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# Enhancement of electron-capture detection of methyl bromide in air by iodination

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## Abstract

An instrumentally simple and cost-effective method for the direct analysis of methyl bromide in ambient air is described. The method is based on the separation of sample components by gas chromatography, the conversion of methyl bromide to methyl iodide by reaction with an inorganic iodide salt, and the detection of the methyl iodide thereby produced by an electron-capture detector. Of the 20 different inorganic salts investigated here for conversion of methyl bromide to methyl iodide, zinc iodide was found to provide the greatest conversion efficiency. In addition, zinc iodide was found to provide high conversion efficiency at a modest reaction temperature, thereby minimizing both the thermal decomposition of compounds within the reaction volume and the level of column bleed introduced to the detector. The reactions of several other brominated and chlorinated organic compounds with zinc iodide have also been characterized. The successful application of this instrument to the quantitative determination of methyl bromide in a local background air sample is then demonstrated.  © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

In studies of the depletion of stratospheric ozone by chlorine- and bromine-containing compounds, methyl bromide has been identified as a particularly important compound [1]. This is because the ozone depletion potential of bromine atoms once carried to the stratosphere is significantly greater than that of chlorine atoms [2–4] and because methyl bromide is thought to be the main carrier of bromine atoms to the stratosphere [5–7]. The atmospheric presence and chemistry of methyl bromide is made additionally interesting and complex by the fact that this compound is known to have several natural and anthropogenic sources and several natural sinks [1,8,9]. It is unfortunate, therefore, that quantitative determinations of methyl bromide concentration at points throughout Earth's atmosphere have proven to be more difficult to obtain than those of many of the other known ozone-depleting halogenated compounds. One reason for these analysis difficulties is that the concentration of methyl bromide in the background atmosphere is relatively low; its average global mixing ratio is thought [1,8,9] to be only about 10 parts per trillion by volume (pptv). Another reason is that electron-capture detection (ECD), which provides an extremely sensitive and cost-effective method for the detection of many atmospheric halocarbons, offers only a modest level of

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sensitivity for the detection of methyl bromide. This is due to the fact that the electron-capture rate constant for methyl bromide is more than two-orders of magnitude lower than those of strongly-responding atmospheric halocarbons [10]. While some improvement in ECD sensitivity to methyl bromide has been demonstrated by use of oxygen-sensitization [11,12], the magnitude of that improvement is not large. For these reasons, perhaps the majority of studies concerning methyl bromide's presence in air [7,9,13] have utilized mass spectrometry (MS) along with gas chromatography (GC) for their analyses, rather than ECD [8,12]. Due to the relatively high cost, complexity, and physical size of mass spectrometers, however, this approach generally requires the collection and transport of an air sample from the sampling point of interest to the facility in which the mass spectrometer is housed. This approach is not only costly in terms of time and equipment, but is also subject to errors caused by the absorption of methyl bromide onto the walls of the air-sampling container. In order to facilitate future characterizations of methyl bromide presence throughout the Earth's atmosphere, an instrumentally simple and cost-effective method that can be applied to the direct and continuous analysis of air at any sampling point of interest is clearly needed. In the present study, a means by which this goal can be achieved is described.

The method that has been developed here is an extension of a GC–ECD-based method previously developed by Watson et al. [14] for the detection of methyl chloride in air. By their method, approximately 80% of the methyl chloride within an air sample was converted to methyl iodide by passage through a ''conversion tube'' containing sodium iodide at a temperature of 350°C. The methyl iodide thereby produced was then detected by ECD. In the present study, the conversion of methyl bromide to methyl iodide is shown to be much more efficiently accomplished when zinc iodide rather than sodium iodide is used and, furthermore, it is shown that this conversion can be efficiently accomplished at a temperature of only 150°C. A lower reaction temperature is advantageous in this application for two reasons. It greatly decreases the possibility that the reaction product, methyl iodide, will be thermally degraded within the conversion tube [15] and it imparts a lower level of background noise to an ECD system that is placed downstream from the conversion tube. We also report here the fate of other brominated and chlorinated compounds upon their passage through the zinc iodide conversion tube. A successful analysis of methyl bromide within a local background air sample by this instrumental configuration is then demonstrated.

