Short communication

Improvements in the detection and analysis of CF_3-containing compounds in the background atmosphere by gas chromatography–high-resolution mass spectrometry

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Abstract

An improved method for the gas chromatography/mass spectrometry analysis of CF_3-containing compounds in air is described. This method replaces a GS-Q porous layer open tubular (PLOT) column previously used with a 30 m×0.32 mm GS-GasPro PLOT column. For this exceedingly volatile set of compounds the GS-GasPro column provides improved peak shapes, better signal-to-noise responses and no coelution of compounds. These improvements have allowed eleven CF_3-containing compounds to be detected in background air, including CF_4 (FC 14), C_2F_6 (FC 116), CF_3Cl (CFC 13), CF_3H (HFC 23), CF_3Br (Halon 1301), C_3F_8 (FC 218), CF_3CF_2Cl (CFC 115), CF_3CHF_2 (HFC 125), CF_3CH_3 (HFC 143a), CF_3CH_2F (HFC 134a), and CF_3CFCl_2 (CFC 114a). Three of these compounds have not been previously detected in background air, to our knowledge. Quantitative determinations for each of these compounds in the background atmosphere of Montana are also reported. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Fluorocarbons

1. Introduction

The presence of halogenated compounds in the Earth's atmosphere has been a significant source of concern during the last two decades due to their potential for stratospheric ozone destruction [1–7] and global warming [8–12]. Some of the most powerful methods that have been developed for the detection of halogenated compounds in real air samples have been based on gas chromatography (GC) with detection by either the electron capture detector (ECD) [13–15] or mass spectrometry (MS)

[16–22]. A method for detecting CF_3-containing compounds in background air by gas chromatography–high-resolution mass spectrometry was recently reported by our laboratory [23]. With this method, a whole air sample (355 atm cm³, 1 atm= $1.013×10^5$ Pa) was preconcentrated at liquid nitrogen temperature followed by introduction to a gas chromatograph equipped with a GS-Q porous layer open tubular (PLOT) column 30 m×0.32 mm. A dual-sector high-resolution mass spectrometer (HRMS) operated in the selected ion monitoring (SIM) mode was used for detection. Due to the large ion optic system of this mass spectrometer, high ion throughput was obtained simultaneously with use of relatively high mass resolution, thereby providing

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very sensitive and specific detection of CF_3-containing compounds in air. A limitation to that method, however, was the relatively poor chromatographic resolution obtained for these very volatile compounds using the GS-Q column, which performed very well in the analysis of other less volatile components of the atmosphere.

O'Doherty et al. [24] recently described the use of a cyclodextrin PLOT column for the separation of hydrohalocarbons and chlorofluorocarbons. They determined retention times for 34 halogenated compounds (8 of which contain the CF_3 group) using GC with either flame ionization detection (FID) or ECD. One ambient air analysis was also shown using GC/ECD. This chromatogram demonstrated the separation of 13 halogenated compounds (none of which contain the CF_3 group) commonly detected in background air. Their report showed promise for the use of the cyclodextrin column in real air analysis for many classes of compounds that are difficult to chromatograph. The present paper describes the use of a GS-GasPro (cyclodextrin) column which provides excellent chromatographic resolution of the CF_3-containing compounds. With the improved method described here, eleven CF_3-containing compounds are now detected in all background air samples.

2. Experimental

A detailed description of the GC–HRMS and associated sample introduction system has been recently provided [23]. Only a brief description of the primary elements of the system will be given here along with the modifications made for the present measurements. The HRMS system is a ZAB-2F (VG Instruments) high-resolution mass spectrometer of the dual (magnetic/electric) sector design with an accelerating voltage up to 8 kV. The gas chromatograph (Hewlett-Packard, Model 5890 series II Plus) has subambient temperature capability with liquid N_2 cooling. The GC contains a GS-GasPro (J&W Scientific, Folsom, CA, USA) PLOT column 30 m×0.32 mm.

Most of the air samples analyzed here were collected 10 km south of Bozeman, Montana, using an oil-less diaphragm pump (KNF Neuberger, model

