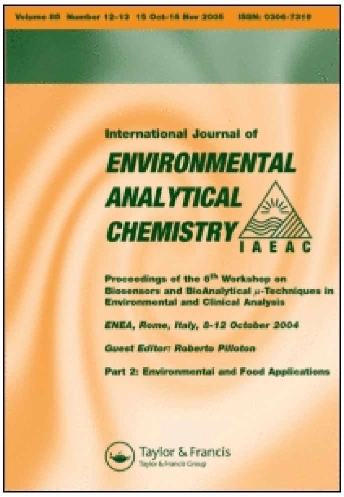

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REPLACEMENT OF CHARCOAL SORBENT IN THE SAMPLING OF VOLATILE ORGANICS FROM STATIONARY SOURCES

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U.S. Environmental Protection Agency Method 0030 for sampling volatile organics from stationary sources (VOST) specifies the use of petroleum-based charcoal in the second sorbent tube. Charcoal has proven to be a marginal performer as a sampling sorbent, partly due to inconsistency in analyte recovery. In addition, commercial availability of petroleum charcoal for VOST tubes has been variable. Lack of data on comparability and variability of charcoals for VOST application has created uncertainty when other charcoals are substituted.

Five potential sorbent replacements for charcoal in Method 0030 were evaluated along with a reference charcoal. Two of the sorbents tested. Ambersorb XE-340 and Tenax GR, did not perform well enough to qualify as replacements. Three candidates, Anasorb 747, Carbosieve S-III and Kureha Beaded Activated Charcoal, performed adequately, and produced statistically equivalent results. Because Anasorb 747 exhibited an excellent combination of performance, availability, and cost, it was selected for use in field tests to follow this study.

KEY WORDS: Sampling, emissions, organics, sorbents, VOST

INTRODUCTION

The Volatile Organic Sampling Train (VOST), U.S. Environmental Protection Agency Method 0030, has been the method of choice for sampling most volatile organic compounds since its introduction[1,2]. Figure 1 is a schematic diagram of the VOST. Two of the key elements of the train are the two sorbent cartridges. These cartridges are the primary devices for collection and concentration of the volatile compounds in the flue gas being sampled. The front sorbent tube contains 1.6 g of Tenax-GC, a polymer of 2,6-diphenylene oxide, one of many porous polymer bead materials often used for sampling or for gas chromatography column packing. The VOST method was designed with the intent of capturing all of the compounds of interest on the front tube, with the back tube serving as a secondary trap in case of breakthrough of the more volatile compounds. In order to minimize potential breakthrough from the second tube, it contains 1.0 g of Tenax-GC, followed by 1.0 g of petroleum-based charcoal.

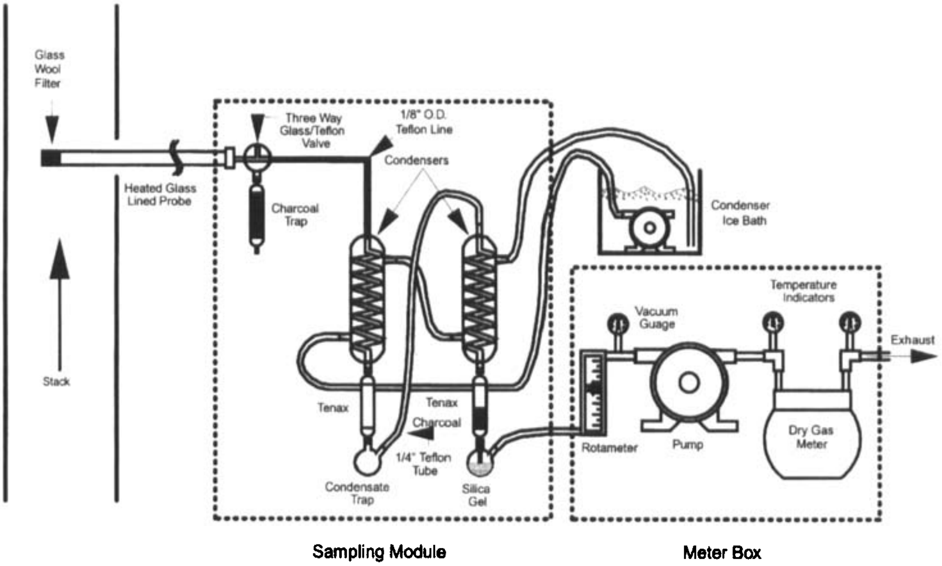


Figure 1 Volatile organic sampling train.

The combination of Tenax-GC followed by charcoal is effective because the Tenax-GC traps all but the most volatile compounds and prevents them from reaching the charcoal, where they would be irreversibly sorbed. The charcoal, in turn, acts as a "safety net" and traps the few compounds which are not quantitatively sorbed by the Tenax-GC. It would be preferable to load both tubes with a single sorbent capable of quantitatively trapping all compounds of interest and exhibiting quantitative release of the compounds upon heating. Unfortunately, all sorbents known to be sufficiently retentive to quantitatively collect compounds boiling below 30°C do not quantitatively release compounds boiling above 30°C upon heating.

Tenax-GC has served well as the primary sorbent in the VOST, and fortunately, most of the compounds of interest from incinerators are trapped on the front tube containing this material[3]. The charcoal has performed adequately, but has been far from ideal in several respects. It has sometimes been contaminated with organic material which has been difficult to remove and which has complicated analysis and limited detection limits. In addition, charcoal has exhibited inconsistency of composition and uncertainty of supply.

