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Determination of 1,3-Butadiene Down to Sub-part-per-million Levels in Air by Collection on Charcoal and High-Resolution Gas Chromatography

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The need for a more sensitive method for the determination of 1,3-butadiene in air led to the development of NIOSH Method 1024, in which samples are collected on tandem 400- and 200-mg coconut-shell charcoal samplers; desorbed in dichloromethane; separated by gas chromatography on an aluminum oxide, porous-layer, open-tubular, fused silica capillary column fitted with a backflushable precolumn; and detected by flame ionization. This article reports the development of the method and an assessment of its performance based on laboratory evaluations and field use. A sample volume of 25 L is recommended for 1,3-butadiene concentrations up to 100 ppm. Samples stored in a freezer are stable; a loss of 1.5 percent per day occurs at ambient temperature. The lower quantitation limit, based on maintaining desorption efficiency ≥ 75 percent, is about 40 μg/sample. The estimated limit of detection is 0.2 μg/sample. The estimated precision of the total sampling and analytical method is 6 percent relative standard deviation. The accuracy is within ± 25 percent, based on the analysis of blind quality control samples ranging from 20 to 663 μg/sample. **Lunsford, R.A.; Gagnon, Y.T.; Palassis, J.; Fajen, J.M.; Roberts, D.R.; Eller, P.M.: Determination of 1,3-Butadiene Down to Sub-part-per-million Levels in Air by Collection on Charcoal and High-Resolution Gas Chromatography. Appl. Occup. Environ. Hyg. 5:310–320; 1990.**

Introduction

In 1977, the National Institute for Occupational Safety and Health (NIOSH) published Method S91 for the sampling and determination of 1,3-butadiene in air.(1) Like its antecedent, NIOSH P&CAM 127,(2) it specified collection on 100/50-mg coconut-shell charcoal tubes, desorption by carbon disulfide, and analysis by packed column gas chromatography. Method S91 was evaluated over concentrations of 500 to 2000 ppm to address the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) of 1000 ppm. Since then, concern about exposure to 1,3-butadiene has intensified. In 1984, based on the induction of multiple-site carcinogenic responses in inhalation exposure studies of rats and mice,(3,4) 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–Time-weighted Average (TLV–TWA) of 10 ppm, proposed in 1984, was adopted in 1986.(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 ppm 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 have been limited for the following reasons. Five of the six investigations resulted in a total of just six samples with detectable 1,3-butadiene. In the other study,(8) done in 1977 using P&CAM 127, more than six weeks elapsed between sampling and analysis, although the samples were presumably 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 ppm 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,

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whose reported concentrations ranged from 0.06 to 5.5 ppm, the median amount found was only four times the reported detection limit. In all subsequent NIOSH investigations for 1,3-butadiene from 1977 through 1983 that utilized P&CAM 127 or Method S91, 1,3-butadiene was detected in only 16 of 77 samples, and the highest levels found were no more than 5 times the reported detection limits.(9)

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 mass collected. Uncorrected low recovery leads 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 might be expected to increase with decreasing analyte concentration, the sample volumes obviously were excessive in some cases. In others, where the mass collected was near the detection limit, breakthrough may have occurred undetected, resulting in underestimation of the actual exposure levels. The evaluation of Method S91 did not include an investigation of storage effects. Loss during storage leads 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. Interferences by other compounds with the same retention time cause overestimation of the actual exposure levels.

In 1984, NIOSH researchers began an industrywide 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 and, subsequently, the development of Method 1024.(10) This article reports the development, evaluation, and initial field usage of the new method, which features collection on tandem coconut-shell charcoal tubes, desorption with dichloromethane, and analysis by high-resolution (capillary) gas chromatography. Other recently developed methods for the determination of 1,3-butadiene in the air are OSHA Method 56,(11) with collection on specially treated coconut-shell charcoal coated with 4-*tert*-butylcatechol and desorption by carbon disulfide, and the Health and Safety Executive (London) MDHS 53,(12) with collection on 13X molecular sieve and thermal desorption. Both of these methods specify analysis by packed column gas chromatography.

Experimental

Reagents

Instrument grade 1,3-butadiene (99.5 mole %) was obtained from Matheson. A certified mixture of 9.51-ppm (± 2%) 1,3-butadiene in nitrogen (can mix # 250) was obtained from Scott Specialty Gases. 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. A carbon molecular sieve, 60/80 mesh Carbosphere, was obtained from Alltech Associates. Glass-distilled dichloromethane preserved with cyclohexene (Product # 300) was obtained from Burdick and Jackson. (1,1-Dichloroethene was identified by retention time and mass spectrometry as a trace contaminant in dichloromethane that grew in over time. The contaminant was not always observable in freshly opened bottles of dichloromethane.)

