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Development of automated gas chromatographic–mass spectrometric analysis for natural volatile organic compounds in the atmosphere

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ABSTRACT

An automated system for the trace determination of natural volatile organic compounds (dimethyl sulphide, bromoform, isoprene and its reaction products) was developed. A volume of 200 ml of air was collected on a small Tenax TA trap cooled electrically to 15°C. After desorption it was subjected to capillary GC–MS (selected ion monitoring) analysis. After each five air analyses, a standard gas generated with permeation tubes was analysed for calibration. With a sampling volume of 200 ml, the detection limits were dimethyl sulphide 2.4, isoprene 1.9 and bromoform 1.3 ppt (v/v) at a signal-to-noise ratio of 3. This method was applied successfully to the monitoring of natural organics at Tsukuba, Japan, where 1800 data sets were obtained during the period July–December 1991.

INTRODUCTION

Naturally derived organics in the atmosphere are now of major interest, as some are intimately involved in global atmospheric chemistry. Dimethyl sulphide (DMS), produced mainly by marine algae, is photochemically oxidized to non-sea salt sulphate in the atmosphere [1], potentially contributing to cloud formation and the Earth's radiation budget [2]. Bromoform and some other bromomethanes, also emitted from the ocean, may be important in the springtime surface-ozone destruction in the Arctic [3]. Isoprene, a biogenic hydrocarbon from terrestrial plants, and its reaction products, methacrolein (MAC) and methyl vinyl ketone (MVK), can contribute to the photochemical production of ozone and organic acids [4]. Globally, they might be a significant source of carbon monoxide and also be important in determining tropospheric OH concentration [5].

As these naturally derived organics are often present at ppt–ppb (v/v) levels in the atmosphere, their measurement is difficult, usually being performed by collection and preconcentration either on adsorbents or in canisters or cryogenic traps, with final analysis by GC. Because the mixing ratios of these compounds are likely to change drastically owing to the fluctuation of source- and sink-strength, serial measurements on-site are necessary to understand better their impact on atmospheric chemistry. To accomplish this, we developed a fully automatic analysis for on-site ambient monitoring of volatile organics, based on capillary GC–MS, especially focused on DMS, bromomethanes and isoprene and its reaction products.

EXPERIMENTAL

The method is based fundamentally on normal cryogenic concentration followed by thermal desorption and GC–MS analysis. Special attention was paid to the reduction of the dead volume, adsorptive losses of organics on sampling lines, undesirable water vapour effects and good chromatographic separation, all necessary for the precise measurement of organics in the ppt range.

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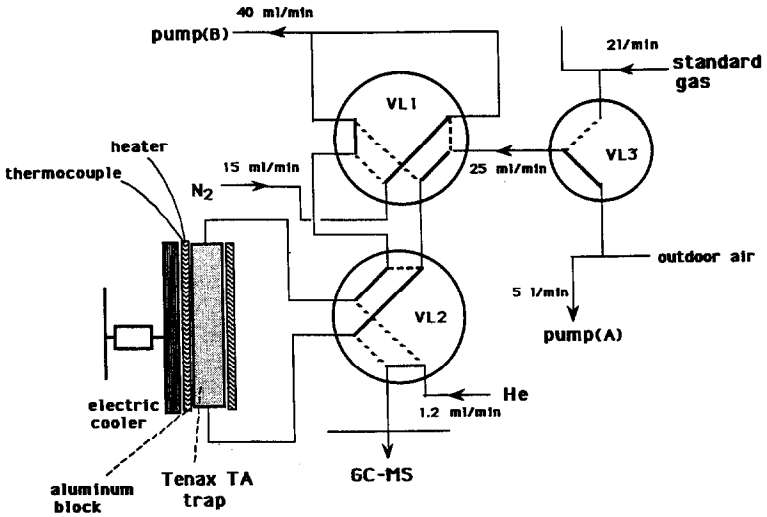

Fig. 1. Schematic diagram of preconcentration system.

Preconcentration unit

The concentration unit for automatic GC analyses of hydrocarbons reported elsewhere [6] was used after some modifications (Fig. 1). Automatic selection of sampling air and standard gas was accomplished by adding another switching valve (VL3). An electric cooler (based on the Peltier effect) was used to lower the trap temperature instead of flushing with liquid CO_2 as in previous work [6]. Electric cooling, which requires no cryogen, is more suitable for field studies, although liquid CO_2 can easily give a much lower temperature. The trap contained 0.08 g of Tenax TA in a stainless-steel tube (5 cm × 4 mm O.D.), set inside a small aluminium block with two ceramic heaters and thermocouples inserted. The electric cooler was mounted on a cylinder and only for cooling was it pressed on the block to lower the trap temperature. Air was drawn in at a high flow-rate (5 l/min) using pump A, and some was supplied to the concentration system, to reduce adsorptive losses of sampled organics on the sampling tube (PTFE). A diaphragm pump (B) drew both sample air and purging nitrogen gas (15 ml/min) at a flow-rate of 40 ml/min, resulting in 25 ml/min of air passing through the trap. All flow-rates were controlled with thermal mass flow controllers.

