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The Neutron Activation Analysis of Mercury in Soil

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A radiochemical neutron activation procedure has been designed for the determination of mercury in soils. After the irradiation of 100 mg of soil it was decomposed with a hydrofluoric and perchloric acid mixture in a platinum crucible, and the mercury was separated radiochemically by solvent extraction from sulfuric acid·potassium iodide media into toluene, followed by precipitation as a sulfide. The radioactivity of ^{197}Hg was measured by using a Ge(Li) detector. The chemical yield, as determined by atomic absorption spectrophotometry, was high enough, and the precision was satisfactory. The detection limit is estimated to be 1—2 ppb [(1—2) $\times 10^{-10}$ g] by this method. The above procedure was applied to the determination of mercury in soils sampled in the Kumamoto and Minamata districts and in between.

The mercury contamination of soil has no less serious an influence on man and his ecosystem than do those of foodstuff, air, and water, so its detailed investigation should be pushed forward. Neutron activation analyses for mercury in various materials have been reported by a number of workers;[1)] however, such analyses for mercury in soil have been few.[2)]

An important step to improve the accuracy and detection limits in the activation analysis of mercury in matrices consists of radiochemical separation. Various methods have been used for separation by many investigators,—for instance, distillation or evaporation,[3–7)] solvent extraction,[8,9)] isotopic exchange,[5)] anion exchange,[10–14)] precipitation,[2,14–16)] deposition,[15,17)] and adsorption.[6)] The present authors investigated a solvent extraction method of mercury with toluene from sulfuric acid·potassium iodide-treated samples to achieve a complete, satisfactory separation.[18)] The procedure was studied in order to determine whether or not it was satisfactory in precision and detection limits. In addition, it was relatively simple and quick. The atomic absorption method was used for the determination of the chemical yield as an auxiliary means.

Because of the volatile nature of mercury and its compounds, the problem of mercury loss from a heated matrix is important; in this study it was checked by means of an atomic absorption method.

The activities of either ^{197}Hg or ^{203}Hg have generally been used for the determination. Because of the more convenient half-life, cross section, and target abundance of ^{197}Hg than ^{203}Hg (64 h, 3.1×10^3 b, 0.146% and 47 d, 4.9 b, 29.8% respectively),[19)] the γ-ray of ^{197}Hg and the X-rays of ^{197}Au were measured by the present procedure.

After the method mentioned above had been established, the contents of mercury in 11 soil samples from Kumamoto and Minamata and in between were determined and discussed.

Experimental

Irradiation Facilities, Instruments, and Reagents. The samples and standards were irradiated in the S-Pipe of the JRR-4 Reactor at the Japan Atomic Energy Research Institute. The thermal neutron flux was 2×10^{13} n cm^{-2} s^{-1}. The activities were measured with a 41.5 cm^3 Ge(Li) detector (ORTEC) coupled to a 4096-channel pulse-height analyzer (Toshiba USC-1 model 10). A Perkin-Elmer model 303 atomic absorption spectrophotometer equipped with a recorder readout was used. The reagents used were of the JIS special grade from Wako Pure Chemical, unless otherwise mentioned. Doubly distilled water was used for the pre-irradiation procedure.

Procedure. *Sample Preparation and Irradiation*: All of the soil samples were taken from 30 cm deep, dried in the atmosphere at room temperature, ground in an agate mortar, and finally passed through a JIS 125 sieve. Into a quartz vial (5 mm$\phi \times 4$ cm), 100 mg of a soil sample was placed. A standard consisted of 5.0×10^{-7} g of mercury (in the form of mercury (II) acetate in 0.1 M acetic acid), which was transferred to a quartz vial with a micropipet and absorbed onto 100 mg of silica powder (from E. Merck, Germany). All the vials were sealed with an oxygen-city gas torch. The above procedure was performed in a dustless room throughout, and the mortar, the quartz vials, and the glassware were washed with *aqua regia* and water prior to use. A standard and five samples were packed together in a polyethylene capsule; this unit was irradiated for 5 h and then left for 24 h in order to permit the short-lived nuclides to decay.

