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AIR SAMPLING METHODS FOR *s*-TETRACHLOROETHANE AND OTHER RELATED CHLORINATED HYDROCARBONS

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SUMMARY

An acid-treated Pittsburgh Activated Carbon (PAC) tube for sampling *s*-tetrachloroethane in air is described that minimizes sample losses through dehydrogenation and dehydrohalogenation reactions. Commercially prepared NIOSH charcoal, untreated PAC, and acid-treated PAC tubes are compared as to their effectiveness in stabilizing *s*-tetrachloroethane. Common homologues and analogues of *s*-tetrachloroethane cause no interference with the gas chromatographic method. In addition the effectiveness of the untreated PAC and acid-treated PAC tubes was also evaluated for four different chlorinated aliphatic hydrocarbons.

INTRODUCTION

The application of charcoal tubes for air sampling of organic vapors is well documented. The NIOSH methods¹ are based on the work of White *et al.*² in which two sections of charcoal, contained in a 4 mm I.D. Pyrex tube and separated by polyurethane plugs, are employed. After sampling, each section is extracted separately with an organic solvent and the extract is analyzed by gas chromatography.

In the course of an investigation to develop air sampling methods for nine C₁-C₂ chlorinated hydrocarbons of interest, a sampling tube, prepared from a 15-lb. lot size of Pittsburgh Activated Carbon (PAC), was found to be an excellent substitute for commercially available NIOSH charcoal tubes. Comparable quantitative data were obtained from both sets of sampling tubes. Our purpose in using PAC were three-fold: (1) to minimize repetitive re-evaluations of analytical parameters with different lots of charcoal or tubes, (2) to have the capability for preparing longer absorption tubes for special applications, and (3) to reduce the cost per sampling tube for our needs. However, the extension of the PAC tube to include air sampling of *s*-tetrachloroethane met with unexpected results. Extensive decomposition of this compound occurred on the sorbent at ambient temperature with a corresponding increase in the decomposition products with time, a response not observed with other chlorinated compounds. The decomposition of *s*-tetrachloroethane was also observed with the NIOSH charcoal tubes, but to a lesser degree. Consequently, an effort was made

to determine the cause of the reaction and to find a sorbent compatible for sampling *s*-tetrachloroethane in air.

In this article, an acid-treated PAC is described for sampling *s*-tetrachloroethane and other related chlorinated aliphatic hydrocarbons in air. In addition, a comparative study on the stability of *s*-tetrachloroethane on NIOSH charcoal, untreated PAC and acid-treated PAC sorbents is presented, and an explanation is given for the cause of the decomposition reaction.

EXPERIMENTAL

Reagents and equipment

A Varian Aerograph Series 2860 gas chromatograph, a Varian Model A-25 recorder, and an Autolab System I computing integrator were used throughout this investigation for quantitative analysis.

A 6.1 m \times 3.2 mm O.D. \times 2.4 mm I.D. stainless-steel tube was packed with 20% (w/w) of OV-101 and 0.1% (w/w) of Carbowax 1500 coated on Supelcoport (80–100 mesh) with a column packer. The packed column was preconditioned at 150° for 24 h with helium before use.

A Varian gas chromatograph–Bendix time-of-flight mass spectrometer (Series 1800 and Model MA-2, respectively), and Du Pont Model 21-104 mass spectrometer were used to identify the major decomposition products from *s*-tetrachloroethane. Fragmentation patterns were obtained at 70 eV ionizing voltage and a 250° source temperature. The mass range was scanned electrostatically.

Granular Pittsburgh Activated Carbon, 12 \times 30 standard mesh size, was purchased from Calgon (Pittsburgh, Pa., U.S.A.) to prepare sampling tubes. Commercially prepared NIOSH sampling tubes, lot 103, were obtained from SKC (Pittsburgh, Pa., U.S.A.).

s-Tetrachloroethane, 1,2-dichloroethane, and trichloroethylene were purchased from Matheson, Coleman & Bell (East Rutherford, N.J., U.S.A.). Spectrograde carbon tetrachloride and tetrachloroethylene were obtained from Mallinckrodt (St. Louis, Mo., U.S.A.) and Chemical Samples Co. (Columbus, Ohio, U.S.A.), respectively. In all cases the indicated purity of these chemicals was >99 mol%. AR grade carbon disulfide was purchased from Mallinckrodt.

