衛生化学
EISEI KAGAKU
34 (4) 335-342 (1988)

Concentration and Distribution of Uranium in Atmospheric Particulates

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(Received January 19, 1988)

The concentration and distribution of uranium in the atmosphere surrounding a nuclear fuel processing factory were examined. Uranium, scandium, and thorium in the atmospheric particulates were determined by instrumental neutron activation analysis (INAA).

The concentration of uranium in the atmosphere surrounding the factory was as low as that in other environments. Significant correlations ($p < 0.01$) between the concentration of uranium and the concentrations of scandium and thorium (derived from ground soil particles) were observed. Approximately 70% of uranium in the atmosphere was found in the coarse particles ($> 2 \mu\text{m}$ in diameter) using an Andersen high-volume sampler. Daily retention of uranium in the respiratory organs was estimated to range from 1.1 to 1.5 ng per person.

The calibration curve for uranium by INAA was linear between 0 and 500 ng. The limit of determination of uranium in the atmospheric particulates by this technique was 1.0 mg kg^{-1} . It was concluded that the cellulose filter was suitable for determination of uranium in atmospheric particulates by INAA because of its low blank value.

Keywords—uranium; atmospheric particulate; neutron activation analysis; particle size; Andersen sampler; respiratory organ; concentration; distribution

Introduction

The Clark number of uranium is 4×10^{-4} (ranking: No. 50). However, uranium is widely distributed in the earth. It has been suggested that manufacturing facilities related to atomic power generation or steam power generation are sources of atmospheric uranium pollution. These institutions are few, so that studies on uranium in the atmosphere have been scanty.¹⁻³⁾ On the other hand, the concentration, the behavior and the states of many elements in the atmosphere have been investigated by analyses of atmospheric particulates.⁴⁻¹⁰⁾ The effects on the respiratory organs have also been reported.⁷⁻¹⁰⁾ In this report,

the concentration of uranium in atmospheric particulates collected near a nuclear fuel processing factory and at other points within Kanagawa Prefecture as controls were determined by instrumental neutron activation analysis (INAA). For comparison, the soil elements, scandium, thorium, and iron, were determined simultaneously. Furthermore, the relation between these elements and their emission sources is discussed based on the particle size distribution obtained with an Andersen high-volume sampler. In addition, the retention of uranium in the respiratory organs was evaluated from the results of particle size fractionation.

Experimental

1. Reagents—Uranium Standard Solution: U_3O_8 (NBS · SRM 950 b, 99.94 %, 294.81 mg) was dissolved in nitric acid and adjusted to 500 ml with deionized water ($0.50 \text{ mg} \cdot \text{U ml}^{-1} \cdot 0.7 \text{ N HNO}_3$).

Reference Rock Samples: Reference rock samples JB-1 and JG-1 (Geological Survey of Japan)¹¹⁾ were used as standards of scandium, thorium, and iron for INAA.

Filter Papers: Uranium contents in three types of filter papers, a glass fiber filter (Gelman A-type), a cellulose filter (Toyo No. 5 A), and a quartz filter (Toyo QR 200), were determined.

2. Apparatus—Air Samplers: High-volume samplers (Kimoto Elec.) and an Andersen high-volume sampler (four stages plus a back-up filter, aerodynamic diameters >7.7 , $7.7-3.3$, $3.3-2.0$, $2.0-1.1$, and $<1.1 \mu\text{m}$) were used.

Gamma Ray Spectrometry: Gamma peaks from nuclides of interest were measured with a Ge (Li) detector (Camberra Co.) coupled with a pulseheight analyzer (Nuclear Data 2400 or ND 66).

Reactor: Samples were irradiated in the RSR (neutron flux, $\phi = 5 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$) of the Rikkyo University TRIGA II reactor.

