Evaluation of Charcoal Tube and SUMMA Canister Recoveries for Methyl Bromide Air Sampling

Heinz W. Biermann and Terrell Barry

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STATE OF CALIFORNIA
Environmental Protection Agency
Department of Pesticide Regulation
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Environmental Hazards Assessment Program
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Disclaimer

Abstract

The performance of two sampling methods for ambient methyl bromide concentrations, charcoal tubes and SUMMA canisters, was determined in a laboratory using simulated field sampling procedures. A gas mixing and handling system was set up to generate controlled flows of air with known amounts of methyl bromide and moisture content. Samples were taken from the air flow inside the system using regular field sampling equipment with typical operating parameters. Initial tests with the charcoal tubes showed breakthrough at very high relative humidity (RH > 90%) and recoveries near zero for extremely dry air (RH < 10%). Most of the data were limited to a humidity range of 20% to 80% and concentrations between 20 ppb and 2000 ppb. Within this range, no major effects of either humidity or concentration were found. The average recovery was 49% ± 7% (s.d.) for the charcoal tubes and 78% ± 12% (s.d.) for the SUMMA canisters.

Also reported are field data about the relative performance of collocated charcoal tubes and SUMMA canisters. A linear regression of the log-transformed concentrations of the two methods indicated that at the 200 ppb level the charcoal tube results were 71% of the SUMMA canister data. This was not significantly different from the same regression done on the laboratory data, where the charcoal tubes yielded 63% of the SUMMA canisters. Adjusting the relative performance of 71% in the field by the laboratory measured recovery of the SUMMA canisters of 78%, gives a net recovery of 55% for the charcoal tubes under field conditions. This net recovery of the field samples is consistent with the laboratory measured recovery of 49%.

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Introduction

The Department of Pesticide Regulation (DPR) established buffer zones around methyl bromide applications based on air monitoring data. The sampling and analysis method used in these monitoring studies consists of trapping of the methyl bromide vapor on charcoal, extraction of the methyl bromide from the charcoal with a solvent and subsequent gas-chromatographic analysis of the liquid.

This report describes a set of tests that quantify the effects of temperature, humidity and concentration on method performance. Because it has been suggested that a sampling method using stainless steel canisters would yield more accurate results, the performance of SUMMA canisters was evaluated also. The core of this study is a design that compared the chemical analysis results to the calculated methyl bromide concentration in the sampled air. Because the conclusions of this comparison depend critically on the accuracy of the calculated air concentration, special care has been taken to document the steps that were taken to ensure the correctness of these calculations. Therefore, this report contains a major subsection about calibration of all equipment used in the preparation of the gas mixtures in the main body of the report. Additional exploratory tests that influenced the design are described in the results section.

Experimental

To test these methyl bromide monitoring methods under operating conditions that are representative of the field sampling procedures, a gas mixing and delivery system was set up. Air samples containing a known fraction of methyl bromide were taken from this system over a periods of six or twelve hours using charcoal tubes and/or stainless steel canisters (SUMMA canisters).

Setup

All samples were prepared at the DPR West Sacramento facility using the gas mixing system shown in Figure 1. Commercial compressed gas tanks containing certified mixtures of methyl bromide in air (Matheson) and commercial tanks of compressed air (Sierra Airgas) were the gas sources. The flows from these two tanks were regulated and monitored by flow controllers (Cole Palmer, Model 32915). The flow from the compressed air tank was split with one part bubbling through water to add moisture to the air. The amount of moisture in the final mixture could be varied using valves with attached flowmeters (Cole Palmer, Model 32460) that determined the ratio of the air going through and bypassing the bulb with water. The moist air was then combined with the flow from the methyl bromide/air mixture in a second bulb. The outflow from this bulb passed through a manifold with eight sampling ports.

The effluent from this manifold could be routed through a glass cell attached to a Fourier Transform Infrared (FTIR) spectrometer (Laser Precision Analytical RFX-75). The glass cell was

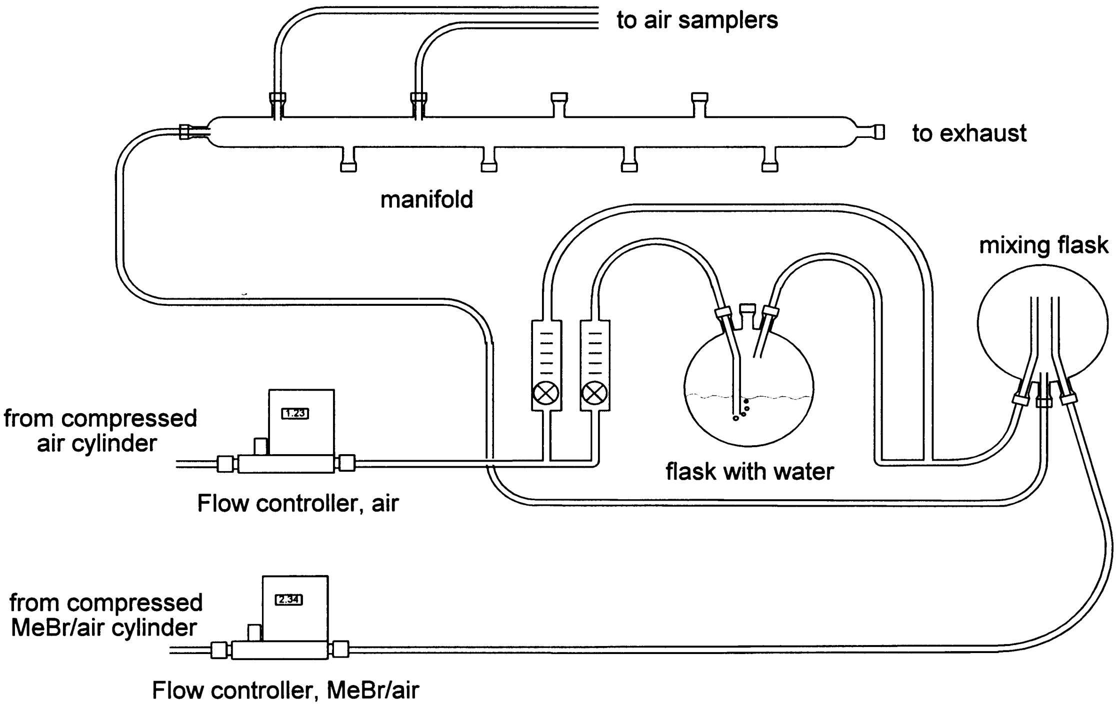

Figure 1 Gas mixing system.

about one meter long with a total volume of about 5500 mL. Inside this cell was a multiple reflection mirror system which created a folded light path with a total length of 25.6 m. This allowed for an independent confirmation of the methyl bromide concentration. Because of the high FTIR detection limit, however, this check was employed only during a few initial tests where the methyl bromide levels were above 500 ppb. Near the end of the exhaust line, inside a ventilated hood, a digital thermohygrometer (Omega, Model RH411) was inserted into the flow to measure the temperature and moisture content of the gas mixture. In addition, a capacitance manometer (MKS Baratron, Model 590HA) monitored the pressure inside the glass manifold. A datalogger (Campbell Scientific, Model 21X) was used to record the output of these instruments. Readings were taken every second for the setpoints and actual readouts of the flow controllers as well as the temperature, pressure and relative humidity of the gas mixture. These readings were then averaged over a one minute interval, copied to permanent storage and later transferred to a computer.

Sampling

In this study, identical to the field sampling procedure, two tubes were set up in sequence: the first contained 400 mg, the second 200 mg petroleum-based charcoal (SKC, Cat. No. 226-38-02). Air was pulled through these cartridges by an air sampling pump (SKC, Model 224-PCXR7). During field sampling, these pumps run off an internal battery. During these tests, however, the internal battery was replaced by an a/c-adapter.

The stainless steel sampling canisters and accompanying flow controllers and vacuum gauges were supplied by Quanterra Environmental Services (City of Industry, Ca.). The volume of the canisters was about six liters and the nominal flow rate about 3.5 ml/min. This low flow is necessary for 24-hour sampling intervals (3.5 ml/min * 1440 min = 5040 ml). Although the flow could have been increased by a factor of four because of the shorter sampling interval of six hours in this study, it was left at 3.5 ml/min which is the preset level of the controller valves which were used also during all DPR field sampling with SUMMA canisters.

The air sampling pumps operated at the same flow as used during field sampling (about 15 ml/min) and, with up to six samplers running simultaneously, pulled up to 90 ml/min from the manifold. Thus, total flow through the system was set to about 120 to 500 ml/min, depending on the desired mixing ratio. Because the total volume of the gas mixing system was about 1500 ml, these flows required an adjustment period of up to one hour between runs. Figure 2 demonstrates the need for this waiting period. The response of the relative humidity in the exhaust from the gas handling system to a sudden change is shown as an indicator for the general mixing behavior of the system. At time zero, the amount of air flowing through the bulb with water was increased without changing the total flow of 212 ml/min. The first response in the relative humidity became apparent after about seven minutes, and it took about 30 minutes before the final level was reached. The approach to this end value can be described very well by an exponential function with a half life of about 3.2 min.

The general steps involved in the sample preparation procedure were:

a) Set gas mixing flows and humidity inside the manifold.
b) Equilibrate flow conditions for at least one hour.
c) Attach charcoal tubes to sampling pumps.
d) Take three replicate measurements of the air flow through each charcoal tube.
e) Connect the charcoal tubes to the ports of the manifold and start sampling.
f) Connect the SUMMA canisters to the manifold
g) Record the initial pressure and open the sampling valve.
h) Sample over a measured amount of time.
i) While sampling, collect and store information about flow rates and humidity using the data logger.
j) After sampling, close the valve on the SUMMA canisters and record the final pressure.
k) After sampling, disconnect the charcoal tubes from the manifold and take three replicate measurements of the flow through the charcoal tubes.
l) Fill out the chain of custody, store the charcoal tubes in a freezer and the SUMMA canisters at room temperature.

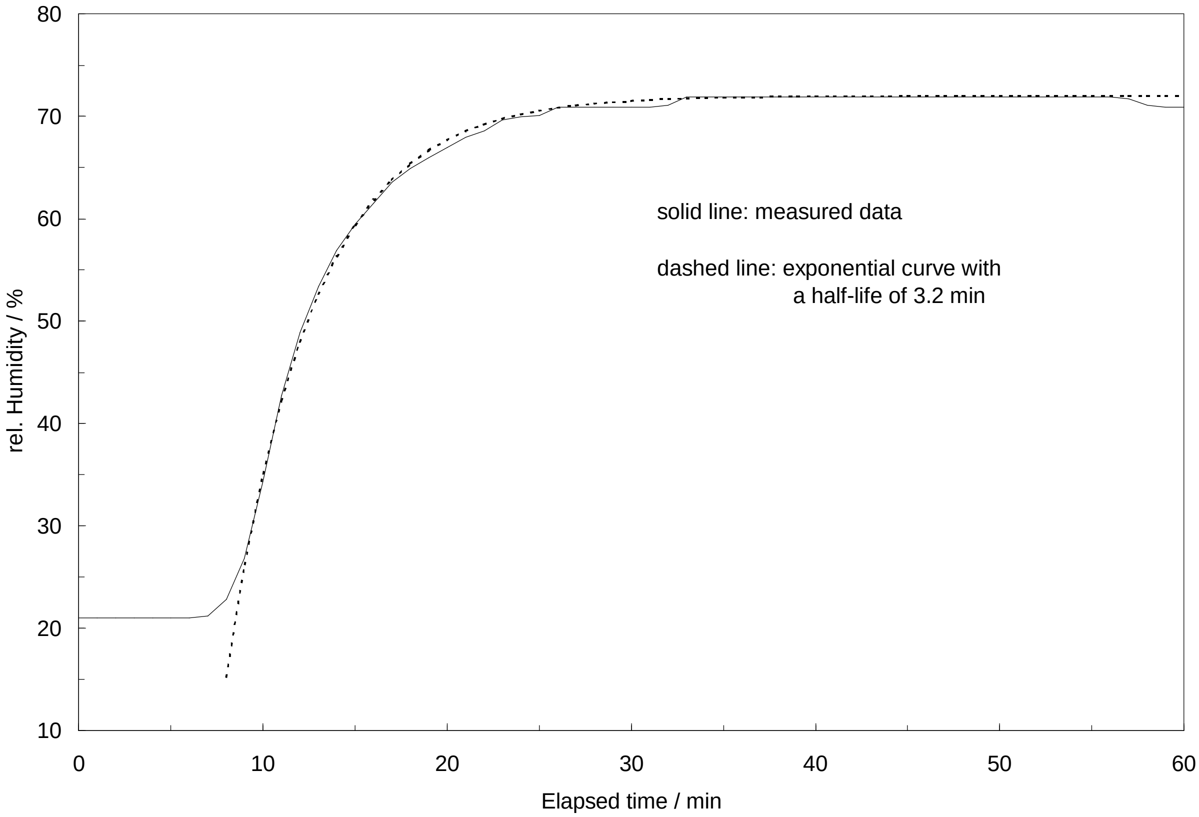

Figure 2 Response of relative humidity in the exhaust to a humidity change in the input.

Calibration

Gas Mixtures

Certified mixtures of methyl bromide in air were obtained from Matheson. One tank was ordered with 2 ppm methyl bromide in June 1997 and another one with 10 ppm in December 1997. When delivered, the mixtures were certified to contain 1.93 ppm and 9.5 ppm, respectively. To verify the accuracy of these mixtures, samples from these tanks were checked by two methods: the CDFA laboratory directly injected gas samples taken from the tanks into a GC without dilution and Quanterra analyzed SUMMA canister samples filled from the two tanks. Table 1 summarizes the results. Because Quanterra had to dilute the samples by factors of about 8 and 40, respectively, to get into the working range of the calibration curve, and because this analysis is subject to the same complications that this study is supposed to investigate, the SUMMA canister results were not used as an independent confirmation of the tank mixtures. All recoveries determined in this report are based on the tank concentrations of 2.12 ppm and 12.3 ppm as determined in the April 1998 set of GC analyses.