To avoid adsorption of components in the sampled air on the valves and connecting tubes, their temperature was maintained at 150°C with a heating cable.

Gas chromatograph–mass spectrometer

GC–MS was performed using a Hewlett-Packard Model 5971 mass-selective detector directly interfaced with an HP 5890 gas chromatograph. A Poraplot Q column (10 m × 0.32 mm I.D.) was used for GC separation. This had been used successfully for the separation of bromomethanes without problems of subambient cooling of the capillary column [7]. The column oven temperature was initially maintained at 55°C for 7 min, then programmed to 210°C at 12°C/min. The flow-rate of helium carrier gas was controlled at 1.2 ml/min by a thermal mass flow controller.

The mass-selective detector was used in the selected ion monitoring (SIM) mode. Table I lists the target compounds with their retention times and monitored ions. The time programme of the monitored ions was m/z 68, 62 and 58 for 10–14 min, m/z 70, 82, 130 and 174 for 14–16.5 min and m/z 94 and 173 for 16.5–23 min. In order to confirm that there was no interference with the target compounds, the qualifier ions in Table I were also monitored in several air analyses.

TABLE I

RETENTION TIMES AND MONITORED IONS FOR THE TARGET COMPOUNDS

Compound	Retention time (min)	Monitored ion (*m/z*)	Qualifier ion (*m/z*)
Dimethyl sulphide (DMS)	12.4	62	(47)
Acetone	12.7	58	(43)
Isoprene	13.1	68	(67)
Methacrolein (MAC)	14.3	70	(41)
Methyle vinyl ketone (MVK)	14.8	70	(55)
3-Methylfuran	14.9	82	(53)
Dibromomethane	15.9	174	(172)
Trichloroethylene	16.0	130	(132)
Dimethyl disulphide (DMDS)	17.2	94	(79)
Bromoform	19.6	173	(171)

Standard gas

A standard gas mixture of DMS, dibromomethane and bromoform at the ppb level was generated using thermostated permeation tubes. Certification of the mixing ratios of the generated standard gas was done from the mass loss of the permeation tubes, measured several times during 5 months. This standard was analysed in the same manner as the atmospheric samples, but with a smaller sampling volume, and was used for calibration during the analytical runs.

To determine components other than DMS, dibromomethane and bromoform, the relative sensitivity was calculated from liquid standard analyses at the beginning and end of the serial measurements. Liquid standard containing *ca.* 100 pg of each standard (DMS, dibromomethane, bromoform, isoprene, trichloroethylene, MAC, MVK) in 0.5 μl of methanol was injected into a 5-ml glass vial on-line via helium to the preconcentration trap. The vial was heated to 100°C and the standards were collected on the trap and then desorbed in the usual way. Both methods provided a good correlation between permeation tubes and the liquid standards for the compounds. Liquid standard was also used for the studies of linearity of the response and detection limits.

Procedure

The time programme of the sequential analyses was as follows. The procedure starts with cooling the trap to 15°C. For quantitative trapping of the target compounds in a 200-ml air sample, 15–20°C was cool enough (see below), and no water filter was required because of the low trapping efficiency of water at this temperature. The next steps are trapping of the air sample (200 ml total) for 8 min, thermal desorption and sweeping the trapped compounds into the capillary column for 7 min and start of the GC–MS analysis. During the analysis, the trap was baked for 5 min under a nitrogen flow. These processes were repeated automatically every 45 min, using a time controller.

After every five air analyses, standard gas was analysed using the same procedure, but with a sampling time of 2 min.

Field study

The method was applied successfully for the automatic measurement of DMS, bromoform, isoprene and its reaction products at Tsukuba, located at 36°05′N, 140°10′E and 50 km inland of the Pacific Ocean. Field research was conducted at the monitoring station of the National Institute for Environmental Studies, adjacent to pine forests and some farms. Some 2–3-week serial measurements were repeated during the period July–December 1991.

