Precise Measurement of Atmospheric Concentration of CH_3Br by GC/ECD

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A precise measurement system of atmospheric CH_3Br at background concentration level was developed for the survey of its spatial and temporal distribution by gas chromatographic separation with dual Porapak Q columns and detection with an electron capture detector.

Methyl bromide (CH_3Br) is an atmospheric trace gas with both natural and anthropogenic sources.[1] It has become of interest recently because of its ability to deplete stratospheric ozone by delivering bromine to the stratosphere. Global average concentration of methyl bromide has been reported as about 10 pptv (pptv=10^{-12} v/v),[2-7] though with large analytical uncertainty. Hence it is necessary to develop more precise and convenient method for measurement of atmospheric CH_3Br.

We developed a precise measurement method of CH_3Br at background concentration level by gas chromatographic (GC) separation with dual Porapak Q separation column system and detection with an electron capture detector (ECD). Sample volume necessary for analysis at background concentration level was 100 to 200 mlSTP, which is much smaller than those reported in previous papers.[2-7] By decreasing sample amount for analysis, we can measure each sample several times to improve reliability. This method enabled simultaneous measurement of CH_3Cl, CH_3I, CFCs, Halons, SF_6, N_2O and CO_2 as well.

Atmospheric sample was collected into an all metal canister equipped with a stainless steel bellows valve, and its aliquot was introduced into the GC/ECD through all metal vacuum line; whole connecting lines were warmed at 50 °C for avoiding losses of trace sticky or polar constituents during the analysis. Cryofocusing method and Valco's switching valves were adopted: after main components in the air (oxygen and nitrogen) were removed by passing through a cold trap (stainless steel tube packed with glass beads) maintained at liquid N_2 temperature in order to prevent the O_2 effect on ECD response, trace constituents trapped in the tube were then introduced to GC by quickly and uniformly heating the tube up to 80 °C in hot water bath. Since CH_3Br has fairly high solubility in water (1.26 g/100 g) and is thermally unstable, other methods (e.g., electric heating) gave worse reproducibility. Each sample was firstly divided into two parts with the pre-column (Porapak Q). Higher boiling point constituents eluted slowly (CFCs and methyl halides) were further separated by the separation column-1 (Porapak Q) maintained at 130 °C and were detected by ECD-1. Lower boiling point constituents (inorganic gases and water) were further separated by the separation column-2 (Unibeads C) also maintained at 130 °C in the same oven and detected by ECD-2 into which was doped methane (5%) to stabilize N_2O response of ECD. Both EC detectors were maintained at 300 °C. The sample volume analyzed was determined from the pressure change in excess volume vessel in which every sample was temporarily introduced at reduced pressure before cryofocusing.

We adopted Porapak Q as the column packing to separate methyl halides (CH_3Br, CH_3Cl, and CH_3I), CFCs and others. Since the boiling point of CH_3Br is, however, very close to those of CFC-114a (CCl_2FCF_3) and CFC-11 (CCl_3F), we found it was impossible to separate these compounds completely with isothermal conditions or ordinary temperature programing of the columns. Other columns such as Porasil D or silica gel column showed similar problems. Halon-1211 ($CBrClF_2$) and CFC-114 ($CClF_2CClF_2$) with near boiling points to CH_3Br, gave close retention volumes in GC separation. Since the concentration of CH_3Br is much smaller than other species at background concentrations and ECD sensitivity to CH_3Br is also smaller (about one tenth to one hundredth), complete separation of CH_3Br from other species with much larger peak areas is necessary for its precise measurement. Since the retention time of polar CH_3Br is less temperature dependent than those of CFCs on Porapak Q column as shown in Figure 2, we separated CH_3Br from other compounds by using two Porapak Q columns temperature controlled very differently. The first column (pre column: 1.0 m) was initially kept at 60 °C for 4 min, then elevated at 12 °C/min up to 115 °C and maintained for 40 min. This relatively low temperature column condition permits complete separation of CH_3Br from CFC-11 thousand times as large. The second column (Porapak Q separation column-1: 1.5 m) was maintained at 130 °C to separate CH_3Br from CFC-114a and to prevent baseline drift by

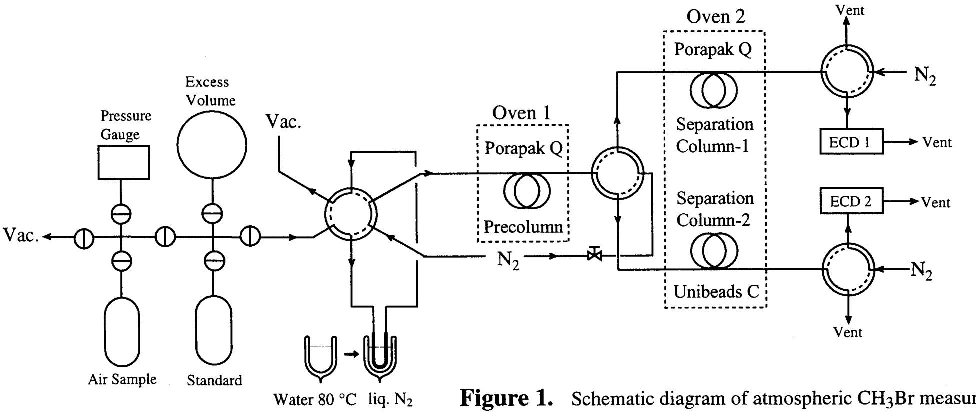

Figure 1. Schematic diagram of atmospheric CH_3Br measurement system.

rapid temperature change of the first column. Thus we obtained the best separation as shown in Figure 3. Each peak in the chromatogram was identified and quantified mainly with the calibration standards prepared in our laboratory and occasionally with commercially available higher concentration standards after dilution. The CH_3Br concentration in the atmospheric sample shown in Figure 3 was, for example, determined as 15.5 pptv from the calibration curve.