## 2. Experimental

### 2.1. Instrumental configuration 1

A schematic diagram of the general experimental setup used for all experiments reported here is shown in Fig. 1. For preliminary testing of the method, gaseous standards prepared in nitrogen gas were introduced to a 2-ml stainless steel sample loop (1/8 in. O.D.; 1 in.=2.54 cm) at atmospheric pressure with a 250-ml glass syringe. By rotation of the six-port valve (Carle Instruments) indicated as valve A, the contents of the sample loop were then passed into gas chromatographic column A by the nitrogen carrier gas that was set to a flow-rate of 40 ml min$^{-1}$. For the preliminary testing of standards, column A was a laboratory-made stainless steel column of 3 m×1/8 in. O.D. that was packed with
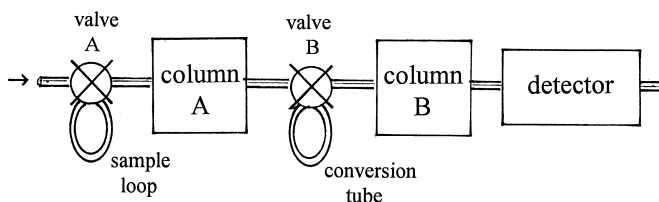


Fig. 1. Generalized schematic diagram of apparatus used both for the initial testing of the conversion tube and for the analysis of methyl bromide in air samples. Details concerning each component used for instrumental configurations 1 and 2 are provided in Experimental.

10% SF96 on Chromosorb W (Alltech). This column was maintained at a constant temperature between 30 and 50°C. After passing through column A, the carrier gas could be made to pass either directly to column B or through the conversion tube and then to column B by appropriate setting of a second six-port valve, labeled valve B. The conversion tube consisted of stainless steel tubing of 6 in.×1/4 in. O.D. It was filled with a mixture of an inorganic iodide salt (usually zinc iodide) and an inert column support material, Chromosorb W (Alltech, 60–80 mesh size). This mixture was made by grinding the inorganic iodide with a mortar and pestle and then combining it with an equal volume of column support material. The support material was included in order to ensure that the carrier gas stream passed freely though the conversion tube. The ends of the conversion tube were plugged with glass wool. The conversion tube was typically maintained at a temperature of 150°C with a heating tape. For the preliminary testing of prepared standards, column B was identical to column A and was maintained at the same temperature. Finally, the effluent from column B was passed into the detector. In the preliminary testing of standards, a flame ionization detector, rather than an electron-capture detector, was used.

### 2.2. Instrument configuration 2

For the analysis of real air samples, several changes were made in the general components indicated in Fig. 1. The volume of the sample loop was increased to 100 ml by use of a longer 1/4 in. O.D. stainless steel tube. A drying tube was inserted between the sampling loop and column A. This tube consisted of 1/4-in. O.D. stainless steel packed with anhydrous magnesium perchlorate (Fisher Scientific). Column A was changed to a GS-Q capillary porous-layer open tubular (PLOT) column (J&W Scientific) of 30 m×0.53 mm I.D. The temperature of the oven that housed column A was programmed. In the analysis of air samples, valve B was set to bypass the conversion tube until all of the oxygen introduced with the air sample had passed through the detector at $t=5$ min. If this precaution was not taken, the conversion tube then emitted an electron-capture-active substance (probably iodine vapor) that significantly elevated the baseline response and back-

ground noise level of the ECD system for several hours after each analysis.

For the analysis of real air samples, satisfactory results could be obtained by the complete elimination of column B. However, it was also noted that the detector baseline was improved somewhat if a short column B was used in order to protect the ECD system from a small amount of an electron-capturing substance that was continuously emitted from the conversion tube. This function was well-served here by a 1.0 m packed column of the type described above for the testing of gaseous standards. For the analysis of real air samples, the detector was changed to an ECD system (Hewlett-Packard, Model 5890). The carrier gas flowing through the total system shown in Fig. 1 was nitrogen and was set at an initial flow-rate of 38 ml min$^{-1}$ (as the temperature of column A is increased, the flow-rate decreases somewhat). No additional detector makeup gas was required. The supply of carrier gas was first passed through oxygen- and water-removing traps (Alltech).

