



## Project Summary

# Field Evaluation of EPA Method 0040 (Volatiles Using Bags)

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A field test was completed to evaluate EPA Method 0040 (Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar® Bags), a method designed to collect volatile organic compounds at concentrations that are above the range of EPA Method 0030 (VOST). Method 0040 is based on the successful results of laboratory studies to develop and refine a sampling train and methodology to collect and analyze volatile organic compounds existing in source emissions between 100 and 1000  $\mu\text{g}/\text{m}^3$ . After demonstrating satisfactory recovery of target compounds in the laboratory, a field evaluation of this method 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 (quad probe). The field evaluation was accomplished by dynamically spiking the sampling trains with specific compounds while simultaneously sampling emissions from a coal combustion source. Analytical data were statistically evaluated according to the procedures of EPA Method 301 (Field Validation of Pollutant Measurement Methods from Various Waste Media). Fifteen of eighteen volatile organic test compounds met Method 301 acceptance criteria for performance of Method 0040.

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*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

A field test was performed to evaluate a method for sampling and analyzing volatile organic compounds from stationary source emissions using EPA Method 0040 (Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar® Bags). Method 0040<sup>1</sup> was designed to collect volatile organic compounds at concentrations between 100 and 1000  $\mu\text{g}/\text{m}^3$  (above the range of EPA Method 0030 [VOST]). The field study was performed using an experimental design for the sampling strategy that follows the statistical approach outlined in EPA Method 301, Field Validation of Pollutant Measurement Methods from Various Waste Media.<sup>2</sup>

The original sampling train used in this study was developed by Radian Corporation, under contract to the U.S. Environmental Protection Agency (Contract No. 68-D1-0010, Work Assignment No. 57). The laboratory development work involved the design of the sampling train, laboratory evaluation of the train using dynamic spiking, and preparation of a standard sampling method in the SW-846 format. The analytical portion of the method was based on gas chromatography/mass spectrometry (GC/MS) to provide qualitative identification of specific compounds and quantitative emissions results based on calibration for individual compounds. A let-

ter report submitted to EPA on June 30, 1994, discussed the results of the laboratory study and provided suggestions for modification of the train for improved operation.

The most important issue raised by the subsequent laboratory studies of the Proposed Method was the correct measurement of the volume collected in the Tedlar® bag and confirmation of this value. In the final laboratory study (Contract 68-D4-0022, Work Assignment 10), 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 between theoretical and observed volume was encountered with the check valve in place. Removal of the check valve resulted in experimentally determined volumes ranging from -1.0 to 3.5% relative standard deviation. Based on these results, the design of the sampling train was changed before the field test, and the Teflon® check valve was replaced with a glass/Teflon® stopcock. An additional thermocouple was also added in the rigid container to monitor the temperature of the sampled gas.

After testing the modified sampling train and demonstrating satisfactory recovery of target compounds in the laboratory, a field evaluation of this revised method was performed to determine and document the systematic error (bias) and random error (precision) of the method under stationary source sampling conditions. Four (4) similar trains were operated simultaneously using a quadruplicate sampling probe (quad probe). The field evaluation was accomplished by dynamically spiking the sampling trains with specific compounds from a certified compressed gas cylinder while simultaneously sampling emissions from a coal combustion source.

## Experimental Approach

The primary objective of this program was to evaluate EPA Method 0040, incorporating the modifications approved by the Work Assignment Manager, under actual field conditions following an experimental design based on EPA's Method 301. Method 0040 was evaluated for sampling and analysis of 18 volatile organic compounds selected from those listed in the Clean Air Act Amendments of 1990 that had previously been tested in the field using the VOST methodology. Additional volatile organic compounds that did not meet Method 301 acceptance criteria in the VOST methodology were also included in the field test of Method 0040. 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. This section describes the experimental approach to accomplish this field test and includes the sampling site description, the sampling approach, the analyte spiking techniques, and analytical procedures.

