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An Internal-Monitor Method for the Activation Analysis of Silver in Palladium with Thermal Neutrons

Yoshinaga OKA, Toyoaki KATO, Hui-Tuh TSAI and Koichi NOMURA

Department of Chemistry, Faculty of Science, Tohoku University, Katahira-cho, Sendai

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An internal-monitor method has been developed to eliminate many of the errors probable with activation analysis. This method involves the measurement of the composed radioactivity of the species to be analyzed and of an appropriate internal-monitor, and the estimation of the ratio of the induced activity of both the species. The present report will describe the principles and the applicability of the method to the determination of a trace amount of silver in palladium by means of thermal neutron irradiation. After the silver activity is chemically separated from the irradiated sample, the γ-ray spectrum corresponding to the mixture of ^{110m}Ag and ^{111}Ag formed by the β^- decay of ^{111}Pd is measured. Synthetic mixtures of silver and palladium with known weight ratios have been prepared to check the accuracy of the method. A good proportionality has been obtained between the ratios of the ^{110m}Ag to ^{111}Ag activities and the ratios of the concentrations. By using this relationship, silver analysis can easily be achieved. Contents of silver in a palladium sample down to about 1 ppm can be determined with a relative error of within ±2%. By this method the errors which arise from neutron flux irregularities and self-shielding effects can be avoided, and no correction for chemical yield is necessary.

Although radioactivation analysis has been widely employed as one of the most sensitive analytical methods for the determination of many elements, the errors accompanying this method are usually significant. A comparative technique is used more frequently than the absolute determination method. An important source of errors can be due to a difference in neutron flux between the sample and the reference. Such differences are to be attributed to neutron flux irregularities and to different self-shielding effects in the substances. To correct for these differences, Leliaert *et al.*[1] have developed a method of activation analysis using an internal standard. This method involves the standard addition of the desired element to a portion of the sample. Both spiked and unspiked samples are irradiated, and the specific activity of the desired element is estimated by means of the activity difference. In activation analysis by charged particles or by high-energy photons, errors from the flux inhomogenuities become serious. When the comparative technique is used, therefore, it is difficult to get a good accuracy even when extreme care and effort are taken. To overcome these errors, Oka *et al.*[2] have developed a method using a matrix species as an internal-monitor in non-destructive activation analysis with bremsstrahlung γ-rays.

A second source of error which is likely to be important is the effect of competing reactions. Interferences may proceed either directly or through second-order nuclear reactions.[3] In addition to these nuclear factors, several additional factors can be expected to lead to serious inaccuracies. These are mainly connected with radiochemical and counting processes. The stage of yield correction can give rise to errors, and in the final stage of radioactivity measurement errors due to poor counting statistics can also be considerable. In ordinary activation analysis, thus, errors effected by these sources are accumulated to a significant extent, so that, in most cases, it is difficult to get an accuracy better than ±5%. The use of an internal-monitor method can, however, eliminate many of the errors probable with activation analysis. This can be illustrated by the determination of trace silver in palladium by means of thermal neutron activation, with radiochemical separation and subsequent γ-ray spectrometry.

Illustration of the Method

The counting rate of the photopeak, A, due to any induced γ-ray emitter is given by:

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[1] G. Leliaert, J. Hoste and Z. Eeckhaut, *Nature,* **182**, 600 (1958); *Anal. Chim. Acta,* **19**, 100 (1958); *Talanta,* **2**, 115 (1959).

[2] Y. Oka, T. Kato and M. Sasaki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.),* **84**, 588 (1963); *ibid.,* **86**, 612 (1965); Y. Oka and T. Kato, *ibid.,* **86**, 835 (1965); *ibid.,* **87**, 1057 (1966); Y. Oka, T. Kato and K. Nomura, *ibid.,* **87**, 147 (1966); Y. Oka, T. Kato and T. Saito, *ibid.,* **87**, 154 (1966); *ibid.,* **88**, 866 (1967); Y. Oka, T. Kato and I. Nagai, *ibid.,* **88**, 871 (1967).

[3] R. C. Koch, "Activation Analysis Handbook," Academic Press, New York (1960), p. 10.

$$A = \varepsilon N \phi \sigma S \tag{1}$$

where N=the number of target nuclei, ϕ=flux of the bombarding particle, σ=a reaction cross section, ε=the photopeak efficiency of counting process, and S=the saturation factor.