N05SVI) and a 6 l electropolished stainless steel container (Idaho Valve and Fitting, Idaho Falls, ID, USA). The whole air samples are introduced to the GC–HRMS system by use of an associated air sampling system. A sample volume (corrected to standard conditions) of 355 atm cm^3 is drawn through a freeze-out loop (GS-GasPro, 22 cm×0.32 mm) cooled to liquid nitrogen temperature. Moisture in the air sample is removed prior to the freeze-out loop to prevent the loop from becoming plugged with ice and to avoid overloading the column with water by passage through a short drying tube containing $Mg(ClO_4)_2$. Experiments performed with and without the drying tube indicate that no sample is lost by using the $Mg(ClO_4)_2$ drying tube. It should be noted however that a significant decrease in the CF_4 response is observed as the sample introduction flow-rate is increased from 40 ml/min to 120 ml/min. This indicates that at higher flow-rates CF_4 is not being trapped with unit efficiency. At a flow-rate of 40 ml/min the CF_4 response is reproducible to less than a 2% deviation and no further increase in response is observed as the flow-rate is lowered. All other compounds showed no significant change in response as the sample introduction flow-rate was changed. After collection of a sample on the freeze-out loop, the loop is rapidly warmed by a heat gun and its contents routed to the GC via a six-port valve. The GC is initially held at $-40°C$ for 4 min, then ramped at $+20°C$/min to the final temperature of $180°C$. The carrier gas (ultra high purity He) inlet pressure is held constant at 12 kPa. The exit end of the GC column is threaded directly into the ion source of the mass spectrometer. The mass spectrometer is set to the SIM mode where the CF_3^+ ion is monitored ($m/z=68.9952$) using a mass resolution of 2200. In order to ensure that the mass spectrometer remains focused exactly on the centroid of the selected mass, the mass scale of the mass spectrometer is recalibrated twice per second throughout the analysis period by a peak-matching technique recently described in detail [23,26].

3. Results and discussion

In the electron impact mass spectrum of CF_3-

containing compounds, the CF_3^+ ion usually has major relative intensity and, therefore, can be used for the detection of this class of compounds. The CF_3^+ single ion chromatogram of a background outside air sample using the GS-GasPro column is shown in Fig. 1. The eleven CF_3-containing compounds shown in this chromatogram are invariably detected in background air samples. It is also noted that with this level of mass resolution ($R = 2200$), almost no responses to other components of the air sample are observed. The GS-GasPro column provides superior chromatographic resolution, no coelution of CF_3-containing compounds, and improved

signal-to-noise detection responses (by at least a factor of 5) relative to the GC column previously used [23]. These improvements have provided lower detection limits for all compounds, more reproducible and reliable peak area determinations, and have resulted in the detection of three CF_3-containing compounds in the background atmosphere which were not detected with the previous analysis system [23]. These three compounds are C_3F_8 (octafluoropropane, FC 218), CF_3CHF_2 (pentafluoroethane, HFC 125), and CF_3CH_3 (1,1,1-trifluoroethane, HFC 143a). These compounds are presently being used as substitutes for ozone-depleting chlorofluorocarbons
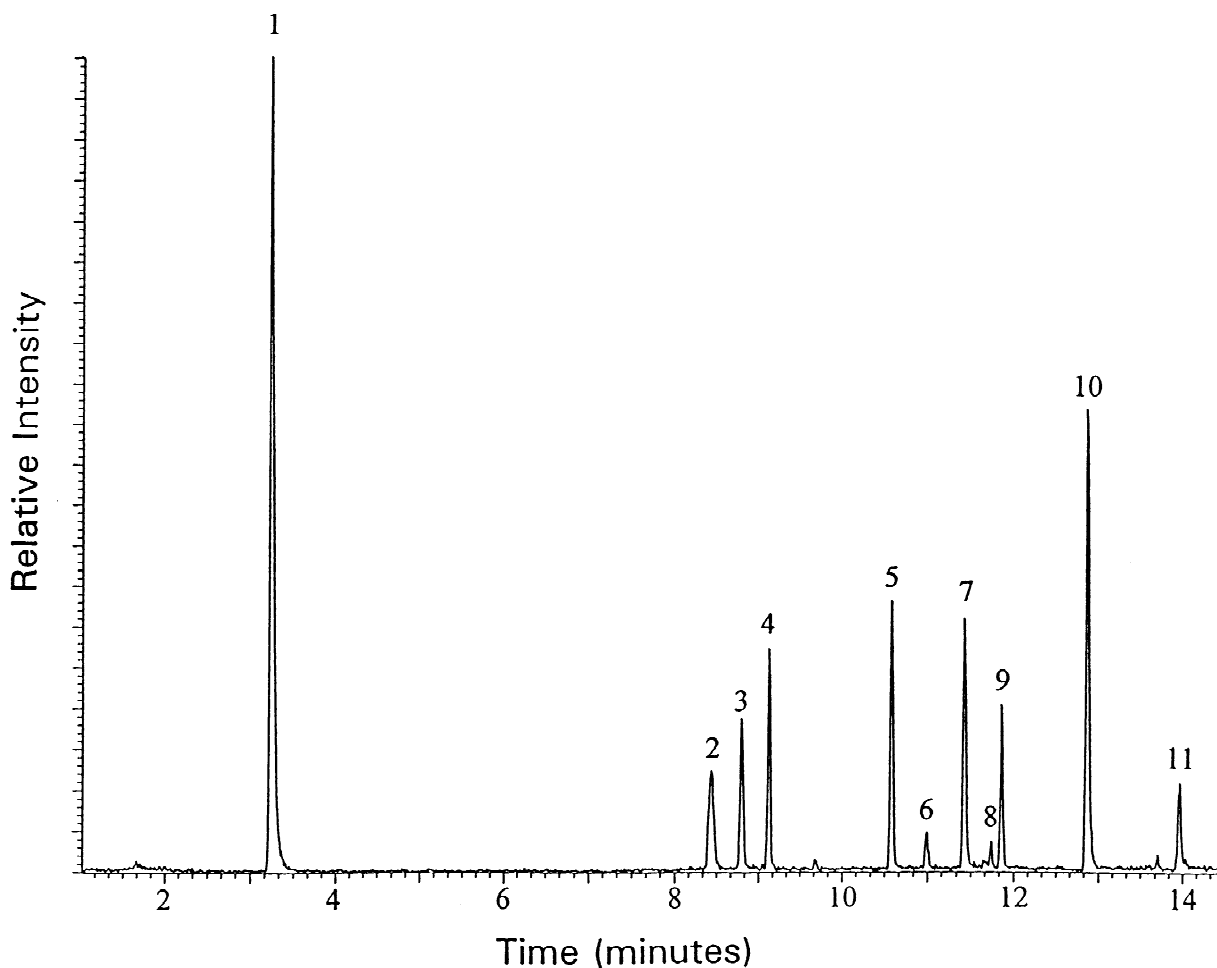

