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Determination of Trace Amounts of Iron, Nickel, and Tin in Zircaloys by X-Ray Fluorescence Spectrometry after Coprecipitation with Hexamethyleneammonium Hexamethylenedithiocarbamate

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A rapid and precise X-ray fluorescence spectrometry is proposed for the determination of the trace amounts of iron, nickel, and tin in zircaloys. A zircaloy sample was dissolved in a mixture of tetrafluoroboric acid and hydrochloric acid, diluted to a definite volume with water. After the addition of 3 cm^3 of 1% (*R*,*R*)-tartaric acid solution as an auxiliary chelating agent and 50 μg of cobalt as an internal standard to an aliquot (less than 200 μg of tin) of the solution, the pH was adjusted to 2 with ammonia solution and 3 cm^3 of 1% hexamethyleneammonium hexamethylenedithiocarbamate (HMA–HMDC) was added. The resulting HMA–HMDC complexes were collected on a membrane filter and dried. The contents of iron, nickel, and tin in zircaloys were calculated by the calibration curves with the ratios of $K\alpha$ intensities for each element to that for cobalt. The coefficients of variation (5 results for each metal) were 2.16, 0.63, and 1.52% for 10, 10, and 200 μg of iron, nickel, and tin, respectively. The analytical results of iron, nickel, and tin in zircaloy samples by the proposed method agreed with the certified values.

Various methods for the determination of chromium,[1] iron,[2] nickel,[3] and tin[4] in zircaloys, including atomic absorption spectrometry[5] for the former three elements, have been reported. Polarographic methods[6,7] for tin and spectrographic methods[8,9] for chromiun, iron, and nickel, have suffered from the interference of lead and from relatively high coefficients of variation, respectively. In the determination of tin by a volumetric[10] or coulometric method,[11] meticulous attention must be given to the reduction of tin(IV). X-Ray fluorescence analysis using an "oxide"[12] or "extraction" method[12] needs troublesome treatment and one using a "nondestructive" method[13] can be easily influenced by a matrix effect or by segregation.

The present paper will describe the determination of trace amounts of iron, nickel, and tin in zircaloys by coprecipitation-X-ray fluorescence spectrometry with hexamethyleneammonium hexamethylenedithiocarbamate (shortened to HMA–HMDC), which didn't react with the zirconium matrix but formed stable complexes with these trace elements in a lower pH range. Cobalt was also used as an internal standard in order to improve the accuracy.

Experimental

Apparatus. The X-ray fluorescence measurements were performed using a Rigaku-Denki Model KG-X with a Philips tungsten target tube; lithium fluoride ($2d$=4.028 Å) was used as the analyzing crystal. The detection of the fluorescence X-rays was accomplished using a scintillation counter. The HMA–HMDC complexes of chromium, iron, nickel, tin, and cobalt were collected on membrane filters TM-80 (25 mm in diameter, 0.8 μm pore size). The pH measurements of sample solutions were carried out using a Hitachi-Horiba M-5 pH meter with a glass electrode.

Reagents. Chromium(VI) standard solution: A 1000 μg/cm^3 solution was prepared by dissolving potassium dichromate (analytical-reagent grade) with hydrochloric acid (1+5) and by diluting with water.

Iron(III) Standard Solution: A 1000 μg/cm^3 solution was prepared by dissolving electrolytic iron with a mixture of nitric acid and hydrochloric acid and by diluting with water.

Nickel(II) Standard Solution: A 1000 μg/cm^3 solution was prepared by dissolving nickel metal (99.9%) with hydrochloric acid (1+1) and by diluting with water.

Tin(IV) Standard Solution: A 2500 μg/cm^3 solution was prepared by dissolving tin metal (99.999%) with hydrochloric acid and by diluting with water.

Zirconium(IV) Standard Solution: A 4000 μg/cm^3 solution was prepared by dissolving zirconium dichloride oxide (analytical-reagent grade) with water.

Cobalt(II) Standard Solution: A 1000 μg/cm^3 solution was prepared by dissolving cobalt nitrate (analytical-reagent grade) with nitric acid and by diluting with nitric acid (1+100). The solution was standardized by EDTA titrimetry.

The above standard solutions were diluted as required.

Tetrafluoroboric Acid Solution: Tetrafluoroboric acid solution was prepared by dissolving 50 g of boric acid in 100 cm^3 of 47% hydrofluoric acid and was retained in a polyethylene bottle.