## 3. Results and discussion

### 3.1. Characterization of conversion tube

In order to determine the most efficient means of converting methyl bromide to methyl iodide, a variety of different iodide salts were first tested for use in the conversion tube using instrumental configuration 1 described in Experimental. With this configuration the flame ionization detector provided a similar level of sensitivity to all compounds of interest and thereby simplified the detection of reaction products and the determination of conversion efficiencies. An illustration of these experiments is provided in Fig. 2 for the reaction of methyl bromide in a conversion tube containing zinc iodide. In chromatogram A the temperature of the conversion tube was set to a relatively low value of 50°C. At this temperature most of the methyl bromide survives passage through the conversion tube and is observed at its retention time of about 225 s. Even at this low temperature, however, a small amount of methyl iodide is produced within the conversion tube, is separated from the unreacted methyl bromide
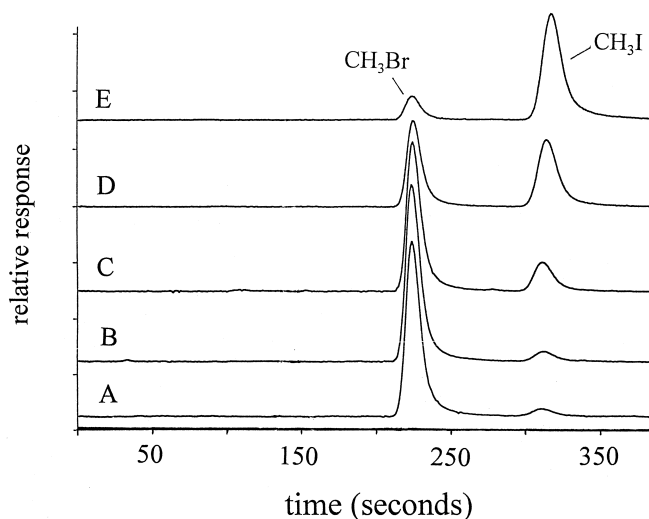
Fig. 2. Chromatograms obtained using instrumental configuration 1 with zinc iodide in the conversion tube for a 10-ppmv sample of methyl bromide in nitrogen gas. Conversion tube temperatures are: (A) 50, (B) 75, (C) 100, (D) 125 and (E) 150°C.

in column B and is detected at a total system retention time of about 310 s. As the temperature of the conversion tube is increased in chromatograms B–E, the efficiencies of methyl bromide conversion to methyl iodide is continuously increased to a maximum value of about 83% at the highest temperature, 150°C. In numerous repetitions of the experiment shown in chromatogram E, the reproducibility of the measured of conversion efficiency was very good (within ±2%) and did not significantly change with large changes in amount of methyl bromide introduced to the conversion tube [in these preliminary experiments, calibration standards varied in concentration from 1 to 100 parts per million by volume (ppmv)].

In addition to zinc iodide, numerous other inorganic iodides were also tested for use in the conversion of methyl bromide to methyl iodide. The conversion efficiencies observed for these inorganic iodides at a conversion tube temperature of 150°C are listed in Table 1. While $ZnI_2$ was found to be most effective, several other inorganic iodides, including LiI, $MgI_2$ and $NiI_2$, also provided conversion efficiencies of greater than 50%. It is interesting to note that NaI, which was used by Watson et al. [14] for the conversion of methyl chloride to methyl iodide, provided an efficiency of only 11% for conversion of methyl bromide to methyl iodide at

150°C. For this reason, we also determined the efficiency of conversion of methyl chloride to methyl iodide by use of NaI and $ZnI_2$ at 150°C and found these to be 1% and 23%, respectively. Therefore, it appears that the present approach using $ZnI_2$ might

