

**Field Evaluation of EPA Proposed Method 0040  
(Sampling and Analysis of Volatile Organic Compounds Using Tedlar® Bags)**

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## **ABSTRACT**

A field test has been performed to evaluate EPA Proposed Method 0040 (Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar® Bags), a method designed for the collection of volatile organic compounds present in a combustion source at concentrations above the range of EPA Method 0030 (VOST). Proposed Method 0040 is based on the results of laboratory studies to develop and refine a sampling train and methodology to collect and analyze volatile organic compounds present in source emissions between 100 and 1000  $\mu\text{g}/\text{m}^3$ . In the laboratory studies, a design for the sampling train was developed, the train was evaluated using dynamic spiking techniques, and a standard sampling method in SW-846 format was prepared. An analytical methodology using gas chromatography/mass spectrometry (GC/MS) was also developed to provide qualitative identification of specific compounds and quantitative results based on calibration for individual compounds.

The original design of the sampling train was modified by removing a Teflon® check valve at the Tedlar® bag inlet to resolve discrepancies in volumes measured by the train. As a result, leak-check procedures in the proposed method were simplified. A field test of the modified methodology was performed to determine and document the systematic error (bias) and random error (precision) of the method under stationary source sampling conditions. Four similar trains were operated simultaneously using a quadruplicate sampling probe, with dynamic spiking of two of the four quad trains with specific volatile organic compounds, while simultaneously sampling emissions from a coal combustion source. Analytical data were statistically evaluated according to the procedures of EPA Method 301. Fifteen of eighteen volatile organic test compounds met Method 301 acceptance criteria for performance while using the Proposed Method 0040.

## **INTRODUCTION**

A field test using the statistical experimental design outlined in EPA Method 301<sup>1</sup> to evaluate a method for sampling and analyzing high-level [i.e., parts per million (ppm) in a stationary source] volatile organic compounds from stationary source emissions using EPA Proposed Method 0040<sup>2</sup> has been completed. Proposed Method 0040 was designed to collect volatile organic compounds (VOCs) at concentrations that are above the concentration range that can be collected by EPA Method 0030<sup>3</sup> (the Volatile Organic Sampling Train, VOST).

The original sampling train used in this field study was developed by ERG staff under contract to the U. S. Environmental Protection Agency. This method for collecting and analyzing VOCs at concentrations between 100 and 1000  $\mu\text{g}/\text{m}^3$  in stationary source emissions was developed and refined in the laboratory. The laboratory development work involved the design of the sampling train, laboratory evaluation of the train using gaseous dynamic spiking techniques, and preparation of a standard sampling method in SW-846 format. The analytical portion of the method is based on gas chromatography/mass spectrometry (GC/MS) and provides qualitative identification of VOCs for characterization of Products of Incomplete Combustion (PICs) as well as quantitative emissions results based on calibration for individual compounds. Additional laboratory studies were performed to address the question of accurate

and reproducible measurement of the volume collected in the Tedlar® bag. In the original laboratory experiments, the volume of air collected by evacuating a nominal 20 liters of air from the rigid container was determined before and after the removal of the Teflon® check valve assembly located just prior to the bag inlet valve. Significant deviation from the theoretical 20 liters collected was encountered with the check valve in place. Removal of the check valve resulted in actual volumes ranging from -1.0 to 3.5 percent relative deviation from the theoretical amount. Therefore, Method 0040 was modified prior to the field test. The Teflon® check valve was replaced with a glass/Teflon® stopcock. Additional thermocouples were also added inside the rigid container to monitor the temperature of the sampled gas.

The field evaluation of the modified method was performed to determine and document the systematic error (bias) and random error (precision) of the method under stationary source sampling conditions.

## **EXPERIMENTAL APPROACH**

Proposed Method 0040 was evaluated for sampling and analysis of the compounds listed in Table 1. EPA Method 301 was used for the statistical design of the sampling strategy and for the statistical evaluation of the results obtained from dynamic spiking of two of four collocated trains. The field evaluation was conducted at a coal-fired power plant. An 800-megawatt unit with an electrostatic precipitator but no caustic scrubber was selected for testing. Since the coal contained 1% sulfur, SO<sub>2</sub> was present in the emissions, as well as particulate matter and NO<sub>x</sub>. The stack temperature was approximately 132°C (270°F).

Unit 2 at this test site had been characterized previously for VOST sampling. Several non-halogenated VOCs had been detected in the VOST samples, but at levels typically found in ambient air and 1% or less of the proposed dynamic spiking levels for Proposed Method 0040.

