PB83-133447

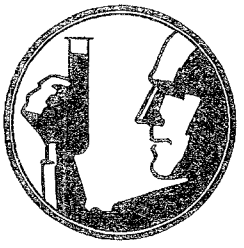
ANALYTICAL METHODS EVALUATION AND VALIDATION FOR VINYLIDENE FLUORIDE, VINYL BROMIDE, VINYL FLUORIDE, BENZENETHIOL, AND *n*-OCTANETHIOL

Research Report for Vinyl Bromide

to

DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service, Centers for Disease Control
National Institute for Occupational Safety and Health
Cincinnati, Ohio 45226

Contract No. 210-79-0100



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50272-101			
REPORT DOCUMENTATION PAGE	1. REPORT NO. 210-79-0100	2. NA	3. Recipient's Accession No. PB82 133447

4. Title and Subtitle
Analytical Methods Evaluation and Validation for Vinylidene Fluoride, Vinyl Bromide, Vinyl Fluoride, Benzenethiol, and n-Octanethiol. Research Report for Vinyl Bromide

5. Report Date
September 1981

6. NA

7. Author(s)
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8. Performing Organization Rept. No.
NA

9. Performing Organization Name and Address
Southern Research Institute
Birmingham, Alabama

10. Project/Task/Work Unit No.
NA

11. Contract(C) or Grant(G) No.
(C) 210-79-0100
(G)

12. Sponsoring Organization Name and Address
NIOSH
Cincinnati, Ohio

13. Type of Report & Period Covered
Contract

14. NA

15. Supplementary Notes
NA

16. Abstract (Limit 200 words)

A sampling and analytical method for vinyl-bromide (593602) determination in air was developed. The method involved use of solid sorbent, coconut based charcoal, desorption of the analyte with absolute ethanol, and gas chromatography/flame ionization detection. Air samples containing vinyl-bromide in concentrations ranging from 1.32 to 56.5 milligrams per cubic meter (mg/cu m), were used to evaluate the procedure. Two alternative extraction procedures were presented: continuous and multiple extraction. Vinyl-bromide was separated from ethylene, acetylene, and 1,3-dibromoethane samples, but not from bromine. Recovery of vinyl-bromide was 90 percent. The method allowed a precision of 9.0 percent Relative Standard Deviation (RSD) over the vinyl-bromide concentration range of 1.32 to 6.38 milligrams per cubic meter (mg/cu m) and 6.3 RSD over the range of 6.38 to 56.5 mg/cu m.

17. Document Analysis a. Descriptors
Anlaytical-methods, Anlaytical-processes, Air-sampling, Analytical-chemistry, Qualitative-analysis

b. Identifiers/Open-Ended Terms

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Available to Public	NA	70
	20. Security Class (This Page)	22. Price

SORI-EAS-81-405

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Research Report for Vinyl Bromide

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Project 4405-R2
September 1, 1981

ABSTRACT

This report describes the development of a sampling and analytical method for the determination of vinyl bromide in air. The developed method is based on the collection of vinyl bromide from air with a solid sorbent, coconut-based charcoal; the desorption of the analyte with absolute ethanol; and the analysis of the extract by gas chromatography with flame ionization detection. The overall method was evaluated in the concentration range of 1.32 to 56.5 mg/m^3 in 6-L air samples. The average bias from the concentration determined by an independent method was about +3% over the entire range of the method. The precision of the overall sampling and analytical method was 9.0% RSD over the vinyl bromide concentration range of 1.32 to 6.38 mg/m^3 and 6.3% RSD over the range of 6.38 to 56.5 mg/m^3.

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AN AIR SAMPLING AND ANALYTICAL METHOD FOR VINYL BROMIDE

I. GENERAL CONSIDERATIONS

A. Background

The need for air sampling and analytical methods for toxic contaminants in the workplace arises from provisions of the Occupational Safety and Health Act of 1970 requiring that regulations be prescribed limiting the exposure of employees to substances or physical agents that may endanger their health or safety. To prescribe such regulations and to ensure compliance, it is necessary to have available sampling and analytical methods suitable for use by employers and by Government personnel.

Vinyl bromide is a potentially toxic workplace contaminant. The available toxicity data have been compiled in a Material Safety Data Sheet presented as Appendix A of this report. A TLV of 250 ppm (1100 mg/m^3)* has been assigned to vinyl bromide by the American Conference of Governmental Industrial Hygienists [B3]. No U.S. Federal standard for workplace exposure to vinyl bromide currently exists. However, NIOSH has recommended that an OSHA standard of 1 ppm (4.4 mg/m^3) be established. This recommendation is based on test results that revealed increased incidences of angiosarcomas of the liver and other cancers in animals [B3].

There is currently no NIOSH-validated method for the sampling and analysis of vinyl bromide. Thus, NIOSH decided to develop and evaluate a method for the compound. This report describes the work that was performed under contract with NIOSH to carry out that task.

B. Research Approach

The general approach to the development of the method involved several steps. First, a literature search for information relating to air sampling and analytical methodology for the compound was performed. Second, an experimental protocol was devised for development of the method according to NIOSH guidelines. The protocol was reviewed by NIOSH. A method was then developed and evaluated according to the revised protocol. Upon the completion of the evaluation of the method, a written description of the method and a sampling data sheet were submitted to NIOSH.

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* In this report all vapor concentrations (given in units of mg/m^3) and all gas flow rates (given in units of L/min) are expressed for 25 °C.

The information gathered in the literature search has been incorporated into an outline that classifies the material according to the following topics:

- Physical and chemical properties.
- Toxicity.
- Manufacture.
- Commercial uses.
- Analytical procedures.
- Air sampling and analytical procedures.
- Properties of candidate sorbent materials.

The outline serves to annotate briefly the information and has been included as the bibliography (Section VII) of this report. Not all of the references listed in the bibliography are cited in the text of this report.

The protocol that was employed in the development and evaluation of the sampling and analytical method was comprised of the following tasks:

- Optimization of the analytical procedure.
- Calibration of the analytical method.
- Screening tests to select the best sorbents. These included the determination of desorption efficiencies of vinyl bromide from solid sorbents by solvent extraction and the determination of the stability of analyte spikes on solid sorbent materials.
- Construction and evaluation of an analyte vapor generator and sampling system (see Appendix B).
- Determination of the capacities of candidate sorbents for vinyl bromide.
- Determination of the stability of vinyl bromide collected from air with the sorbent of choice.
- Determination of the accuracy and precision of the analytical procedure, including the extraction step.
- Determination of the accuracy and precision of the total sampling and analytical method.

The developed method was tested and modified until it was considered valid. The following criteria were employed for validation:

- The efficiency of the desorption of vinyl bromide from the sorbent of choice with an appropriate solvent had to be at least 0.8.

- The bias of the method from a reliable independent method had to be no more than about ±10%.

- The relative standard deviation (RSD) of the overall sampling and analytical procedure had to be no greater than the value necessary to ensure that the average result was within ±25% of the "true" result. For a bias of ±10%, the RSD should be no greater than 8%; however, for a non-biased method, the RSD should be no greater than about 10% [11].

- The mean of the results obtained with exposed sorbent tubes that were stored for 1 d could not differ statistically at the 0.05 significance level from the mean of results obtained with exposed tubes that were stored for 7 or 14 d.

One other specific task in the development and evaluation of the method was to find the lowest level of vinyl bromide that could be extracted from the sampling medium with at least an efficiency of 0.8 and with an RSD of 10%. This level was to be called the lowest analytically quantifiable level (LAQL). The lower concentration limit of the method was then to be defined as the LAQL in the recommended air sample volume. As is discussed below, a value was assigned to the LAQL that gave a higher extraction efficiency and a lower RSD than required.

The details of the analytical method developed for vinyl bromide are presented in this report in Appendix D (Method Description) and Appendix E (Sampling Data Sheet).

II. DEVELOPMENT AND EVALUATION OF THE ANALYTICAL METHOD

Gas chromatography was chosen as the analytical method for determining vinyl bromide on the basis of previous NIOSH work. Bales determined vinyl bromide in workplace air by gas chromatography using a procedure similar to that given in NIOSH Method P&CAM No. 127 [D1], and NIOSH recommended the use of gas chromatography with flame ionization detection (FID) using a 20-ft SE-30 column for the determination of vinyl bromide [B3].

We utilized four separate gas chromatographs during the development and validation of a method for vinyl bromide. A Hewlett-Packard Model 5750 GC with FID was used in the preliminary desorption efficiency and stability tests with candidate solid sorbents. A Tracor Model 560 GC with a Tracor Model 700A Hall electrolytic conductivity detector was used in the determination of the weight capacities of selected solid sorbents. A Perkin-Elmer Model Sigma 2 GC with FID was used in the determination of the LAQL, the stability of VBr collected from air on charcoal, the accuracy and precision of the analytical procedure, and the accuracy and precision of the total sampling and analytical method. In addition, another Hewlett-Packard Model 5750 GC was briefly employed to evaluate the response of an electron capture detector (ECD) to vinyl bromide.

We encountered persistent instrumental problems with the Hewlett-Packard gas chromatographs early in the development of the method. For this reason we switched to the use of the Tracor GC. However, recurrent instrument problems and lack of sensitivity with the Tracor GC caused us to switch again to another instrument—the Perkin-Elmer Sigma 2 with FID. This instrument operated satisfactorily and gave the best response to vinyl bromide of any of the instruments evaluated.

The detection limits for vinyl bromide found with the various combinations of gas chromatographs and detectors are as follows:*

- HP 5750 with FID: 13 ng
- HP 5750 with ECD: 40 ng
- Tracor 560 with Hall detector: 9 ng
- Perkin-Elmer Sigma 2 with FID: <1 ng

The most satisfactory sensitivity for vinyl bromide was found with the Perkin-Elmer Sigma 2 instrument. However, the sensitivities of the other chromatographs were adequate for the determinations made with them during the sorbent screening tests.

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* The detection limit was defined as the quantity of vinyl bromide in a single injection that gave a peak height approximately twice the background noise level.

A. Selection of Appropriate Operating Conditions

The optimum operating conditions for the determination of vinyl bromide were obtained with the Perkin-Elmer Sigma 2 gas chromatograph with FID. Similar operating conditions were used with the Hewlett-Packard Model 5750 GC and the Tracor Model 560 GC. The operating conditions used were as follows:

- Chromatograph: Perkin-Elmer Sigma 2.
- Detector: flame ionization (FID).
- Column: 6-m long by 2-mm i.d. nickel column packed with 10% FFAP on 80/100 mesh, acid-washed DMCS Chromosorb W.
- Carrier gas: nitrogen, 25 mL/min.
- FID air flow rate: ∿400 mL/min.
- FID hydrogen flow rate: ∿90 mL/min.
- Column temperature: isothermal at 50 °C for 3 min, programmed at 40 °C/min to 225 °C and maintained at 225 °C for 5 min.*
- Injection port temperature: 140 °C.
- FID temperature: 240 °C.
- Injection volume: 5 µL.

In addition to the 10% FFAP analytical column, two other GC columns were also evaluated. These columns were:

(1) a 6-m long by 2-mm i.d. nickel column packed with 10% SE-30 on 80/100-mesh, acid washed DMCS Chromosorb W, and

(2) a 4-m long by 2-mm i.d. nickel column packed with 80/100 mesh Porapak Q.

