The Determination of 1,3–Butadiene in Workplace Air: Reevaluation of NIOSH Method S91 and Development of NIOSH Method 1024

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Evidence that 1,3–butadiene is a potential occupational carcinogen, teratogen, and possible reproductive hazard has prompted a reassessment of the risks of exposures to low levels. A reevaluation of NIOSH Method S91 indicated a lower quantitation limit of about 3.4 ppm in 6-L samples. The breakthrough volume was less than 8 L at a concentration of 80 ppm in humid air. As reported here, a new sampling and analytical method, NIOSH Method 1024, was developed which utilizes collection on tandem 400- and 200-mg coconut-shell charcoal samplers, desorption in methylene chloride, and a sensitive, selective analysis by high-resolution gas chromatography with flame-ionization detection. Air volumes up to 25 L may be sampled, permitting quantitation of full-shift exposures ranging from 0.4 to 10 ppm. The range may be extended up to 100 ppm by diluting desorbed samples. The limit of detection was about 0.2 µg per sample or 0.005 ppm for 25-L samples. There was an average loss of 1.5% per day for 1,3–butadiene loadings of 26 µg stored at ambient temperature. However, there was no significant loss when samplers were stored in a freezer below -4 °C for one through 21 days.

In 1977, the National Institute for Occupational Safety and Health (NIOSH) published Method S91 for the sampling and analysis of 1,3–butadiene in air (*1*). It addressed the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) of 1000 ppm, and was evaluated over concentrations of 500 to 2000 ppm. Since then, concern about exposure to 1,3–butadiene has increased markedly. In 1984, based on the induction of multiple-site carcinogenic responses in inhalation exposure studies of rats and mice (*2-4*), NIOSH recommended that 1,3–butadiene be regarded as a potential occupational carcinogen, teratogen, and possible reproductive hazard (*5*). Based on the same animal studies, the American Conference of Governmental Industrial Hygienists (ACGIH) proposed a suspect carcinogen_(A2) classification for 1,3–butadiene (*6*); a Threshold Limit Value (TLV) of 10 ppm, proposed in 1984, was adopted recently (*7*). Clearly, the risks of exposure to 1,3–butadiene needed to be reevaluated based on the new toxicological information and the extent of worker exposure.

Six NIOSH Health Hazard Evaluations, conducted between 1972 and 1979, reported exposures ranging from 0.06 to ≥46 ppm (*5*). While the exposure levels were obviously much lower than the OSHA PEL, the use of these historical data for risk assessment would be limited for the following reasons. Five of the six investigations resulted in a total of just six samples with detectable 1,3–butadiene. Reported concentrations ranged from 0.8 to 2.1 ppm. The other survey, conducted in 1977 at a synthetic rubber plant, provided the bulk of the data. In this case, more than six weeks elapsed between sampling and analysis, though the samples presumably were refrigerated. 1,3–Butadiene was undetected in 18 of the 70 samples. In the five most heavily loaded samples, with reported concentrations ranging from ≥18 to ≥46 ppm, severe breakthrough occurred. (1,3–Butadiene was not regarded as an important hazard at that time; the nominal sample volumes of 48 or 96 L were designed for sampling other substances, e.g., benzene.) In the remaining 47 samples, whose reported concentrations ranged from 0.06 to 5.5 ppm, the median amount found was only 0.04 mg, or four times the reported detection limit. Since then, through 1983, 1,3–butadiene was detected in only 16 of the 77 samples so analyzed in studies conducted by NIOSH investigators, and the highest levels found were no more than five times the reported detection limits.

Since the performance of the sampling and analytical methods had not been evaluated at such low levels, several factors could have adversely affected the validity of the data:

- The recovery or desorption efficiency of an analyte generally decreases with the amount collected, especially at low levels. Uncorrected low recovery would lead to underestimation of the actual exposure levels.
- For the majority of the samples, the sample volume greatly exceeded the maximum of 1 L recommended in Method S91. While the breakthrough volume would increase with decreasing analyte concentration, the volumes sampled obviously were excessive in some cases. In others, where the amount collected was near the detection limit, breakthrough may have occurred undetected, resulting in underestimation of the actual exposure levels.

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- The evaluation of Method S91 did not include an investigation of storage effects. Losses during storage would lead to underestimation of the actual exposure levels.
- While Method S91 performed adequately at high levels, at trace levels the possibilities for chemical interference are enhanced greatly. Chromatographic interferences from other light hydrocarbons could cause overestimation of the actual exposure levels.

NIOSH researchers, through an interagency agreement with the U.S. Environmental Protection Agency, began an industry-wide study of 1,3–butadiene monomer and polymer plants for the purpose of establishing the current extent of worker exposure and effectiveness of control technology. The effort included a reevaluation of Method S91. This communication reports the results of the reevaluation and the subsequent development of Method 1024 (*8*). This method features collection on tandem coconut-shell charcoal tubes, desorption with methylene chloride, and high-resolution gas chromatographic analysis. Other recently developed methods for the determination of 1,3–butadiene in air are: OSHA Method 56 (*9*), with collection on specially cleaned coconut-shell charcoal coated with 4-*tert*-butylcatechol and desorption by carbon disulfide; and Health and Safety Executive (London) MDHS 53, with collection on 13X Molecular Sieve and thermal desorption (*10*). Both of these methods specify analysis by packed column gas chromatography.

EXPERIMENTAL SECTION

Reagents. Instrument grade 1,3–butadiene (99.5 mole %) was obtained from Matheson, East Rutherford, NJ. A certified mixture of 9.51 ppm (±2%) 1,3–butadiene in nitrogen (can mix # 250) and mixtures of hydrocarbons at approximately 15 ppm in nitrogen (can mix #s 1-8, 30) were obtained from Scott Specialty Gases, Plumsteadville, PA. n–Hexane, 99+%, was obtained from Aldrich, Milwaukee, WI. Glass-distilled carbon disulfide (Cat. # CX0396-1) was obtained from MCB, Cincinnati, OH. Glass-distilled methylene chloride (Product # 300) was obtained from Burdick & Jackson, Muskegon, MI. Coconut-shell charcoal tubes (Lot 107, Cat. # 226-01 and Lot 120, Cat. # 226-37) and petroleum-coke charcoal tubes (Lot 104, Cat. # 226-38 and 226-38-02) were obtained from SKC, Eighty-Four, PA. A carbon molecular sieve, 177/250-µm (60/80-mesh) Carbosphere, was obtained from Alltech Associates, Deerfield, IL.

Apparatus. House air for simulated sampling was purified, humidified, and distributed through a jacketed mixing chamber and 12-port manifold. The air flow into the system was set to 10 L/min by a mass flow controller from Tylan Corp., Carson, CA, and the humidity level was maintained at 80% relative humidity by a Hydrocon precision electro-humidity reader-controller from Phys-Chemical Research Corp., New York, NY. Sampling pumps were Models SP–1, SP–2, and SP–4 from Anatole J. Sipin Co., New York, NY. Ultraviolet and visible absorbance measurements were made on Models 25 and 26 spectrophotometers from Beckman Instruments, Fullerton, CA.