### **Field Sampling**

The sampling train used in the field evaluation study is shown in Figure 1. A quad probe was used with four similar sampling trains. The quad probe consists of four similar heated sampling probes that can be inserted in the stack as one unit. This configuration allows the simultaneous collection of stack gas in four similar trains, with gaseous dynamic spiking in two of the trains.

Prior to shipment to the field test site, all glass components of the sampling train were cleaned according to the procedures described in Proposed Method 0040, wrapped in aluminum foil, and segregated to prevent contamination. Tedlar® bags were cleaned and blanked according to the procedures of Proposed Method 0040; 10% of the bags were analyzed by GC/MS to verify that appropriate cleaning criteria had been met.

All Tedlar® bags and rigid containers were leak-checked prior to transport to the test site. The rigid containers were evacuated to a vacuum of approximately 25" Hg and allowed to stand for 30 minutes while a vacuum gauge was monitored. All containers were leak-free. Each container and the corresponding lid were uniquely numbered so these two components were always used as a unit. In addition, each Tedlar® bag was filled almost to capacity with clean nitrogen, sealed, and allowed to stand overnight. Each bag was visually inspected for leaks. The nitrogen in 10% of these bags was analyzed to demonstrate the absence of VOCs that were to be dynamically spiked. After leak-checks, each bag was uniquely numbered, attached to the Quick-Connect® fitting on a rigid container lid, re-evacuated, and sealed in the corresponding rigid container. Containers and bags were then transported to the test site. Dry gas meters were leak-checked and calibrated. Other preparations included leak-checking the sampling umbilicals, temperature readout calibration, and checking the operation of other associated sampling equipment.

Sampling trains were assembled in the field laboratory without Tedlar® bags and associated rigid containers. The bags in containers were transported separately to the sampling location and installed in the sampling train after the probe was positioned in a single stack port.

Each heated train component was heated to 130°C, and each sampling train was leak-checked in the field according to the simplified leak-check procedures. Samples were collected by evacuating the rigid container of the Tedlar® bag, withdrawing stack gas through the quad probe. The front end of the quad probe was positioned in the center of the stack and remained in that location during each day of testing. Traversing was not required for this method evaluation study since the true concentration of the components of the stack gas was of no interest to this program. The sampling flow rate always exceeded the dynamic spiking flow rate by at least a factor of 2 to ensure that all of the spiked VOCs were carried totally into the sampling trains.

The sampling flow rate was set to a nominal 0.33 Lpm and a sample was collected for one hour simultaneously in each of the sampling trains. At the end of one hour, the rigid container was isolated from the rest of the train and the trains were leak-checked. Each rigid container was opened to visually inspect the Tedlar® bag to determine if it had been filled to approximately 80% of capacity, indicating the sample had been collected. Since no condensate was observed in any of the trains during any of the sampling runs, no condensate was collected. Samples were shipped daily by ground transport to the laboratory to ensure that the Tedlar® bag samples remained above 0°C and that the samples could be analyzed within 72 hours of sampling. Two quad runs were scheduled and performed each day of sampling to ensure that laboratory analytical capacity would not be exceeded. On three of the four days of sampling, the rigid containers were heated to maintain the temperature above 0°C.

In addition to the eleven quad sampling runs performed for method evaluation, four field blanks (one for each of the sampling trains) were taken. The field blanks were transported and analyzed with the stack gas samples. Two Tedlar® bags, filled with high purity nitrogen and labeled as laboratory blanks, were left in the laboratory under the same storage conditions as the field samples.

### **Dynamic Spiking Procedures**

The compounds dynamically spiked in the field (Table 1) were contained in a commercially prepared and certified compressed gas cylinder. The concentration of each VOC in the cylinder was verified by GC/MS before field use. During each quad sampling run, spiking gas was continuously introduced into two of the four sampling trains through two fine metering valves. The flow rate of the spiking gas into the sampling trains was nominally 80 mL/min to introduce approximately 20 ppm of each VOC over the sampling period of one hour. Each gas metering system was equilibrated for approximately 30 minutes before the start of sampling. The gaseous spike was introduced into each train at a point immediately after the probe and before the filter and condenser. The regulator and tubing leading to each sampling train were maintained at a temperature of 130-140°C.

### **ANALYSIS**

Gaseous samples in Tedlar® bags were analyzed by GC/MS, using an injection loop to inject a constant volume of sample into the GC. Analytes were cryofocused and then introduced onto the head of a fused-silica DB-1 (0.32 mm ID, 60 m length, 1 µ film thickness) capillary column.