All three column packing materials were chosen for evaluation on the basis of their prior use in the determination of vinyl halides. Porapak Q was used in the first phase of this contract in the determination of vinylidene fluoride and vinyl fluoride. Ten percent FFAP is the column packing material in NIOSH Method P&CAM No. 127 for organic solvents. This method was used by Bales

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* Vinyl bromide was eluted from the column within 3 min at 50 °C; the column temperature was then increased to 225 °C to elute ethanol, which was subsequently chosen as the extraction solvent in the sorbent desorption procedure.

for the determination of vinyl bromide [D1]. Ten percent SE-30 is the column packing material in NIOSH Method No. 178 for vinyl chloride.

The column packed with 10% FFAP was selected over the other two columns because the Porapak Q column gave an extremely noisy GC response at the high temperature required to elute vinyl bromide (200 °C) from the column and because the SE-30 column would not completely separate vinyl bromide from ethanol, which was subsequently selected as the extraction solvent in the sorbent desorption procedure.

The gas chromatographic procedures were evaluated for interferences by injecting 1-mL aliquots of gas mixtures of vinyl bromide in nitrogen into the GC's. Two sources of vinyl bromide were used: gaseous vinyl bromide (98% purity) obtained from the Linde Division of Union Carbide and a certified gas mixture of 994 ppm vinyl bromide in nitrogen obtained from Matheson Gas Products. Several potential interferents were injected in a few experiments. The compounds injected were ethylene, acetylene, bromine, and 1,2-dibromoethane (ethylene dibromide). These compounds were selected because they are either starting materials or intermediates in the commercial preparation of vinyl bromide. The 10% FFAP column was able to separate vinyl bromide from all of the potential interferents except bromine.

B. Calibration of the Gas Chromatographic Method for Vinyl Bromide

The GC response to vinyl bromide was usually calibrated by injecting aliquots of standard solutions of vinyl bromide in ethanol into the GC and measuring the peak heights of the GC responses to vinyl bromide. A concentrated stock solution of vinyl bromide in ethanol was first prepared according to the following procedure:

- Several milliliters of absolute ethanol was transferred to a volumetric flask, and the flask was accurately weighed on an electronic balance.
- The flask and its contents were chilled to near 0 °C in an ice-water bath.
- A small volume of prechilled liquid vinyl bromide at (at ~0 °C) was transferred to the volumetric flask with a prechilled syringe.
- The flask was stoppered and allowed to warm up to room temperature.
- The flask was reweighed on the electronic balance, and the weight of vinyl bromide added to the flask was determined from the weight difference of the flask.
- The flask was diluted to the mark with absolute ethanol and the solution in the flask was thoroughly mixed by shaking.

Vinyl bromide standards were then prepared by serial dilution of the stock solution with absolute ethanol. Aliquots of the ethanol solutions of vinyl bromide were withdrawn by syringe and injected into a gas chromatograph.

The standard solutions were refrigerated when they were not in use and appeared to be stable for several days, although fresh standards were routinely prepared daily during the course of the investigation. Detailed stability determinations were not made, however, of the vinyl bromide standard solutions.

The calibration curve for vinyl bromide concentration versus peak height obtained with the Perkin-Elmer Sigma 2 GC is shown in Figure 1. The curve was found to be linear over the concentration range tested (0.25 to 50 µg/mL), with a correlation coefficient of 0.9998.

Similar curves were obtained for the determination of solution standards with the HP 5750 with FID and the Tracor 560 with the Hall detector. With the HP 5750 with FID operating under similar GC conditions as the Perkin-Elmer Sigma 2, except that the column temperature was 80 °C, a plot of peak height versus concentration was linear over the concentration range of 4 to 80 µg/mL with a correlation coefficient of 0.9998. With the Tracor 560 operating under GC conditions similar to those of the HP 5750 with FID and with detector operating parameters recommended by the manufacturer, again a plot of peak height as a function of vinyl bromide concentration was linear in the concentration range of 4 to 400 µg/mL with a correlation coefficient of 0.9993.

The Tracor 560 was also calibrated with vinyl bromide gas standards in nitrogen. The standards were prepared by diluting the 994 ppm (4371 mg/m^3) vinyl-bromide-in-nitrogen certified gas mixture with nitrogen in sealed glass flasks. A graduated gastight syringe was employed in the preparation and transfer of vinyl bromide gas standards. With 1-mL injections, the GC response (peak height) was found to be linear with respect to vinyl bromide concentration over the range of 40 to 400 mg/m^3 with a correlation coefficient of 0.9995.

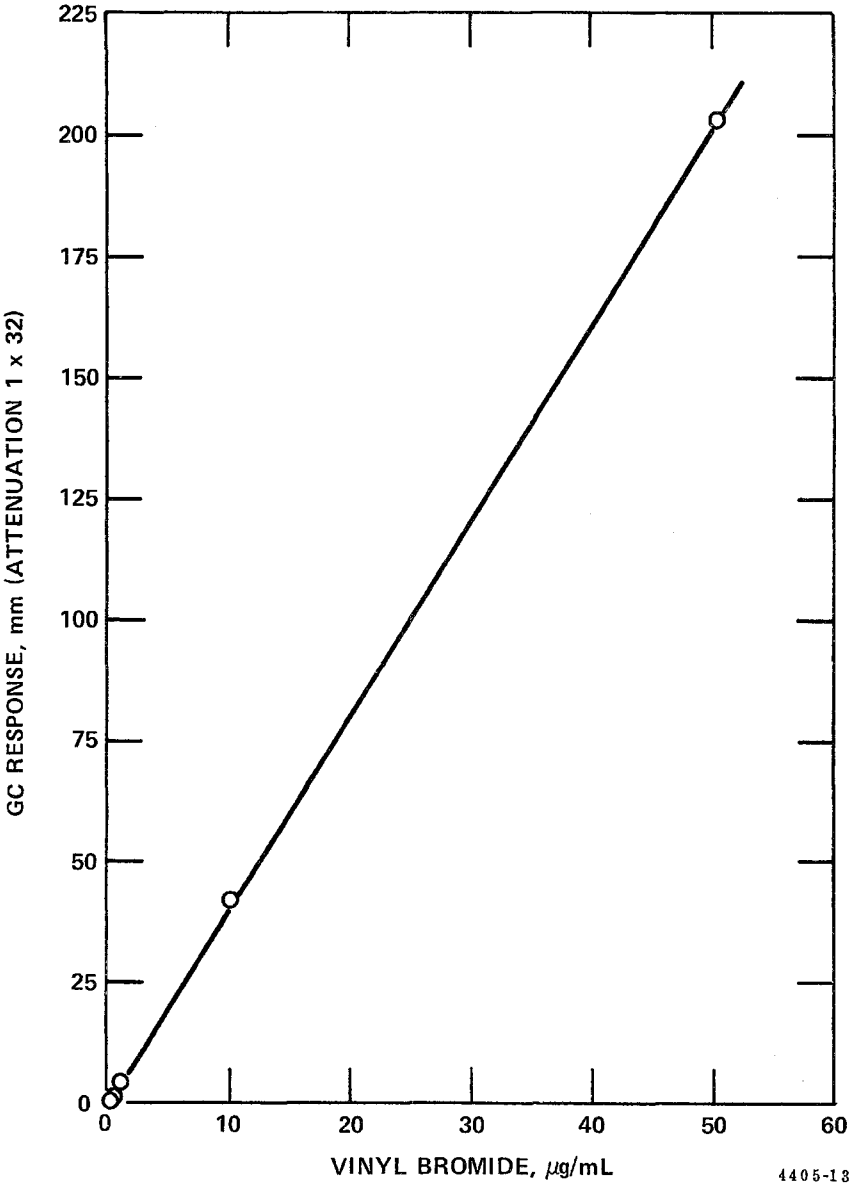

Figure 1. GC calibration curve for vinyl bromide with 5-µL injection volumes.

III. SELECTION OF COLLECTION MEDIUM AND PRELIMINARY EVALUATION

A. Description of Candidate Sorbents

Several nonreactive sorption media were evaluated for the collection of vinyl bromide from air. The sorbent materials that were investigated are listed and briefly described in Table I.

B. Selection of Extraction Solvent

Several organic solvents were evaluated as extraction solvents for vinyl bromide: acetone, acetonitrile, carbon disulfide, chloroform, cyclohexane, ethanol, methanol, *n*-propanol, and toluene. Of these solvents, only ethanol, *n*-propanol, and toluene were able to be separated from vinyl bromide in the determination of dilute solutions of the analyte by the GC procedures described above. All three solvents eluted at longer retention times than vinyl bromide, but ethanol had a shorter retention than either *n*-propanol or toluene and was thus selected as the extraction solvent. As discussed in subsequent sections of this report, ethanol was found to readily extract vinyl bromide from charcoal at all of the vinyl bromide levels evaluated in the development of a method.

C. Desorption Efficiency and Stability Tests

Vinyl bromide was expected to be readily adsorbed by most of the candidate sorbent materials. Thus the weight capacities of many of the sorbents for vinyl bromide were expected to be satisfactory. The suitability of a particular sorbent material was initially judged, therefore, on the recovery of sorbed vinyl bromide from the sorbent material by solvent extraction. The term "desorption efficiency" was applied to the recovery of vinyl bromide from spiked sorbent samples obtained after 1 d of storage. For sorbent samples stored for more than 1 d, the recovery was then considered to be related not only to the "desorption efficiency" but also to the "stability" of the analyte on the sorbent.

1. Experimental procedure

Screening tests were conducted to determine the recoveries of vinyl bromide from spiked sorbent tubes of the candidate sorbent materials.

The Porapak porous polymer sorbent materials were cleaned prior to use by Soxhlet extraction. Several grams of each sorbent was extracted with an acetone-methanol solution for 6 h. The material was then extracted for 6 h with methanol alone and dried under vacuum at 70 to 100 °C. The other sorbent materials evaluated were not subjected to any pretreatment prior to use.

For most of the candidate sorbent materials, several 4-mm i.d. Pyrex tubes were each packed with a 150-mg sorbing section and a 50-mg backup section of sorbent. With Carbosieve B and Tenax GC, each tube was packed with a 70-mg

Table I. Description and Identification of the Nonreactive Sorbents Evaluated for Vinyl Bromide

Sorbent	Specific surface area, m^2/g	Average pore diameter, Å	Description	Tested mesh size	Lot no.	Supplier
Charcoal— SKC 226-01-01	-[a]	-[a]	activated coconut charcoal	20/40	107	SKC, Inc.
Charcoal— Barnebey-Cheney 580-26	-[a]	-[a]	activated petroleum charcoal	16/24	M-2749	Barnebey-Cheney
Silica gel	100-800	22-220	dehydrated, polymerized silica	60/80	2-0290	Supelco, Inc.
Carbosieve B	1000	20-24	carbon molecular sieve	45/60	296-43A	Supelco, Inc.
Ambersorb XE-340	400	6-300	synthetic carbonaceous spheres	20/40	6-9674	Rohm and Haas
Ambersorb XE-347	350	<6-300	synthetic carbonaceous spheres	20/40	6-9675	Rohm and Haas
Ambersorb XE-348	500	<6->300	synthetic carbonaceous spheres	20/40	6-9676	Rohm and Haas
Porapak Q	850	75	copolymer of ethylvinylbenzene and divinylbenzene	50/80	838	Supelco, Inc.
Porapak R	780	76	polymer of 1-ethenyl-2-pyrrolidinone	50/80	1736	Supelco, Inc.
Porapak T	450	91	polymer of ethyleneglycodimethylacrylate	50/80	1400	Supelco, Inc.
Tenax GC	19	-	polymer of 2,6-diphenyl-p-phenylene oxide	20/40	-	Applied Science Division Milton Roy Company Laboratory Group A

a. Value unavailable. Charcoals typically have a specific surface area of several hundred to one thousand square meters per gram.

sorbing section and a 30-mg backup section. The two sorbent beds in each tube were held in place and separated with glass wool plugs. A 5-μL aliquot of an 8.07-mg/mL solution of vinyl bromide in ethanol was deposited in one of the glass wool plugs in each tube while approximately 3 L of air free of vinyl bromide was drawn through the tube at a rate of about 0.2 L/min. The vinyl bromide was vaporized and transferred onto the sorbent material. The exposed tubes were then sealed with Teflon tape and plastic caps and were stored in the dark at 25 °C. After a particular spiked sorbent material had been stored for a given period of time (ranging from 1 to 13 d), three tubes of the sorbent were extracted in ethanol. Each sorbent sample was extracted ultrasonically for 30 min with 1 mL of ethanol. Each ethanol extract was then analyzed for vinyl bromide by the gas chromatographic procedure. The Hewlett-Packard Model 5750 GC with FID was used to determine the vinyl bromide in the ethanol extracts.

