A-2.1.2 Study on the origin of methylbromide by radio carbon isotope measurement

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Abstract

To determine the origin of methylbromide (MeBr) in the atmosphere, C-14 dating method using accelerator mass spectrometry (AMS) is being attempted. Two large-volume samplers for the collection of methylbromide in the atmosphere, including a transportable system based on a silica gel pre-water trap, several water trap systems and a methylbromide trap by molecular sieve-type active carbon cooled by dry ice, and a pump for high volume sampler, were constructed and their performances were evaluated. A small SIM peak corresponding to methylbromide was detected in the collected samples, though the absolute amount was not enough for the AMS ^{14}C measurement. Further purification of this fraction is being attempted by the combination of a cooled injection system (CIS) and a preparative capillary gas chromatography (PCGC). Attempts were also made for two orders reduction of necessary amount of samples for the AMS measurement. Reduction by one order was attained by the present graphitization system with data correction based on the standard produced under the same condition (same carbon/iron catalyst ratio). An additional order reduction was attempted by constructing a new graphitization system with much smaller volume of reaction chamber.

Key Words Methylbromide, carbon dating by AMS

1. Introduction

Among ozone-layer destructive substances, methylbromide is unique in the point that it has both natural and anthropogenic sources. Based on the current knowledge, anthropogenic methylbromide, mainly for soil fumigant, is estimated to contribute to around one fifth of the total methylbromide in the atmosphere[1]. However there still remain considerable uncertainties in this estimate, and efforts are needed to reduce this uncertainty in order to make better plan to control the emission of methylbromide and other ozone-destructive substances and to prevent further destruction of ozone-layer in the stratosphere.

In the present research, a novel approach to elucidate the contribution of anthropogenic methylbromide was investigated, i.e., analysis of ^{14}C content in the methylbromide in the atmosphere. Anthropogenic methylbromide, from fossil fuels, is expected to contain virtually no ^{14}C while the natural one produced by biological activity is expected to contain modern carbon level $^{14}C(^{14}C/^{12}C=1.2 \times 10^{-12})$. It is expected, therefore, that one can estimate the contribution of anthropogenic source by analyzing ^{14}C ratios in the natural methylbromide. Major obstacle in this experiment is its extremely low concentration. It is generally reported that methylbromide concentration in the atmosphere is around 10 pptv level[1]. Even using accelerator mass spectrometry (AMS), one usually needs about 1 mg carbon samples for the analysis[2]. This means that at least 200,000m^3 air have to be sampled for the collection of enough amount of methylbromide; this is a formidable procedure considering the fact that a few tons of water vapor included in this volume of air has to be removed during sampling. If the necessary volume is reduced to two orders of magnitude, however, the above procedure will become much more realistic. In the present research, the following three themes were selected and tackled with for the analysis of ^{14}C in atmospheric methylbromide; 1) development of the analytical procedure for the ^{14}C analysis of 10 microgram level carbon samples, 2) development of large volume sampling device for the collection of methylbromide from 2000m^3 air, and 3) development of purification procedure of methylbromide from the trapped atmospheric compounds.

2. Experimental

Charcoal used for the trap of methylbromide was a molecular-sieve type, spherical active carbon. Silica gel and calcium chloride were chemical grade materials. Air sampling device was composed of stainless steel, alminium or glass. No plastic materials were used except for O-lings which are made of Viton@.

A purification system was composed of a Gerstel cooled injection system (CIS), a Hewlett Packard 6890 gas chromatograph with liquid nitrogen oven cooling system and FID detector, and a Gerstel preparative fraction collector (PFC).

^{14}C analysis was performed by the accelerator mass spectrometer (AMS) facility (made by National Electrostatics Corp., USA) called NIES-TERRA (National Institute for Environmental Studies – Tandem accelerator for Environmental Research and Radiocarbon Analysis)[3].

3. Results and Discussion

1) Small sample analysis by AMS

(a) Analysis of ^{14}C in commercial methylbromide

As a first step for the AMS analysis of environmental methylbromide, a sample preparation procedure was checked by analyzing ^{14}C in commercial methylbromide (Wako

Pure Chemicals). The sample was successfully oxidized to carbon dioxide and then reduced to graphite. The $^{14}C/^{12}C$ ratio of the sample was found to be 2.5×10^{-15}, showing that the commercial product was originated from fossil fuels.

(b) Improvements of precision and accuracy

The precision of the AMS analysis is theoretically limited by the total count, N, of ^{14}C (based on Poison distribution; i.e., relative standard deviation = $N^{-1/2}$). To establish pretreatment and analytical procedures for highest precision and accuracy, extensive modifications have been done, including change of design of graphitization tube, improvement of cathode wheel design and positioning system, increase of extraction voltage by changing the amprifier, and stripper canal change to a wider bore sized one (8 mm i.d. to 11 mm i.d.)[4]. After these modifications, satisfactory results could be obtained on a series of standards (IAEA C1 to C8; HOx II was used as a reference) on both precision (RSD=0.24 % for HOx II) and accuracy (all the data matched with the standard/reference values within RSD).