The temperature dependence of the ECD response to CH_3Br was examined at 200-300 °C. Its sensitivity increased with the increase in the detector temperature up to 250 °C and then remained nearly constant. On the other hand, sensitivities of CFCs increased with the increase in temperature even at higher temperatures. Although Khalil's group used O_2 doping to ECD for CH_3Br measurement,[8] we could not obtain remarkable improvement for CH_3Br, while CH_3Cl and HCFC-22 showed fairly large enhancement instead. The baseline noise increased with O_2 amount by factor of ten with 0.03% O_2 doping, and the signal-to-noise (S/N) ratio for CH_3Br with O_2 doping became much lower than that without O_2 doping (i.e., N_2 carrier gas only). Accordingly we did not adopt O_2 doping for CH_3Br measurement.

We observed instability of ECD response with column conditioning. Methyl halides appear to be more sensitive to impurities in ECD response; it is important to remove impurities completely in the carrier gas for precise measurement of CH_3Br and CH_3Cl. Even though the GC baseline seems to be stable, ECD responses to methyl halides are enhanced unstably with impurities from the column depending on column conditioning. It was necessary to make column conditioning in strictly the same manner. Otherwise, the ECD response to CH_3Br varied sometimes as much as 50%. Both columns were baked at 180 °C for 60 min before each analysis. By this procedure, the reproducibility was improved to ±5%.

We have collected and stored atmospheric samples in both the northern and southern hemispheres since 1980. In such samples have been confirmed stabilities of CFCs, halons, and many trace species. However, we found that methyl halides were unstable during prolonged storage. Regarding the atmospheric samples collected in Hokkaido, the CH_3Br concentration was nearly reproducible in the samples stored for a month, while in the samples stored more than one year it showed quite large variation and mostly higher values than expected from the current average concentration. Similar kind of phenomena has been briefly reported by Montzka's group,[9] while its details and causes are not mentioned. Similar problem was also encountered with CH_3Cl and CH_3I during storage in metal containers.

By using this system, we have analyzed several kinds of air samples collected in Japan. The results will be published elsewhere.

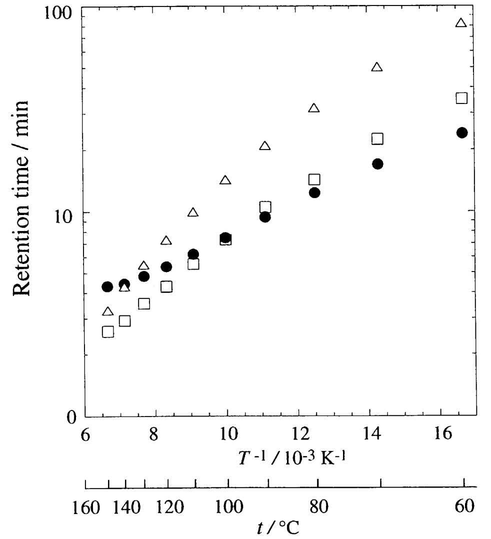

Figure 2. Temperature dependence of retention times of some halocarbons on Porapak Q column (1.0 m).

● CH_3Br ; △ CFC-11 (CCl_3F) ; □ CFC-114a (CCl_2FCF_3).

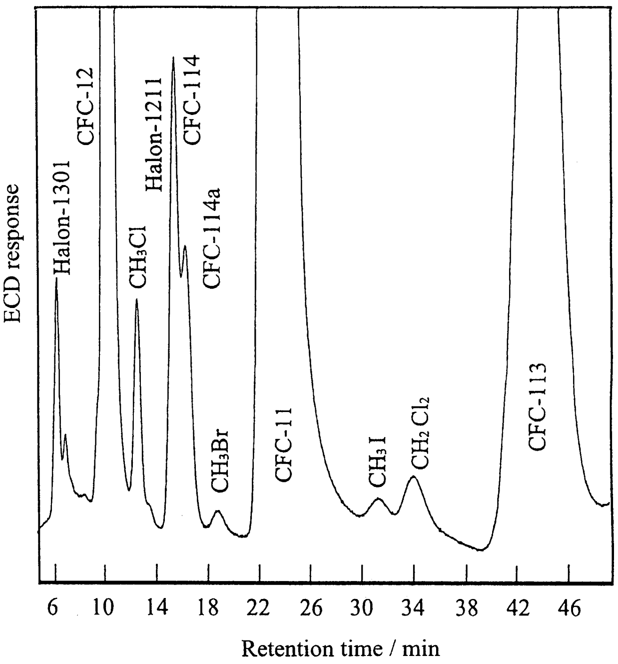

Figure 3. Typical ECD chromatogram of atmospheric methyl bromide and other halocarbons.

Sample size: 170 mlSTP; sample was collected at Katsu-ura on Dec. 8, 1995. Precolumn: Porapak Q (1/8" o.d., 1 m long), 60 °C (4 min), then 12 °C/min to 115 °C. Separation column: Porapak Q (1/8" o.d., 1.5 m long), constant at 130 °C. Carrier gas: N_2 99.9995%, 40 ml/min.

References and Notes

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