2. Experimental results

The results of the recovery screening tests are presented in Table II. The minimum acceptable recovery of vinyl bromide from the spiked sorbents is 80% for all storage periods. The results in Table II clearly indicate that acceptable vinyl bromide recoveries were found only with SKC 226-01-01 coconut charcoal. Both the desorption efficiency and the recovery of vinyl bromide after 6 d of storage averaged 95%, with relative standard deviations of 4.6 and 4.7% respectively. All of the vinyl bromide recovered from the spiked coconut-charcoal sorbent tube was found in the sorbing layer of charcoal. No vinyl bromide was recovered from the backup section.

D. Capacity Tests

On the basis of the desorption efficiency and stability tests described in the previous section, the only sorbent material that merited additional evaluation was SKC 226-01-01 coconut charcoal. Weight capacity determinations of SKC coconut charcoal for vinyl bromide were made with three types of sorbent tubes: two-layer sorbent tubes packed with 100- or 150-mg sorbing layers and 50-mg backup layers of charcoal; single-layer sorbent tubes packed with 100, 150, or 400 mg of charcoal; and commercial charcoal tubes containing a 400-mg sorbing layer and a 200-mg backup layer (SKC 226-09). The tubes containing 100- or 150-mg sorbing layers were 4 mm i.d.; those containing 400-mg sorbing layers were 6 mm i.d.

In these tests vinyl bromide was sampled from a test atmosphere generator. A description of the vapor generator and sampling system is given in Appendix B of this report.

1. Experimental procedure

During each weight capacity determination, the vinyl bromide test atmosphere was sampled simultaneously through two sorbent tubes in parallel. The test atmosphere was sampled through both tubes at the same rate by means of separate critical orifices attached to a vacuum pump. One tube contained an adsorbing layer and a backup layer of charcoal. The second tube had dimensions identical to those of the first tube but was packed only with an adsorbing

Table II. Recovery of Vinyl Bromide (VBr) from Candidate Sorbent Materials by Solvent Extraction with Ethanol after Various Storage Periods[a]

Sorbent[b]	Length of storage, d	Average weight of VBr recovered,[c] µg	Average Recovery, %	RSD, %
SKC 226-01-01	1	38.4	95	4.6
coconut charcoal	6	38.3	95	4.7
Barnebey-Cheney 580-26	1	32.2	80	12.0
petroleum charcoal	7	25.8	64	8.1
Ambersorb XE-340	10	11.2	27	4.0
Ambersorb XE-347	3	11.9	29	8.5
Ambersorb XE-348	3	17.8	44	4.2
Carbosieve B[d]	1	27.8	69	15.1
Silica Gel	1	0.0	0	-
Tenax GC[d]	1	0.0	0	-
Porapak Q	13	0.0	0	-
Porapak R	13	0.0	0	-
Porapak T	13	0.0	0	-

a. Each sorbent tube was spiked with 40.4 µg of vinyl bromide.

b. Each sorbent tube was packed with a 150-mg sorbing layer and a 50-mg backup layer of the indicated sorbent except where noted.

c. For each sorbent material, three spiked sorbent tubes were extracted and analyzed after each indicated storage period.

d. Sorbent tubes were packed with a 70-mg sorbing layer and a 30-mg backup layer.

layer of charcoal (the same amount as was used in the adsorbing layer of the two-section tube). The second tube also had a sidearm at right angles to the cylindrical axis of the packed portion of the tube on the pump side of the charcoal bed. The sidearm was capped with a rubber septum. A gastight syringe was used to monitor the generator effluent that was sampled through the single adsorbing layer of this sorbent tube to determine the breakthrough of vinyl bromide. This was done by withdrawing aliquots of the sampling stream through the septum with a gastight syringe and analyzing the gas aliquots for vinyl bromide by GC.

Each tube was inserted into the sampling chamber of the test atmosphere generator so that the packed sorbent layers of each tube were totally within the chamber and thus maintained at the same temperature as the test atmosphere (40 °C). The vinyl bromide test atmosphere was sampled through the two sorbent tubes until the vinyl bromide concentration in the effluent of the single-layer tube reached 5% of that in the test atmosphere generator. The concentration of vinyl bromide in the test atmosphere generator was calculated from the concentration of a certified gas mixture of vinyl bromide in nitrogen (994 ppm v/v) and the measured flow rates of the gas mixture and the dilution air entering the generator.

After the vinyl bromide test atmosphere had been sampled through the two sorbent tubes, each charcoal layer in the exposed tubes was separately extracted in absolute ethanol. The amount of vinyl bromide in each ethanol extract was then determined by GC. All of the GC analyses performed in these determinations were made with a Tracor Model 560 gas chromatograph equipped with a Model 700A Hall electrolytic conductivity detector.

2. Experimental results

The results of the weight capacity determinations for vinyl bromide on SKC coconut charcoal are given in Tables III, IV, and V. Table III summarizes the average weight capacities and breakthrough volumes for vinyl bromide found with the various quantities of SKC coconut charcoal evaluated. Tables IV and V list the detailed breakthrough and recovery data for SKC 226-09 coconut charcoal sampling tubes.

An acceptable value for the capacity of a sorbent for vinyl bromide can be estimated from the exposure limit of 4.4 mg/m^3 (4.4 µg/L) for vinyl bromide recommended by NIOSH. Since the minimum sampling time required for successful validation of a NIOSH method is 2 h, and a typical low sampling rate is 0.05 L/min, a desirable minimum value for the capacity of a sorbent tube should be about 25 µg with a corresponding minimum breakthrough volume of about 6 L. All of the determined weight capacities were significantly greater than the estimated minimum value for the capacity of a vinyl bromide sorbent tube. However, the breakthrough volumes were greater than the desired minimum volumes only with the sorbent tubes containing a 400-mg sorbing layer of charcoal. Thus, on the basis of the breakthrough results, it appeared that an acceptable sampling method for vinyl bromide could be based on the use of an SKC 226-09 charcoal sampling tube, which contained a 400-mg sorbing layer of coconut charcoal and a 200-mg backup layer.

Table III. Summary of the Average Weight Capacities and Breakthrough Volumes for Vinyl Bromide (VBr) on SKC Coconut Charcoal

Quantity of charcoal in sorbent tube, mg sorbent layer/ backup layer	VBr generator concentration, µg/L	Sampling rate, mL/min	Weight capacity, mg	Breakthrough volume, L
100/50	190	200 or 50	0.5	2.5
150/50	950	200 or 50	3.2	3.5
400/200	125	200	1.3	10.4

Table IV. Breakthrough Data for Vinyl Bromide (VBr) on SKC Coconut Charcoal[a]

Sorbent sample set no.	Concn of VBr in generator,[b,c] µg/L	Sampling rate, L/min	Breakthrough time,[d] min	Breakthrough volume,[e] L	Weight capacity,[f] mg
1	120	0.20	40	8.0	0.96
2	130	0.20	34	6.8	0.88
3	130	0.20	60	12.0	1.56
4	130	0.20	41	8.2	1.07
5	130	0.20	66	13.2	1.72
6	130	0.20	60	12.0	1.56
7	130	0.05	245	12.3	1.60

a. Commercial SKC 226-09 charcoal tubes with the 400-mg sorbing sections intact but with the 200-mg backup sorbent sections removed were used in all of the determinations listed in this table.

b. Relative humidity >80%.

c. Calculated from measured flow rates of the dilution air and the standardized gas mixture of VBr in nitrogen (994 ppm v/v) entering the generator.

d. The time required for the VBr concentration in the sampling tube effluent to reach 5% of that in the tube influent.

e. Sampling rate multiplied by breakthrough time.

f. Breakthrough volume multiplied by VBr generator concentration.

Table V. Recovery of Vinyl Bromide (VBr) from SKC Coconut Charcoal

Sorbent sample set no.	Type of breakthrough indicator[a]	Weight of VBr recovered, µg: Sorbent layer	Breakthrough indicator[b]	Total	Weight of VBr sampled,[c] µg	% Recovery[d]
1	Syringe sampler	1080	20	1100	1060	104
	Backup sorbent section	1020	310	1330	1120	119
2	Syringe sampler	780	60	840	1080	78
	Backup sorbent section	880	40	920	1130	81
3	Syringe sampler	1660	10	1670	1410	118
	Backup sorbent section	1540	40	1580	1460	108
4	Syringe sampler	1250	40	1290	1180	109
	Backup sorbent section	1260	10	1270	1230	103
5	Syringe sampler	1640	30	1670	1520	110
	Backup sorbent section	1520	50	1570	1590	99
6	Syringe sampler	1090	7	1100	1120	98
	Backup sorbent section	1040	9	1050	1160	91
7	Syringe sampler	1300	6	1390	1250	111
	Backup sorbent section	1270	226	1500	1250	120

a. The syringe sampler is described in the text. The backup section contained 200 mg of SKC coconut charcoal.

b. The amount of VBr that broke through the sorbent layer of the syringe sampler was estimated graphically from a plot of percent breakthrough versus sampling time.

c. The product of the independently determined VBr generator concentration and the total volume sampled.

d. Relative to the "true" weight of VBr sampled as determined by the independent method. Not corrected for desorption efficiency.

After consultation with the Project Officer, we chose 6 L, or approximately two-thirds of the average breakthrough volume of 10.4 L found with the SKC 226-09 charcoal sampling tube, as the recommended sampling volume for vinyl bromide. This is a conservative estimate of the recommended sampling volume, and the relatively high temperature at which the samples were collected (40 °C), provides an additional margin of safety in the sampling.

This recommended sampling volume was chosen to compensate for possible reduction of the capacity of the sorbent tube under potentially harsh field sampling conditions.

The recoveries of vinyl bromide from the exposed charcoal sampling tubes relative to the expected recoveries calculated from the sampling volumes and the concentration of vinyl bromide in the test atmosphere averaged 104% with a relative standard deviation of 13%.

E. Determination of the Volume of Extraction Solvent

Although we were able to efficiently extract vinyl bromide from 150-mg charcoal beds with only 1 or 2 mL of ethanol in the preliminary desorption efficiency and stability tests, we were unable to duplicate these recoveries in later experiments using the same small volume of ethanol to extract vinyl bromide from 400-mg charcoal beds. Thus we performed a series of experiments to determine the minimum volume of ethanol necessary to efficiently extract vinyl bromide from the sorbing layer of SKC 226-09 charcoal sampling tubes.