The dynamic generating system for producing known concentrations of a specific analyte in air was accomplished with a Model 309 calibration system manufactured by Analytical Instrument Development (AID; West Chester, Pa., U.S.A.).

Helium and ultrapure hydrogen in H-size cylinders were purchased from Matheson Company. Air was obtained from Los Alamos Scientific Laboratory Gas Facility, prepared by mixing liquified oxygen and nitrogen to 21% oxygen. For flow controls, all cylinders were equipped with pressure regulators and needle valves.

Hamilton syringes (10 μ l), volumetric pipettes, and vials (3- and 20-ml capacity) with screw caps equipped with Mininert valves were used to prepare the solutions.

Methods

Various analytical parameters were initially investigated to optimize the gas chromatographic conditions for analysis. A mixed liquid phase, consisting of 20% (w/w) of OV-101 and 0.1% (w/w) of Carbowax 1500 coated on Supelcoport (80–100

mesh), separated the chlorinated hydrocarbons³ in a test mixture composed of 1,2-dichloroethane, carbon tetrachloride, trichloroethylene, tetrachloroethylene, and *s*-tetrachloroethane. However, to achieve the desired separation of solvent and analytes for quantitation, a column longer than 3 m was required and a 6.1 m × 3.2 mm O.D. stainless-steel column was found to be the best compromise. Based on peak symmetry and separation, air and helium flow-rates of 350 and 30 ml/min produced chromatograms that were best suited for analysis. Using these conditions, the hydrogen flow-rate was varied and tested with the five-component mixture at four different concentrations to establish the influence of hydrogen flow-rate on the peak areas of the analytes. A maximum signal (counts) for all compounds occurred at a hydrogen flow-rate of 30 ml/min at column temperatures of 80° and 125°.

Previous work had shown that the volume of CS₂ solvent usually influences the peak area of the sample. To control this effect, a constant volume of solvent (1 μl) was used to introduce samples and standards into the gas chromatograph. Calibration curves for each of the five compounds were found to be linear within the concentration range of interest.

Identification of decomposition products. The identification of the major decomposition products of *s*-tetrachloroethane absorbed on PAC and NIOSH charcoal sorbents was verified by relative retention time measurements and mass spectrometric data. Known samples and CS₂ extracts from *s*-tetrachloroethane-NIOSH charcoal (sample A) and *s*-tetrachloroethane-PAC samples (sample B) were analyzed under identical conditions. From the relative retention times shown in Table I, the decomposition products are tentatively identified as trichloroethylene and tetrachloroethylene, the latter being present in trace quantity (less than 0.1 μg/ml of CS₂). To verify the chromatographic data mass spectrometric analyses were also performed on samples A and B.

Table II lists the partial fragmentation patterns of the organic chlorides of interest. As can be seen, each compound has a major peak in its spectrum relatively

TABLE I

RELATIVE RETENTION TIME MEASUREMENTS OF *s*-TETRACHLOROETHANE AND OTHER RELATED COMPOUNDS

Compound	Known sample	Relative retention time	
		Sample A	Sample B
Methylene chloride	0.19		
Carbon disulfide, 1st peak	0.20	0.20	0.21
Carbon disulfide, 2nd peak	0.23	0.23	0.24
Chloroform	0.27		
1,2-Dichloroethane	0.30		
1,1,1-Trichloroethane	0.31		
Carbon tetrachloride	0.34		
Trichloroethylene	0.38	0.38	0.39
1,1,2-Trichloroethane	0.50		
Tetrachloroethylene	0.66	0.66*	0.66*
1,1,1,2-Tetrachloroethane	0.78		
<i>s</i> -Tetrachloroethane (ref. compound)	1.00	1.00	1.00

* Only trace amount (less than 0.1 μg/ml of CS₂).

TABLE II
 PARTIAL FRAGMENTATION PATTERNS OF C₂-CHLORIDES AND CS₂ EXTRACT SAMPLES
 — = Contribution of less than 0.5 %.

