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Leodegario de Garcia Cilindro
Iowa State University

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NEUTRON ACTIVATION ANALYSIS FOR IRIDIUM, PALLADIUM AND SILVER IN PLATINUM

by

Leodegario de Gracia Cilindro

A Dissertation Submitted to the
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DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

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Head of Major Department

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Dean of Graduate College

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Of Science and Technology
Ames, Iowa

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INTRODUCTION

Nature and Purpose of this Investigation

The possible significant influence of some impurities on the chemical behavior of platinum in its compounds furnished the motivation for this investigation. Impurities consisting of the elements of the platinum family, in particular, may be present even in a carefully purified laboratory platinum stock due to the inherently difficult chemistry of these platinum elements and their closely similar chemical behavior. These impurities may occur in micro- and submicroquantities, i.e., at too low a concentration to be determined by most of the conventional methods of quantitative analysis. Three common impurities in platinum, namely, iridium, palladium and silver have favorable nuclear properties (1) that can enable neutron activation analysis to be a highly sensitive and specific method for the quantitative determination of these elements. Iridium-191 with a 37.3% natural abundance has a thermal neutron activation cross section of 750 barns (1 barn = 10^{-24} cm^2) to form iridium-192 with a half-life of 74 days; palladium-108, 26.71% abundant, has a thermal neutron activation cross section of 12 barns to form palladium-109 with a half-life of 14 hours; silver-109, 48.65% abundant, has a thermal neutron activation cross section of 2 barns to form silver-110m with a half-life of 253 days. All of these product radionuclides decay with characteristic incident gamma-ray energies. Radioactivity measurements can therefore be performed with a gamma-ray scintillation spectrometer, thus a further enhancement of the sensitivity and specificity of neutron activation analysis for these elements can be obtained.

Platinum in its native form is commonly found in alluvial deposits in the presence of the other Group VIII metals and their neighbors, gold, silver and copper. Some of these metals may remain with the platinum fraction in the recovery of platinum from its ore concentrates. Moreover, commercially available platinum metal is often alloyed with the other metals in its family and with gold, silver, copper and nickel to improve its physical properties. Therefore any platinum from a "recovered" source invariably contains impurities. There are of course well known analytical methods of separating platinum from other elements, the most outstanding of which are those of Gilchrist and Wichers (2) and of Schoeller and Powell (3). But although these methods are indeed reliable, they are admittedly tedious, particularly those involving the separation of the elements of the platinum family from one another. Furthermore, due to the closely similar chemical behavior of these elements, the separation in some cases may not be complete. For instance, Jowanovitz _et_ _al_. (4) of this laboratory, using radiochemical tracer techniques in a critical evaluation of the method of Gilchrist and Wichers (2) for separating iridium from platinum by precipitation of iridium(IV) hydroxide, observed that ca. 0.2% of iridium-192 activity was not removed from platinum even after three precipitations. Consequently, even a carefully prepared platinum stock may still contain trace impurities.

The influence of impurities on the chemical behavior of platinum in its compounds may be significant. Iridium, most notably, has indeed a striking catalytic effect on the reactions of platinum compounds due to the readily reversible one-electron oxidation-reduction couple of iridium(III) and iridium(IV). Klason (5), for example, noted that the oxalate reduction of $[PtCl_6]^{2-}$ to $[PtCl_6]^{4-}$ required the presence of at least a trace of iridium. Rich and Taube (6) observed that iridium impurities inhibited the photo-induced exchange of chloride between $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$ and between Cl^- and $[PtCl_6]^{2-}$. Traces of other metals which have several oxidation states like iridium can likewise catalyze platinum(IV) reactions. It is also likely that traces of some metal ions may act as reducing agents to form platinum(II) which in turn is well known to catalyze exchange reactions (7,8,9) and substitution reactions (10,11) of platinum(IV) complexes.

The current exchange and kinetic studies being undertaken at this laboratory on some systems involving platinum(II) and platinum(IV) complexes suggested the need for a quantitative determination of trace impurities that may occur in the platinum stock material. Indeed, in an earlier work done at this laboratory (9), iridium activity was repeatedly noted in platinum-195 radioisotopic tracer utilized for exchange studies. Consequently, this investigation was carried out in order to: 1) establish the amount of iridium, palladium and silver impurities of the current platinum stock; 2) demonstrate a practical and sensitive technique for the simultaneous neutron activation analysis of these three elements in a platinum sample matrix.

Neutron Activation Analysis

Activation analysis is a method of elemental analysis based on the principle that when a material is bombarded by the nuclear particles produced in a nuclear reactor, particle accelerator or other suitable source, some of the atoms present in the material will interact with the bombarding particles and be converted into radioactive isotopes of the same element or of different elements depending on the nature of the bombarding particles. The radioactive isotope thus formed can be characterized by its half-life and the type and energy of the radiation it emits. A quantitative measure of this radiation can then be a measure of the quantity of the parent isotope present in the irradiated material.

Neutron activation analysis utilizes neutrons as the activating particles. The source of these neutrons is generally the nuclear reactor, although in recent years fast neutron generators have been gaining popularity in the analysis of elements with atomic number lower than 10. Under favorable circumstances portable low-yield neutron sources such as RaBe or SbBe sources can also be used.

The method of activation analysis was used as early as 1936 when Hevesy and Levi (12,13) determined dysprosium and europium in rare earth mixtures using a 300-millicurie RaBe neutron source. In 1938, Seaborg and Livingood (14) utilized deuterons accelerated in a cyclotron in analyzing for parts-per-million amounts of gallium in very pure iron. The development and application of activation analysis achieved a steady increase after the Second World War with the advent of high-flux nuclear reactors and the simultaneous technological demand for materials of high purity. This fact is of course attributable to the high sensitivity attainable by activation analysis at high neutron fluxes. In 1951, Leddicotte and Reynolds (15) started using activation analysis on a routine scale at the Oak Ridge National Laboratory. Numerous applications of activation analysis have been reported since then in a wide variety of fields including metallurgy, geochemistry and biochemistry and even in specific problem areas such as archeological applications and forensic chemistry. In most of these applications, the emphasis has been on trace analysis (less than 0.001%) although minor constituent analysis (0.001-1%) has also been reported using low-level neutron sources. Some excellent review articles (16-21) and comprehensive bibliographies (22-27) on the techniques and applications of activation analysis have appeared in the recent literature.

The method of activation analysis differs from other analytical methods primarily in that it exploits the nuclear properties rather than the atomic or chemical properties of an element. This enables the characterization from one another of elements which are normally similar in atomic or chemical properties. Thermal (0.025 ev) neutrons, available in a nuclear reactor, are especially desirable for trace analysis. Since radiative neutron capture is practically the only nuclear reaction that can take place at thermal energies, the radioisotopes formed have the advantage of being isotopic with the target elements.

The mathematical equations which describe the activation of a nucleus, and the growth of radioactive products in general, have been elegantly presented by various authors, among them, Friedlander, Kennedy and Miller (28). For the particular case in which the isotope of an element to be determined is transmuted to a radioactive nuclide by bombarding the sample with neutrons in a nuclear reactor, the induced radioactivity is given by the equation

$$A = \frac{6.02 \times 10^{23}\, W\sigma_{act}\phi\theta[1-\exp(-\lambda t)]\exp(-\lambda T)}{M} \qquad (1)$$

where ϕ is the neutron flux, σ and θ are the activation cross section and isotopic abundance, respectively, of the target isotope, W and M are the weight and the atomic mass, respectively, of the element being determined, λ is the decay constant of the radionuclide produced, and t and T are the bombarding and cooling times, respectively. The term $[1 - \exp(-\lambda t)]$ is commonly referred to as the "saturation factor" since it expresses the fraction of the maximum radioactivity produced in time t. It is evident from the above equation that the weight W of the element can be determined from the measured absolute disintegration rate A once the neutron flux is known, the activation cross section σ being a fixed quantity for any particular nuclide and nuclear reaction.