Ten sorbent tubes (SKC 226-09 charcoal sampling tubes containing a 400-mg sorbing layer and a 200-mg backup layer) were each spiked with 40 µg of vinyl bromide. Two of the spiked sorbent tubes were extracted with 1 mL of ethanol, two tubes with 2 mL, two tubes with 5 mL, two tubes with 10 mL, and two tubes with 15 mL. Two additional sorbent tubes were each spiked with 1550 µg of vinyl bromide and then extracted with 50 mL of ethanol. Each charcoal bed was extracted ultrasonically for 45 min. The vinyl bromide contents of the ethanol extracts were then determined by the GC analytical method, and the vinyl bromide recoveries were calculated.

The results of this recovery experiment are listed in Table VI.

Table VI. The Effect of the Volume of Extraction Solvent on the Recovery of Vinyl Bromide (VBr) from Spiked Charcoal Tubes

Spiking level, µg VBr	Extraction volume, mL EtOH	Average VBr recovery, %
40	1	63
40	2	71
40	5	74
40	10	82
40	15	92
1550	50	98

On the basis of these results we chose 15 mL as the minimum volume of ethanol needed to efficiently extract vinyl bromide from spiked or exposed sorbent tubes in the sampling and analytical method. The selection of 15 mL represented a trade-off between small extraction volume and high desorption efficiency (>90%).

F. Determination of the LAQL

The lowest analytically quantifiable level (LAQL) of vinyl bromide is defined as the lowest level of vinyl bromide that can be extracted from the chosen sampling medium (coconut charcoal) with an efficiency of at least 0.80 and a relative standard deviation (RSD) of 10% or less. The LAQL was determined by the experimental procedures described in the following paragraphs.

The first step in the procedure was the determination of the smallest quantity of vinyl bromide that could be determined in a 15-mL aliquot of ethanol by the GC analytical procedure with an RSD of 10%. This amount, X, was found to be 3.75 µg for a 5-µL injection volume.

Six SKC-226-09 charcoal sampling tubes (400-mg sorbing layer and 200-mg backup layer of coconut charcoal) were then spiked with known amounts of vinyl bromide. Two of the sorbent tubes were spiked with 7.5 µg of vinyl bromide, two with 75 µg of vinyl bromide, and two with 750 µg of vinyl bromide. These amounts of vinyl bromide corresponded to 2X, 20X, and 200X, respectively. The spiked sorbent tubes were stored for 1 d. Each tube was then extracted with 15 mL of ethanol, and the ethanol extracts were analyzed for vinyl bromide by the GC analytical method described in Section II for the Perkin-Elmer Sigma 2 with FID. Vinyl bromide standards for the GC analyses were prepared by injecting 2X, 20X, and 200X amounts of vinyl bromide into separate 15-mL aliquots of ethanol.

The results of the LAQL spiking experiments are summarized in Table VII. All recoveries were 86% or higher. In addition, although there are only two values at each spiking level, the test results at each level are very precise. The recoveries ranged no more than ±5% of the average of the two results at each test level. On the basis of these results, the LAQL was estimated to be <7.5 µg of vinyl bromide (2X). However, because we expected more variability to be introduced into the determination of vinyl bromide by the air sampling procedure than by the sorbent extraction procedure, we chose 7.5 µg of vinyl bromide as a practical value of the LAQL.

Table VII. Results of the LAQL Spiking Experiments with Vinyl Bromide (VBr)

Sorbent tube No.	Weight of VCr added to charcoal, µg	Weight of VBr recovered, µg	Recovery, %
1	750 (200X)	690	92
2	750 (200X)	719	96
3	75 (20X)	67.2	90
4	75 (20X)	67.5	90
5	7.5 (2X)	6.45	86
6	7.5 (2X)	6.63	88

G. Recovery of Vinyl Bromide from Sorbent Tubes Spiked at the LAQL

After the LAQL was determined, twelve sorbent tubes were spiked near the chosen LAQL and stored at room temperature. Six of the tubes were analyzed after 1 d and six after 8 d. The results of this spiking experiment are listed in Table VIII. The weight of vinyl bromide recovered from each of the six sorbent tubes stored for 1 d averaged 6.9 µg (89% recovery) with a standard deviation of 0.3 µg (RSD = 5.0%). The weight of vinyl bromide recovered from each of the six tubes stored for 8 d averaged 7.2 µg (93% recovery) with a standard deviation of 0.3 µg (RSD = 3.8%). The vinyl bromide recoveries for the tubes stored for 1 d were compared with the recoveries of the tubes stored for 8 d by means of Student's *t* test. The difference between the means did not differ statistically at the 5% significance level.

Table VIII. Recovery of Vinyl Bromide (VBr) from SKC 226-09 Charcoal Tubes Spiked at the LAQL (7.75 µg)

Storage time, d	Vinyl bromide found, µg	Recovery,[a] %	Average recovery, % (RSD)
1	6.64	85.6	89.1 (5.0%)
	6.36	82.1	
	7.18	92.6	
	7.18	92.6	
	6.91	89.2	
	7.18	92.6	
8	7.55	97.4	92.1 (3.8%)
	7.23	93.3	
	7.23	93.3	
	6.92	89.3	
	6.76	87.2	
	7.15	92.3	

t (observed) = 1.296[b]
t (critical) = 2.228

a. VBr found/VBr added.

b. Student's t test at the 0.05 significance level for a two-tailed test.

IV. EVALUATION OF ALTERNATIVE EXTRACTION PROCEDURES

The sensitivity of the sampling and analytical method for vinyl bromide could be significantly increased if the volume of ethanol required to extract vinyl bromide from charcoal could be significantly decreased. In the method that has been developed, vinyl bromide is desorbed from exposed charcoal in a single extraction with 15 mL of ethanol. At the Project Officer's suggestion two alternative extraction procedures were briefly evaluated: (1) a continuous extraction technique in which a given volume of ethanol is percolated through an exposed charcoal tube and (2) a multiple-extraction procedure in which exposed charcoal is successively extracted with several fresh aliquots of ethanol. Neither technique, however, appeared to give significantly greater desorption efficiencies than were obtained in a single-batch extraction with an equivalent volume of ethanol.

A. Continuous Extraction Procedure

The continuous extraction of vinyl bromide from the charcoal was evaluated by the following procedure. In each test, the backup charcoal layer of an SKC 226-09 charcoal sampling tube was removed, and the sorbing charcoal layer was spiked with 77 μg of vinyl bromide. After the charcoal was spiked, ethanol was pumped through the sorbent tube at a constant rate with a syringe pump into the end of the tube opposite the end where the vinyl bromide spike was deposited. Each of three different syringe pumping rates was tested: 0.33, 0.99, or 2.00 mL/min. Four or five successive fractions of ethanol extract were collected, and the vinyl bromide content of each fraction was determined by GC. The volume of each of the first three fractions collected was 1 mL, the volume of the fourth fraction was 2 mL, and the volume of the fifth fraction (collected only in the experiment with a pumping rate of 0.99 mL/min) was 3 mL.

In order to compare the continuous extraction procedure with the single-extraction batch procedure, a separate experiment was performed in which the sorbing layer of an SKC 226-09 charcoal sampling tube was spiked with 77 μg of vinyl bromide and the charcoal extracted with 5 mL of ethanol in a single extraction.

For the continuous extraction procedure, the percent of the vinyl bromide initially spiked on each charcoal bed that was found in each of the collected ethanol fractions is given in Table IX for each pumping rate evaluated. The table indicated that for each ethanol flow rate, the largest percentage of vinyl bromide recovered was found in the first 1-mL fraction of ethanol extract collected. The percentage of vinyl bromide recovered decreased greatly in each succeeding ethanol fraction collected, so that little additional vinyl bromide was extracted after 5 mL of ethanol had been pumped through the exposed sorbent bed.

Table IX. Recoveries of Vinyl Bromide (VBr) from Spiked Charcoal Tubes in Successive Ethanol Fractions Collected at Various Pumping Rates*

Fraction collected	Volume of fraction, mL	VBr recovery, %, at the specified pumping rates		
		0.33 mL/min	1.00 mL/min	2.00 mL/min
1	1	41	45	36
2	1	10	16	15
3	1	3	8	6
4	2	1	3	2
5	3	-	1	-
Cumulative recovery (%) after eluting 5 mL of ethanol through spiked charcoal bed		55	72	59

* Each tube was spiked with 77 µg of VBr (in ethanol).

The cumulative vinyl bromide recovery in the first 5 mL of ethanol collected is also listed in Table IX for each pumping rate. The cumulative recoveries range from 55 to 72%. In the single-extraction batch procedure, the vinyl bromide recovery with 5 mL of ethanol was 70%. Thus the continuous extraction technique does not appear to have any significant advantage over the single-extraction procedure in terms of extraction efficiency.

B. Multiple-Extraction Procedure

To evaluate briefly the multiple-extraction procedure, the sorbing layer of one SKC 226-09 charcoal sorbent tube was spiked with 77 µg of vinyl bromide, and the exposed charcoal bed was successively extracted with three 2-mL portions of ethanol. Each ethanol extract was analyzed separately for vinyl bromide by GC. A second charcoal tube was also spiked with 77 µg of vinyl bromide and was extracted with 6 mL of ethanol in a single extraction.

In the multiple-extraction procedure the greatest fraction of vinyl bromide was recovered in the first extract. Much smaller fractions were recovered in the two succeeding extractions. The cumulative vinyl bromide recovery after the three 2-mL extractions (for a total extraction volume of 6 mL) was 66%. The vinyl bromide recovery found with a single 6-mL extraction was 75%. Thus, the multiple-extraction procedure appears to be no more efficient than the single-extraction procedure.

The results given in the previous paragraph are somewhat surprising. Calculations based on the vinyl bromide recoveries given in earlier reports on this contract indicate that greater than 90% recovery should be obtained from three 2-mL extractions. While it would certainly have been of interest to investigate the apparent discrepancy between our calculations and the experimental results, we did not feel that it would be fruitful to investigate a multiple-extraction procedure any further due to the increased complexity that a multiple-extraction procedure would introduce into a method for vinyl bromide.

V. EVALUATION OF THE TOTAL METHOD

The purpose of this portion of the research was to validate the method developed in previous work for the determination of vinyl bromide vapor in air. The accuracy and precision of the analytical procedure, including the solvent desorption step, were determined over a wide range of vinyl bromide levels with vinyl bromide/ethanol solution spikes. The long-term storability of vinyl bromide sorbed from a test atmosphere was then determined. Finally, the accuracy and precision of the total sampling and analytical method was assessed with test atmospheres over a wide range of concentrations of vinyl bromide in air.

A. Accuracy and Precision of the Analytical Procedure

Twelve SKC 226-09 coconut-charcoal sampling tubes (400-mg sorbing layer and 200-mg backup layer of charcoal) were spiked with known amounts of vinyl bromide. Six of the tubes were spiked with 35.5 μg of vinyl bromide and six were spiked with 355 μg of vinyl bromide. These amounts of vinyl bromide corresponded to approximately 5 x LAQL and 45 x LAQL, respectively. The exposed tubes were sealed with teflon tape and plastic caps and stored in the dark for 1 d at about 25 °C. Each sorbent section was then extracted with 15 mL of absolute ethanol in an ultrasonic bath for 30 min. The extracts were then analyzed for vinyl bromide by the GC analytical method.