HMA–HMDC Solution: A 1% ethanol solution was prepared by dissolving HMA–HMDC which had been synthesized and recrystallized by Busev's method.[14]

All the other chemicals used were of analytical-reagent grade; deionized-distilled water was used throughout the work.

Proposed Procedure. A zircaloy standard sample, 0.2 g, was dissolved in a mixture of 1 cm^3 of tetrafluoroboric acid and 14 cm^3 of hydrochloric acid (1+1) on a sand bath, and diluted to 100 cm^3 with water. After an aliquot (less than 200 μg of tin; corresponding to 10 mg of zircaloys) was pipetted into a 100 cm^3-beaker, 3 cm^3 of 1% (*R*,*R*)-tartaric acid solution as an auxiliary chelating agent and 50 μg of cobalt as an internal standard were added; the total volume of the solution should be around 50 cm^3 with water. The pH of the solution was adjusted to 2 with ammonia solution (1+3). Three cm^3 of 1% HMA–HMDC ethanol solution was mixed into the solution. The resulting HMA–HMDC complexes for chromium, iron, nickel, tin, and cobalt were allowed to stand for 20 min at room temperature. After the HMA–HMDC complexes were collected on a membrane filter, the precipitate was washed with 10 cm^3 of water three times and dried at room temperature. The precipitate on the filter, covered with a Mylar film, was fixed onto an aluminium holder and fitted with a titanium mask to remove the scattered background intensity. The X-ray intensity for each element was measured three times for 20 s, operating at 40 kV and 20 mA. The counting was performed for the $K\alpha$ lines of each HMA–HMDC complex for chromium, iron, nickel, tin, and cobalt at the 2θ angles of 69.34°, 57.49°, 48.64°, 14.03°, and 52.81°, respectively. The background correction of each element was made by the blank values measured in a similar manner to that described above. The amounts of the four elements were calculated from their calibration curves, which gave the ratios of the average X-ray intensities for chromium, iron, nickel, and tin to that for cobalt.

Results and Discussion

Effect of the pH on the Formation of HMA–HMDC Complexes. The maximum X-ray intensity of each element was examined for the solutions containing 50 μg each of chromiun, iron, nickel, and cobalt, and 250 μg of tin. The pH range was varied from 1 to 5 with the proposed procedure. The results obtained are shown in Fig. 1. The maximum constant X-ray intensities were shown in the pH range of 1 to 5 for nickel and cobalt, and in that of 1.5 to 5 for chromium and tin. For iron, its maximum constant intensity was found in the pH range of 1.5 to 4. In 1 and 2 molar media of hydrochloric acid, chromium and iron showed an abrupt decrease of their X-ray intensities. The pH range of 1.5 to 4 is available for the formation of HMA–HMDC complexes of these elements; we carried out the experiment at pH 2.

*Effect of Adding Amounts of (*R,R*)-Tartaric Acid Solution.* Though HMA–HMDC reacts with tin(IV) to form a complex, the X-ray intensity of its complex shows a poor reproducibility of the results obtained. When (*R*,*R*)-tartaric acid was added to the solution containing tin, reproducible results were obtained. (*R*,*R*)-Tartaric acid, therefore, seems to be effective for tin as an auxiliary chelating agent in the formation of the tin–HMA–HMDC complex. To the solutions containing 20 μg each of chromium, iron, and nickel, 200 μg of tin, and 50 μg of cobalt, 1% (*R*,*R*)-tartaric acid solution was added in the range of 1 to 5 cm^3 and the X-ray intensities of the elements were measured using the proposed procedure. As shown in Fig. 2, the five elements recorded constant X-ray intensities with no marked variations due to tin. Three cm^3 of 1% (*R*,*R*)-tartaric acid solution, therefore, was used.

