September, 1987] © 1987 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 60, 3195—3198 (1987) 3195

The Iodine Content of Atmospheric Aerosols as Determined by the Use of a Fluoropore Filter® for Collection

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(Received February 7, 1987)

Atmospheric aerosols were collected onto a Fluoropore filter in order to determine the iodine by means of instrumental neutron activation analysis. The collection filter was found to be the best material among the nine filters examined, for it has the lowest blank values for iodine as well as for other halogens and sodium. The iodine concentrations in Tokyo were found to be 1.7—12.7 ng m^{-3}. Of the soluble iodine, 10% or less was in the form of IO_3^-.

Among the radionuclides released from nuclear fuel reprocessing plants, radioiodine is of special concern because of its high fission yield, its volatility, and its accumulation in the human thyroid. An extraordinary long half-life of ^{129}I (1.6×10^{7} y) necessitates the knowledge of the geochemical cycle of stable iodine in order to assess the behavior of ^{129}I in the environment and to estimate internal exposure through food ingestion.

The concentrations of aerosol iodine have been reported to be from several to several tens ng m^{-3}.[1–8] However, in most of the reported cases, the filter blank of iodine was not sufficiently low as compared with the amount of iodine collected on the filter, suggesting the potential inaccuracy of the reported values of the iodine concentration. This paper deals with the choice of an appropriate collection filter and the determination of stable iodine in atmospheric aerosols.

The present study examined nine filters for the blank iodine by means of instrumental neutron activation analysis; it demonstrated that the Fluoropore AF07P filter had the lowest iodine blank values. This filter was employed as the collection material for atmospheric aerosol in Tokyo. The aerosol was analyzed for iodine and some other elements, such as bromine, sodium, and aluminum, in order to obtain information regarding the environmental behavior of iodine.

Experimental

Three kinds of filters were analyzed by means of the instrumental neutron activation method: (a) filters prepared for standards, (b) filters for blank contents, and (c) filters with collected aerosols on them.

Standard Samples. Standard solutions of iodine, bromine, and chlorine were prepared by dissolving the respective potassium salts in twice-distilled water. For the iodine solution, the pH was adjusted to 8 with lithium hydroxide so as to prevent any iodine from being lost from the solution. Each of the solutions was impregnated uniformly onto a cellulose filter (Toyo 7) of the same size and shape as the other samples. For the standard of sodium and aluminum, powder of Standard Rock JG-1 (Porphyrite biotite granodiorite: Na, 2.51; Al, 7.53%), prepared by the Geological Survey of Japan, was caused to adhere onto a cellulose filter (Toyo 7) in the way described above.

Table 1. Filter Blanks Determined by Instrumental Neutron Activation Analysis

Filter	Element				
	I	Br	Cl	Na	Al
	ng cm^{-2}				
Sumitomo Fluoropore AF07P	0.044±0.021[a]	<0.08[b]	7.5± 0.6	1.2± 0.4	1.9± 0.1
Whatman 41	0.14 ±0.07	2.3±0.2	509 ±11	130 ± 6	22 ± 1
Toyo 7	0.21 ±0.05	4.8±0.2	322 ± 8	87 ± 4	5.2± 0.5
Toyo 51A	0.21 ±0.06	4.1±0.2	474 ±11	53 ± 4	3.1± 0.5
Gelman	<0.46	<1.4	216 ±16	183 ±11	—
Millipore HA	<0.54	2.5±0.6	1190 ±50	352 ±16	—
Sartorius SM	0.50 ±0.21	2.1±0.7	382 ±24	290 ±15	—
Nuclepore	2.4 ±0.5	503 ±7	34 ± 5	11 ± 3	2.5± 1.2
Palflex 2500QST	<1.7	<6.4	457 ±38	3890 ±60	32400 ±500

a) The ± values indicate the counting errors. b) Lower limit of detection.

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Filter Blanks. Table 1 covers the analyzed nine filters. The filters were subjected to the analysis without any particular treatment.

Filters with Collected Aerosols on Them. A Fluoropore AF07P filter (Sumitomo Electric Industries, 22.8×17.7 cm) was employed as the aerosol-collection material (aerosol collection efficiency: 99.9%).[9] Atmospheric aerosol was collected for from three to ten hours by means of a high-volume air sampler set on the rooftop of the Institute of Public Health, Tokyo (about 15 m above the ground).