Table 1 Analysis results for methyl bromide in the compressed air tanks.

Method	Level / ppm (0 ± s)	Comment
2 ppm tank:		
manufacturer's certificate	1.93	
GC, direct injection	2.21 ± 0.05	July 97, average of 4 injections
GC, direct injection	2.12 ± 0.04	April 98, average of 7 injections
Summa canister	1.63 ± 0.01	April 98, average of 4 samples
10 ppm tank		
manufacturer's certificate	9.5	
GC, direct injection	12.3 ± 0.6	April 98, average of 7 injections
Summa canister	11.0 ± 0.0	April 98, average of 4 samples

Flow Controllers

Four precision gas flow controllers were available for the mixing of the gases; their full scale ratings were 5, 50, 200 and 500 ml/min. Only two of these controllers were used in any given run. One of the two with the lower ratings was used for the methyl bromide / air mixture, one of the two with the higher ratings for the dilution air. The volumetric gas flow through the line was metered and compared to a setpoint. The gas flow was then adjusted by a proportional control valve until it matched the setpoint. The stated accuracy of these controllers was 2% of full scale. However, the NIST traceable calibration sheets supplied with the controllers indicated that the maximum deviation at full scale was 1% and at 1/4 of full scale 3% (see Appendix A). The flows of all controllers were also checked against an Accuflow Digital Calibrator (SKC, model 712). In this case, the readings of the Accuflow Digital Calibrator were compared to the stored readings of the flow controller on the datalogger, not to the digital readout on the flow controller itself. This way, any additional errors introduced by the datalogger are included in the comparison. This procedure was chosen because all flow values presented in this study are taken from the datalogger. Table 2 summarizes the calibration check data. The full data set is shown in Appendix A.

Table 2 Summary of the flow controller calibration check

Controller ml/min rating	Readout difference compared to Digital Calibrator		
	full scale	half scale	quarter scale
5*)	1.0%	6.3%	10.5%
50	0.4%	2.8%	4.4%
200	2.6%	1.0%	0.1%
500	0.0%	1.0%	0.5%

*) indirect calibration procedure, see text

The 5 ml/min flow controller could not be checked with the Accuflow Digital Calibrator directly because the minimum readable flow on the calibrator is about 7 ml/min. In order to obtain a calibration check at 5 ml/min and less, a fixed flow of 22 ml/min was added from the 50 ml/min controller to the flow of the 5 ml/min controller. Two readings were made: one of the fixed offset flow and one of the combined flows. The nominal flow of the 5 ml/min controller was then determined from the difference in the two readings. Thus for low flows, the small uncertainty of 0.05 ml/min in the measurement of the 22 ml/min flow translates into a large relative error for the difference.

Air Sampling Pumps

The flows of the SKC sampling pumps were checked with the Accuflow Digital Calibrator before and after each sampling period. The sampling volume was determined from the average of three flow measurements before the sampling period plus three flow measurements after the sampling period and the run time of the pump as displayed on the readout of the pump. These flow checks were done with the actual sampling tubes attached but not connected to the gas mixing system (i.e., room air was flowing through the sampling tubes for about three minutes before and after each run). While each set of three consecutive readings often gave identical flow values, there was a difference of up to 3% in the measurements before and after a run.

Thermo-Hygrometer

The manufacturer of the Thermo-Hygrometer states that the accuracy of the sensor is 3% in the relative humidity range of 20% to 90%. The only calibration check performed during this study was an informal comparison of the readout of this unit with the readout from a Campbell Scientific weather station. At an ambient humidity of about 60%, the two instruments agreed within about 2% RH, which translates to a 3% relative deviation.

Flow Controllers and Gauges for SUMMA canisters

The flow controllers and pressure gauges used in the sampling procedure for the SUMMA canisters were supplied and calibrated by Quanterra. The flow rate through the controller is quite unimportant, as long as the canister does not fill up during the sampling period. An accurate measure of the pressure difference before and after the sampling, however, is crucial to an accurate estimate of the air concentration. The gauges supplied by Quanterra had scales from -30" of Hg (i.e., vacuum) to +30 psi (note the change in units at ambient pressure). Most gauges had divisions marked for every 2" of Hg on the vacuum side of the scale. Thus, pressure readings could be estimated to the nearest 0.5" with an overall uncertainty of 1" for the difference measurement. Pressure changes during the six hour sampling periods were about 6". This yields an estimated error in the amount of air captured of about 15%. This error could have been reduced if the flow controller had been set to a higher flow to maximize the capacity of the canister for this sampling time. No adjustments were made, however, because pressure changes of about 6" over six hours were the conditions under which the samplers were used in the field trials.

Error Estimation for the Methyl Bromide Concentration

To determine the overall performance of the sampling and analysis methods, one has to know precisely how much methyl bromide was in the sampled air. The concentration inside the manifold was calculated from the tank concentration and the flow rates through the two flow controllers:

$$C_{manifold} = C_{tank} * \frac{F_{MeBr}}{F_{MeBr} + F_{air}}$$

where $C_{manifold}$ and C_{tank} are the methyl bromide concentrations in the manifold and in the compressed air tank with the methyl bromide / air mixture, respectively. F_{MeBr} and F_{air} are the measured flows for the methyl bromide / air mixture and the dilution air, respectively.

The flows F_{MeBr} and F_{air} were regulated and monitored by the gas flow controllers. Based on the accuracy stated by the manufacturer (2% of full scale), the maximum error for the methyl bromide dilution ratio varied between about 4% (both controllers near full scale) and about 12% (one of the controllers at 1/5 of full scale). Both the NIST traceable calibration data and the flow check with the Accuflow Digital Calibrator, however, indicate that the maximum error does not exceed about 4%, independent of the flow through each controller.

Additional uncertainties occur during the sampling from this manifold. The amount of methyl bromide on the charcoal tubes varies with the sampling time and the sampling flow:

$$A_{tube} = C_{manifold} * F_{tube} * t_{run}$$

where A_{tube} is the amount of methyl bromide in the sampling tube, $C_{manifold}$ the methyl bromide concentration in the gas mixing system as calculated above, F_{tube} the gas flow through the sampling tube and t_{run} the sampling time.

For the SUMMA canisters, the crucial measurements in the determination of the amount sampled are the two pressures before and after the sampling period:

$$A_{canister} = C_{manifold} * \alpha * V_{canister} * (P_{after} - P_{before})$$

where $A_{canister}$ is the amount of methyl bromide in the SUMMA canister, α a conversion factor, $V_{canister}$ the fixed volume of the canister, P_{after} and P_{before} the two pressures. It is necessary to measure the two pressures exactly because the laboratory pressurizes the canister during the analysis process to about two atmospheres. This enables them to draw a sample from the canister without using a vacuum system, but they have to know the dilution factor from the pressure ratio to back calculate the original concentration.

Table 3 summarizes the maximum errors in the parameters of these equations. The only error that is not based on information provided by a manufacturer or derived from comparison data obtained in this study is the concentration of methyl bromide in the compressed gas tank. This error is based on FTIR measurements of methyl bromide in the effluent from the gas mixing system (as described in the Results and Discussion section). The FTIR data yielded a concentration that varied only by 3% from the calculated concentration based on an assumed tank concentration of 2.12 ppm. Considering that the FTIR calibration matches a commercial reference spectrum to within 1% (see Appendix B), and that the calculated dilution has a maximum error of 4%, the actual disagreement between the FTIR data and the tank concentration cannot be higher than 8%.

Taking the above uncertainties for the two methods into account, the worst case error in the amount (or concentration) of methyl bromide forwarded for chemical analysis is about 15% for the charcoal tubes (terms 1 through 4 in Table 3) and about 27% for the SUMMA canisters (terms 1, 2 and 5 in Table 3). The higher uncertainty for the SUMMA canister samples is not inherent to the method, it is just that the sampling procedure had not been optimized for our operating conditions, as explained above. These worst case error is unlikely, because they represent the sum of a sequence of independent errors, all contributing maximally in the same direction.

Table 3 Error sources in the calculation of the methyl bromide concentration.

Error Source	Error Term	Error Magnitude
1) tank concentration	C_{tank}	8%
2) flow controller	$F_{MeBr} /(F_{MeBr} + F_{air})$	4%
3) air sampler flow	F_{tube}	3%
4) run time	t_{run}	0.3%
5) canister pressure	$(P_{after} - P_{before})$	15%

Chemical Analysis

The charcoal tubes were sent to the California Department of Food and Agriculture (CDFA) laboratory for analysis using method #39.0, revised 3/10/97 (Determination of methyl bromide Desorbed from Charcoal Tubes). The SUMMA canisters were shipped to Quanterra and analyzed using EPA method TO-14 (Volatile Organics by GCMS)

Statistical Analysis

Three separate sets of statistical analyses were performed on different subsets of the data: storage stability, concentration/humidity matrix and field comparison. All statistical analyses were conducted using MINITAB 12 statistical software (MINITAB, 1998). Detailed descriptions of the procedures are provided in the respective discussion sections and in Appendix H.

Results and Discussion

The first part of this section describes exploratory tests that were done to see if certain environmental or sampling conditions had any effect on the analysis result. These are single tests of two to four replicate samples each that form the basis for the final design presented later on. These tests also include valuable information about the accuracy of the gas mixing process. The main section consists of a matrix of methyl bromide samples taken at three concentrations and three relative humidities. The final part compares the results of these laboratory tests with field data on the relative performance of charcoal tube and SUMMA canister samples.

Two sets of units are used in this report. The results of the charcoal tube analyses are reported by the laboratory as micrograms per sample (µg/sample), the results of the SUMMA canisters and all FTIR measurements are reported in parts per billion (ppb). These different units have been retained in this report because they represent the most direct measurement for the respective methods. Whenever comparisons between the methods are made, µg/sample are converted to µg/l based on the known sample volume collected by the charcoal tubes. A fixed conversion factor of 258 is then applied to convert µg/l to ppb.

Exploratory tests

The tests described in this section were done to help in the planning of a statistical design for the main part of the study. Because of the small number of samples involved and the somewhat arbitrary selection of test conditions, the results of these preliminary tests were not subjected to a thorough statistical analysis.

During these exploratory tests, no relative humidity probe was available. But a FTIR spectrometer was set up to measure methyl bromide concentrations and to estimate absolute water content in the gas mixture. These FTIR measurements provide independent evidence for the accuracy of the calculated methyl bromide mixing ratio and verify that observed effects were not caused by artifactual changes inside the gas handling system. Information about the calibration and data analysis procedure for the FTIR are provided in Appendix B. The data tables in this section show only mean values, the complete data sets are listed in Appendix C.

The first set of tests explored if dry tank air could be used or if moisture had to be added to the gas mixture. Two sets of four replicate samples each were run at near 0% and 40% relative humidity (RH). The methyl bromide concentration in the sampling manifold was 5.48 µg/l (1.41 ppm), based on the tank concentration of 2.12 ppm and the measured flows from the methyl bromide tank and the dilution air. With a run time of 12 hours and targeted sampling flows of 15 ml/min, about 60 µg of MeBr should have been collected by the charcoal tubes. Because the actual flow rates of the air samplers varied slightly, each sampling tube collected a different amount of air and thus the 'MeBr spiked' column in Table 4 lists different values for each replicate sample. The data show that the recovery for the dry air samples is noticeably (t = -30.00, p = 0.00) lower than for the moist air (28% vs. 58%, respectively).

Table 4 Charcoal tube results for 1410 ppb spikes.

Humidity %	Volume L	MeBr spiked µg	Result µg	Recovery %
0	11.7	64.4	16.7	26
0	10.9	59.6	18.0	30
0	11.5	63.2	17.3	27
0	10.7	58.4	16.8	29
			mean=	28
40	11.7	64.0	37.1	58
40	10.8	59.5	34.3	58
40	11.3	61.9	35.3	57
40	10.5	57.8	34.0	59
			mean=	58

During these two tests, FTIR spectra were taken of the gas mixture after passing through the sampling manifold. The air exchange rate in the sampling chamber of the FTIR was about 1.5 hours. To ensure that the air in the FTIR chamber was representative of the air in the manifold, only the last eight spectra, representing the last two hours of the twelve hour test, were analyzed. Figure 3 shows the spectrum of the dry air and a scaled methyl bromide reference spectrum. The scaling factor (determined using the procedure described in Appendix B) corresponds to a methyl bromide concentration of 1.37 ppm (i.e., a recovery of 97%). Both the dry air and the moist air gave nearly identical results, evident in Figure 4 where the two methyl bromide spectra are overlaid. In addition, Figure 4 shows an FTIR spectrum of air containing 1.41 ppm methyl bromide after passing through a single charcoal tube. No traces of methyl bromide are visible. Based on an estimated FTIR detection limit of 0.3 ppm, the trapping efficiency of the single charcoal tube was at least 79%:

$$\text{trapping efficiency (\%)} = 100 * \frac{\text{amount trapped}}{\text{amount in air}} = 100 * \frac{(1.41 - 0.3)}{1.41} = 78.7\%$$

These FTIR results indicate that the low recoveries of 28% and 58% are not due to problems with the collection of methyl bromide on the charcoal and that the difference in the recoveries is not due to a change in the air concentration. Quite in contrast to the low recoveries in this test, the two 50 µg quality control spikes prepared internally by the chemistry laboratory yielded recoveries of 93% and 94%.