Chromatographic analyses were performed on Hewlett-Packard (Avondale, PA) Models 5840A and 5880A gas chromatographs. The carrier gas, 99.995% helium, from Union Carbide, Danbury, CT, was purified with a Model H36GG2 "go-getter" from General Electric, Pleasanton, CA. The HP 5840A gas chromatograph was equipped with dual packed column inlet systems and flame-ionization and thermal conductivity detectors. To enable the introduction of gases, one or more sample injection valves were at times installed in a carrier gas line just before an injection port. The valves used included a Model 7010 with 200-, 50-, and 10-µL sample loops and a Model 7410 with 2- and 0.5-µL loops, both from Rheodyne, Cocati, CA, as well as a 10-port valve from Valco, Houston, TX. One 2-mL loop on the Valco valve was fitted with a tee and septum. This permitted the introduction of gas samples by gas-tight syringe at ambient pressure. Separations were obtained on several columns, including a 1.7-m x 2-mm ID glass column packed with 177/250-µm (60/80-mesh) acetone-washed Chromosorb 102 (Alltech Stock # 2408W) and 6.1-m x 3.2-mm OD stainless steel columns from Supelco, Bellefonte, PA, packed with 10% SP-1000 on 149/177-µm (80/100-mesh) Supelcoport or 10% FFAP on 149/177-µm (80/100-mesh) Chromosorb W-AW.

The HP 5880A gas chromatograph was equipped with packed column and dual split-splitless capillary inlet systems and flame-ionization detectors. Separations were obtained with the FFAP column mentioned above or a 50-m x 0.32-mm ID fused-silica porous-layer open-tubular (PLOT) column coated with KCl-deactivated aluminum oxide (Cat. # 7515) from Chrompack, Bridgewater, NJ. The latter column was protected from high-boiling or polar contaminants through the use of a backflushable 10-m x 0.50-mm ID fused-silica precolumn coated with a 1.8-µm film of CP WAX 57 CB (Chrompack Cat. # 7648).

Reevaluation of Method S91 and Sorbent Comparisons. The potential for interference problems when using the chromatographic conditions specified in Method S91 were evaluated as follows. Samples of the hydrocarbon mixtures in nitrogen were injected by gas-tight syringe into the HP 5840A gas chromatograph using the SP-1000 or FFAP column at an oven temperature of 50 or 80 °C, respectively. The carrier flow was 30 mL/min. The injection port temperature was 140 °C and the flame-ionization detector temperature was 200 °C.

Recoveries at low loadings, using the sampler and eluent specified in Method S91, were determined by the phase-equilibrium method. Analyses were performed using the HP 5880A gas chromatograph, FFAP column, and flame-ionization detector. The injector and detector temperatures were 250 °C, the helium flowrate was 30 mL/min, and the column temperature was initially 52 °C for 3 min, then programmed at 30 °C/min to 240 °C and held 1 min. Standard solutions were prepared by gas-tight syringe injections of 0.4-mL aliquots of 1,3–butadiene gas into sealed vials containing 1 mL of carbon

disulfide. Analyses of replicate standards indicated that transfers of the pure gas by syringe were incomplete to varying degrees. This conclusion was based on the observation that obvious outliers always were characterized by low results. Therefore, a single-point calibration was based on the standard providing the greatest response. For each loading tested, five vials containing 1 mL of carbon disulfide were prepared. For three of the vials, 100 mg of coconut-shell charcoal were added. The remaining two vials served as controls. All five vials were injected with identical portions of 1,3–butadiene standard solution. Depending on the loading desired, the amounts of standard solution added ranged from 11 to 220 µL. After sitting overnight, the samples and controls were analyzed. The difference in the average amounts found in the controls and samples was considered retained by the sorbent. This amount plus the average amount found in 1 mL of sample was taken to be the loading. The desorption efficiency was derived from the ratio of the amount in 1 mL of sample solution to the loading.

Relative 1,3–butadiene recoveries were measured for three sorbents — carbon molecular sieve, petroleum-coke charcoal, and coconut-shell charcoal. The same analytical conditions were used except for a slightly modified temperature program. Samplers were used as purchased or were prepared by packing 100-mg sorbent sections into 4-mm ID glass tubing. They were loaded either by passing through identical volumes of the certified mixture of 1,3–butadiene in nitrogen or by injecting aliquots of 1,3–butadiene in air from a Tedlar bag into the samplers as laboratory room air was drawn through. They were extracted either with 5 mL of carbon disulfide or 1 mL of methylene chloride, both containing 0.01% (v/v) n–hexane as an internal standard for the chromatographic analysis. Because of continued difficulties in preparing standard solutions for calibration, the amounts of 1,3–butadiene recovered were calculated by the internal standard method, using an assumed response factor of 1.00 for 1,3–butadiene relative to n–hexane.

The capacities of carbon molecular sieve, coconut-shell charcoal, and petroleum-coke charcoal were compared by exposing the tested sampler to a constant concentration of 1,3–butadiene in humid air while monitoring the UV absorbance of the effluent from the sampler. A 40-L Tedlar bag was filled with humid air. After pure 1,3–butadiene was transferred by gas-tight syringe into the bag, the atmosphere was allowed to equilibrate for more than 30 min. The 100- or 400-mg sampler was connected by short pieces of flexible plastic tubing to the bag and to a 1-cm quartz flow cell mounted in a spectrophotometer, which was set to monitor the observed 1,3–butadiene absorbance maximum at 217 to 219 nm. The outlet of the flow cell was connected to a calibrated pump set for a flow of 50 to 100 mL/min. The volume sampled was calculated from the sampling rate and time. The concentration of the bag atmosphere was monitored occasionally by removing the sampler from the line to obtain a direct reading. Breakthrough was deemed to occur when the absorbance of the sampler effluent reached 5% of that observed directly from the bag. The concentration of 1,3–butadiene in the bag was calculated from the observed absorbance, assuming an ambient temperature of 22 °C, barometric pressure of 750 mm Hg, and a value of 14600 L–mole^{-1}-cm^{-1} for the molar absorptivity of 1,3–butadiene, which was estimated from the maximum occurring at 215.8 nm in a published vapor phase spectrum (*11*).

Evaluation of Method 1024. There were five tests of the precision and accuracy of the total sampling and analytical method. Simulated samples and media standards were prepared by loading the front tubes from 400/200-mg sets of charcoal tubes. Known amounts of 1,3–butadiene were placed inside the front of the tube as laboratory air was pulled through by a sampling pump for 2 min at a flow of 150 to 200 mL/min. Three different techniques were used to deliver 1,3–butadiene: (1) A calibrated Rheodyne sample injection valve/loop was filled with pure 1,3–butadiene and flushed with inert gas flowing at 50 mL/min; (2) A gas-tight syringe was used to transfer an appropriate amount of a standardized 1,3–butadiene-He mixture; (3) A gas-tight syringe was used to transfer a 40-µL aliquot of standard solution. Blank media standards and simulated samples were prepared by going through all the steps except for the actual transfer of 1,3–butadiene.