The results of the spiking experiments at approximately 5 x LAQL and 45 x LAQL and the results of the spiking experiments performed previously at the LAQL (Section III.F.) are summarized in Table X. The results indicate that the recovery of vinyl bromide with this analytical procedure is quantitative, with close to 90% recovery at all test levels. The precision of the results in the entire range of the tests was found to be homogeneous by application of Bartlett's test ($\chi^2 = 2.4$), and the RSD's of the test results at each level were pooled to give a pooled standard deviation $\overline{RSD}_1$ of 4.0%. The average desorption efficiency over the 7.75- to 335-μg range was 0.910.

B. Determination of the Stability of Sorbed Vinyl Bromide at the LAQL after Collection from Air

To test the stability of sorbed vinyl bromide when collected from air, SKC 226-09 charcoal sampling tubes were exposed to test atmospheres of vinyl bromide and stored for up to 14 d at room temperature. Each charcoal sampling tube contained a 400-mg sorbing section of coconut charcoal and a 200-mg backup section.

The vinyl bromide concentration in the test atmosphere was maintained at 1.32 mg/m^3 over the exposure period. A certified mixture of vinyl bromide in nitrogen (4390 mg/m^3) was introduced into the test atmosphere generator with a syringe pump at a rate of 0.99 mL/min. The mixture was then diluted with humidified air at a rate of 3300 mL/min to give a vinyl bromide concentration of 1.32 mg/m^3 in the test atmosphere. The temperature of the test atmosphere was maintained at 25 °C, and the relative humidity of the test atmosphere

Table X. Accuracy and Precision of Desorption and Analysis Procedure for Vinyl Bromide (VBr)[a]

	7.75-µg spike		35.5-µg spike		355-µg spike	
	VBr found, µg	Desorption efficiency[b]	VBr found, µg	Desorption efficiency[b]	VBr found, µg	Desorption efficiency[b]
	6.64	0.856	31.0	0.873	330	0.930
	6.36	0.821	32.0	0.901	352	0.992
	7.18	0.926	32.0	0.901	309	0.870
	7.18	0.926	32.8	0.924	330	0.930
	6.91	0.892	32.8	0.924	337	0.949
	7.18	0.926	32.8	0.924	327	0.921
Average	6.91	0.891	32.2	0.908	331	0.932
Std dev	0.35	0.044	0.7	0.020	14	0.040
RSD,%	-	5.0	-	2.3	-	4.3

$\overline{DE}$[c] = 0.910

$\overline{RSD_1}$[d] = 4.0%

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a. SKC coconut charcoal sampling tubes (Catalog No. 226-09) were spiked with the indicated quantities of VBr.

b. VBr found/VBr added.

c. Average desorption efficiency.

d. Pooled precision.

was 80%. Approximately 6 L of test gas was sampled simultaneously through six charcoal sampling tubes at a nominal rate of 0.2 L/min. The procedure was repeated for three sets of tubes. About 8 µg of vinyl bromide ($\sim$ 1 x LAQL) was collected by each tube.

The ends of the exposed tubes were wrapped with Teflon tape and sealed with plastic caps and stored in the dark at room temperature (24 to 27 °C). Six of the charcoal tubes were analyzed for vinyl bromide after 1 d, six were analyzed after storage for 8 d, and six were analyzed after storage for 14 d. The gas chromatographic analytical method employed the Perkin-Elmer Sigma 2 with FID.

The results of the storage tests are presented in Table XI. The average recoveries of vinyl bromide from exposed charcoal tubes after 1, 8, or 14 d of storage were 109, 100, and 95%, respectively. There was no statistical difference at the 0.05 significance level for a two-tail *t*-test between the mean vinyl bromide concentration determined in either the 8-d or 14-d storage test and the mean vinyl bromide concentration determined in the 1-d storage test. The variability in the results was acceptable for the 1-d and 8-d storage tests (i.e., RSD <10%) but was higher than desired for the 14-d storage test (RSD = 15%).

C. Accuracy and Precision of the Total Sampling and Analytical Method

Twelve SKC 226-09 coconut charcoal sample tubes were exposed to test atmospheres of vinyl bromide and stored for 1 d. The tubes were then extracted with 15 mL of absolute ethanol, and the ethanol extracts were analyzed for vinyl bromide by the GC analytical method developed with the Perkin-Elmer Sigma 2 with FID. Six of the tubes were exposed to a test level of 6.38 mg/m^3 of vinyl bromide, and six were exposed to a test level of 56.5 mg/m^3. The temperature of the test atmosphere was 25 °C and the relative humidity was >80%. At each concentration level, each of the six charcoal sample tubes was simultaneously exposed to approximately 6 L of the test atmosphere at a nominal sampling rate of 0.2 L/min. At the 6.38-mg/m^3 concentration, an average of 5.72 L of the test gas was sampled; this corresponded to the sampling of an average of 36.5 µg of vinyl bromide, or approximately 5 times the LAQL. At the 56.5 mg/m^3 concentration level, an average of 5.76 L of the test gas was sampled; this corresponded to the sampling of an average of 326 µg of vinyl bromide, or approximately 40 times the LAQL.

The vinyl bromide concentration in the test atmosphere generator was determined from the concentration and measured flow rate of a certified gas mixture of vinyl bromide in nitrogen and the measured flow rate of dilution air. This method is known as delivery rate calibration and is the independent method that we employed for determining the "true" value of the vinyl bromide concentration.

The results of the test atmosphere sampling experiments at approximately 5 x LAQL and 40 x LAQL and the results of the sampling experiments performed previously at the LAQL are summarized in Table XII. The vinyl bromide recoveries

Table XI. Stability of Sorbed Vinyl Bromide (VBr) on SKC Coconut Charcoal

Sample Set No.[a]	VBr conc. found, mg/m^3 after the indicated no. of days storage[b,c]		
	1	8	14
1	1.24	1.15	1.02
	1.33	1.23	1.03
2	1.63	1.41	1.42
	1.51	1.41	1.43
3	1.46	1.44	1.28
	1.44	1.29	1.35
Mean	1.44	1.32	1.26
Std. dev.	0.14	0.12	0.19
RSD, %	9.7	9.1	15.1
Avg. recovery, %	109	100	95
t (observed)	-	1.543[d]	1.909[e]
t (critical)	-	2.228	2.228

a. The VBr concentration in the test atmosphere was determined to be 1.32 mg/m^3 during the exposure of all sample sets on the basis of the concentration and measured flow rate of a certified gas mixture of VBr in nitrogen and the measured flow rate of dilution air. The temperature of the test atmosphere was 25 °C and the relative humidity was >80%.

b. Commercial SKC 226-01 charcoal sampling tubes were used in all of the determinations. Each tube contained a 400-mg sorbing layer and a 200-mg backup layer. No measurable amounts of VBr were found in any of the backup sections.

c. All results were corrected for a desorption efficiency of 0.89.

d. Comparison of means between the results of 1- and 8-d experiments by the Student's *t* test at the 0.05 significance level for a two-tailed test.

e. Comparison of means between the results of 1- and 14-d experiments by the Student's *t* test at the 0.05 significance level for a two-tailed test.

Table XII. Accuracy and Precision of the Sampling and Analysis of Vinyl Bromide in Air

Test level,[a] mg/m^3		Quantity found,[b] µg	Volume sampled, L	Calc'd concn,[b] mg/m^3	Recovery,[c] %
1.32		6.85	5.54	1.24	94
		6.85	5.13	1.34	102
		9.79	6.02	1.63	123
		8.31	5.51	1.51	114
		8.81	6.02	1.46	111
		7.83	5.44	1.44	109
	Average	8.07	5.61	1.43	109
	Std dev	-	-	0.14	10.0
	RSD, %	-	-	-	9.2
6.38		28.6	4.79	5.97	94
		39.8	6.09	6.54	103
		36.3	6.12	5.93	93
		40.7	6.19	6.58	103
		35.7	5.44	6.56	103
		35.2	5.68	6.20	97
	Average	36.1	5.72	6.30	99
	Std dev	-	-	0.30	4.8
	RSD, %	-	-	-	4.8
56.5		257	4.73	54.3	96
		348	6.22	55.9	99
		348	6.15	56.6	100
		353	6.36	55.5	98
		311	5.51	56.4	100
		314	5.61	56.0	99
	Average	322	5.76	55.8	99
	Std dev	-	-	0.8	1.5
	RSD, %	-	-	-	1.5

a. Determined on the basis of the concentration and measured flow rate of a certified gas mixture of VBr in nitrogen and the measured flow rate of dilution air (delivery rate calibration).

b. The results reported have been corrected for the desorption efficiency.

c. Relative to the concentration found by delivery rate calibration.

at all of the test levels were close to 100% with relative standard deviations less than 10%. The precisions of the vinyl bromide recoveries at the three test levels were not homogeneous (χ^2 = 11.1); thus the relative standard deviations of the test results at the three levels could not be pooled. However, the RSD's of the results at the 1.32 mg/m^3 test level and the 6.38 mg/m^3 test level were homogeneous and could be pooled (χ^2 = 1.80, $\overline{RSD}_2$ = 7.34). Similarly, the RSD's of the results at the 6.38 mg/m^3 test level and the 56.5 mg/m^3 test level were also homogeneous and could be pooled (χ^2 = 5.12, $\overline{RSD}_2$ = 3.56). The pooled relative standard deviation ($\overline{RSD}_1$) of the total method (which consists of the composite variations in sampling and analysis, desorption efficiency, and the pump error) was calculated to be 9.0% over the vinyl bromide concentration range of 1.32 to 6.38 mg/m^3 and 6.3% over the concentration range of 6.38 to 56.5 mg/m^3.

The bias of the developed sampling and analytical method with respect to the independent method was small. The bias was +9% at the 1.32 mg/m^3 test level, -1% at the 6.38 mg/m^3 test level, and 1% at the 56.5 mg/m^3 test level. Thus, the average bias was about +3%.

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F2. "Vinyl Chloride"--Physical and Chemical Analysis Branch Method No. 178. In NIOSH Manual of Analytical Methods, 2nd ed., DHEW (NIOSH) Publication No. 77-157-A. U.S. Department of Health, Education, and Welfare:Cincinnati, Ohio, 1977; Vol 1, pp 178-1 to 178-10.

F3. "Vinylidene Chloride"--Physical and Chemical Analysis Branch Method No. 266. In NIOSH Manual of Analytical Methods, 2nd ed., DHEW (NIOSH) Publication No. 77-157-A. U.S. Department of Health, Education, and Welfare:Cincinnati, Ohio, 1977; Vol. 4, pp 266-1 to 266-9.

A P P E N D I X A

Material Safety Data Sheet

Vinyl Bromide
(Incomplete)

VINYL BROMIDE

4*	POTENTIALLY SERIOUS HEALTH HAZARD
3	MODERATELY FLAMMABLE
1	SLIGHTLY REACTIVE

MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION

MANUFACTURER'S NAME ETHYL CORP.,	REGULAR TELEPHONE NO. 504-388-7556 EMERGENCY TELEPHONE NO.
ADDRESS Industrial Chemicals Div. 451 Florida St., Baton Rouge, LA 70801	
TRADE NAME Vinyl Bromide	
SYNONYMS Bromethylene; bromoethane; VBr	

II HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	%	HAZARD DATA
Vinyl bromide		Possible Carcinogen
(May contain a polymerization inhibitor, such as hydroquinone monomethyl ether)	0.05	Dependent on specific inhibitor used.