For two species, I and II, in a homogeneous sample:

$$\frac{A_{\mathrm{I}}}{A_{\mathrm{II}}} = \frac{(\varepsilon N \phi \sigma S)_{\mathrm{I}}}{(\varepsilon' N' \phi \sigma' S')_{\mathrm{II}}} \tag{2}$$

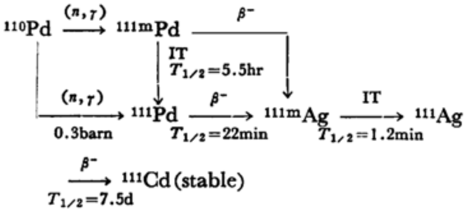
Accordingly,

$$\frac{W_{\mathrm{I}}}{W_{\mathrm{II}}} = K \frac{A_{\mathrm{I}}}{A_{\mathrm{II}}} \tag{3}$$

where the W's are the weights of the target elements and K is a constant.

The ratio of the photopeak activities attributed to these two species is a linear function of the ratio of the concentrations. Hence, the combination of an unknown (I) with a properly chosen internal-monitor (II) allows an accurate determination.

In the case of silver in palladium matrix, it can be assayed by γ-ray spectrometry through the induced $^{110\mathrm{m}}$Ag in an irradiated sample. Palladium, on the other hand, gives seven radionuclides as (n, γ) reaction products: ^{103}Pd, $^{107\mathrm{m}}$Pd, ^{107}Pd, $^{109\mathrm{m}}$Pd, ^{109}Pd, $^{111\mathrm{m}}$Pd, and ^{111}Pd. However, the major radionuclides are represented by the following sequences:



When the silver activity is separated from the irradiated sample, therefore, a composite γ-ray spectrum which corresponds to both the 253-day $^{110\mathrm{m}}$Ag and the 7.5-day ^{111}Ag as the β^--decay product of ^{111}Pd is measured. By detecting the photopeak activities of both nuclides at an identical time after each irradiation,4) the following relationship can be obtained:

$$\frac{W_{\mathrm{Ag}}}{W_{\mathrm{Pd}}} = K' \frac{A_{\mathrm{Ag\text{-}110m}}}{A_{\mathrm{Ag\text{-}111}}} \tag{4}$$

Now if R_W is the ratio of concentrations and R_{A_0} is the ratio of the measured photopeak areas related at the end of the irradiation, Eq. (4) becomes:

$$R_W = K' R_{A_0} \tag{5}$$

The constant, K', can be determined by irradiating synthetic mixtures of silver and palladium with known compositions. By using this relationship, it is possible to determine the content of silver in a palladium sample provided that the irradiation period and the counting process are identical to those of the standard mixtures. It is obvious that this internal-monitor method offers several advantages with regard to accuracy and precision over ordinary activation analysis: i) Since results can be calculated on the basis of the activity ratios, the effects of flux irregularities and self-shielding are cancelled out. ii) Since the correction for yield is not necessarily taken into account, the errors arising in this stage can be avoided completely. iii) The effects of the (n, p) and the (n, α) reactions induced by fast neutrons give no trouble.

Experimental

Materials and Irradiation. A series of synthetic palladium-silver mixtures was prepared in the following manner. Fifty milligrams of palladium powder was weighed into a quartz tube with an internal diameter of 6 mm, and then known amounts of an aqueous silver nitrate solution were added. After evaporation to dryness, the tube was sealed. The palladium powder was processed from 99.99% palladium metal as follows. The metal was dissolved in aqua regia, evaporated nearly to dryness, repeatedly evaporated with additional conc. hydrochloric acid, and then subjected to anion exchange purification.5) Palladium was eluted from a Dowex 1×8 column with an aqueous ammonium chloride-ammonia mixture. The metallic powder was precipitated from this eluate by reduction with formic acid, repeatedly washed with water, and dried in a vacuum. The aqueous silver nitrate solution was prepared by dissolving a reagent purified by repeated recrystallizations. Proper dilution with water was made from this just before use. The hydrochloric acid, nitric acid, and water were all redistilled. All the other chemicals were of a guaranteed grade.

Two kinds of electrolytic palladium plates were tested for their silver contents. From these samples, small pieces of approximately 30 mg were cut out and analyzed. The samples, a series of the synthetic mixtures, and 50 mg of the original palladium powder were put together in an aluminum capsule for pile irradiation. The irirradiation was performed for 72.8hr in the JRR-2 reactor of the Japan Atomic Energy Research Institute. The reactor was operated at 10 MW, providing a thermal neutron flux of 2.5×10^{13} n/cm^2/sec at the irradiation site. After the irradiation, the samples were subjected to the radiochemical procedure for the isolation of the silver activities.

