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Neutron Activation Analysis of Traces of Palladium, Gold, and Iridium in Supernates from the Refining of Precious Metals

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In the refining of precious metals it is desirable to be able to determine amounts of the elements remaining in solution after various precipitations. Neutron-activation analysis can be used advantageously in this field, and in the present report the application of the method for the determination of traces of palladium, gold and iridium is described. The nuclear reactor BEPO at Harwell was used as the source of neutrons and each of the three elements could be determined with high sensitivity in a 0.5-ml aliquot of a sample solution. Results of analyses of microgram and submicrogram quantities of palladium, gold and iridium in the solutions under investigation showed good precision.

INTRODUCTION

In the extraction and refining of precious metals it is important to be able to determine traces of the elements which may be present in various residual solutions and effluents. Sensitive analytical techniques may be required in this connection and the application of radioactivation to such problems has proved advantageous. In the work reported here a description is given of a neutron-activation method whereby traces of palladium, gold, and iridium can be determined in a small sample of solution. The procedure involves irradiation of the sample, together with comparison standards containing known amounts of the selected elements, in a nuclear reactor, separation of activities from elements in the sample, and comparison of separated activity from a sample with the corresponding activity from a standard.[1,2]

The nuclear characteristics of palladium, gold, and iridium on irradiation in a source of thermal neutrons are listed in Table I. In the present study measurement of gamma radiation from ^{198}Au was used in the determination of gold. For palladium, beta particles from ^{109}Pd or, alternatively, Ag *X*-rays accompanying the decay of ^{109m}Ag in equilibrium with ^{109}Pd were counted. Gamma rays from ^{192}Ir were measured in the analyses of iridium. The fact that the half-lives of ^{109}Pd, ^{198}Au and ^{192}Ir are 13.6 h, 2.70 d, and 74.4 d, respectively, made it desirable to perform analyses in the order palladium, gold, iridium.

EXPERIMENTAL

Irradiation of samples and standards

Aliquots of sample solutions (0.5 ml.) were accurately pipetted into cylindrical aluminium capsules of 6-mm diameter. In each case the liquid was carefully eva-

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TABLE I

Nuclear Data for Thermal Neutron Activation of Palladium, Gold and Iridium

Target nuclide	Abudance %	Isotopic activation cross section, barns	Radioactive product of thermal neutron activation	Radiation and energy, MeV	Half-life
^{102}Pd	0.96	4.8	^{103} Pd	EC (to ^{103m}Rh) γ 0.0402 to 0.498	17.0 d
^{108}Pd	26.71	0.2 12	^{109m}Pd ^{109} Pd	ITγe 0.188 β^- 1.03 (to ^{109m}Ag)	4.75 m 13.6 h
^{110}Pd	11.81	0.05 0.2	^{111m}Pd ^{111} Pd	IT; β^-; γ 0.17 β^- 2.15. Parent of ^{111}Ag (7.5 d)	5.5 h 22 m
^{197}Au	100	99	^{198} Au*	β^- 0.29 (1%), 0.96 (99%), 1.37 (0.025%) γ 0.412 (95.6%), 0.68 (1.1%), 1.09 (0.26%)	2.70 d
^{191}Ir	37.3	250	^{192m}Ir	IT e$^-$ (γ) 0.056 (Q_{IT}) (99.9%) β^- 0.056 ($\sim$ 0.1%)	1.42 m
		750	^{192} Ir	β^- 0.24 (6%), 0.54 (40%) 0.67 (50%); EC (4%) γ 0.296 (30%), 0.308 (29%), 0.316 (83%), 0.468 (53%), 0.588 (6%), 0.605 (12%),, 0.613 (7%)	74.4 d
^{193}Ir	62.7	1.20	^{194} Ir	β^- 0.98 (9%), 1.91 (15%) 2.24 (68%) others γ 0.328 (24%) (others 0.293 to 2.048)	19 h

* ^{198}Au has the large thermal neutron cross section of 26,000 barns, so that on irradiation of gold in a high flux ^{199}Au (3.15 d) is formed in addition to ^{198}Au.

porated to dryness and the capsule was sealed. Comparators were prepared by successively weighing out and evaporating to dryness 0.1-ml aliquots of very dilute standard solutions of Au(III), Pd(II), and Ir(IV) in an aluminium capsule. Containers of samples and standards were packed together with silica wool in standard screw-top aluminium cans (2.5-cm. diam. × 7.5-cm. long) and sent to the Atomic Energy Research Establishment, Harwell, for activation. Irradiations were for six days in a flux of 1.2×10^{12} thermal neutrons cm^{-2} sec^{-1} in the nuclear reactor BEPO.

Radiochemical separation

Because the samples for analysis contained a variety of constituents, many radionuclides were produced by the neutron irradiation. As a result, gamma spectral studies of the samples, as delivered from Harwell, were inadequate for determinations. owing to the superposition of different spectra. A chemical procedure employing carriers was used,[3–5] therefore, to separate the desired radionuclides so that they could be measured satisfactorily by scintillation spectrometry or by Geiger-Müller counting.