Instrumental Neutron Activation Analysis. The filters were sealed in polyethylene bags previously washed with nitric acid. A number of bags were put into a polyethylene capsule and irradiated in the Rikkyo University TRIGA II Reactor at a flux rate of 1.5×10^{12} n cm^{-2} s^{-1} for 10 minutes. The samples were cooled for five minutes after irradiation and then counted by means of a Ge(Li) detector (volume: 55 cm^3) for five minutes.

Results and Discussion

Concentrations of Blank Filters. The blank contents of iodine and the other elements are listed in Table 1, which shows that Fluoropore AF07P (polytetrafluoroethylene) has the lowest blank iodine, 0.04 ng cm^{-2}, one or two orders of magnitude lower than any other filters analyzed. The same thing goes for the other determined elements. In addition, this filter is designed for air filtration and so it designed to have a small pressure drop (0.69 Pa s m^{-1}), as small as that of the commonly used quartz-fiber filter. All of these findings establish the appropriateness of this filter for collecting aerosol iodine.

S/N Ratio of Iodine Concentrations. The accuracy of the observed iodine concentrations is directly affected by the blank value of iodine for the filter employed. The accuracy is quantified as the S/N ratio, where signal and noise correspond to the iodine content per unit of area of the filter with collected aerosol on it and to the blank value of iodine for the filter itself. This ratio was applied to the present results and the previously reported data. When the blank value was not reported by the original authors, it was replaced in this work by the corresponding blank values.

The S/N ratios are listed in Table 2. The present work is characterized by a high S/N ratio, around 100, whereas most of the other works have had smaller ratios, 1—10. It follows that our measured iodine concentrations are exceedingly reliable.

Table 2. Values of Iodine in Aerosols vs. in Blank Filter (S/N ratio)

Filter	Blank / ng cm^{-2}	S/N ratio	Authors
Sumitomo Fluoropore AF07P	0.044[a]	97	This work S 1
		150	S 2
		51	S 3
		33	S 4
		160	S 5
		110	S 6
		240	S 7
Whatman 41	0.14[a]	≈100	W. John et al.[4]
		≈16	R. Dams et al.[10]
Delbag polystyren	<0.5	>30	N. K. Aras et al.[7]
Whatman 541	0.65	6.9	W. Maenhaut and W. H. Zoller[11]
Nuclepore	0.94	14.6	W. Maenhaut and W. H. Zoller[11]
	2.4[a]	≈5	K. A. Rahn et al.[6]
Millipore EA	1	≈1	R. A. Duce et al.[3]
Millipore AA	14	≈1	T. Kato et al.[12]

a) Determined by this work.

Evaluation of Iodine Volatilization in the Neutron Irradiation Process. Iodine loss by means of volatilization might be suspected in the process of neutron irradiation. In order to examine this problem, the iodine content was compared between two pieces of filters with collected aerosol. A filter with collected aerosol was cut into two pieces of equal size. One piece was impregnated with a lithium hydroxide solution before irradiation to prevent the iodine from volatalizing, while the other was not treated thus. Two samples, S2 and S3, were thus compared. The respective iodine contents for the treated and not-treated filter pieces were as follows: S2: 7.4±0.4 and 6.6±0.4; S3: 11.5±0.5 and 11.9±0.5 ng cm^{-2}. No significant difference between the treated and untreated pieces was noted, indicating that no such treatment was necessary to apply the samples in this study.

Atmospheric Concentration of Iodine in Aerosols. Table 3 shows the atmospheric concentrations of iodine in the aerosol collected in Tokyo. The iodine concentrations ranged between 1.7 and 12.7 ng m^{-3}. For the other elements, the factors of air to air fluctuation were one order, about the same as that of iodine. In the present work, samples were analyzed for several tens of cubic meters.

The obtained iodine concentrations are in the range of reported values not only for Tokyo but also for various sites in the world (ng m^{-3}): 3.2—15.4 (Tokyo),[8] 1.32—>24.6 (Hawaii),[1] 1.5—5.2 (Hawaii),[2] 0.3—9.4 (Alaska),[3] 4.7—10 (San Francisco),[4] 2—10 (Massachusetts),[5] and 2.2—5.1 (New York).[6]

Different Mechanisms of Iodine and Chloride in Aerosols. The principal source of iodine in the atmosphere has been reported to be marine.[13,14] However, soil-derived iodine and surface soil particles in air are collected together with airborne particles. For that reason, their iodine content can be calculated on the basis of the aluminum concentrations listed in Table 3, which range from 56 to 338 ng m^{-3}, assuming that the average contents of aluminum and iodine in