Radiochemical Procedure. The radiochemical procedure for the isolation of the silver activities is diagrammed in Table 1.

Separations were performed for each sample after ^{111}Pd had been allowed to decay to ^{111}Ag completely. The final aqueous layer was drained into a polyethylene tube for γ-ray spectrometric measurements.

γ-Ray Measurements. For the γ-ray spectrometric measurements, a $1^1/_2''\phi \times 1^1/_2''$ NaI(Tl) crystal

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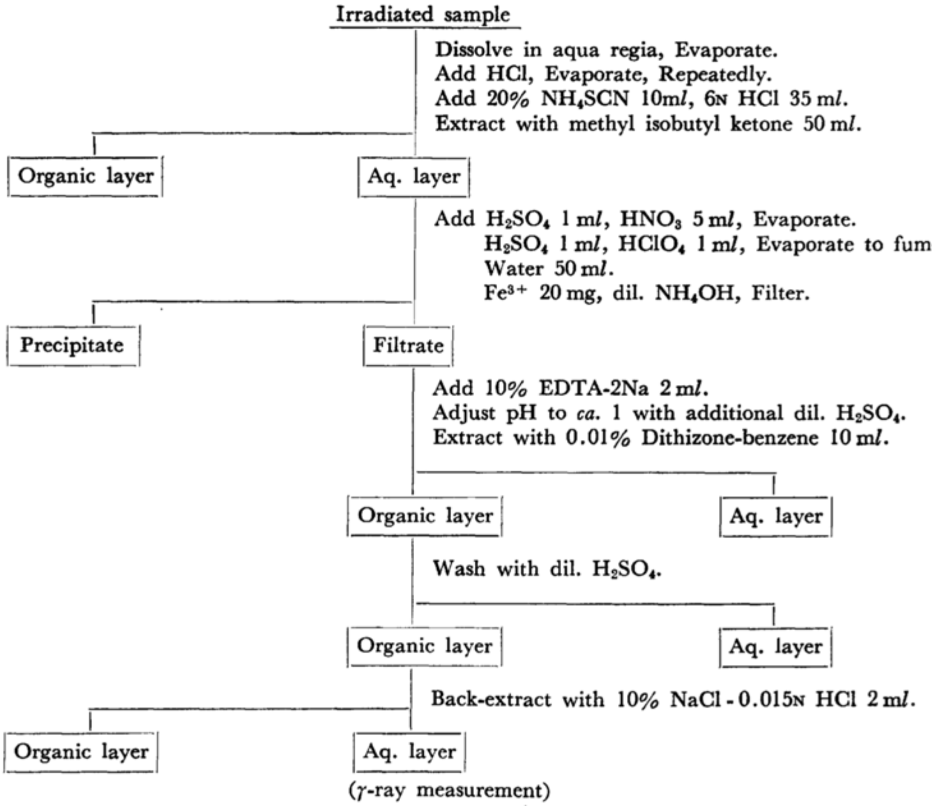
4) For comparison, these activities were corrected for decay to the end of the irradiation, as will be described later.

5) W. M. MacNevin and W. B. Crummett, *Anal. Chem.*, **25**, 1628 (1953).

TABLE 1. SEPARATION SCHEME FOR RADIOSILVER FROM IRRADIATED PALLADIUM


Irradiated sample
Dissolve in aqua regia, Evaporate.
Add HCl, Evaporate, Repeatedly.
Add 20% NH_4SCN 10m*l*, 6N HCl 35 m*l*.
Extract with methyl isobutyl ketone 50 m*l*.
Organic layer
Aq. layer
Add H_2SO_4 1 m*l*, HNO_3 5 m*l*, Evaporate.
H_2SO_4 1 m*l*, $HClO_4$ 1 m*l*, Evaporate to fume.
Water 50 m*l*.
Fe^{3+} 20 mg, dil. NH_4OH, Filter.
Precipitate
Filtrate
Add 10% EDTA-2Na 2 m*l*.
Adjust pH to *ca.* 1 with additional dil. H_2SO_4.
Extract with 0.01% Dithizone-benzene 10 m*l*.
Organic layer
Aq. layer
Wash with dil. H_2SO_4.
Organic layer
Aq. layer
Back-extract with 10% NaCl - 0.015N HCl 2 m*l*.
Organic layer
Aq. layer
(γ-ray measurement)

coupled with a 800-channel pulse-height analyzer made by the Tokyo Shibaura Electric Co., Ltd., Japan, was used. The peeling-off method6) was employed to determine the accurate photopeak areas from the γ-ray spectra obtained.