3. Sample—The atmospheric particulates were collected with high-volume samplers (flow rate; $1.3 \text{ m}^3 \text{ min}^{-1}$) over the ground (1 m above ground level) in Yokosuka City and Odawara City, and at the roof of our laboratory (20 m above ground level, Yokohama City) and Kanagawa Prefectural Environmental Center (12 m above ground level, Hiratsuka City) from November, 1982 to December, 1983. The Andersen high-volume sampler was employed to collect atmospheric particulates graded according to particle size at the laboratory from November, 1984 to July, 1985, and then in Yokosuka City on August, 1985. Surface (0–10 cm in depth) soils were sampled at several points in Yokosuka City. The soils were sieved through a stainless steel sieve ($<0.053 \text{ mm}$ in diameter) after being dried at room temperature. Both the atmospheric particulates collected on the filters and the soils were ashed at 500°C in an electric furnace.

4. Method—Instrumental Neutron Activation

Analysis (INAA): Uranium, scandium, thorium, and iron in the atmospheric particulates were determined simultaneously by INAA. The ashed atmospheric particulates (10–100 mg) were taken and put in a double-folded polyethylene bag ($15 \times 20 \text{ mm}$), and then irradiated for 18 h in a cadmium capsule in the Rikkyo University TRIGA II reactor. After 7–10 d, gamma spectrometry was carried out. The peaks at 228.2 keV and 277.6 keV from ^{239}Np (T 1/2; 2.35 d) which is the daughter of ^{239}U (T 1/2; 23.5 min) was measured to evaluate uranium. Those of 889.4 keV from ^{46}Sc (T 1/2; 84.0 d), 311.9 keV from ^{233}Pa (T 1/2; 27.0 d) which is the daughter of ^{233}Th (T 1/2; 23.4 min), and 1098.6 keV from ^{59}Fe (T 1/2; 45.0 d) were also determined. Uranium and thorium in the soils were determined by this technique in the same way.

Results and Discussion

1. Filter Paper for Collecting Atmospheric Particulates

A glass fiber filter on a high-volume sampler is usually used for collecting atmospheric particulates. However, there are large quantities of sodium, potassium and other impurities in glass fiber filters. So they would not be suitable for determination of uranium by INAA. There are few reports about uranium contents in filters.^{12,13)} In this study, uranium contents in three typical filters, a glass fiber filter, a cellulose filter and a quartz filter, were determined by INAA. Scandium, thorium and iron contents in a cellulose filter were determined simultaneously. The results and literature values are shown in Table I.

Uranium contents in the glass fiber filter, the quartz filter, and the cellulose filter were 2.6 ng cm^{-2} , 10.0 ng cm^{-2} , and $8 \times 10^{-3} \text{ ng cm}^{-2}$ respectively. The cellulose filter was suitable for determination of uranium because of its low blank value. The contents of scandium and thorium in the cellulose filter, $6 \times 10^{-3} \text{ ng cm}^{-2}$ and $2 \times 10^{-3} \text{ ng cm}^{-2}$, respectively, were of the same order as that of uranium. The

TABLE I. Uranium, Scandium, Thorium and Iron Contents in Some Typical Filters

Filter material	Contents (ngcm ⁻²)			
	Uranium	Scandium	Thorium	Iron
Cellulose (Toyo No. 5 A)	8×10^{-3}	6×10^{-3}	2×10^{-3}	57.0
Glass Wool (Gelman A-type)	2.6	-	-	710 ^{a)}
Quartz (Toyo QR 200)	10.0	-	-	110 ^{b)}

a) atomic absorption spectrometry (AAS).¹⁴⁾b) AAS; Palleflex.¹⁴⁾

content of iron, 57.0 ngcm⁻², was one order lower than the literature values for glass fiber and quartz filters.¹⁴⁾ The use of a cellulose filter with a high volume sampler may result in severe pressure drops.¹²⁾ The result obtained from an investigation of the relation between the sampling times and the flow rate showed the flow rate had decreased to 70 % at 8 h. Thus, operation of the sampler was terminated at 8 h.