A second test was run at a lower methyl bromide concentration of 0.82 µg/l (210 ppb) with an additional humidity level near 100% (see Table 5). While the recoveries at midrange humidity are nearly identical for the two concentration levels, the recoveries for dry air are basically zero in this second test. At the very high humidity level, breakthrough onto the second tube was observed. These data indicate that this method has problems at both ends of the humidity range. Because the saturated air was the only condition under which breakthrough onto the second tube was found, the information about the second tube will not be listed in the following tables.

A third set of tests was run to mimic field sampling conditions more closely by moving the gas handling system outdoors. Field procedures call for two six-hour samples followed by twelve-hour samples. Because applications are done in the early morning hours, the two six-hour samples are usually taken in the morning and afternoon, the first twelve-hour sample over night. In this controlled outdoor test, for convenience sake, the twelve-hour night sample was collected first. A steady flow of air containing 0.82 µg/l methyl bromide was maintained inside the sampling manifold for the entire 24 hour period at a relative humidity of about 40%. This methyl bromide level translates to about 9 µg for the twelve hour run and about 4.5 µg each for the two six hour runs. During the initial twelve-hour run, two of the four air sampling pumps malfunctioned. The following two six-hour periods were run with only three replicates because only one spare sampler was available. Table 6 summarizes the analysis results. Surprisingly, the two six hour samples had much lower recoveries than the twelve hour sample (25% and 22% vs. 47%). A possible explanation for this discrepancy is the decay of methyl bromide during high daytime temperatures, as this data set was generated on one of the last hot days in fall of 1997. Data on the hydrolysis of methyl bromide indicate that under these temperature and humidity conditions, the half life of methyl bromide may have been less than 12 hours (Gan et al., 1995).

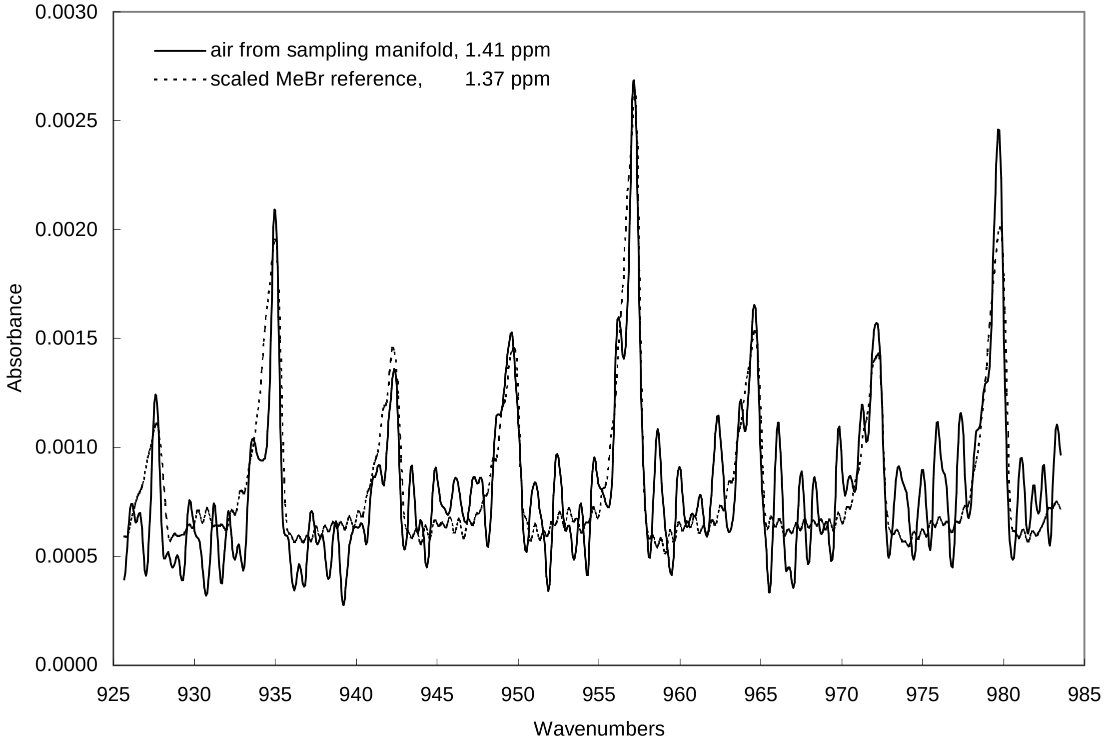

Figure 3 FTIR spectrum of methyl bromide in dry air with a scaled reference.

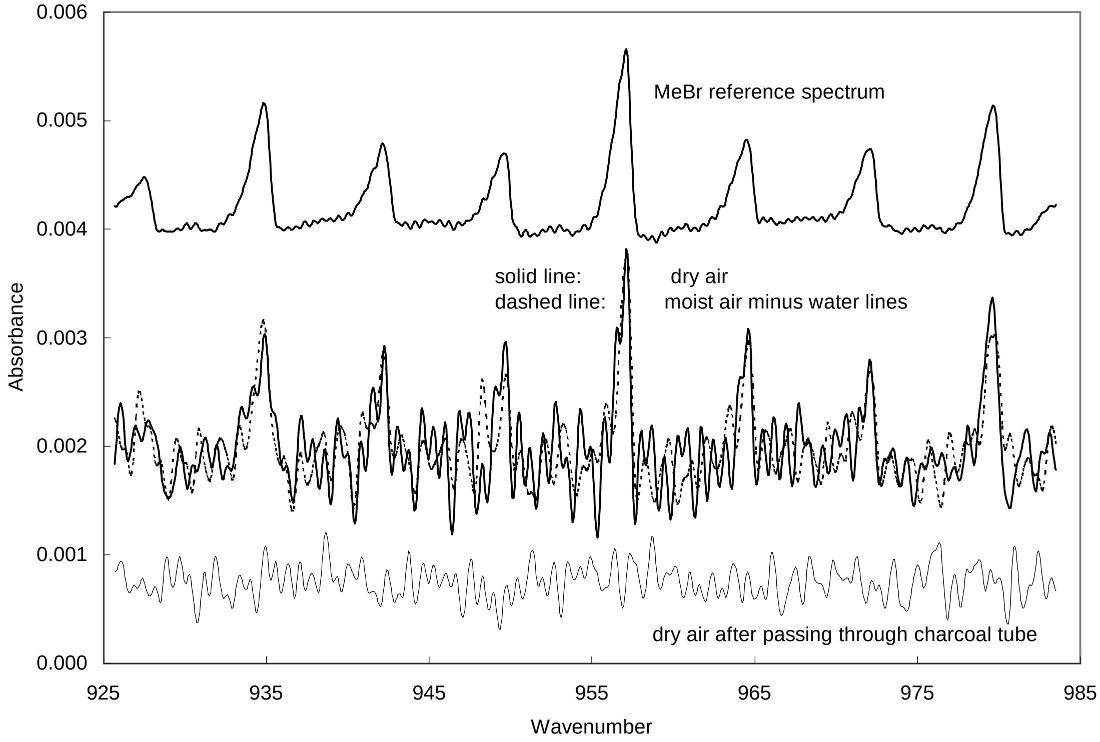

Figure 4 FTIR spectra of dry and moist air with identical MeBr concentrations.

Table 5 Charcoal tube results for 210 ppb spikes.

Humidity %	Volume L	MeBr spiked µg/sample	Result µg/tubeA	µg/tubeB	µg/sample	Recovery %
0	8.2	6.76	0.00	0.00	0.00	0
0	10.9	9.00	0.20	0.00	0.20	2
0	11.8	9.71	0.26	0.00	0.26	3
0	9.7	8.01	0.00	0.00	0.00	0
					mean= SD=1.5	1
50	8.3	6.80	3.68	0.00	3.68	54
50	10.9	9.00	4.49	0.00	4.49	50
50	11.8	9.71	6.11	0.00	6.11	63
50	11.3	9.30	5.55	0.00	5.55	60
					mean= SD=5.8	57
100	11.9	9.77	3.89	1.04	4.93	50
100	10.9	8.94	3.90	0.56	4.46	50
100	11.7	9.65	3.45	1.14	4.59	48
100	11.3	9.30	3.35	0.42	3.77	41
					mean= SD=4.3	47

Table 6 Charcoal tube results for 210 ppb spikes run outdoors.

Period	Volume L	MeBr spiked µg/sample	Result µg/sample	Recovery %
night	10.9	8.98	4.38	49
(12 hrs)	11.6	9.50	4.25	45
			mean=	47
morning	5.8	4.77	1.11	23
(6 hrs)	5.0	4.14	1.07	26
	5.7	4.65	1.18	25
			mean=	25
afternoon	5.8	4.74	0.97	21
(6 hrs)	5.3	4.40	1.00	23
	5.9	4.82	1.04	22
			mean=	22

One additional set of tests was run to check if the low recoveries observed so far were caused by the choice of the extraction solvent, ethyl acetate. Spikes were prepared using the same conditions as used during the six hour outdoor runs, but the sample extraction procedure was modified by the laboratory to use carbon disulfide. The recoveries were about 45% at 40% RH and 3% for very dry air (RH < 7%) with carbon disulfide, compared to about 57% and 1%, respectively, for ethyl acetate. This indicates that the recoveries can not be improved by switching solvents from ethyl acetate to carbon disulfide.

Storage Stability

Typically, up to four replicate samples were prepared in a single six hour run. This small number of samples per day would allow the analytical laboratory to extract samples prepared over a period of one week in a single day. To verify that the analysis of samples with different storage times would not cause a bias in the results, a storage stability study was undertaken. A constant concentration of about 710 ppb methyl bromide in air was maintained in the gas handling system for a period of seven days. On each of the seven days, two replicate six hour samples were taken under low humidity conditions (about 20% to 30% RH) during the morning. Then the humidity was raised to about 60% to 70% and a second set of two replicate samples was taken during the evening hours. Afterwards, the humidity was lowered again. All samples were put into a freezer immediately after sampling and stored there at about -20EC. At the end of the week, one of the two replicate samples was selected and forwarded to the laboratory for immediate extraction. Thus, this one extraction set contained two data points per day: one each for the two humidity levels. The second set of replicates was submitted to the laboratory after an additional week in the freezer, yielding storage stability data for a combined period of 14 days. A second set of data using the same study design was taken with a fixed concentration of about 95 ppb methyl bromide. Figure 5 shows the percent recovery as a function of storage time for the four test conditions (high/low concentration and high/low humidity). The full data set is listed in Appendix D.

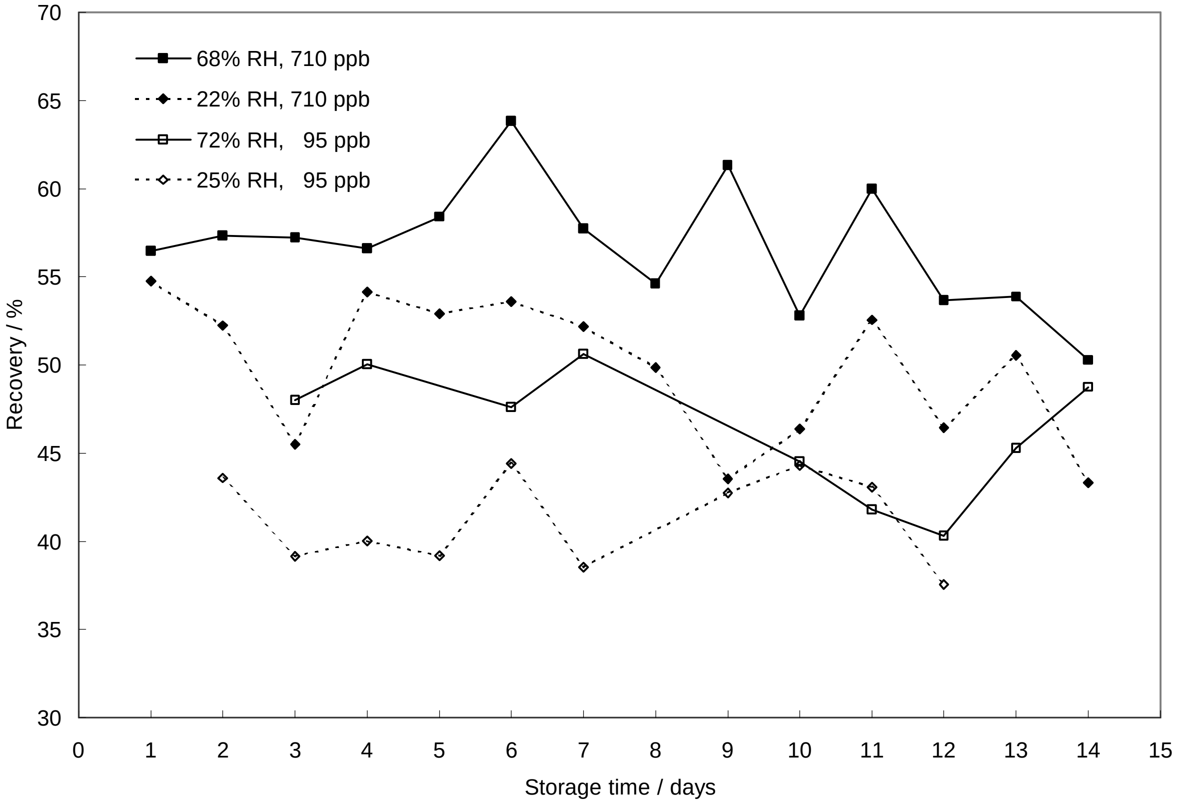

Figure 5 Storage stability of methyl bromide on charcoal at -20EC.