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 Corporation, and the humidity level was maintained at 80 percent relative humidity by a Hydrocon precision electro-humidity reader-controller from Phys-Chemical Research Corporation. Ultraviolet (UV) and visible absorbance measurements were made with Beckman Models 25 and 26 spectrophotometers. Chromatographic analyses were performed on Hewlett-Packard Models 5840A and 5880A gas chromatographs. 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, as well as a 10-port valve from Valco. One 2-ml loop on the Valco valve was fitted with a tee and septum to permit the introduction of gas samples by gas-tight syringe at ambient pressure. Separations were obtained on a 1.7-m × 2-mm i.d. glass column packed with 60/80 mesh acetone-washed Chromosorb 102. The HP 5880A gas chromatograph was equipped with packed column and dual split-splitless capillary inlet systems and flame ionization detectors. Separations were obtained on a 6.1-m × 3.2-mm o.d. stainless steel column packed with 10 percent FFAP on 80/100 mesh Chromosorb W-AW or a 50-m × 0.32-mm i.d. fused silica, porous-layer, open-tubular (PLOT) column coated with KCl-deactivated aluminum oxide. The latter column was protected from high-boiling or polar contaminants through the use of a backflushable 10-m × 0.50-mm i.d. fused silica precolumn coated with a 1.8-μm film of CP WAX 57 CB.(13)

Sorbent Capacity Comparisons

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. Samplers were used as purchased or were prepared by packing 100- or 400-mg sorbent sections into 4- or 6-mm i.d. glass tubing, respectively. 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 at least 30 min. A sampler was connected by short

TABLE I. Simulated Samples and Standards for Precision and Accuracy Tests

	Simulated Samples[A]			Calibration Range (Number of Levels)[B]	
Test	Loading (µg/sample)	Number of Back Tubes	Air Volume (L)	Media Standards[C] (µg/sample)	Standard Solutions[D] (µg/sample)
1	125[E]	0	0	51–152 (3)[F]	56 to 168 (3)[G]
2	463	2	22.3 to 27.9	1.6–472 (5)	4.4 to 435 (4)
3	45.3	1	27.3 to 32.4	1.6–475 (5)	0.87 to 458 (6)
4	4.64	1	24.6 to 28.4	1.6–476 (5)	0.88 to 464 (6)
5	4.71	1	24.8 to 25.4	125–481 (2)	112 to 1760 (3)
				1.1–18 (3)[H]	0.28 to 18 (4)[I]

[A] Standardized 1,3-butadiene–helium mixture was transferred to the sorbent tube, the indicated number of back sorbent tubes were attached, and humid air from the 12-port sampling manifold was drawn through the assembly. Six replicates were prepared for each test.

[B] Three replicates were prepared at each level.

[C] Sorbent tubes were loaded by calibrated valve/loop.

[D] Pure 1,3-butadiene was bracketed between water plugs in a gas-tight syringe and transferred into septum-capped vials of dichloromethane.

[E] Sorbent tubes were loaded by calibrated valve/loop.

[F] Sorbent tubes were loaded with standardized 1,3-butadiene–helium mixture. Five replicates were prepared at each level.

[G] Four replicates were prepared at each level.

[H] Sorbent tubes loaded with aliquots of the three highest level standard solutions.

[I] Prepared by dilution of the three highest level standard solutions.

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 1,3-butadiene absorbance maximum at 217–219 nm. The outlet of the flow cell was connected to a calibrated pump set for a flow of 50–100 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 UV absorbance reading. Breakthrough was deemed to occur when the absorbance of the sampler effluent reached 5 percent of that observed directly from the bag. The concentration of 1,3-butadiene in the bag was calculated from the observed absorbance, assuming 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.(14)

Precision and Accuracy Tests

Simulated samples and media standards were prepared by loading the front tubes from 400/200-mg sets of charcoal

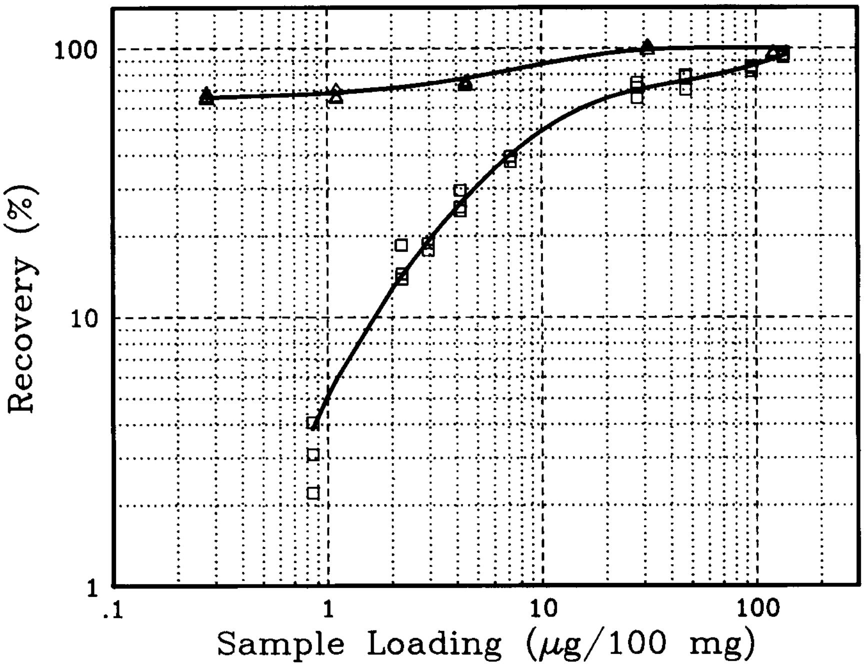

FIGURE 1. Recovery versus sample loading for the desorption of 1,3-butadiene from 100 mg coconut-shell charcoal by 1 ml carbon disulfide (squares) or from 400 mg coconut-shell charcoal by 4 ml dichloromethane (triangles). Solid lines are curves empirically fitted to the data.