(c) Analysis of smaller amount of samples down to 100 microgram range[5]

A series of standards, i.e., HOx II and ANU sucrose, from 2 mg down to 0.1 mg carbon, were processed to graphite with fixed amount of iron powder (catalyst), and were analyzed by AMS. The results are shown in Figure 1 and 2. The raw $^{14}C/^{12}C$ data (standardized based on the 1.1 mg C HOx II data) showed a clear decline in accordance with the decrease of sample amount. The corrected value of ANU sucrose by the HOx II data with same carbon/iron ratio (Figure 2), however, is basically identical each other irrespective of the sample amount, showing that this isotopic fractionation can be corrected. Essentially the same phenomena were observed by changing carbon/iron ratio without decreasing the amount of samples, suggesting that some matrix effects in the ion source rather than during graphitization process are responsible on this phenomenon.

(d) New graphitization system for down to 10 microgram carbon samples

In the above experiment, background data, i.e., contamination level during graphitization step, were found to be around one to several micrograms modern carbon level[5]. This will seriously affect the analysis of 10 microgram level samples. In order to decrease this background level, and also to optimize the reaction condition, a smaller graphitization system in which the reaction volume was decreased from the original 22.1 ml to 3.7 ml, was made and a series of samples down to 10 micrograms carbon were processed. The performance will be evaluated in the next ^{14}C AMS measurement.

(e) Investigation on a gas ion source

The AMS system at NIES has another experimental ion source, called gas ion source, for the ionization of negative carbon ion from carbon dioxide gas directly[6]. This source is expected to be useful for the analysis of smaller amount of samples as it can handle with a small volume of CO_2 gas without processing it to solid graphite. Promising results of the

source were obtained on sensitivity, precision and accuracy by analyzing several CO_2 gases produced from standard[7]. Further study will be need for the efficient introduction of small volume of samples and for the reduction of tailing effects.

2) Development of large volume samplers

The adsorption and detachment conditions of active carbon beads for methylbromide were investigated. A small column packed with the beads at 5cm thickness retained methylbromide well even at room temperature, and the adsorbed methylbromide detached at 160 C within 30 min. From the result, detachment condition for the trap was set at 160 C for 2 hrs. However, the trap efficiency at room temperature in a large scale was found to be insufficient, and the cooling system for the trap and the water-removal system were developed.

A transportable trap system based on silica-gel primary water trap, four-stage secondary water trap cooled by dry ice, two stage final water trap packed with silica gel and calcium chloride cooled by dry ice, and an active carbon trap cooled by dry ice, was made. By sucking air using high-volume pump, up to 900 m^3 air could be passed within two days. The temperature of the trap was kept at –15 to –20 C during the operation. The GC/MS chromatogram of the trapped materials is shown in Figure 3 together with the chromatogram of authentic methylbromide. A small peak at m/z=94 and 96 corresponding to methylbromide was detected in the trapped material Although the total amount was not enough for the AMS analysis, the fraction is now being purified by the following system.

3) Purification of methylbromide

A combination of cooled injection system with a high resolution capillary gas chromatograph and 6 port trapping system (PFC) was established for the purification of methylbromide from the trapped material, and its performance was evaluated by purifying particular compound from the standards containing variety of n-alkanes. The results were quite satisfactory. Several improvements/modifications were done for the handling of volatile materials by the system, and the purification of trapped methylbromide is now underway.

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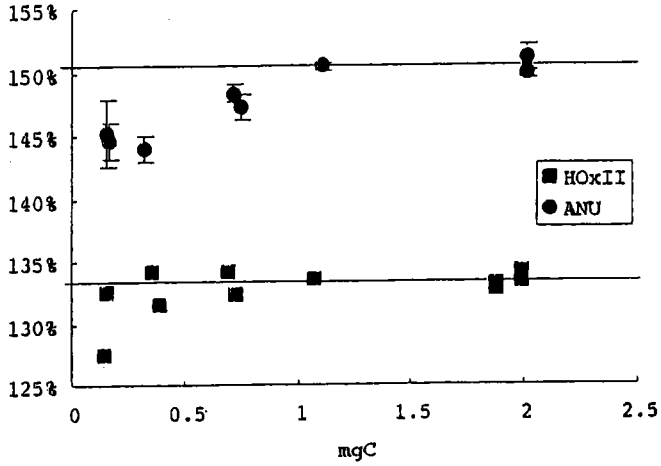

Figure 1 Changes of $^{14}C/^{12}C$ ratio of the standards, NIST HOx II and ANU Sucrose, in accordance with the sample amounts (expressed as the weight of carbon)

