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Analysis of brominated compounds in background air by gas chromatography–high-resolution mass spectrometry

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Abstract

The application of a gas chromatography–high-resolution mass spectrometry (GC–HRMS) system to the detection and quantitative analysis of bromine-containing compounds in the Earth's atmosphere is described. By this technique, air samples are introduced to the HRMS system by GC while the HRMS system is tuned to the exact masses of the ions expected in the electron impact spectrum of each compound. By the method described here, the mass spectrometer is assured of focusing precisely on the centroid of the exact mass selected because the mass scale is continuously (two times per second) recalibrated during the chromatographic analysis using *n*-dodecane as a mass reference. By this technique, the positive identification and quantitative analysis of several brominated compounds consistently found in the background air of rural Montana is demonstrated. In addition, a large volume standard addition technique is described and shown to be well-suited to the quantitative analysis of atmospheric components that have extremely low concentrations. Most of the brominated compounds identified here are present in background air at the sub parts-per-trillion (ppt) level. One of them, CF_2Br_2 , is shown to have an atmospheric presence of only about 40 parts per quadrillion (ppq). Detection limits for all of the brominated compounds identified here were very low (in the low ppq range) and even lower detection limits could be achieved, if desired, by use of sample volumes that are larger than those routinely used here (340 cm^3). © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the last two decades, it has been shown that bromine atoms are being transported to the stratosphere by a variety of organic compounds and that these bromine atoms then contribute significantly to the destruction of stratospheric ozone [1–

12]. While the concentration of bromine in the stratosphere is about two orders of magnitude lower than that of chlorine, bromine is thought to be about 40- to 100-times more effective at destroying ozone than is chlorine [13]. Primary carriers of organic bromine in the troposphere have been shown [12] to include CF_3Br (Halon 1301), CF_2BrCl (Halon 1211), $\text{C}_2\text{F}_4\text{Br}_2$ (Halon 2402), CH_3Br , CH_2Br_2 , CHBr_3 and CH_2BrCl . Very small amounts of CF_2Br_2 (Halon 1202) have also been detected in some background air samples [14,15]. The atmospheric Halons, which are thought to have only anthro-

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pogenic sources, have relatively long atmospheric lifetimes and relatively high ozone depletion potentials [7]. While methyl bromide is known to have both natural and anthropogenic sources [9] the other hydrogen-containing brominated compounds listed above are thought to have only natural sources of significance. A detailed summary of what is currently known about the known sinks, sources, atmospheric lifetimes, ozone depletion potentials and atmospheric concentrations of most of these compounds can be found in a recent study by Schauffler et al. [12] of the transport of these compounds to the tropical tropopause. A conclusion of that study was that in order to accurately evaluate the transport of bromine to the stratosphere, the concentrations of the individual bromine-containing compounds should be determined in the regions and time intervals of interest.

The methods that have been most widely used for the trace analysis of brominated compounds in the atmosphere have been based on the separation of sample components by gas chromatography (GC) along with selective detection by either electron-capture detection (ECD) or mass spectrometry (MS). In a recent report from our laboratory [16] an analysis system based on GC detection by high-resolution mass spectrometry (HRMS) was also described. While mass spectrometers capable of high mass resolution have been applied to the detection of trace atmospheric halocarbons [17–20] a unique feature of the present system is that the mass calibration scale is continuously recalibrated (two times per second) during the analysis. This additional feature of the measurement ensures that the exact mass selected for observation coincides precisely with the mass centroid of the ion of interest no matter what level of mass resolution is selected for use. In the present study, a demonstration of this GC–HRMS system to the analysis of brominated compounds in local background air samples is provided. In addition, a standard addition calibration system that has also been recently developed in our laboratory specifically for the quantitative determination of ultra-trace atmospheric components is also described and applied to the quantitative determination of the atmospheric brominated compounds detected.

2. Experimental

2.1. GC–HRMS analysis system

The GC–HRMS system has recently been recently described in detail [16] in an application to the detection and analysis of CF_3 -containing compounds in the atmosphere. Only a brief summary of its essential elements will be provided here along with an account of the alterations that were made for the present project. The HRMS system is a ZAB-2F (VG Instruments) high-resolution mass spectrometer of the dual (magnetic/electric) sector design with an accelerating voltage of up to +8 kV. The gas chromatograph (Hewlett-Packard, Model 5890 series II Plus) has subambient temperature capability with liquid N_2 cooling. Whole air samples are introduced to the GC–HRMS system by use of an associated air sampling system. A sample volume of 340 cm^3 (at 1 atm pressure; 1 atm = 101 325 Pa) is drawn through a freeze-out loop cooled to liquid nitrogen temperature. This coiled loop consisted of 0.125 in. O.D. stainless steel tubing of approximately 10 in. in length and was packed with glass beads (1 in. = 2.54 cm). With this loop, trapping efficiencies of unity were observed for all except the most volatile compound, CF_3Br . This was evidenced by the observation that the amount of each compound (except CF_3Br) collected on the sample loop did not vary with changes in the flow-rate of the sample through the loop or with changes in the length of time vacuum was applied to the collected sample prior to its transfer to the GC. The transfer lines to and from the freeze-out loop were made from deactivated fused-silica capillary of 0.53 mm I.D. and were about 2 m in length. The water content of the original whole-air samples was removed prior to freeze-out by passage of the air sample through a short drying tube containing $\text{Mg}(\text{ClO}_4)_2$. The drying tube did not affect the transport of the brominated compounds to the freeze-out loop as evidenced by its lack of a detectable affect when relatively small volume ($<50 \text{ cm}^3$) samples were analyzed with and without inclusion of this trap. After collection of a sample on the freeze-out loop, the loop was warmed by a heat gun and its contents were routed to the GC

system by the turn of a six-port valve. The sample compounds were focused on the head of the column by cooling a short piece of the column to liquid nitrogen temperature. At the start of each chromatographic analysis, the focusing portion of the column was then rapidly warmed to ambient temperature with a water bath.

The GC system contained a J&W DB-VRX column 60 m×0.25 mm I.D. with a film thickness of 1.4 μm . The following temperature program was used. The oven was initially held at 30°C for 5 min, following by a temperature ramp of 15°C/min to 220°C, where the temperature was maintained for the remainder of the analysis. A pressure program was also used in order to reduce the time necessary for transport of the analytes from the freeze-out loop to the GC system. The initial pressure was set at 200 kPa and held for 5.0 min. The pressure was then ramped downward at a rate of 10 kPa/min to 100 kPa where it was held for the remainder of the analysis. The exit end of the capillary GC column was threaded directly into the ion source of the mass spectrometer.

In order to monitor the intensity of a specific single ion of interest with the highest possible level of quantitative reproducibility while maintaining a moderate to high level of mass resolution, it was found necessary to continuously recalibrate the controlling fields of the mass spectrometer in order to insure that the mass spectrometer focuses precisely at the exact mass of interest. We have recently described [16] a method by which this can be done using *n*-dodecane, continuously introduced to the ion source during the analysis, as a mass reference. By control and variation of the electric fields of the mass spectrometer, the mass scale can then be recalibrated frequently (typically two times per second) during the entire chromatographic analysis. This electric field method of mass spectrometer control is most effective when the masses of the group of ions to be monitored are similar to that of one of the reference ions of *n*-dodecane. Therefore, if more than one ion is to be simultaneously monitored by the present method, those ions will typically be within a cluster of $\text{Br}^{79}/\text{Br}^{81}$ isotopic ions or within a group of chemically distinct ions that happen to differ in mass by less than about 10%.