Quantitative calculations were based on the injection of a 5 mL sample from the Tedlar® bag, at a nominal concentration of 200-600 ng on column on the basis of field-spiked values. Appropriate dilutions from the spiking cylinder were used to prepare calibration standards. All standards were prepared in Tedlar® bags and stored at ambient temperatures. A 5-mL gaseous aliquot of the internal standards (bromochloromethane, 1-bromo-4-fluorobenzene, chlorobenzene-d<sub>3</sub>, and 1,4-difluorobenzene) was cryofocused along with each sample prior to introduction onto the capillary column. The response factors were verified daily. Tedlar® bag field samples were stored at laboratory ambient temperature and analyzed within 72 hours of sampling to meet the method-specified hold time. All field samples were analyzed and the results were used in the statistical calculations.

Repeated analysis of several samples verified the stability of the VOCs over time in a source matrix. Percent change from the original analysis was determined by comparing area counts of the subsequent analyses to the original analysis. The percent difference for every compound on each of the

subsequent analysis days is the same within experimental error, indicating that the compounds were stable in the Tedlar® bags for at least 10 days following the initial analysis.

## RESULTS AND DISCUSSION

The theoretical concentration of each analyte in the spiked trains was calculated by determining the amount of dilution of the volume of gas spiked into each Tedlar® bag. The volume of spiked gas was calculated by multiplying the average of the spiking gas flow rate (values from pre- and post-sample collection) in mL/min by the length of the spiking period (nominally 60 min). This value was then divided into the sum of the dry gas meter volume and the spiking volume to determine a dilution factor. This dilution factor (nominally a value of 5) was then divided into the concentration of each analyte contained in the spiking gas cylinder (nominally 100 ppm).

The percent recovery for each VOC was calculated by dividing the analyzed value by the theoretical value and multiplying by 100. Recoveries for each quad run are shown in Table 1, with mean and standard deviation. Using a criterion of acceptable recoveries from 50-150%, all compounds except bromomethane fell in the acceptable range. Using a precision criterion of percent relative standard deviation less than 50, all compounds except 1,3-butadiene and dichlorodifluoromethane performed successfully.

The results of the Method 301 statistical calculations are shown in Table 2. Using the acceptance criteria of EPA Method 301, all the compounds met acceptance criteria except bromomethane, 1,3-butadiene, and dichlorodifluoromethane.

## CONCLUSIONS

The Proposed Method 0040 sampling train performed successfully in its modified configuration. Modification of the method leak-check procedures was successful. These modifications should therefore be made a part of the Method. The total volume of sample collected in the Tedlar® bags of the dynamically-spiked sampling trains was determined by summing the volume read by the dry gas meter and the volume of spike gas added. This measurement approach was confirmed by calculating the percent recovery of deuterated analogs of several of the VOCs that were injected as a liquid spike into the bags during the collection of the samples.

## REFERENCES

1. EPA Method 301. Protocol for the Field Validation of Emission Concentrations from Stationary Sources. U. S. Environmental Protection Agency. EPA 450/4-90-0015. April, 1991.
2. Proposed Third Update to SW-846 Manual, Published for Public Comment, Federal Register July, 1995.
3. "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, D.C. November, 1986.

## DISCLAIMER

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**Table 1. Summary of spiked compound recoveries.**

Compound	Mean <sup>a</sup>	%RSD
1,1,1-Trichloroethane	92.9	23.9
1,1,2-Trichloroethane	94.5	21.4
1,1-Dichloroethane	93.7	21.8
1,1-Dichloroethene	92.8	24.1
2,2,4-Trimethylpentane	105	22.8
Allyl chloride	82.0	25.6
Benzene	98.0	24.9
Bromomethane	168	31.6
1,3-Butadiene	52.9	56.9
Carbon tetrachloride	101	21.6
Chloromethane	123	22.9
Dichlorodifluoromethane	51.1	60.9
<i>n</i> -Hexane	94.0	20.5
Methylene chloride	93.4	25.8
Toluene	84.7	29.8
Trichlorofluoromethane	121	24.4
Vinyl chloride	109	25.3
Vinyl bromide	112	26.4