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 150–200 ml/min. Three different techniques were used to deliver 1,3-butadiene: a calibrated Rheodyne sample injection valve/loop was filled with pure 1,3-butadiene and flushed with inert gas flowing at 50 ml/min; a gas-tight syringe was used to transfer an appropriate amount of a standardized 1,3-butadiene–helium mixture; a gas-tight syringe was used to transfer a 40-μL aliquot of a standard solution. Blank media standards and blank simulated samples were prepared by going through all the steps except for the actual transfer of 1,3-butadiene. Experimental details for five accuracy and precision tests are given in Table I.

The actual capacities of the Rheodyne sample injection valve/loop combinations were measured by diluting aliquots of stock dye solution from the sample injection valves to known volumes and determining the original volumes spectrophotometrically.(15) The standardized mixtures of 1,3-butadiene in helium were prepared by introducing approximately nine volumes of helium and one volume of 1,3-butadiene into a 1-L Tedlar bag. The precise concentrations were determined by gas chromatographic analysis, using the HP 5840A gas chromatograph, Chromosorb 102 column, and thermal conductivity detection.(15)

Storage Stability

Sets of six media standards were prepared at weekly intervals by dosing with pure 1,3-butadiene gas via the 10-μL valve/loop. Three standards were stored at ambient temperature, and three standards and one 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 day following preparation of the fourth set, all the tubes were extracted and analyzed. The calibration was based on the results for the media standards stored one day in the freezer.

Capacity Check by Pulse Method

The outlet end of a 400-mg, coconut-shell charcoal sampler was connected to vacuum through the 200-μL Rheodyne valve and a critical orifice. A known volume, 700 μL, of 1,3-butadiene was introduced by gas-tight syringe into the sampler 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. The response was calibrated 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 percent of the TWA influent concentration. The experiment was repeated with a fresh sampler, using 2.5 mL of 1,3-butadiene.

Field Sampling and Analysis

The procedures given in Method 1024(10) were observed with the following additions or exceptions. Sampling pumps were calibrated after each day's sampling. Full-shift samples were taken for 8 hours at 50 ml/min. Short-term, task-specific samples were taken at 500 ml/min. At the end of each shift, the samples were placed in a freezer. For shipment, they were packed in an insulated container cooled by ice sealed in plastic bags. Upon arrival, they were again placed in a freezer. For the analyses, the HP 5880A gas chromatograph was equipped with a 7673A autosampler. Water chilled to 10°C was circulated through the sampler trays to control the temperature of the samples. Calibrations over the range of 1.1–440 μg per sample were obtained from the analyses of the media standards by linear regression with s^{-2} weighting, where s was the estimated standard deviation. For each set of samples, which were desorbed with the same batch of dichloromethane, the response due to the contaminant, 1,1-dichloroethene, was monitored. When the response was unusually low, i.e., deviating by more than two standard deviations from the average, this was taken as an indication of faulty injection. For these samples, the 1,1-dichloroethene response was used as an internal standard to adjust the 1,3-butadiene response. Two sets of blind quality control samples were prepared and stored in a freezer. Generally, four blind samples were analyzed along with each set of field samples.

Results and Discussion

Development of Method 1024

The first efforts at developing the new method were directed towards improving the recovery. Slight improvements in recovery from coconut-shell charcoal were obtained by increasing the volume of solvent, carbon disulfide, used to desorb samples or by adding an internal standard (*n*-hexane) or a π-electron donor (benzene) to the solvent. However, recoveries were improved greatly by desorbing with dichloromethane. The lower curve in Figure 1 shows percent recovery versus 1,3-butadiene loading for the conditions specified in Method S91.(15) The upper curve in Figure 1 shows percent recoveries obtained by desorbing with dichloromethane. The dichloromethane preservative, cyclohexene, may have had a role in improving the recovery; however, this was not investigated. Thus, dichloromethane was selected as the desorbent for all subsequent work.

Many commonly used adsorbents, such as porous polymers and graphitized carbons, are not practical for sampling compounds as volatile as 1,3-butadiene; they are not sufficiently retentive. While some of the inorganic adsorbents might have proven satisfactory,(12) this study was limited to two charcoals, petroleum-coke and coconut-shell, and a carbon molecular sieve. Comparative recovery measurements on these sorbents revealed no significant differences.(15) The results of breakthrough volume determinations, given in Table II, indicated that the performances of carbon molecular sieve and coconut-shell charcoal were about equal and were superior to that of the petroleum-coke charcoal. However, the use of carbon mo-

TABLE II. Breakthrough Volume Measurements for Selected Sorbents[A]

Sorbent	Bed Size[B] (mg)	Sampling Flowrate (ml/min)	Influent Concentration (ppm)	Breakthrough Volume (L)
Carbon molecular sieve	100	54	31	16
Coconut-shell charcoal	100	54	31	>13[C]
	100	54	38	>10[C]
	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

[A] 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.