Results and Discussion

Radiochemical Process. The recovery of radiosilver in each step in Table 1 was studied using ^{110m}Ag as a tracer. The results are shown in Table 2. Although about 27.5% of the radiosilver was coprecipitated with ferric hydroxide, this scavenging technique made possible a successful decontamination from other radionuclides.7) The final recovery was about 70%. In the final chloride solution, a composite γ-ray spectrum which corresponded to the mixture of ^{110m}Ag and ^{111}Ag, as shown in Fig. 1-(1), was obtained. The decay curve followed on the 0.342 MeV photopeak area showed a half-life of 7.5 days, corresponding to the literature value of ^{111}Ag.8)

TABLE 2. RECOVERY OF SILVER ACTIVITY IN SEPARATION STEP OF TABLE 1

Chemical step	^{110m}Ag recovery, %			
				Mean
Filtrate in ferric hydroxide scavenging	70.3	75.6	71.6	72.5
Dithizone extraction	98.8	99.7	99.4	99.7
Back extraction with chloride solution	97.5	97.3	96.8	97.2

R_W *vs.* R_{A_0}. The marked difference in the energy of γ-rays emitted from ^{110m}Ag and ^{111}Ag permits a γ-ray spectrometric determination of silver in palladium. From the composite spectra obtained from silver-palladium mixtures, photopeak areas were measured on the 0.342 MeV γ-rays for ^{111}Ag, and on the 0.656 and 0.885 MeV γ-rays for ^{110m}Ag.

These values were corrected for decay to the end of the irradiation,9) and the R_{A_0}'s were computed on the basis of the illustration given earlier in this paper. At that time, the correction coefficient for silver in the original palladium, α,10)

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6) W. S. Lyon, Jr., ed., "Guide to Activation Analysis," D. Van Nostrand Co., Princeton, N. J. (1964), p. 104.

7) This technique was especially effective for the removal of ^{192}Ir .

8) Nuclear Data Sheets, Natl. Academy of Science-Natl. Research Council, Washington, D. C. (1961).

9) For convenience, the ^{111}Ag activities were determined by interpolating the counting rates to the end of the irradiation using a half-life of 7.5 days.

10) The α values obtained under the present conditions were 9.49×10^{-5} from the 0.656 MeV peak and 4.77×10^{-5} from the 0.885 MeV peak.

TABLE 3. R_W *vs.* R_{A_0} FOR SILVER-PALLADIUM MIXTURES

R_W	R_{A_0} From 0.656 MeV peak	R_{A_0} From 0.885 MeV Peak	R_W/R_{A_0} From 0.656 MeV peak	R_W/R_{A_0} From 0.885 MeV peak
1.73×10^{-4}	2.03×10^{-3}	9.54×10^{-4}	8.53×10^{-2}	1.81×10^{-1}
2.73×10^{-5}	3.24×10^{-4}	1.46×10^{-4}	8.42×10^{-2}	1.87×10^{-1}
1.30×10^{-5}	1.49×10^{-4}	7.02×10^{-5}	8.72×10^{-2}	1.85×10^{-1}
4.02×10^{-6}	4.68×10^{-5}	2.18×10^{-5}	8.60×10^{-2}	1.87×10^{-1}
2.51×10^{-6}	2.87×10^{-5}	1.33×10^{-5}	8.74×10^{-2}	1.89×10^{-1}
		Mean:	8.60×10^{-2}	1.86×10^{-1}
		Std. dev.:	$\pm0.12\times10^{-2}$ ($\pm1.4\%$)	$\pm0.03\times10^{-1}$ ($\pm1.6\%$)

TABLE 4. RESULTS OF SILVER ANALYSES

Sample	R_{A_0} From 0.656 MeV peak	R_{A_0} From 0.885 MeV peak	Silver content, ppm From 0.656 MeV peak	Silver content, ppm From 0.885 MeV peak	Mean	Average
A	8.83×10^{-5}	3.96×10^{-5}	7.5_9	7.3_7	7.4_8	$7.4_5\pm0.0_3$
	8.78×10^{-5}	3.91×10^{-5}	7.5_5	7.2_7	7.4_1	
	8.76×10^{-5}	3.97×10^{-5}	7.5_3	7.3_8	7.4_6	
	8.74×10^{-5}	3.91×10^{-5}	7.5_2	7.2_7	7.4_0	
	8.78×10^{-5}	3.97×10^{-5}	7.5_5	7.3_8	7.4_7	
B	1.54×10^{-4}	6.99×10^{-5}	13.3	13.0	13.2	13.2
	1.55×10^{-4}	7.04×10^{-5}	13.3	13.1	13.2	
	1.56×10^{-4}	6.99×10^{-5}	13.4	13.0	13.2	