Compound	Nominal mass (m/e)															
	60	61	62	63	82	83	84	94	95	96	98	130	131	166		
1,2-Dichloroethylene (<i>cis,trans</i>)	21-24	100	9-10	23	—	—	1	—	2-3	67-73	43-47	—	—	—		
1,1-Dichloroethane	2	7	5	100	1	11	—	—	—	—	5	—	—	—		
1,2-Dichloroethane	3	12	100	19	—	—	—	—	—	—	14	—	—	—		
Trichloroethylene	67	5	21	—	—	1	—	—	100	7	—	60	2	—		
Tetrachloroethylene	1	—	—	—	9	5	38	—	1	24	4	2	74	100		
<i>s</i> -Tetrachloroethane	8	7	3	2	—	100	1	—	7	4	—	—	5	3		
Sample A (halide only)	34	13	—	—	—	100	—	—	7	5	—	1	3	2		
Sample B (halide only)	71	17	—	—	—	100	—	—	18	12	—	8	3	2		

free from interferences from either CS_2 or other chlorides. Comparison of the mass spectral data of samples A and B with those of the calibration data revealed the presence of trichloroethylene and dichloroethylene decomposition products. Dichloroethylene was not observed on the chromatogram as it is obscured by the CS_2 solvent peak and could not be resolved for identification purposes. The tetrachloroethylene product was not detected by mass spectrometry because of its low concentration in the extract as mentioned above. A reasonable explanation for the presence of these products is that two simultaneous reactions of *s*-tetrachloroethane must occur on the sorbent. The dehydrohalogenation reaction of *s*-tetrachloroethane leads to trichloroethylene and dichloroethylene products, while the dehydrogenation reaction produces tetrachloroethylene.

Attempts were made to modify the PAC sorbent so that the final product would stabilize the collected *s*-tetrachloroethane sample and would have a capacity to retain *s*-tetrachloroethane at the 1-TLV (Threshold Limit Value, 5-ppm) concentration in air at a sampling rate of 0.2 l/min for an 8-h period. Various treatments were tested on PAC, and the acid-treated PAC sorbent proved to be acceptable for air sampling of *s*-tetrachloroethane.

Preparation of acid-treated PAC sorbent and sampling tube. 12 g of PAC and 50 ml of 1 N HCl were refluxed for 2 h and then washed several times with distilled water. The PAC was refluxed with 250 ml of water for an additional hour. The sorbent was filtered and rinsed with distilled water. To activate the sorbent, the PAC was packed in a pyrex tube and purged with helium while heating the tube in an oven maintained at 250° for 16 h.

The acid-treated PAC was packed in a 4 mm I.D. pyrex tube as two separate sections with the same physical dimensions as the commercial NIOSH charcoal tube. The first section contained 90 mg of sorbent and the second section 30 mg. Quartz-wool plugs were used in place of the polyurethane foam plugs to retain and separate the sections. These sampling tubes were sealed with plastic caps for storage before use.

Sampling and analytical procedure. An air sample containing *s*-tetrachloroethane or other chlorinated hydrocarbons is drawn through the acid-treated PAC tube at 0.2 or 1 l/min and the sample is collected on the first section. After sampling, each section with its quartz-wool plugs is transferred into a 3-ml vial and 1 ml of CS_2 is added for extraction. Immediately, the vial is capped with a Mininert valve and the sample is agitated occasionally for 30 min. A 1- μ l aliquot of the extract is introduced into the gas chromatograph equipped with a 6.1-m 20% OV-101 and 0.1% Carbowax 1500 column for analysis. Column temperature is controlled at 80° for 1,2-dichloroethane and carbon tetrachloride analysis and 125° for trichloroethylene, tetrachloroethylene and *s*-tetrachloroethane analysis. Inlet and detector temperatures are held at 140° and 150°, respectively. Flow-rates of helium, hydrogen and air are maintained at 30, 30 and 350 ml/min, respectively. Peak area of the analyte is measured with an Autolab System I computing integrator and related to concentration via a calibration curve prepared previously with standards.