Method 0030 specifies petroleum charcoal from SKC Lot 104 or equivalent, but gives no procedure for determining equivalency. Petroleum-based charcoal was chosen because it is slightly hydrophobic and, therefore, does not retain water as readily as coconut charcoal and its sorption properties are not sensitive to the presence of water. Petroleum charcoal also shows less tendency than coconut charcoal to irreversible sorption of compounds sampled. Lot 104 charcoal became unavailable several years ago, VOST users have sometimes had difficulties obtaining petroleum charcoal in any form. Coconut charcoal has sometimes been substituted, with uncertain effect upon both sampling and analysis.

The goal of this project was to find and test a sorbent with sorption and recovery behavior at least as good as petroleum charcoal, with better consistency of properties and availability, and hopefully with lower contaminant levels and water sensitivity.

EXPERIMENTAL

Materials. The six sorbent materials tested were obtained from U.S. sources. Some of the sorbents are also available from other U.S. suppliers, and most are likely available from other suppliers outside the U.S. Petroleum-based charcoal (SKC Lot 208), Ambersorb XE-340 and Anasorb 747 were obtained from SKC, Inc., 334 Valley View Road, Eighty Four, PA 15330-9614, U.S.A. Carbosieve S-III was obtained from Supelco, Inc., Supelco Park, Bellefonte, PA 16823-0048, U.S.A. Tenax-GR was obtained from Alltech Associates, Inc., 2051 Waukegon Road, Deerfield, IL 60015, U.S.A. Kureha Beaded Activated Carbon (grade BAC-G-70R) was obtained from Kureha Chemical Industry Co., Ltd., 420 Lexington Ave., New York, NY 10170, U.S.A.

Two cylinders of certified analysis gas standards were obtained from Scott Specialty Gases, 6141 Easton Road, Plumsteadville, PA 18949, U.S.A. Cylinder 1 contained 19 of the test analytes, while Cylinder 2 contained the remaining 4. The certified analysis concentrations were used in all recovery calculations. The analytes and their concentrations are discussed in subsequent sections.

Phase One. The project was carried out in two experimental phases. Phase One was a screening study designed to determine the suitability of a series of sorbents for more extensive testing. Phase Two included dynamic spiking and recovery studies of a modified VOST.

Five sorbents were tested in the phase one screening study. Petroleum-based charcoal (SKC Lot 208) was chosen as the reference material to represent the original SKC Lot 104, which is no longer available. The other four sorbents tested were Ambersorb XE-340, Anasorb 747, Carbosieve S-III and Tenax-GR. Suppliers' literature gives the following descriptions of the sorbents. Ambersorb XE-340 is a hydrophobic carbonized resin bead. Anasorb 747 is a beaded active carbon with a very regular pore size and structure which should contribute to consistent performance characteristics. Carbosieve S-III is a carbon molecular sieve which is widely used in conjunction with Carbopak sorbent in commercial analytical sorbent traps. Tenax-GR, not to be confused with Tenax-GC, is a new material only recently made commercially available. Tenax-GR consists of Tenax with graphite incorporated into the particles. The intent of the manufacturer was apparently to produce a sorbent with the virtues of both consituents.

Unlike methods for semivolatile organics, the VOST has an upper limit on the boiling point of compounds for which it is applicable. Method 0030 states this upper limit to be 100°C, but the VOST can be effectively applied to compounds with slightly higher boiling points. The reasons why the VOST cannot be applied to unlimited higher boiling compounds relate to the sorption of these compounds on particulate matter and on train components. The tendency of organic compounds to sorb onto particulate matter depends on a number of factors. At a given temperature, the two most relevant to this discussion are the nature of the particulate, and the boiling point of the compound. For a given type of particulate matter, the higher boilers sorb more readily and more strongly. Not only should particulate-bound material be sampled isokinetically, but it is discarded during VOST sample recovery. Because the VOST was designed for volatile compounds, no attempt is made to recover sorbed materials from either the particulate catch or from the probe or cooler/condenser walls.

For a time after publication of Method 0030, the upper limit for application of the method was thought to be in the 130°C to 140°C range. The VOST probe should always be operated at a temperature above the boiling point of the compound of interest, so a few sampling projects were carried out with probe temperatures approaching 140°C to maximize the number of compounds effectively collected. It is difficult to operate the front part of the VOST above 140°C and still maintain adequate cooling of the sorbent in the following section. Recent data[4] have shown that the presence of fairly high levels of soot in the stack increases sorption effects and recovery losses measurably for compounds boiling above approximately 125°C. The best current advice is to limit sampling with VOST to compounds boiling below 132°C in low soot situations and below 121°C in the presence of high soot concentrations.