Neutron activation analysis may be carried out in one of two ways: by an absolute method or by a comparator method. The absolute method requires a knowledge of the absolute disintegration rate which in turn requires accurate information on the neutron flux, the activation cross section of the target nuclide and the half-life of the radionuclide produced. This method finds only limited application since the measurement of the actual neutron flux is rather difficult and the activation cross sections for most nuclides are not reliable. Moreover, the activation equation assumes that the neutron flux is constant throughout the sample matrix. This is not always true particularly in a matrix where nuclides with high neutron absorption cross sections are present. These nuclides may attenuate the neutron flux considerably thus causing a smaller flux being experienced by atoms well within the sample than by those close to the surface. This self-shielding effect is usually evaluated experimentally although semi-empirical calculations have been made for specific sample matrices (29-31). This effect can be minimized to a certain extent by reducing the size of the sample or by diluting the sample with an inert matrix. Also, the use of internal standards (32,33) may in some cases correct for neutron flux variations.

In actual practice, the comparator method of activation analysis is generally used since it does not require an accurate knowledge of the neutron flux and the activation cross section. In this method a standard material that contains a known amount of the element to be determined is irradiated simultaneously in the same irradiation position with the material to be analyzed. The radioactivity induced in the element to be determined in the sample is then compared with that induced in the element to be determined in the comparator. The amount of an element to be determined is given by the simple equation

$$\frac{W_s}{W_c} = \frac{A_s}{A_c} \tag{2}$$

where W_s and W_c are the weights of the element of interest in the sample and in the comparator, respectively, and A_s and A_c are the corresponding induced radioactivities. To further simplify the analysis, the activities in both the sample and the comparator can be measured under identical conditions to normalize the effects of counter geometry and counter efficiency. The absolute disintegration rates A_s and A_c can then be replaced by the corresponding observed counting rates R_s and R_c, corrected for decay if necessary. Thus Equation 2 becomes

$$\frac{W_s}{W_c} = \frac{R_s}{R_c} \quad . \tag{3}$$

In instances where self-shielding effects are considerable the comparator should ideally have a matrix of the same size and composition as that of the sample, as illustrated by the work of Speecke and Maes (34).

If the radioactivity induced in other components of the sample does not interfere with the measurement of the radioactivity induced in the element to be determined, a non-destructive analysis can be made. In this case, the radioactivity of the irradiated sample is measured directly without making any pre-counting chemical separation. An extensive review of the techniques of non-destructive activation analysis has been made by Adams and Hoste (19).

In most matrices, however, the radioactivity induced in other components of the sample does interfere with the measurement of the radioactivity induced in the element to be determined. A destructive analysis must therefore be made, in which case, the sample is dissolved after being irradiated, and the various constituents are separated by precipitation, ion exchange, solvent extraction, or other methods. The isolation of the radionuclide of the desired element, particularly in quantitative analyses for trace elements, is commonly done by "carrier" separation methods. Carrier methods involve the addition of a small amount of material containing an inactive stable element to the solution of the irradiated material to serve as a carrier of the radionuclide of the element throughout the separation. The use of carriers makes possible ordinary analytical manipulations on a milligram scale. Moreover, after the addition of carriers, chemical separations need not be quantitative. The chemical yield of the separation is determined by comparing the actual weight of the element obtained after the chemical separation to the weight of the same element that could be obtained theoretically from the amount of carrier material added. This chemical yield can be denoted by a factor, Y, and incorporated in Equation 3 to give

$$\frac{W_s}{W_c} = \frac{R_s/Y_s}{R_c/Y_c} = \frac{Y_c R_s}{Y_s R_c} \qquad (4)$$

where Y_s and Y_c are chemical yield factors of the element of interest in the sample and in the comparator, respectively.

It is evident from Equation 1 that in neutron activation analysis, irradiation of the sample at the highest neutron flux possible for the longest period of time practical insures the production of the maximum amount of radioactivity, thus attaining high sensitivity. Although this is indeed the case, irradiation in a high neutron flux entails some inherent problems that should be contended with to improve the accuracy of the analysis. Primarily, under high neutron flux conditions some neutron-induced second-order nuclear reactions can take place leading to significant interferences, particularly in the determination of a trace element, because they produce additional amounts of the measured radionuclide. Second-order interference may be produced by successive reactions of the type

$$ {}_{Z}E^{A}(n,\gamma)\ {}_{Z}E^{A+1} \begin{array}{l} \xrightarrow{\beta^-} {}_{(Z+1)}E^{A+1}(n,\gamma)\ {}_{(Z+1)}E^{A+2} \\ \xrightarrow{\beta^+,EC} {}_{(Z-1)}E^{(A+1)}(n,\gamma)\ {}_{(Z-1)}E^{A+2} \end{array} . \qquad (5) $$

Thus, if an element ${}_{(Z+1)}E$ or ${}_{(Z-1)}E$ is to be determined in a sample matrix with large amounts of ${}_{Z}E$, the above reactions may add significantly to the amount of the radionuclides actually formed from the element being determined. The extent of this second-order interference can be calculated, as demonstrated by Ricci and Dyer (35). This interference can be totally avoided in some favorable cases by making a proper choice of the radionuclide that will represent the element to be determined in the activation analysis.

Another problem that may arise in a high neutron flux irradiation results from the possible occurrence of threshold reactions induced by fast neutrons (greater than 0.1 Mev). This is particularly significant in irradiations done in a nuclear reactor where high thermal neutron flux irradiation positions have correspondingly high fast neutron fluxes. Threshold reactions can produce $_{(Z-1)}E$ and $_{(Z-2)}E$ nuclides from an $_{Z}E$ parent by (n,p) and (n,α) reactions which can cause serious interferences in the analysis. This situation is most pronounced in the thermal neutron activation analysis of the transition elements, where the atomic numbers of the impurities usually differ by 1 or 2 units from that of the matrix. Difficulties encountered with threshold reaction interferences have been reviewed by Durham _et_ _al_. (36) and by Maslov (37). In instances where the fast neutron flux is known, the extent of threshold reaction interferences can be calculated. A table of estimated cross sections for (n,p), (n,α) and (n,2n) reactions has been published by Roy and Hawton (38). Experimentally, the extent of these interferences can be calculated by irradiation with and without cadmium shielding to suppress the thermal neutron flux. On the other hand, reactor fast neutrons are sometimes utilized in the activation analysis of some elements whose threshold reactions can provide better sensitivities than thermal neutron activation, as shown by Yule *et al.* (39).

The half-life of the radionuclide produced in neutron activation also affects the sensitivity of the method. As can be deduced from Equation 1, the half-life is incorporated in the saturation factor (as a result of the relation $\lambda = \frac{0.693}{T_{1/2}}$), and therefore predetermines the length of irradiation necessary. Also, the half-life limits the time available after bombardment for chemical separations prior to measurement of the radioactivity.

In neutron activation analysis, therefore, there are several conditions that can be varied, namely, the neutron flux, the length of irradiation time and the choice of the radionuclide that will represent a certain element. By optimizing these conditions, the differences in nuclear properties between the element to be analyzed and those in the sample matrix may be magnified, thus making the analysis even more sensitive.

In the majority of the early activation analysis work, tedious chemical separations were necessary in order to prepare pure counting samples because activity measurements were usually done in GM tube counting systems. Qualitative identification of the radionuclides in this case was difficult and decay- and absorption measurements provided the only means of improving the specificity of the analysis. The development of gamma-ray scintillation spectroscopy using NaI(Tl) crystal detectors, first with single channel, and later on with multichannel analyzers greatly extended the scope of activation analysis. With scintillation counting systems, it became possible to measure specifically different radionuclides in a mixture and to conveniently characterize these nuclides not only by their half-lives but also by the energies of the gamma rays associated with their decays. Thus the necessity of complete chemical separations in activation analysis could often be avoided since most radionuclides decay with the emission of characteristic gamma rays. General information on the techniques of gamma-ray scintillation spectroscopy including a compilation of gamma-ray energy spectra of various nuclides obtained with a NaI(Tl) crystal detector is given in a book by Crouthamel (40) and in a recently published catalogue by Heath (41). Further refinements in gamma-ray scintillation spectroscopy were attained in recent years with the application of electronic computers to the evaluation of spectroscopic data. Least squares fitting programs have been developed specifically for problems in activation analysis by Auboin, Junod and Laverlochere (42), Munzel (43) and Coulomb and Schiltz (44). Least squares fitting has also been used for the analysis of multicomponent decay curves (45,46).