Effect of Adding Amounts of HMA–HMDC Solution. The X-ray intensities of the five elements were examined by adding from 1 to 6 cm^3 of 1% HMA–HMDC solution and using the proposed procedure. The results obtained are shown in Fig. 3. The addition of less than 2 cm^3 of HMA–HMDC solution

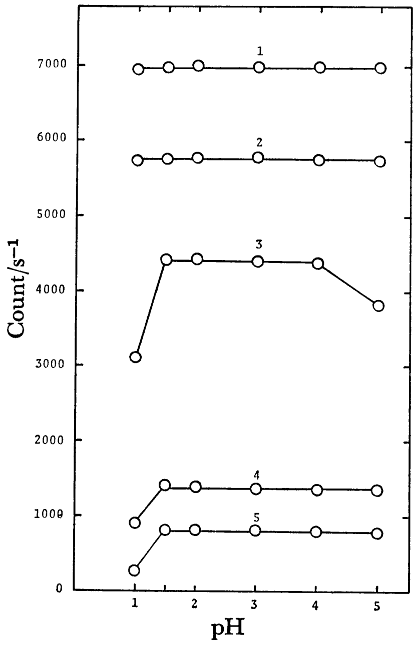

Fig. 1. Effect of the pH on the formation of HMA–HMDC complexes.
1: Ni, 2: Co, 3: Fe, 4: Cr, 5: Sn.

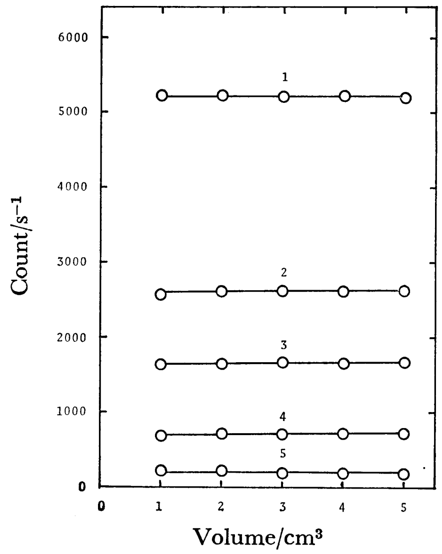

Fig. 2. Effect of adding amounts of 1% (*R*,*R*)-tartaric acid solution.
1: Co, 2: Ni, 3: Fe, 4: Sn, 5: Cr.

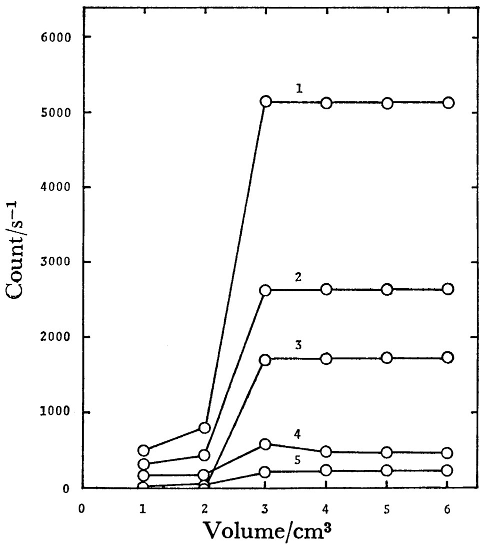

Fig. 3. Effect of adding amounts of 1% HMA–HMDC solution.
1: Co, 2: Ni, 3: Fe, 4: Sn, 5: Cr.

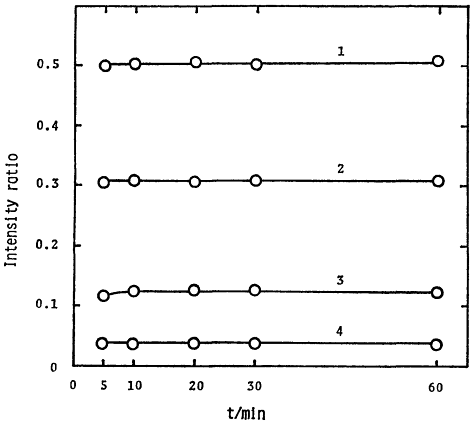

Fig. 4. Effect of aging time of the complexes.
1: I_{Ni}/I_{Co}, 2: I_{Fe}/I_{Co}, 3: I_{Sn}/I_{Co}, 4: I_{Cr}/I_{Co}.

gives extremely low X-ray intensities for each element because a part of the precipitate must pass through membrane filters. The addition of more than 4 cm^3 of HMA–HMDC solution makes the filtration of the precipitate more difficult, because of the fine particles of the complexes, and gives lower X-ray intensities of tin. Three cm^3 of 1% HMA–HMDC was thus added.