III PHYSICAL DATA mol. wt. = 106.96

BOILING POINT, 760 mm Hg 15.85 °C	MELTING POINT -137.8 °C
SPECIFIC GRAVITY (H_2O = 1) 1.529 at 11 °C	VAPOR PRESSURE 1000 mm Hg at 20 °C
VAPOR DENSITY (AIR = 1) 3.7	SOLUBILITY IN H_2O, 0.565 g/100 mL
% VOLATILES BY VOL. 100%	EVAPORATION RATE (BUTYL ACETATE = 1)
APPEARANCE AND ODOR Colorless gas or colorless liquid; pungent odor	

* Tentitive assignment. VBr is a possible carcinogen.

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)	None (open cup)		AUTOIGNITION TEMPERATURE	None reported	
FLAMMABLE LIMITS IN AIR, % BY VOL.	LOWER	9%	UPPER	15%	
EXTINGUISHING MEDIA	CO_2 , dry chemical, or water spray				
SPECIAL FIRE FIGHTING PROCEDURES	None reported				
UNUSUAL FIRE AND EXPLOSION HAZARD	Dangerous, when exposed to heat or flame Explosion hazard unknown				

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA: TLV (air) 250 ppm; Recommended air standards TWA: 1 ppm; Ceiling level: 5 ppm/15 min

ROUTES OF EXPOSURE

INHALATION: TCLo (rat) = 250 ppm/1Y TFX:NEO; TD (rat) = 10 ppm TEX:ETA

SKIN CONTACT: -

SKIN ABSORPTION: -

EYE CONTACT: -

INGESTION: LD50 (rat) = 400 mg/kg

EFFECTS OF OVEREXPOSURE

ACUTE OVEREXPOSURE: Moderate irritation of skin, eyes, and mucous membranes; has produced drowseness and sluggishness in rats.

CHRONIC OVEREXPOSURE: Has caused a significant increase in liver cancer in rats

EMERGENCY AND FIRST AID PROCEDURES

EYES: Rinse with water for 15 min; obtain medical attention as soon as possible

SKIN: Wash immediately with soap and water

INHALATION: Move to fresh air, perform artificial respiration if required

INGESTION: -

NOTES TO PHYSICIAN

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

Can react vigorously with oxidizing materials

INCOMPATIBILITY Oxidizing agents, catalysts for vinyl polymerization, such as peroxides, strong acids, aluminum chloride

HAZARDOUS DECOMPOSITION PRODUCTS

Hydrogen bromide, carbon monoxide

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

Polymerizes rapidly in sunlight to form a mixture of polymers

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

None reported

NEUTRALIZING CHEMICALS

None reported

WASTE DISPOSAL METHOD

None reported

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS

Effective hood or ventilation system

SPECIFIC PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY (SPECIFY IN DETAIL) Dependent upon vinyl bromide concentration. For a concentration $\leq$ 10 ppm - chemical cartridge respirator

EYE

Safety goggles or glasses with side shields

GLOVES

Neoprene gloves

OTHER CLOTHING AND EQUIPMENT One vinyl bromide manufacturer has recommended that neoprene gloves and boots be worn by employees opening process lines and repairing pumps, and that a one-piece nylon suit, vinyl coated on both sides, with attached neoprene boots and gloves be worn by empolyees entering a reactor vessel or tank.

IX SPECIAL PRECAUTIONS

PRECAUTIONARY STATEMENTS

The available information on vinyl bromide suggests that it is carcinogenic and may induce the same type of characteristic tumor that is associated with exposure to vinyl chloride.

OTHER HANDLING AND STORAGE REQUIREMENTS

Keep away from heat, flames and sparks. Store and use with adequate ventilation.

PREPARED BY: Ralph B. Spafford
H. Kenneth Dillon

ADDESSS: Southern Research Institute
P.O. Box 3307-A
Birmingham, Alabama 35255

DATE: August, 1981

A P P E N D I X B

Vapor Generation System

TEST ATMOSPHERE GENERATOR AND SAMPLING SYSTEM

A. Test Atmosphere Generator

The test atmosphere generator was designed to produce vinyl bromide concentrations in the range of about 1 to 1100 mg/m^3.* The generator consisted of a gas delivery system, a dilution system, and test atmosphere sampling chamber. The components of the generator were connected by glass, stainless steel, or teflon tubing and compression fittings. The components of the generator are described in the following paragraphs and are illustrated in Figure 2.

1. Gas delivery system

Vinyl bromide was introduced into the system by one of two methods depending on the concentration of vinyl bromide required in the test atmosphere. To produce vinyl bromide concentrations of 4 mg/m^3 or greater in the test atmosphere, a certified gas mixture of 4371 mg/m^3 of vinyl bromide in nitrogen (Linde Division, Union Carbide Corporation) was metered through a precision valve and rotameter that allowed constant and reproducible flows in the range of 10 to 500 mL/min. To produce vinyl bromide concentrations of less than 4 mg/m^3 in the test atmosphere, a certified gas mixture of 4371 mg/m^3 vinyl bromide in nitrogen was introduced into the system from a glass syringe at an accurately known and calibrated rate with a Sage Model 341 syringe pump (Sage Instrument Co., Cambridge, Mass.)

2. Dilution system

The dilution system included flowmeters to control the flow of air into the mixing chamber, a large gas washing tower for humidifying air, and a mixing chamber for combining the vinyl bromide and nitrogen mixture with the dilution air. The dilution air was cleaned of organic vapor impurities with charcoal. A replaceable particle filter with a pore size of 0.2 μm was employed to remove particulate contaminants. The air was also dried with a heatless fractionator containing molecular sieves. The filtered air was split into two streams, one that was humidified and another that was not. The humidified and dry airstreams were recombined before they were introduced as dilution air into the mixing chamber. The humidity of the dilution air was controlled by regulating the volume flow rate of air through each of the two streams. The total volume flow rate of the dilution air was adjustable from about 2 L/min to about 10 L/min.

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* All vapor concentrations (given in units of mg/m^3) and all gas flow rates (given in units of L/min) are expressed for 25 °C.

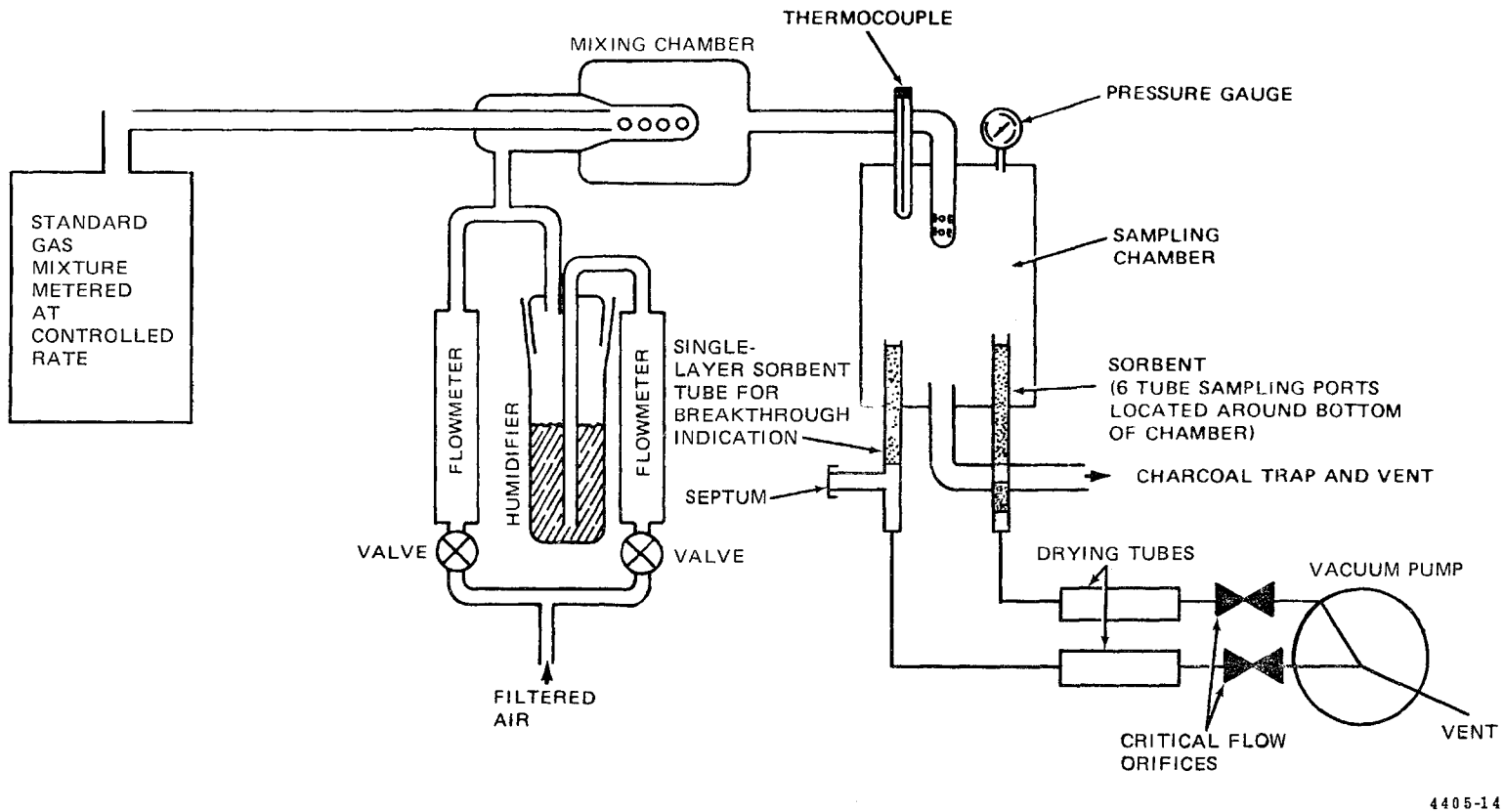

Figure 2. Vapor generator and sampling system.

3. Test atmosphere sampling chamber

The test atmosphere sampling chamber consisted of a cylindrical glass chamber about 15 cm in length and 10 cm in diameter. The ends of the cylinder were fitted with specially designed Teflon discs. One disc had an axial opening for the introduction of the vinyl bromide and air mixture and additional openings for temperature and pressure measurements. The other disc had an axial opening for chamber exhaust and seven smaller openings for sampling located about 2.5 cm from the axis of the cylinder. Sorbent tubes were inserted directly into the sampling chamber through the smaller openings. The tubes fit tightly without the use of sleeves or connectors.

B. Sampling System

The sampling system consisted basically of a sorbent tube, a drying tube, a critical orifice, and a vacuum pump connected in series. The test atmosphere was sampled from the sampling chamber through a solid sorbent tube at a constant rate by means of a critical orifice and vacuum pump. During the weight capacity determinations, a single-layer sorbent tube was used to monitor the breakthrough of vinyl bromide from a packed sorbent tube. This was done by withdrawing aliquots of the sampling stream from a septum-capped sidearm connected to the outlet of the single-layer tube with a gastight syringe and by then analyzing the gas aliquots for vinyl bromide by GC. This syringe sampler technique was described in detail in Section III.D.1. of the report. The initial concentration of vinyl bromide in the sampling chamber was determined by the delivery rate calibration technique described in the text of the report.