With the very high neutron fluxes now available in new research reactors, the inherent sensitivity of the neutron activation analysis technique has resulted in great emphasis on the use of this method to the determination of extremely low concentrations of various elements in a variety of matrices. Using a thermal neutron flux of about 10^{12} n/cm^2-sec, some 60 elements can be detected down to levels of about 5 micrograms or less, in a one-hour irradiation and with gamma-ray measurement in a scintillation spectrometer (47). With neutron fluxes in excess of 10^{14} n/cm^2-sec now attainable in more modern reactors, detection levels of 10^{-11} to 10^{-12} gram for some elements are not unusual. Calculated and experimental sensitivities have been reported by several investigators (22,48,49,50) for the neutron activation analysis of various elements.

Neutron Activation Analysis for Iridium, Palladium and Silver in Platinum

The feasibility of the simultaneous neutron activation analysis for iridium, palladium and silver in platinum can be ascertained from a consideration of the nuclear properties of these elements.

In Table 1, a list is given of some of the stable nuclides of the elements of interest including those of the sample matrix and the radionuclides that are produced through an (n,γ) reaction (1).

Table 1. Nuclear properties of the constituents of iridium, palladium, silver and platinum subject to activation by thermal neutrons

Target nuclide	Natural abundance (%)	Activation cross section (10^{-24} cm^2)	Product radio-nuclide	Product half-life
Ir^{191}	37.3	250	Ir^{192m}	1.4 m
		750	Ir^{192}	74 d
Ir^{193}	62.7	112	Ir^{194}	19 h
Pd^{102}	0.96	3.2	Pd^{103}	17.0 d
Pd^{106}	27.33	0.25	Pd^{107m}	21 s
Pd^{108}	26.71	0.2	Pd^{109m}	4.7 m
		10.4	Pd^{109}	14 h
Pd^{110}	11.81	0.020	Pd^{111m}	5.5 h
		0.36	Pd^{111}	22 m
Ag^{107}	51.35	33	Ag^{108}	2.4 m
Ag^{109}	48.65	2	Ag^{110m}	253 d
		97	Ag^{110}	24 s
Pt^{190}	0.0127		Pt^{191}	3.0 d
Pt^{192}	0.78	<16	Pt^{193m}	4.4 d
		0.08	Pt^{193}	<500 y
Pt^{194}	32.9	1.2	Pt^{195m}	4.1 d
Pt^{196}	25.3	0.05	Pt^{197m}	82 m
		~ 1	Pt^{197}	20 h
Pt^{198}	7.21	4.0	Pt^{199}	30 m

Basing on the natural abundance and activation cross section of the parent nuclide and the half-life of the daughter radionuclide, it can be deduced that Ir^{192}, Pd^{109} and Ag^{110m} are the most practical radionuclides that can be used to represent the corresponding elements to be determined. For the particular application under investigation, the use of the short-lived radionuclides can be ruled out due to the foreseeable radiochemical separations that would be required. It appears that Ir^{194} can also be used to represent iridium; however, this particular nuclide is produced together with Ir^{192} in the activation process and the radioactivity measurement of the iridium samples would involve a strictly simultaneous determination for both the sample being analyzed and the corresponding irradiation standard sample in order to normalize the effect of the time-varying activity ratio of Ir^{194} and Ir^{192}. This is obviously an inconvenient technique. On the other hand, the use of Ir^{192} alone is easily made possible by allowing Ir^{194} to decay.

The decay schemes of Ir^{192}, Pd^{109} and Ag^{110m} are shown in Figure 1 (1). Only the major branches of the decay are shown for clarity. It can be seen that all these radionuclides decay with the emission of characteristic gamma rays thus allowing the use of scintillation spectroscopic techniques in the measurement of their radioactivities. Ir^{192} has two modes of decay, ca. 96% by β^--emission and the rest by EC (electron

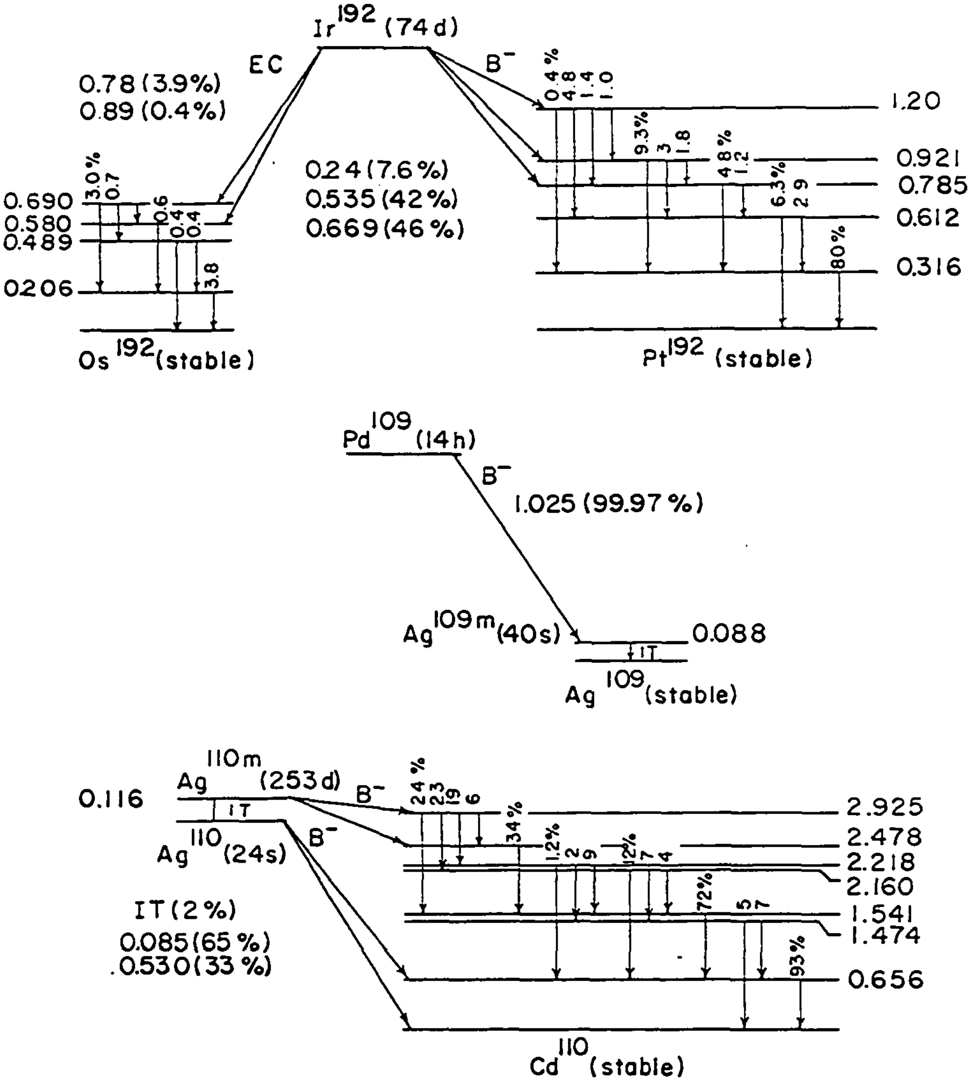


Figure 1. Decay schemes of Ir^{192}, Pd^{109} and Ag^{110m}

capture) with associated gamma rays of various energies, the most intense of which are those with energies of 0.316 and 0.469 Mev. Pd^{109} with a half-life of 14 hours decays by β^--emission to the metastable state Ag^{109m}, the latter de-exciting with a half-life of 40 seconds to stable Ag^{109} with the emission of a 0.088 Mev gamma ray; since the half-life of the parent nuclide is greater than that of the daughter nuclide, transient equilibrium is established in the system, the effective half-life being that of the parent, 14-hr. Pd^{109}. Ag^{110m} decays mainly by β^--emission with associated gamma rays of various energies, the most intense of which have energies of 0.656 and 0.885 Mev.