Table 1
Efficiencies of methyl bromide to methyl iodide conversion observed with use of instrumental configuration 1 and various inorganic iodides within the conversion tube at 150°C

| Inorganic iodide | Conversion efficiency (%) |
|---|---|
| $ZnI_2$ | 83 |
| LiI | 80 |
| $MgI_2$ | 67 |
| $NiI_2$ | 53 |
| $CoI_2$ | 31 |
| $MnI_2$ | 31 |
| $PbI_2$ | 29 |
| AgI | 20 |
| $CuI_2$ | 17 |
| $BaI_2$ | 15 |
| CsI | 15 |
| RbI | 12 |
| NaI | 11 |
| KI | 9 |
| $SrI_2$ | 7 |
| $CdI_2$ | 5 |
| $BiI_3$ | 4 |
| $NH_4I$ | 0 |
| $SnI_2$ | 0 |
| $SnI_4$ | 0 |

also provide an excellent means of determining methyl chloride in air.

## 3.2. Effect of conversion tube on other halogenated compounds

In assessing the utility of the present method for real air analysis, it is of interest to consider what would happen to other classes of halogenated compounds that might also be present in an air sample as they are passed through the conversion tube. For this reason, the efficiencies of conversion for the additional compounds listed in Table 2 were also determined. The percentage of the reactant compound destroyed (obtained by a comparison of responses observed with and without inclusion of the conver-sion tube) is indicated in the first column. In the second column the corresponding percentage yield of the iodinated substitution product is indicated. For those cases where the amount of iodinated product was found to be less than the amount of reactant lost, an addition reaction product or two were also detected in the chromatograms at a retention time(s) less than that of the reactant compound. This additional product(s) was assumed to be an alkene in which one or two halogen atoms had been eliminated from the reactant molecule.

In assessing the information provided in Table 2, it is clear that primary alkyl bromides, as well as methyl and ethyl chloride, tend to be converted to the corresponding alkyl iodides by the zinc iodide conversion tube at 150°C. It is also noted that

Table 2
Extent of reaction and product distributions for reactions of various halogenated compounds with zinc iodide in the conversion tube at 150°C

| Compound | Amount reacted (%) | Iodo product (%) |
|---|---|---|
| $CH_3Br$ | 82 | 82 |
| $CH_3CH_2Br$ | 64 | 64 |
| $CH_3CH_2CH_2Br$ | 82 | 82 |
| $CH_3CH(CH_3)CH_2Br$ | 72 | 21 |
| $CH_3CHBrCH_3$ | 100 | 7 |
| $CH_3CHBrCH_2CH_3$ | 100 | 1 |
| $CH_2Br_2$ | 0 | 0 |
| $CH_2BrCH_2Br$ | 21 | 0 |
| $CH_2BrCH_2CH_2Br$ | 53 | 28 |
| $CH_3CBr_2CH_3$ | 100 | 0 |
| $CH_3Cl$ | 23 | 23 |
| $CH_3CH_2Cl$ | 7 | 7 |
| $CH_2=CHCl$ | 0 | 0 |
| $CH_3CH_2CH_2Cl$ | 0 | 0 |
| $CH_3CHClCH_3$ | 74 | 60 |
| $CH_2=CClCH_2CH_2CH_3$ | 0 | 0 |
| $CH_3CHClCH_2CH_3$ | 99 | 3 |
| $CH_3CCl(CH_3)CH_3$ | 100 | 0 |
| $CHCl_3$ | 0 | 0 |
| $CCl_4$ | 0 | 0 |
| $CH_3CHCl_2$ | 0 | 0 |
| $CH_3CCl_3$ | 28 | 5 |
| $CHClBr_2$ | 0 | 0 |
| $CH_2BrCH_2Cl$ | 6 | 0 |
| $CF_3Br$ | 0 | 0 |
| $CF_2Br_2$ | 0 | 0 |
| $CFBr_3$ | 0 | 0 |
| $CHFBr_2$ | 0 | 0 |
| $CFClBr_2$ | 0 | 0 |
| $CF_2ClBr$ | 0 | 0 |
| $CF_2Cl_2$ | 0 | 0 |
| $CFCl_3$ | 0 | 0 |

secondary alkyl bromides and chlorides are destroyed in the conversion tube even more easily than their primary analogs. These secondary halides are not quantitatively converted to the corresponding secondary alkyl iodides, however, since a significant fraction of their reaction products were smaller molecules assumed to be alkenes formed by competitive elimination reactions. Dibromomethane undergoes no reaction within the conversion tube while 1,2-dibromoethane undergoes only an elimination reaction to form ethene. With respect to the application of this conversion tube to air analysis, it is particularly important to note that all of the highly or totally halogenated methanes that are listed in the lower portion of Table 1 are not affected by passage though the conversion tube.