2. Uranium in Atmospheric Particulates by INAA

Fluorometric analysis is the most popular method for the determination of uranium in environmental samples. INAA, however, can simultaneously determine some co-existing elements in the samples. As shown in Fig. 1, the calibration curve for uranium by INAA was linear between 0 and 500 ng. Figure 2 shows the gamma ray spectra of the atmospheric particulates measured for 2000 s. The peaks due to ²³⁹Np (the daughter of ²³⁹U), ²³³Pa. (that of ²³³Th), ⁴⁶Sc, and ⁵⁹Fe were observed clearly.

In the case of determination of certain elements in rocks or soils by INAA, ²⁴Na can cause serious interference. However, the activity of ²⁴Na irradiated in a cadmium capsule with epithermal neutrons is relatively decreased because uranium is one of elements with a high cross-section of resonance absorption.¹⁵⁾ In a cadmium capsule, the activity of ²⁴Na decreased to about 1/23 of that without a cadmium capsule. When 20 mg of atmospheric particulates

Fig. 1. Calibration Curve for Standard Uranium by Neutron Activation Analysis

Fig. 2. Gamma Ray Spectra of Atmospheric Particulates Irradiated for 18 h with Neutrons

was measured for 2000 s, the limit of determination of uranium by this technique was 1.0 mg kg⁻¹.

3. Concentration of Uranium in Atmospheric Particulates Obtained near the Nuclear Fuel Processing Factory

To evaluate uranium pollution derived

TABLE II. Concentrations of Uranium, Scandium, Thorium and Iron in Atmospheric Particulates at Various Points

Point	Uranium (ngm ⁻³)	<i>n</i>	Scandium (ngm ⁻³)	<i>n</i>	Thorium (ngm ⁻³)	<i>n</i>	Iron (μgm ⁻³)	<i>n</i>
Yokosuka N ^{a)}	0.11±0.05	10	0.68±0.52	9	0.27±0.20	9	3.4±1.6	9
Yokosuka S ^{b)}	0.14±0.08	10	0.82±0.63	10	0.34±0.34	10	3.9±2.3	10
Yokohama	0.11±0.05	5	1.43	2	0.28±0.11	5	4.8	2
Hiratsuka	0.11	2	1.13	2	0.14	2	3.1	2
Odawara	0.13	2	0.85	2	0.40	2	4.0	2
Literature value	0.090 ^{b)} (0.07—0.11)		0.3 ^{b)} (0.08—0.64)		0.02—1.24 ^{d)}		0.05—12.4 ^{d)}	

a) N: north of the factory.

b) S: south of the factory.

from the factory, the concentrations of uranium, scandium, thorium and iron in samples col-

Fig. 3.—A

Fig. 3.—B

Fig. 3.—C

Fig. 3. Relation between Concentration of Particles and Concentration of Uranium (A), Concentration of Uranium and Concentration of Scandium (B), and, Concentration of Uranium and Concentration of Thorium in Atmospheric Particulates (C)

A: $Y=2.0X+23.1(r=0.953)$, B: $Y=7.7X-102(r=0.869)$,
C: $Y=3.5X-120(r=0.935)$.

lected near the factory and elsewhere from November, 1982 to December, 1983 were evaluated. In Yokosuka City, two sampling points, located north and south of the factory, were selected. In this area, the prevailing wind is northwest. Yokohama, Hiratsuka, and Odawara City were used as control points. The concentrations are shown in Table II.

Uranium concentration to the north of the factory was at nearly the same level as that to the south. Moreover, there was little difference in uranium concentration between the atmosphere surrounding the factory and those of samples from Yokohama City, Hiratsuka City and Odawara City; all were about 0.1 ngm^{-3} . Furthermore, the concentrations of scandium, thorium, and iron in the atmosphere surrounding

the factory were approximately equal to those at other points in Kanagawa Prefecture. The concentrations of these elements were similar to the natural levels reported by Hithaya *et al.*³⁾ and Mamuro and Mizohata.⁴⁾

4. Sources of Uranium in the Atmosphere

4-1 Correlation between the Concentration of Uranium and the Concentrations of Other Elements—

The correlation between

TABLE III. Distribution of Uranium and Other Elements in Size-Fractionated Atmospheric Particulates