## Test Site Description

The field evaluation was conducted at a coal-fired power plant with four boiler units equipped with electrostatic precipitators but no caustic scrubbers. This site was selected because the source produced the primary components of a combustion matrix (moisture, sulfur dioxide, oxides of nitrogen and particulates) without any of the targeted volatile organic compounds to interfere with the interpretation of spiked compound concentrations. The stack temperature was measured during a previous presurvey and found to be approximately 132°C (270°F). Sampling was performed at Unit 2 because prior sampling efforts performed by ERG had already characterized Unit 2. Unit 2 also has a large sampling platform and easy access to sampling ports, and the plant personnel provided support and cooperation for the test series.

## Sampling

Sampling procedures were consistent with EPA Method 0040. The sampling train (Figure 1) was modified by employing a quad probe system which contained four similar heated sampling probes that could be inserted into the stack as one unit. This multiple probe 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 sampling site, all glass components of the sampling train were cleaned, wrapped in aluminum foil, and segregated to prevent contamination. Tedlar® bags were cleaned and blanked according to the procedures of EPA Method 0040 with 10% of the bags analyzed by GC/MS to verify that appropriate cleaning criteria were met. All Tedlar® bags and rigid containers were leak checked prior to transport to the test site.

The rigid containers for the Tedlar® bags were evacuated to approximately 25 inches of mercury (in. Hg) and allowed to stand for 30 minutes while monitoring a vacuum gauge. All containers were found to be leak free. Each container with corresponding lid was numbered so these two components were always used as a unit. In addition each bag was filled almost to capacity with clean nitrogen, sealed and

allowed to stand overnight. A visual inspection of each bag indicated that they were leak free. Each bag was then numbered, attached to the inlet quick-connect fitting on a rigid container lid, re-evacuated and sealed in the rigid container. The containers and bags were then ready to be transported to the test site.

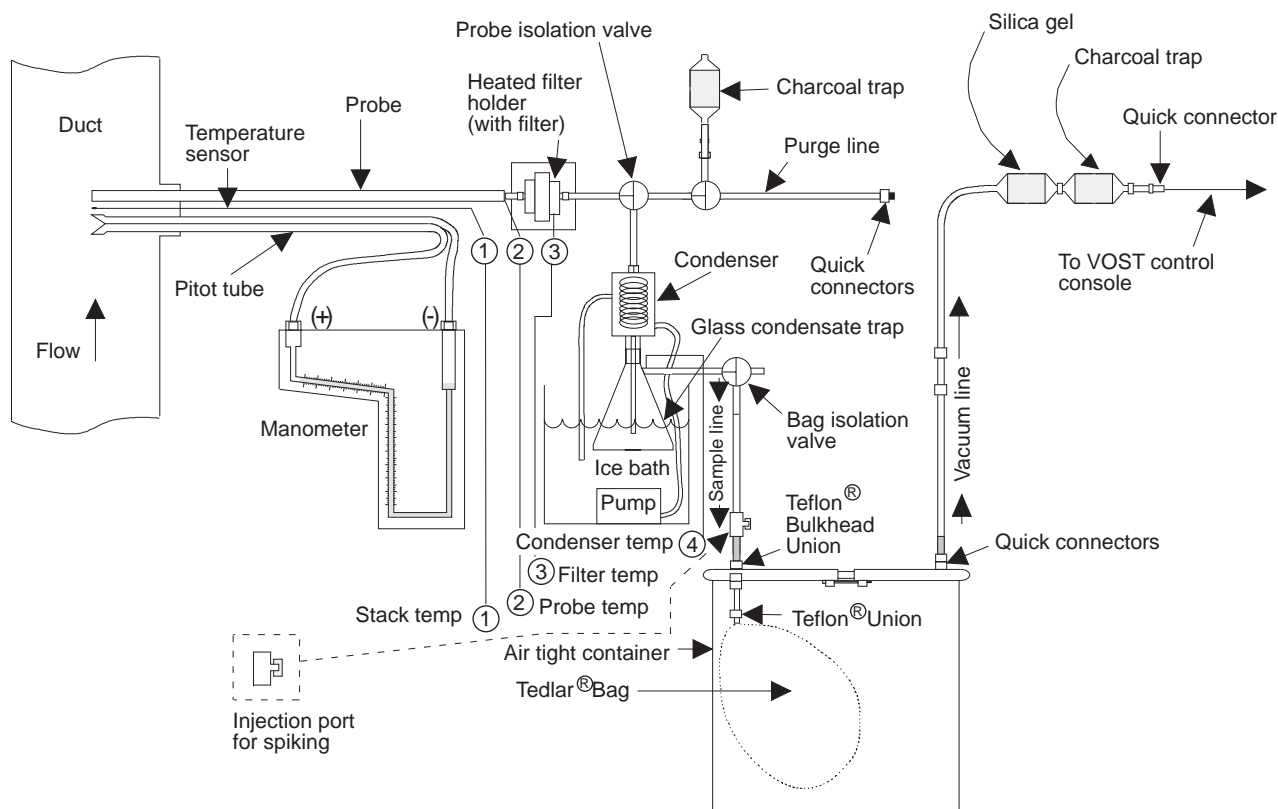
Dry gas meters were leak checked and calibrated prior to transport to the field site and the results of the calibrations kept in dedicated laboratory notebooks. The remaining preparation included leak checking the sampling umbilicals, temperature readout calibration, and functional checks of other associated sampling equipment.