<sup>a</sup> Average of 22 samples

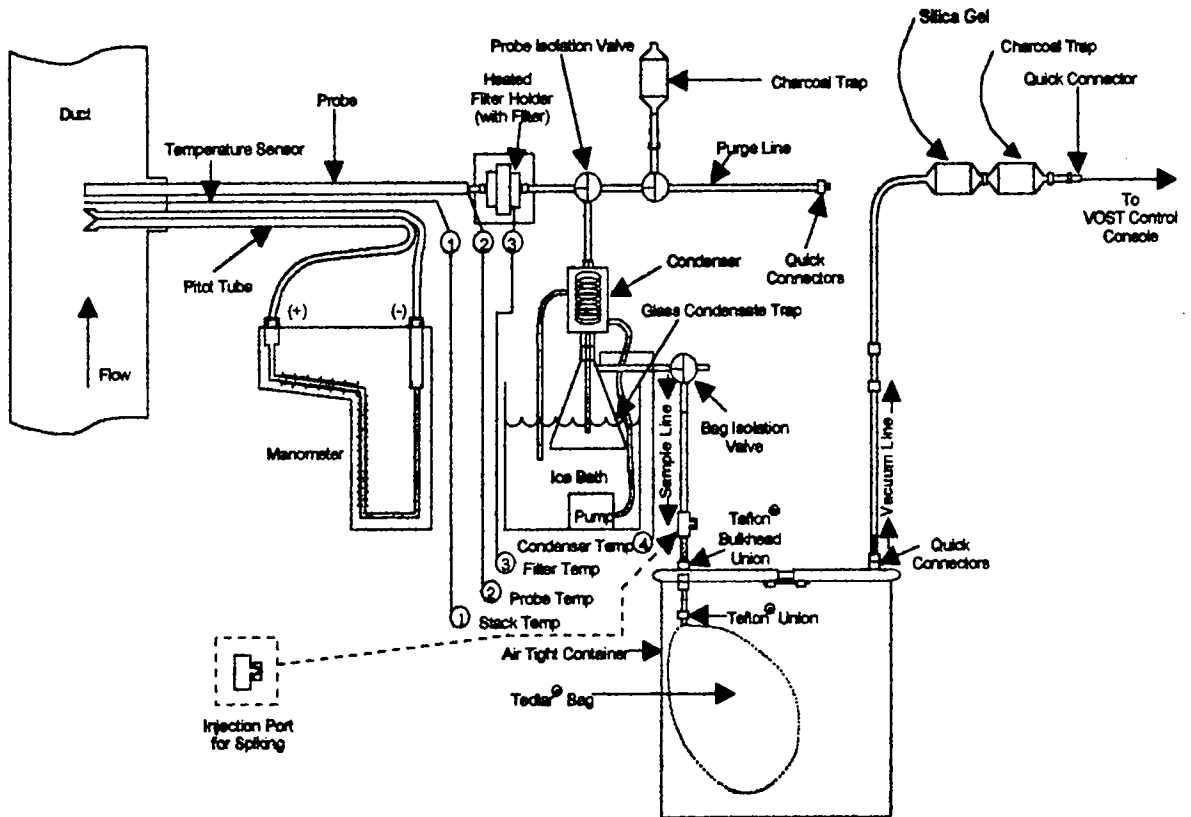
**Table 2. Summary of Method 301 statistical calculations.**

Compound	Bias Significant ?	Correction Factor	Precision, %RSD
1,1,1-Trichloroethane	No	--- <sup>a</sup>	15.0
1,1,2-Trichloroethane	No	--- <sup>a</sup>	16.6
1,1-Dichloroethane	Yes	1.12	15.0
1,1-Dichloroethene	Yes	1.14	17.1
2,2,4-Trimethylpentane	No	--- <sup>a</sup>	13.2
Allyl chloride	Yes	1.29	18.0
Benzene	No	--- <sup>a</sup>	14.9
Bromomethane	Yes	0.66 <sup>b</sup>	17.1
1,3-Butadiene	Yes	1.81 <sup>b</sup>	41.5
Carbon tetrachloride	No	--- <sup>a</sup>	14.6
Chloromethane	Yes	0.83	23.3
Dichlorodifluoromethane	Yes	2.14 <sup>b</sup>	70.8 <sup>c</sup>
<i>n</i> -Hexane	Yes	1.11	13.9
Methylene chloride	Yes	1.12	23.2
Toluene	Yes	1.22	29.8
Trichlorofluoromethane	Yes	0.84	14.0
Vinyl chloride	No	--- <sup>a</sup>	17.6
Vinyl bromide	No	--- <sup>a</sup>	20.6

<sup>a</sup>Calculation of a Correction Factor is not required if bias is not significant.

<sup>b</sup>Correction factor outside of Method 301 criteria for an acceptable method.

<sup>c</sup>%RSD outside of Method 301 criteria for an acceptable method.



**Figure 1. Proposed Method 0040 train configuration.**

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