2.2. Standard addition calibration system

In the calibration of an instrument's response to atmospheric components whose concentrations are in the low- and sub-ppt level, a formidable challenge is presented by the generation of reliable calibration standards. In addressing this challenge, we have taken an approach that is based on the principle of standard addition [21] rather than on the preparation of static gas standards. A disadvantage of this approach is that it is both labor and equipment intensive and requires several analyses in order to make a single determination. Its advantage is that it inherently provides a degree of compensation for unknown or poorly characterized sources of systematic error, if such exist, that might become particularly important when the concentration of the sought-for-substance in the whole air sample is exceedingly small. For example, if an unknown, but constant fraction of any analyte of interest is adsorbed onto any of the surfaces that it is exposed to during the entire analysis process (such as those within sample containers or the air sampling and chromatographic system), that source of systematic error will be negated in the standard addition method.

Our standard addition sampling device is located in an open field about 10 km south of the community of Bozeman, Montana, and consists of a corrugated steel cylinder of 5.9 ft. diameter and 11.9 ft. length (1 ft.=30.48 cm). When performing an analysis, a very large (9245 dm^3) air sample is captured within this cylinder by allowing ambient air to pass freely through the cylinder for many hours and then capping the ends of the cylinder with two polypropylene 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 6- dm^3 stainless steel air-sampling container (SilcoCan, Restec). The standard addition vessel was then spiked at least four times with a known amount (typically between 1 and 100 parts per million) of a primary standard containing the compound(s) of interest in nitrogen gas using a 1.00- cm^3 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. After each addition, an air sample was taken into another 6-dm³ 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 the MSU Mass Spectrometry Facility for analysis by GC–HRMS. All of the air-sampling containers used for sample transport were evacuated in the laboratory by connection to a vacuum system prior to use. In this way a sample could be taken in the field simply by opening the single valve in each container. In evacuating the containers prior to sampling, it is noted that care was taken not to pump on a container too long (containers were routinely evacuated only until the residual pressure was reduced to 0.5 Torr; 1 Torr = 133.322 Pa). This is because the residual water vapor that tends to stick to the interior surfaces of the container serves to passivate the interior surfaces against future analyte absorption.

The primary standards that were used in the standard addition experiments described above were prepared in our laboratory by the dilution of the pure compound of interest into a 20-dm³ glass carboy containing nitrogen gas. Two of the compounds analyzed here, CH₃Br and CF₂ClBr, are gases in the pure form and, therefore, were introduced volumetrically as gases to carboy. In order to correct for the non-ideal behavior of these pure gases, correction factors were deduced from estimates of the second virial coefficients for these and closely related substances [22]. Thus, in order to change from concentrations units of parts per million by volume (ppmv) to the desired unit of parts per million by mole ratio (ppm), conversion factors of 1.019 and 1.017 were used for CH₃Br and CF₂ClBr, respectively. All of the other compounds were introduced volumetrically as liquids to the carboy so that the corresponding molar quantity could be obtained from the known densities of each liquid. The combined uncertainties associated with the preparation of the primary standards and the subsequent injection of specific gas volumes of these standards into the standard addition vessel are thought to be the main contributors to the overall uncertainties in the quantitative measurements to be reported here. From these considerations the quantitative measurements

to be reported here are estimated to be accurate to within about ±10%.

3. Results and discussion

3.1. Detection and identification of brominated compounds

The discussions to follow will be facilitated by the eight electron impact mass spectra shown in Fig. 1. Inspection of these spectra indicates that all of these bromine-containing compounds have at least minor fragment ions of nominal mass 79 and 81, due to the Br⁺ ion, in their mass spectra. In Fig. 2, two single ion chromatograms are shown where the mass spectrometer has been tuned to the exact mass $m/z = 80.9163$ of the ion, ⁸¹Br⁺, using two different resolution settings. With use of resolution, $R = 1000$, in Fig. 2A, at least 14 distinct peaks are observed, with a coelution of two compounds observed at a GC retention time of about 4 min. As will be shown below, the eight peaks indicated with check marks, are not due to compounds that contain bromine atoms and, therefore, constitute unwanted interferences in the present study. With an increase in mass resolution to $R = 2000$ in Fig. 2B, a great simplification of the single ion chromatogram has been caused. With this higher level of mass resolution, the intensities of all of the checked peaks in Fig. 2A have been greatly reduced and most of the major peaks now observed are due to the brominated compounds of interest. Only two of the minor peaks observed now have check marks indicating that these are not due to bromine-containing compounds. Proof for each of the compound identifications indicated in Fig. 2B is based on retention times and the additional ion chromatograms to be provided below. The great simplification that has been caused by a change from $R = 1000$ to $R = 2000$ in Fig. 2A and B was expected [16] and is due to the distinct mass deficiency of the bromine atoms relative to those of carbon and hydrogen atoms.

Additional proofs the assignments of all of the brominated compounds indicated in Fig. 2B, except CF₃Br, are provided by the single ions chromatograms shown in Figs. 3–9. We have not included

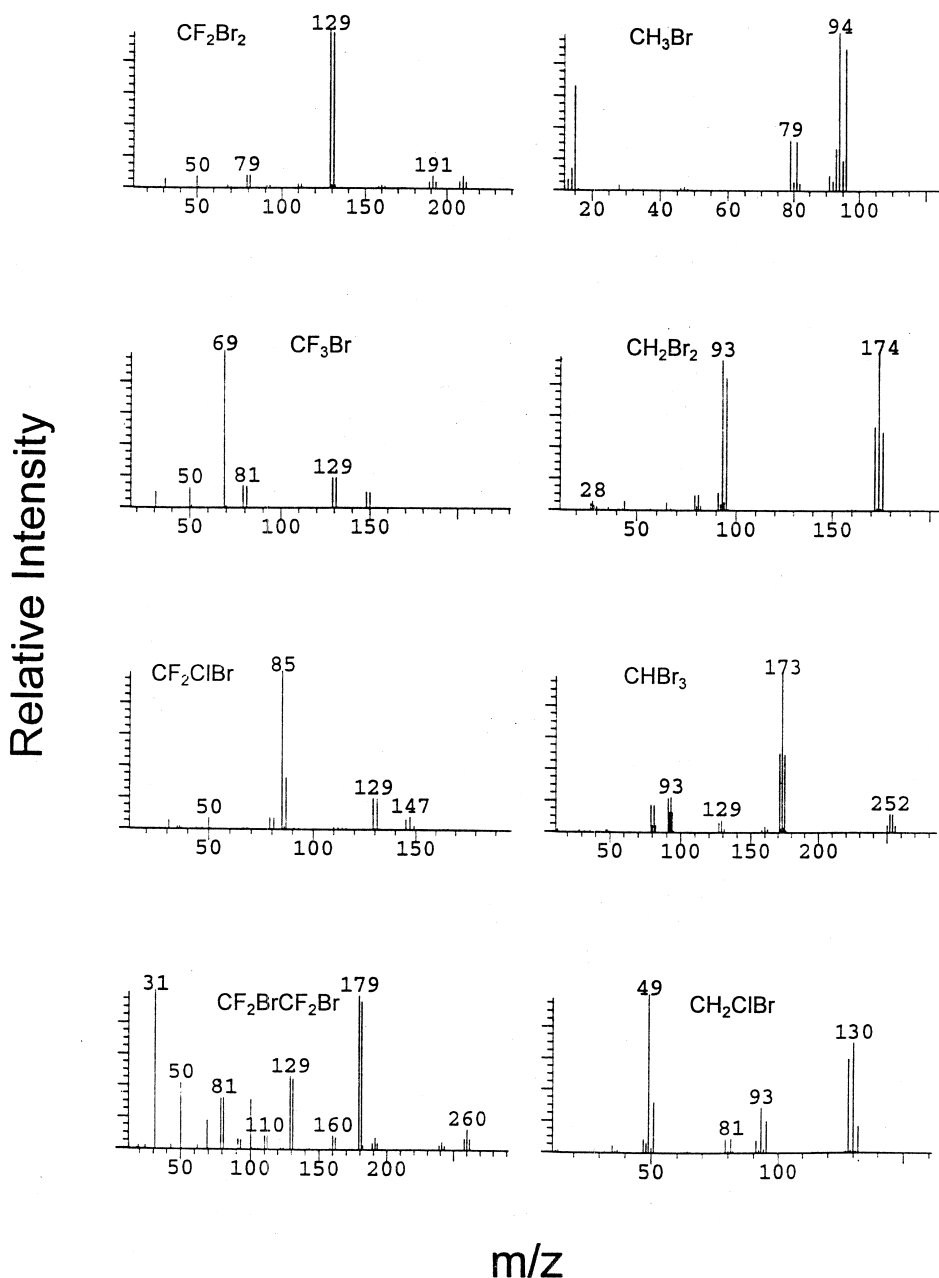


Fig. 1. Electron impact mass spectra of eight compounds detected in local background air samples. Obtained from the NIST Library of Electron Impact Mass Spectra.