Fig. 1. CF_3^+ ($m/z = 68.9952$) single ion chromatogram of a background air sample at a mass resolution of 2200. The peak identities are; 1. CF_4 (FC 14), 2. C_2F_6 (FC 116), 3. CF_3Cl (CFC 13), 4. CF_3H (HFC 23), 5. CF_3Br (Halon 1301), 6. C_3F_8 (FC 218), 7. CF_3CF_2Cl (CFC 115), 8. CF_3CHF_2 (HFC 125), 9. CF_3CH_3 (HFC 143a), 10. CF_3CH_2F (HFC 134a), 11. CF_3CFCl_2 (CFC 114a).

in a wide variety of industrial and commercial applications [25].

Confirmations of the identities of the compounds indicated in Fig. 1 were based on the retention time of pure standards and on the single ion detection of each compound using all of the other major peaks in their known electron impact mass spectra [23]. In addition, when the mass resolution of the HRMS was increased from 2200 to 4500 all of the responses observed in the single ion chromatogram using $m/z=68.9952$ had the same relative peak intensities. This provides additional conformation for the suggestion that the major peaks shown in Fig. 1 are, in fact, due to the CF_3^+ ion and CF_3-containing compounds and are not due to any other interfering substances [23,26].

For four of the compounds shown in Fig. 1 (CF_3CF_2Cl, CF_3CH_2F, CF_3CFCl_2, and CF_3CHF_2), the CF_3^+ ion is not the major ion observed in their electron impact mass spectrum. Therefore, the detection limits for these compounds are generally improved somewhat when the most abundant ion for that compound is monitored rather than the CF_3^+ ion. The detection limits for all compounds shown in Fig. 1 lie within the range from 0.5 to 5 parts per quadrillion (ppq) by volume when the most abundant ion of each compound is monitored and all other conditions are set to those described in the experimental section.

Quantitative determinations of all eleven compounds in background air were performed using a large sample standard addition method, which has been previously described in detail [26]. In brief, standards of all eleven compounds were made at the low ppm level. All compounds were initially taken in the pure gaseous state and diluted into nitrogen or helium. Concentrations were determined on a volumetric basis. 1.0 or 2.0 ml aliquots of the standard were then successively added to a very large volume (9245 l) background air sample. After each of the five standard additions, a sample was taken into a 6 l air sampling canister (SilcoCan, Restek Corp., Bellfonte, PA, USA) and later analyzed by the HRMS system. These samples were collected in March and April, 2000, approximately 10 km south of Bozeman, Montana. The concentrations of CF_3-containing compounds in these samples were found to be 82 ± 8 pptv for CF_4, 3.6 ± 0.3 pptv for C_2F_6,

3.6 ± 0.3 pptv for CF_3Cl, 18 ± 2 pptv for CF_3H, 3.7 ± 0.3 pptv for CF_3Br, 0.26 ± 0.03 pptv for C_3F_8, 7.9 ± 0.8 pptv for CF_3CF_2Cl, 1.5 ± 0.1 pptv for CF_3CHF_2, 3.2 ± 0.3 pptv for CF_3CH_3, 21 ± 2 pptv for CF_3CH_2F, and 7.9 ± 0.8 pptv for CF_3CFCl_2. The uncertainty indicated for each compound is due either to the uncertainty (at the 95% confidence limit) of a linear regression analysis of the standard addition samples or to our estimate of the error associated with the preparation of our standards (thought to be approximately 10% [26]), whichever is larger. Changes in the response for all compounds on different sampling dates were within the limits of uncertainty indicated above. Therefore, the above concentrations are thought to be representative of the average concentrations over the March through April time period. Also, the responses for all compounds varied negligibly when compared to samples obtained from Cape Mears, Oregon on similar sampling dates. This suggests that any local sources of these compounds in Bozeman, Montana were of negligible importance.

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