RESULTS AND DISCUSSION

Desorption efficiency of CS_2 for *s*-tetrachloroethane absorbed on NIOSH charcoal and acid-treated PAC was evaluated by static testing. Known amounts of

sample were applied on 90 mg of sorbent contained in a 1-ml volumetric flask. These samples were stoppered and allowed to equilibrate at room temperature for 24 h after which extraction was accomplished by adding 1 ml of CS₂. After 30 min with occasional shaking, the extract was analyzed gas chromatographically. Results from this study are summarized in Table III. With both types of sorbents, quantitative recovery of *s*-tetrachloroethane was achieved with CS₂ extraction.

TABLE III

DESORPTION STUDY OF CS₂ FOR *s*-TETRACHLOROETHANE ON NIOSH CHARCOAL AND ACID-TREATED PAC SORBENTS

Sorbent	Number of determinations	<i>s</i> -Tetrachloroethane		
		Amount applied (mg)	Average amount found (mg)	Average recovery (%)
Acid-treated PAC	3	0.30	0.29	96.7
Acid-treated PAC	3	0.50	0.49	98.0
Acid-treated PAC	3	1.00	0.98	98.0
Acid-treated PAC	3	1.60	1.56	97.5
				97.6 ± 0.6
NIOSH charcoal	3	0.30	0.29	96.7
NIOSH charcoal	3	1.00	0.96	96.0
NIOSH charcoal	3	1.60	1.55	96.8
				96.5 ± 0.4

Of equal importance is the capacity of the sorbent to retain *s*-tetrachloroethane. A dynamic testing method was selected to apply known amounts of sample on the sorbent. A diffusion cell was charged with *s*-tetrachloroethane (>99%) and placed in an AID generator. The conditions were found to produce a 1-TLV (5-ppm) concentration of this material in air at flow rates of 0.2 and 1 l/min, and air samples were collected on commercially prepared NIOSH charcoal tubes and acid-treated PAC tubes with the same configuration. As shown in Table IV, each sampling tube is effective in collecting a 1-TLV air concentration of *s*-tetrachloroethane at the specified sampling rates for an 8-h period with essentially no break-through into the second section.

TABLE IV

COLLECTION EFFICIENCY OF ACID-TREATED PAC AND COMMERCIALY PREPARED NIOSH CHARCOAL TUBES FOR *s*-TETRACHLOROETHANE IN AIR

Sampling tube	No. of determinations	Conc. of <i>s</i> -tetrachloroethane (ppm)	Sampling rate (l/min)	Length of sampling (min)	Amount found (wt. %)	
					1st Section	2nd Section
Acid-treated PAC	4	5	0.2	480	100	0
NIOSH	4	5	0.2	480	100	0
Acid-treated PAC	4	5	1	480	99.9	0.1
NIOSH	4	5	1	480	100	0

Since sample storage is also an important parameter for consideration, another set of samples was collected from the AID generator. A 10-l air sample containing 5 ppm *s*-tetrachloroethane was collected at a flow-rate of 1 l/min through each sampling tube and these tubes were capped and stored for varying lengths of time (up to 7 days) prior to analysis, to determine the stability of *s*-tetrachloroethane. The data are shown graphically in Fig. 1. Typical chromatograms (from samples stored for 3 days) are reproduced in Fig. 2.