CF_3Br in the present study because its analysis by our HRMS system has already been described in a previous study of CF_3 -containing compounds in

background air. In addition, CF_3Br is the only compound that was not quantitatively trapped on the freeze-out loop used in the present study (see Ex-

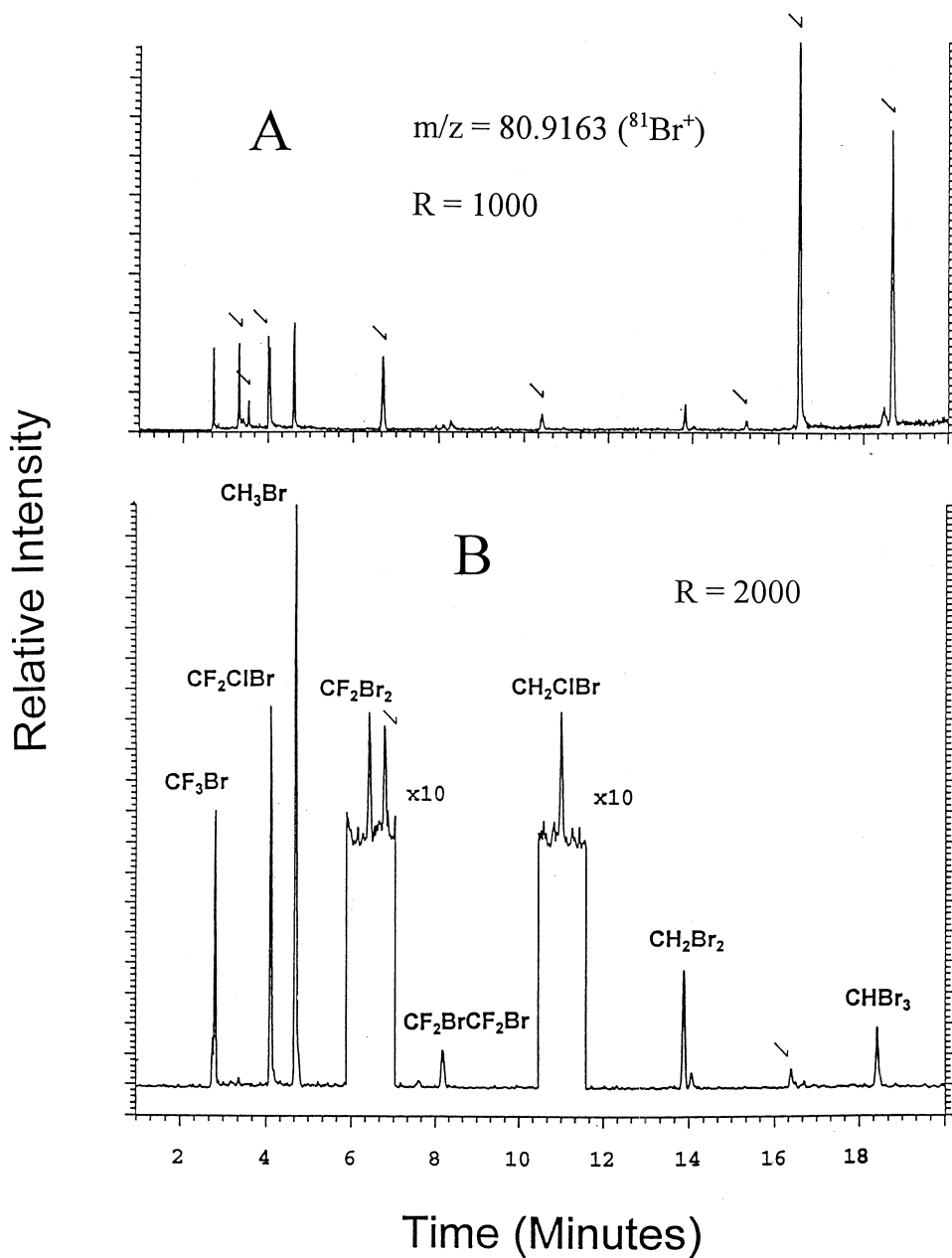


Fig. 2. $^{81}\text{Br}^+$ single ion chromatograms using mass resolutions of $R=1000$ (A) and $R=2000$ (B). In each chromatogram, the relative responses are normalized to the maximum response observed under each condition. In chromatogram B, the attenuation of the recorder has been increased momentarily at $t=6$ min and $t=10.5$ min by a factor of $\times 10$ in order to see more clearly the responses to CF_2Br_2 and CH_2ClBr . The volume of air sampled is 340 cm^3 . The peaks indicated by check marks are those due to compounds that do not contain bromine atoms.