Sampling trains were assembled in the field laboratory, without Tedlar® bags or their rigid containers. Tedlar® bags in rigid containers were transported separately to the sampling location and positioned in the sampling train after the probe was inserted in the stack port. Sampling was started after all sampling trains were completely assembled and leak checked.

Each heated train component was brought to 130°C and each train was leak checked in the field by following the procedures outlined in Method 0040. Each probe of the quad assembly was capped, and the train (excluding the bag and rigid container) was evacuated to 10 in. Hg. Any leaks were located and repaired until all trains were found to be leak free. Each rigid container was then inspected to verify that the previously evacuated bags were still leak free.

Sampling was performed by evacuating the rigid container containing the Tedlar® bag. Stack gas was withdrawn from a single port in the stack through the four (4) probe quad assembly and directed to four similar sampling trains as shown in Figure 1. 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. The true concentration of the components of the stack was of no interest to this program and, therefore, traversing was not required. The sampling flow rate always exceeded the spiking rate by at least a factor of 2 to ensure that all of the spiked analytes were carried totally into the sampling train. Two of the trains of each quad run were spiked and two were unspiked. Eleven (11) quad runs were performed. On three of the four days of sampling, the rigid containers were heated to maintain the temperature above 0°C.

The sampling flow rate was set to a nominal 0.33 L/min and sample was collected for one hour simultaneously in each



**Figure 1.** Schematic of the Method 0040 sampling train.

train. At the end of each one-hour sampling run, the rigid container was isolated from the rest of the train and then 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 that sample had been collected. No condensate was observed in any of the trains during any of the sampling runs, so no condensate samples were collected. However, each condensate flask was rinsed with organic-free water after each run. Sample transport to the laboratory was scheduled for every day of sample collection to ensure that the Tedlar® bag samples remained above 0°C. After the completion of sample recovery, the next quad run was performed as discussed above.

In addition to the eleven quad samples taken for method evaluation, four field blanks, one for each of the trains, were taken following the procedures of Method 0040. These field blank samples were transported and analyzed with the stack gas samples. Two Tedlar® bags were filled with high purity nitrogen, labeled as laboratory blanks, and left in the laboratory

under the same storage conditions as the field samples. Samples were transported daily from the test site to the laboratory.

### **Dynamic Spiking**

To evaluate the complete sampling and analytical methodology for Method 0040, it was necessary to perform dynamic spiking in the field. To ensure the performance of the spiking equipment and the sampling techniques under controlled conditions, Method 0040 trains were set up in the laboratory and dynamically spiked using the proposed apparatus prior to field deployment. In the field evaluation test, the same certified standard cylinder and the same dynamic spiking procedures were used.

