



Project Summary

VOST Charcoal Specification Study

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The volatile organic sampling train (VOST) methodology incorporates SW-846 sampling Method 0030 and SW-846 analytical Method 5040 or 5041. VOST is currently one of the leading methodologies available for the sampling and analysis of volatile principal organic hazardous constituents and products of incomplete combustion from stationary sources at very low levels. However, revisions to the original method are necessary to maintain VOST as a viable regulatory tool. Method 0030 states that the VOST sampling tube set must consist of a front tube containing Tenax® (a 2,6-diphenylene oxide polymer) and a rear tube containing sequential bed of Tenax® and SKC Lot 104 petroleum-based charcoal "or equivalent." However, the method does not identify a specific equivalent, nor does the method supply the performance specifications that would allow determination of an equivalent. Lot 104 petroleum-based charcoal is no longer commercially available and has not been available for several years. Laboratories are presently using a wide range of substitutes, usually coconut-based charcoal, and there is a wide range of performance from batch to batch of charcoal in one laboratory and from laboratory to laboratory. To provide performance specifications and identify a replacement for SKC Lot 104 charcoal, a VOST charcoal specification study was initiated. The following carbon-based candidate sorbents were considered: Tenax-GR (a graphitized Tenax); a Petroleum-based Charcoal;

Amborsorb® XE-340 (hydrophobic carbonized resin bead); Anasorb® 747 (beaded active carbon with very regular pore size); Carbosieve® S-III (carbon molecular sieve); and a Beaded Activated Charcoal (BAC) with a very regular pore size.

The results indicated that Tenax-GR showed significantly poorer performance than the other candidates in preliminary experimental results. Amborsorb did not retain the gaseous volatile organic compounds tested as well as the others, and recovery of vinyl chloride was very low at all levels of spiking. Carbosieve was eliminated as a candidate replacement because of cost and handling problems. The petroleum-based charcoal was eliminated because of difficulties in handling a finely-divided powder. The availability of Anasorb® 747 proved to be the deciding factor between it and the BAC. Performance, cost, ease of handling, and plentiful supply make Anasorb® 747 a good choice for replacement of SKC Lot 104.

This Project Summary was developed by EPA's National Exposure Research 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

The Volatile Organic Sampling Train (VOST) is used for sampling principal organic hazardous constituents and prod-

ucts of incomplete combustion from stationary sources. The sampling protocol for the VOST is presented in SW-846 Method 0030. The sampling train uses solid sorbents for collection of volatile organic compounds. The solid sorbents used in the VOST are Tenax GC®, a phenylene oxide polymer, and charcoal. The combination of sorbents is required because very volatile organic compounds such as vinyl chloride are not trapped efficiently by Tenax® and require the use of a carbon-based sorbent for efficient collection. VOST samples are analyzed by thermal desorption followed by purge and trap gas chromatography/mass spectrometry, according to SW-846 Method 5040 or 5041.

VOST sampling and analytical protocols are periodically revised to address the development of new technology and improved procedures. For example, Method 5041 was written to address the application of megabore® capillary column technology to the analysis of VOST tubes. An aspect of the VOST sampling protocol that has required revision is the use of the specified carbon-based sorbent (SKC Lot 104 petroleum-based charcoal). SKC Lot 104 petroleum-based charcoal is no longer commercially available. Method 0030 specifies that "an equivalent" may be used but contains no specifications for an equivalent. To revise the methodology and provide an appropriate substitute for the SKC Lot 104 petroleum-based charcoal, which is no longer available, the U.S. Environmental Protection Agency and Radian Corporation initiated a VOST Charcoal Specification Study to define the performance characteristics of petroleum-based charcoal, identify and test potential candidate sorbents, and recommend a replacement sorbent for SKC Lot 104 charcoal for VOST applications.

On the basis of discussions with sorbent manufacturers and users, a comprehensive literature search, and a preliminary round of laboratory feasibility testing, five candidate sorbents were selected for extensive laboratory testing. These sorbents were

- Reference: Lot 208 petroleum-based charcoal (SKC);
- Anasorb® 747 (SKC);
- Amborsorb® XE-340 (SKC);
- Carbosieve® S-III (Supelco); and
- Beaded activated charcoal (BAC, from Kureha, Japan).

In the laboratory, the sorbents would be tested under simulated field conditions.

Results and Discussion

To determine the adsorptive capacity and recovery efficiency of each of the candidate sorbents, a thermal desorption

study was performed. Using flash evaporation of the analytes in methanol solution (the protocol for spiking surrogate compounds onto VOST tubes prior to analysis according to SW-846 Method 5041), analytes listed in Method 5041 were spiked onto VOST tubes containing the candidate sorbents. The spiked tubes were thermally desorbed at 250°C, 300°C, and 350°C. Recoveries of spiked analytes were determined at each desorption temperature to determine both the optimum desorption temperature for each candidate sorbent and the feasibility of using a single tube containing only the candidate sorbent rather than the tube containing sequential beds of Tenax® and carbon-based sorbent presently used in Method 0030.