A statistical analysis was performed to identify significant effects. The first test was to check the difference in recovery between duplicate tubes analyzed seven days apart. A two-way analysis of variance with both concentration and humidity as random effects was used (Table 7). Because this is a controlled condition experiment (performed in the laboratory) the usual p-value of p = 0.05 is used as the yardstick to determine significant effects. With this criterion, the analysis shows no significant effects of concentration or humidity on the difference between recoveries on duplicate samples analyzed seven days apart. This analysis supports the use of the grand mean difference in recovery between the duplicate tubes analyzed seven days apart to represent potential storage losses. The mean difference in recovery between duplicates analyzed 7 days apart is -2.6%. This mean difference is statistically significantly different from zero (t = -3.10, df = 22, p = 0.0055). However, for practical purposes, and as will be shown in further analyses below, this reduction in recovery is small compared to the recovery reductions due to other factors. This analysis shows that a storage period of seven days does not have a substantial effect on method recovery. An additional analysis was performed to look at the whole 14 day period.

Table 7 Two-way analysis of variance on the difference in percent recovery between duplicate samples analyzed seven days apart, concentration and humidity are random effects.

Source	DF	SS	MS	F	p-value
Concentration	1	26.7	26.7	0.50	0.61
Humidity	1	15.1	15.1	0.28	0.69
Conc*Hum	1	53.8	53.8	3.84	0.07
Error	18	252.9	14.0		
Total	21				

Regression analysis of the data in Figure 5 shows that there is no significant trend in recovery with days of storage for any of the four combinations of concentration and humidity (Table 8). The results of this analysis support conducting analysis of variance directly on the recoveries at each concentration and humidity level.

Table 8 Summary of regressions expressing percent recovery as a function of days in storage for each of four combinations of concentration and humidity.

Concentration	Humidity	intercept	Slope	Slope p-value	R^2
95 ppb	20%	37.5%	0.02	0.94	0.1%
95 ppb	75%	46.6%	0.45	0.13	29.9%
710 ppb	20%	49.0%	0.47	0.05	28.5%
710 ppb	75%	54.5%	0.33	0.14	17.5%

The results of the analysis of variance are shown in Table 9. A two-factor analysis of variance was conducted with concentration and humidity both designated as random effects. The analysis results indicate that there is no significant interaction between concentration and humidity on recovery. However, there is a marginally significant effect of concentration level (p = 0.04) and a

Table 9 Two-way analysis of variance on percent recovery, concentration and humidity are random effects.

Source	DF	SS	MS	F	p-value
Concentration	1	396.7	396.7	204.7	0.04
Humidity	1	224.0	224.0	115.6	0.06
Conc*Hum	1	1.94	1.94	0.22	0.65
Error	21	187.5	8.93		
Total	24				

non-significant effect of humidity level (p = 0.06) on recoveries. Table 10 shows the mean recoveries in a two-way table. Because there is no significant interaction between these two main effects, they may be examined separately. The mean high concentration recovery is 49% and the mean low concentration recovery is 41%, a difference of about 8%. The mean high humidity recovery is 49% and the mean low humidity recovery is 42%, a difference of about 7%.

Table 10 Mean recoveries for each treatment combination and weighted marginal means. Sample sizes for each cell are shown in parentheses.

	23% Humidity	70% Humidity	Marginal Mean
95 ppb	38.0 (6)	43.5 (5)	40.5 (11)
710 ppb	45.5 (7)	52.1 (7)	48.8 (14)
Marginal Mean	42.0 (13)	48.5 (12)	45.1 (25)

Concentration/humidity matrix

The range of concentrations and relative humidities in this matrix is based on the range of values seen in our previous field studies. Three concentration levels were selected at about 20 ppb, 210 ppb and 2300 ppb. For moisture content, three relative humidity level of about 20 %, 50 % and 80 % were targeted. Besides the charcoal tubes, analyzed by the CDFA laboratory, SUMMA canister samples, analyzed by Quanterra, were collected also. Three replicate samples per method were taken for every concentration/humidity combination.

After starting this matrix of nine combinations, it was realized that the low concentration of 20 ppb, representing two times the reporting limit of the CDFA laboratory, could be too low for the charcoal tube analysis because the exploratory tests had shown that recoveries often were below 50%. Thus, after the first run, the low level was changed to about 35 ppb. After the samples for all nine sets in the matrix were collected, one replicate sample each was submitted for analysis to the respective laboratories. The other replicates were submitted sequentially at one week intervals. Thus, the final set exceeded the length of the storage stability study, but the originally planned spacing of four days could not be achieved due to scheduling problems. Table 11 shows the average result for each concentration/humidity combination. The full data set is listed in Appendix E.

Table 11 Summary data for the concentration/humidity matrix.

RH / %	MeBr / ppb			Recovery / %		Ratio
	spiked	reported				
		charcoal	Summa	charcoal	Summa	c/S
22	19	0	10	0	54	----
24	36	15	27	41	74	0.56
55	36	18	24	50	67	0.74
81	35	18	23	50	64	0.78
23	219	84	170	38	77	0.49
52	218	99	183	45	84	0.54
80	217	104	160	48	74	0.65
22	2350	1210	2000	51	85	0.61
53	2340	1340	2000	57	85	0.67
79	2330	1330	1970	57	84	0.68

The concentration/humidity matrix analysis was according to a three-way ANOVA with mixed effects. The three factors are method (SUMMA or charcoal), concentration and humidity. Method is a fixed effect, while concentration and humidity are random effects. Thus the ANOVA is under a mixed model. In addition, one observation was missing from the SUMMA method so the model is unbalanced. However, given the potential total number of observations is 54 and that only one cell has one missing value, therefore, the sample size for each treatment combination is nearly equal. Therefore, the degree of unbalance may be assumed to not be great enough to substantially effect the results. Mixed models are potentially affected by deviations from other assumptions of ANOVA, specifically, the assumptions of normality and homogeneous variance.

The data did not depart significantly from normality according to the Ryan-Joiner test (R=0.98, p=0.06, conducted with lumped data). This test is similar to the Shapiro-Wilks test. The variances between the main effects were homogenous according to a simple F-test (method, F = 2.086, p=0.07) and Bartlett's Test (concentration, B=1.41, p=0.50; humidity, B=0.96, p=0.62). The F-test and Bartlett's test were used since the data are assumed to conform to normality.

Table 12 shows the results of analysis of variance on the mixed model. The results indicate that there is a significant difference between mean recovery for the two methods. There are no other significant effects. The mean recovery for the charcoal tube method is 48.8% with a standard deviation of 7% and a coefficient of variation (CV) of 14%. These results for the charcoal tube method are consistent with the results obtained in the storage stability experiment where the grand mean recovery was 45.1% (Table 10). The mean recovery for the SUMMA method is 77.5% with a standard deviation of 12% and a CV of 15%.

Table 12 Three-way analysis of variance, mixed model on percent recovery. Method is a fixed effect; concentration and humidity are random effects.

Source	DF	Adjusted SS	Adjusted MS	F	p-value
Method	1	10692.6	10692.6	31.55	0.009
Concentration	2	1424.9	712.5	4.09	0.233
Humidity	2	118.0	59.0	0.36	0.743
Method*Conc	2	383.3	191.6	5.65	0.068
Method*Hum	2	362.7	181.4	5.35	0.074
Conc*Hum	4	64.9	16.2	0.48	0.753
Method*Conc*Hum	4	135.6	33.9	0.56	0.690
Error	35	2099.6	60.0		
Total	52	15496.4			

One can compare these average recoveries with the worst case error estimates from the Calibration section. With the high worst case error of 27% for the SUMMA canisters, it cannot be ruled out that the average recovery of about 78% was caused by bias in the sample preparation procedures. For the charcoal tubes, however, the low average recovery of about 49% is so far away from 100% that it cannot be explained by calibration errors alone. Even if one would apply the worst case error of 15% in the sample preparation to the charcoal tube results, the average recovery would only increase to about 56%.

Laboratory quality control spikes

Lab-internal quality control spikes were analyzed by each laboratory along with every batch of submitted samples. The data are listed in Appendix F. The CDFA laboratory ran 32 quality control spikes distributed over three levels: 1 µg/tube, 5 µg/tube and 50 µg/tube. The average recoveries for the 1 µg and 5 µg spikes were 63% and 71%, respectively, with no significant trend during the course of this study. The recoveries for the 50 µg spikes, however, started out at 93% for the first batch and 81% for the second batch, the remaining six control samples varied around an average of 71%. These results are higher than the air sample based recoveries determined in this study which yield an overall average of 49%.

Quanterra analyzed eight quality control samples (three at 9 ppb and five at 45 ppb), each of them on two separate detectors. The average recovery was 107% for either detector. This compares to the average air sample based recovery of 78% measured in this study. Neither of the laboratory control sets match the recoveries determined from samples prepared under simulated field conditions.

This difference is not surprising because the lab-internal spikes are a quality control measure for the analysis steps performed by the laboratory (i.e., extracting methyl bromide from charcoal tubes). They are not geared to verify or control procedures done outside the lab. For example, the methyl bromide levels used in the spiking procedure are based on liquid solutions of methyl bromide in a solvent, not on a gaseous mixture as used in this study. Thus, the methyl bromide is introduced into the air stream passing through the charcoal tube as a short-term, high-level pulse and not as a steady, low-level concentration.

Therefore, the laboratory control samples cannot be used as a correction factor for actual field samples (note that Quanterra's control samples routinely yield values above 100%). At best, they can be used to track laboratory performance. But even an odd result in the control samples does not imply that the whole analysis batch is suspect. For example, there was no corresponding change in the sample recovery when the control recovery of the CDFA laboratory dropped from 94% to 71%.

Field Comparison

While this laboratory study on the performance of charcoal tube and SUMMA canister analysis was going on, five field studies were conducted where SUMMA canister samples were taken during methyl bromide fumigations monitored by the DPR. The complete data set is listed in Appendix G. Average charcoal/SUMMA ratios from the five studies were 0.62 (8 pairs), 0.58 (8 pairs), 0.78 (12 pairs), 0.94 (34 pairs) and 0.82 (9 pairs). These field data are also shown in Figure 6, together with the laboratory data generated in this study.

Simple linear regression analysis was performed on these data where Charcoal tube and SUMMA samples were collected side-by-side. A total of 70 samples, with observed concentrations ranging from near the reporting limit of each method (charcoal tube: 10 ppb at six hours, SUMMA canister: 2 ppb) to approximately 1200 ppb, were available for the comparison. This range of observed concentrations was within the range of concentrations used in the laboratory matrix study, allowing a further comparison of the regression results from the field with those from the laboratory study.

An initial regression analysis was conducted on the 70 pairs of field samples. The resulting regression equation was:

$$\text{charcoal (ppb)} = -5.3 + 0.788*(\text{SUMMA (ppb)})$$

The intercept was not significantly different from zero ($t = -0.42$, $p = 0.673$, $S_a = 12.55$) and the slope was significantly different from zero ($t = 22.62$, $p = 0.000$, $S_b = 0.0348$). The $R^2 = 88.3\%$. An examination of the residual plot and an analysis of the residuals by regression techniques indicated that violation of the assumption of homogeneity of variance was present. In addition, the four pairs of observations with high concentrations were highly influential in the fit of the regression equation. A logarithmic transformation is appropriate for these conditions. A second regression analysis on transformed data was conducted, resulting in the regression equation:

$$\log_{10}(\text{charcoal (ppb)}) = 0.098 + 0.893*(\log_{10}(\text{SUMMA (ppb)}))$$

The intercept was not significantly different from zero ($t = 0.96$, $p = 0.342$, $S_a = 0.10$) and the slope was significantly different from zero ($t = 18.76$, $p = 0.00$, $S_b = 0.048$). The $R^2 = 83.8\%$. Examination of the residual plot and an analysis of the residuals by regression techniques indicated that under the conditions of the logarithmic transformation no violation of the assumption of homogeneity of variance was present.

Regression analysis was also performed on the laboratory matrix experiment results. A total of 26 pairs of charcoal/SUMMA results were available for the analysis. An initial regression analysis was conducted on the 26 pairs of laboratory samples. The resulting regression equation was:

$$\text{charcoal (ppb)} = -3.3 + 0.648*(\text{SUMMA (ppb)})$$

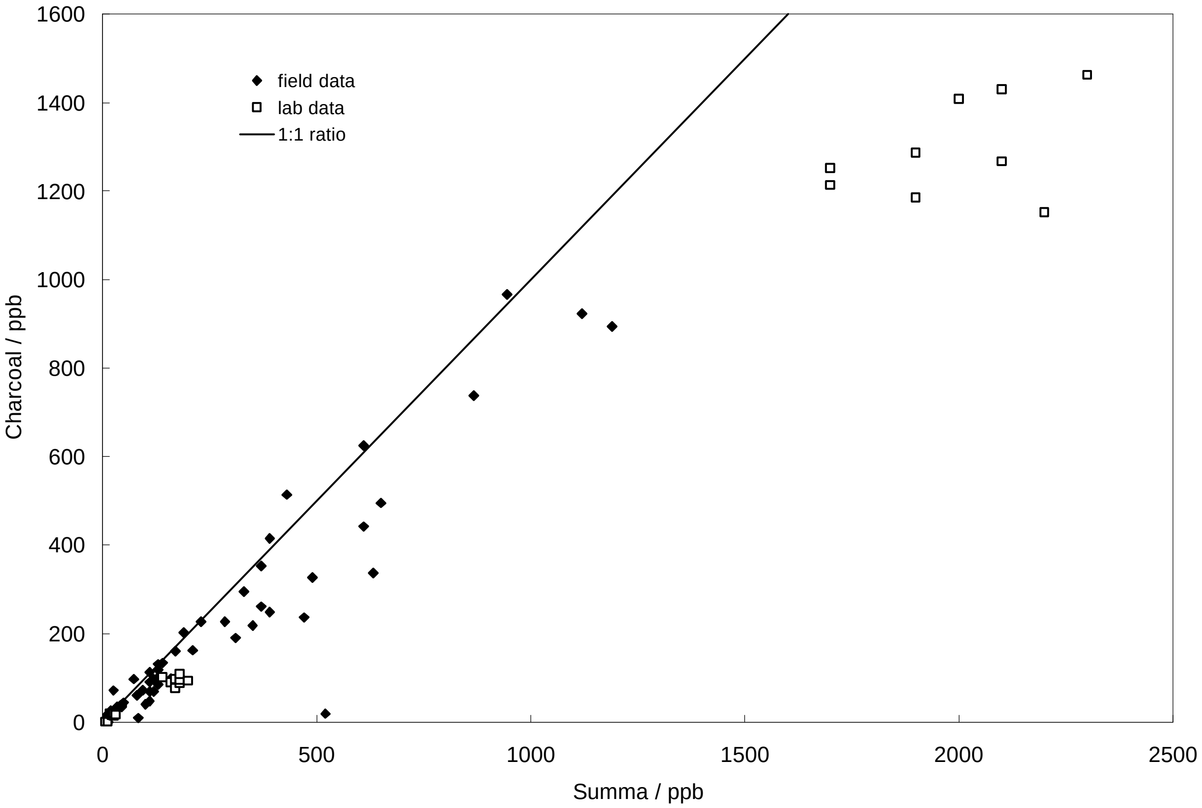

Figure 6 Comparison of SUMMA canister and charcoal tube analyses of paired samples.