A P P E N D I X C

Summary of Statistical Terms and Formulas

Summary of Statistical Terms and Formulas

The statistical terms and formulas employed in this report were adapted from those given in Appendix A of the "Documentation of the NIOSH Validation Tests".* The major deviation from the format given in that reference was that the relative standard deviation (RSD) instead of the coefficient of variation (CV) was used to express precision. The appropriate formulas were modified accordingly.

Mean - Arithmetic mean or average, defined as the sum of all the observations divided by the number of observations (n).

Standard deviation - Defined as the positive square root of the variance, which is defined as the sum of squares of the deviations of the observations from the mean ($\bar{x}$) divided by one less than the total number of observations (n-1).

$$\text{std dev} = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}}$$

RSD - Relative standard deviation, defined as the standard deviation divided by the mean and multiplied by 100.

$$\text{RSD, \%} = \frac{\text{std dev}}{\text{mean}} \times 100$$

RSD_1^j - Relative standard deviation for the samples in the determination of the desorption efficiency at one of the spiking levels (the j^{th} level).

RSD_2^j - Relative standard deviation for the sorbent samples exposed to the test gas at one of the concentration levels (the j^{th} level).

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* Taylor, D.G.; Kupel, R.E.; Bryant, J.M. "Documentation of the NIOSH Validation Tests"; National Institute for Occupational Safety and Health: Cincinnati, Ohio, April 1977, DHEW (NIOSH) Publication No. 77-185, pp. 1 to 11.

$\overline{RSD}$ - Pooled relative standard deviation. The value is derived from the relative standard deviations obtained from the analysis of samples at each of the test levels. The mathematical equation is expressed as:

$$\overline{RSD} = \sqrt{\frac{\sum_{j=1}^{n} f_j \, (RSD^j)^2}{f}}$$

where: f_j = degrees of freedom, equal to number of observations minus one, at the j^{th} spike or concentration level.

RSD^j = Relative deviation of the observations at the j^{th} level.

$$f = \sum_{j=1}^{n} f_j$$

$\overline{RSD}_1$ - Pooled relative standard deviation calculated as above based on data for the determination of the desorption efficiency.

$\overline{RSD}_{A+\overline{DE}}$ - This is a derived correction to include error due to the use of the desorption efficiency factor which is an average of 6 values at each level.

$$\overline{RSD}_{A+\overline{DE}} = \overline{RSD}_1 \sqrt{7/6} = 1.0801 \, \overline{RSD}_1$$

$\overline{RSD}_2$ - Pooled relative standard deviation based on the data for all of the sorbent samples exposed to the test gas.

$\overline{RSD}_s$ - Pooled relative standard deviation in the sample collection procedure. The value is dependent on the data from the sorbent samples spiked with analyte and the sorbent samples exposed to the test gas.

$$\overline{RSD}_s = \sqrt{(\overline{RSD}_2)^2 - (\overline{RSD}_1)^2}$$

$\overline{RSD}_p$ - Relative standard deviation due to the pump error; assumed to be equal to 5%.

$\overline{RSD}_T$ - Relative standard deviation of the total procedure that consists of the composite variations in sampling and analysis, desorption efficiency, and the pump error.

$$\overline{RSD}_T = \sqrt{(\overline{RSD}_S)^2 + (\overline{RSD}_{A+DE})^2 + (\overline{RSD}_P)^2}$$

or:

$$\overline{RSD}_T = \sqrt{(\overline{RSD}_2)^2 - (\overline{RSD}_1)^2 + 1.1667\,(\overline{RSD}_1)^2 + (5)^2}$$

Grubbs' Test for Rejection of an Observation

This test is applied in order to determine if one of the observations should be rejected as being an outlier. The following equation was used for the test:

$$B_1' = \frac{x - \bar{x}}{s} \text{ or } \frac{\bar{x} - x}{s}$$

where: x = observation being tested.

$\bar{x}$ = mean of all observations.

s = standard deviation based on $n-1$ degrees of freedom for n observations.

For any six observations, a value can be rejected if $B_1' \geq 1.944$. The B_1' limit is based on a 1% significance level (i.e., a B_1' value calculated from the data can be expected to exceed 1.944 only 1% of the time if the observation is a legitimate one conforming to the underlying theory.)

Bartlett's Test for Homogeneity

This test is applied in order to test the feasibility of "pooling" the relative standard deviations. The following equation for χ^2 with $k-1$ degrees of freedom was used:

$$\chi^2 = \frac{f \ln (\overline{RSD}_i)^2 - \sum_{j=1}^{n} f_j \ln (RSD_i^j)^2}{1 + \frac{1}{3(k-1)} \left[\left(\sum_{j=1}^{n} 1/f_j \right) - 1/f \right]}$$

where: i = 1 or 2. When i= 1, the precision of the desorption efficiency tests applies. When i = 2, the precision of the results with sorbent samples exposed to test atmospheres applies; thus:

$$\overline{RSD}_i = \overline{RSD}_1 \text{ or } \overline{RSD}_2$$

$\overline{RSD}_i^j$ = relative standard deviation at the j^{th} level for i = 1 or 2.

f_j = degrees of freedom associated with $(RSD_i^j)^2$ and equal to the number of observations at the j^{th} level minus one (for i = 1 or 2).

$$f = \sum_{j=1}^{n} f_j$$

k = number of variances being tested.

In order to pass Bartlett's test at the 1% significance level, χ^2 must be less than or equal to 6.64 when k = 2, 9.21 when k = 3, or 11.34 when k = 4.

A P P E N D I X D

Analytical Method

VINYL BROMIDE

Analytical Method

Analyte:	Vinyl bromide	Method No.: P&CAM 349
Matrix:	Air	Range: 1.32 to 56.5 mg/m^3 (at 25 °C)
Procedure:	Adsorption on activated charcoal, desorption with ethanol, analysis by GC/FID	Precision: 0.090 over the range 1.32 to 6.38 mg/m^3; 0.063 over the range 6.38 to 56.5 mg/m^3
Date Issued:	5/15/81	Classification: E (proposed)
Date Revised:		

1. Synopsis

   1.1 A known volume of air is drawn through a coconut charcoal tube to adsorb the vinyl bromide vapor present.

   1.2 The charcoal in the tube is transferred to a small vial where the vinyl bromide is desorbed with 15 mL of absolute ethanol.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The height or area of the resulting peak for vinyl bromide is determined and compared with the peak heights or peak area obtained from the injection of standards.

2. Working Range, Sensitivity, and Detection Limit

   2.1 The overall method was evaluated by collecting 6-L samples of test atmospheres containing vinyl bromide in the range of 1.32 to 56.5 mg/m^3 at 25 °C and a relative humidity of >80%. The amounts of vinyl bromide collected ranged from 8.07 to 322 µg per 400-mg bed of charcoal.

   2.2 The slope of the analytical calibration curve was 0.804 mm peak height per ng of vinyl bromide for an attenuation of 1 x 32 with a Perkin-Elmer Sigma 2 gas chromatograph.

2.3 The lowest analytically quantifiable level for this method was determined to be about 7.75 µg of vinyl bromide per sorbent sample extracted with 15 mL of absolute ethanol. This corresponds to a lower level of quantitation in air samples of 1.3 µg/m^3. The instrumental detection limit was about 0.25 µg/mL of vinyl bromide in ethanol for a 5-µL injection volume; the relative standard deviation of replicate determination of standards at this level was 10%.

2.4 The breakthrough volume of the sorbent tube was found to be approximately 10 L with a sampling rate of 0.2 L/min at a vinyl bromide concentration of about 130 mg/m^3, a sampling temperature of 40 °C, and a relative humidity of greater than 80%. The recommended sampling volume is 6 L to compensate for possible reduction of the capacity of the sorbent tube under potentially harsh field sampling conditions.

3. Interferences

3.1 The chromatographic operating conditions described below will separate vinyl bromide from ethylene, acetylene, and 1,3-dibromoethane, but not from bromine.

3.2 When two or more substances are known or suspected to be present in the air sampled, the identities of the substances should be transmitted with the sample because the substances may interfere with the determination of vinyl bromide.

3.3 Any substance that has the same retention time as vinyl bromide with the gas chromatograph operating conditions described in this method can interfere with the analysis. Therefore retention time data cannot be considered as proof of chemical identity.

3.4 If the possibility of interference exists, changing the separation conditions (column type, column temperature, carrier has flow rate, etc.) may circumvent the problem.

4. Precision and Accuracy

4.1 For the overall sampling and analytical method, the pooled relative standard deviation (RSD) for the replicate measurements was 9.0% over the range of 1.32 to 6.38 mg/m^3 and 6.3% over the range of 6.38 to 56.5 mg/m^3. The pooled RSD for the analytical method was 4.0% for 18 sorbent samples spiked with 7.75 to 355 µg of vinyl bromide and stored for 1 d.

4.2 The concentration of vinyl bromide in the test atmosphere was determined on the basis of the concentration and measured flow rate of a certified gas mixture of vinyl bromide in nitrogen and the measured flow rate of dilution air (delivery rate calibration).

4.3 Samples of vinyl bromide on coconut charcoal were found to be stable at 25 °C for up to 14 d. The samples were stored in the dark.

5. Advantages and Disadvantages

5.1 The sampling device is small, portable, and involves no liquids. Many of the potential sources of interference are avoided by the analytical procedure. The samples are analyzed by means of a quick instrumental method.

5.2 One disadvantage is that the precision of the method is limited by the reproducibility of the pressure drop across the tubes. Variations in pressure drop will affect the flow rate. The reported sample volume will then be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 Personal sampling pump capable of accurate performance (±5%) at 0.05 to 0.2 L/min and calibrated with a representative tube in the line.

6.2 Sorbent tubes: SKC Catalog No. 226-09 (SKC, Inc., Eighty-Four, PA 15330) or equivalent. These sorbent tubes are 100 mm long by 8 mm o.d. glass tubes packed with a 400-mg sorbing section and a 200-mg backup section of coconut-based charcoal. The sorbing section is preceded in the tube by a glass wool plug held in place with a metal spring. The sorbing section and backup section are separated by a polyurethane foam plug. There is also a foam plug placed near the outlet end of the tube to hold the backup sorbent section in place. The pressure drop across a typical tube is about 1.1 in. H_2O (0.3 kPa) at a sampling rate of 0.2 L/min.

6.3 Gas chromatograph with flame ionization detector.

6.4 A 6-m long by 2-mm i.d. nickel column packed with 10% FFAP on 80/100-mesh acid-washed DMCS Chromosorb W.

6.5 Glass serum vials, 15 mL, with crimp-on caps containing Teflon-lined silicone rubber septa.

6.6 Pipets and volumetric glassware of convenient sizes for making dilutions.

6.7 Ultrasonic bath.

6.8 Syringes, 10 µL.

7. Reagents

7.1 Vinyl bromide (liq.), 98% purity or better.

7.2 Ethanol, absolute.

8. Procedure

8.1 Cleaning of Equipment: All nondisposable glassware used for the laboratory analysis should be thoroughly cleaned and rinsed with 50% nitric acid, tap water, and distilled water (in that order). The glassware should then be dried.

8.2 Collection and Shipping of Samples

8.2.1 Immediately before sampling, break open the ends of the tube to provide openings that are at least 2 mm in diameter.

8.2.2 Connect the tube to the sampling pump with Tygon or rubber tubing. The smaller section of charcoal is the backup layer and is positioned nearer the sampling pump.