RESULTS AND DISCUSSION

Analytical method

Figure 2 shows chromatograms of an air sample. The chromatographic separation is excellent with-

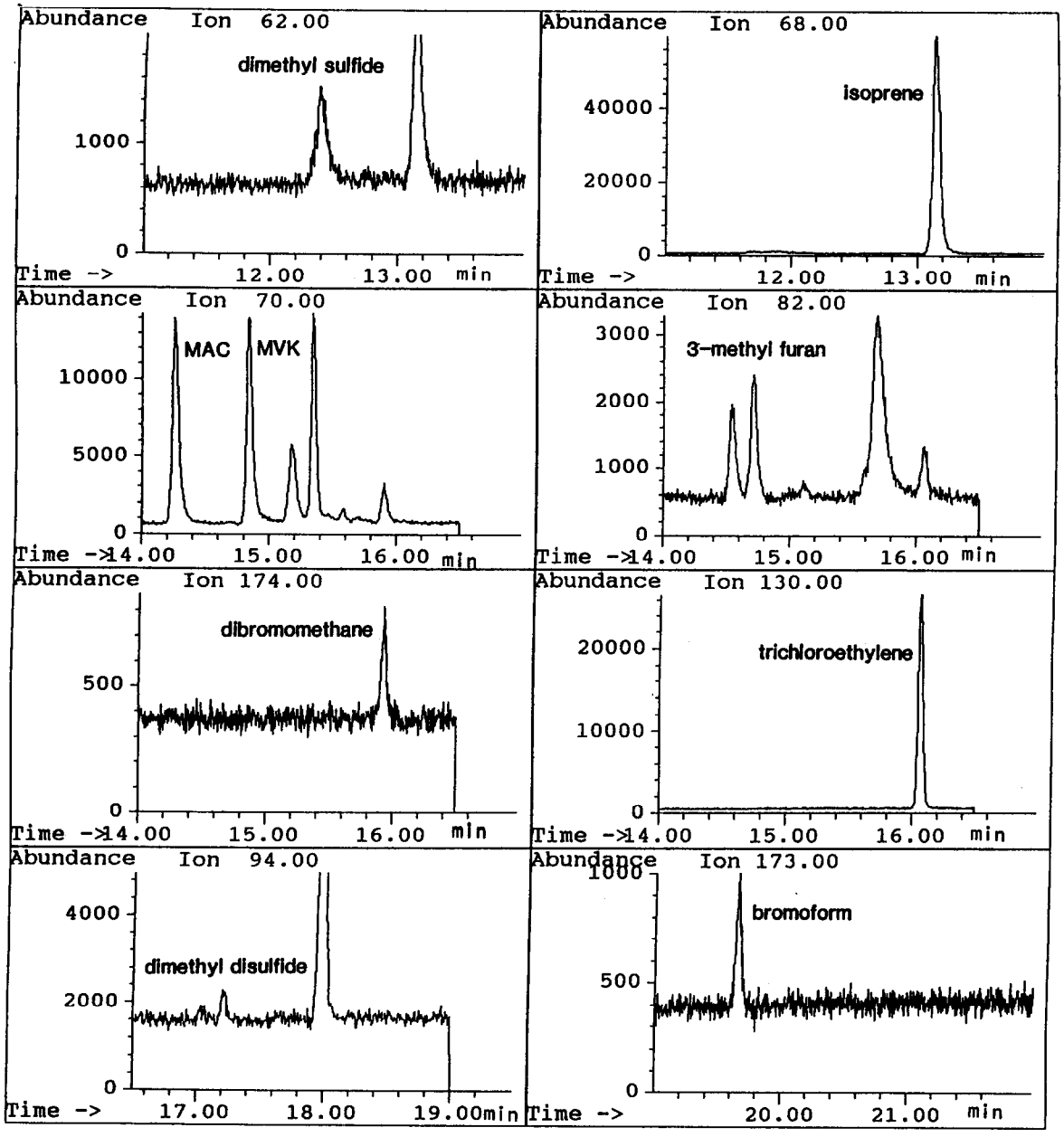

Fig. 2. Ion chromatograms of an air sample (200 ml) collected at Tsukuba at 13:18 h on August 31st, 1991.

out cryogenic cooling of the capillary column. The peak width of DMS is larger than those of the other compounds, but can be improved by lowering the initial temperature to 40–45°C and focusing more precisely on the top of the colum.

The method was validated by determining breakthrough volume, recovery, linearity of detector response and detection limit.