The gamma-ray energy spectra of Ir^{192}, Pd^{109} and Ag^{110m} are shown in Figures 2,3 and 4. These spectra were obtained with a multichannel pulse height analyzer using a NaI(Tl) crystal detector. Ir^{192} can be characterized by three prominent photopeaks in its energy spectrum corresponding principally to energies of 0.316, 0.469 and 0.605 Mev. The spectrum of Pd^{109} has two main peaks with energies of 0.022 and 0.088 Mev, the lower energy peak being due to the K X-ray emission of the Ag^{109} decay daughter. The spectrum of Ag^{110m} has also two prominent peaks corresponding to energies of 0.656 and 0.885 Mev.

Table 1 also indicates that neutron irradiation would certainly induce considerable activity in the platinum sample

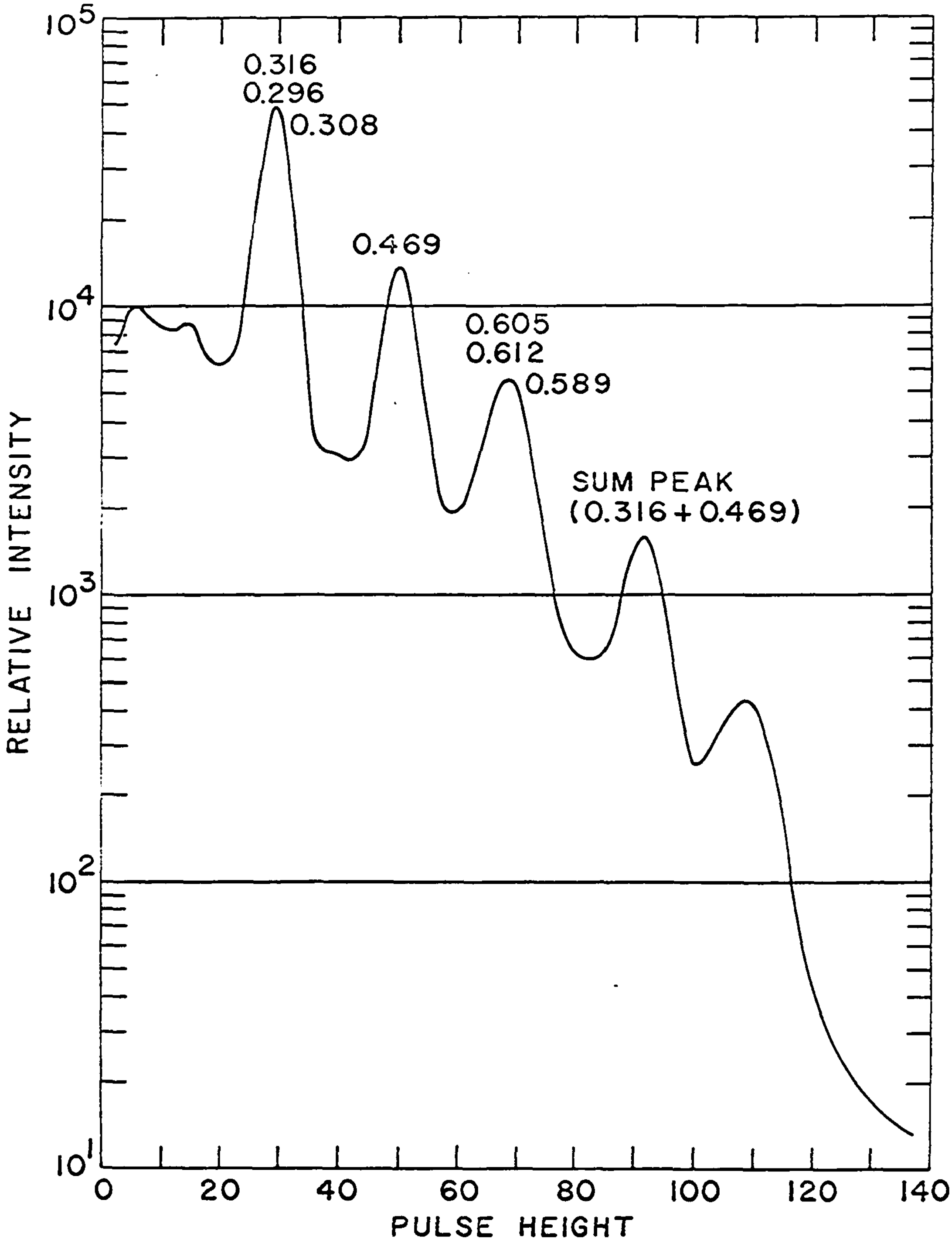


Figure 2. Gamma-ray energy spectrum of Ir^{192}

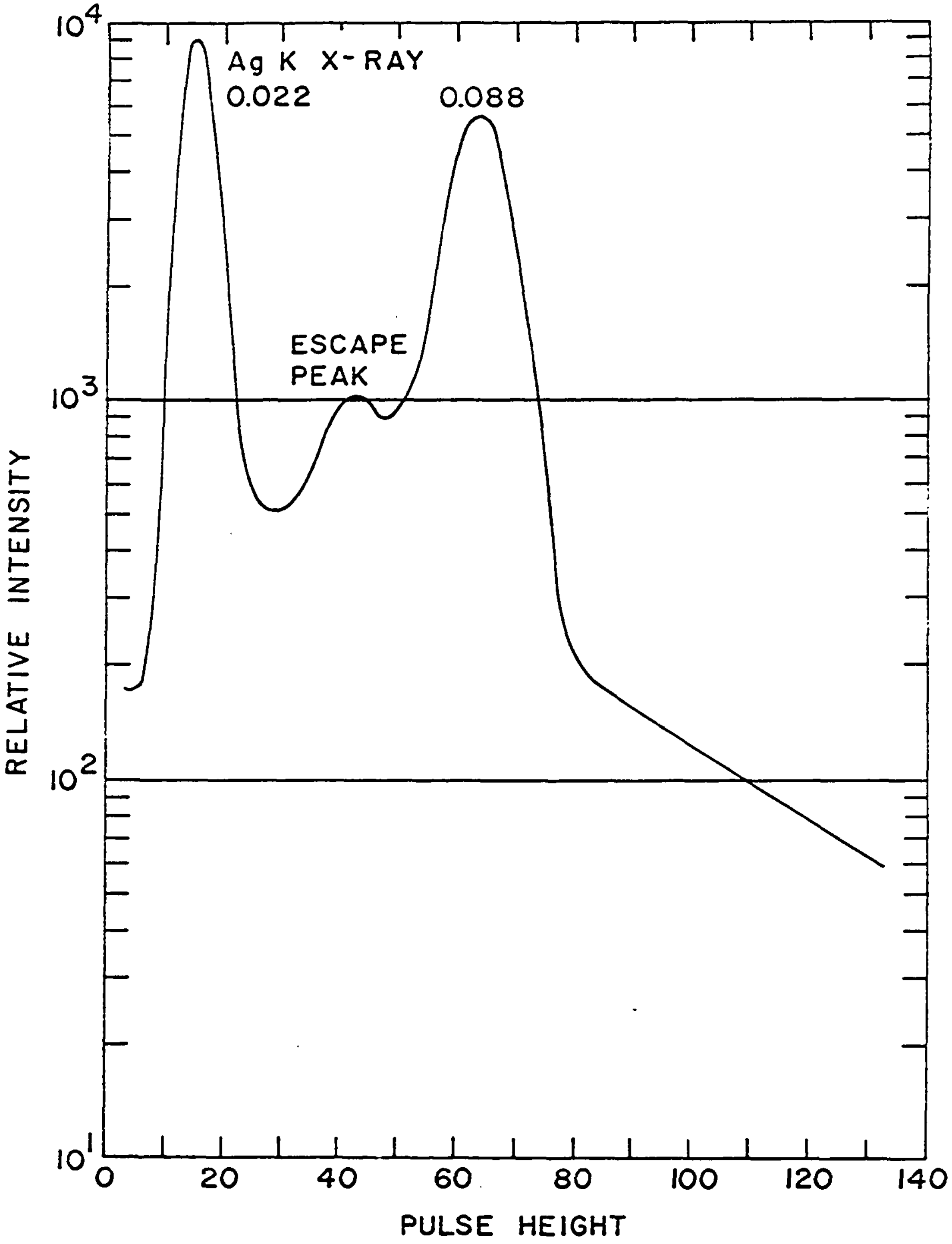


Figure 3. Gamma-ray energy spectrum of Pd^{109}

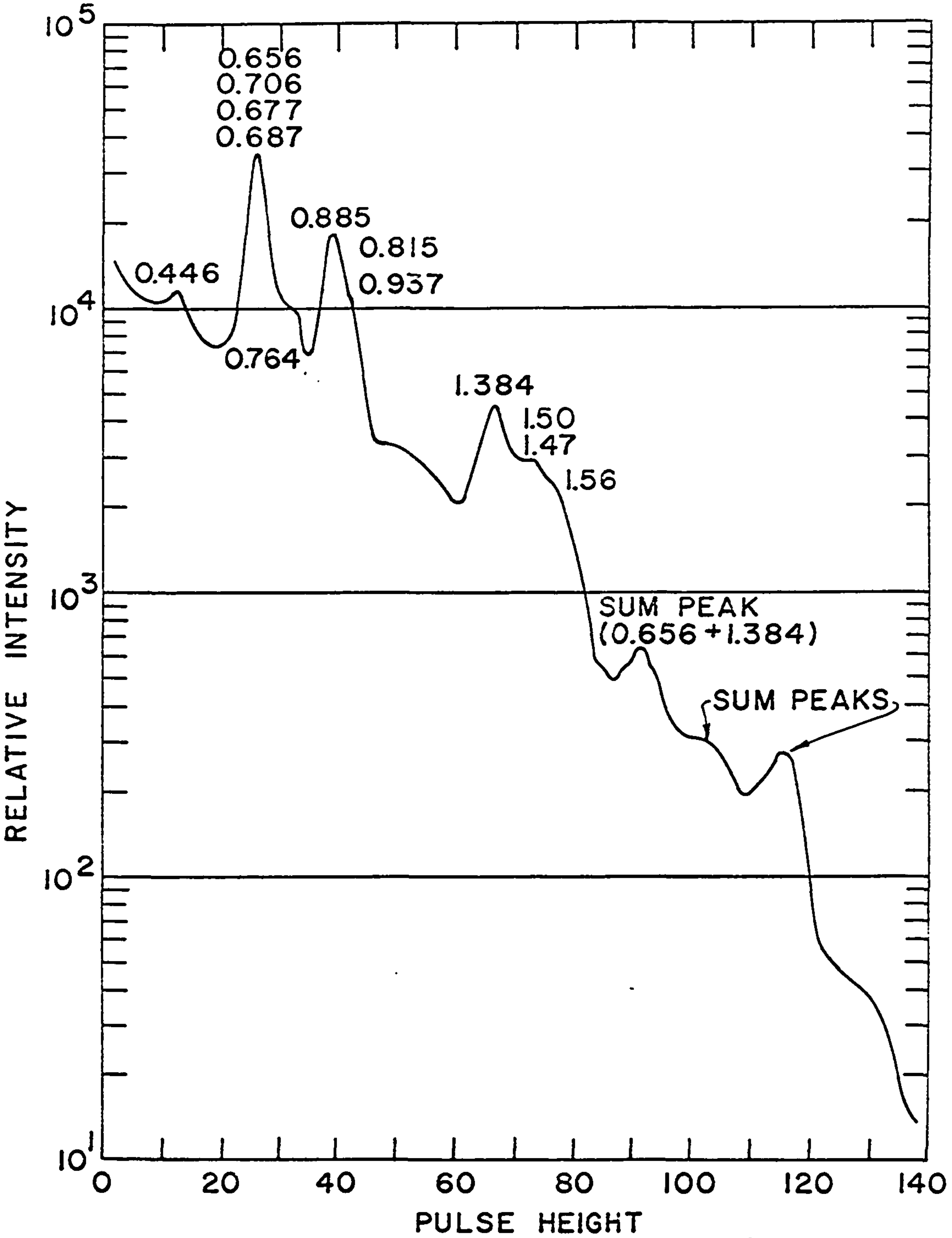


Figure 4. Gamma-ray energy spectrum of Ag^{110m}

matrix due to the formation of the radionuclides Pt^{193m}, Pt^{195m}, Pt^{197m}, Pt^{197} and Pt^{199}. Of these nuclides, the short-lived components Pt^{197m} (82 min.) and Pt^{199} (30 min.) both decay to radioactive daughters, Pt^{197} (20 h.) and Au^{199} (3.15 d.). Inasmuch as the elements