Decomposition and Radiochemical Separation: The main components of the soil seemed to be mineral granules and humus, to which mercury as a contaminant seemed to adhere *via* natural water beside that involved in the soil in nature. In any case, it was necessary to decompose the components completely for the following extraction procedure.

Irradiated vials were washed with 6 M nitric acid, water, and acetone before opening. The contents were then thoroughly transferred to a 20 ml platinum crucible. Onto the matrix 1.00 mg of mercury (in the form of mercury(II) chloride in 0.1 M hydrochloric acid) was added as a carrier. With 2 ml of 46% hydrofluoric acid and 1.5 ml of 60% perchloric acid, the sample was decomposed at 160 ± 5 °C for 45 min in an oil bath. Then 1 ml of a saturated boric acid solution was pipetted into the crucible, and the mixture was heated again for 5 min. The decomposed sample solution was transferred to a 50 ml volumetric flask, and subsequently diluted with 15 ml of 20 M sulfuric acid, 1 ml of a 5.0×10^{-2} M potassium iodide solution, and water to make 6.0 M sulfuric acid and a 1.0×10^{-3} M potassium iodide solution. The mixture was transferred to a 100 ml separatory funnel. With 10 ml of toluene added, it was shaken for 3 min by means of a mechanical shaker and then allowed to stand. After the aqueous phase had been discarded, the organic phase was washed with a 50 ml portion of the aqueous 6.0 M sulfuric acid and a 1.0×10^{-3} M potassium iodide solution. A 1 ml aliquot of the organic phase was taken for atomic absorption spectrometry in order to ascertain the recovery. With 50 ml of a 200 μg/ml mercury

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solution (in the form of mercury(II) chloride in 0.1 M hydrochloric acid), radioactive mercury was stripped from the remaining phase, precipitated with hydrogen sulfide, and filtered by means of suction on 25 mmϕ filter paper (Toyo Roshi No. 5C).

A standard sample was processed in a manner similar to that used for soil samples.

γ-Ray Spectrometry: The filter paper with the precipitates was heat-sealed in a polyethylene sheet, and its radioactivity was measured with a Ge(Li) detector for 1000 s. For quantitations, conventional peak integration and background subtraction were applied to the 68.8 keV X-ray from ^{197}Au, and to the composite peak of the 77.6 keV γ-ray of ^{197}Hg and 78.0 keV X-ray from ^{197}Au.

Results and Discussion

The Determination of Mercury Retention after Decomposition. To determine mercury retention after decomposition process, 1 ml of a mercury(II) chloride solution (10.0 mg Hg/ml), 2 ml of 46% hydrofluoric acid, and 1.5 ml of 60% perchloric acid were added to 100 mg of soil in a 20 ml platinum crucible. Covered, it was heated in an oil bath at an appropriate temperature until the contents appeared to be transparent; then the contents were cooled to room temperature and diluted to 50 ml in a volumetric flask with water. The mercury concentration was subsequently measured by atomic absorption spectrometry.

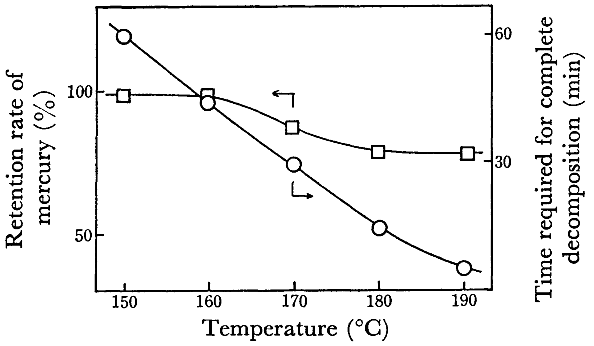

Fig. 1. Retention rate of mercury after complete decomposition of soil in a platinum crucible and the time required for *vs.* temperature. The initial contents: 100 mg of soil, 10.0 mg of mercury in the form of mercury-(II) chloride, 2 ml of 46% hydrofluoric acid, and 1.5 ml of 60% perchloric acid. Determined with an atomic absorption method.