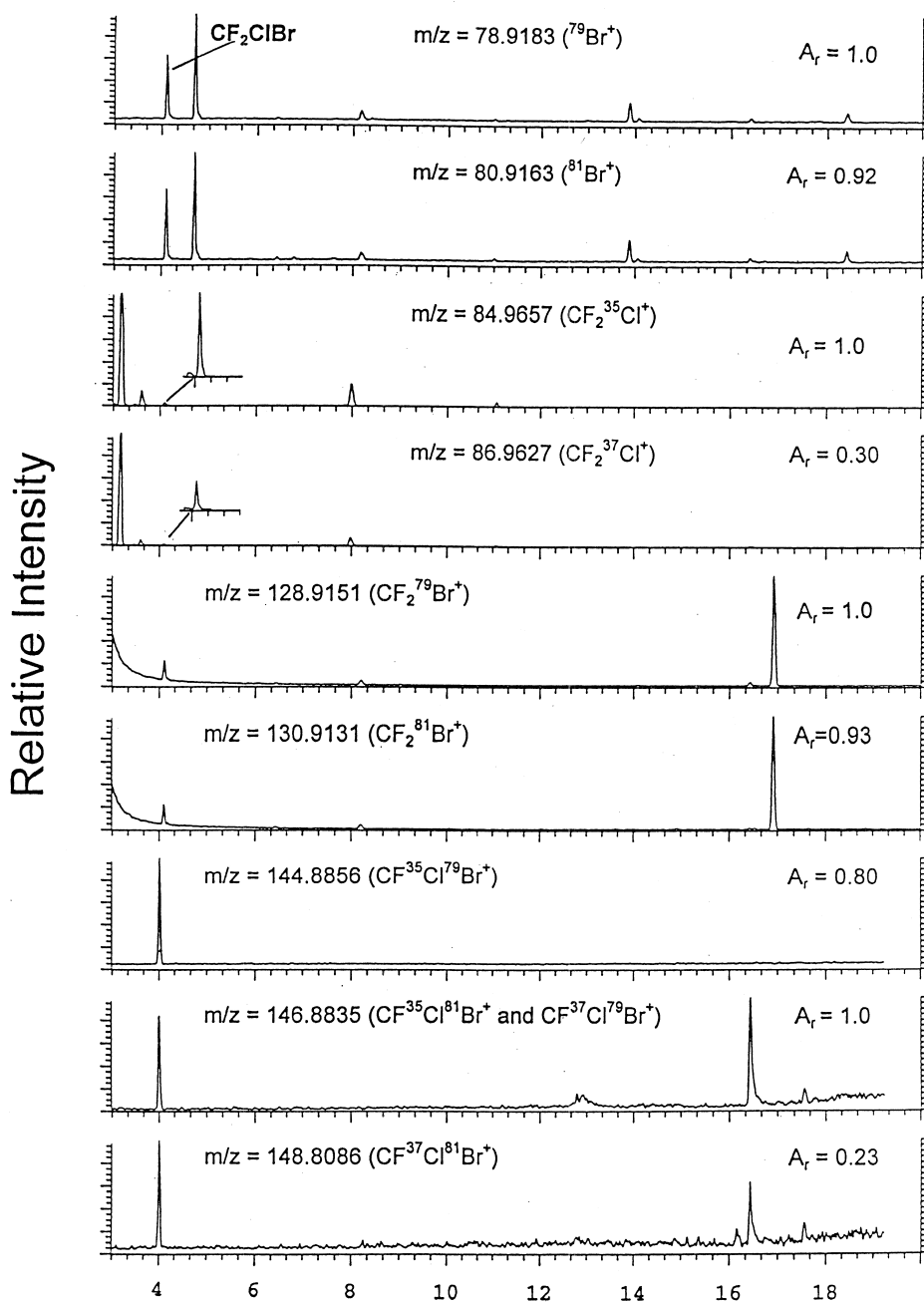


Fig. 3. Single ion chromatograms for each of the nine major ions in the mass spectrum of CF_2ClBr (see Fig. 1) using a mass resolution of 2000. All ions within an isotopic cluster group were monitored simultaneously during a single GC analysis. Within each of these groups, the A_r values listed indicate the magnitude of a given response to CF_2ClBr relative to that obtained using the most abundant ion in that group (for which A_r is assigned a value of 1.0).

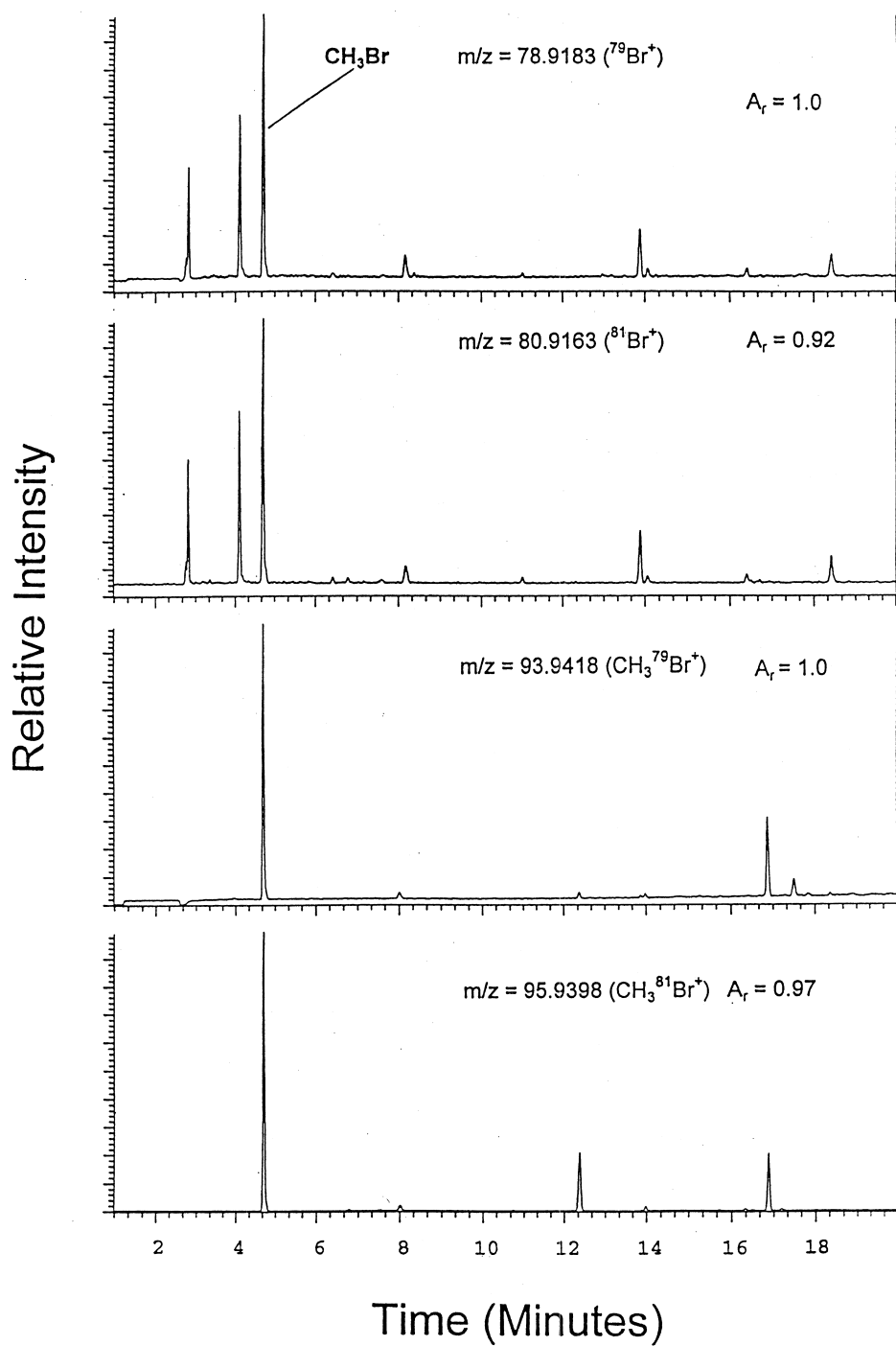


Fig. 4. Single ion chromatograms using the four major ions in the mass spectrum of CH₃Br.