to be determined were expected to occur in the sample material only in trace quantities, their neutron activation analysis in the platinum matrix would obviously involve a destructive method using suitable chemical separations to get rid of most if not all of the platinum radioactivities.

The possible interferences on the gamma-ray energy spectrometry of the radionuclides of the elements to be determined that can arise from contaminant activities induced in the sample matrix can be inferred from the decay schemes of the platinum radionuclides shown in Figure 5 (1). It appears that no serious interference on the spectra of Ir^{192} and Ag^{110m} can be caused by the gamma rays of any of the platinum radionuclides if moderately satisfactory decontamination factors are attained by chemical separating. For instance, Pt^{195m}, one of the predominant radionuclides in the matrix, has gamma rays with energies of 0.099, 0.129 and 0.130 Mev., considerably lower than the energies of the principal gamma rays of either Ir^{192} or Ag^{110m}. Moreover, all the platinum radionuclides have half-lives much shorter than either of Ir^{192} or Ag^{110m}, hence they could be eliminated simply by

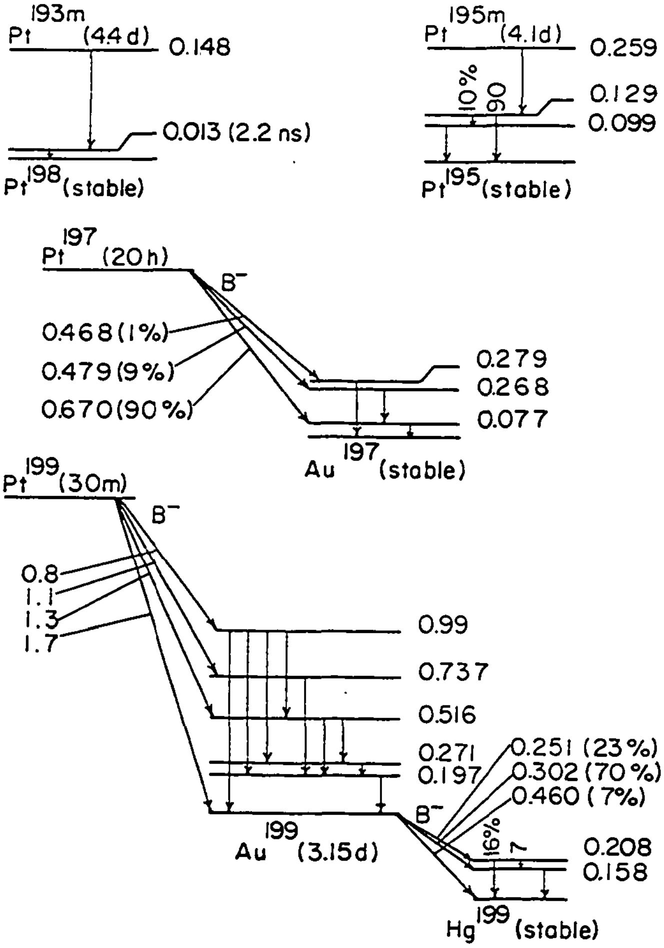


Figure 5. Decay schemes of the Pt radionuclides

allowing them to decay.