Standard solutions were prepared by injecting aliquots of 1,3–butadiene gas into sealed vials, chilled in an ice-water bath and containing methylene chloride. A special technique was used to assure quantitative transfer. A gas drying tube was submerged in a beaker of freshly distilled, deionized water and the small end was closed with a serum cap. 1,3–Butadiene was captured in the drying tube by the displacement of water. A piece of plastic tubing fitted over the serum cap was filled with water. Aliquots of gas withdrawn by gas-tight syringe were bracketed with plugs of water taken from above the serum cap. The quantities transferred were corrected for the vapor pressure of water and the compressibility of 1,3–butadiene (*8,12*).

The samples and media standards were extracted by dumping the charcoal sections into 5-mL vials chilled in ice-water and containing 4 mL of methylene chloride. The vials were closed immediately with crimp-on seals and polytetrafluoroethylene-lined septa and allowed to stand at least 30 min at room temperature to complete the desorption. Aliquots of standard solutions and desorbed samples and media standards were transferred into chilled autosampler vials and sealed in preparation for analysis on the HP 5880A gas chromatograph, which was equipped with a 7672A automatic injector set for 1-µL injection. The injector temperature was 200 °C, the detector 250 °C. The capillary inlet systems had been modified to enable use of a backflushable pre-column. The construction and operation of the modified inlet system has been described elsewhere (*8,13*). The gauge pressure at the head of the analytical column was set to 185 kPa, providing a flow of approximately 4 mL/min through the analytical column. Nitrogen was used as the make-up gas. The forward and reverse flows through the pre-column were set to 10 mL/min. Typically, the time between injection and backflush was set to 1.2 min and the column oven was

programmed to hold an initial temperature of 50 °C for 2 min, rise to 120 °C at 20 °C/min, hold 5 min, rise to 200 °C at 30 °C/min, and hold 5 min before recycling.

In the first test, six samples were loaded with 125 μg of 1,3–butadiene by the Rheodyne valve/loop. Five media standards were prepared at each of three levels by loading tubes with 250-, 500-, and 750-μL aliquots of standardized 1,3–butadiene-He mixture. Standard solutions were prepared from 25-, 50-, and 75-μL aliquots of pure gas in 4 mL of solvent, four at each level. The samples, media standards, and standard solutions were analyzed after storage overnight at ambient temperature.

In the second test, six samples were loaded with 463 μg in 2.62-mL aliquots of 1,3–butadiene-He mixture. Two back sections were attached to each sample and to one blank, and clean, humid air from the 12-port sampling manifold was drawn through the assemblies until 22.3 to 27.9 L had been sampled. Three media standards at each of five levels were loaded using the Rheodyne valves. Standard solutions ranging from 1.10 to 110 μg/mL were prepared in triplicate by transferring 2- to 200-μL aliquots of pure gas into 4 mL of solvent. The tubes were capped, stored in a freezer overnight, extracted, and analyzed along with the standard solutions on the following day.

In the third and fourth tests, triplicate standard solutions ranging from 0.221 to 116 μg/mL were prepared from 10- to 210-μL aliquots of pure gas in 4 to 100 mL of solvent. In the third test, the samples were loaded with 45.3 μg in 140 μL of 1,3–butadiene-He mixture, only one back section was used, and 27.3 to 32.4 L of humid air were sampled. In the fourth test, the samples were loaded with 4.64 μg in 35 μL of 1,3–butadiene-He mixture, one back section was used, and 24.6 to 28.4 L of humid air were sampled. Otherwise, the procedures of the second test were followed.

In the fifth test, the samples were loaded with 4.71 μg in 20 μL of 1,3–butadiene-He mixture and were exposed, with one back section attached, to 24.8 to 25.4 L of humid air. The procedures of the second test were followed except that the preparation of the media standards and standard solutions was modified. Triplicate standard solutions in three concentrations ranging from 28 to 440 μg/mL were prepared by transferring 50- to 200-μL aliquots of pure gas into 1 to 4 mL of solvent. Lower standards ranging from 0.07 to 4.4 μg/mL were prepared by diluting 10 to 40 μL of the higher standards in 4 mL of solvent. This provided better precision for the lower standards. The two highest levels of media standards were prepared as before, but the three lower levels were loaded using 40-μL aliquots of the three highest standard solutions.

The actual volumes of the Rheodyne sample injection valve/loop combinations, including the internal volume of the valves, were determined in several ways. Gravimetric determinations, based on the masses of nonvolatile residue from aliquots of aqueous saline solution of known concentration delivered by the "50-μL" loop, gave volumes of 53.1 and 55.3 μL. In another method, the HP 5840A gas chromatograph, Chromosorb 102 column, and thermal conductivity detector were used to measure the relative responses from injections of air by gas-tight syringe versus valve. Calibrations in this manner gave estimates of 218.5 μL for the "200-μL" loop, 56.8 and 58.2 μL for the "50-μL" loop, 13.8 and 14.1 μL for the "10-μL" loop, and 2.8 μL for the "2-μL" loop. In the same way, but using 1,3–butadiene instead of air, the "50-μL" loop volume was calculated to be 57.8 μL. The most precise determinations were accomplished by a spectrophotometric method. A stock solution of 1% Fast Green FCF (93% dye content) in a phosphate buffer of pH 6.9 was prepared. Standard solutions were prepared, four at each of four levels, by diluting 20–, 25–, 30-, and 35-μL aliquots of the stock solution with the buffer solution in 50-mL volumetric flasks. The volumes delivered by the syringe were gravimetrically verified to be accurate within 1.5%. The standards provided a calibration of absorbance versus volume for absorbances ranging from about 0.6 to 1 at 626 nm. Three measurements were made for each valve/loop combination by filling the valve with the stock dye solution, flushing the aliquot into a volumetric flask, diluting to the mark with buffer solution, and measuring the absorbance. The dilutions were "0.5-μL" to 1 mL, "2-μL" to 5 mL, "10-μL" to 25 mL, "50-μL" to 100 mL, and "200-μL" to 500 mL. The valve/loop volumes determined from the dilution ratios and measured absorbances were: "0.5-μL", 0.71 ± 0.03 μL; "2-μL", 2.11 ± 0.07 μL; "10-μL", 11.40 ± 0.07 μL; "50-μL", 54.86 ± 0.07 μL; "200-μL", 210.5 ± 0.9 μL. The values measured by the latter method were assumed to be the most accurate and were used in subsequent calculations.