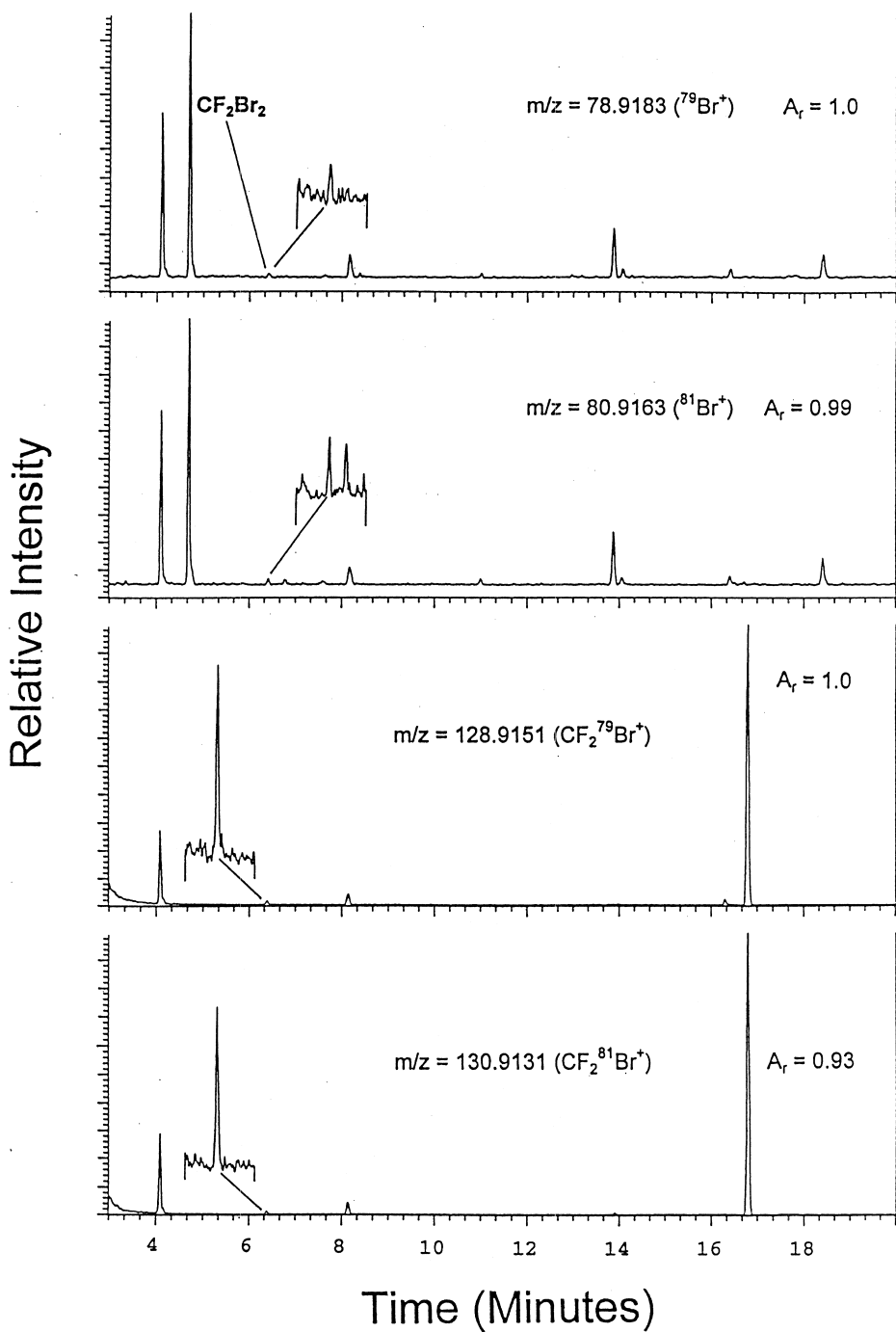


Fig. 5. Single ion chromatograms using the four major ions in the mass spectrum of CF_2Br_2 .

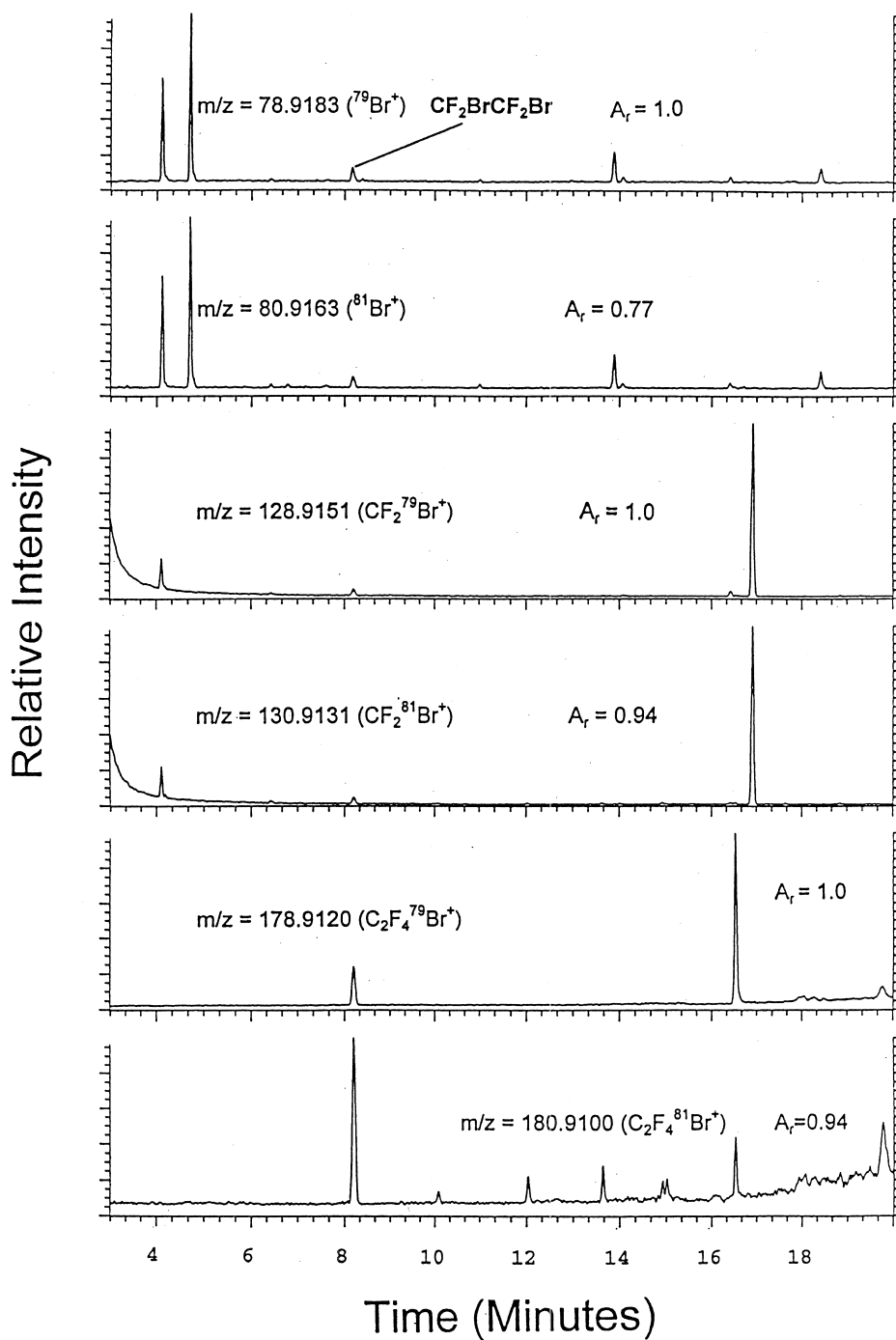


Fig. 6. Single ion chromatograms using the six major ions in the mass spectrum of $\text{CF}_2\text{BrCF}_2\text{Br}$.