Serious interferences, however, can be expected in the case of the gamma-ray spectrometry of Pd^{109}. First, Pd^{109} has a half-life shorter than any of the platinum radionuclides except that of Pt^{199}, but this nuclide decays to 3.15-day Au^{199}. This precludes aging of the palladium counting samples as a means of eliminating any interfering platinum radioactivity. Secondly, the gamma rays of the platinum radionuclides, such as those of Pt^{195m} (0.099 Mev) and of Pt^{197} (0.077 Mev), have energies close enough to the 0.088 Mev gamma ray of Pd^{109}. To further aggravate the situation, associated with the decay of the platinum radionuclides are the K X-rays of platinum (from isomeric transition) and gold (from decay by β^--emission) which have emission energies of 0.067 and 0.069 Mev, respectively (51). All of these interfering radiations will appear as peaks in the gamma-ray energy spectrum superimposed on the slopes of the 0.088 Mev photopeak of Pd^{109}. These interference problems could at least be minimized by monitoring the activity of Pd^{109} on the basis of its 0.022-Mev Ag K X-ray emission peak. This approach has actually been reported by Herak and Morris (52) when they analyzed for palladium in platinum ore concentrates by neutron activation. In this Ag X-ray-based activity measurement, it should however be realized that the other radionuclides of palladium produced by (n,γ) reactions as shown in Table 1 all have associated

X-rays that can also contribute some interferences. Pd^{103}, for instance, decaying by EC with a half-life of 17.0 days to Rh^{103} will have corresponding 0.020-Mev rhodium K X-rays (51). Pd^{111m} (22 min.) and Pd^{111} (2.4 min.) eventually decay to the radioactive Ag^{111} nuclide (β^--emitter, 7.5 days), which in turn have associated 0.023-Mev cadmium K X-rays (51). These interfering activities could be eliminated by proper radiochemical purification methods combined with decay data evaluation techniques.

In neutron activation analysis for trace impurities, special care must be taken in selecting the irradiation times and the sample weights for a particular neutron flux in order to obtain sufficient activity of the impurities and a matrix activity low enough for safe handling in a conventional radiochemical laboratory. This is especially important in a platinum matrix, as shown from preceding considerations, where a high activity is induced in the matrix by neutron irradiation. To establish the detection limits for the elements of interest in this work, the activities induced in 1 ppm of each of the elemental impurities in a 100-mg platinum sample were calculated, using pertinent data listed in Table 1, for a 24-hour neutron irradiation at a flux of 10^{13} thermal neutrons/cm^2-sec. Results are shown in Table 2. It must be emphasized that the induced activities shown are theoretically derived values and are therefore merely indicative of the relative

Table 2. Activities induced in 1 ppm of each of some impurities in 100 mg of platinum sample after a 24-hour irradiation at 10^{13} neutrons/cm^2-sec

Impurity radionuclide	Half-life	Induced activity (dpm)	Saturation factor
Ir^{192}	74 d	4.9×10^5	0.0094
Pd^{109}	14 h	7.8×10^5	0.70
Ag^{110m}	253 d	9×10^2	0.0027

detection limits of the elements involved; the actual experimental sensitivities depend mainly on the chemical separations and activity measurements associated with the analysis. Nevertheless, with a conservative counting efficiency estimate of 10%, a value which is easily attainable in gamma-ray spectrometry, iridium and palladium can be detected down to levels below 1 ppm for the bombardment conditions used. Pd^{109}, although appearing to have the highest detection sensitivity, has the shortest half-life and would therefore limit the time of the radiochemical separations necessary in the analysis.

The saturation factors, also shown in Table 2, indicate that the detection sensitivities of Ir^{192} and Ag^{110m} can be considerably improved by irradiating the sample for longer periods. Although this is indeed the case, the irradiation period is however limited by the hazardously high radioactivity level induced in the sample matrix, as depicted in Table 3. As shown in the table, immediately after irradiation 100 mg of

Table 3. Activities induced in 100 mg of platinum after a 24-hour irradiation at 10^{13} neutrons/cm^2-sec

Radionuclide	Half-life	Induced activity (mc)	Activity after cooling 2 hours (mc)
Pt^{193m}	4.4 d	1.6	1.6
Pt^{195m}	4.1 d	5.3	5.2
Pt^{197m}	82 m	1.1	0.4
Pt^{197}	20 h	11.8	11.0
Pt^{199}	30 m	24.1	1.5
Totals		43.9	19.7

platinum in the matrix would have an activity of 44 mc (1 mc = 2.22×10^9 dpm) consisting of β^-- and γ-radiation. Even if the sample is allowed to decay for 2 hours to eliminate most of the 30-minute Pt^{199} activity, the matrix would still have an activity of 20 mc.

In the light of all the considerations cited in the preceding discussions on the nuclear properties of the elements of interest and of the sample matrix, it is apparent that the main aspect of this investigation was the development of a suitable destructive method of neutron activation analysis using chemical separations with high decontamination factors, particularly in the analysis for palladium.

The use of a high neutron flux and a long irradiation time, *e.g.*, of the order of two half-lives of Pd^{109}, was obviously necessary in the analysis for ppb amounts of palladium. Under these conditions, the effects of possible associated interferences, namely, second-order (n,γ) reactions and threshold reactions, must be considered. The results of the analysis for palladium and silver cannot be affected by these interferences, their atomic numbers being very well below that of platinum. However, in the case of the determination for iridium these interferences may have significant effects since iridium has an atomic number only one unit less than that of platinum.

An interference can be caused by second-order (n,γ) reactions on Pt^{190} in the matrix, as follows:

$$Pt^{190}\ (n,\gamma)\ Pt^{191} \xrightarrow{\beta^+,\ EC} Ir^{191}\ (n,\gamma)\ Ir^{192}\ . \qquad (6)$$

Unfortunately, calculations for the extent of this interference, similar to those demonstrated by Ricci and Dyer (35), cannot be performed because of the lack of pertinent literature data. It was assumed in this investigation that this type of interference had only a negligible effect, if any, on the Ir^{192} activities observed in the samples analyzed, considering the fact that the natural abundance of Pt^{190} in platinum metal is only 0.0127%.

An interference due to fast neutrons can also arise from the possible extensive occurrence of (n,p) threshold reactions on Pt^{192} producing Ir^{192}. For this reaction, the threshold energy required for the incident neutron is 0.65 Mev and the potential barrier for proton emission is 10.3 Mev. The cross section for this reaction had not been reported, but Miller (53) who determined the (n,p) reaction cross sections of some nuclides of iron, cobalt and nickel concluded that the large reaction Q-values and potential barrier values of nuclides of the heavy elements of Group VIII suggest that their (n,p) reaction cross sections should be very small, *e.g.*, less than one millibarn. This small cross section, and the fact that Pt^{192} has a natural abundance of only 0.78% in platinum metal, would make the interference from (n,p) threshold reactions negligibly small. Indeed, in work done by Jowanovitz *et al.* (4) on a neutron activation analysis for iridium in platinum, no interference from (n,p) reactions was observed in 24-hour irradiations with an epithermal neutron flux of 1.6×10^{13} neutrons/cm^2-sec.

Review of Neutron Activation Methods and Related Radiochemical Techniques for Iridium, Palladium and Silver

The analytical procedures commonly used for the elements of the platinum family including iridium and palladium are rather difficult particularly when all or even several of these elements are present in a sample. The methods of separation generally used for these elements are those due to Gilchrist and Wichers (2) and Schoeller and Powell (3).