The standardized mixtures of 1,3–butadiene in helium were prepared by introducing approximately 9 volumes of helium and one volume of 1,3–butadiene into a 1-L Tedlar bag. The precise concentration of the 1,3–butadiene-He mixture was determined as follows. Aliquots were injected into the 10-port valve on the HP 5840A gas chromatograph with the Chromosorb 102 column at 160 °C and the thermal conductivity detector at 180 °C. Typically, six replicate injections of two different volumes of the 1,3–butadiene-He mixture were interspersed with six injections of 54.9 μL of pure 1,3–butadiene by the Rheodyne valve/loop. The volumes of the mixture were chosen to give responses closely bracketing the response due to the pure 1,3–butadiene. Linear regression of the mixture data yielded an equation which, when solved for the volume giving a response equal to that observed for the 54.9 μL of pure 1,3–butadiene, lead to the concentration of the 1,3–butadiene-He mixture.

To check the storage stability, six media standards were prepared at weekly intervals using the 11.4-μL valve/loop. Three tubes were stored at ambient temperature and three tubes and a blank were stored in a freezer at less than -4 °C. Three media standards at each of three other loadings were prepared along with the fourth set and placed in the freezer. On the following day, all the tubes were extracted and analyzed. The calibration was based on the results for the media standards stored 1 day in the freezer.

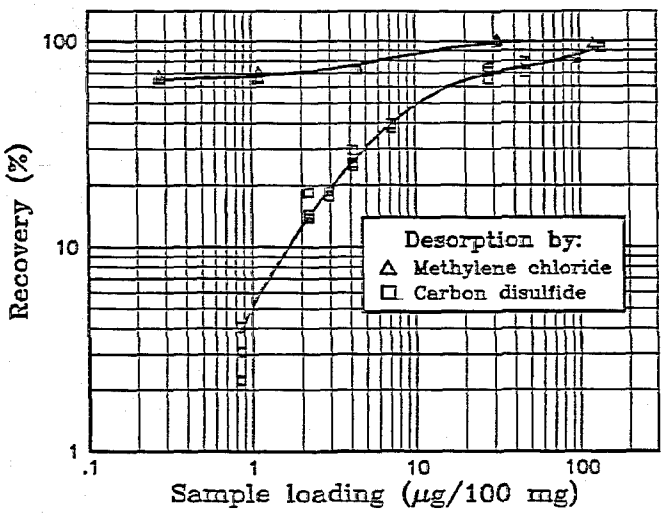

Figure 1. Recovery versus sample loading for the desorption of 1,3–butadiene from 100 mg coconut-shell charcoal by 1 mL carbon disulfide or from 400 mg coconut-shell charcoal by 4 mL methylene chloride. Solid lines are curves empirically fitted to the data.

The breakthrough volume for the 400-mg coconut-shell charcoal sampler was rechecked by challenging the sampler with an initial pulse of pure 1,3–butadiene rather than a constant concentration. The outlet end of a sampler was connected to vacuum through the 200-μL Rheodyne valve and a critical orifice. A known volume, 0.7 mL, of 1,3–butadiene was introduced by gas-tight syringe into the tube inlet, which was then connected to an aluminized bag containing humid air. Periodically, the valve was used to inject an aliquot of the effluent for gas chromatographic analysis by the HP 5840A with Chromosorb 102 column and flame-ionization detection. Calibration was achieved by using the same valve to inject aliquots of the certified mixture of 1,3–butadiene. The breakthrough volume was estimated from the sampling rate and the time at which the effluent concentration reached 5% of the time-weighted average influent concentration. The experiment was repeated with a fresh sampler, using 2.5 mL of 1,3–butadiene.

RESULTS AND DISCUSSION

Reevaluation of Method S91. The reassessment of Method S91 included investigations of recovery, breakthrough volume, and potential chromatographic interferences. The lower curve in Figure 1 shows percent recovery versus 1,3–butadiene loading, as determined by the phase-equilibrium method, for the sampler and eluent specified in Method S91. If the lower quantitation limit is determined by the level at which recovery falls below 75%, a limit of 45 μg per sample is indicated. The volume of air that would have to be sampled to collect that amount is, of course, dependent on the concentration. For example, the current ACGIH TLV of 10-ppm (*7*) could be measured with a 2-L air sample. However, several labor unions submitted petitions to OSHA for an Emergency Temporary Standard of 1 ppm or less (*14*), which would require at least a 20-L air sample. (OSHA subsequently denied the petitions.) Another factor related to the required breakthrough volume is loading by co-contaminants in the occupational environment. In the case of 1,3–butadiene, ten other light hydrocarbons could easily be present at similar concentrations. Thus, measurements of 10 ppm 1,3–butadiene may expose a nonselective sorbent to a total hydrocarbon concentration of more than 100 ppm. The evaluation of breakthrough volume at relatively high levels seemed advisable to assure a robust sampling method. The breakthrough volume for the S91 sampler was less than 5 L for approximately 450-ppm 1,3–butadiene in air at ambient temperature and 80% relative humidity. At about 80 ppm, breakthrough occurred before 8 L was sampled. A conservative estimate of the lower quantitation limit for Method S91 appears to be about 3.4 ppm, based on a 6-L sample volume.

TABLE I. Retention Times of 1,3–Butadiene and Other Light Hydrocarbons on Packed Columns of SP–1000 and FFAP

compounds	retention time on SP-1000[a] (min)	retention time on FFAP[b] (min)
butane	2.41	2.17
1-butene	2.53	2.23
2-methylpropene	2.53	2.25
ethyne	2.57	2.23
2-methylbutane	2.61	2.28
cis-2-butene	2.70	2.34
3-methyl-1-butene	2.73	2.34
pentane	2.74	2.30
2,2-dimethylbutane	2.88	2.40
1,3-butadiene	2.90	2.42
1-pentene	2.98	2.44
2-methyl-1-butene	3.08	2.50
propyne	3.12	2.50
2-methylpentane	3.13	2.51
cis- and *trans*-2-pentene	3.22	2.56
3-methylpentane	3.32	2.59
2-methyl-2-butene	3.37	2.62
4-methyl-1-pentene	3.46	2.66
hexane	3.47	2.64

Gas samples in nitrogen were analyzed on an HP 5840A gas chromatograph using 6.1-m x 3.2-mm OD stainless steel columns and a carrier flow of 30 mL/min. [a]10% loading on 149/177-μm (80/100-mesh) Supelcoport at 50 °C. [b]10% loading on 149/177-μm (80/100-mesh) Chromosorb W-AW at 80 °C.

Another potential shortcoming of Method S91 is that the packed column gas chromatographic analysis is subject to interference. Table I lists retention times for 1,3–butadiene and other hydrocarbons under two different sets of conditions. Based on the peak width for 1,3–butadiene, substances eluting within 0.1 min would interfere severely. The potential for interference drops off as the separation increases to 0.2 min.

TABLE II. Comparisons of Recovery from Selected Sorbents

sorbent	number of samples	average amount recovered (μg)	standard deviation (μg)
carbon molecular sieve	7	2.10[a]	0.25
coconut-shell charcoal	7	2.07[a]	0.16
coconut-shell charcoal	5	2.16	0.26
petroleum-coke charcoal	5	1.97	0.19
coconut-shell charcoal	3	0.054	0.005
petroleum-coke charcoal	3	0.048	0.007
coconut-shell charcoal	3	0.054[b]	0.008
petroleum-coke charcoal	3	0.045[b]	0.006

Samples on 100 mg of sorbent were desorbed with 1 mL of 0.01% n–hexane in methylene chloride and analyzed within 1 day. [a]Samples were desorbed with 5 mL of 0.01% n–hexane in carbon disulfide. [b]Samples were stored 6 days before desorption.