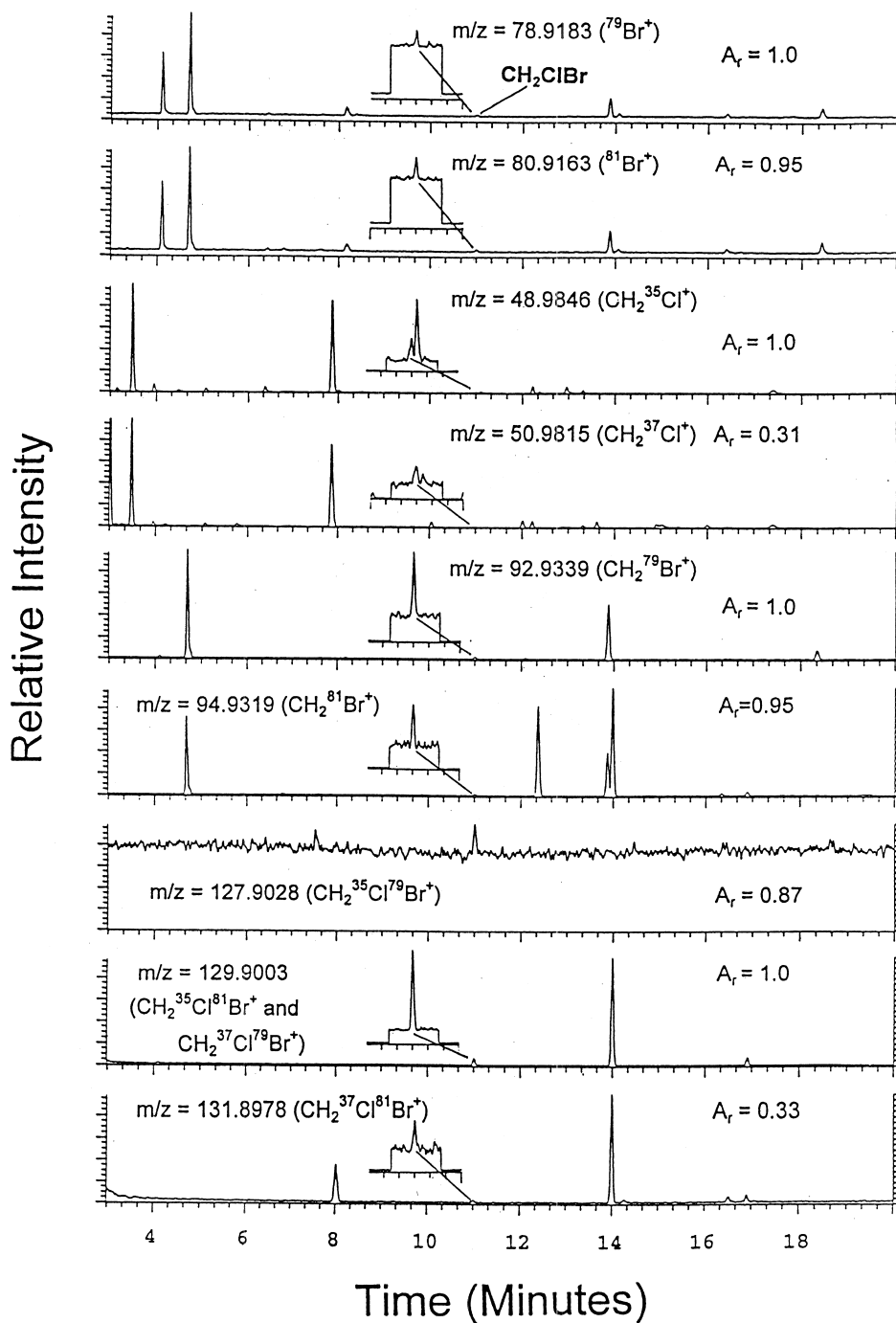


Fig. 7. Single ion chromatograms using the nine major ions in the mass spectrum of CH_2ClBr .

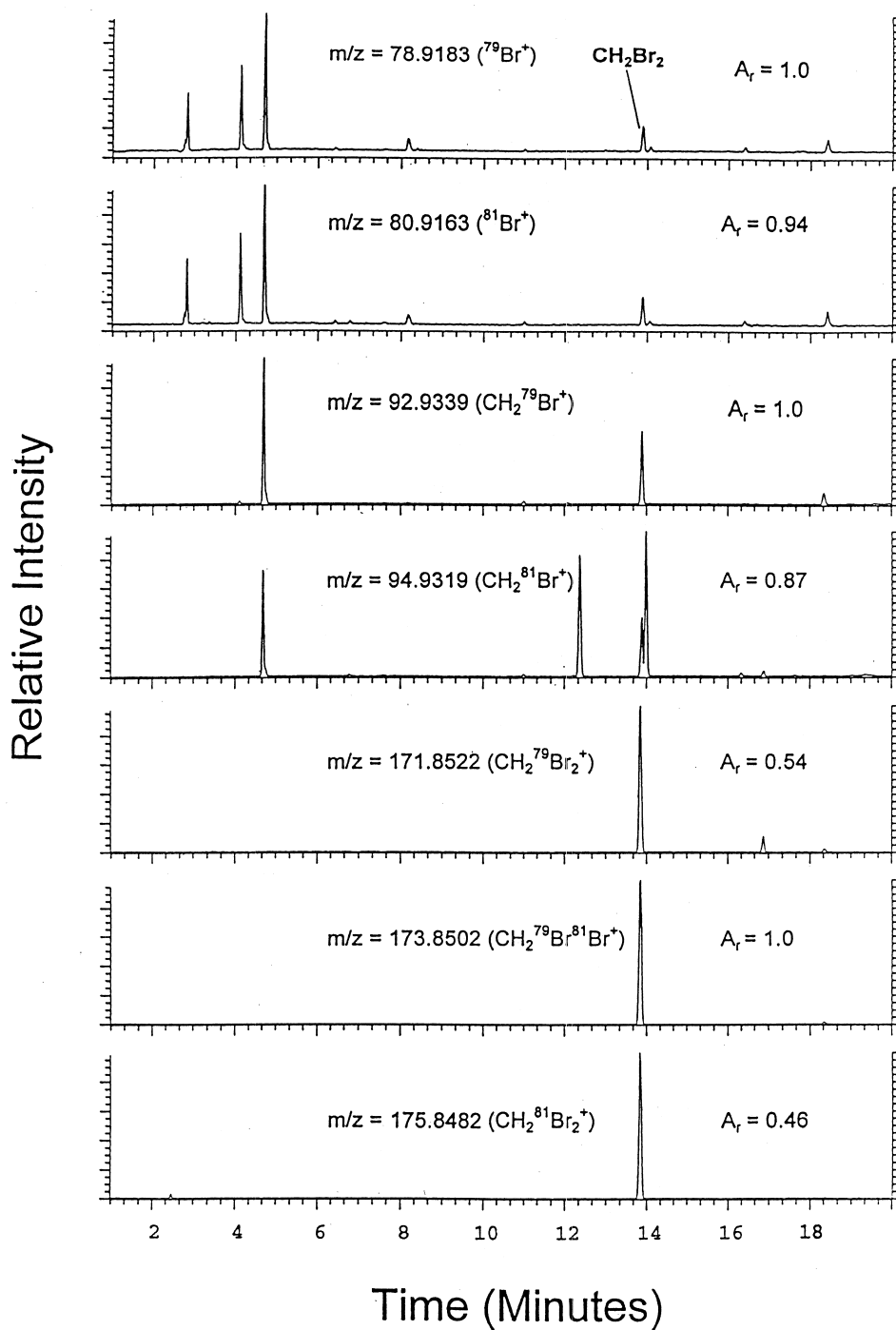
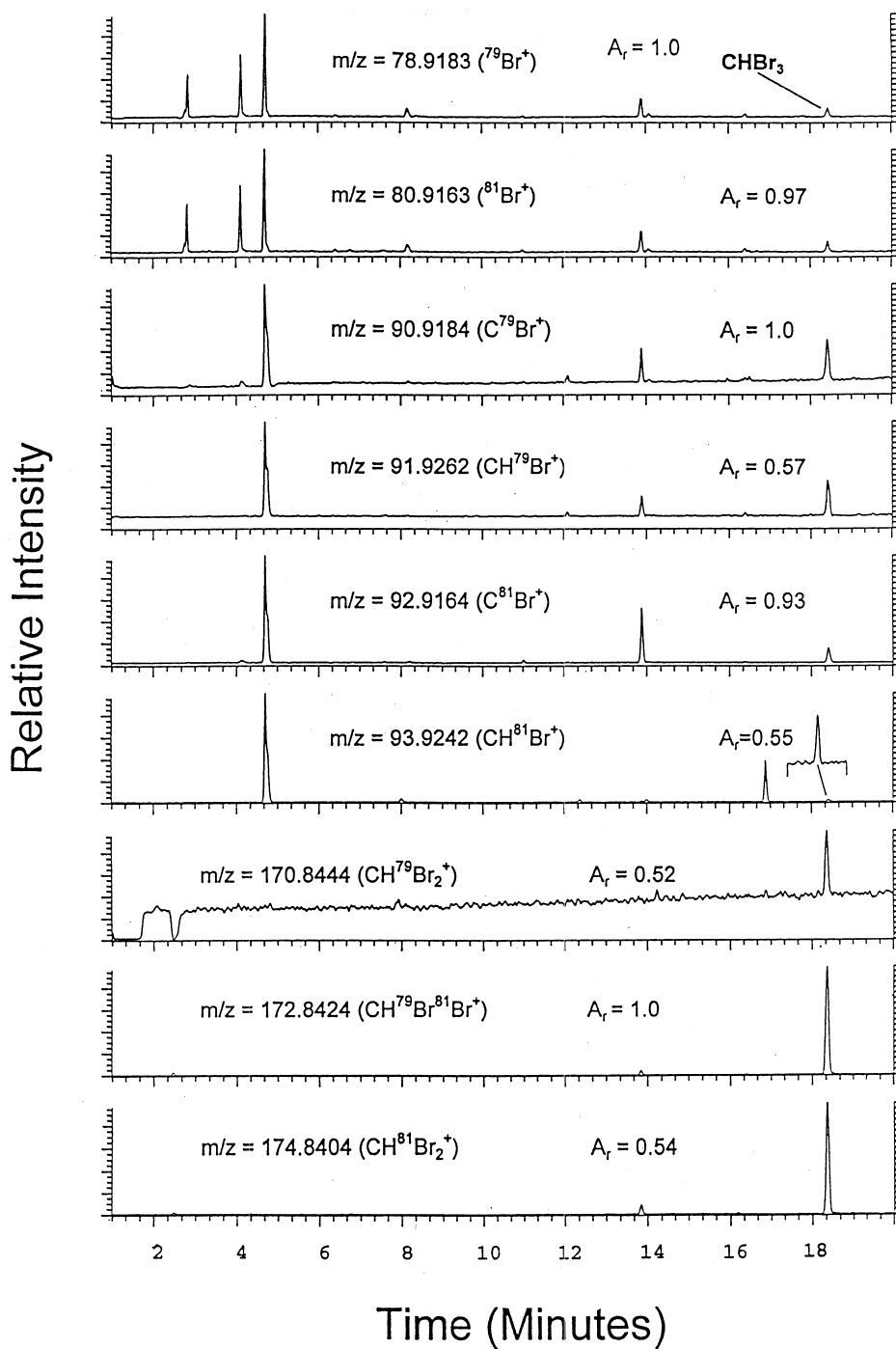