The intercept was not significantly different from zero (t = -0.17, p = 0.869, S_a = 19.80) and the slope was significantly different from zero (t = 38.69, p = 0.000, S_b = 0.0168). The R^2 = 98.4%. An examination of the residual plot and an analysis of the residuals by regression techniques indicated that a violation of the assumption of homogeneity of variances was present. A logarithmic transformation is appropriate for this condition. A second regression analysis was conducted, resulting in the regression equation:

$$\log_{10}(\text{charcoal (ppb)}) = -0.163 + 0.984*(\log_{10}(\text{SUMMA (ppb)}))$$

The intercept was significantly different from zero (t = -3.20, p = 0.004,S_a = 0.05), indicating a bias. The slope was significantly different from zero (t = 47.04, p = 0.00, S_b = 0.021). The R^2 = 98.9%. Examination of the residual plot and an analysis of the residuals by regression techniques indicated that under the conditions of the logarithmic transformation no violation of the assumption of homogeneity of variance was present.

As a final analysis, a comparison of the two regression equations shown below was conducted.

Field data - $\log_{10}(\text{charcoal (ppb)}) = 0.098 + 0.893*(\log_{10}(\text{SUMMA (ppb)}))$

Laboratory data - $\log_{10}(\text{charcoal (ppb)}) = -0.163 + 0.984*(\log_{10}(\text{SUMMA (ppb)}))$

A comparison of the two slopes showed that they were not significantly different ($t = -1.38$, $p = 0.09$, $S_{b1-b2} = 0.66$). This means that the two regression lines are either parallel (if the intercepts are significantly different) or the two regression lines are independent estimates of a common regression line. A comparison of the two intercepts showed that they were not significantly different ($t = 1.70$, $p = 0.05$). This means that the two lines have the same elevation. Therefore, the two regressions have neither different slopes nor different elevations. The analysis indicates that these two regression lines are independent estimates of a common regression line. The common regression line can be calculated, with a common slope and a common intercept weighted for the differences in sample size. The common regression equation is shown below:

$$\log_{10}(\text{charcoal (ppb)}) = -0.005 + 0.930*(\log_{10}(\text{SUMMA (ppb)}))$$

For this common regression equation, the intercept is not significantly different from zero ($t = -0.069$, $p = 0.53$, $S_a = 0.0724$) and the slope is significantly different from zero ($t = 28.61$, $p = 0.00$, $S_b = 0.0325$). The R^2 is 89.8%. In addition, the slope is significantly different from 1.0 ($t = 2.15$, $p = 0.02$).

The common regression equation, which includes paired charcoal tube and SUMMA canister measurements from both field and laboratory studies, can be used to estimate the relative measured concentrations. Based on an assumed SUMMA canister reading of 200 ppb, the regression would estimate 140 ppb for the charcoal. This represents a ratio of 0.70 between the charcoal and SUMMA measurements at 200 ppb. Taking into account the average recovery of the SUMMA canister samples determined in this study (about 78%), the regression estimate at 200 ppb leads to a charcoal recovery of 55% (78% x 0.70), which is consistent with the laboratory based average charcoal recovery of 49%. A similar result also occurs when the field data only regression is used, which is independent of the laboratory generated charcoal tube data. In this case, the field data only regression leads to a ratio of 0.71 between the charcoal tube and SUMMA canister measurements at 200 ppb and the estimated charcoal recovery would then be 55% (78% x 0.70).

Summary and Conclusions

These tests show that the measurement of ambient levels of methyl bromide using adsorption on charcoal tubes has some limitations. For extremely dry air (<10% RH), recoveries drop to near zero, and with very moist air near the dew point, breakthrough occurs. In the more moderate relative humidity range of about 20% to 80%, the average recovery of the charcoal tube method was 49%, indicating that the ambient levels of methyl bromide are underestimated by a factor of about two. This conclusion was substantiated by using the results of the field comparisons to adjust the laboratory based SUMMA canister recovery, a calculation which was independent of the laboratory generated charcoal tube data.

The recoveries measured in this study also show that the lab-internal quality control spikes are not a good measure of the performance under field conditions. The main reason for this is that the laboratory quality control is concerned mainly with the analysis procedure performed in the laboratory and does not adequately cover sampling, storage or other effects occurring before the samples arrive at the laboratory. This is especially evident in the laboratory recoveries reported by Quanterra, as they are routinely above 100%.

Even though this study tried to simulate field sampling procedures as closely as possible, being an indoor study, it could not take into account all factors that influence field measurements. For example the single outdoor experiment where the recovery for the daytime samples was markedly lower than for the nighttime samples. Perhaps, as discussed earlier, this effect can be explained by the observed decay of methyl bromide under elevated daytime temperatures. If the use of charcoal tubes for the determination of ambient methyl bromide levels is continued, this effect needs further study. Especially because outdoor sampling effects are not covered by laboratory-internal quality control spikes.

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Appendices

A) Flow Controller Calibration Data

NIST traceable calibration data provided by the manufacturer of the flow controllers.

Actual Flow ml/min	Readout ml/min	Deviation %
5 ml/min:		
0	.00	0.0%
1.22	1.25	2.5%
2.49	2.50	0.4%
4.95	5.00	1.0%
50 ml/min:		
0	0.0	0.0%
12.5	12.5	0.0%
24.8	25.0	0.8%
49.8	50.0	0.4%
200 ml/min:		
0	0	0.0%
51	50	-2.0%
100	100	0.0%
202	200	-1.0%
500 ml/min:		
0	0	0.0%
126	125	-0.8%
250	250	0.0%
500	500	0.0%

Calibration check for 5 mL/min flow controller

Because flows less than about 7mL/min cannot be measured by the Accuflow meter, a fixed flow was added through the 50mL/min flow controller. Readings of the fixed flow were taken between each set of flow measurements in this sequence:
set 5 mL/min controller to zero, read fixed flow only
set 5 mL/min controller to 0.5 mL/min, read combined flows
set 5 mL/min controller to zero, read fixed flow only,
set 5 mL/min controller to 1.0 mL/min, read combined flows, etc.

The average fixed flow from before and after each combined reading was subtracted from that combined reading to obtain the flow of the 5 mL/min controller.

Setpoint mL/min	Accuflow mL/min	Datalogger mL/min
0	0.00	0.09
0.5	0.43	0.51
1.0	0.92	1.00
1.5	1.34	1.51
2.0	1.89	2.00
2.5	2.36	2.50
3.0	2.89	3.00
3.5	3.40	3.50
4.0	3.98	4.00
4.5	4.42	4.49
5.0	4.88	4.93

Calibration check for 50 mL/min flow controller

Setting mL/min	Accuflow mL/min	Datalogger mL/min
0	0.00	0.15
7.5	7.34	7.71
10.0	9.89	10.31
12.5	12.30	12.84
15.0	14.83	15.39
17.5	17.20	17.81
20.0	19.77	20.44
22.5	22.21	22.86
25.0	24.74	25.45
27.5	27.24	27.95
30.0	29.74	30.34
32.5	32.26	32.89
35.0	34.73	35.42
37.5	37.40	37.90
40.0	40.06	40.39
42.5	42.53	42.80
45.0	45.16	45.30
47.5	47.67	47.76
50.0	50.39	50.20

Calibration check for 200 mL/min controller

Setting mL/min	Accuflow mL/min	Datalogger mL/min
0	0.00	0.752
10	10.09	10.578
20	19.70	20.118
30	30.27	30.492
40	40.69	40.782
50	50.54	50.498
60	60.44	60.114
70	70.93	70.5
80	81.57	80.9
90	90.84	89.9
100	101.00	100
110	111.14	110.3
120	121.00	119.88
130	131.43	130.3
140	141.43	139.94
150	152.00	150.4
160	161.71	159.86
170	172.14	170.28
180	181.43	179.8
190	192.57	189.96
200	205.14	199.84

Calibration check for 500 mL/min controller

Setting mL/min	Accuflow mL/min	Datalogger mL/min
0	0.00	1.070
24	26.37	24.472
50	52.06	50.668
75	77.07	76
100	101.00	100.34
125	126.57	125.9
150	150.86	150.48
174	173.86	174.4
200	199.29	200.46
226	224.86	226.4
250	247.86	250.28
275	272.29	275.12
299	297.14	299.9
324	323.43	324.32
350	352.43	350.26
376	375.29	376.32
400	400.71	400.46
426	426.00	426.25
450	449.14	450.4
474	472.43	474.3
500	501.00	501

B) FTIR measurements

Air concentrations are calculated from the FTIR spectra using the formula:

$$C_{air} = \frac{f * A_{ref}}{L}$$

where C_{air} is the methyl bromide concentration in the sampling volume, f is the scaling factor that matches a reference spectrum to the current sample spectrum, A_{ref} is the amount of methyl bromide in the reference spectrum and L is the absorption path length. The factor f is a dimensionless number obtained from a least-squares fitting procedure that matches the height and shape of the methyl bromide peaks in a reference spectrum to a sample and from the amount of methyl bromide in the reference spectrum. A_{ref} is expressed as a path-integrated concentration with the units ppm-meter.

The accuracy and the precision of the determined air concentration depend on three factors: the error in the concentration of the reference spectrum, the measurement of the total absorption path length and the goodness of the fit. The first two factors are constant throughout this study. Of these, the absorption path length is obtained by a simple measurement of the distance between the mirrors in the multiple reflection system times the number of reflections plus a measured offset. Assuming a readout error of 1 mm, the path length can be determined with an accuracy of about 1%.

The methyl bromide reference spectrum was prepared at the West Sacramento facility in 1991 by Martina Green. To check its accuracy, this reference spectrum was used to determine the methyl bromide concentration in a commercial reference spectrum (Infrared Analysis, Inc.) for which the vendor lists a path-integrated concentration of 660 ppm-m. The concentration of the DPR reference spectrum is 868 ppm-m. The least-squares fit of the DPR reference to the commercial reference yielded a fitting factor of 0.753 which gives a calculated concentration of 654ppm-m. Thus, the DPR reference used in this study agrees with the commercial reference to within 1%.

The third factor, the coefficient of the least-squares fit, has an influence on the analysis result that varies somewhat with the signal to noise ratio in the spectra and effects mainly the precision. A systematic bias, however, can be introduced if the spectra contain extraneous features like absorption lines of other compounds or noise spikes. Because the spectra in this study were taken from clean gas mixtures under controlled conditions, this problem did not occur here.

C) Raw Data for the exploratory tests

All operating conditions, datalogger files and laboratory results were entered into an Excel spreadsheet. The following tables contain abbreviated printouts of these files. Omitted in this printout are the six replicate measurements of the flow speed for each air sampler (only the average is listed) and the raw data from the data logger (one-minute readouts of the flows and environmental conditions).