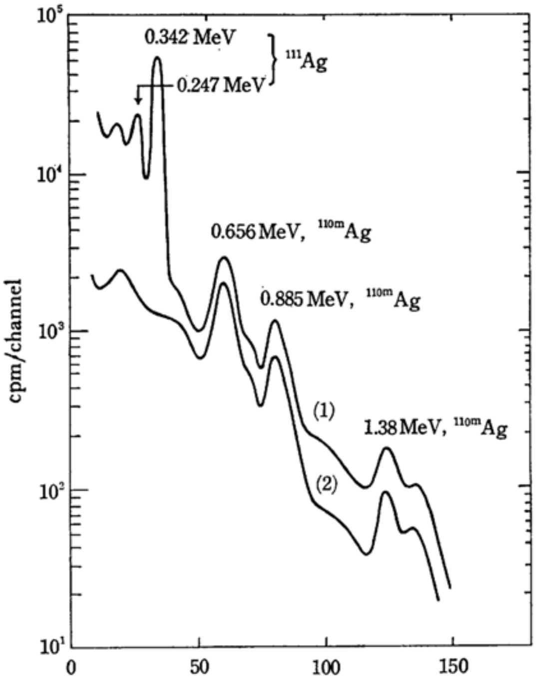

Fig. 1. γ-Ray spectra of radiosilver; (1) separated from irradiated silver-palladium mixture (Ag/Pd$=1.73\times10^{-4}$), 37 days after irradiation, and (2) standard ^{110m}Ag spectrum.

was introduced in Eq, (4); thus we obtained:

$$\frac{W_{\mathrm{Ag}}}{W_{\mathrm{Pd}}} = K'\left(\frac{A'_{\mathrm{Ag\text{-}110m}}}{A_{\mathrm{Ag\text{-}111}}} - \alpha\right)_{t=0} \qquad (6)$$

where:

$$\alpha = \left(\frac{A_{\mathrm{Ag\text{-}110m}}}{A_{\mathrm{Ag\text{-}111}}}\right)_{\mathrm{original}}$$

On the standard series, the relation between the weight ratios and the corrected photopeak activity ratios was calculated. Table 3 shows these experimental results. In each case, a good proportionality was obtained between R_{W} and R_{A_0}. Relative standard deviations of $\pm1.4\%$ for the 0.656 MeV peak and $\pm1.6\%$ for the 0.885 MeV peak were obtained under the present conditions. The present results show that an accurate determination can be expected when using these relationships.

The separation procedure diagrammed in Table 1 can isolate the silver activity without any contamination of undesired activities; hence, the individual silver photopeak areas were measured with minimum relative errors. When a minimum photopeak area of 50 cpm is selected as the limit of detection, silver contents in palladium down to about 0.8 ppm (0.04 μg in a 50-mg sample) from the 0.656 MeV peak and down to about 2 ppm (0.1 μg in a 50-mg sample) from the 0.885 MeV peak can be determined with relative errors of within ±2%.

Silver Analysis. This method of silver analysis was tested on electrolytic palladium plates. After irradiation, samples were cooled for about 10 days, and then subjected to radiochemical procedure. As Table 4 shows, a good agreement in the silver contents was obtained, indicating satisfactory precision in the method.

Applicability of the Method. In general cases, where the atomic number of the element to be analyzed is higher by one unit than that of the matrix element, and where the nuclear characteristics of the (n, γ) reaction product of the former and the secondary β^--decay product from the latter are favorable for subsequent γ-ray spectrometric measurements, it is possible to use the present method in the determination. For example, the determinations of gold in platinum and of antimony in tin by the thermal neutron activation technique can be performed. Moreover, the technique of combining an unknown with an additional internal-monitor offers a general applicability.

Further application of this method would be found in the activation with high-energy photons by which the neutron defficient radionuclide is formed by the (γ, n) process. This primary product undergoes in the main β^+ and/or EC decay to produce a secondary nuclide. When this secondary activity is combined with the (γ, n) reaction product from the element to be analyzed, it is possible to determine the element in question with an atomic number smaller by one unit than that of the species chosen as the internal-monitor.