Table 1 serves two purposes, it lists the compounds tested and it reports the results of the detection limit study discussed in a later section. Twelve test compounds, shown in Table 1, were selected to serve as a representative set of volatile organics with boiling points throughout and slightly below the practical range of Method 0030. Since the VOST utilizes sequential sorbent tubes containing different sorbents, it is necessary that a front tube, as described below, and a back tube be paired before sampling and tracked as a unit in the laboratory records. Analysis of the tubes may be carried out with the paired tubes connected as a unit, or with the front tube and back tube analyzed separately. The former approach costs less and produces better detection limits, while the latter provides more information about analyte distribution between the two tubes. The Phase One analyte recovery and detection limit study utilized VOST tube pairs prepared as specified in Method 0030, with each of the twelve candidate sorbents substituted for the charcoal. The front tube of each pair was packed with 1.6 g of Tenax-GC, and the rear tube was loaded with 1.0 g of Tenax-GC followed by 1.0 g of candidate sorbent. Analytes were loaded onto clean VOST tube pairs by a flash vaporization technique described in Method 0030 and in greater detail in Method 5041[5]. The technique is briefly described here for the convenience of the reader. The paired tubes were connected to a heated injection port so that the flow of high purity nitrogen carrier gas entered the front Tenax-GC tube and exited from the rear of the back tube containing the candidate sorbent. The target analytes (25 ng of each) in methanol solution were then introduced

Table 1 Analyte detection limits in nanograms, phase one method detection limit study.

Target Compounds	*Petroleum Charcoal*	*Ambersorb XE-340*	*Anasorb 747*	*Carbosieve S-III*	*Tenax-GR*
Chloromethane	82	64	482	490	12
Chlorobenzene	8	16	9	10	32
Vinyl chloride	5	26	10	9	3
1,1-Dichloroethene	16	17	6	14	52
Chloroform	10	5	6	9	43
Toluene	122	117	132	79	102
Methylene chloride	35	306	77	386	46
1,1,1-Trichloroethane	6	14	13	39	44
Carbon Tetrachloride	7	10	15	33	43
Benzene	16	43	60	9	75
Trichloroethene	7	6	5	8	44
Tetrachloroethene	7	10	5	11	40

into the injection port with a microliter syringe. The carrier gas, flowing at 10 mL/min, swept the volatilized compounds onto the sorbent tubes during a 1 minute period. After spiking the tubes in this manner, they were disconnected from the injection port and further treated in order to better simulate sampling conditions and to thus promote realistic distribution of the compounds throughout the tube pair. Each tube pair was purged for 20 min with a total of 20 L of high purity nitrogen at ambient temperature. Sample tubes were sealed and stored until analysis.

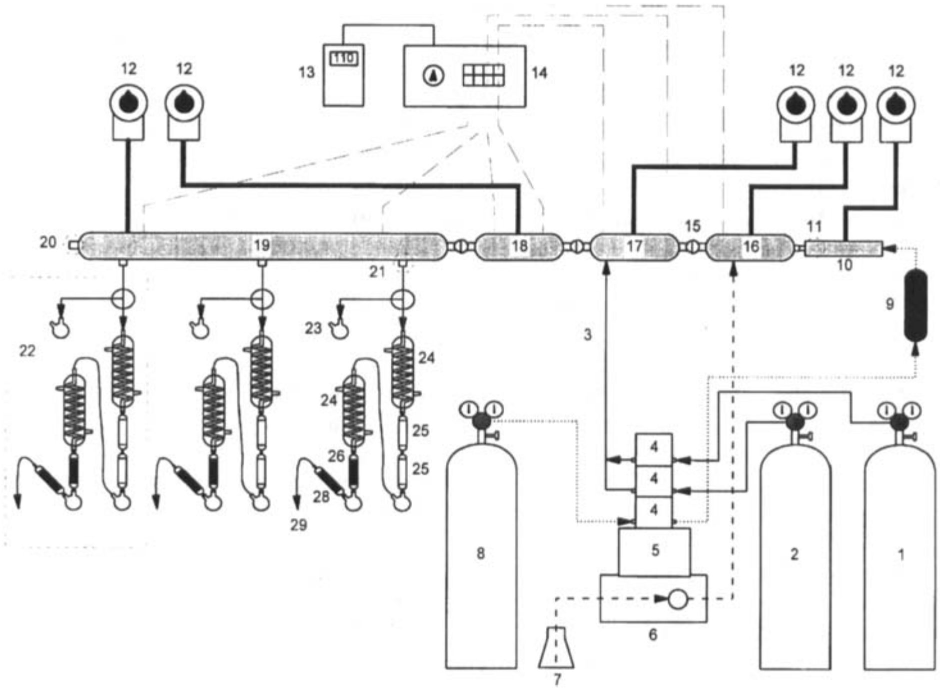
Analysis of these compounds on the sample tubes prepared by the procedure described above, was performed using Method 5041[4], with the following modifications. The performance of each candidate sorbent was evaluated for analyte recovery and compared against a maximum recovery obtained by purging analytes and internal standards from water. Daily gas chromatograph-mass spectrometer (GC-MS) calibration checks were performed by introducing analytes and internal standards into water. For analyses of samples, internal standards were spiked into the purge water. A single calibration check was compared to a five-point calibration curve, and each daily calibration check was compared to the calibration standard of the previous day. Recovery of the compounds of interest from water was used as the standard reference for recovery of the compound from the spiked sorbent tube. All analyses were performed using a Finnigan-MAT 4500 GC-MS interfaced to a Tekmar purge and trap unit. Sample tubes were desorbed by heating with the gas flow in the direction opposite to the direction of sampling, as described in Method 5041. The analytical conditions for GC-MS described in Method 5041 were used.