Sample	Volume	Dust	Uranium		Scandium		Thorium		Iron	
	(m^3)	(μgm^{-3})	(pgm^{-3})	(%)	(pgm^{-3})	(%)	(pgm^{-3})	(%)	(ngm^{-3})	(%)
1985.4/30—5/8 (Yokohama)										
Stage 1		18.1	45	42.9	388	47.7	165	37.8	898	38.2
2		7.6	21	20.0	144	17.7	82	18.8	444	18.9
3		4.7	11	10.5	90	11.0	53	12.2	296	12.6
4		2.5	7	6.6	47	5.8	54	12.4	241	10.3
Back-up filter		8.8	21	20.0	145	17.8	82	18.8	471	20.0
Total	2294	41.7	105		814		436		2350	
1985.5/10—5/28 (Yokohama)										
Stage 1		9.1	21	39.6	172	42.7	41	33.3	485	43.0
2		3.5	8	15.1	77	19.1	18	14.7	181	16.0
3		1.9	7	13.2	42	10.4	14	11.4	148	13.1
4		1.0	6	11.3	25	6.2	10	8.1	97	8.6
Back-up filter		4.5	11	20.8	87	21.6	40	32.5	217	19.2
Total	3754	19.9	53		403		123		1128	
1985.6/4—6/27 (Yokohama)										
Stage 1		13.3	28	32.9	278	39.6	80	28.6	1500	41.3
2		5.7	21	24.7	118	16.8	56	20.0	800	22.0
3		3.1	8	9.4	76	10.8	27	9.6	300	8.3
4		2.3	10	11.8	87	12.4	51	18.2	350	9.6
Back-up filter		7.5	18	21.2	143	20.4	66	23.6	680	18.7
Total	1701	31.8	85		702		280		3630	
1985.7/1—7/28 (Yokohama)										
Stage 1		6.2	12	50.0	138	45.8	39	38.2	610	43.6
2		3.3	4	16.7	64	21.3	18	17.7	200	14.3
3		1.2	2	8.3	26	8.6	10	9.8	200	14.3
4		1.2	2	8.3	24	8.0	10	9.8	170	12.1
Back-up filter		4.2	4	16.7	49	16.3	25	24.5	220	15.7
Total	5281	16.2	24		301		102		1400	
1985.8/6—8/10 (Yokosuka)										
Stage 1		12.4	20	54.1	237	51.3	78	54.5	1030	51.0
2		4.8	8	21.6	86	18.6	21	14.7	370	18.3
3		2.3	2	5.4	37	8.0	12	8.4	200	9.9
4		2.0	2	5.4	29	6.3	8	5.6	130	6.4
Back-up filter		3.5	5	13.5	73	15.8	24	16.8	290	14.4
Total	3198	25.0	37		462		143		2020	

Four stages plus a back-up filter : aerodynamic diameters >7.7 , $7.7-3.3$, $3.3-2.0$, $2.0-1.1$ and $<1.1 \mu\text{m}$.

the concentration of uranium and the concentrations of scandium and thorium (so-called soil elements⁸⁾) were examined (Fig. 3). There were clear correlations at the 1% level of significance. Further, the concentration ratio of uranium to thorium (Th/U) in the atmosphere, 2.1 ± 0.5 (mean $\pm$ S.D., $n=9$), was approximately equal to that in the surface soils sampled in Yokosuka City, 2.5 ± 0.4 ($n=9$). Thus, it was suggested that the behavior of uranium in

the atmosphere was the same as that of scandium and thorium.

4-2 Uranium Concentrations in Size-Fractionated Atmospheric Particulates—In order to determine the sources of elements in the atmosphere, it is important to know the concentrations in particulates of various size fractions. Particle size distributions in the atmosphere at urban sites were found to be generally bimodal, with peaks at 4–5 μm and

Fig.4.—A

Fig. 4.—B

Fig. 4.—C

Fig. 4. Ratios and Concentrations of Some Elements in Coarse Particles and Fine Particles in Atmospheric Particulates

A : uranium, B : scandium, C : thorium.