[B] Bed diameters were 4 mm for 100-mg sections and 6 mm for 400-mg sections.

[C] Experiment ended before breakthrough occurred.

lecular sieve was rejected because of its relatively high cost. Thus, it appeared 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 for concentrations up to 100 ppm, and the ability to quantitate down to 0.5 ppm when desorbed with dichloromethane 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 × 3.2-mm o.d. stainless steel column packed with 20 percent SP-2100 on 80/100 mesh Supelcoport. Since *n*-butane and butenes interfered with the quantitation of 1,3-butadiene, a better separation was sought. An Al_2O_3/KCl PLOT column was selected because it provided, at an oven temperature of 120°C, baseline separation of 1,3-butadiene from the other hydrocarbons typically present in the field samples. Chromatography of 34 other light hydrocarbons and halocarbons revealed no interferences.(15)

The third and fourth sets of field samples were analyzed using the Al_2O_3/KCl PLOT column. This revealed further problems. During the course of the analyses, there was a reversal in the elution order of 1,3-butadiene and 1,1-dichloroethene. 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 a backflushable precolumn.(13) The modified analytical procedure was used for the subsequent evaluation of the method.

A problem that had hampered early efforts to evaluate the overall accuracy and precision of the method involved calibration. Ordinarily, standard solutions of a soluble gas could be prepared by using gas-tight syringes to inject known volumes of gas into a suitable solvent. However, 1,3-butadiene is liquified 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 about twice the force exerted through the vapor pressure of 1,3-butadiene. For smaller syringes, the force required to move the plunger was even more dominant. 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 dichloromethane, the problem was solved by bracketing the 1,3-butadiene gas between plugs of water. Expulsion of the water assured complete delivery of the gas.

Table III gives the results of the five tests of total method precision and accuracy described in Table I. The precisions (relative standard deviations) 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. Accuracy or bias in the method was evaluated by considering the desorption efficiencies and recoveries shown in Table III. The desorption efficiencies, based on analyses of the samples versus the standard solutions, were expected to be similar to the desorption efficiencies typically observed for media standards. The recoveries, based on analyses of the samples versus the media standards, were expected to be quantitative. In the first two tests, the recoveries were acceptably close to 100 percent 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

TABLE III. Precision and Accuracy Tests[A]

Test	Sample Loading (μg/sample)	Recovery[B] (%)	Desorption Efficiency[C] (%)	Relative Standard Deviation[D]
1	125	102.2	96.8	0.016
2	463	101.6[E]	91.3[E]	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

[A] Six samples were prepared for each test and analyzed in duplicate.

[B] Average amount found, calibrated against media standards, divided by sample loading.

[C] Average amount found, calibrated against standard solutions, divided by sample loading.

[D] RSD of the analytical response.

[E] Includes amounts found on first back sections, which averaged 1.24% of the total.

TABLE IV. Linearity and Precision of Standard Solution Analyses

Loading (μg/sample)	Observed Response[A] (area counts)	Relative Standard Deviation[B]	Calculated Response[C] (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] RSD of the analytical response.

[C] Based on a linear 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.

used to prepare the samples, media standards, and standard solutions. However, the simulated samples in tests three through five showed recoveries increasingly distant from 100 percent. Furthermore, the desorption efficiencies in tests three and five were larger than those typically observed for the media standards. For example, the 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,(16) the linearity of the standard solution calibration can provide an independent check on the accuracy of the lower-level standards. Table IV shows the linearity and precisions obtained for the standard solutions analyzed in the fifth test, whose concentrations covered the widest range and were extended to the lowest level. The observed deviations from linearity can be explained reasonably by small systematic or random errors in preparation. Also, the zero intercept (−4 ± 6 area counts) indicates a lack of significant bias in the preparation of the standards at the lowest concentrations. 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 V 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 lowest two levels by a valve with internal loops. If the standard solution calibration was correct, then the latter valve must have been delivering more 1,3-butadiene than was calculated from the measured volumes of the valve/loop combinations. Thus, the low recovery listed for the fourth test in Table III can be explained by the apparent error in the preparation of the media standards. Because sample injection valves provided the most convenient means to prepare media standards, their use in Method 1024 would have been desirable. However, the inability to determine the effective volume accurately forced abandonment of the technique.

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 was correct, then, as the intended sample loading decreased, the relative amount actually loaded onto the sorbent in preparing the simulated samples must have been increasingly more than was calculated from the volume of 1,3-butadiene–helium mixture transferred by gas-tight syringe. This would also account for the greater than 100 percent 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 a change in desorption efficiency. However, aside from 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. And, 1,3-butadiene was not detected in any of the blank samples exposed to the humid air.

The accuracy of the proposed sampling and analytical method, as indicated by the recoveries in Table III, 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. The apparent positive bias at 45.3 μg per sample, or 0.82 ppm in 25 L, was probably due to error in the independent method of preparing the samples rather than bias in the sampling and analytical method. The analyses of blind quality control samples during subsequent field usage of Method 1024, as reported below, indicated acceptable accuracy down to 20 μg per sample, or 0.4 ppm in 25 L of air.