Effect of Aging Time of the Complexes. The aging time required to obtain quantitative complex formation was examined for the same solutions by varying the time over the range from 5 to 60 min. As shown in Fig. 4, the maximum constant ratios of X-ray intensities for chromium, iron, nickel, and tin to that for cobalt were obtained after more than 10 min of aging time. The complexes were thus allowed to stand for 20 min at room temperature.

Calibration Curves. The calibration curves were made for chromium, iron, nickel, and tin as follows. Fifty μg of cobalt as an internal standard and 60 mg of zirconium were added to the solutions containing 5—150 μg of chromium, 5—100 μg each of iron and nickel, and 50—200 μg of tin. By using the proposed procedure, the ratios of X-ray intensities for the elements to be determined to that for cobalt were plotted against the amounts of the elements. The calibration curves were linear in the concentration range of up to 100 μg of iron and nickel, and up to 150 μg of chromium. For tin, a reproducible result could not be obtained in the absence of (*R*,*R*)-tartaric acid, but the calibration curve was linear up to 300 μg in the presence of 3 cm^3 of 1% (*R*,*R*)-tartaric acid solution as an auxiliary chelating agent.

The calibration curves of applying zircaloy samples were also made as follows. To the solutions containing 2—15 μg each of chromium and nickel, 5—30 μg of iron and 50—300 μg of tin, also added were 1 cm^3 of 5% tetrafluoroboric acid solution, 10 mg of zirconium, 3 cm^3 of 1% (*R*,*R*)-tartaric acid solution and 50 μg of cobalt. The procedure mentioned above was then carried out. The calibration curves, which are used for the determination of the amounts less than 300 μg of tin, 15 μg of nickel, and 30 μg of iron in 10 mg aliquots of zircaloy sample, are shown in Fig. 5. For chromium, however, a nonlinear relationship was found with a lowering of sensitivity.

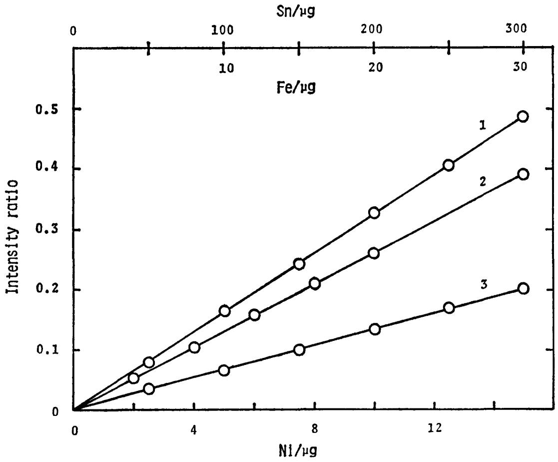

Fig. 5. Calibration curves.
1: I_{Fe}/I_{Co}, 2: I_{Ni}/I_{Co}, 3: I_{Sn}/I_{Co}.

TABLE 1. COMPARISON OF THE PROPOSED METHOD WITH OTHER METHODS

Element	Element added (μg)	Proposed method (μg)	Other method (μg)
Fe	20.0	20.0	20$^{a)}$
Ni	20.0	19.8	20$^{a)}$
Sn	240.0	243.4	240$^{b)}$

a) Determined by atomic absorption spectrometry. b) Determined by extraction spectrophotometry with oxine.

Precision and Detection Limits. The precision of the proposed method was examined for the solution containing 10 μg each of iron and nickel, and 200 μg of tin. The coefficients of variation for iron, nickel, and tin in five determinations were 2.16, 0.63, and 1.52%, respectively.

The detection limits of iron, nickel, and tin were 1.4×10^{-2}, 5.5×10^{-3}, and 3.0×10^{-1} μg, respectively; these amounts correspond to the X-ray intensities that are equal to three times standard deviations of their backgrounds.

Comparison of the Proposed Method with Other Methods. For the solutions containing 20 μg each of iron and nickel or 240 μg of tin, the analytical data obtained by the proposed method were compared with those by atomic absorption spectrometry or spectrophotometry. The results obtained are shown in Table 1. The results by the proposed method agreed with those by other methods.

Effect of Diverse Elements. HMA–HMDC forms complexes with chromium(VI), iron(III), nickel, and tin as well as cobalt, but does not form a complex with zirconium matrix; these complexes can be separated from zirconium by the filtration of them. Negligible interferences of excitation and absorption occurred among the elements studied, because these elements were measured below several hundreds micrograms in total amounts as a thin film.