Fig. 8. Single ion chromatograms using the seven major ions in the mass spectrum of CH_2Br_2 .

Fig. 9. Single ion chromatograms using the nine major ions in the mass spectrum of CHBr_3 .

perimental) and, therefore, determinations of the concentration of this compound could not be reliably performed with the present analysis system. In Figs. 3–9, all of the major ions expected for each of the other compounds shown in Fig. 1 have been monitored, again using a resolution setting of $R=2000$ and it is noted that responses are, indeed, observed at the expected retention times using all of the expected ions. In obtaining these chromatograms, sets of ions that have very similar masses were simultaneously monitored (see Experimental) and the relative peak areas (A_r) observed within each of these groups of ions are also indicated on each chromatogram. These relative peak area values are all seen to be in good agreement with the mass spectra shown in Fig. 1 and, therefore, provide additional verifications of the assignments. Again, a notable feature of all of the chromatograms shown in Figs. 3–9 is the great simplicity that is obtained with use of this level of mass resolution. As was demonstrated in Fig. 2, the complexity of these single ion chromatograms were also found to increase significantly when the resolution of the mass spectrometer was lowered to the levels of $R=1000$ or less. For each chromatogram in Figs. 3–9, the magnitude of the observed responses shown for each peak have been normalized relative to the most intense peak observed at that exact mass. It is noted that for all compounds, except CF_2Br_2 , at least one of the ions monitored resulted in the strongest response observed over the entire chromatogram. This result is noteworthy considering the fact that all of these compounds have atmospheric presences in the low or sub parts per trillion range. The signal quality observed for CF_2Br_2 in Fig. 5 is also noteworthy considering its exceeding small presence in the atmosphere (to be determined below).

3.2. Quantitative determinations of the brominated compounds

Quantitative determinations were performed using the standard addition apparatus and method described in Experimental. A typical example of the results thereby obtained is shown in Fig. 10 for the case of CF_2Br_2 . The ion that was monitored for these analyses was the ion of $m/z=130.9131$ which provided the best signal-to-noise response to this com-

pounds (see Fig. 5). As shown in Fig. 10, a near-linear response to CF_2Br_2 was observed over the entire concentration range of added CF_2Br_2 (a least-squares analysis of these data indicates a linear correlation coefficient of $R^2=0.996$). A measure of the concentration of CF_2Br_2 in the original sample is provided by the point at which the best-fit line shown in Fig. 10 passes through the y-axis at a value of -0.038 ppt. We believe that the greatest source of uncertainty concerning the absolute accuracy of this and all measurements reported here is that associated with the preparation of the primary standards used for the standard additions. As indicated in Experimental, our estimate of the uncertainty of the primary standards is about $\pm 10\%$. Therefore, we also estimate that the uncertainty of the present measurements are about $\pm 10\%$.

An essential requirement of the standard addition method of analysis illustrated in Fig. 10 is that the sensitivity of the instrument's response to CF_2Br_2 must remain very constant over the period of several hours that was required to analyze six different samples. The fact that mass resolution had been set to a relatively high magnitude of $R=2000$ during these measurements makes this requirement a particularly challenging one. From the high correlation coefficients routinely obtained in these measurements, however, it is clear that the continuous (two calibrations per second) mass calibration procedure used here successfully focuses the mass spectrometer precisely on the exact mass of interest in each analysis. In order to additionally assure ourselves of this important point, we have periodically analyzed the same sample repeatedly in exactly the same way with use of resolution levels of $R=2000$ and higher over the course of an entire day. Invariably, a very consistent response magnitude was observed. For example, the methyl bromide content of one sample was measured once an hour for a period of 8 h using the ion of $m/z=95.9398$ with $R=2000$ (as illustrated in Fig. 4). The relative standard deviations of the responses thereby obtained were less than 1% and were thought to be limited primarily by small variations in the amount of sample introduced to the GC system rather than by variations in the sensitivity of the mass spectrometer, itself. We have also performed this type of experiment without use of the continuous mass calibration scheme described here.