Table VI gives the linearity and precision of the media standards from the fifth test. Again, the precision appeared to be independent of the loading. The nonlinearity of the response, due to the variation in desorption efficiency, is evident. Therefore, multilevel calibration or curve fitting should be used for quantitating unknowns against media standards.

The lower limit of quantitation for a method usually is determined by the analytical sensitivity. However, for Method 1024, the desorption efficiency was the limiting factor.

TABLE V. Desorption Efficiency from Media Standards Loaded by Valve/Loop[A]

Loading[B] (μg/sample)	Average Amount Found[C] (μg/sample)	Desorption Efficiency (%)
1.61	3.42	212
4.76	5.50	115
25.8	22.5	87.2
124	120	96.6
476	441	92.6

[A] Three media standards were prepared at each level.

[B] Calculated from volume of valve/loop.

[C] Calibrated against standard solutions.

TABLE VI. Linearity and Precision of Media Standard Analyses

Loading (µg/sample)	Observed Response[A] (area counts)	Relative Standard Deviation[B]	Calculated Response[C] (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] RSD of the analytical response.

[C] Based on linear regression, weighted assuming constant relative standard deviation.

While calibration of samples versus media standards automatically corrects for the decrease in desorption efficiencies at lower sample loadings, there is always the possibility that atmospheric co-contaminants collected with the samples will improve the desorption efficiency and cause the results to be too high. Setting a lower bound on the desorption efficiency limits the magnitude of such an error. The upper curve in Figure 1 indicates that the desorption efficiency falls below 75 percent 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. Thus, 20 µg per sample was recommended as the lower limit of quantitation for Method 1024.

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 detection limit 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 detection limit for the overall method could only be estimated because the desorption efficiency was not determined for such low levels. If a 30 percent recovery from the sorbent is assumed, the overall detection limit would be about 0.2 µg per sample, or 0.005 ppm in a 25-L sample.

Figure 2 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, which simulated collection of 0.5 ppm 1,3-butadiene from 25 L of air, 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 percent confidence limits, −0.10 ± 0.35 percent per day, suggested no loss. However, for the samples stored at ambient temperature, the slope was significant, −1.55 ± 0.60 percent per day. If one assumes that no loss 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 treated coconut-shell charcoal coated with 4-*tert*-butylcatechol (TBC).[11] It was 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 conclu-

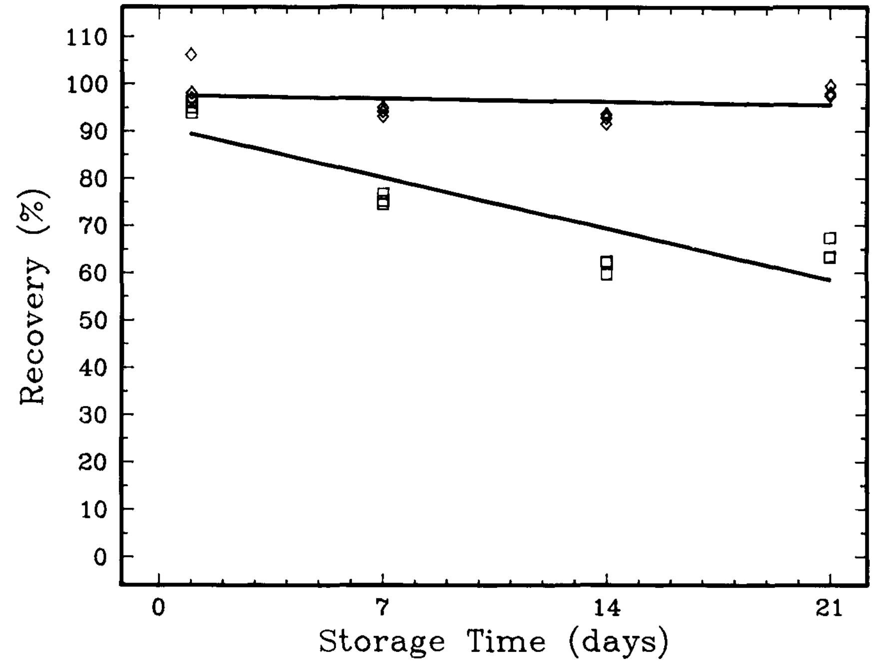

FIGURE 2. Linear regression of recovery on storage time at ambient temperature (squares) or in a freezer below −4°C (diamonds) for 26-µg loadings of 1,3-butadiene on 400-mg coconut-shell charcoal samplers.