8.2.3 Place the charcoal tube in a vertical position during sampling to prevent channeling through the tube.

8.2.4 Air being sampled should not be passed through any hose or tubing before entering the tube.

8.2.5 Sample the air at 0.05 to 0.2 L/min.* Measure and report the flow rate and time or volume sampled. The maximum volume sampled should not exceed 6 L.

8.2.6 Record the temperature and pressure of the air being sampled.

8.2.7 Immediately after sampling, seal the ends of the tubes with Teflon tape and plastic caps.

8.2.8 To obtain a blank sample, process one unused charcoal tube in the same manner as the samples (break, seal, and transport) but do not sample air through this tube. Submit one blank sample tube for every ten samples with a minimum of three blank tubes.

8.2.9 If samples are shipped to a laboratory, pack them tightly to minimize tube breakage during shipping.

8.2.10 Ship nine to twelve unopened charcoal tubes so that desorption efficiency studies can be performed on the same type and lot of charcoal used for sampling.

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* Although the lowest sampling rate used in the development of a method for vinyl bromide was 0.05 L/min, a lower sampling rate such as 0.025 L/min may increase the possible sample time.

8.3 Analysis of Samples

8.3.1 Preparation of Samples. Transfer the sorbing section and backup section of each sorbent tube to separate 15-mL vials. Discard the metal spring. Place the glass wool plug into the vial containing the sorbing section and the foam plugs into the vial with the backup section.

8.3.2 Desorption of Samples. After the two sections of a tube are transferred to small vials, pipet 15 mL of the solvent into each vial. Crimp a serum cap into place on each vial immediately after the solvent has been added. Extract the sealed sorbent samples in an ultrasonic bath for 30 min at room temperature.

8.3.3 GC Conditions

- Carrier gas: nitrogen, 25 mL/min.
- FID air flow rate: 400 mL/min.
- FID hydrogen flow rate: 30 mL/min.
- Injection port temperature: 140 °C.
- Column temperature: isothermal at 50 °C for 3 min, programmed at 40 °C/min to 225 °C and maintained at 225 °C for 5 min.
- Detector temperature: 240 °C.
- Under these conditions, the analyte elutes in 3.0 min.

8.3.4 Injection. Inject a 5-µL aliquot of a sample extract or standard into the gas chromatograph by the solvent flush technique. Use 1 µL of ethanol as the solvent flush. Maintain a 1-µL air gap between the solvent flush and the 5-µL aliquot.

8.3.5 Quantitation of GC Response. Multiply the peak height by the attenuator setting necessary to keep the peak on scale. Read the result from a standard curve prepared as discussed in Section 9. If the peak height indicates an apparent concentration outside of the linear range of the calibration curve, dilute the sample solution appropriately for reanalysis. (The product of peak height and attenuator setting was found during the development of the method to be linear over the concentration range of about 0.25 to 50 µg/mL.)

8.4 Determination of Desorption Efficiency

8.4.1 Importance of Determination. The desorption efficiency of a particular compound may vary between laboratories and batches of charcoal. Also, for a given batch of charcoal the desorption efficiency may vary with the weight of contaminant adsorbed. The charcoal used for the study of this method gave an average desorption efficiency of 0.910 with a pooled RSD of 4.0% for loadings of 7.75 to 355 µg of vinyl bromide on 400-mg beds of sorbent material.

8.4.2 Procedure for Determining Desoprtion Efficiency. Determine the desorption efficiency at three levels with a minimum of three samples at each level. Two of the levels should reflect the extremes of the analytical range while the third is an intermediate level. Dissolve vinyl bromide in ethanol to give stock solutions with concentrations such that 7.8 to 355 µg of vinyl bromide will be injected onto the sorbent in no more than 5 µL of a stock solution. Inject an aliquot of the appropriate solution into the front sorbing section of a sorbent tube while sampling 6 L of analyte-free air through the tube at 0.2 L/min. Cap the tube and store it overnight at room temperature to ensure complete adsorption of the analyte onto the sorbent material. Prepare a standard at each level by injecting an identical amount of the corresponding stock solution into 15 mL of absolute ethanol. Analyze the samples and standards as described in Section 8.3.

The desorption efficiency at each level is the ratio of the average amount found to the amount taken. A blank correction is not expected to be necessary but should be checked. The desorption efficiency curve is constructed by plotting the amount of vinyl bromide found in a sample versus the desorption efficiency.

9. Calibration and Standardization

9.1 Prepare a concentrated stock solution of vinyl bromide in ethanol by the following procedure:

9.1.1 Transfer several milliliters of absolute ethanol to a volumetric flask and weigh the flask accurately on an electronic balance.

9.1.2 Chill the flask and its contents to near 0 °C in an ice-water bath.

9.1.3 Transfer a small volume of prechilled vinyl bromide (at 0 °C) to the volumetric flask with a prechilled syringe.

9.1.4 Stopper the flask and allow it to warm up to room temperature.

9.1.5 Reweigh the flask on an electronic balance and determine the weight of vinyl bromide added to the flask from the weight difference of the flask.

9.1.6 Dilute the vinyl bromide-ethanol solution in the flask to the mark with absolute ethanol and mix the solution thoroughly by shaking.

9.2 Prepare a series of working standards varying in the concentration over the range of interest by serial dilution of the stock solution with ethanol.

9.3 Prepare fresh working standards daily; the stock solution may be stable for several days if stored in an airtight container and refrigerated when not in use. However, no detailed stability data are available. Analyze the five working standards under the same instrumental operating conditions and during the same time period as the samples. To establish a calibration curve, plot the concentration of the standards in µg/mL versus peak height.

10. Calculations

10.1 Determine the sample concentration from the standard curve.

10.2 Determine the sample weight in micrograms by multiplying the sample concentration by the sample volume.

10.3 Blank corrections are not expected to be necessary. If the analysis shows a blank correction is needed, make the correstion as follows:

$$W_F = W_s - W_b$$

where: W_F = corrected amount (µg) on the front section of the sorbent tube.

W_s = amount (µg) found on the front section of the sorbent tube.

W_b = amount (µg) found on the front section of the blank absorbent tube.

Follow a similar procedure for the backup section.

10.4 Make correction for desorption efficiency as follows:

$$M_F = \frac{W_F}{D}$$

where: M_F = corrected amount (µg) in the front section.

W_F = amount (µg) after blank correction.

D = desorption efficiency corresponding to the weight W_F.

10.5 Express the concentration, C, of vinyl bromide in the air sampled in mg/m^3, which is numerically equal to $\mu g/L$.

$$C = \frac{M_F + M_B}{V}$$

where: M_F = corrected amount (μg) of vinyl bromide found on front section.

M_B = corrected amount (μg) of vinyl bromide found on backup section.

V = volume (L) of air sampled.

10.6 If desired, the results may be expressed in ppm by volume

$$C(ppm) = C(\mu g/L) \times \frac{24.45}{106.96} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where: P = pressure (torr) of air sampled.

T = temperature (°C) of air sampled.

24.45 = molecular volume (L/mol) at 25 °C and 760 torr.

106.96 = molecular weight of vinyl bromide.

11. Reference

Spafford, R.B.; Dillon, H.K. "Analytical Methods Evaluation and Validation for Vinylidene Fluoride, Vinyl Bromide, Vinyl Fluoride, Benzenethiol, and n-Octanethiol: Research Report for Vinyl Bromide"; NIOSH Contract No. 210-79-0100; Southern Research Institute: Birmingham, Alabama; September 1981.

A P P E N D I X E

Sampling Data Sheet

NIOSH SAMPLING DATA SHEET NO. ____ Class ____

May 15, 1981

Substance: Vinyl bromide

Standard: A standard has not been established.

Analytical Method

A known volume of air is drawn through a tube containing coconut charcoal to trap the vinyl bromide vapor present. The analyte is desorbed from the sorbent with ethanol and then determined in an aliquot of the solution using a gas chromatograph with a flame ionization detector. The backup section is used as a breakthrough indicator. The complete sampling and analytical method referenced below has been tested with air containing concentrations of the analyte of 1.32 to 56.5 mg/m^3 at 25 °C and at a relative hummdity of 80% or greater. Details are provided in the reference given below.

Sampling Equipment

1. Personal sampling pump, capable of accurate flow (±5%) in the recommended range of sampling flow rates (0.025 to 0.2 L/min). The pump is calibrated at the recommended sampling flow rates with a recommended sampling tube in line.

2. Sorbent tubes: SKC Catalog No. 226-09 (SKC, Inc., Eighty-Four, PA 15330) or equivalent. These sorbent tubes are 110 mm long by 8 mm o.d. glass tubes packed with a 400-mg sorbing section and a 200-mg backup section of coconut-based charcoal. The sorbing section is preceded in the tube by a glass wool plug held in place with a metal spring. The sorbing section and backup section are separated by a polyurethane foam plug. There is also a foam plug placed near the outlet end of the tube to hold the backup sorbent section in place. The pressure drop across a typical tube is about 1.1 in. H_2O (0.3 kPa) at a sampling rate of 0.2 L/min.

Sample Size

The volume of air sampled should not exceed 6 L.

Sampling Procedure

1. Immediately before sampling, break the ends of the tube to provide an opening that is at least 2 mm (one-half the internal diameter of the tube).

2. Connect the tube to the sampling pump with Tygon or rubber tubing. The smaller section of sorbent is the backup section and is positioned nearer the sampling pump.

3. Place the sorbent tube in a vertical position during sampling to prevent channeling.

4. Air being sampled should not be passed through any hose or tubing before entering the tube.

5. Sample is taken at 0.05 to 0.2 L/min.* Measure and report the flow rate and time or volume sampled.

6. Record the temperature and pressure of the air being sampled.

7. Immediately after sampling, seal the ends of the tube with Teflon tape and plastic caps. Store the tube in the dark.

8. For every ten samples taken, process one sorbent tube in the same manner as the samples (break, seal, and transport). Do not sample air through this tube. The tube should be labeled as a blank. A minimum of three blank tubes are required for every set of samples submitted for analysis.

9. If samples are shipped to a laboratory, pack them tightly to minimize tube breakage during shipping.

10. Ship nine to twelve unopened sorbent tubes so that desorption efficiency studies can be performed on the same type and lot of charcoal used for sampling.

Special Considerations

1. Where two or more compounds are known or suspected to be present in air, the identities of the substances should be transmitted with the sample.

2. The pumps should not be operated more than 8 h continuously without recharging the battery.

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* Although the lowest sampling rate used in the development of a method for vinyl bromide was 0.05 L/min, a lower sampling rate such as 0.025 L/min may increase the possible sample time.

Bulk Samples

If samples of material containing vinyl bromide are shipped to the laboratory, they should be submitted in glass containers with Teflon-lined caps. Do not transport these samples in the same container with sorbent tubes.

Shipping Instructions

Capped sorbent tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping. Never transport, mail, or ship the bulk sample in the same container as the sample or blank tubes. When the samples are received by the laboratory, they can be stored for at least 1 week at room temperature (25 to 30 °C) without loss of vinyl bromide from the samples. If tubes are refrigerated, store them in an airtight container to prevent contamination by the diffusion of chemicals through the plastic end caps.

Reference

Spafford, R.B.; Dillon, H.K. "Analytical Methods Evaluation and Validation for Vinylidene Fluoride, Vinyl Bromide, Vinyl Fluoride, Benzenethiol, and n-Octanethiol: Research Report for Vinyl Bromide"; NIOSH Contract No. 210-79-0100; Southern Research Institute: Birmingham, Alabama; September 1981.