TABLE III. Breakthrough Volume Measurements for Selected Sorbents

sorbent	bed size[a] (mg)	sampling flowrate (mL/min)	influent concentration (ppm)	volume (L)
carbon molecular sieve	100	54	31	16
coconut-shell charcoal	100	54	31	>13
	100	54	38	>10
	100	97	82	8
	100	59	451	5
	400	89	56	31
	400	89	106	35
petroleum coke charcoal	100	97	72	5
	400	89	106	18
	400	89	136	12

1,3-Butadiene atmospheres were prepared and sampled at 22 °C and 80% relative humidity. The breakthrough volume was determined when the UV absorbance of the effluent reached 5% of the influent. [a]Bed diameters were 4 mm for 100–mg sections and 6 mm for 400–mg sections.

Development of Method 1024. The first efforts at developing the method were directed towards recovery. Carbon disulfide containing n–hexane as an internal standard slightly improved the recovery, as did increasing the volume or adding a π-electron donor (benzene). However, recoveries were improved greatly by desorbing with methylene chloride. The upper curve in Figure 1 shows percent recovery versus sample loading for the desorption of 1,3–butadiene from coconut-shell charcoal with methylene chloride. (It may be significant that the methylene chloride was preserved with cyclohexene. However, the role cyclohexene may play in improving the recovery was not investigated.) Thus, methylene chloride was selected as the eluent for all subsequent work.

Many commonly used adsorbents, such as porous polymers, graphitized carbons, etc., are not practical for sampling volatile compounds like 1,3–butadiene — they are not sufficiently retentive. While some of the inorganic adsorbents might have proven satisfactory (*10*), this study was limited to two charcoals, petroleum-coke and coconut-shell, and a carbon molecular sieve. Table II gives the results of comparative recovery measurements on these sorbents. Table III lists the results of breakthrough volume determinations. It appeared that the carbon molecular sieve and coconut-shell charcoal were about equally good, and superior to the petroleum-coke charcoal. However, the use of carbon molecular sieve was rejected, because of its relatively high cost. Thus, it was concluded that a 400-mg primary section of coconut-shell charcoal would provide adequate recovery for a 20-μg loading of 1,3–butadiene, a breakthrough volume of at least 25 L, and the ability to quantitate down to 0.5 ppm when extracted with methylene chloride in a proportion of 1 mL per 100 mg of sorbent. The use of a separate 200-mg backup section was chosen to eliminate the possibility of migration from front to back sections during shipment or storage.

As the laboratory evaluation of the method was continuing, the industrial hygiene studies of four 1,3–butadiene monomer production plants began. Samples from the first two surveys were analyzed by gas chromatography on a 6.1-m x 3.2-mm OD stainless steel column packed with 20% SP-2100 on 149/177-μm (80/100-mesh) Supelcoport. Butanes and butenes interfered with the quantitation of 1,3–butadiene, prompting the search for a better separation. A 2-m x 3.2-mm OD stainless steel column packed with 0.19% picric acid on 149/177-μm (80/100-mesh) GP Carbopak was unsatisfactory, because methylene chloride interfered. The carrier flow was too low on a 9-m x 3.2-mm OD stainless steel column packed with 23% SP-1700 on 149/177-μm (80/100-mesh) Chromosorb P-AW. A 25-m x 0.32-mm ID fused-silica capillary coated with a bonded 5-μm film of methyl silicone would not separate 1,3–butadiene from n–butane except at sub-ambient oven temperatures. Finally, an Al_2O_3/KCl PLOT column was selected, because it provided baseline separation of 1,3–butadiene from the other light hydrocarbons present in field samples at an oven temperature of 120 °C. Using the latter column, a large number of hydrocarbons and halocarbons were chromatographed to check for potential interferences. The elution order is given in Table IV. The separation of 1,3–butadiene from the immediately adjacent peaks due to pentane and vinylidene chloride is shown in Figure 2.

TABLE IV. Elution Order of 1,3–Butadiene and Possible Hydrocarbon or Halocarbon Interferences on an Al_2O_3/KCl PLOT Column

compounds	Kovats retention indices[a]
propane	300
dichlorodifluoromethane	341
cyclopropane	342
propylene	346
acetylene	353
isobutane	390
butane	400
chlorodifluoromethane	415
propadiene	440
trans-2-butene	440
1,2-dichlorotetrafluoroethane	441
1-butene	445
isobutene	453
cis-2-butene	461
neopentane	471
cyclopentane	489
methylacetylene	491
isopentane	491
pentane	500
1,3-butadiene	503
vinylidene chloride	513
3-methyl-1-butene	526
trans-2-pentene	533
1-pentene	544
2-methyl-1-butene	550
cis-2-pentene	555
trichlorofluoromethane	575
1,1,2-trichloro-1,2,2-trifluoroethane	575
2,2-dimethylbutane	578
cyclohexane	583
2,3-dimethylbutane	587
2-methylpentane	588
dichloromethane	591
3-methylpentane	591
hexane	600

Data were obtained for gas samples injected (1 to 15 split ratio) into a Tracor MT560 gas chromatograph using a 50-m x 0.32-mm ID column, 205 kPa carrier (helium) head pressure, and 120 °C oven temperature. [a]These indices are intended only as a general indication of the relative retention. Indices may vary, depending on the moisture content of the carrier, which was not determined. Also, as the column ages, irreversibly retained material may change the retention order.

The third and fourth sets of field samples were analyzed using the Al_2O_3/KCl PLOT column. This revealed a severe problem. During the course of the analyses, there was a reversal in the elution order of 1,3–butadiene and vinylidene chloride, which is a contaminant in methylene chloride. For a time, 1,3–butadiene could not be quantitated because of the interference. Also, there was considerable variability in retention time due to the presence of moisture in the field samples and consequent deactivation of the aluminum oxide. These problems were circumvented by adding an automated, backflushable pre-column, which stripped injected samples of water and any high-boiling or polar compounds that might be retained irreversibly by the aluminum oxide column. Since even volatile semi-polar compounds, e.g., methylene chloride, could be stripped and backflushed, potential interferences were reduced. In addition, by backflushing the solvent, the analysis time was reduced greatly. A discussion of the backflushable pre-column modification has been presented elsewhere (*13*). The modified analytical procedure was used for the subsequent evaluation of the method.

