Development of the analytical method for sulfur isotope in SO_2 gas

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1. Introduction

Sulfur is a major source of acid deposition. Usually sulfur is emitted as SO_2 and it is oxidized to SO_4^{2-} in atmosphere. S isotopic analysis of water and particulate samples were conducted in many studies. But gaseous SO_2 was rarely used for isotopic study. Isotopic ratio of SO_2 is strongly influenced by emission source near the sampling point. Because most of SO_2 emitted far from sampling point is oxidized to SO_4^{2-} during transportation. It is possible to distinguish domestic emission from transboundary emission. Moreover, dry deposition processes of SO_2 and particulate SO_4^{2-} and their interactions with tree canopy could be discussed more precisely. Isotopic analysis of SO_2 is considered as a powerful method to investigate the behavior of S in the atmosphere and ecosystems. We studied about the analytical method for S isotope in SO_2.

2. Method

(1) Equipment

SO_2 concentration in Japan is very low (e.g. annual 0.02ppb at Sado). We need to collect air sample at least $1m^3$ that is the amount we can obtain 1.2mg of $BaSO_4$ precipitation enough for isotopic analysis. High volume air sampler is generally used to collect around $1m^3$ of air sample. It uses filter, so we examined filter collection of SO_2 by K_2CO_3 filter generally used to collect SO_2 in filter-pack method.

(2) Filters

We used quarts filter for particulate SO_4^{2-} and K_2CO_3 filter for gaseous SO_2 next to it. K_2CO_3 filter is made on the basis of EANET manual. But to get enough flow rate for high volume air sampler, the size of K_2CO_3 filter is larger (20×26 cm, same size with quarts filter) than the manual and already dried before sampling.

(3) Flow rate/leak test

Under flow rate 100~400 L/min in this system, we confirmed weather sampling can be carried out stably. And we checked leak using two K_2CO_3 filters.

(4) Sample treatment

On the basis of EANET manual, the sample was extracted with 0.05% H_2O_2aq and filtered. Then 2N HCl was added and concentrated to remove CO_3^{2-}. Next 1%(w/w)$BaCl_2$ was added. We filtered forming $BaSO_4$ precipitation. We examined the method to get $BaSO_4$ precipitation and to remove the components from K_2CO_3 filter.

3. Results

(1) Sampling and sample treatment

Sampling could be conducted under flow rate 100~400 L/min. Sampling efficiency was about 80%..

Several conditions to get $BaSO_4$ precipitation ware examined, it could be gotten by the method as below.

Filter was cut and ultrasonic extracted with 0.05% H_2O_2aq 30 minutes and filtered. 2.5 ml of 2N HCl was added and concentrated to around 10 ml. Then 1 ml of heated 1 %(w/w) $BaCl_2$ was added under pH 4~6. Next evaporated all solvent and added 10 ml of water. $BaSO_4$ precipitation was observed. After put for one night, the precipitation was separated by centrifuge 3,600 rpm for 10 minutes and we removed the solvent. The precipitation was washed twice by 10 ml of water and filtered. At last the filter was ashed for four hours in muffle furnace in 800 ℃ .

(2) Actual analysis

We used two K_2CO_3 filters and collected 2160.2 m^3 of air sample under flow rate 300 L/min. 3.80 mg of particular SO_4^{2-} and 0.89 mg (first) and 0.14 mg (second) of SO_4^{2-} from SO_2 were obtained. $\delta^{34}S$ of particular SO_4^{2-} was 8.64 ‰and that of SO_2 from the first filter was -1.54 ‰. The amount of precipitation from second filter was not enough for isotopic analysis. This difference was caused by effect of sea salt mainly. But nss- $\delta^{34}S$ of particular SO_4^{2-} was 4.78 ‰. It was still higher than SO_2. It suggested that nss- SO_4^{2-} contains both transboundary SO_4^{2-} and domestic SO_4^{2-}. According to the relevant literature, domestic SO_2 may have negative isotopic values because of imported oil from Middle East. Considering that this sampling was carried out in January, possible effect of transboundary SO_2 with higher isotopic values should also be taken into account for source identification of the collected SO_2.
We would like to discuss at the conference with the latest data.

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