Table 3. Atmospheric Concentrations of I, Br, Cl, Na, and Al in Aerosols

Sample No.	Air volume	Date	Element				
			I	Br	Cl	Na	Al
	m^3		ng m^{-3}				
S1	230	14/7/83	7.5±1.1[a]	20.6±4.6	2510±120	2810±80	—
S2	525	29/10/83	5.0±0.3	14.6±1.3	789± 21	892±20	338±6
S2-T[b]			5.7±0.3	14.6±1.3	699± 20	827±19	335±6
S3	375	1/11/83	12.7±0.5	26.8±2.1	2160± 40	1970±40	265±6
S3-T[b]			12.4±0.5	24.0±2.1	2020± 40	1920±40	270±5
S4[c]	14.9	13/11/83	1.7±0.3	4.0±1.0	402± 19	187±14	56±3
S5	1230	12-13/3/84	4.6±0.5	—	—	—	—
S6	1345	21-22/3/84	3.0±0.3	—	—	—	—
S7	1172	23-24/3/84	7.3±0.6	—	—	—	—

a) The ± values indicate the counting errors. b) Treated with a LiOH solution before irradiation. c) Collected by means of a low-volume air sampler.

Table 4. Water-soluble-I and IO_3^--I in Aerosols

Sample No.	Total (T_I)	Water-soluble(S_I) (in IO_3^- form: S_{IO_3})	Residue(R_I)	Recovery(S_I+R_I)
	ng m^{-3}			
S5	4.6±0.5[a]	2.0 ±0.1 (0.19±0.03)	1.2±0.2	3.3±0.2
S6	3.0±0.3	1.4 ±0.1 (0.15±0.02)	1.4±0.3	2.8±0.3
S7	7.3±0.6	3.3 ±0.1 (0.10±0.03)	4.3±0.4	7.5±0.4

a) The ± values indicate the counting errors.

soil are 71 g kg^{-1} and 5 mg kg^{-1} respectively.[15] The calculated values are 0.024 (S2), 0.019 (S3), and 0.004 (S4) ng m^{-3} respectively. Thus, the contribution of soil particles to the total iodine content of aerosols is negligibly small. Most of the iodine in aerosols may thus be of marine origin.

The principal source of chloride in the atmosphere has been also considered to be marine, but recently there was appeared an anthropogenic supply of chloride, formed from the hydrogen chloride emitted from incinerating plants. At the same site over a period from June, 1979, to July, 1982, one of the present authors determined the particle-size distributions for chloride and other components in order to ascertain the seasonal variation of the chloride distribution.[16] On a monthly averaged basis, the chloride in the coarse-particle region was 78, 61, and 27% of the total chloride for July, October, and November respectively. On the basis of these values, the chloride concentration in aerosols of marine origin can be postulated. The calculated values of I/Cl (by weight) in marine-origin aerosols are 0.38—2.2×10^{-2}, but the I/Cl (by weight) in sea water is 3.2×10^{-6}.

If the behavior of iodine through transport is the same as that of chloride, the same order of magnitude of I/Cl in aerosols should be expected as in sea water, but the result indicates an extraordinarily high ratio (by a factor of about 10^3). This is in accord with similar observations of the total I/Cl ratios in aerosols and precipitation reported by many researchers[1,3,5,13] and strongly suggests a different behavior of iodine through transport from that of chloride.

A Simple Fractionation of Iodine Species. Atmospheric aerosol probably contains various sorts of iodine compounds. Aerosol iodine was tentatively fractionated into water-soluble and insoluble residues, and iodate was collected so as to be determined for the former fraction.

Two equivalent pieces were cut out of a sample filter in the manner described before. One piece was analyzed for total iodine (T_I). The other was subjected to ultrasonic extraction with water: iodine was determined for the water extract (S_I) and for the insoluble residue (R_I). This measurement was applied to three samples.

The extraction was satisfactory because no appreciable chlorine, all of which could be regarded water-soluble, was observed for the insoluble residue. The water-soluble fraction was further passed over the anion-exchange resin (Dowex 2-X8) to separate the iodate fraction (S_{IO_3}), which was them analyzed for iodate.[17,18]

Table 4 indicates that the recovery was almost satisfactory, that only 42—73% of the iodine was water-soluble, and that 10% or less of the soluble iodine was iodate, IO_3^-.

The existence of the IO_3^- form in aerosols was established in the present work, although there could be various kinds of iodine compounds in the atmosphere.

We are grateful to Mr. Hiroyuki Takagi for his help in the Gamma-ray measurements.

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