Breakthrough volume. The breakthrough volume was determined by extrapolating the retention vol-

umes of each compound on Tenax TA used as a GC column. DMS has the smallest breakthrough volume for Tenax TA of the five compounds examined. That of DMS was 24, 12 and 6.8 l per gram of Tenax TA at 0, 10 and 20°C, respectively, corresponding to 1.9 l 960 ml and 540 ml breakthrough volumes for the trap containing 0.08 g of Tenax TA. Therefore, under these sampling conditions, where 200 ml of air was collected at 15°C, 100% of these compounds in the sample can be trapped. Quantitative sampling (sampling volume smaller than breakthrough volume) was also confirmed directly by trapping standards on the trap, passing a known volume of helium through it and analysing as for atmospheric samples.

Recovery. The recovery efficiencies for the compounds from the trap were determined by changing the thermal desorption time for the collected standards on the Tenax TA trap to the capillary GC column. It was found that 7 min was sufficient to desorb all the compounds with helium carrier gas (1.2 ml/min) at 210°C. Quantitative recovery was also confirmed by comparison with direct injection of the liquid standard onto the capillary GC column.

The relative standard deviation of five analyses of standard gas was excellent: 2.4 % for DMS, 1.5% for dibromomethane and 0.49% for bromoform.

Linearity and detection limit. Linearity in the range 10 pg–2 ng was excellent for all the compounds. Detection limits at a signal-to-noise ratio of 3 were determined by extrapolation from the analysis of 10 pg of standards and were 1.3 pg for DMS, 1.6 pg for dibromomethane, 2.9 pg for bromoform and 1.2 pg for isoprene. Based on a 200-ml air sample, the relative detection limits by volume are 2.4 ppt for DMS, 1.0 ppt for dibromomethane, 1.3 ppt for bromoform and 1.9 ppt for isoprene.

The analytical procedure described above was developed for naturally derived organics. It is also applicable to trichloroethylene, tetrachloroethylene, benzene and some other anthropogenic organics. Given the trapping efficiency of Tenax TA and the adsorptive property of the Poraplot Q column, this method is potentially useful for non-polar organic compounds with boiling points approximately in the range 30–160°C.

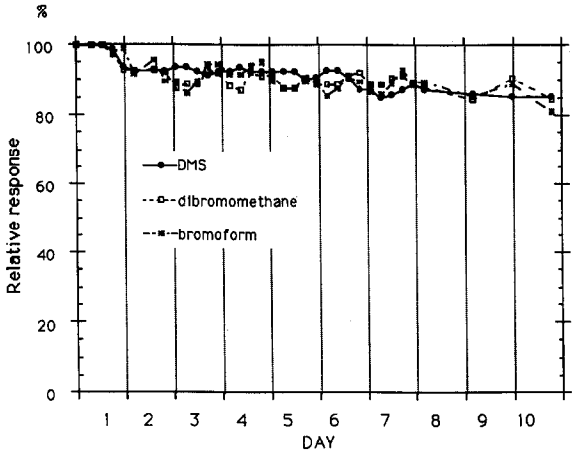

Fig. 3. Change of response of detector for standard gas after tuning. Analysis of a standard was performed after every five air analyses, except for on the 8th–10th days, where it was performed after every 21 air analyses. Monitored ions are *m/z* 62 for DMS (●), *m/z* 174 for dibromomethane (□) and *m/z* 173 for bromoform (×).

Serial measurements of naturally derived organics in the atmosphere

The response for standard gas was generally stable, although it showed a gradual decrease. The raw data for the responses for the standards during a serial measurement with no adjustment for of the mass-selective detector are shown in Fig. 3. Therefore, tuning of the mass-selective detector was not often required (usually once every 1–2 weeks), demonstrating its practical usefulness for field monitoring. The change in response for DMS (*m/z* 62) differs from those for dibromomethane (*m/z* 174) and bromoform (*m/z* 173) (Fig. 3). This may have resulted from a change in the relative response of high mass to low mass.

During the July–December 1991 field study 1800 data sets were obtained. These appear the first to be on-site automatic serial measurements for bromoform, DMS and the reaction products of isoprene using GC–MS. Our objective here was not a precise study of the variation of these compounds; those results will be reported elsewhere. However, as an example, the variations of isoprene, DMS and bromoform over 1 week are shown in Figs. 4–6.

The diurnal variations of isprene, DMS and bromoform differed. The mixing ratio of isoprene was much higher in daytime than at night (Fig. 4),

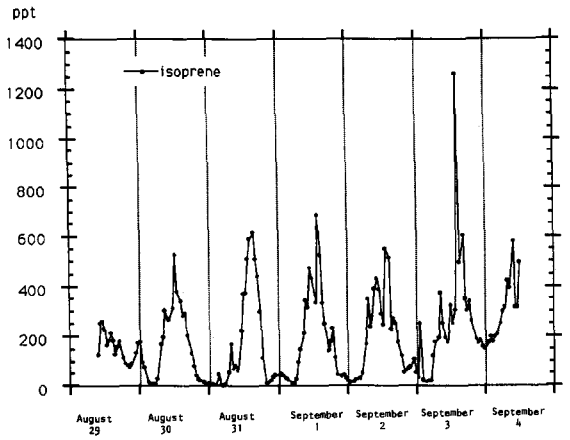

Fig. 4. Variation of the mixing ratio of isoprene in the atmosphere (Tsukuba, August 29th–September 4th, 1991).