### 3.3. Analyses of methyl bromide in air

By alteration of the generalized instrument shown in Fig. 1 to instrumental configuration 2 described in Experimental, the methyl bromide content of air

samples could be determined. Examples of the chromatograms thereby obtained for a local background air sample are shown in Fig. 3. The first chromatogram shown in Fig. 3A was obtained with valve B positioned so that the conversion tube was bypassed at all times. At time $t=0$, valve A (see Fig. 1) was turned so that the contents of the 100-ml sample loop were passed through the drying tube and onto column A, and the following temperature program of column A was initiated: (1) hold at 24°C for 9 min (during this period, many components of the air sample, including $CH_3Br$, are transfer to and immobilized on the head of column A); (2) at $t=9$ min, increase temperature rapidly to 80°C; (3) hold temperature at 80°C until $t=15$ min (by this time, $CH_3Br$ has passed though the ECD system), (4) at $t=15$ min, increase temperature rapidly to 150°C and hold until $t=35$ min (this step serves simply to rid the column of the less volatile components of the air sample).

As seen in Fig. 3A, the ECD response is saturated for the first 5 min due to the passage of oxygen
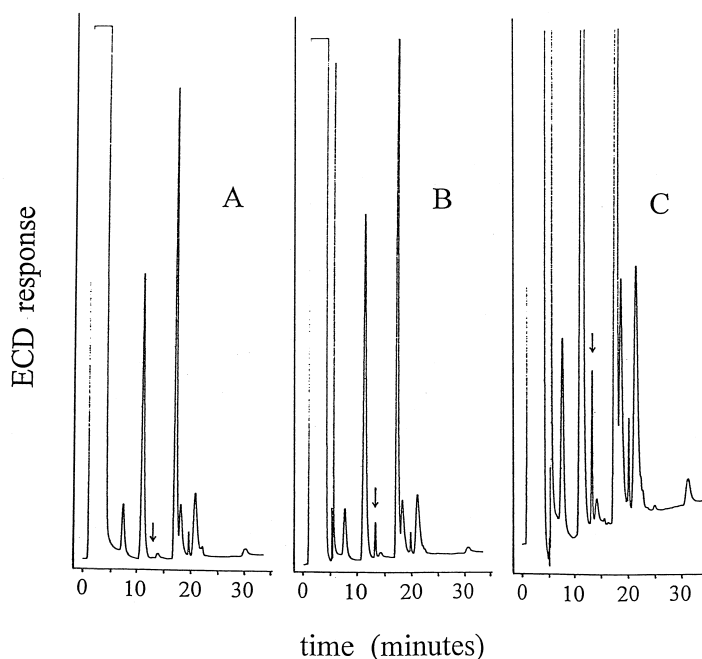


Fig. 3. Repeated analyses of a local background air sample using instrumental configuration 2 with the conversion tube bypassed (A) and with the conversion tube included (B and C) in the chromatographic flow stream. The arrows indicate the expected retention time of methyl bromide. Chromatogram C was obtained by repeating the analysis shown in chromatogram B, but with use of a 4× more sensitive recorder attenuation. The GC temperature program used is described in Section 3.3.