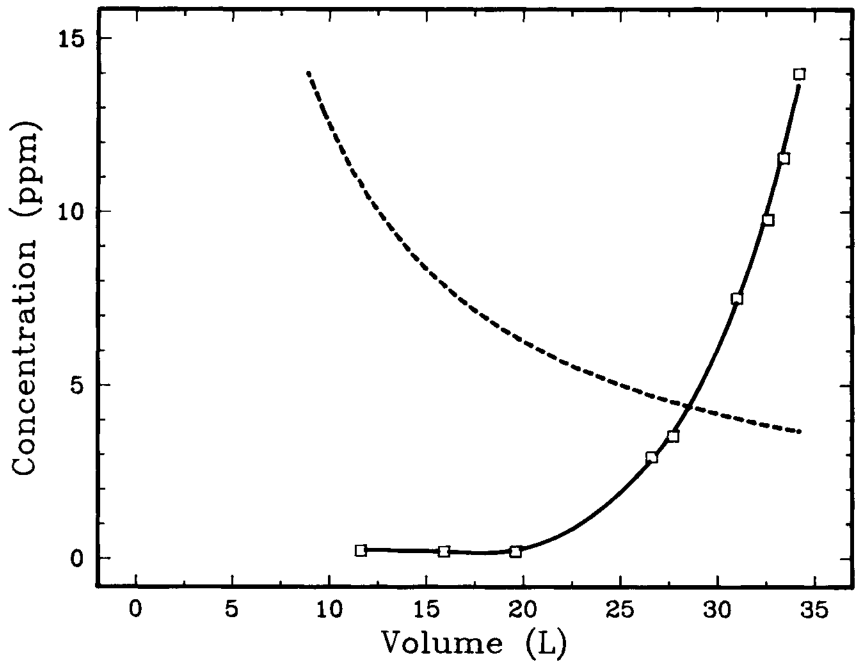

FIGURE 3. Breakthrough volume for a 400-mg coconut-shell charcoal sampler exposed to 2.5 ml of 1,3-butadiene gas followed by air at 80% relative humidity, given by the intersection of the effluent concentration (squares) with the line (dashed) representing 5% of the time-weighted average influent concentration.

sions. The average daily loss of 1,3-butadiene from TBC-coated charcoal during 17 days' storage at ambient temperature was 1.36 percent.(17,18) While this appears to be less than the 1.50 percent 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 1.0 percent. For both sorbents, storage at ambient temperature should be avoided to minimize losses.

Two final tests of breakthrough volume were conducted. Figure 3 shows the results of one in which 2.5 ml of pure 1,3-butadiene were 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 may be the worst case for breakthrough at a given 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.

Field Sampling and Analysis

Industrial hygiene surveys of five polymer production plants located near the Louisiana and Texas Gulf Coasts were conducted between June and September 1986, using Method 1024 to determine exposure to 1,3-butadiene.(19) As a result of the surveys, 621 samples, including 37 field blanks, were submitted for analysis. The front sections and selected back sections were analyzed over a period of about six months. The samples were divided into 20 sets, each set including additional laboratory blanks, 3 to 4 blind quality control samples, and 3 standard solutions and 3 media standards at each of five levels. The stability of the chromatographic system was demonstrated by the completion of approximately 2000 analyses without any significant change in chromatographic performance.

The analytical precisions and the linearity of the standard solution calibrations are summarized in Table VII. The relative standard deviations were nearly 2 times those observed during the laboratory evaluation (see Table IV), and there was some indication for higher relative standard deviations at the lower levels. On the whole, the standard solution calibrations were linear, as indicated by the overall mean relative deviations from linearity. The 95 percent confidence intervals for the individual mean deviations indicate the range of deviations from linearity that could

TABLE VII. Precision and Linearity Data from Twenty Standard Solution Calibrations*

Calibration Level (μg/sample)	Pooled RSD of Analytical Response	95% Confidence Intervals for Relative Deviation from Linearity: Overall Mean (%)	95% Confidence Intervals for Relative Deviation from Linearity: Individual Means (%)
1.08–1.10	0.093	−0.2 ± 2.1	− 5.2– 4.9
4.32–4.40	0.074	0.0 ± 2.2	−13.3–13.2
17.3–17.6	0.059	−2.0 ± 1.5	− 9.1– 5.2
108–110	0.055	0.2 ± 1.4	− 5.4– 5.8
432–441	0.071	−1.9 ± 1.7	−10.0– 6.2
overall pooled RSD 0.072			

*For each calibration, three standards were analyzed at each of the five levels. Each calibration line was determined by linear regression, weighted assuming constant relative standard deviation. For each level of each calibration, the relative standard deviation (RSD) of the analytical response and the mean relative deviation from linearity were determined.

TABLE VIII. Precision and Desorption Efficiency Data from Twenty Media Standard Calibrations*

Calibration Level (μg/sample)	Pooled RSD of Analytical Response	95% Confidence Intervals for Desorption Efficiency	
		Overall Mean (%)	Individual Means (%)
1.08–1.10	0.109	60.4 ± 3.0	41–80
4.32–4.40	0.080	66.4 ± 2.2	52–81
17.3–17.6	0.050	70.5 ± 1.8	58–84
108–110	0.064	86.2 ± 1.9	75–97
432–441	0.037	91.2 ± 1.3	82–100
overall pooled RSD	0.072		

*For each calibration, three standards were analyzed at each of the five levels. For each level of each calibration, the relative standard deviation (RSD) of the analytical response and the mean desorption efficiency were determined. For calculating desorption efficiency, the amount recovered was determined by the calibration line derived from standard solutions analyzed concurrently.

be expected for a single calibration.