Set #	Rep #	Pump #	Comment	Start date	Run time	Pump flow	Volume	MBr flow	Air flow	RH	Lab result		MBr meas.		MBr calc.		Recovery
					min	mL/min	L	mL/min	mL/min	%	ug (A)	ug (B)	ug/sample	ug/L	ug/sample	ug/L	%
1	1	132		8/14/97	720	16.3	11.7	90	45	0	16.70	0.00	16.70	1.42	64.36	5.48	25.9
1	2	151		8/14/97	720	15.1	10.9	90	45	0	18.00	0.00	18.00	1.66	59.62	5.48	30.2
1	3	138		8/14/97	720	16.0	11.5	90	45	0	17.30	0.00	17.30	1.50	63.17	5.48	27.4
1	4	85		8/14/97	720	14.8	10.7	90	45	0	16.80	0.00	16.80	1.58	58.43	5.48	28.8
1		268	room air	8/14/97	720	14.6	10.5				0.00	0.00	0.00	0.00	N/A		
2	1	132		8/15/97	720	16.2	11.7	90	45	40	37.10	0.00	37.10	3.18	63.96	5.48	58.0
2	2	151		8/15/97	718	15.1	10.8	90	45	40	34.30	0.00	34.30	3.16	59.45	5.48	57.7
2	3	138		8/15/97	714	15.8	11.3	90	45	40	35.30	0.00	35.30	3.13	61.86	5.48	57.1
2	4	85		8/15/97	712	14.8	10.5	90	45	40	34.00	0.00	34.00	3.23	57.79	5.48	58.8
3	1	132		8/19/97	720	16.5	11.9	20	180	100	3.89	1.04	4.93	0.41	9.77	0.82	50.5
3	2	151		8/19/87	720	15.1	10.9	20	180	100	3.90	0.56	4.46	0.41	8.94	0.82	49.9
3	3	138		8/19/97	720	16.3	11.7	20	180	100	3.45	1.14	4.59	0.39	9.65	0.82	47.5
3	4	85		8/19/97	720	15.7	11.3	20	180	100	3.35	0.42	3.77	0.33	9.30	0.82	40.5
4	1	132	pump stopped	8/20/97	498	16.6	8.3	20	180	50	3.68	0.00	3.68	0.45	6.80	0.82	54.1
4	2	151		8/20/97	720	15.2	10.9	20	180	50	4.49	0.00	4.49	0.41	9.00	0.82	49.9
4	3	138		8/20/97	720	16.4	11.8	20	180	50	6.11	0.00	6.11	0.52	9.71	0.82	62.9
4	4	85		8/20/97	720	15.7	11.3	20	180	50	5.55	0.00	5.55	0.49	9.30	0.82	59.7
5	1	132	pump stopped	8/21/97	495	16.6	8.2	20	180	0	0.00	0.00	0.00	0.00	6.76	0.82	0.0
5	2	151		8/21/97	720	15.2	10.9	20	180	0	0.20	0.00	0.20	0.02	9.00	0.82	2.4
5	3	138		8/21/97	720	16.4	11.8	20	180	0	0.26	0.00	0.26	0.02	9.71	0.82	2.7
5	4	85	pump stopped	8/21/97	620	15.7	9.7	20	180	0	0.00	0.00	0.00	0.00	8.01	0.82	0.0
6	1	132	outdoor/night	8/27/97	700	15.6	10.9	20	180		4.38	0.00	4.38	0.40	8.98	0.82	48.8
6	2	151	no flow after run	8/27/97	700	14.4	10.1	20	180		ND		N/A	N/A	8.29	0.82	N/A
6	3	138	outdoor/night	8/27/97	700	16.5	11.6	20	180		4.25	0.00	4.25	0.37	9.50	0.82	44.7
6	4	85	no flow after run	8/27/97	700	14.5	10.2	20	180		ND		N/A	N/A	8.35	0.82	N/A
7	1	132	outdoor/morning	8/28/97	345	16.8	5.8	20	180		1.11	0.00	1.11	0.19	4.77	0.82	23.3
7	2	268	outdoor/morning	8/28/97	345	14.6	5.0	20	180		1.07	0.00	1.07	0.21	4.14	0.82	25.8
7	3	138	outdoor/morning	8/28/97	345	16.4	5.7	20	180		1.18	0.00	1.18	0.21	4.65	0.82	25.4
8	1	132	outdoor/afternoon	8/28/97	345	16.7	5.8	20	180		0.97	0.00	0.97	0.17	4.74	0.82	20.5
8	2	268	outdoor/afternoon	8/28/97	345	15.5	5.3	20	180		1.00	0.00	1.00	0.19	4.40	0.82	22.7
8	3	138	outdoor/afternoon	8/28/97	345	17.0	5.9	20	180		1.04	0.00	1.04	0.18	4.82	0.82	21.6
9	1	133	carbon disulfide	10/15/97	360	14.9	5.4	20	180	35	1.94	0.00	1.94	0.36	4.41	0.82	44.0
9	2	82	carbon disulfide	10/15/97	360	15.1	5.4	20	180	35	2.06	0.00	2.06	0.38	4.47	0.82	46.1
9	3	83	carbon disulfide	10/15/97	360	15.2	5.5	20	180	35	2.14	0.00	2.14	0.39	4.50	0.82	47.5
9	4	271	carbon disulfide	10/15/97	360	15.3	5.5	20	180	35	1.91	0.00	1.91	0.35	4.53	0.82	42.2
10	1	133	carbon disulfide	10/15/97	360	13.9	5.0	20	180	8	0.11	0.00	0.11	0.02	4.12	0.82	2.6
10	2	82	carbon disulfide	10/15/97	360	14.7	5.3	20	180	8	0.14	0.00	0.14	0.03	4.35	0.82	3.2
10	3	83	carbon disulfide	10/15/97	360	15.4	5.5	20	180	8	0.11	0.00	0.11	0.02	4.56	0.82	2.5
10	4	271	carbon disulfide	10/15/97	360	15.3	5.5	20	180	8	0.11	0.00	0.11	0.02	4.53	0.82	2.4

D) Raw data for the storage stability tests

sampling date	start time	run time min	flow ml/min	volume L	MeBr flow mL/min	Air flow (corr.) mL/min	MeBr - calc ug (ppb for Summa)	RH %	storage days	MeBr - lab ug (ppb for Summa)	recovery %
23-Oct-97	9:40	360	15.1	5.4	50.3	101.3	14.8	22	14	5.84	39.5
23-Oct-97	9:40	360	14.8	5.3	50.3	101.3	14.5	22	7	6.92	47.6
23-Oct-97	16:45	360	16.7	6.0	50.4	102.5	16.3	71	14	7.51	46.2
23-Oct-97	16:45	360	14.6	5.2	50.4	102.5	14.2	71	7	7.53	53.0
24-Oct-97	9:00	366	15.1	5.5	50.3	101.3	15.1	22	6	7.39	48.9
24-Oct-97	9:00	366	14.6	5.3	50.3	101.3	14.5	22	13	6.7	46.1
24-Oct-97	16:30	360	14.4	5.2	50.4	102.5	14.1	71	6	8.26	58.6
24-Oct-97	16:30	360	14.6	5.2	50.4	102.5	14.2	71	13	7.03	49.5
25-Oct-97	9:00	360	14.3	5.1	50.3	101.3	14.0	23	12	5.95	42.4
25-Oct-97	9:00	360	14.7	5.3	50.3	101.3	14.4	23	5	6.96	48.2
25-Oct-97	16:00	360	13.7	4.9	50.3	102.4	13.4	67	5	7.18	53.6
25-Oct-97	16:00	360	14.7	5.3	50.3	102.4	14.4	67	12	7.07	49.3
26-Oct-97	7:08	360	13.7	4.9	50.3	101.3	13.5	25	11	6.46	48.0
26-Oct-97	7:08	360	14.6	5.3	50.3	101.3	14.4	25	4	7.1	49.4
26-Oct-97	14:33	360	13.8	5.0	50.3	102.3	13.5	66	11	7.42	55.1
26-Oct-97	14:33	360	14.7	5.3	50.3	102.3	14.3	66	4	7.44	51.9
27-Oct-97	7:33	383	15.5	5.9	50.3	101.3	16.2	23	3	6.73	41.5
27-Oct-97	7:33	383	14.7	5.6	50.3	101.3	15.3	23	10	6.49	42.3
27-Oct-97	15:05	360	17.6	6.3	50.4	102.3	17.2	66	10	8.33	48.5
27-Oct-97	15:05	360	14.7	5.3	50.4	102.3	14.3	66	3	7.53	52.5
28-Oct-97	7:58	360	15.9	5.7	50.3	101.2	15.6	20	9	6.21	39.7
28-Oct-97	7:58	360	14.7	5.3	50.3	101.2	14.5	20	2	6.89	47.6
28-Oct-97	15:25	360	15.2	5.5	50.4	102.4	14.8	68	2	7.81	52.6
28-Oct-97	15:25	360	14.7	5.3	50.4	102.4	14.3	68	9	8.06	56.3
29-Oct-97	7:23	360	15.1	5.4	50.3	101.2	14.9	20	8	6.76	45.4
29-Oct-97	7:23	360	14.6	5.3	50.3	101.2	14.4	20	1	7.18	49.9
29-Oct-97	14:40	350	15.1	5.3	50.4	102.4	14.3	67	1	7.42	51.8
29-Oct-97	14:40	350	14.7	5.1	50.4	102.4	13.9	67	8	6.98	50.1
30-Oct-97	7:50	363	15.2	5.5	9.4	201.0	2.0	25	7	0.714	35.1
30-Oct-97	7:50	363	14.7	5.3	9.4	201.0	2.0	25	14	broken	N/A
30-Oct-97	15:29	360	15.1	5.4	9.4	203.0	2.0	69	7	0.925	46.5
30-Oct-97	15:29	360	14.6	5.3	9.4	203.0	1.9	69	14	0.863	44.8
31-Oct-97	6:53	360	15.1	5.4	9.4	200.8	2.0	23	6	0.725	36.3
31-Oct-97	6:53	360	14.6	5.3	9.4	200.8	1.9	23	6	0.865	44.5
31-Oct-97	14:36	360	15.1	5.4	9.4	202.5	2.0	71	13	0.828	41.5
31-Oct-97	14:36	360	14.6	5.3	9.4	202.5	1.9	71	6	0.841	43.7
31-Oct-97	14:36	360			9.4	202.5	94.5	71	10	74	78.3
1-Nov-97	8:03	360	15.2	5.5	9.4	200.8	2.0	22	12	0.688	34.2
1-Nov-97	8:03	360	14.7	5.3	9.4	200.8	2.0	22	5	0.696	35.7
1-Nov-97	8:03	360			9.4	200.8	95.2	22	10	68	71.5
1-Nov-97	14:57	360	15.1	5.4	9.4	203.2	2.0	73	12	0.743	37.4
1-Nov-97	14:57	360	14.7	5.3	9.4	203.2	1.9	73	12	0.709	36.8
2-Nov-97	7:58	360	15.1	5.4	9.4	201.2	2.0	32	11	0.785	39.3
2-Nov-97	7:58	360	14.6	5.3	9.4	201.2	1.9	32	4	0.706	36.5
2-Nov-97	14:38	360	15.0	5.4	9.4	203.7	2.0	73	11	0.758	38.5
2-Nov-97	14:38	360	14.5	5.2	9.4	203.7	1.9	73	4	0.88	46.1
2-Nov-97	14:38	360			9.4	203.7	94.0	73	8	61	64.9
3-Nov-97	8:03	360	15.1	5.4	9.4	200.9	2.0	25	3	0.716	35.7
3-Nov-97	8:03	360	14.6	5.2	9.4	200.9	1.9	25	10	0.78	40.4
3-Nov-97	8:03	360			9.4	200.9	95.1	25	3	67	70.5
3-Nov-97	14:50	360	15.0	5.4	9.4	203.2	2.0	72	3	0.871	44.2
3-Nov-97	14:50	360	14.5	5.2	9.4	203.2	1.9	72	10	0.783	41.0
4-Nov-97	7:35	364	15.0	5.5	9.4	200.9	2.0	25	9	0.786	38.9
4-Nov-97	7:35	364	14.6	5.3	9.4	200.9	2.0	25	2	0.776	39.7

E) Raw data for the concentration/humidity matrix

Charcoal tube analyses:

Date	Days	Volume	MeBr	MeBr	Air flow	MeBr				Recovery	RH
sampled	in		tank	flow	corrected	calculated	reported	calculated	reported		
	storage	l	ppb	ml/min	ml/min	ug/sample	ug/sample	ppb	ppb	%	%
26-Jan-98	8	5.32	2120	3.7	417	0.38	0	19	0	0.0	22
26-Jan-98	15	5.54	2120	3.7	417	0.40	0	19	0	0.0	22
26-Jan-98	22	5.48	2120	3.7	417	0.40	0	19	0	0.0	22
27-Jan-98	7	5.24	2120	8.2	481	0.72	0.383	36	19	53.0	55
27-Jan-98	14	5.29	2120	8.2	481	0.73	0.365	36	18	50.0	55
27-Jan-98	21	5.58	2120	8.2	481	0.77	0.366	36	17	47.5	55
27-Jan-98	7	5.24	2120	8.2	484	0.72	0.385	35	19	53.5	81
27-Jan-98	14	5.45	2120	8.2	484	0.75	0.341	35	16	45.6	81
27-Jan-98	21	5.54	2120	8.2	484	0.76	0.390	35	18	51.3	81
28-Jan-98	6	5.23	2120	8.2	478	0.73	0.326	36	16	44.8	24
28-Jan-98	13	5.42	2120	8.2	478	0.75	0.311	36	15	41.3	24
28-Jan-98	20	5.47	2120	8.2	478	0.76	0.291	36	14	38.3	24
28-Jan-98	6	5.47	2120	45.3	393	4.65	1.85	219	87	39.7	23
28-Jan-98	13	5.27	2120	45.3	393	4.49	1.82	219	89	40.5	23
28-Jan-98	20	5.57	2120	45.3	393	4.75	1.64	219	76	34.6	23
29-Jan-98	5	5.41	2120	45.4	395	4.58	1.96	218	93	42.8	52
29-Jan-98	12	5.53	2120	45.4	395	4.68	2.31	218	108	49.3	52
29-Jan-98	19	5.30	2120	45.4	395	4.49	1.98	218	96	44.1	52
29-Jan-98	5	5.26	2120	45.3	398	4.43	2.07	217	101	46.7	80
29-Jan-98	12	5.50	2120	45.3	398	4.63	2.45	217	115	53.0	80
29-Jan-98	19	5.46	2120	45.3	398	4.59	2.02	217	95	44.0	80
30-Jan-98	4	5.29	12300	45.3	191	48.33	24.9	2354	1213	51.5	22
30-Jan-98	11	5.60	12300	45.3	191	51.13	27.5	2354	1266	53.8	22
30-Jan-98	18	5.50	12300	45.3	191	50.25	24.6	2354	1152	49.0	22
2-Feb-98	1	5.27	12300	45.3	193	47.90	28.8	2341	1407	60.1	53
2-Feb-98	8	5.52	12300	45.3	193	50.14	30.6	2341	1429	61.0	53
2-Feb-98	15	5.38	12300	45.3	193	48.83	24.7	2341	1184	50.6	53
2-Feb-98	1	5.37	12300	45.3	194	48.55	26.8	2330	1286	55.2	79
2-Feb-98	8	5.20	12300	45.3	194	47.03	29.5	2330	1462	62.7	79
2-Feb-98	15	5.52	12300	45.3	194	49.90	26.8	2330	1251	53.7	79