Simultaneous Determination of the Trace Amounts of Chromium, Iron, Nickel, and Tin in Zircaloys. The analytical results of chromium, iron, nickel, and tin

TABLE 2. ANALYSIS OF ZIRCALOYS

Zircaloys	Element found (%)				Certified values[a] (%)			
	Fe	Ni	Sn	Cr	Fe	Ni	Sn	Cr
Z-9	0.138	0.057	1.45	—	0.148	0.057	1.47	0.097
Z-11	0.200	0.021	1.83	—	0.209	0.021	1.83	0.041
Z-12	0.128	0.095	0.91	—	0.129	0.094	0.92	0.013
Z-13	0.134	0.061	1.48	—	0.136	0.058	1.48	0.098

a) Certified by Japan Atomic Energy Research Institute.

in zircaloy standard samples, JAERI Z-9, Z-11, Z-12, and Z-13, are shown in Table 2, along with their values certified by the Japan Atomic Energy Research Institute. The content of tin is fairly high in zircaloy samples used, compared with the contents of chromium, iron, and nickel, and the intensities of their *K*α lines are more sensitive than that of tin. Thus 10 mg of sample was sufficient for the determination of their elements, with no addition of standard material. When chromium exists in a trivalent state in the zircaloy samples, the complex formation with HMA–HMDC would not proceed. The oxidations of chromium with hydrogen peroxide, potassium periodate, ammonium persulfate, and potassium permanganate were thus tried, but no effective results were obtained. The analytical results of the other three elements obtained by the proposed method were in agreement with their certified values.

The proposed method is free from the interference by the zircaloy matrix and has advantages in speed (about 2 h), simplicity and precision compared with other chmical methods.

References

1) The Committee on Analytical Chemistry of Nuclear Fuels and Reactor Materials, "Analysis of Zirconium and Its Alloys," JAERI 4050, Japan Atomic Energy Research Institute (1969), pp. 35—39.

2) The Committee on Analytical Chemistry of Nuclear Fuels and Reactor Materials, "Analysis of Zirconium and Its Alloys," JAERI 4050, Japan Atomic Energy Research Institute (1969), pp. 43—47.

3) The Committee on Analytical Chemistry of Nuclear Fuels and Reactor Materials, "Analysis of Zirconium and Its Alloys," JAERI 4050, Japan Atomic Energy Research Institute (1969), pp. 95—99.

4) The Committee on Analytical Chemistry of Nuclear Fuels and Reactor Materials, "Analysis of Zirconium and Its Alloys," JAERI 4050, Japan Atomic Energy Research Institute (1969), pp. 111—119.

5) The Committee on Analytical Chemistry of Nuclear Fuels and Reactor Materials, "Analysis of Zirconium and Its Alloys," JAERI 4050, Japan Atomic Energy Research Institute (1969), pp. 36, 37, 45, and 97.

6) R. T. Clark, *Analyst*, **85**, 245 (1960).

7) T. Mukoyama, T. Yamane, N. Kiba, and M. Tanaka, *Anal. Chim. Acta*, **61**, 83 (1972).

8) N. E. Gordon, Jr., and R. M. Jacobs, *Anal. Chem.*, **25**, 1605 (1953).

9) R. F. Farrell, G. J. Harter, and R. M. Jacobs, *Anal. Chem.*, **31**, 1550 (1959).

10) M. Kawahata, H. Mochizuki, R. Kajiyama, and M. Ishii, *Bunseki Kagaku*, **11**, 963 (1962).

11) T. Yoshimori, I. Matsubara, T. Tanaka, K. Yoshida, K. Tanaka, and T. Tanabe, *Bull. Chem. Soc. Jpn.*, **44**, 731 (1971).

12) R. W. Ashley and R. W. Jones, *Anal. Chem.*, **31**, 1632 (1959).

13) T. Matsumura, N. Kotani, and T. Goto, *Bunseki Kagaku*, **17**, 933 (1968).

14) A. I. Busev, V. M. Byr'ko, A. P. Tereshchenko, N. N. Novikova, V. P. Naidina, and P. B. Terent'ev, *Zh. Anal. Khim.*, **25**, 665 (1970).