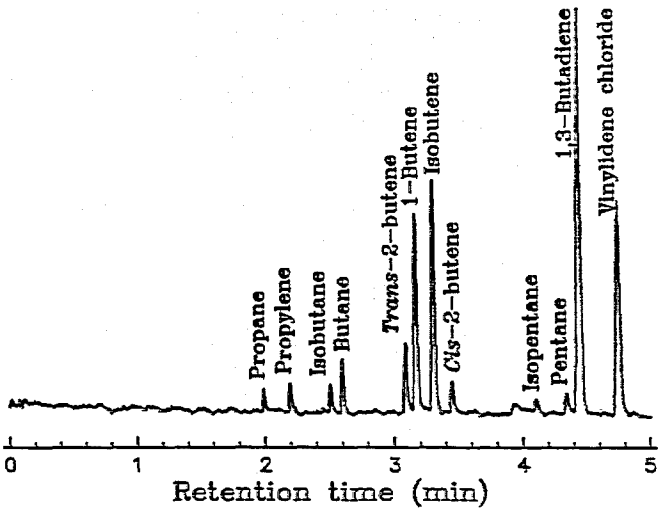

Figure 2. Separation of a typical 1,3–butadiene field sample on a 50-m x 0.32-mm ID Al_2O_3/KCl PLOT column at 120 °C.

Evaluation of Method 1024. A problem that had hampered previous efforts to evaluate the overall accuracy and precision of the method involved calibration. Ordinarily, standard solutions of a soluble gas could be prepared easily by using gas-tight syringes to inject known volumes of gas into a suitable solvent. However, 1,3–butadiene is liquefied very easily at ambient temperature and the corresponding liquid volume is so small that the entire syringe contents can be condensed into just a part of the needle. Measurement of the force required to move a 1-mL gas-tight syringe plunger revealed that it was several times greater than the force exerted through the vapor pressure of 1,3–butadiene. For smaller syringes, the situation was even worse. Thus, it was impossible to determine reliably whether a measured quantity of gas actually was delivered, either by the feel of the syringe or by the qualitative observation of bubbling beneath the surface of the receiving solvent. It is likely that partial blockage of the needle with flakes of polymer shed from the gas-tight seal frequently prevented quantitative transfer. Since 1,3–butadiene is only slightly soluble in water, and likewise, water in methylene chloride, a solution to the problem was to bracket the 1,3–butadiene gas between plugs of water. Expulsion of the water assured complete delivery of the gas.

TABLE V. Overall Accuracy and Precision Tests

test	sample loading (μg)	recovery[a] (%)	desorption efficiency[b] (%)	relative standard deviation[c]
1	125	102.2	96.8	0.016
2	463	101.6[d]	91.3[d]	0.047
3	45.3	112.3	102.9	0.048
4	4.64	80.3	103.8	0.011
5	4.71	129.4	91.2	0.023
			pooled RSD	0.033

Six samples were prepared for each test and analyzed in duplicate. [a]Average amount found, calibrated against media standards, divided by sample loading. [b]Average amount found, calibrated against standard solutions, divided by sample loading. [c]Of the analytical response. [d]Includes amounts found on first back sections, which averaged 1.24% of the total.

Table V gives the results of five tests in which simulated samples, media standards, and standard solutions of known concentrations were prepared independently, by the procedures indicated in Table VI, and then analyzed to test the precision (relative standard deviation) and bias of the total method. The precisions for the samples appeared to be independent of loading at the levels tested. Combining the pooled precision (0.033) with an assumed sampling pump precision of 0.05 gave 0.060 as the estimated precision of the total method.

Possible bias in the method was evaluated by considering the desorption efficiencies and recoveries shown in Table V. The desorption efficiencies, based on analyses of the samples versus the standard solutions, were expected to correspond with desorption efficiencies observed for the media standards. The recoveries, based on analyses of the samples versus the media standards, were expected to be 100%. In the first two tests, the recoveries were acceptably close to 100% and the desorption efficiencies were as expected. For these tests, the reasonable agreement between the analyses of the independently prepared samples, media standards, and standard solutions implied accuracy for the total method as well as for the independent procedures used to prepare the samples, media standards, and standard solutions. However, tests three through five showed recoveries increasingly distant from 100% and desorption efficiencies that were larger than expected. Typical desorption efficiencies, observed for the media standards in the fifth test, are shown in the upper curve of Figure 1. Thus, at the lower levels, the accuracy of the total method and/or some of the preparation procedures was in doubt.

Since the flame-ionization detector provides the broadest linear dynamic range of all gas chromatographic detectors (*15*), the linearity of the standard solution calibration can provide an independent check on the accuracy of the lower-level standards. Table VII and Figure 3 show the linearity and precision obtained for the standard solutions analyzed in the fifth test, whose concentrations covered the widest range and were extended to the lowest levels. The observed deviations from linearity can be explained reasonably by small systematic or random errors in preparation. Also, as shown in Figure 4, the negligible intercept indicates a lack of significant bias in the preparation of the standards at the lowest concentration. On this evidence, it was assumed that the preparation of the standard solutions was accurate and that calibrations based on the standard solutions could be used to evaluate the results of the other procedures.

TABLE VI. Preparation Procedures Used in the Precision and Accuracy Tests

test	preparation method for samples	media standards	standard solutions
1	loop	dilute gas	water plug
2	dilute gas	loop	water plug
3	dilute gas	loop	water plug
4	dilute gas	loop	water plug
5	dilute gas	loop/standard sol'n[a]	water plug[b]

The preparation methods designated loop, dilute gas, and water plug are defined as follows. Loop refers to transfer of pure 1,3-butadiene gas by means of a calibrated valve/loop. Dilute gas refers to transfer by gas-tight syringe from a standardized 1,3–butadiene–He mixture. Water plug refers to transfer of pure 1,3–butadiene gas by gas-tight syringe, using water plugs to bracket the gas. [a]Highest two levels prepared by valve/loop. Three lowest levels prepared by loading with aliquots of standard solution. [b]Lower concentrations prepared by dilution of higher concentrations.

TABLE VII. Linearity and Precision of Standard Solution Analyses

loading (μg)	observed response[a] (area counts)	relative standard deviation	calculated response[b] (area counts)	deviation from linearity (%)
0.28	171	0.044	169	1.29
1.10	651	0.038	679	-4.19
4.40	2662	0.049	2740	-2.85
17.7	10664	0.023	10984	-2.91
112	73300	0.006	69522	5.43
448	285789	0.049	276860	3.23
		pooled RSD 0.038		

[a]Average of three independent analyses. [b]Based on a least squares regression, weighted assuming constant relative standard deviation, which gave a slope of 621 ± 9 area counts/μg and an intercept of -4 ± 6 area counts.

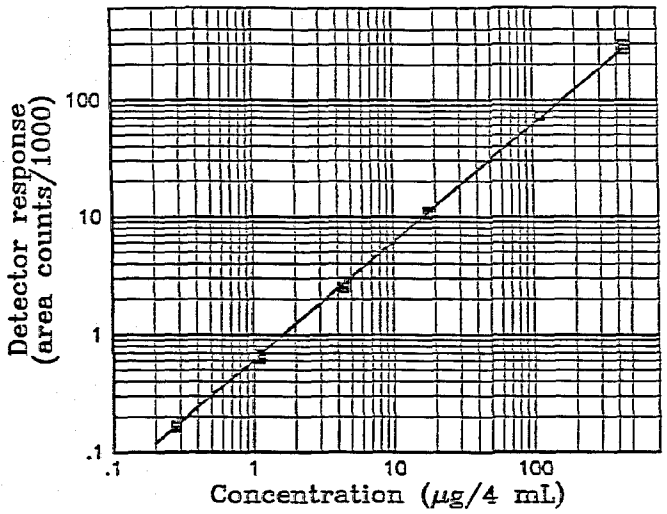

Figure 3. Log-log plot of detector response versus concentration for standard solution analyses. Table VII summarizes the data and gives the slope and intercept of the fitted line.