SUMMA canister analyses:

Date filled	Days in storage	MeBr tank ppb	MeBr flow ml/min	Air flow corrected ml/min	MeBr calculated ppb	MeBr reported ppb	Recovery %	RH %
26-Jan-98	24	2120	3.7	417	19	12	64.5	22
26-Jan-98	25	2120	3.7	417	19	5.9	31.7	22
26-Jan-98	26	2120	3.7	417	19	12	64.5	22
27-Jan-98	23	2120	8.2	481	36	27	75.9	55
27-Jan-98	24	2120	8.2	481	36	21	59.1	55
27-Jan-98	24	2120	8.2	481	36	24	67.5	55
27-Jan-98	23	2120	8.2	484	35	27	76.3	81
27-Jan-98	24	2120	8.2	484	35	24	67.8	81
27-Jan-98	24	2120	8.2	484	35	17	48.1	81
28-Jan-98	22	2120	8.2	478	36	31	86.5	24
28-Jan-98	23	2120	8.2	478	36	22	61.4	24
28-Jan-98	24	2120	8.2	478	36	27	75.4	24
28-Jan-98	22	2120	45.3	393	219	180	82.0	23
28-Jan-98	23	2120	45.3	393	219	160	72.9	23
28-Jan-98	24	2120	45.3	393	219	170	77.5	23
29-Jan-98	21	2120	45.4	395	218	200	91.6	52
29-Jan-98	21	2120	45.4	395	218	180	82.4	52
29-Jan-98	23	2120	45.4	395	218	170	77.9	52
29-Jan-98	21	2120	45.3	398	217	140	64.5	80
29-Jan-98	22	2120	45.3	398	217	n/a	n/a	80
29-Jan-98	23	2120	45.3	398	217	180	83.0	80
30-Jan-98	20	12300	45.3	191	2354	1700	72.2	22
30-Jan-98	20	12300	45.3	191	2354	2100	89.2	22
30-Jan-98	22	12300	45.3	191	2354	2200	93.5	22
2-Feb-98	17	12300	45.3	193	2341	2000	85.4	53
2-Feb-98	17	12300	45.3	193	2341	2100	89.7	53
2-Feb-98	19	12300	45.3	193	2341	1900	81.2	53
2-Feb-98	17	12300	45.3	194	2330	1900	81.5	79
2-Feb-98	18	12300	45.3	194	2330	2300	98.7	79
2-Feb-98	19	12300	45.3	194	2330	1700	73.0	79

F) Raw Data for the laboratory quality control spikes

Charcoal tube extractions by the CDFA laboratory:

extraction date	ID #	spike ug	result ug	recovery %
9/8/97	97-0649	1	0.682	68.2
11/6/97	97-1854	1	0.58	58.0
11/6/97	97-1855	1	0.662	66.2
11/13/97	97-1872	1	0.644	64.4
11/13/97	97-1873	1	0.591	59.1
11/13/97	97-1878	1	0.595	59.5
11/13/97	97-1879	1	0.626	62.6
8/25/97	97-0932	5	3.61	72.2
9/8/97	97-0648	5	3.7	74.0
10/30/97	97-1842	5	3.53	70.6
10/30/97	97-1843	5	3.71	74.2
10/30/97	97-1848	5	3.68	73.6
10/30/97	97-1849	5	3.99	79.8
11/6/97	97-1860	5	3.45	69.0
11/6/97	97-1861	5	3.54	70.8
11/6/97	97-1866	5	3.49	69.8
11/6/97	97-1867	5	3.8	76.0
2/3/98	97-2740	5	2.78	55.6
2/3/98	97-2741	5	3.3	66.0
2/10/98	97-2748	5	3.61	72.2
2/10/98	97-2749	5	3.85	77.0
2/17/98	97-2756	5	3.41	68.2
2/17/98	97-2757	5	3.62	72.4
8/18/97	97-0351	50	46.4	92.8
8/18/97	97-0352	50	47.2	94.4
8/25/97	97-0933	50	40.7	81.4
2/3/98	97-2738	50	35.6	71.2
2/3/98	97-2739	50	34.4	68.8
2/10/98	97-2746	50	36.9	73.8
2/10/98	97-2747	50	37.9	75.8

SUMMAcanister analyses by Quanterra:

analysis	QC lot	spike	result		recovery	
date	#	ppb	DCS1	DCS2	DCS1	DCS2
6/11/97	06 NOV 97-C1	8.97	8.68	8.98	97	100
10/11/97	10 NOV 97-C1	8.97	9.28	9.10	103	101
11/11/97	11 NOV 97-C1	8.97	9.44	9.34	105	104
2/18/98	18 FEB 98-B1	44.8	49.2	50.0	110	112
2/19/98	19 FEB 98-B1	44.8	49.5	50.8	110	113
2/20/98	20 FEB 98-B1	44.8	48.1	49.1	107	110
2/21/98	21 FEB 98-B1	44.8	48.8	46.1	109	103
4/17/98	17 APR 98-B1	44.8	52.2	49.5	117	110

G) Raw Data for the field comparisons

summa	charcoal	ratio	test id
28	17	0.60714	0
180	173	0.96111	0
220	47	0.21364	0
290	158	0.54483	0
350	120	0.34286	0
390	223	0.57179	0
480	453	0.94375	0
490	384	0.78367	0
11	17	1.54545	1
44	34	0.77273	1
83	9	0.10843	1
110	47	0.42727	1
110	69	0.62727	1
390	248	0.6359	1
470	236	0.50213	1
520	19	0.03654	1
7	7	1	2
9	5	0.55556	2
17	11	0.64706	2
44	38	0.86364	2
80	60	0.75	2
93	72	0.77419	2
286	226	0.79021	2
632	337	0.53323	2
867	738	0.85121	2
945	966	1.02222	2
1120	922	0.82321	2
1190	894	0.75126	2
16	15	0.9375	3
18	26	1.44444	3
25	22	0.88	3
26	71	2.73077	3
29	23	0.7931	3
33	28	0.84848	3
41	38	0.92683	3
49	43	0.87755	3
73	97	1.32877	3
110	90	0.81818	3
110	113	1.02727	3
120	96	0.8	3
120	69	0.575	3
130	101	0.77692	3
130	130	1	3
130	118	0.90769	3

SUMMA	Charcoal	Ratio	Test ID
130	85	0.65385	3
140	133	0.95	3
160	98	0.6125	3
170	160	0.94118	3
190	201	1.05789	3
210	162	0.77143	3
230	226	0.98261	3
310	190	0.6129	3
330	294	0.89091	3
350	218	0.62286	3
370	353	0.95405	3
370	261	0.70541	3
390	415	1.0641	3
430	514	1.19535	3
490	326	0.66531	3
610	624	1.02295	3
610	441	0.72295	3
650	495	0.76154	3
28	24.5	0.875	4
17	18.7	1.1	4
46	34.8	0.75652	4
14	12	0.85714	4
13	12	0.92308	4
10	13.4	1.34	4
36	31.7	0.88056	4
20	20	1	4

H) Statistical analysis procedures

Three separate sets of statistical analyses were performed: 1) storage stability analysis; 2) three factor analysis of variance with the factors of method, concentration, and humidity; 3) regression analysis on air concentrations collected in the field by collocated charcoal tube and SUMMA canister samplers. Each analysis will be discussed below. All statistical analysis was conducted using MINITAB 12 statistical software (MINITAB, 1998) .

1) Storage stability analysis. This analysis consists of three sequential analyses. The experiment was designed to produce duplicate tubes that were subsequently held for various lengths of time but extracted seven days apart.

The first statistical analysis was performed on the difference in recovery between the initial tube and its duplicate tube held seven days longer. A balanced two factor analysis of variance was used to tests whether there was a significant effect of either MeBr concentration or humidity on the difference in recovery. Both factors were considered as random effects and Adjusted Sum of Squares (Type III SS) were used to perform the F-tests. When the ANOVA is balanced, the SS are identical for Type I, Type II and Type III SS. However, the designation of the factors as random effects requires that the two-way interaction be used to perform the F-tests on the main effects in the ANOVA.

The second statistical analysis was a linear regression expressing percent recovery as a function of days in storage for each of the four combinations of concentration and humidity. The slope of the regression function characterizes the change (if any) of recovery with days of storage. The third analysis was a balanced, two-factor ANOVA on percent recovery with the factors of concentration and humidity. Both concentration and humidity were designated as random effects, therefore, the F-test for the main effects employed the two-way interaction mean square as the denominator.

2) Three factor, mixed effects analysis of variance with the factors of method, concentration, and humidity. Mixed models are potentially affected by deviations from assumptions of ANOVA, specifically the assumptions of normality and homogeneity of variance. Therefore the Ryan-Joiner test for normality (similar to the Shapiro-Wilks test) and Bartlett’s test for homogeneity of variance were employed before the ANOVA was performed. The concentration/humidity matrix data from the two methods (charcoal tube and SUMMA canister) was analyzed according to the experimental design of a three-factor ANOVA. In this design, method is designated as a fixed effect because interest is specifically in the recovery obtained using each of these two methods. Concentration and humidity are both designated as random effects because the interest is in the recoveries characteristic of each method at the levels of concentrations and humidity potentially measured in the field. These considerations require the used of a mixed-model ANOVA. The unrestricted form of the mixed-model is used. In addition, the design is slightly unbalanced due to one missing cell. However, this degree of unbalance is not likely to substantially effect the results (Milliken and Johnson, 1984).

Because this ANOVA is a three-way mixed model, there are some hypotheses that will have no exact- F test. In these cases the Pseudo-F tests will be employed (Hicks, 1984; Bennett and Franklin, 1954). A Pseudo-F test is constructed using the Expected Mean Squares (EMS) to obtain the F tests for the factor of interest as the numerator and a linear combination of the appropriate error terms, according to the hypothesis, as the denominator. The appropriate denominator is the linear combination of EMS producing an F test that results in a ratio isolating the factor of interest in the numerator. A table of the EMS and the Pseudo-F tests for this ANOVA is shown below (Tables H1 and H2). These Pseudo-F tests do not have exact degrees of freedom. An equivalent number of degrees of freedom, based upon the linear combination of EMS, must be found according to a procedure developed by Satterthwaite (1946). The process for obtaining the approximate degrees of freedom for each Pseudo-F tests is shown in Formula H1.

3) Regression analysis on air concentrations collected in the field by collocated charcoal tube and SUMMA canister samplers. Simple linear regression was performed on data collected from field monitoring studies where charcoal tube and SUMMA samples were collected side-by-side. The regression models fit express the charcoal tube concentration measured in the field (ppb) as a function of the SUMMA canister concentration (ppb) measured at the collocated sampler. All regression models were tested for violations of assumptions of linear regression. Transformations to logarithmic scale were performed when necessary.

Unbalanced, Unrestricted, Three-Way Mixed Model

Table H1: Expected Mean Squares (EMS)

Source	EMS
1 Method	$s_e^2 + 2.92s^2_{mhc} + 8.76s^2_{mh} + 8.76s^2_{mc} + f_m$
2 Concentration	$s_e^2 + 2.92s^2_{mhc} + 5.84s^2_{ch} + 8.76s^2_{mc} + 17.53s^2_c$
3 Humidity	$s_e^2 + 2.92s^2_{mhc} + 5.84s^2_{ch} + 8.76s^2_{mh} + 17.53s^2_h$
4 MethodxConcentration	$s_e^2 + 2.92s^2_{mhc} + 8.76s^2_{mc}$
5 MethodxHumidity	$s_e^2 + 2.92s^2_{mhc} + 8.76s^2_{mh}$
6 ConcentrationxHumidity	$s_e^2 + 2.92s^2_{mhc} + 5.84s^2_{ch}$
7 MethodxConc.xHum	$s_e^2 + 2.92s^2_{mhc}$
8 Error	s_e^2

Table H2: Derivation of Pseudo-F tests using linear combinations of MS from Table H1 (above) as shown

Source	Error DF†	Error MS	Synthesis of Error MS
Method	3.28	338.9	0.999*(4) + 0.999*(5) - 0.998*(7) - 0.001*(8)
Concentration	1.62	174.01	(4) + 0.999*(6) - 0.999*(7)
Humidity	1.60	163.73	(5) + 0/999*(6) - 0.999*(7)
Method*Conc.	4.02	33.92	0.999*(7) + 0.0013*(8)
Method*Hum.	4.02	33.92	0.999*(7) + 0.0013*(8)
Conc.*Hum.	4.00	33.89	(7)
Meth*Conc*Hum	35.00	59.99	(8)

Formula H1: Satterthwaite's Degrees of Freedom:

$$Error\ DF\ \ '\ \ v\ \ '\ \ \frac{(MS)^2}{a_1^2\ [\,(MS)_1^2/v_1\,]\ \%\ a_2^2\ [\,(MS)_2^2/v_2\,]\ \%\ \ldots\ldots\ \%}$$

Appendix I

The Determination of Volatile Organic Compounds (VOCs) in Ambient Air by GC/MS - Scan Mode

I. Method

A. Source

"EPA Compendium Method TO-14. The Determination of Volatile Organic Compounds (VOCs) in Ambient Air using SUMMA Passivated Canister Sampling and Gas Chromatographic Analysis."