The modifications to Method 5041 were necessary for this study in order to obtain recovery data for each of the candidate sorbents. The calibration procedure in Method 5041 requires spiking of standards onto the sorbent tubes, and recovery by the same analytical techniques used for the analytes of interest. While the Method 5041 approach has the advantage of compensating for recovery losses during routine VOST operation, it would have precluded quatitation of those recovery losses as needed in this study. By comparing the amount of each analyte recovered from heat desorption of the sorbent tubes to quantities recovered from water, rather than quantities from the same sorbent, an accurate recovery was obtained.

Reference 7 contains the U.S. Environmental Protection Agency definition of method detection limit (MDL) along with procedures for determination of the MDL. The reference states that, "The method detection limit (MDL) is defined as the minimum concentration of a substance that can be reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte"[7]. Although the MDL method described in the reference[7] is most often applied to analytical methods for pollutants in water and wastewater, the authors have found that it provides useful information when evaluating candidate sorbents for use in sampling trains. In addition to a detection limit, each MDL study produces a value for the recovery efficiency of each analyte from the sorbent tested. For a given application, the best sorbents typically exhibit recovery efficiencies in the range of 80 to 120%, and will produce an MDL low enough to meet the requirements of the method being tested. For VOST applications the MDL needs to be on the order of nanograms. A detection limit study for the test analytes was performed for each sorbent. Each study was carried out according to instructions given in reference 7. Seven sets of tubes were analyzed for each candidate sorbent.

Phase One resulted in selection of Petroleum Charcoal, Ambersorb XE-340, Anasorb 747 and Carbosieve S-III for additional study. A fifth candidate sorbent, Kureha Beaded Activated Carbon (BAC), was added to the four selected in Phase One, and the five sorbents were tested further in Phase Two.

Phase Two. Phase Two consisted of dynamic spiking and recovery studies of a modified VOST loaded with Tenax-GC and with each of the sorbents being evaluated. A modified VOST configuration was adopted in order to give greater protection against breakthrough of the non-gaseous analytes which had displayed poor recovery from the candidate sorbents in the early phases of the project. Any of these compounds breaking through the Tenax-GC would be poorly recovered from the candidate sorbent and would therefore exhibit low overall recovery. This configuration consisted of front and middle tubes containing Tenax-GC, and a full tube of candidate sorbent in the back. The arrangement of the three tube VOST assemblies is illustrated in Figure 2.



1. Analyte cylinder #1
2. Analyte cylinder #2
3. Heated lines
4. Mass flow meters
5. Mass flow controller
6. HPLC H_2O pump
7. H_2O (purified)
8. Nitrogen carrier gas
9. Charcoal trap for carrier gas
10. Carrier gas pre-heater
11. Heating tape (wrapped around all chambers)
12. Variac rheostats
13. Thermocouple readout
14. Thermocouple switch box
15. Thermocouple wells
16. Carrier gas moisturizing chamber
17. Analyte spiking/primary mixing chamber
18. Secondary mixing chamber
19. Manifold
20. Excess sampling stream exit line
21. Sampling port (attaches to VOST train)
22. VOST sampling train (three identical)
23. Charcoal trap
24. Condensers
25. Tenax-GC sample tubes
26. Candidate sorbent sample tube
27. Condensate traps
28. Silica gel trap
29. Exit to meter boxes

Figure 2 Dynamic spiking apparatus.

Before assembly of the VOST units, the sorbent tubes were cleaned and checked for contamination as follows. The apparatus used for cleaning VOST tubes is shown in Figure 3. A high temperature (capable of attaining an upper temperature of at least 350°C) oven purged with inert gas was modified with twenty 1/4" Swagelok® ports to attach tubes for cleaning. Gas flow through each port was individually monitored by a 0–100 mL/min rotameter, using a purge gas of high purity nitrogen. Gas lines shown in Figure 3 were 1/8" stainless steel tubing. The rotameters were anchored to an aluminium plate, and the system could be expanded to 25 cleaning ports. After assembly, the cleaning system was purged for 24 hours with high purity nitrogen, then heated with purging to approximately 300°C. Random purge gas samples were taken at the cleaning ports using a precleaned SUMMA®-polished canister; the samples were taken both before and after heating. Analysis of the contents of the canisters by GC-MS showed no detectable levels of residual contaminants.

The carbon-based sorbents (SKC Lot 208 petroleum-based charcoal, Ambersorb XE-340, Anasorb 747, Carbosieve S-III, and BAC) were all cleaned identically. Each VOST tube was connected to a port in the oven so that the flow of purge gas would be opposite to the direction of gas flow during spiking. Carbon-based sorbents were thermally purged at 300°C for 18–24 hours, under a nitrogen flow of 80–100 mL/min. After cleaning a batch of tubes of the same sorbent, one tube was analyzed by GC-MS. Only insignificant trace amounts of various organic analytes were found. To address the concern that the cleaning of the tubes might be only surface cleaning (i.e., contaminants embedded in the structure of the sorbent could migrate to the surface of the sorbent particle over time), candidate sorbent tubes which had been cleaned and then sealed in glass culture tubes with Teflon®-lined screw caps for 48 hours were re-analyzed 48 hours after cleaning. No appreciable amounts of contaminants were found.

