audit standards. In addition to validation of Method 23, the most significant outcome of the investigation regarded the reliability of Tedlar bags. By contrast, mylar bags produced unacceptable results; measured concentrations were consistently lower when compared to Tedlar bag samples.

Experimental Method

The field evaluations were conducted at a metal degreasing facility using TCE and at a plant which manufacturers EDC.

Sampling variables were selected based on their likelihood of occurring under actual field conditions. Some variations were controllable, such as changes in the sampling rate or the type of bag used, whereas others were subject to chance, such as ambient temperature, sunlight exposure, or moisture condensation. The variables studied in the field were as follows:

1) Sampling and storage temperature,
2) Moisture removal,
3) Tedlar or mylar bags,
4) Sample volume,
5) Exposure to sunlight,
6) Storage time before analysis.

All gas samples were collected in pairs, using identical sampling trains. One sampling train was always operated in strict adherence to Method 23, i.e., protected from heat, shielded from sunlight during removal of the bag, sampled to obtain a full bag, and analyzed within 30 to 60 min. The second sampling train was varied in one or more of the above conditions. At each site both high level and low level concentrations were sampled and analyzed by GC with flame ionization detection.

Hydrocarbon-free nitrogen was injected into the GC system between analyses to demonstrate that no contamination remained from previous samples. The standards shown below were analyzed frequently to maintain a constant calibration.

The concentrations of the working standards were as follows:

EDC (ppm)	TCE (ppm)
1024	49.6
51.7	9.18
9.66	

The accuracy and linearity of the GC analysis used in this program were demonstrated through the use of EPA audit samples. The concentration of the audit samples were not disclosed until after they were analyzed during the field test. One audit cylinder was also sampled with the Tedlar bag and compared against the audit value to determine sampling system loses.

Possible effects of excessive moisture on source samples were determined by injecting distilled water into Tedlar bags that contained 25 ppm EDC and 50 ppm TCE and measuring the concentrations after water dispersion. Also, silica gel was evaluated as a moisture preconditioner in a 35-1 sample of EDC.

Results and Discussion

The results of the Method 23 evaluation are shown in Tables 1 and 2. Source concentrations sampled in bags were not significantly affected by variations in heat, light, and sample volume. The difference in the analytical results fell within the magnitude of precision for the Method.

When mylar sample bags were used, consistently lower values were obtained. These variations far exceeded reasonable levels of precision (±10%) for Method 23. The decay of mylar bag samples was significant, as compared to the minimal decay of Tedlar bag samples.

The values of field analysis of audit samples were compared to actual audit values, with close agreement. Results were as follows:

TCE		
Audit value	Field analysis	% diff.
14.9	15.2	+2.0
566	517	−8.7
EDC		
Audit value	Field analysis	% diff.
9.2	9.75	+6.0
438	448	+2.3

Another factor considered in this evaluation was the possible effect of moisture content in the sample. The effect of condensing moisture in the sampling train could not be demonstrated since the only

Table 1. TCE Field Evaluation Results

Test no.	Train A (ppm)	Train B (ppm)	Variations in Train B	Percent variation
1	280	272	½ Volume/sunlight exposure	−2.8
2	345	195	½ Volume/mylar bag	−43.5
3	338	192	Heat/mylar bag	−43.2
4	369	373	Heat/sunlight exposure	+1.1
5	32	33	½ Volume	+3.1
6	34	20	Mylar bag	−41.2
7	43	40	Heat	−7.0
8	51	52	Sunlight exposure	+2.0

Table 2. EDC Field Evaluation Results

Test no.	Train A (ppm)	Train B (ppm)	Variations in Train B	Percent variation
4*	1816	1821	None	+0.3
5	1764	1699	Heat/½ volume	−3.7
6	1796	1459	Mylar/½ volume	−18.8
7	1764	1538	Heat/mylar bag	−12.8
9	16.1	16.2	Heat	+0.6
10	17.08	15.48	Mylar bag	−9.4

*Test nos. 1-3 contained nondetectable levels of EDC.

source containing moisture contained non-detectable levels of EDC. However, the injection of distilled water into bag samples did not measurably affect the gas concentrations.

Silica gel, as a moisture conditioner, adsorbed a significant amount of the organics being sampled (about 95% of the EDC from a 35-1 sample). Moisture preconditioning should be achieved with a coil condenser, and only where necessary to prevent blockage of the sampling train.

It was determined that significant errors could be caused by leaks in the rigid sample containers, the probe, or bag connection. Depending on its size, a leak in the rigid container could produce results ranging from a reduction in the sample volume to loss of the entire sample. Leaks in the probe or bag connection, on the other hand, diluted the sample. An on-site procedure for early detection of leaks was devised to eliminate these problems from the sampling train.

Sample degradation over time was not determined to be a major problem for samples contained in Tedlar bags. Regression analysis of the data collected indicated that TCE samples held in Tedlar bags degrade at an average rate of approximately 1% per day whereas samples in mylar bags degrade at a rate of 2% per day.

Conclusions and Recommendations

1. EPA Reference Method 23 using Tedlar bags produced satisfactory precision; variations ranged from 0.6% to 7.06%. Mylar bags, however, yielded reduced concentrations ranging from 9% to 43% lower than the Tedlar bag counterpart. Mylar bags are not recommended for use in this method.
2. Field variations of low sample volume, heat, and sunlight exposure did not significantly affect the results when Tedlar bags were used.
3. A rigorous leak check procedure should be performed immediately before a sampling run.
4. A container that is reliable, lightweight, leak-proof, and economical should be developed for integrated sampling.
5. It is not necessary to remove moisture from samples to perform Method 23.

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The complete report, entitled "Field Validation of EPA Reference Method 23," (Order No. PB 83-214 551; Cost: $10.00, subject to change) will be available only from:
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