Walsh and Hausman (54) made a systematic summary of the known analytical chemistry of the platinum metals. The various methods for the determination of these metals were also critically reviewed by Beamish, including volumetric methods (55), gravimetric methods (56,57) and titrimetric methods (58). In his reviews, Beamish commented that the number of gravimetric methods reported for these metals were considerably more than the number of recorded volumetric methods, and that many of the proposed volumetric methods can be considered useful only when applied to the isolated platinum metal constituent and applied under carefully controlled conditions. Most of the titrimetric methods applicable to these metals had been developed only recently, with electrometric techniques involving electrogenerated titrants taking precedence.

So far, a literature survey clearly indicates that for the separation of iridium and palladium from the other platinum metals and their subsequent quantitative determination, precipitation techniques had been the most widely utilized.

Iridium can be quantitatively separated from platinum by a controlled hydrolysis of its chloro complex in the presence of bromate, with the eventual precipitation of the hydrated Ir(IV) oxide.

For the separation and determination of palladium the most common reagent used is dimethylgloxime. The dimethylglyoxime complex of this metal is formed in dilute acid solution, is sparingly soluble in water and dilute HCl or HNO_3, soluble in ammonia, chloroform and benzene, and decomposed in concentrated

HNO_3 and in aqua regia. The use of dimethylglyoxime as a precipitating reagent specific for palladium can be found in general references (2,54,59).

A promising method of separation of the platinum metals from one another and from other metals that can be easily adapted to radiochemical work is by the use of ion exchange resins. Following the unique success achieved by ion exchange techniques in the separation of the rare earth metals by Spedding and coworkers (60,61), several investigators studied the behavior of the metals toward cation and anion exchange resins. Kraus _et al_. (62,63) showed that iridium as Ir(III) can be separated from Pt(IV) and Pd(II) by first adsorbing them from a dilute chloride solution onto the anion exchange resin Dowex 1, and then using 10 N HCl as a column eluant, with Ir(III) desorbing from the column and Pt(IV) and Pd(II) remaining on the column. Iridium, palladium, platinum and also rhodium were reportedly separated from each other by Stevenson and co-workers (64) by adsorbing the perchlorate forms of these metals in a Dowex 50 cation resin column and subsequently eluting the column with HCl solutions of varying molarities. Blasius and Wachtel (65) used the anion exchange resin Permutit E. S. in the hydroxide form to separate palladium from platinum and iridium from platinum. The anion exchange resin Dowex 2 was used by MacNevin and Crumett (66) to adsorb and separate the chloro complexes of palladium, platinum, rhodium and iridium by selective elutions with aqueous ammonia-ammonium chloride. Berman and McBride (67) measured the distribution coefficients of the chlorides of the platinum metals relative to the anion exchange resin Amberlite IRA-400 and reported separations of various combinations of rhodium, iridium, palladium and platinum. In the majority of these ion exchange works, submilligram quantities of the metals were used. The separations, in most cases, were not quantitative, with chemical yields generally below 90%. Nevertheless, the results of these investigations indeed suggest that ion exchange techniques can be integrated with a Gilchrist-Wichers (2) scheme for an improved and less tedious separation of the platinum metals from one another and from other metals.

The preparation, structure and general behavior of ion exchange resins are described in several reference books, such as those by Kunin and Meyers (68) and by Samuelson (69). A comprehensive report on the adsorption coefficients on an anion exchange resin of most of the metals in their various oxidation states from chloride media was made by Kraus and Nelson (70). Adsorption coefficients of the metals from HCl solutions and from $HClO_4$ solutions on a cation exchange resin were also reported by Nelson and co-workers (71).

The general radiochemistry of iridium, palladium, silver and platinum have been critically reviewed in a series of monographs published by the National Academy of Sciences-National Research Council (72,73,74,75). Included in these reviews are descriptions of the general chemistry of the element, nuclear properties, methods of dissolution, safety practices, and also condensed details for representative radiochemical studies.

Some investigations have already been done on the application of neutron activation techniques to the determination of iridium and palladium in various matrices including platinum. As usual, the emphasis has been on trace analysis. Some of these applications have been particularly useful for the examination of the efficiency of analytical treatments of the platinum metals in general, and for determining the losses and distribution of these metals in the various stages of industrial methods for their recovery and purification.

The neutron activation analysis for iridium and palladium in a platinum matrix that have been reported so far are briefly reviewed below:

Iridium

Kamemoto _et_ _al_. (76) determined 4.5 to 90 microgram amounts of iridium in 50-milligram samples of platinum, rhodium, palladium and gold by a non-destructive method. The samples and iridium standard were irradiated for 2 hours with a flux of 3 x 10^{11} neutrons/cm^2-sec. After allowing the samples to decay for 20 to 40 days, the gamma-ray spectra were measured with a 256-channel pulse height analyzer. Iridium was determined by comparing the photopeaks of Ir^{192} in the standard.

Germagnoli and Airoldi (77) reported the determination of 1.18 $\pm$ 0.34 x 10^{-5} milligrams of iridium per milligram of a very pure sample of platinum by using two techniques of nuclear activation. One method involved the use of the gamma-ray activity of Au^{199} resulting from the decay by β^{-}-emission of Pt^{199} as an internal standard to calculate the number of platinum atoms; iridium concentration was determined from the gamma-ray activity of Ir^{192}. The second method involved the prior decay of the platinum activity over a period of 49.9 days after which the Ir^{192} gamma-ray activity was measured; an independently measured value of the neutron flux was used in the calculation for the concentration of iridium.

Jowanovitz et al. (4) of this laboratory developed a highly sensitive destructive neutron activation technique for the determination of traces of iridium in platinum. The platinum sample and freshly precipitated hydrated iridium oxide as standard were irradiated for periods of at least 12 hours with a thermal flux of 2 x 10^{12} neutrons/cm^2-sec. The radiochemical separation used involved the dissolution of the platinum sample to yield the chloride form, addition of $[IrCl_6]^{2-}$ carrier, extraction of interferring Au^{199} with ethyl acetate, and precipitation of iridium as the hydrated

Ir(IV) oxide. Ir^{192} activity was measured with a gamma-ray spectrometer. Iridium impurities of 0.04 ppm were obtained. No interference from (n,p) processes was evident at this impurity level.

Submicrogram amounts of iridium and osmium were simultaneously determined by Morris and Killick (78) in powder samples of platinum and palladium. The samples and standards were irradiated for 1 week with a thermal flux of 10^{12} neutrons/cm^2-sec. Chemical separations using carriers were used wherein iridium was finally precipitated as the hydrated Ir(IV) oxide followed by ignition to the metal form. The gamma-ray activity of Ir^{192} was measured with a scintillation counter. Values of 0.097- 11.1 ppm were reported for iridium.

Palladium

The determination by neutron activation analysis of traces of palladium, in concentrations ranging from 0.3 to 3 ppm, was reported by Killick and Morris (79). The samples and standard were irradiated with a thermal flux of 10^{12} neutrons/cm^2-sec for periods of up to 3 days. Chemical separations using carriers were employed, involving precipitation of palladium with dimethylglyoxime, repeated precipitation as the hydrated Pd(II) oxide, removal of silver activity with silver carrier, and solvent extraction of Au^{199}. The β^--radiation of 13.5-hour Pd^{109} was measured with a thin end-window GM counter. The time needed for chemical separation ensured the removal of the shorter-lived Pd^{111}.

Iridium and palladium

Palladium, iridium and gold in submicrogram and microgram quantities were determined by Herak and Morris (52) in residues from the recovery of platinum metals from ores. Irradiation of samples and standards were done with a flux of 1.2×10^{12} neutrons/cm^2-sec for 6 days. Radiochemical separations with appropriate carriers were used; gold was extracted with isopropyl ether, palladium was precipitated with dimethylglyoxime and iridium was precipitated as the hydrated Ir(IV) oxide, in that order. For palladium, the β^--radiation of Pd^{109} or alternatively the K X-rays associated with the equilibrium mixture of Pd^{109} and Ag^{109m} were measured. For iridium, the gamma rays of Ir^{192} were used.