through the detector. At about $t=7$ min, another peak whose origin is not presently known is also observed while column A is still at room temperature. After the temperature of column A begins to increase at $t=9$ min, the transport of at least three electron-capture-active compounds to the detector is noted to occur during the time window between 10 and 15 min. The large peak observed at $t=11$ min is due primarily to $CF_2Cl_2$ which is known to have an atmospheric concentration of about 530 pptv at this time [16]. While it is known that $CH_3Cl$ also has an expected retention time of $t=11$ min and has an atmosphere presence of about 600 pptv, $CH_3Cl$ does not contribute significantly to the response observed at $t=11$ min, because the electron-capture rate constant for methyl chloride is extremely low even at the elevated detector temperature of 300°C [10]. The expected retention time of methyl bromide is 12.5 min under these conditions and is marked with an arrow. A very small peak due to electron-capture by methyl bromide is noted at this retention time. At $t=14$ min, a slightly larger peak is observed at the retention time expected for $CF_2ClBr$, a compound that is presently thought to have an atmospheric presence of about 3.5 pptv [17]. At $t=15$ min, the temperature of column A is rapidly increased to 150°C in order the rid the column of other less volatile components of the air sample. Therefore, after $t=15$ min the passage of numerous ECD-active compounds, many of which are not chromatographically resolved from each other, is noted. The first of these peaks at about $t=17$ min is thought to be due primarily to $CFCl_3$, which is known to have an atmospheric presence of about 275 pptv [16].

In Fig. 3B, the same background air sample was analyzed again in the same manner as used for Fig. 3A, except that after the passage of oxygen though the detector at $t=5$ min, valve B was turned so that the effluent from column A then passed through the conversion tube containing zinc iodide at 150°C (the disturbance noted at $t=5$ min is due to a momentary pressure surge caused by the change in valve B). From this point in time onward, only a few changes in this chromatogram compared to that shown in Fig. 3A are noted. A trivial change is that the retention times associated with all observed peaks are increased slightly (by about 20 s) by the addition of the conversion tube to the total chromatographic flow

line. Most importantly, at the expected retention time of converted methyl bromide (again indicated by an arrow), a significantly improved response is noted. This increased response is consistent with our expectation that a majority of the methyl bromide within the sample has been converted to methyl iodide by passage through the conversion tube and that the rate of electron-capture by the methyl iodide is much greater than that of methyl bromide (rate constants for electron attachment to methyl iodide and methyl bromide have been reported [10] to be $1.1 \cdot 10^{-7}$ and $2.5 \cdot 10^{-9}$ ml$^{-1}$ s$^{-1}$, respectively, at 312°C). The only other significant changes that are noted to be caused by inclusion of the conversion tube in Fig. 3B are that the magnitudes of the two large peaks in Fig. 3A at $t=11$ and 17 min have been increased somewhat in Fig. 3B. This effect on the peak at $t=11$ min was expected due to the conversion of some of the methyl chloride, which coelutes at this retention time with $CF_2Cl_2$, to methyl iodide (see Table 1). The observed increase in the peak at $t=17$ min suggests that some unknown compound also coelutes with $CFCl_3$ at $t=17$ min and that this unknown compound also undergoes some degree of iodination as it passes through the conversion tube. It is noted that the peak due to $CF_2ClBr$ at $t=14$ min in Fig. 3A is not increased in Fig. 3B, as expected (see Table 1). The chromatogram shown in Fig. 3C was obtained by repeating the analysis that lead to Fig. 3B. For Fig. 3C, however, the attenuation of the strip-chart recorder was set four-times more sensitive in order to indicate more clearly the signal-to-noise quality of the methyl bromide response, again indicated by an arrow.

Several additional experiments were performed in order to test the applicability of the present method for quantitative determinations of methyl bromide in air samples. As a test of the reproducibility of the method, a single air sample was analyzed once every hour for a period of 8 h. The relative standard deviation of the eight peak height responses thereby obtained for methyl bromide within this sample was 2%. This suggests that if an accurate methyl bromide air standard is available for calibration, the methyl bromide concentration within an unknown air sample could be determined by this method to an accuracy on the order of a few percent from single measurements of the sample and standard.