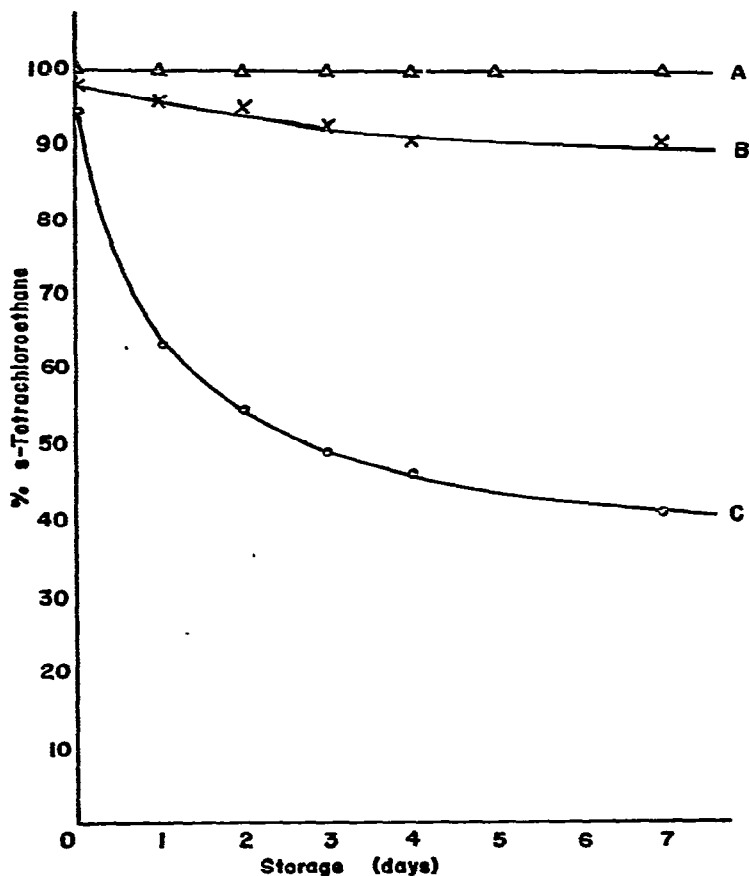


Fig. 1. Storage study of *s*-tetrachloroethane on NIOSH and PAC sorbents. A = Acid-treated PAC sampling tube; B = commercially prepared NIOSH charcoal sampling tube; C = untreated PAC sampling tube. Each point represents an average of 3-4 determinations.

It can be seen that the untreated PAC is unacceptable for sampling *s*-tetrachloroethane as only 41% of the original sample is recovered after 7 days of storage. With the commercial NIOSH charcoal tubes, 90% of *s*-tetrachloroethane is recovered at the end of the same time period. However, with longer storage, greater losses can be anticipated. On the other hand, the acid-treated PAC produces the best results. As Fig. 1 indicates, 98.7% of the *s*-tetrachloroethane is found after 7 days of storage. On