The analytical precisions and desorption efficiencies observed for the media standards are summarized in Table VIII. Here, the relative standard deviations were nearly 3 times those observed during the laboratory evaluation (see Table VI), and the trend towards larger relative standard deviations at the lower levels was more evident. From the overall means, it appeared that the desorption efficiency usually fell below 75 percent somewhere between 20 and 110 μg per sample. Thus, a safer estimate of the lower quantitation might be 40 μg per sample. The 95 percent confidence intervals for the individual means show the range of mean desorption efficiencies that could be expected from a single calibration.

The field samples were collected under conditions of high ambient temperature and humidity. The morning low temperatures ranged from 21° to 26°C. The mean and standard deviation were 23.8° ± 1.5°C. The corresponding relative humidities ranged from 80 to 97 percent and averaged 91 ± 6 percent. The afternoon high temperatures ranged from 31° to 37°C and averaged 32.9° ± 2.1°C. The corresponding relative humidities ranged from 39 to 70 percent and averaged 55 ± 10 percent. For any given day, the absolute humidity was relatively constant. Based on all the measurements of ambient temperature and relative humidity, the absolute humidity ranged from 15.5 to 22.3 mg/L and averaged 19.9 ± 1.6 mg/L. Thus, the environmental conditions provided a rigorous test of the sampler capacity. For each set of samples, about one-sixth of the back (200-mg) tubes, those corresponding to the most heavily loaded front (400-mg) tubes, were analyzed to check for breakthrough. For the 108 samples checked, the median sample volume was 22 L. 1,3-Butadiene was detected in 25 of the back tubes analyzed. Only two samples showed severe breakthrough, i.e., where the amount found on the back tube exceeded 10 percent of that found on the front tube. For these two samples, the breakthrough was probably related to excessive concentration (≥ 280 ppm) in one case and sample volume (43.4 L) in the other. For the rest of the samples in which breakthrough was detected, multiple linear regression indicated no significant correlation between the severity of breakthrough and either the 1,3-butadiene concentration (2.2–99.6 ppm), the mass of 1,3-butadiene collected on the front tube (110–4160 μg), or the volume of air sampled (10.7–23.1 L). Thus, for the most part, breakthrough appeared to occur at random. Possible causes could be channeling of sample through the sorbent or reduced capacity for 1,3-butadiene due to the collection of atmospheric co-contaminants.

The recoveries obtained for the 77 blind quality control samples and the number of days they were stored prior to analysis are shown in Figure 4. Three results, those falling outside two standard deviations, were determined to be outliers at the 2.5 percent significance level by one-sided Grubbs tests.(20) The low value is probably the result of physical sample loss, either during preparation or analysis. The two high values were obtained from the analysis of one set of samples. All the blind samples analyzed with that set gave the highest recoveries observed for their respective loadings, so there may have been a calibration problem for that set of samples. The outliers were not considered in the subsequent analysis of the data. Table IX summarizes the recoveries by loading levels and over all levels. The overall mean recoveries were all close to 100 percent but increased by about 11 percent in going from the lowest to highest loadings. Thus, the bias appeared to range from −3.9 percent to +7.4 percent. However, since the bias seemed to be a function of the concentration, it probably arose from the use of linear regression rather than curve fitting or multilevel methods for the calibration. Note that in Table VI, linear regression resulted in overestimation of the analytical response of the media standards at 17.7 μg/sample, and underestimation at 481 μg/sample. Nevertheless, the 95 percent confidence intervals for the individual recoveries were consistent with accuracies of ± 25 percent overall and for each individual level except one.

From Figure 4, it appeared that the blind quality control samples experienced no significant loss during storage for up to 134 days in a freezer. The sample stability was further investigated by regression of recovery on days stored. The results are summarized in Table X. For the individual lev-

TABLE IX. Recovery Data from Blind Quality Control Samples*

Loading (μg/sample)	Number of Samples	95% Confidence Interval for	
		Overall Mean Recovery (%)	Individual Recoveries (%)
19.9–21.9	12	96.5 ± 3.2	85.4–107.5
48.6–52.6	14	96.1 ± 5.1	77.0–115.3
104–110	14	99.4 ± 3.1	87.7–111.1
199–209	14	102.9 ± 5.4	82.6–123.2
398–438	13	104.2 ± 6.7	80.1–128.4
663	7	107.4 ± 5.5	92.8–122.0
Over all levels:			
19.9 to 663	74	100.6 ± 2.0	83.1 to 118.0

*For each sample, the amount found was calibrated against media standards analyzed concurrently. The recovery was the amount found divided by the loading.

TABLE X. Linear Regression of Recovery on Number of Days Stored for Blind Quality Control Samples

Loading (μg/sample)	95% Confidence Interval for the Slope (% per day)	Projected Maximum Loss or Gain After 60 Days	
		Loss (%)	Gain (%)
19.9–21.9	0.065 ± 0.075	− 0.6	+ 8.4
48.6–52.6	0.005 ± 0.127	− 7.3	+ 7.9
104–110	−0.002 ± 0.091	− 5.6	+ 5.3
199–209	0.026 ± 0.179	− 9.2	+12.3
398–438	0.228 ± 0.205	+ 1.4[A]	+26.0
663	0.018 ± 0.247	−13.7	+15.9
Over all levels:			
19.9 to 663	0.036 ± 0.051[B]	− 0.9	+ 5.2

[A] Minimum gain instead of maximum loss.