As an additional test of the present method, it was incorporated into a standard addition scheme that has been recently developed in our laboratory specifically for the quantitative determination of atmospheric halocarbons whose concentrations are exceedingly low. The standard addition sampling device is located in an open field about 10 km south of the community of Bozeman, MT, USA, and consists of a corrugated steel cylinder of 3.6 m×1.8 m diameter. A very large (9200 l) air sample was captured within this cylinder on 26 February 1998, by allowing air to pass freely through the cylinder for many hours and then capping the ends of the cylinder with two vinyl tarps. In order to verify later that the air sample thereby captured was not contaminated by its container, an additional sample of ambient air was simultaneously taken into a 2-l stainless steel air-sampling container whose interior surfaces had been pretreated by the SUMMA process. The standard addition vessel was then spiked three times with a known amount (139 ppmv in nitrogen gas) of methyl bromide using a 1-ml gas-tight syringe. After each addition, the contents of the large container were thoroughly stirred with a fan that is manually operated by a handle extending through the container

wall. Also after each addition, an air sample was taken into another 2-l air-sampling container via a side port in the standard addition vessel. After the above sequence of steps, the air samples thereby obtained were transported to our research laboratory for analysis by the new method described here. The magnitude of the responses (peak heights) thereby provided by the ECD-based method with conversion of methyl bromide to methyl iodide by zinc iodide are shown in Fig. 4. A linear response to methyl bromide is observed over the concentration range of added methyl bromide, from 0.0 to 43 pptv. By extrapolation of the least-squares line thereby formed to the origin of the y axis, the concentration of methyl bromide in the unspiked sample is deduced to be equal to 15.5 pptv with a least-square intercept uncertainty of 1.5 pptv. This results indicates that the concentration of methyl bromide in the specific sample analyzed here is about 50% greater than average global levels which have been reported to be about 10 pptv [1]. This result was expected due to two factors. Methyl bromide levels are expected to be about 35% greater in the northern hemisphere during the spring months [9] and a ground-level sample collected on the floor of the broad valley
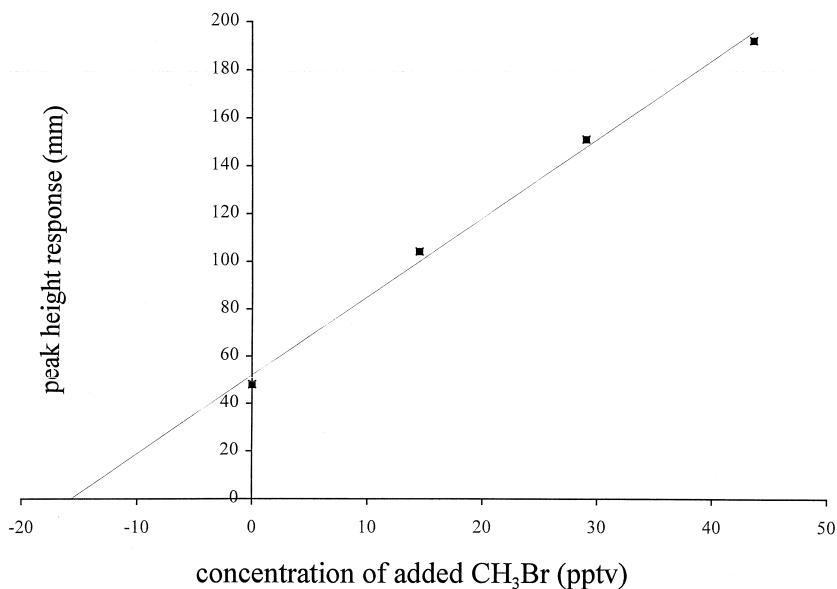


Fig. 4. ECD responses to methyl bromide in a local air sample and to the air sample after three standard additions of methyl bromide. The x-axis intercept obtained by extrapolation of the line formed by least-squares analysis of these determinations provides the concentration of methyl bromide in the original air sample.

surrounding Bozeman, might be expected to include some additional methyl bromide due to local agricultural activities.

In summary, we believe that we have demonstrated here a relatively simple instrumental means by which the methyl bromide content of background air could be continuously and directly monitored at any sampling site of interest that offers a source of electrical power and physical protection from the elements. With ongoing refinements of its chromatographic components, additional improvements in the levels of sensitivity, reproducibility and sampling frequency demonstrated here are expected.

## Acknowledgements

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