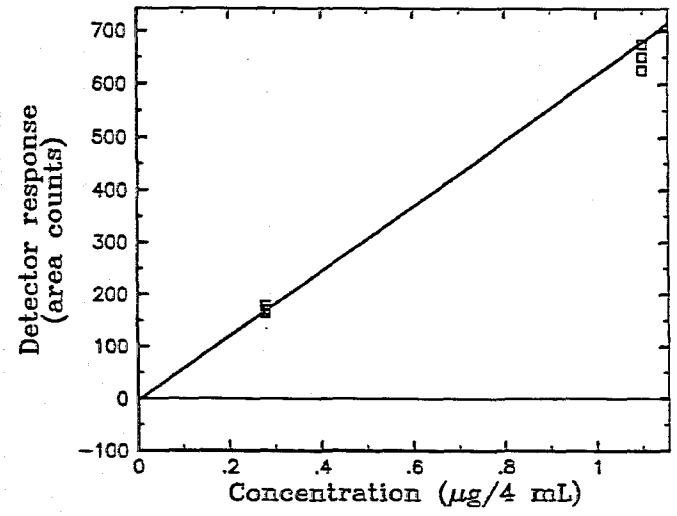

Figure 4. The same line and data as in Figure 3, plotted linearly and scaled to show the intercept and two lowest concentration levels.

Table VIII gives the desorption efficiencies from the media standards in the fourth test. The three highest concentration levels were prepared using a valve with external loops and the lower two levels by a valve with internal loops. If the standard solution calibration is correct, then the latter valve must have been delivering more 1,3–butadiene than was calculated based on the measured volumes of the valve/loop combinations. Thus, the low recovery listed for the fourth test in Table V can be explained by the apparent error in the preparation of the media standards.

As was noted previously, the desorption efficiencies observed for the samples in tests three and five were larger than the desorption efficiencies typically observed for media standards. Again, if the standard solution calibration is correct, then this implies that as the sample loading decreased, the amount actually loaded onto the samples was increasingly more than was calculated from the volume of 1,3–butadiene-He mixture transferred by gas-tight syringe. This would account for the greater than 100% recoveries in the third and fifth tests. Alternatively, a difference between the treatment of the samples and media standards may have increased the apparent recovery from the samples at low levels through chemical interference or change in desorption efficiency. However, that does not seem likely. Besides the method of loading with 1,3–butadiene, the only difference between the samples and the media standards was the exposure of the samples to humid air. Many previous experiments with media standards demonstrated that the addition of water before or during desorption did not affect the desorption efficiency. 1,3–Butadiene was not detected in any of the blank samples exposed to the humid air.

TABLE VIII. Desorption Efficiency from Media Standards Loaded by Valve/Loop

loading[a] (μg)	average amount found[b] (μg)	desorption efficiency (%)
476	441	92.6
124	120	96.6
25.8	22.5	87.2
4.76	5.50	115
1.61	3.42	212

Three media standards were prepared at each level. [a]Calculated from volume of valve/loop. [b]Calibrated against standard solutions.

Surface effects may have contributed to the apparent error in media standards and samples at the lower levels, since the ratio of surface area to volume in the measuring devices was much larger for the preparation of the lower-level samples and media standards. However, adsorption of a 1,3–butadiene monolayer can not account for the additional amounts delivered. In the case of the Rheodyne Model 7410 valve, which was used to load the two lowest levels of media standards, the ends of the internally mounted loop fit through holes in a polyimide rotor. Absorption into the polyimide is a possibility, but the amount absorbed probably would depend on the exposure time, leading to greater imprecision than was observed. Formation of an interstitial condensed phase, e.g., between the surfaces of the loop and rotor, is yet another possible explanation for the excessive amounts delivered.

Based on the results reported in Table V, the accuracy appeared to be acceptable at levels of 463 and 125 μg per sample, which would correspond to concentrations of 8.4 and 2.3 ppm, respectively, in 25-L air samples. Much of the apparent positive bias at 45.3 μg per sample, or 0.82 ppm in 25 L, may be due to error in the independent method of preparing the samples rather than bias in the proposed sampling and analytical method.

TABLE IX. Linearity and Precision of Media Standard Analyses

loading (μg)	observed response[a] (area counts)	relative standard deviation	calculated response[b] (area counts)	deviation from linearity (%)
1.10	453	0.025	424	6.69
4.42	1857	0.042	2249	-17.43
17.7	8226	0.019	9546	-13.83
125	79005	0.020	68508	15.32
481	289803	0.007	264130	9.72
	pooled RSD	0.025		

[a]Average of three independent analyses. [b]Based on a least squares regression, weighted assuming constant relative standard deviation.

Table IX gives the linearity and precision of the media standards from the fifth test. Again, the precision appeared to be independent of the loading. The non-linearity of the calibration, due to the variation in desorption efficiency, is evident. Therefore, multi-level calibration or curve fitting should be used for quantitating unknowns.

In estimating the lower limit of quantitation, the desorption efficiency of the media standards was considered. The upper curve in Figure 1 indicates that the desorption efficiency falls below 75% at a loading of about 5 μg per 100 mg of charcoal, i.e., 20 μg per sample or 0.4 ppm in a 25-L sample. Since results at lower loadings could be subject to significantly larger error if the collection of atmospheric co-contaminants increased the desorption efficiency, 20 μg per sample was chosen as the lower limit of quantitation.

A 10:1 signal to noise ratio was observed for the flame-ionization detector responses to injections of standard solutions corresponding to 0.28 μg per sample. This implied an analytical limit of detection of about 0.06 μg per sample, 14 pg 1,3–butadiene injected, or 6 pg delivered to the analytical column, based on a 2:1 signal to noise ratio. The limit of detection for the overall method could only be estimated because the desorption efficiency was not determined for such low levels. Assuming a 30% recovery from the sorbent, the overall limit of detection would be about 0.2 μg per sample.