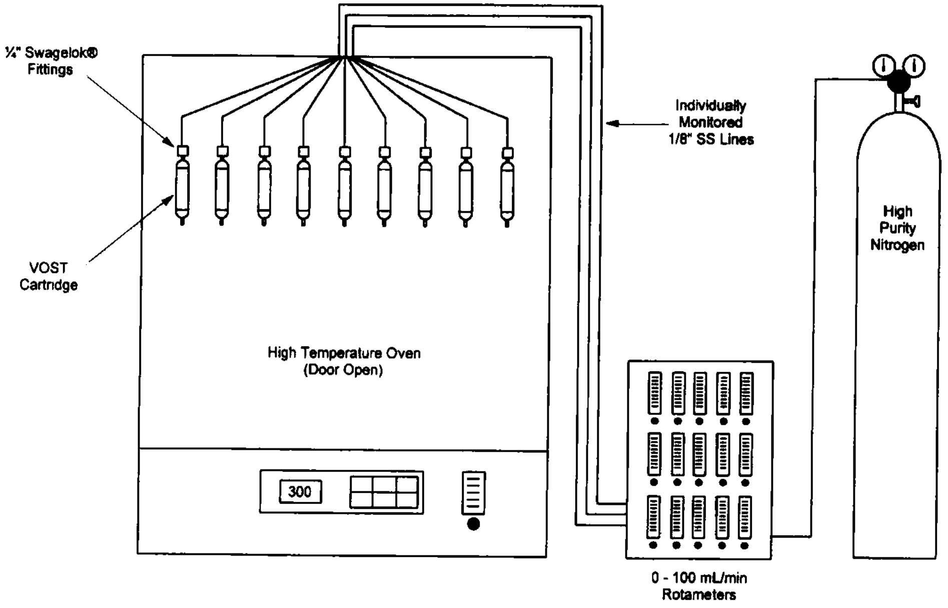


Figure 3 Desorption oven for cleaning VOST tubes.

According to the manufacturer's specifications, Tenax-GC can be cleaned at 300°C for 2–3 hours with a nitrogen flow rate of 80–100 mL/min. When Tenax-GC tubes were cleaned according to this procedure, GC-MS analysis showed the presence of detectable amounts of benzene, toluene, styrene, and alkylstyrenes, all indicative of decomposition of the Tenax-GC polymer. When the desorption temperature was decreased to 250°C and the purge time lengthened to 8–12 hours using the same gas flow, the polymer decomposition products were not observed upon GC-MS analysis. Analysis indicated that the tubes were clean. This lower temperature cleaning procedure was used for all Tenax-GC tubes employed in the dynamic spiking study described below.

The dynamic spiking study was designed to provide a comprehensive picture of the performance characteristics of each of the candidate sorbents in realistic VOST applications. The system operated at approximately 175°C and test gas moisture content was adjusted to 11%, in order to be consistent with a hot moist flue gas. The dynamic spiking apparatus consisted of four major sections, a carrier gas moisturizing section, a spiking and primary mixing chamber, a secondary mixing chamber and a sampling manifold. Figure 2 is a diagram of the dynamic spiking apparatus showing three modified VOST samplers in position for an experimental run. The spiking apparatus features the following parts: The Carrier Gas Preheater (#10 in Figure 2) was designed to heat the carrier gas entering the spiking system to prevent the condensation of moisture. The Carrier Gas Moisturizing Chamber (#16 in Fugure 2, shown in closeup in Figure 4) produced hot, moisturized carrier gas at a temperature of 175–204°C. Nitrogen carrier gas was admitted at the front, and clean HPLC-grade water was metered into the chamber through a small jet positioned at the center of the carrier gas stream. The analyte spiking and primary mixing chamber (#17 in Figure 2, shown in closeup in Figure 5) received moisturized carrier gas through a curved downspout in order to ensure mixing. Analytes were metered into the chamber outside of the direct flow of the carrier gas to avoid aspiration. Two cylinders of certified standard analytes were used. The outputs of the two cylinders were teed together after the individual lines passed through mass flow controllers. The common line from the tee was an 1/8" Teflon® line. The mixing chamber was heated to 150–175°C. The Secondary Mixing Chamber (#18 in Figure 2, shown in closeup in Figure 6) acted as a final mixing chamber for moisture, analytes, and carrier gas. This chamber was also heated to 150–175°C.

The Sampling Manifold (#19 in Figure 2, shown in closeup in Figure 7) had a 1/2" open end and three stopcock ports to which modified VOST trains were attached. The sampling manifold was heated to 150°C and had a 1/2" Teflon® line attached at the end to release gases exiting from the chamber into a hood.

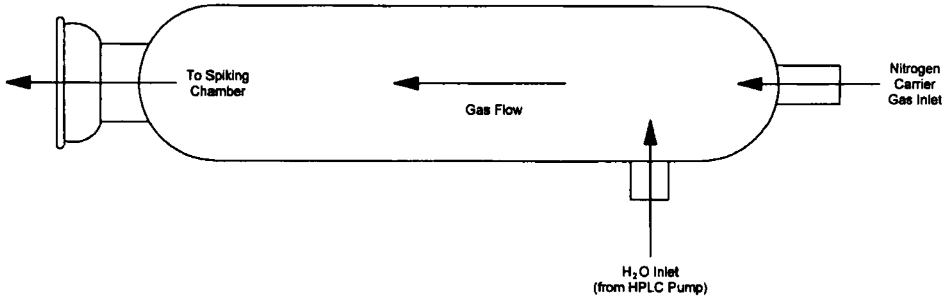


Figure 4 Carrier gas moisturizing chamber.