The compounds dynamically spiked into two of the Method 0040 sampling trains were contained in a compressed gas cylinder. The cylinder was commercially prepared at a concentration of 100 ppm for each analyte, as verified by GC/MS. A second similar compressed gas cylinder was purchased and verified to be available as a backup. During each quad sampling run, spiking gas was continuously introduced into two of the four Method 0040 trains through two fine-metering

valves. The flow rate of spiking gas into each train was nominally 80 mL/min, resulting in the introduction of approximately 20 ppm of each compound into the sampling train over a sampling period of one hour while stack gas was collected at 0.33 liter/min (i.e., nominal 5 liters of spiking gas with 20 liters of stack gas in a 30-liter Tedlar® bag). 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 train were maintained at a temperature of 130 - 140°C (266 - 284°F).

A three-way glass and Teflon® valve (glass tee) was used to introduce the spiking gas into the trains. During the conditioning period and between each of the runs, the valve was used to by-pass the train and allow gas to exit through a charcoal trap to the ambient air. The valve position was then changed to deliver the spiking gas into the train for a specified period of time. The sequence of events for each spiking run was as follows:

- Leak check each train;

- Adjust spiking gas flow rate to a nominal 80 mL/min with the fine metering valve;
- Measure the flow rate of the spiking gas at each of the two trains designated for spiking using a bubble flow meter. Make the measurement in triplicate and average the values;
- Record the initial meter reading, start all four trains simultaneously, connect the rigid containers to the meter box and the sampling train, adjust the sampling flow to a flow rate of 0.333 L/min, and sample for one hour;
- Immediately after the start of the sampling run, divert the spiking gas into the two spiked trains by moving the valve and activate a stop watch;
- Spike the deuterated analogs if appropriate;
- After a one-hour sampling period, move valve back, record the elapsed time from the stop watch, stop the sampling pump and isolate the rigid container/Tedlar® bag from the train, and measure the spiking flow in triplicate and average;
- Perform a post-leak check on all trains; and
- Recover train: Collect any condensate into a 40 mL vial and label all recovered train components.

Prior to the field test, the spiking gas flow rate to be delivered to each train was calculated to be a nominal 80 mL/min to provide a nominal concentration of 20 ppm of each compound in the bag (approximately a 1:5 dilution of a 100 ppm cylinder spike gas). The analysis of a 5 mL aliquot of each sample with the analytes at a concentration of 20 ppm provided results in the range of the GC/MS calibration curve.

Selected quad trains were also spiked with isotopically labeled (deuterated) compounds as field spike samples. Benzene- $d_6$ , hexane- $d_{14}$ , and 2,2,4-trimethylpentane- $d_{18}$  were spiked into the Tedlar® bags. A 10  $\mu$ L amount of a methanol solution containing these compounds was spiked through an injection tee at the point where the stack gas enters the Tedlar® bag. These isotopically labeled field spikes were used to verify the volume of gas collected in the Tedlar® bags.

## Analysis

Gaseous samples in Tedlar® bags were analyzed by GC/MS, using an injection

loop to introduce a constant volume of sample into the GC. Analytes were cryofocused and then introduced onto the head of the analytical column. Analysis was performed using a fused silica capillary column, DB-1, under analytical conditions following the guidelines of EPA Method 8260.<sup>3</sup> Electron ionization (EI) mass spectrometry was used.

Calculations of compound concentrations were based on the injection of a 5 mL sample from the Tedlar® bag, a nominal concentration range 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. The initial five-point calibration for the GC/MS analysis was performed over the range of approximately 20-1000 ng for each compound of interest. All standards were prepared in Tedlar® bags and stored at ambient temperature. Daily verification of the response factors was performed following the guidelines in Draft Method 5041.<sup>4</sup>

Tedlar® bag samples were stored at laboratory ambient temperature and analyzed within 72 hours of sampling to meet the method hold time requirements. A 5 mL gaseous aliquot of the internal standards (bromochloromethane, 1-bromo-4-fluorobenzene, chlorobenzene- $d_5$ , and 1,4-difluorobenzene) was cryofocused along with each sample prior to introduction onto the GC column.

Six complete and valid quad runs (24 Tedlar® bags) are required to satisfy the requirements of EPA Method 301, the field validation protocol. Eleven quad sampling runs were collected to provide additional samples in case of loss or breakage. All samples were analyzed and results are reported and used in the statistical calculations.