For all of the carbon-based sorbents tested, the laboratory spiking/desorption study demonstrated that the recovery of non-gaseous volatile organic analytes using thermal desorption is poor at any of the desorption temperatures tested. Since non-gaseous volatile organic analytes are efficiently trapped by the carbon-based sorbents but are not quantitatively released by thermal desorption, Tenax®-GC must be used to trap non-gaseous volatile organic analytes. The tube containing sequential beds of Tenax® and charcoal is used in Method 0030 because organic analytes such as methylene chloride can show some distribution on the second tube of the VOST sampling train. If this second tube is entirely carbon-based sorbent, the organic compounds will not be recovered. If the back tube of the VOST train contains only carbon-based sorbent, two Tenax® tubes in front of the carbon-based sorbent will be required to ensure that non-gaseous volatile organic compounds can be recovered by thermal desorption.

A sorbent cleaning study was performed to develop a procedure for initial cleaning/conditioning for the carbon-based sorbent and to evaluate the feasibility of regeneration of the sorbent after use. A high temperature oven (ambient to 360°C) was modified for sorbent cleaning with 20 individually regulated stainless steel gas lines, each capable of 0 to 100 mL/min of inert gas flow. Tenax® tubes were thermally desorbed at 250°C for 8-12 hours. This temperature was selected to be well above the Tenax® desorption temperature of 180°C in the VOST analytical protocol yet well below the manufacturer's upper temperature limit of 350°C for Tenax®. Carbon-based sorbents, with a higher upper temperature limit, were cleaned at 300°C for 18 to 24 hours. All sorbents were desorbed under a flow of 80 to 100 mL/min of high purity nitrogen.

After the cleaning process, a percentage of the tubes were checked for cleanliness by gas chromatography/mass spectrometry (GC/MS) analysis. The cleaning conditions described above were sufficient to condition new tubes or to regenerate used VOST tubes after reasonable use.

A preliminary dynamic spiking study was performed to determine correct parameters for a major dynamic spiking study. It was also necessary to evaluate the reproducibility and accuracy of spiking VOST tubes through a simulator at various analyte concentration levels. Using a modified three-tube VOST configuration (Tenax®/Tenax®/carbon-based sorbent), triplicate spiking experiments were conducted at three spiking levels (approximately 100 ng, 200 ng, and 300 ng). The VOST tube sets were analyzed separately (front/middle/back) by GC/MS to determine both total recovery and distribution of spiked analytes among the three cartridges.

Conclusions

The data were subjected to statistical analysis to differentiate the performance of the candidate sorbents. No statistically significant differences were found for the whole range of analytes at any spiking level. Amborsorb® XE-340 demonstrated very poor recoveries for vinyl chloride compared to the reference sorbent and the other candidate sorbents. The other three candidate sorbents all behaved similarly and were comparable in performance to SKC Lot 208. Sorption/recovery data that can be used as a basis for selection of an alternative to SKC Carbon Lot 104 are shown in Table 1.

In Table 1, chloromethane shows the high and erratic recoveries that have characterized this compound in laboratory and field studies that include a carbon-based sorbent. The compound is apparently being formed on the sorbent tubes. The other gaseous organic analytes, vinyl chloride, bromomethane, and chloroethane, show reasonably reproducible recoveries at all concentration levels.

The standard SW-846 Method 5041 VOST calibration procedure, where analytes, surrogate compounds, and internal standards are spiked onto the tubes by flash evaporation immediately prior to analysis, should not be used in the analysis of a sorbent tube containing only carbon-based sorbent because analyte recoveries are not quantitative with increasing boiling point of the analyte. A calibration study was therefore conducted to determine an appropriate method of calibration for VOST analyses using the modified three-tube configuration. Five-point

Table 1. Mean Percent Recoveries from Sampling Runs for Reference Sorbent (SKC Lot 208) and Candidate Carbon-Based Sorbents (100/200/300 ng Spiking Level)