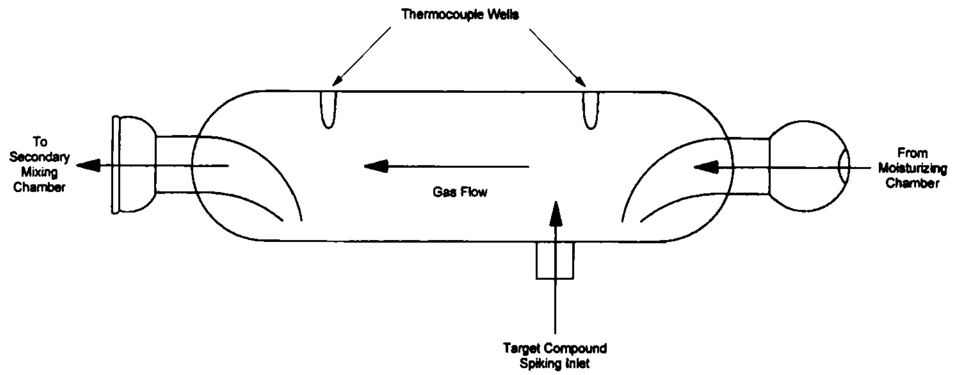


Figure 5 Spiking and primary mixing chamber.

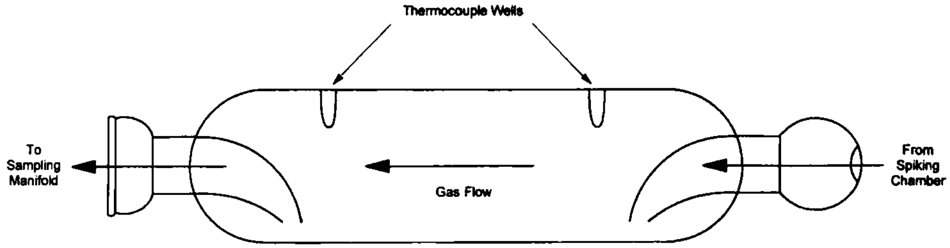


Figure 6 Secondary mixing chamber.

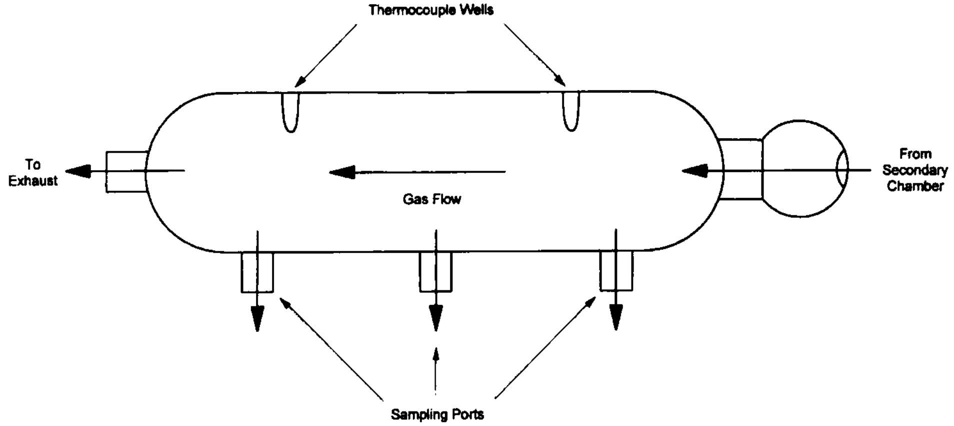


Figure 7 Sampling manifold.

The Dynamic Spiking System was calibrated for a flow of 5 L/min of carrier gas, with expected spiking flows of analytes of approximately 6, 12, and 18 mL/min (for final analyte values of 100 ng, 200 ng, and 300 ng, respectively). The certified standard analytes in the two cylinders and their concentrations are shown in Table 2.

The gas stream from the dynamic spiking system was sampled using the three tube modified VOST, following procedures in Method 0030. Three VOST units collected samples simultaneously for each candidate sorbent at each spiking level. Experiments were conducted at spiking levels of approximately 100 ng, 200 ng, and 300 ng. These spike levels represent normal levels encountered during actual field sampling with the VOST. Collection of multiple spiking levels is often used in evaluation of gas phase collection systems in order to provide information whether the performances of the delivery system and the collection system are sensitive to spike level.

Lower spike levels were used in Phase One than in Phase Two because a detection limit study was an important part of the initial screening. Detection limit studies, because of their very nature, must be carried out at the lower end of the operating range. In Phase Two, the VOST tubes collected 1 L/min of sample for 20 minutes, giving a 20 L sample. The tubes were then sealed, and either analyzed immediately or stored at 4°C in a refrigerator dedicated to VOST samples. Each three tube modified VOST functioned as a unit, but the tubes were analyzed separately in order to provide analyte distribution information. Analysis was by the modification of Method 5041 used in Phase One, except that carbonaceous sorbents and Tenax-GC were heat desorbed at 250°C.

Table 2 Volatile organic analytes used in dynamic spiking experiments.