[B] Result from multiple linear regression of recovery on loading and days stored. The slope and 95% confidence interval for recovery on loading was 0.017 ± 0.009% per μg.

els, only one slope of recovery versus days stored was significant, indicating a slight gain over time. Overall, the slope was insignificant and the 95 percent confidence interval projected over a 60-day period suggested a maximum loss of 0.9 percent or maximum gain of 5.2 percent.

Conclusions

The development of Method 1024 in conjunction with an industrywide field study provided an unusual opportunity to assess the performance of the method based on actual field use as well as the usual laboratory evaluation. In some respects, the results from the field analyses confirmed or extended those obtained by laboratory evaluation: the expectations for sample capacity and stability based on laboratory evaluations were confirmed with the field samples; the laboratory evaluation of bias was inconclusive below 125 μg/sample, but the analyses of the blind quality control samples confirmed the accuracy down to 20 μg/sample. In other respects, the field results exposed shortcomings in the laboratory evaluation. First, the need for a backflushable precolumn to protect the analytical column was revealed only through the analyses of field samples; in the same way, the ruggedness of the resulting chromatographic system was established. Second, the precisions for the analyses of standard solutions and media standards decreased in going from the laboratory evaluation to the routine analysis of field samples. If this behavior is typical, as might be expected, then methods which just meet accuracy criteria based on laboratory evaluations of precision and bias[(21)] may not actually provide the desired accuracy during routine field use.

Perhaps the most interesting observation concerned the variation in desorption efficiency from one calibration to another. Was the variation primarily due to experimental error in determining the desorption efficiency? If so, calibration of the field samples on the basis of the concurrently analyzed standard solutions, with correction by the overall mean desorption efficiencies, might provide the most accurate results. Or was there truly a variation in desorption efficiency from one calibration to another? In

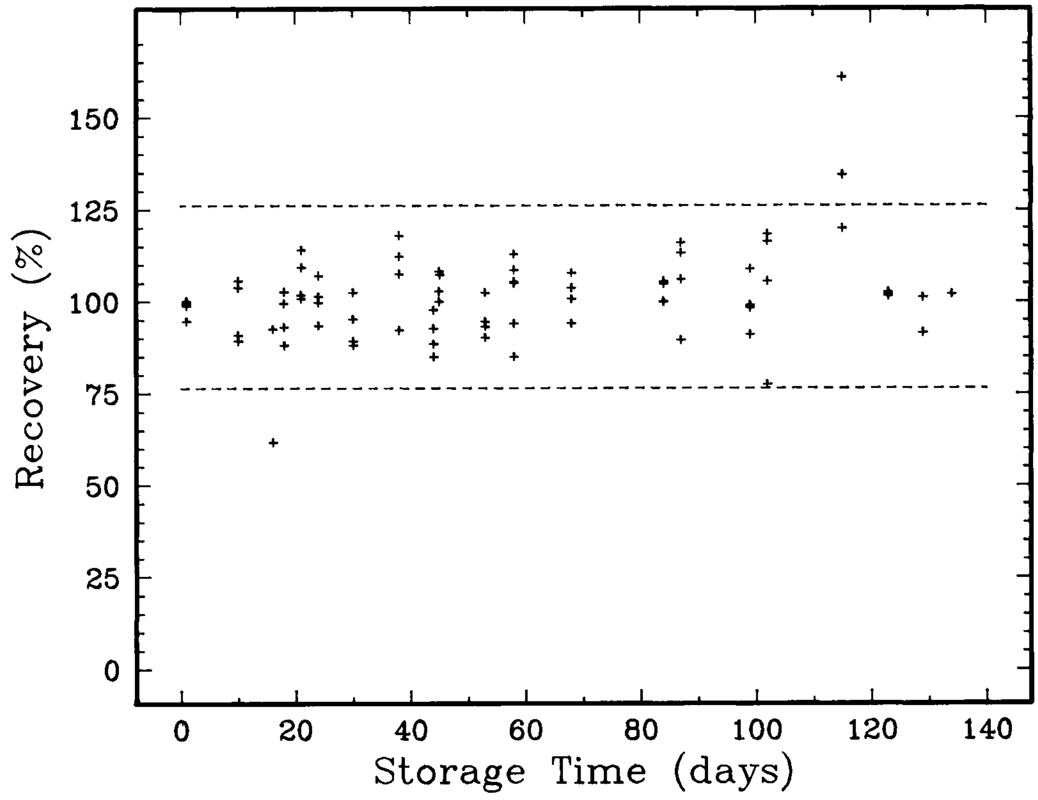

FIGURE 4. Sample storage stability as indicated by recovery from the blind quality control samples versus storage time. The dashed lines indicate ± 2 standard deviations from the overall mean recovery.

that case, calibration of field samples against concurrently analyzed media standards should provide the most accurate results. We intend to explore the issue by recalculating the results for the blind quality control samples using alternative calibration methods.

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