B. Description

An air sample is metered through a mass flow controller onto a cryogenically cooled trap. After an aliquot of the internal standard and aliquot of the sample has been trapped, a valve is switched and the trap is heated to purge the trap's contents onto the gas chromatography column. The target compounds are analyzed with a mass spectrometer operated in the Scan mode.

C. Deviation from Source Method

TO-14 recommends the use of a .32 mm column couple directly to the MSD. With the HP system, the MSD can only handle flow of the 1 ml/min or less. The .32 mm column provides ~ 3 ml/minute. Quanterra uses a .53 mm column through a jet separator.

TO-14 describes an inlet system that uses a vacuum to pull a slip stream sample through the trap. Quanterra uses the pressure of the sample canister to drive the sample through the trap. If the sample is in a Tedlar bag, the sample is pulled through the trap with a vacuum pump.

II. Analytes and Reporting Limits

Compounds		Reporting Limits ppb (vol/vol)
Dichlorodifluoromethane	Freon 12	2.0
Chloromethane		4.0
1,2,-Dichloro-1,1,2,2-Tetrafluoroethane	Freon 114	2.0
Vinyl Chloride		2.0
Bromomethane		2.0
Chloroethane		4.0
Trichlorofluormethane	Freon 11	2.0
1,1-Dichloroethene		2.0
Carbon Disulfide		10
1,1,2-Trichloro-1,2,2-Trifluoroethane	Freon 113	2.0
Acetone		10
Methylene Chloride		2.0
trans-1,2-Dichloroethene		2.0
1,1-Dichloroethane		2.0
Vinyl Acetate		10
cis-1,2-Dichloroethene		2.0
2-Butanone		10
Chloroform		2.0
1,1,1,-Trichloroethane		2.0
Carbon Tetrachloride		2.0
Benzene		2.0
1,2-Dichloroethane		2.0
Trichloroethene		2.0
1,2-Dichloropropene		2.0
Bromodichloromethane		2.0
cis-1,3-Dichloropropene		2.0
4-Methyl-2-Pentanone		10
Toluene		2.0
trans-1,3-Dichloropropene		2.0
1,1,2-Trichloroethene		2.0
Tetrachloroethene		2.0
2-Hexanone		30
Dibromochloromethane		2.0
1,2-Dibromoethane		2.0
Chlorobenzene		2.0
Ethylbenzene		2.0
Total Xylenes		2.0
Styrene		2.0
Bromoform		2.0
1,1,2,2-Tetrachloroethane		2.0
Benzyl Chloride		10
4-Ethyl Toluene		2.0
1,3,5-Trimethylbenzene		2.0
1,2,4-Trimethylbenzene		2.0
1,3-Dichlorobenzene		2.0
1,4-Dichlorobenzene		2.0
1,2-Dichlorobenzene		2.0
1,2,4-Trichlorobenzene		20
Hexachlorobutadiene		4.0

III. Equipment

A. Gas chromatograph - capable of subambient temperature programming for the oven and with the jet separator option (Hewlett Packard 5890).

B. Mass-selective detector - equipped with computer and appropriate software (Hewlett Packard 5970B with HP-1000 RTE-A data system and Hewlett Packard 5972, windows based chemstation with enviroquant).

C. Cryogenic trap with temperature control assembly (Nutech 8533, Entech 2000).

IV. QA/QC Requirements

A. An initial calibration curve consisting of a system blank and a minimum five (5) standards is run in the linear working range of the instrument. The lowest calibration standard level is at or near the reporting limit for each analyte of interest.

B. Each 12 hour shift, the mass spectrometer must meet the tuning criteria described in Table 4 of EPA Compendium Method TO-14.

C. After tuning, a single point check standard must be analyzed. Ninety percent of the target compound response factors must be within 30% of the five point calibration curve average response factors. If the check standard fails to meet this criterion, a new five point calibration curve must be run. This daily one point check standard response factors are used to quantitate the results of the samples for that shift.

D. A laboratory control sample (LCS) must be analyzed after the check standard. This sample will onsist of the target VOCs prepared in a separate canister at a concentration that differs from that of the check standard. Five compounds will be used to assess control for the LCS: methylene chloride, 1,1-dichloroethene, trichloroethene, toluene and 1,1,2,2-tetrachloroethane. The percent recovery for the five control compounds must be within a window established using historical lab data.

E. For each lot of 20 samples analyzed, a duplicate control sample (DCS) must be analyzed after the LCS. The DCS sample is identical to the LCS in composition and source. The recovery criterion must be met. In addition, the relative percent difference (RPD) for the LCS and DCS must be < 20% or a value established using historical lab data.

F. A system blank of HC free air must be analyzed after the LCS or DCS. The blank results must indicate that there are no target compounds present above the target compounds reporting limits.

SUMMARY OF CALIBRATION PROCEDURES

Method	Parameter	QC Performed	Frequency	Acceptance Criteria	Corrective Action
TO-14 (GC/MS)	Volatile Organics	Check of instrument tuning criteria using BFB	Every 12 hours	Refer to SOP	1) Retune instrument. 2) Repeat BFB analysis
		Multipoint calibration (minimum 5 points)	Initially and as required	90% of target compounds less than or equal to 30% RSD. Min RF = 0.05	1) Evaluate system 2) Recalibrate as necessary 3) Reprepare standards
		Continuing calibration check standard	Every 12 hours	90% of target compounds less than or equal to 30% Diff; Min RF = 0.05	1) Evaluate system 2) Repeat calibration check 3) Recalibrate as necessary 4) Reprepare standards
		Humid N_2 blank	Daily after standard or LCS/LCSD analyses	< RL of target analytes	1) Run system blank 2) Reanalyze air blank 3) Clean system and repeat

SUMMARY OF INTERNAL QUALITY CONTROL PROCEDURES

Method	Parameter	QC Performed	Frequency	Acceptance Criteria	Corrective Action
TO-14 (GC/MS)	Volatile Organics	Method blank (Humid N_2 blank)	1 per 20 samples	All target analytes < RL	1) Run system blank 2) Reanalyze method blank
		System blank	As required	All target analytes < RL	1) Run until system is clean
		LCS/LCD pair	5%	Refer to SOP	1) Evaluate system to ensure proper performance 2) Reanalyze LCS 3) Assess impact on data
		Internal Standards	Every sample	Between 50% and 200% of the continuing calibration internal standard pack area	1) Evaluate system 2) Check areas in QC samples 3) Note in narrative

BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15% to 40% of mass 95
75	30% to 60% of mass 95
95	Base peak, 100% relative abundance
96	5% to 9% of mass 95
173	< 2% of mass 174
174	> 50% of mass 95
175	5% to 9% of mass 174
176	> 95% but < 101% of mass 174
177	5% to 9% of mass 176

CONTROL LIMITS FOR LABORATORY CONTROL SAMPLES AND LABORATORY CONTROL SAMPLE DUPLICATES FOR GASES

			Laboratory-Established Control Limits	
Analytical Method	Spiking Compounds	Nominal Spike Concentrations	Percent Recovery	Relative Percent Difference
Volatile Organic Compounds TO-14	Methylene Chloride	50 ppb	80 - 120	20
	1,1-dichloroethene	50 ppb	70 - 120	20
	Trichloroethene	50 ppb	80 - 120	20
	Toluene	50 ppb	70 - 120	20
	1,1,2,2-tetrachloroethane	50 ppb	60 - 130	20

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APPENDIX J

California Dept. of Food and Agriculture
Center for Analytical Chemistry
Environmental Monitoring Section
3292 Meadowview Road
Sacramento, CA. 95832
(916) 262-2080 Fax (916) 262-1572

Method #: 39.0
Original Date: 07/30/79
Revised: 03/10/97
Page 1 of 5

Determination of Methyl Bromide Desorbed from Charcoal Tubes

Scope: This method describes the desorption and determination of methyl bromide from charcoal air sample tubes. It is intended solely for the use by the California Department of Food and Agriculture, Chemistry Laboratory Services.

Principle: Methyl bromide (MeBr) in the air that has been absorbed onto activated charcoal is desorbed from the charcoal with ethyl acetate. Subsequently, MeBr is quantified using a gas chromatograph equipped with a HP-5 megabore capillary column and an electron capture detector (ECD).

Reagents, Equipment and Instrument:

Reagents:

1. Ethyl acetate, Fisher, pesticide grade
2. Methyl bromide, analytical grade
3. Charcoal tubes - SKC #226-38-02 SKC West: phone (714) 992-2780

Equipment:

1. Test tubes, 25 mL, with teflon-liner caps
2. Assorted pipettes and micro-syringes
3. Volumetric flasks, 100 mL
4. Small triangular file
5. Thermolyne Vortex Maxi Mixer II
6. Forceps
7. Glass syringe, 5 mL
8. Nylon Acrodisc®, 0.2 µm, Gelman.
9. Airchek Sampler, Model 224-PCXR7, with a flow about 15 mL/min

Reagents, Equipment and Instrument: continued

Instrument:

Hewlett Packard 5890 Series II Gas Chromatagraph with autosampler and equipped with an electron capture detector.

Analysis:

Sample Extraction:

1. Remove samples from frozen storage. Allow samples to stand at room temperature for 20-30 minutes before starting extraction of methyl bromide.
2. Fold a sheet of white paper into quarters, reopen and place under the test tube to catch spills.
3. Pipette a known volume of ethyl acetate into a labeled test tube. A volume of 10 mL for tube A and 5 mL for tube B is suggested.
4. Remove caps from a charcoal sample tube. Score the tube with a file just above the spring wire and break the glass tube.
5. With a forceps, immediately remove the spring wire only and place it in the test tube.
6. Placing the large broken end of the charcoal tube in the mouth of the test tube containing a known volume of ethyl acetate, insert a Pasteur pipette from the opposite end and push the glass wool and charcoal into the test tube. Immediately cap the test tube.
7. Extract MeBr from charcoal by mixing for 30 seconds using a vortex mixer.
8. Allow the mixture to stand for 3-5 minutes. Filter 1.5 -2 mL of the mixture through a Nylon Acrodisc and collect the solution in an autosampler vial. Store the remaining sample in a freezer.
9. Determine methyl bromide using a glc method.
10. If the peak height of the sample is greater than that of the highest standard, dilute the extract and rerun the standards and the filtered dilute extract.
11. Blank. Score a charcoal tube (A) with a file just above the spring wire and break the glass tube. Next score the tip of the opposite end of the same tube and break the tube at the end.
12. Follow steps 5-9 above.

Analysis:

Sample Extraction: continued

13. Spike. Turn the Airchek Sampler to ON. Score a charcoal tube (A) with a file in a similar manner as the Blank. Place the broken tip of the charcoal tube onto the Airchek Sampler. Place a micro-syringe needle about 1 cm below the glass wool and slowly add a known amount of methyl bromide onto the charcoal.

14. After 10-20 seconds, follow steps 5-9 above.

Instrument Conditions:

Hewlett Packard 5890 Series II GC equipped with ECD
Column: HP-5 (5% phenyl-methyl polysiloxane) 30 m x 0.537 mm x 2.65 µm
Carrier gas: helium; Flow rate: 17 mL / minute
Injector: 220 °C splitless
Detector: 320 °C
Septum purge: 2 mL / minute
Temperature Program: Initial Temp: 50 °C held for 2 minutes
Rate: 70 °C / minute
Final Temp: 210 °C held for 0.5 minute
Injection volume: 3 uL
Retention time of MeBr: 1.1 ± 0.1 minute

Calculations:

Calculate the amount of MeBr present in a charcoal sample tube as follows:

1) without dilution

$$\mu g\ \mathbf{MeBr} = \frac{(\text{peak ht sample})\ (\eta g \text{ std injected})\ (\text{sample final volume, mL})}{(\text{peak ht standard})\ (\mu L \text{ injected})}$$

2) with dilution

$$\mu g\ \mathbf{MeBr} = \frac{(\text{peak ht sample})\ (\eta g \text{ std injected})\ (\text{sample final volume,mL})}{(\text{peak ht standard})\ (\mu L \text{ injected})} \text{ x dilution factor}$$

Method Performance:

Minimum Detection Limit:

The minimum detectable level was 0. 2 µg at a S/N = 4.

Validation:

Charcoal tubes were spiked at two levels of MeBr, 1 and 20 µg. Spiked samples were extracted with ethyl acetate and the amount of MeBr in the extract was subsequently determined.

Recoveries of methyl bromide are:

Spike levels	% Recovery	Ave	SD	CV
1 µg	86.2	85.7	3.83	4.47
	89.2			
	81.6			
20 µg	82.2	83.9	1.99	2.38
	83.2			
	86.1			

Discussion:

High humidity may affect trapping efficiency. When the amount of water in the air is so large that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Experiments using toluene indicate that high humidity severely decreases the breakthrough volume (2).

Check each bottle of ethyl acetate on the GC for any interfering peaks before using for extracting samples. Any bottle of ethyl acetate found to contain interfering peaks is unsuitable for use in this work.

Methyl bromide is highly volatile. Consequently on extraction of MeBr, test tubes must be tightly capped. **Do Not Use Caps Without A Teflon Liner**.

Each analytical run contained standards ranging from approximately 0.04 to 2 µg/mL (eg.04,0.08, 0.16, 0.32, 0.64 and 1.2 µg/mL). This range of 5-6 standards was run after every ten samples

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UPDATED BY: Robert B. Lew

Robert B. Lew

TITLE: Agricultural Chemist I

ADAPTED BY: Paul Lee

TITLE: Agricultural Chemist III

APPROVED BY: Catherine Cooper

Catherine Cooper

TITLE: Agricultural Chemist III, Supervisor