Analyte	*Concentration in cylinder, ppm*
Cylinder #1	
Chloromethane	0.97
Vinyl chloride	0.93
Bromomethane	0.93
Chloroethane	0.98
1,1-Dichloroethene	0.69
Methylene chloride	0.68
Iodomethane	0.83
1,1-Dichloroethane	0.92
Chloroform	1.00
1,1,1-Trichloroethane	1.02
Carbon tetrachloride	0.97
1,2-Dichloroethane	1.10
Trichloroethene	0.95
1,2-Dichloropropane	1.12
1,3-Dichloropropene (cis + trans)	1.22
1,1,2-Trichloroethane	1.07
Tetrachloroethene	1.10
Chlorobenzene	1.21
Cylinder #2	
Trichlorofluoromethane	1.03
Benzene	1.02
Toluene	1.05
n-octane	1.05

RESULTS AND DISCUSSION

Phase One. As previously mentioned, seven replicate sets of tubes were analyzed in Phase One. Average values are used in this paper, but all data are included in reference 6. Table 1 presents the detection limits determined by this study. Since detection limit as defined by the protocol used[7] is a complex function of both sensitivity and reproducibility, it can serve as an important measure of the effectiveness of the sorbents being tested. This use of the MDL as a quality discriminator in a preliminary study should not be confused with the in-stack detection limit of the VOST in field situations. Here, the "method" for which MDL was determined consists only of the spiking of sorbents with standard solutions and analysis by the procedures described. In general, the lower the detection limit in Table 1, the better the sorbent performed. Some caution must be exercised, however, in applying this principle. Although the 3 ng detection limit for vinyl chloride would ordinarily indicate excellent performance of Tenax-GR, it is accompanied, in this case, by an entirely unacceptable recovery of only 2% as shown in Table 3.

Table 3 shows the recoveries for the test analytes. The chloromethane, toluene, benzene and methylene chloride results were generally poor, and cannot be used for sorbent performance comparisons. For the remaining test compounds, all the candidate sorbents showed acceptable performance except that both Ambersorb XE-340 and Tenax-GR displayed low recovery of vinyl chloride. The very low recovery of chloromethane from Tenax-GR is the single instance in which the chloromethane data may be used, since they strongly indicate breakthrough of the low boiling compound. Based on the acceptable performance indicated by the MDL and recovery study, Petroleum Charcoal, Ambersorb XE-340, Anasorb 747 and Carbosieve S-III were selected for further study in Phase Two.

Phase Two. Table 4 shows recoveries from the 100 ng, 200 ng, and 300 ng spiking experiments. The values shown are averages of triplicate sampling runs. They represent total recovery, obtained by adding the recovered amount from each of the three sorbent tubes for each single sampling run. Each of the values in Table 4 is an indication of the laboratory performance of the three tube VOST sampler with respect to each test compound when loaded with Tenax-GC and each of the candidate sorbents as described

Table 3 Average percent recoveries for target analytes phase one method detection limit study.

Target compounds	*Petroleum charcoal*	*Ambersorb XE-340*	*Anasorb 747*	*Carbosieve S-III*	*Tenax-GR*
Chloromethane	247	164	1017	710	15
Chlorobenzene	80	76	76	79	87
Vinyl chloride	87	47	94	77	2
1,1-Dichloroethene	102	90	101	87	99
Chloroform	102	100	88	92	102
Toluene	484	340	299	313	327
Methylene chloride	176	389	215	491	222
1,1,1-Trichloroethane	101	114	98	120	104
Carbon tetrachloride	102	109	88	105	100
Benzene	117	247	138	95	197
Trichloroethene	98	100	89	87	96
Tetrachloroethene	96	91	88	85	94

Table 4 Mean percent recoveries from triplicate sampling runs 100/200/300 ng spiking level.

Organic analyte	*Boiling point, °C*	*SKC Lot 208*	*Anasorb 747*	*Ambersorb XE-340*	*Carbosieve S-III*	*BAC Kureha*
Chloromethane	–24	5784/4055/2014	646/410/470	117/142/181	738/371/364	1197/397/161
Vinyl chloride	–13	69/65/85	71/87/88	3/3/13	74/82/91	74/74/75
Bromomethane	4	78/61/46	45/38/35	30/42/49	38/54/56	20/22/35
Chloroethane	12	47/52/60	37/49/69	56/59/90	38/49/74	37/38/58
Trichlorofluoromethane	24	97/99/120	93/98/113	126/126/142	97/100/117	100/88/104
1,1-Dichloroethene	31	79/80/96	77/84/99	86/72/111	85/77/106	96/80/101
Methylene chloride	40	139/97/100	125/101/105	154/106/111	129/96/106	152/94/101
Iodomethane	42	56/70/74	71/69/81	70/64/78	68/57/70	68/61/80
1,1-Dichloroethane	58	83/80/93	76/85/94	87/83/95	84/80/97	89/89/96
Chloroform	61	89/78/86	79/80/88	92/81/89	92/77/89	95/85/89
1,1,1-Trichloroethane	75	80/75/87	78/78/91	90/77/91	81/72/91	88/78/92
Carbon tetrachloride	77	70/71/82	68/74/86	78/70/86	74/63/85	80/76/88
Benzene	80	108/87/100	90/96/99	179/147/164	125/84/99	109/94/103
1,2-Dichloroethane	83	78/68/76	71/70/77	80/69/75	86/68/77	84/77/80
Trichloroethene	87	96/87/97	81/90/94	90/85/92	94/86/96	97/97/99
1,2-Dichloropropane	96	86/79/88	73/79/86	83/81/86	86/80/87	83/87/88
cis-1,3-Dichloropropene	104	51/56/61	47/55/60	52/57/62	59/57/60	49/61/60
Toluene	111	99/83/79	78/95/88	112/114/105	100/91/88	93/83/92
Trans-1,3-dichloropropene	112	63/71/76	59/65/74	64/70/80	70/70/74	57/76/79
1,1,2-Trichloroethane	113	85/23/89	74/80/85	82/85/89	89/84/86	78/90/89
Tetrachloroethene	121	80/83/84	68/84/91	79/88/91	88/88/94	87/94/95
n-octane	125	133/115/95	95/104/95	105/108/106	108/104/102	108/93/100
Chlorobenzene	132	79/79/86	64/78/83	78/77/84	84/81/86	82/88/87