As is shown in Fig. 1, the retention rate of mercury (in the form of mercury(II) chloride) after the complete decomposition of the soil was 98% up to 160 °C and dropped toward higher temperatures, and the time required for complete decomposition became approximately 15 min shorter with each 10 °C elevation in temperature. This indicates that the optimum conditions for complete decomposition without loss were at 160 °C for 45 min.

The Determination of Extraction Curve of Mercury(II). The extractability of mercury(II) was examined as follows. To a 10 ml graduated test tube with a ground stopper, 0.5 ml of a mercury(II) chloride solution (1.00 mg Hg/ml) and appropriate volumes of 20 M sulfuric acid and either a 5.0×10^{-3} M or a 5.0×10^{-1} M potassium iodide solution were added. The contents were diluted to the 5 ml mark with water. With 5 ml of toluene added, the tube was dipped in a water bath at 20 °C for 15 min, shaken vigorously by hand for 3 min, and then allowed to stand. Each phase was then separated, centrifuged, and submitted to atomic absorption measurement.

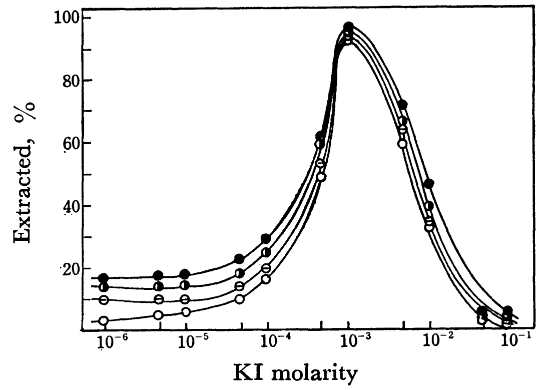

Fig. 2. Extraction curves of mercury into toluene as functions of potassium iodide and sulfuric acid concentrations. The initial mercury concentration: 100 μg/ml in the form of mercury(II) chloride in aqueous phase. Temperature: 20 °C. Determined with an atomic absorption method. ●: 8.0, ◑: 6.0, ⊖: 4.0, ○: 2.0 M sulfuric acid.

The extraction curves of mercury in Fig. 2 indicate that the maximum extraction was obtained at approximately 1×10^{-3} M potassium iodide. This concentration is somewhat higher than that reported by Byrne and Gorenc.[18] The differences in initial mercury concentration and temperature between the present method and that in the literature are 100 μg/ml, and 20 °C, and 1 μg/ml, and 25 °C, respectively.

Examples of the γ-spectra during and after the radiochemical separation procedure are given in Figs. 3 and 4 respectively. Figure 3 shows a typical spectrum of the extracted toluene phase, while Fig. 4 shows one of the final mercury sulfide precipitate. Both spectra indicate typical photopeaks of 68.8 keV (^{197}Au X-ray),

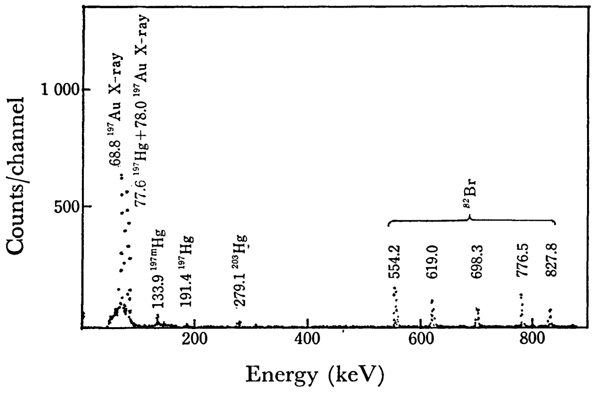

Fig. 3. An example of γ-ray spectrum of the toluene extract. Thermal neutron flux: 2×10^{13} n cm^{-2} s^{-1}, Time of irradiation: 5 h, Time of decay: 30 h, Counting time: 1000 s. Measured with a Ge(Li) detector.