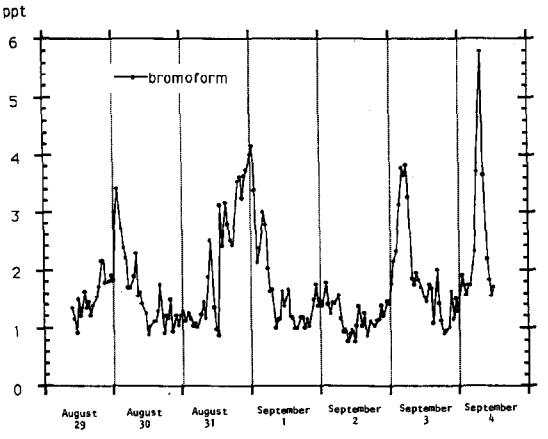

Fig. 5. Variation of the mixing ratio of DMS in the atmosphere (Tsukuba, Augst 29th–September 4th, 1991).

whereas DMS and bromoform were most abundant at night or in the early morning (Figs. 5 and 6).

A higher mixing ratio of isoprene in clear daylight hours was observed previously in forest air [8]. This was explained by isoprene emission being greatly increased in the daytime, although chemical reaction and dilution are also active. It is reasonable to assume, therefore, that the mixing ratio of isoprene was relatively low, even in the daytime on cloudy days (August 29th). Two reaction products of isoprene, methacrolein and methyl vinyl ketone, showed afternoon maxima, just after the maximum of isoprene.

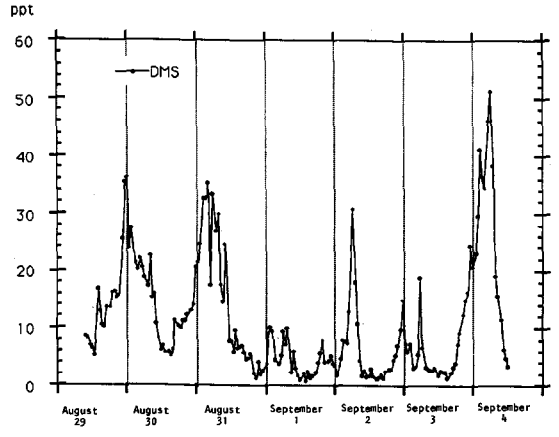

Fig. 6. Variation of the mixing ratio of bromoform in the atmosphere (Tsukuba, August 29th–September 4th, 1991).

A much higher mixing ratio was observed at night than during the day for DMS (Fig. 5). In clean marine air, Andrea *et al.* [9] reported tha the mixing ratio of DMS in the afternoon was about one third lower than that during the night maxima. This agreed with model simulations involving OH oxidations of DMS in the atmosphere. In this study, however, a much more significant diurnal variation was often observed. Possible explanations for the greater differences of the DMS mixing ratio between day and night at Tsukuba are (1) the atmosphere over land is much more stable at night, thereby suppressing dilution and leading to a high mixing ratio, and (2) the loss of DMS through atmospheric reaction with OH and ozone occurring during transportation from the ocean to Tsukuba was lower at night.

Another marine organic compound, bromoform, is decomposed through photolysis in the atmosphere. This is effective only in daytime. Therefore, its mixing ratio is also expected to be higher at night owing to suppressed dilution and photolysis at that time, which is similar to the condition for DMS. However, the diurnal variations of bromoform and DMS are not always coincident (for example, August 30th–31st). This results mainly from the change in the relative strength of their source: DMS is emitted from the soil and the ocean, whereas the ocean is considered the only source for bromoform. Even in the ocean, the relative ratio of DMS and bromoform in sea-water might change daily.

CONCLUSIONS

The automated preconcentration–GC–MS system described here is a very powerful method for trace determinations of such natural volatile organic compounds as bromoform, isoprene and DMS. The detection limits for these compounds in a 200-ml of sample air were *ca.* 2 ppt at a signal-to-noise ratio of 3. The response of the mass-selective detector was stable enough to be compensated for by occasional standard gas analyses.

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