in the previous section. The coefficients of variation were generally less than 25%. A complete set of statistical tables is included in the project report[6], along with all raw data and information on analyte distribution among the three sorbent tubes of each VOST sampler. The scope of this paper does not allow presentation of the very large data set generated, but the summary information in Table 4 can be used to evaluate the performance of the candidate sorbents.

The usual criterion for acceptability of analyte recoveries for the VOST method in the field is a recovery of 50 to 150%, with a coefficient of variation of 50% or less[8]. Because the dynamic spiking experiments were performed in a laboratory under a controlled environment, minimal acceptable recovery should be higher, perhaps in the range 70–130%. Table 5 shows the number of analytes meeting the more stringent 70–130%. When judged by this criterion, the candidate sorbents each performed adequately for 15–20 of the 23 analytes tested.

Table 5 Number of analyte recoveries within 70–130% range.

	Spiking level		
	100 ng	*200 ng*	*300 ng*
Petroleum charcoal	15	17	19
Anasorb 747	15	17	19
Ambersorb XE-340	16	15	17
Carbosieve S-III	18	16	20
BAC	16	18	19

Study of Table 4 reveals several patterns in the data. The chloromethane recoveries are unacceptably high for all sorbents tested. The failure mechanism which caused these very high and erratic results is unknown at present, but subsequent laboratory and field studies[9] have shown similar chloromethane results with the three tube VOST and with Method 0030. Laboratory contamination did not appear to be the cause of the high recoveries, since cleaned sorbent tubes and control blanks showed no detectable chloromethane. Further research into the phenomenon will be necessary before either version of the VOST can be recommended for sampling of chloromethane. Most of the recoveries for vinyl chloride, bromomethane, and chloroethane were poor but not unreasonable. Anasorb 747, Kureha BAC and Carbosieve S-III showed acceptable performance with respect to vinyl chloride. Because of the poor to marginal performance on the other two compounds, it is recommended that any three tube VOST field data for bromomethane or chloroethane be regarded as tentative unless proven with dynamic spiking at the test site. The poor performance with respect to the three compounds is probably related to their low boiling points, as evidenced by the fact that most of the higher boiling compounds were recovered adequately. it is not known whether the low results were due to sorbent breakthrough or an analysis failure. When judged by the 70–130% criteria, cis-1,3-dichloropropene shows unacceptable recoveries while the trans isomer of the same compound exhibits marginally acceptable results. Since neither compound is in the low boiling point range usually associated with breakthrough, the problem is probably an analytical recovery difficulty. The increased reactivity usually associated with double bonds may well be the explanation. Ambersorb XE-340 exhibited extremely poor recovery of vinyl chloride, and was somewhat more susceptible than the other candidate sorbents to the production of benzene and toluene when subjected to thermal stress of heat desorption.

To test the similarity of performance of the candidate sorbents other than Ambersorb XE-340, the data from Table 4 for the other four sorbents were subjected to a statistical Analysis of Variance (ANOVA). Recoveries of all analytes except chloromethane were included in the analysis. Within a given spiking level, there was no statistically significant difference in the recoveries from the four sorbents.

Further study of Tables 4 and 5 reveals that the 300 ng analyte spikes were recovered adequately in slightly more cases than those at the 100 ng or 200 ng levels. The generally close agreement of the recoveries at each spike level for each sorbent and analyte is evidence that there was no systematic volumetric error in blending the gases introduced by the dynamic spiking apparatus.

CONCLUSIONS

Phase One. Tenax-GR performed poorly with respect to recovery of low boilers, and was eliminated from phase two testing. Ambersorb XE-340 exhibited marginal performance for low boilers, but was carried forward, partly because of excellent performance with respect to the compounds in the middle range of boiling point applicability. The other candidates were similar in performance and were carried forward to Phase Two.

Phase Two. It was shown that VOST tube sets in a modified three tube configuration could be used to accurately and reproducibly collect target analytes from a gas stream produced by a simulated stack gas dynamic spiking apparatus. A dynamic spiking study demonstrated that Ambersorb XE-340 performed very poorly for vinyl chloride and is not an acceptable replacement for charcoal in the VOST. A statistical evaluation of the sorbent recoveries confirmed that at a given dynamic spiking level, performance differences for the other three candidates and the reference charcoal, measured in terms of percent recoveries of analytes, were not significant. Based on performance alone, any of these three would be an acceptable replacement for charcoal in the VOST. Because Anasorb 747 exhibited an excellent combination of performance, availability, and cost, it was selected for use in field tests of the three-tube VOST.

FURTHER WORK

Draft Method 0031, a draft three-tube VOST method using Anasorb 747 has been written, and is under review as an alternative to Method 0030. A field test has been performed in which Draft Method 0031 was evaluated along with Method 0030[9,10].

NOTICE

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