Table 1. Mercury contents in soils collected at 11 spots between Kumamoto and Minamata cities

Spot No.	1	2	3	4	5	6	7	8	9	10	11
Mercury found (ppm)	1.87	1.01	0.74	0.84	1.03	1.32	1.25	10.3	4.9	0.36	6.6

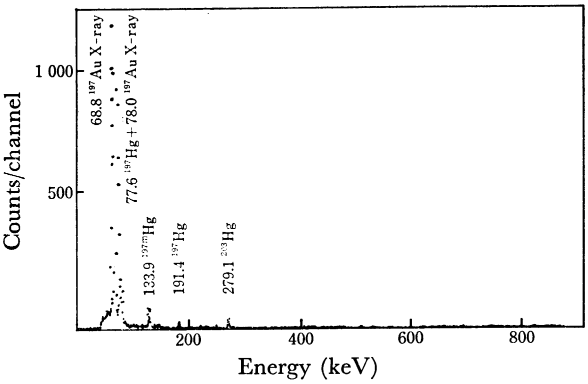

Fig. 4. An example of γ-ray spectrum of the final mercury sulfide precipitate. Time of decay: 32 h. Other conditions were the same as in Fig. 3.

77.6 keV (^{197}Hg) +, 78.0 keV (^{197}Au X-ray), and others emitted by radioactive mercuries.[20] The probable spectral overlaps of these photopeaks with those emitted by ^{169}Yb (63.5 keV), ^{182}Ta (67.7 keV), ^{153}Sm (69.6 keV), and ^{187}W (71.9 keV) were considered, but they gave no problem in this work because no others emitted by any nuclide could be detected in the spectra. In Fig. 3 there exist photopeaks emitted by ^{82}Br, which might be extracted in an oxidized form. The peak heights of radioactive mercury in Fig. 4 were about twice those in Fig. 3 as a result of the improvement in the self-shielding and geometry.

The amount of mercury in the soil was calculated by means of the following equation;

Mercury contents in soil (ppm)

$$= 5.0\times 10^2 \times \frac{1}{W_x}\cdot\frac{C_x\varepsilon_s}{C_s\varepsilon_x}\exp\{1.08\times 10^{-2}\times(t_x - t_s)\}$$

where W_x is the weight of irradiated soil (mg),

C_x and C_s are the counts/1000 s of a sample and a standard respectively,

ε_x and ε_s are the absorbances of a sample and a standard with atomic absorption respectively, and

t_x and t_s are the elapsed times after the irradiation of a sample and a standard respectively (h).

The procedure described above was applied to the determination of the mercury contents in the soil sample of Spot No. 7 in Table 1, with irradiation in a capsule. The average mercury concentration, based on five replicate analyses, was 1.25 ppm, with a relative standard deviation of 3.7%. The precision was thus satisfactory. The recovery averaged 82%. The detection limit (twice the square root of the background counts under the peak of interest) is estimated at 1—2 ppb [(1—2) $\times 10^{-10}$ g in 100 mg of a sample] by this method.

Furthermore, the proposed procedure was applied to the determinations of the mercury contents in 11 soil samples, which were collected on March 3, 1975, along National Route 3 between Kumamoto and Minamata cities. Duplicate analyses were made on each of the samples except for Spot No. 7; the results are summarized in Table 1. All of the procedure after irradiation was done in two days by two persons. The average of 11 determinations was 2.7 ppm, extremely high compared to those in the literature.[2] The results show that the contamination of soil with mercury has spread all over the area.

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