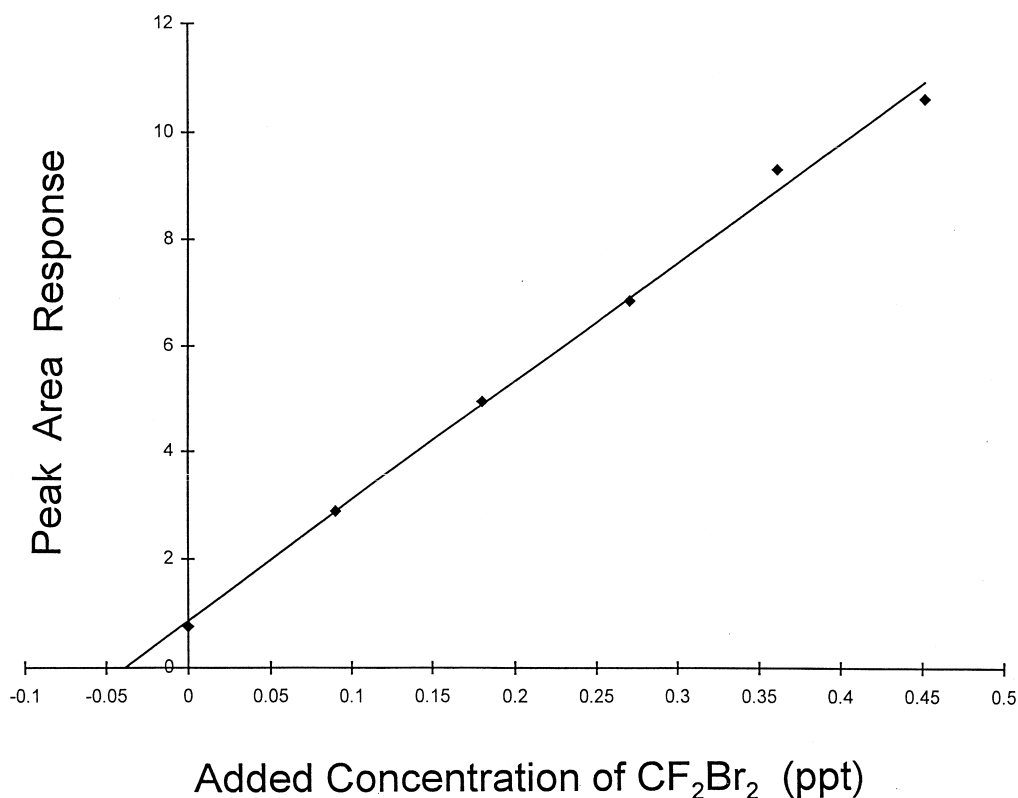


Fig. 10. Peak area responses to CF₂Br₂ observed for a set of standard addition samples collected on 16 January 1998. The exact mass monitored was $m/z=130.9131$ (CF₂⁸¹Br⁺) at a mass resolution of $R=2000$.

In these experiments the electronic stability of the mass spectrometer, itself, was called upon to focus on the exact mass of the selected ion in the analysis of the same sample repeatedly analyzed over the course of several hours. Using a mass resolution level of $R=2000$, the apparent sensitivity varied significantly in these experiments to a degree that would not be appropriate for quantitation by the standard addition method. When the level of mass resolution was doubled to $R=4000$, the mass spectrometer then completely missed the selected ion of interest during many of the repeated analyses if the continuous mass recalibration procedure described here was not used.

Quantitative determinations of seven of the brominated compounds detected here were performed by the standard addition method described above and the results of these measurements are shown in Table 1. Also indicated in Table 1 are the ions that

provided the best signal-to-noise response to each compound, the detection limit for each compound estimated from the magnitudes of the response and baseline noise observed in each analysis (assuming that a signal-to-noise ratio of 3 is necessary for detection), and the linear correlation coefficient, R^2 , determined from the full standard addition data set obtained for each analysis. It is noted that the detection limits to all of these compounds extended down into the low and even sub parts per quadrillion range. In view of the fact that a volume of air much larger than 340 cm³ could be sampled, if desired, the detection limit to any of these compounds could be additionally lowered simply by use of larger sample volumes (the only inconvenience associated with use of a larger air sample is that the time required for the sample's passage through the freeze-out loop is proportionately increased). It is also noted in Table 1 that the linear correlation coefficients, R^2 , are very

Table 1

Concentrations of several brominated compounds determined in local background air samples by GC–HRMS with calibration by the standard addition method

Compound	<i>m/z</i> of selected ion	Detection limits (ppq) ^a	Date	<i>R</i> ²	Concentration (ppt)
CF ₂ Br ₂	130.9131	5	10/24/97	0.996	0.039
			11/10/97	0.995	0.036
			1/16/98	0.996	0.038
			1/23/98	0.987	0.038
			2/10/98	0.987	0.040
5/5/98	0.996	0.049			
CF ₂ BrCF ₂ Br	178.9120	5	10/24/97	0.990	0.45
			11/10/97	0.988	0.41
			5/5/98	0.998	0.47
CF ₂ ClBr	144.8856		8/27/98	0.998	2.93
CH ₃ Br	95.9398	10	9/1/98	0.992	16.6
			9/9/98	0.998	15.4
CH ₂ Br ₂	173.8502	0.6	9/17/98	0.995	0.81
CHBr ₃	172.8424	0.6	9/18/98	0.996	0.24
CH ₂ ClBr	129.9003	5	10/5/98	0.997	0.089

^a Detection limits for each compound in a 340-cm³ whole air sample assuming a signal-to-noise ratio of 3 to 1 is necessary for minimal detection.

high in all cases. Again, this is direct evidence of the high stability of the mass spectrometer that has been achieved at *R*=2000 by the method of continuous mass recalibration used here.

Because very few reports of the detection of CF₂Br₂ in background air samples have previously appeared in the refereed literature [14,15] the concentration of this compound in local background air was determined at six different times between the Fall of 1997 and the Spring of 1998. The average of these measurements was 0.040 ppt with a standard deviation of 0.005 ppt. No other quantitative determinations of this compound in background air have been previously reported in the open literature, to our knowledge. Also, to our knowledge, the source of CF₂Br₂ in background air is not known.

Measurements of CF₂BrCF₂Br in local background air were made at three different times in the Fall of 1997 and the Spring of 1998. Each of these determinations was close to the average observed value of 0.44 ppt. This compound is known to have been used as a fire extinguishant and has been shown to have increased slightly in the atmosphere in recent years [10]. In January of 1997 its global average surface mixing ratio was reported to be 0.45 ppt [10].

One quantitative determination of CF₂ClBr was

made here by the standard addition method in the Fall of 1998 in which an atmospheric presence of 2.9 ppt was indicated. This compound has also been used extensively as a fire extinguishant and has had a relatively constant concentration in background air in recent years [10]. In January of 1997, its global average surface mixing ratio was reported to be 3.5 ppt [10].

The concentration of CH₃Br was determined here twice in the Fall of 1998 by the standard addition method with results of 16.6 and 15.4 ppt. Methyl bromide is known to have both natural and anthropogenic sources [9] and a global average surface mixing ratio of about 10 ppt [23,24] with an average northern to southern hemispheric ratios of about 1.2 to 1.4. Therefore, the present measurements are slightly higher than would be expected from previously reported global averages and might reflect a local influence possibly from forest fires burning in the states of Montana and Idaho during the time of these measurements.

The last three compounds listed in Table 1, CH₂Br₂, CHBr₃ and CH₂ClBr, are naturally occurring with relatively little information available as to their detailed sources and mixing ratios throughout the atmosphere. Most previous determinations of

CH₂Br₂ have fallen between 0.5 and 1.5 ppt [25–27] Those of CHBr₃ have generally been less than 2 ppt [26] and those of CH₂ClBr have generally been less than 0.5 ppt [26]. Therefore, the present measurements of each of these three compounds fall within these relatively broad ranges of previous measurements.

4. Conclusions

The GC–HRMS analysis system and the standard addition calibration method described here has been found to be well-suited to the ultra trace analysis of brominated compounds in the Earth's atmosphere. The use of a moderate level of mass resolution ($R=2000$) greatly simplifies the single Br⁺ ion chromatograms that are particularly useful for the initial interrogation of air samples in that it almost eliminates unwanted chemical interferences from the multitude of other trace components of air that do not containing bromine atoms. At the same time a very high level of response reproducibility is simultaneously obtained with use of $R=2000$ by the method of continuous exact mass recalibration described here. This high level of response reproducibility allows use of the standard addition method for quantitative determinations, a method that is particularly well suited to the analysis of air components whose concentrations are exceedingly low. In the future, one of our primary uses of this instrumentation will be to detect, identify and quantify trace components of the Earth's atmosphere whose presence has not yet been well characterized or even acknowledged. Such measurements will provide an additional source of baseline information concerning compounds that might become implicated later in ongoing investigations of chemically-influenced atmospheric phenomena such as stratospheric ozone depletion and global warming. The approaches to analysis and calibration that have been demonstrated here are expected to be well suited to this task.

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