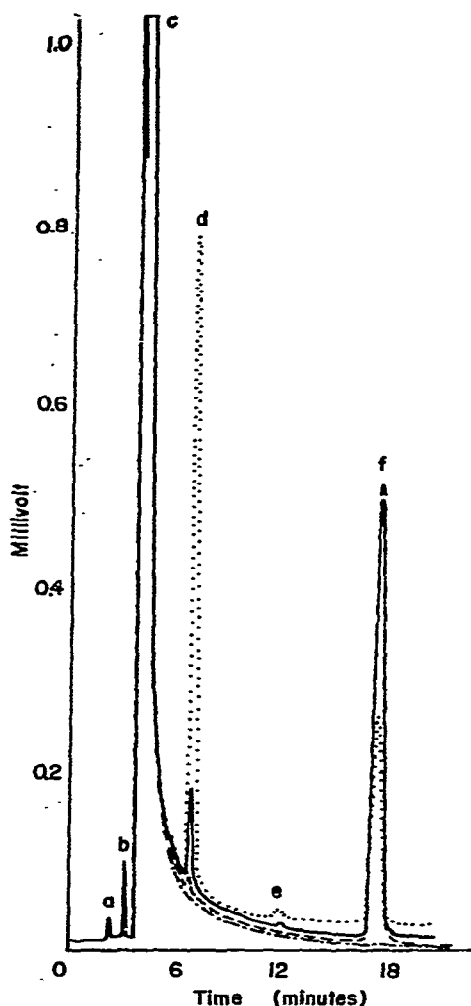


Fig. 2. Chromatograms of CS_2 extracts. Chromatographic conditions: Column, $6.1 \text{ m} \times 3.2 \text{ mm O.D.} \times 2.4 \text{ mm I.D.}$ 20% OV-101 + 0.1% Carbowax 1500 on 80-100-mesh Supelcoport; temperatures: column, 125° ; inlet, 140° ; detector, 150° ; flow-rate of helium (carrier gas), 30 ml/min; hydrogen flow-rate, 30 ml/min; air flow-rate, 350 ml/min; recorder speed, 25.4 cm/h; electrometer range, 10^{-12} A/mV , attenuation, $\times 16$. Sample: 5 ppm *s*-tetrachloroethane in air collected on sorbent and stored for 3 days. Sample size: $1 \mu\text{l}$ of a 1-ml CS_2 extract analyzed by gas chromatography. — = Commercial NIOSH charcoal tube; \cdots = untreated PAC tube; - - - = acid-treated PAC tube; - · - = blank (PAC- CS_2 extract). a and b are unknowns present in PAC- CS_2 extract; c = CS_2 ; e = tetrachloroethylene; d = trichloroethylene; f = *s*-tetrachloroethane.

this basis, the acid-treated PAC is the sorbent of choice for sampling *s*-tetrachloroethane in air. However, the NIOSH charcoal may also be improved by similar treatment, but this was not evaluated.

To assure the reproducibility of the acid-treatment procedure, three separate batches (12 g each) of PAC were prepared and tested. Three sets of samples were collected, stored, and extracted with CS_2 for analysis. Table V summarizes the results.

TABLE V
REPRODUCIBILITY OF PAC ACID TREATMENT
Concentration of *s*-tetrachloroethane, 5 ppm.

<i>Batch no.</i>	<i>No. of determinations</i>	<i>Storage time (day)</i>	<i>Amount found (wt. %)</i>
1	4	0	99.2
2	4	0	99.3
3	4	0	99.4
1	4	1	99.1
2	4	1	99.1
3	4	1	99.2
1	4	2	99.0
2	4	2	99.0
3	4	2	99.2
1	4	3	99.0
2	4	3	98.9
3	4	3	99.0
1	4	4	98.9
2	4	4	98.9
3	4	4	99.0
1	4	5	98.9
2	—	—	—
3	—	—	—
1	2	7	98.8
2	3	7	98.6
3	4	7	98.8

In all cases, essentially identical results were obtained. Hence, the acid-treatment procedure is reproducible. With each batch of sorbent approximately 80 sampling tubes can be prepared.

Four chlorinated hydrocarbons previously tested with untreated PAC sorbent were retested with acid-treated PAC tubes to compare the collection efficiency of this sorbent toward these compounds. As can be seen in Table VI, both types of PAC sorbents have similar collection efficiencies towards 1,2-dichloroethane, carbon tetrachloride, trichloroethylene and tetrachloroethylene and both are acceptable for air-sampling purposes.

Since the decomposition reactions dictate the choice of sorbent, the cause of these reactions was briefly investigated. Spectrographic analysis was performed on the residue recovered from the PAC-HCl extract. High concentrations of alkali and alkaline-earth metals were found along with small amounts of transition metals. The latter are active catalysts for dehydrogenation reactions⁴, and the former, because of their basicity, are responsible for the dehydrohalogenation reaction⁵. Hence, caution should be exercised in extending a given sorbent for air sampling purposes based on homologues and analogues. The sample-sorbent system must be evaluated for each analyte as we have done with *s*-tetrachloroethane.

Potential interferences from nine closely related chlorinated compounds (see

TABLE VI

COLLECTION EFFICIENCY OF ACID-TREATED AND UNTREATED PAC FOR OTHER HALOGENATED ALIPHATIC HYDROCARBONS

A = acid-treated, U = untreated PAC. Sampling rate, 1 l/min.

Sorbent	Conc. in air*	No. of determinations	Length of sampling (min)	Amount found (wt. %)	
				1st Section	2nd Section
A	50 ppm of 1,2-dichloroethane	4	60	99.5	0.5
U		3	60	99.4	0.6
A	10 ppm of carbontetrachloride	4	200	98.8	1.2
U		3	200	99.1	0.9
A	100 ppm of trichloroethylene	4	45	97.6	2.4
U		4	45	99.0	1.0
A	100 ppm of tetrachloroethylene	4	45	99.7	0.4
U		4	45	99.7	0.3

* 1975 TLV's.

Table I) were tested with *s*-tetrachloroethane on the gas chromatographic system. No interferences were observed on the chromatogram. However, other compounds having the same retention time as *s*-tetrachloroethane can be expected to interfere.

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