An outline of the procedure is as follows:

Samples were taken into solution in the presence of known mg amounts of palladium, gold, iridium and platinum carriers. Gold(III) was then extracted into isopropyl ether from 6*M* hydrochloric acid solution.[6] The aqueous phase was treated with sodium nitrite and base metals were precipitated as hydrous oxides, the precious metals remaining in solution as complex nitrites.[7] After decomposition of the nitrites with hydrochloric acid, palladium was precipitated as the dimethylglyoxime complex.[8] Iridium was subsequently precipitated from solution as the hydrous dioxide by bromate hydrolysis.[9]

The precipitate of palladium as the dimethylglyoxime complex was dissolved in aqua regia and palladium was precipitated as metal from dilute hydrochloric acid solution by addition of hypophosphorous acid.[7] The metal was dissolved in nitric acid and, following a silver chloride scavenge, palladium was reprecipitated as the dimethylglyoximate. The precipitate was washed, mounted on a weighed aluminium counting tray, dried, and weighed to determine the chemical yield for palladium.[8]

The isopropyl ether extract containing gold was washed with 3*M* hydrochloric acid in the presence of iridium carrier. After three such washes, the ether was removed by evaporation. The residue was taken up in 6*M* hydrochloric acid, iridium carrier was added, and gold(III) was reextracted with a fresh portion of isopropyl ether. The organic phase was separated and washed with 3*M* hydrochloric acid, after which the ether was evaporated off in the presence of hydrochloric acid. Gold was precipitated as the metal from the resulting aqueous solution by the addition of sulphurous acid. The metal after washing with water and ethanol was mounted on a tared aluminium tray for counting, dried, and weighed to determine the chemical yield for gold.[10]

The precipitate of hydrous iridium(IV) oxide was dissolved in hydrochloric acid and iridium metal was precipitated by addition of calomel in the presence of bromide and iodide.[11] After ignition and reduction in an atmosphere of hydrogen, the metal was mounted on a tared aluminium tray for counting and the chemical yield for iridium was determined by weighing.[9]

Measurement of radioactivity

In the present work the separated precipitates of palladium dimethyl glyoximate were usually counted at constant geometry with a Geiger-Müller counter of the type EHM 2/S. All measured counting rates were corrected for paralysis, background, and chemical yield, and for decay between counting precipitates from samples and comparators. The sources for counting were of similar weights, and their activities could be compared without the need for correction for self absorption. Radiochemical purity was demonstrated by plotting decay curves; these were parallel straight lines corresponding to a halflife of 13.6 ± 0.5 hours. An alternative method of counting was used in some experiments in which the intensity of the photopeak due to 22 keV Ag *X*-rays emitted from the precipitates was measured by scintillation spectrometry using a NaI(Tl) crystal 7.5 cm. diam. × 0.625 cm. thick with a beryllium window 0.2 mm. thick. Analytical results obtained from the two methods of counting were in good agreement.

The final precipitates of gold from samples and standards were counted by gamma ray spectrometry using a 7.5 cm × 7.5 cm. NaI(Tl) crystal and a 100-channel pulse-height analyser. The intensity of the photopeak due to 0.411 MeV gamma rays was measured. The observed counting rates were corrected for background and chemical yield and for any decay of significance between counting of precipitates from samples and standards.

The purified samples of iridium were also counted at constant geometry by gamma scintillation spectrometry. The method of radiation measurement was similar to that described by Morris *et al.*[12] and the count rates (corrected for background) were corrected for chemical yield.

In each case the mass of the element X in the sample could be obtained from the relationship:

$$\frac{\textbf{Mass of X in sample}}{\textbf{Mass of X in standard}} = \frac{\textbf{Corrected activity of radionuclide formed from X in sample}}{\textbf{Corrected activity of radionuclide formed from X in standard}}$$

RESULTS AND DISCUSSION

The concentrations of palladium, gold and iridium found in aliquots of three different solutions from the Acton Rafinery of the International Nickel Company (Mond) Limited are shown in Table II. These results give an indication of the precision obtainable by the neutron activation procedure. Potential sources of error such as discussed by Plumb and Lewis[13] should have been avoided in the method. Self-shielding differences between samples and standards were insignificant. It was also ascertained, by reference to the literature[14] and from previous exprience,[8–10] that significant amounts of the radionuclide counted as a measure of a particular element could not have been produced from nuclear reactions of other elements.

TABLE II

Palladium, gold and iridium concentrations of aliquots of residual refining solutions determined by neutron - activation analysis

	Palladium µg litre^{-1}	Gold µg litre^{-1}	Iridium mg litre^{-1}
Solution 3	10.5	1.27	13.6
	11.5	1.24	13.3
	10.4	1.35	13.0
	11.4	1.31	13.4
Solution 4	22.8	3.47	6.13
	23.5	3.58	5.97
	23.2	3.39	6.43
	23.0		
Solution 5	403	0.76	2.52
	399	0.82	2.44
	402	0.81	2.52
	396	0.88	2.43

The present study has demonstrated that neutron activation can be used to determine palladium, gold and iridium in submicrogram amounts in a small aliquot of a solution containing several constituents. The results can be used to assess the effectiveness of separation and recovery processes in the purification of precious metals.

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IZVOD

Neutronska aktivaciona analiza tragova paladiuma, iridiuma i zlata u matičnim otopinama kod rafinacije plemenitih metala

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Opisana je primjena neutronske aktivacione analize za određivanje tragova paladiuma, iridiuma i zlata u matičnim otopinama kod pročišćavanja plemenitih metala.

Kao izvor neutrona korišten je nuklearni reaktor BEPO u Harwellu. Sva tri elementa određivana su u uzorcima od po 0,5 ml otopine. Dobiveni rezultati analize mikrogramskih i submikrogramskih količina paladiuma, iridiuma i zlata pokazuju veliku osjetljivost i tačnost kod određivanja navedenih elemenata u otopini.

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