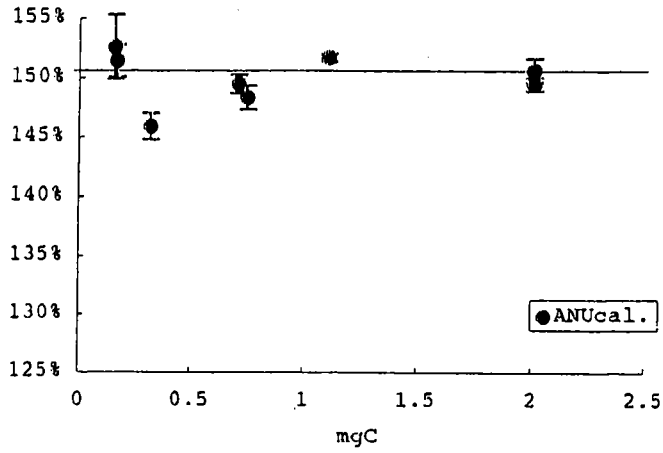

Figure 2 $^{14}C/^{12}C$ ratio of ANU Sucrose corrected with the data of HOx II produced under the same condition (same C/Fe ratio)

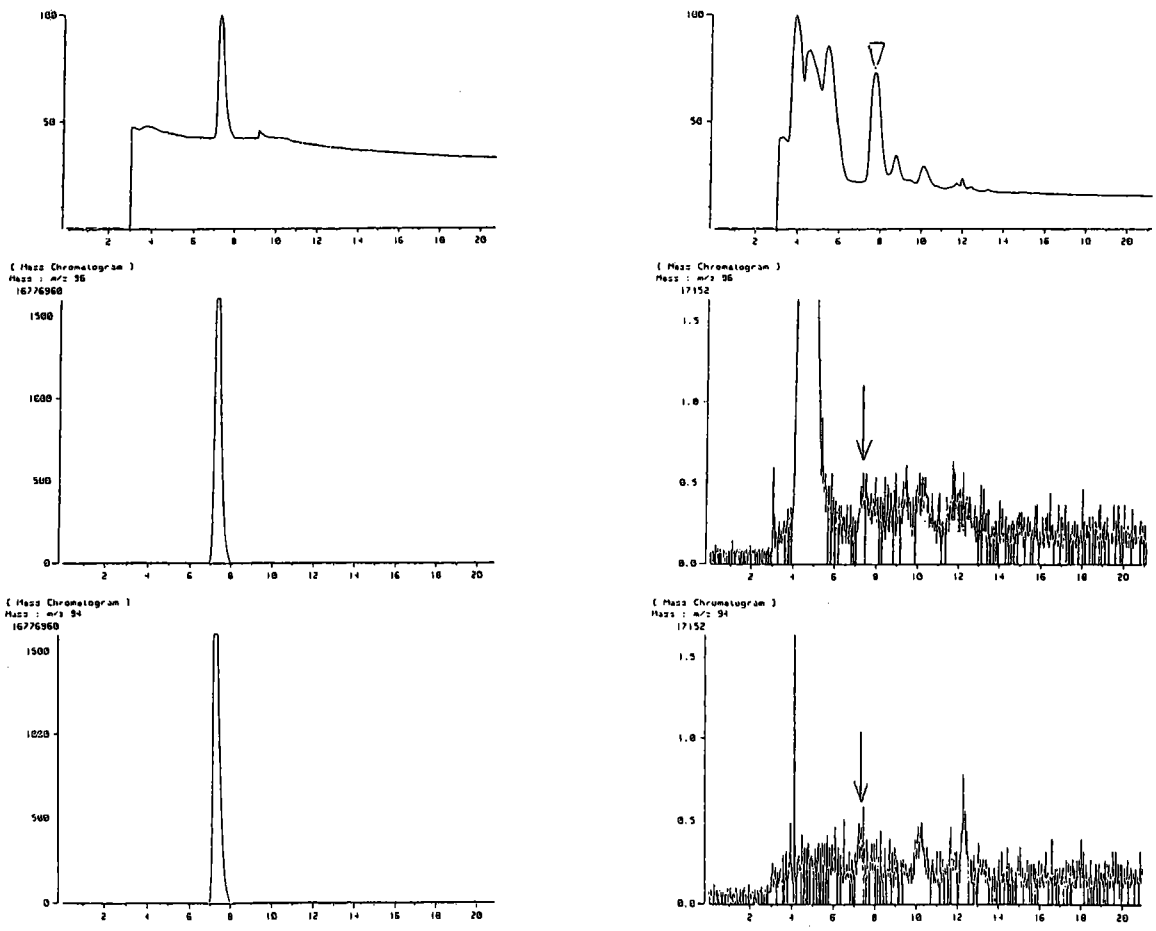

Figure 3 GC/MS chromatograms of authentic methylbromide (left) and trapped compounds (right) A small peak in the right middle (m/z=96) and right lower (m/z=94) figures correspond to methylbromide.