## Results and Discussion

All samples were analyzed within the 72-hour hold time specified in Method 0040. The GC/MS system was calibrated using the same compressed gas standard used for spiking in the field. The concentration of each of the compounds in the cylinder was a nominal 100 ppm. Dilutions of this 100 ppm standard were made in Tedlar® bags covering the range of 5 ppm to 100 ppm (or approximately 20 ng to 1000 ng on column). The expected concentration of each analyte in the bag samples was a nominal 20 ppm. Therefore, a five mL sample aliquot from each bag sample used for analysis was expected to provide 200-600 ng on column depending on the specific compound. All analytical results were presented as ppm.

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 get 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). No target analytes were detected in the unspiked trains.

The percent recovery of each compound for each spiked train was calculated by dividing the analyzed value by the theoretical value and multiplying by 100. Using the criterion of 50 to 150% as acceptable recovery, all compounds except bromomethane fell within this range. Using the precision criterion (%RSD less than 50), all compounds except dichlorodifluoromethane performed successfully. Dichlorodifluoromethane and 1,3-butadiene exhibited recoveries that were generally low and variable while bromomethane exhibited a high recovery with an acceptable precision. The recoveries of bromomethane for the initial runs were in the range of 200-250% showing a definite decreasing trend down to approximately 90% by Runs 10 and 11.

Using EPA Method 301 acceptance criteria of precision  $\leq 50\%$  relative standard deviation with a correction factor between 0.70 and 1.30, the following compounds met the criteria for acceptability: 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1-dichloroethane, 1,1-dichloroethene, 2,2,4-trimethylpentane, allyl chloride, benzene, carbon tetrachloride, chloromethane, *n*-hexane, methylene chloride, toluene, trichlorofluoromethane, vinyl chloride, and vinyl bromide. The three compounds that did not meet Method 301 acceptance criteria were bromomethane, 1,3-butadiene, and dichlorodifluoromethane.

## Conclusions and Recommendations

Based on the results of the sampling and analysis of the samples collected using Method 0040 and the protocol provided in EPA Method 301, the following conclusions are drawn:

- Acceptable method precision (less than 50% relative standard deviation) was observed for all compounds tested except dichlorodifluoromethane.



- The accuracy or bias of the method as measured by the recovery of the spiked compounds relative to the theoretical amount spiked was found not to be significantly different for seven compounds (1,1,1 trichloroethane, 1,1,2- trichloroethane, 2,2,4-trimethylpentane, benzene, carbon tetrachloride, vinyl bromide and vinyl chloride). These compounds, therefore, do not require a correction factor and the method is acceptable for the determination of these compounds from stationary sources.
- The bias of the method for eight compounds was found to be significantly different from zero (1,1-dichloroethane, 1,1-dichloroethene, allyl chloride, chloromethane, hexane, methylene chloride, toluene and trichlorofluoromethane). However, each bias could be corrected by applying a correction factor to the result. Correction factors between 0.70 and 1.30 are acceptable following EPA 301 criteria. Using the appropriate correction factor the method is acceptable for these compounds.
- The bias of the method for three compounds (bromomethane, 1,3-

butadiene and dichlorodifluoromethane) was found to be significantly different from zero and could not be corrected through the use of a correction factor that was within the acceptable range of 0.70 to 1.30. Therefore, the method is not acceptable for these compounds.

- The total volume of sample collected in the Tedlar® bags for the dynamically spiked trains was determined by summing the dry gas meter volume and the volume of spike gas added. This approach was confirmed by calculating the percent recovery of the deuterated analogues of several of the target compounds that were injected as a liquid spike during the collection of the samples.
- The fundamentals of Method 0040 were acceptable.

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## References

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2. Method 301, "Field Evaluation of Pollutant Measurement Methods from Various Waste Media," *Federal Register*, Volume 57, Number 250, December 29, 1992, pp 61998-62002.
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*The complete report, entitled "Field Evaluation of EPA Method 0040 (Volatiles Using Bags)," (Order No. PB98-133085, Cost: \$28.00, subject to change) will be available only from*

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