Ratio (left bar) : : coarse particles ($>2\ \mu\text{m}$ in diameter), : fine particles ($<2\ \mu\text{m}$ in diameter).

Concentration (right bar) : : coarse particles ($>2\ \mu\text{m}$ in diameter), : fine particles ($<2\ \mu\text{m}$ in diameter).

lower than $1\ \mu\text{m}$ in diameter.⁷⁾ Size distributions of elements have been classified into three groups:⁸⁾ 1) a peak only at $4\text{--}5\ \mu\text{m}$ in diameter, 2) peaks at $4\text{--}5\ \mu\text{m}$ and in particles smaller than $2.1\ \mu\text{m}$ in diameter, 3) a peak only in particles smaller than $2.1\ \mu\text{m}$ in diameter. Concentrations of uranium, scandium, thorium, and iron in size-fractionated atmospheric particulates in Yokohama City and Yokosuka City collected from November, 1984 to July, 1985 were determined. Concentrations are shown in Table III.

As shown in the table, there is no linearity between the sampling period and the collected volume, because these samplings were not done continuously.

Nearly 70% of uranium in the atmosphere was in particles above $2\ \mu\text{m}$ in diameter (coarse particles) and 40–50% was in particles above $7\ \mu\text{m}$ in diameter collected on the first stage of the Andersen high-volume sampler. The

distributions of scandium, thorium, and iron derived from the ground soil particles blown into the air were similar to that of uranium in Yokosuka City, where the factory is, and that in Yokohama City (control). The concentrations of the elements and the concentration ratios of the coarse particles to the fine particles in nine samples collected with the Andersen high-volume sampler are shown in Fig. 4. In this figure, the ratios are shown on the left and the concentrations of elements are showed on the right.

Generally, coarse particles, derived from natural sources such as soils, and fine particles derived from artificial emission sources.⁸⁾ As shown in Fig. 4 A, approximately the same ratio was seen in nine samples even though the concentrations were different. These results suggested that the sources of uranium in the atmosphere were the same in all the areas examined.

5. Evaluation of the Retention of Uranium in the Respiratory Tract

The retention of uranium in the respiratory organs was estimated on the basis of the above results and the curve of retention rate.¹⁶⁾ It was calculated that the total retention of uranium in the human respiratory organs might be 1.1 to 1.5 ng per person per day. Particles bellow 1.1 μm in diameter are collected efficiently in the lungs. As the particle size distribution bellow 1.1 μm in diameter could not be determined with the Andersen high-volume sampler, the curve of particle size and retention rate was used. The retention of uranium present in particles of bellow 1 μm size in the lungs was estimated to be 0.1 to 0.3 ng from the retention curve, regarding the maximum rates, as 60 %, and the minimum rate as 25 %.

Conclusions

1. The calibration curve for uranium by INAA was satisfactorily linear between 0 and 500 ng. The limit of determination of uranium by this technique was 1.0 mg kg^{-1} .
2. A cellulose filter was suitable for determination of uranium in the atmosphere by INAA because of its low uranium content, $8 \times$

$10^{-3} \text{ ng cm}^{-2}$, compared with a glass fiber filter or a quartz filter.

3. Significant correlations between uranium and the soil-derived elements scandium and thorium were found.

4. Approximately 70 % of uranium, scandium, thorium and iron in the atmosphere was found in the coarse particles ($>2 \mu\text{m}$ in diameter) using the Andersen high-volume sampler, so that the major source of uranium in the atmosphere is considered to be the ground soil particles.

5. The daily total retention of uranium in the human respiratory organs was estimated to range from 1.1 to 1.5 ng per person, calculated from the uranium concentrations of size-fractionated atmospheric particulates and the retention rates of particles of various sizes in the human respiratory tract.

Acknowledgement The authors are indebted to the staff of the Institute for Atomic Energy of Rikkyo University for use of the reactor and the staff of Kanagawa Prefectural Environmental Center for sampling the atmospheric particulates.

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