Organic Analyte	SKC Lot 208	Anasorb® 747	Ambersorb® XE-340	Carbosieve® S-III	BAC Kureha
chloromethane	5784/4055/2014	646/410/470	117/142/181	738/371/364	1197/397/161
vinyl chloride	69/65/85	71/87/88	3/3/13	74/82/91	74/74/75
bromomethane	78/61/46	45/38/35	30/42/49	38/54/56	20/22/35
chloroethane	47/52/60	37/49/69	56/59/90	38/49/74	37/38/58
trichlorofluoromethane	97/99/120	93/98/113	126/126/142	97/100/117	100/88/104
1,1-dichloroethene	79/80/96	77/84/99	86/72/111	85/77/106	96/80/101
methylene chloride	139/97/100	125/101/105	154/106/111	129/96/106	152/94/101
iodomethane	56/70/74	71/69/81	70/64/78	68/57/70	68/61/80
1,1-dichloroethane	83/80/93	76/85/94	87/83/95	84/80/97	89/89/96
chloroform	89/78/86	79/80/88	92/81/89	92/77/89	95/85/89
1,1,1-trichloroethane	80/75/87	78/78/91	90/77/91	81/72/91	88/78/92
carbon tetrachloride	70/71/82	68/74/86	78/70/86	74/63/85	80/76/88
benzene	108/87/100	90/96/99	179/147/164	125/84/99	109/94/103
1,2-dichloroethane	78/68/76	71/70/77	80/69/75	86/68/77	84/77/80
trichloroethene	96/87/97	81/90/94	90/85/92	94/86/96	97/97/99
1,2-dichloropropane	86/79/88	73/79/86	83/81/86	86/80/87	83/87/88
cis-1,3-dichloropropene	51/56/61	47/55/60	52/57/62	59/57/60	49/61/60
toluene	99/83/79	78/95/88	112/114/105	100/91/88	93/83/92
trans-1,3-dichloropropene	63/71/76	59/65/74	64/70/80	70/70/74	57/76/79
1,1,2-trichloroethane	85/23/89	74/80/85	82/85/89	89/84/86	78/90/89
tetrachloroethene	80/83/94	68/84/91	79/88/91	88/88/94	87/94/95
n-octane	133/115/93	95/104/95	105/108/106	108/104/102	108/93/100
chlorobenzene	79/79/86	64/78/83	78/77/84	84/81/86	82/88/87

Note: All sorbent tubes were desorbed at 250°C. Mean recoveries are calculated from duplicate sampling runs at each spiking level.

calibration curves were created under four sets of conditions:

- Analytes, surrogate compounds, and internal standards spiked in water with the sorbent tube desorbed thermally according to the Method 5041 protocol;
- Analytes, surrogate compounds, and internal standards spiked on one Anasorb® tube, which is then desorbed thermally according to the Method 5041 protocol;
- Analytes, surrogate compounds, and internal standards spiked on one Tenax® tube, which is then desorbed thermally according to the Method 5041 protocol; and

- Analytes, surrogate compounds, and internal standards spiked on a paired set of Tenax® front tube and Anasorb® back tube, with the pair then desorbed thermally according to the Method 5041 protocol.

Calibration curves obtained under each set of conditions were evaluated for acceptable compound recoveries and percent standard deviation for response factors for the spiked analytes. The evaluation showed that the calibration curve determined from spiking analytes and standards into water was superior in recovery and reproducibility and that the curve generated with paired Tenax® and Anasorb® was acceptable within the specifications of Method 5041. Calibration curves origi-

nating from Tenax® only and from Anasorb® only did not meet the acceptance criteria of Method 5041.

On the basis of the laboratory test results and the following considerations, a replacement carbon-based sorbent could be selected:

- Anasorb® 747 showed consistent performance, low cost, and availability of an abundant supply.
- SKC Lot 208 petroleum-based charcoal, the reference sorbent, showed performance equivalent to all of the other candidate sorbents. However, batch-to-batch variability of petroleum-based charcoal has historically been high. If alternative sorbents with equivalent performance are

available, another choice of sorbent is preferable to petroleum-based charcoal.

- Because of its poor recovery for vinyl chloride, Amborsorb® XE-340 was eliminated.
- Because of its high cost (twenty times as expensive as the other candidate sorbents), Carbosieve® S-III was eliminated; other less

costly sorbents demonstrated equivalent performance.

- BAC charcoal was eliminated because of concern over long-term availability from a foreign supplier.

Anasorb® 747 was selected as the replacement sorbent for petroleum-based charcoal because of its consistent performance, low cost, and abundant supply for the foreseeable future. A field study with dynamic spiking is required to compare

the performance of the modified VOST train (three sorbent tubes) with the standard VOST train. The GC/MS calibration should be performed with analytes and internal standards spiked into water, with surrogate compounds spiked on the tube(s) being analyzed. VOST tubes from the modified train may be analyzed individually, or the Tenax® tubes may be paired and the Anasorb® tube analyzed individually.

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Robert G. Fuerst is the EPA Project Officer (see below).

The complete report, entitled "VOST Charcoal Specification Study," (Order No. PB96-175252; Cost: \$47.00, subject to change) will be available only from

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