Figure 5 shows the results of linear regressions on the recovery data from samples stored up to 21 days at ambient temperature or in a freezer below -4 °C. Since the samples were prepared at weekly intervals and analyzed together in one set, the week-to-week correlation in the positions of the two sets of data relative to the corresponding regression lines implied a systematic error in the preparation of the samples. Since the external loop had to be refitted for each sample set, this variation may have resulted from differences of fit within the connections. For the refrigerated samples, the slope and its 95% confidence limits, -0.10 ± 0.35, suggested no loss. However, for the samples stored at ambient temperature, the slope was significant, -1.55 ± 0.60. If one assumes that no loss

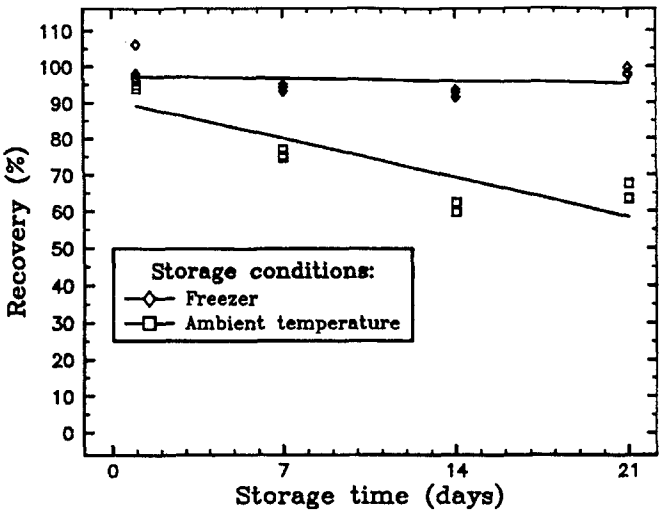

Figure 5. Linear regression of recovery on storage time at ambient temperature or in a freezer below -4 °C for 26-μg loadings of 1,3–butadiene on 400-mg coconut-shell charcoal samplers.

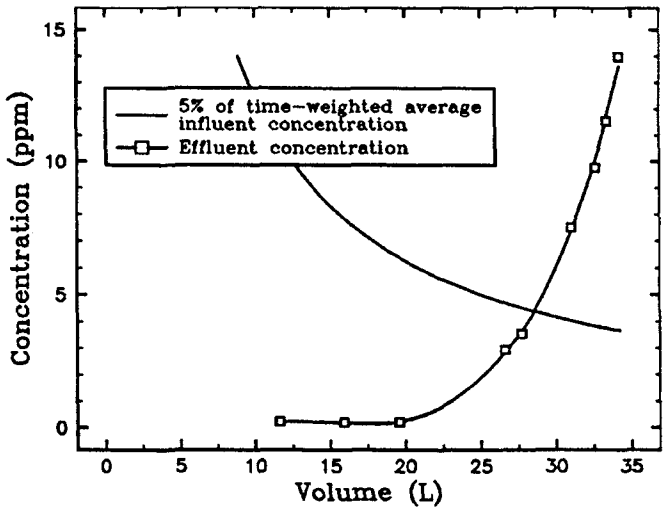

Figure 6. Breakthrough volume determination for a 400-mg coconut-shell charcoal sampler exposed to 2.5 mL of 1,3–butadiene gas followed by air at 80% relative humidity.

occurred for the refrigerated samples, then their recoveries from week-to-week can be used to correct for the variability in sample preparation. Applying this correction to the ambient temperature data results in an estimated daily loss of 1.50 ± 0.41 percent per day.

A dramatic improvement in sample stability has been reported for samples collected on a specially cleaned coconut-shell charcoal coated with 4-*tert*-butylcatechol (TBC) (*9*). The authors also concluded that collection on uncoated charcoal would be inadequate at low ppm levels because of poor sample stability. Our results do not support these conclusions. The average daily loss of 1,3–butadiene from TBC-coated charcoal during 17 days storage at ambient temperature was 1.36% (*16,17*). While this appears to be significantly less than the 1.50% reported above for uncoated charcoal, the additional

loss due to storage for one week at ambient temperature on uncoated versus coated charcoal would be only one percent. For both sorbents, unnecessary storage at ambient temperature should be avoided to minimize losses.

Two final tests of breakthrough volume were conducted. Figure 6 shows the results of one in which 2.5 mL of pure 1,3–butadiene was introduced into a 400-mg charcoal tube, which was then connected to the source of humid air. This procedure simulated high initial and no subsequent exposure, which would be a worst case scenario for breakthrough at a given time-weighted average (TWA) concentration. The breakthrough volume, given by the intersection of the two curves, was 28.5 L for a TWA concentration of 88 ppm. The other experiment, in which 0.7 mL of 1,3–butadiene was introduced, gave a breakthrough volume of 35 L for a TWA concentration of 20 ppm.

CONCLUSIONS

One of the most important observations resulting from this work relates to problems in preparing standards directly from 1,3–butadiene gas and accurately measuring small volumes of the gas. These difficulties may occur not only with 1,3–butadiene, but also with other gases that are easily liquefiable, e.g., methyl bromide, ethylene oxide, vinyl chloride. Industrial hygiene chemists need to be aware of such potential calibration problems so that they may recognize and avoid them if they occur. For 1,3–butadiene, bracketing the gas between water plugs in a gas-tight syringe provided a basis for an accurate and reproducible calibration, which could be monitored by observing the precision of multiple independent standards and the linearity of the flame-ionization detector response to standard solutions.

The laboratory evaluation of Method 1024 indicated that it should be useful for determining full-shift TWA exposures to 1,3–butadiene in humid air at concentrations ranging from approximately 0.4 to 10 ppm, the upper limit of the calibration range, for 25-L samples. If desorbed samples are diluted so that they fall within the calibration range, the sampler's capacity should permit quantitation of levels up to 100 ppm. Samples should be refrigerated at temperatures below -4 °C during shipping and storage to minimize loss.

While any chromatographic conditions are acceptable if they provide adequate sensitivity and separation of 1,3–butadiene from environmental co-contaminants, the combination of backflushable pre-column and aluminum oxide fused-silica capillary analytical column offers two major advantages:

- The enhanced sensitivity provided by the high-resolution chromatography should enable detection down to 0.005 ppm in 25 L.
- The enhanced selectivity provided by gas-solid chromatography should minimize the need for expensive confirmatory techniques, e.g., gas chromatography/mass spectrometry.

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16. Abstract (Limit: 200 words)

NIOSH Method S91 for the determination of 1,3-butadiene (106990) in air was reevaluated, and a new method was developed. Method S91 was reevaluated with respect to recovery, breakthrough volume, and potential chromatographic interferences. Limitations to Method S91 included the fact that the lower quantitation limit appeared to be about 3.4 parts per million (ppm) and the packed column gas chromatographic analysis was subject to interference. The new method developed, Method 1024, employed collection on tandem coconut shell charcoal tubes, desorption with methylene-chloride, and high resolution gas chromatographic analysis. Evaluation of Method 1024 indicated that it should be useful for determining full shift time weighted average exposures in humid air at concentrations ranging from 0.4 to 10ppm. The sampler's capacity should permit quantitation of levels up to 100ppm if desorbed samples are diluted so that they fall in the calibration range. In the chromatographic process, the combination of backflushable precolumn and aluminum-oxide fused silica capillary analytical columns offered the advantages of enhanced sensitivity, enabling detection down to 0.005ppm in 25 liters, and enhanced selectivity, limiting the need for confirmatory techniques.

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