The chemistry of silver of interest to radiochemists is well known and can be found in standard analytical reference books, such as those by Hillebrand et al. (80) and by Vogel (59). So far, no previous work has been reported on the neutron activation analysis for silver in a platinum matrix. But unlike those of the platinum elements, the methods for the radiochemical separations of silver are well-established, due to such highly selective techniques as isotopic exchange, electrodeposition and precipitation. Of these techniques, isotopic exchange has found the widest utility because it gives very high decontamination factors with most radioactive species. An extensive evaluation and discussion of the isotopic exchange behavior of silver including some radiochemical applications has been made by Sunderman and Meinke (81).

NEUTRON SOURCES

The samples analyzed in this investigation were irradiated at the Ames Laboratory Research Reactor (ALRR). This is a 5-megawatt tank-type reactor, fueled with fully enriched U^{235}, cooled and moderated with heavy water. The reactor core assembly consists primarily of the uranium fuel elements within the heavy water tank and surrounded by a stainless steel thermal shield within a light water tank. A total of 35 experimental facilities, including radiation ports, beam tubes, vertical thimbles, rabbit tubes and a thermal column, penetrate the concrete shielding to permit access to the reactor core for irradiation. One of the vertical thimbles (V-5) was used in the irradiation of samples throughout this work. This thimble is about 14 inches from the center of the core. At this location, the thermal neutron flux is approximately 3×10^{13} neutrons/cm^2-sec when the reactor is operating at its full power of 5 megawatts. The cadmium ratio is approximately 20.

Some isotopic tracers used in preliminary studies in connection with this work were obtained by irradiation of the corresponding materials at the Iowa State University Training Reactor (UTR-10). This is a heterogeneous, tank-type reactor, which is cooled with light water and moderated with light water and graphite. The total U^{235} content of the core is 3 kg present in 90% enrichment. A pneumatic tube which terminates against one of the two tank cores permits convenient access to the highest flux possible by means of a "rabbit" sample holder. This reactor can provide a maximum power of 10 kilowatts with a corresponding thermal flux of 8 x 10^{10} neutrons/cm^2-sec in the rabbit.

During the early stage of this work when ALRR was not yet in operation, some irradiations requiring high fluxes were done in the CP-5 reactor at Argonne National Laboratory. Locations in the graphite zone of this reactor were utilized, which were quoted to have a thermal flux of approximately 2 x 10^{12} neutrons/cm^2-sec and an epithermal flux of about 10^{10} neutrons/cm^2-sec.

COUNTING EQUIPMENT

All radioactivity measurements in this study were done in a gamma-ray scintillation spectrometer system consisting of a multichannel pulse height analyzer using a NaI(Tl) crystal detector and accessories for data storage and read-out.

The analyzer was a Radiation Instrument Development Laboratory (RIDL) Model 34-12B Transistorized 400-Channel Pulse Height Analyzer consisting basically of an amplifier, an analog-to-digital (ADC) converter, a computer with a ferrite memory core, a cathode ray tube (CRT) display, and control circuitry for automatic operation. Integrated with the analyzer is a timing system which permits counting in either of two modes: in the live time mode, the timer operates only during the time when the ADC is accepting counts, with automatic compensation for analyzer dead time; in the clock time mode, the timer indicates elapsed clock time during operation, this mode also permitting dead time compensation through an external dead time indicator. Data storage and read-back accessories include an RIDL Model 52-35 magnetic tape recorder and a Tally Model 420/424 paper tape recorder. The data stored in the analyzer memory can be read out in a Friden printer which also permits integration of the counts in desired regions of the gamma-ray energy spectra. A spectrum in the analyzer memory can likewise be automatically plotted with a Mosely Co. Model

2D-2 X-Y Recorder.

The gamma-ray scintillation detector was a 3" diameter NaI(Tl) crystal optically coupled to a photomultiplier tube.

The gamma-ray energy resolution η of this spectrometer system, defined as

$$\eta = \frac{\text{full width at half-maximum, } \Delta E\text{, of } Cs^{137} \text{ line}}{\text{average energy, } \bar{E} \text{ (0.662 mev)}} , \qquad (7)$$

was 9.2%.

MATERIALS

Platinum Stock

The high-purity platinum stock analyzed in this investigation was reclaimed from commercial grade platinum by Mary Ann Tucker of this laboratory.

The chemical procedure followed in the reclamation process is routinely used in this laboratory and is specifically designed to remove iridium from platinum. Details of the procedure are cited below:

1. Reduce the platinum compounds (solid or in solution) to platinum metal by making the solution basic (pH 10) with NaOH and adding a few drops of hydrazine.
2. Coagulate the platinum and allow the sediment to settle. Decant off the supernatant solution and wash the residue with several aliquots of water, decanting off each washing until most of the NaOH is gone (check pH with pH paper).
3. Add concentrated HCl to the residue and digest for one-half hour. Decant off the HCl and repeat digesting with more HCl until the supernatant HCl becomes only slightly colored (very light yellow) after digestion. Important: wash the residue with several aliquots of distilled water, decanting off each one, until no more chloride ion can be observed in the supernate

(check with $AgNO_3$).

4. Repeat step 3 using concentrated HNO_3. Two or three washings with distilled water will be sufficient after the HNO_3 no longer becomes colored.
5. Add enough HCl to the residue to little more than cover it. Bring to a boil and add about one-third as much concentrated HNO_3 slowly. The solution should become a deep red color with no residue left. Filter the solution if any residue does remain.
6. Evaporate the solution to near dryness and add concentrated HBr. Heat again to dryness. Repeat this process at least three times.
7. To the hot solution of $H_2[PtBr_6]$ add excess KBr and allow to cool slowly.
8. Separate the precipitate and recrystallize it from water three times. It will be necessary to continually boil down the mother liquors as $K_2[PtBr_6]$ is appreciably soluble in water.
9. Finally, reduce the $K_2[PtBr_6]$ crystals to platinum metal by repeating step 1.

Reagents

Iridium used in the preparation of the irradiation standard and the carrier solution was purchased from K & K Laboratories, Inc. in the form of $Na_2[IrCl_6]$ powder. Palladium was purchased from Engelhard Industries, Inc. as $PdCl_2$ powder.

All other chemical reagents used in this study were normally of reagent analytical grade. Water used in the preparation of the standard and carrier solutions was drawn from the distilled water tap and redistilled from alkaline permanganate.

Ion Exchange Resin

The anion exchange resin Dowex 1-X8 used in the radiochemical separations was purchased from J. T. Baker Chemical Co. A "Baker Analyzed" reagent, this resin is in chloride form with a particle size of 100-200 mesh. The rated total exchange capacity (wet volume basis) is 1.3 milliequivalents per ml.

EXPERIMENTAL

Preparation and Standardization of Carrier Solutions

Iridium(III)

Na_2IrCl_6 powder was dissolved in water and the solution was made slightly acidic with HCl. The solution was warmed and SO_2 gas was bubbled through slowly for about 30 minutes to reduce Ir(IV) to Ir(III). The reduction was indicated by a change in the color of the solution from dark red to light yellow. To further insure that no more $[IrCl_6]^{2-}$ species was left, the solution was adsorbed in a Dowex 1-X8 anion resin column and eluted with 8 N HCl. With this treatment only $[IrCl_6]^{3-}$ would be eluted out leaving any $[IrCl_6]^{2-}$ adsorbed in the resin column. The eluate was evaporated to a small volume and diluted to mark in a graduated cylinder to make a solution containing <u>ca</u>. 5 mg of iridium per ml.

The $[IrCl_6]^{3-}$ solution was standardized by an indirect iodometric titration method. Two-ml aliquots of the solution were taken and diluted to 100 ml in a 250-ml Erlenmeyer flask. The solution was warmed and iridium was oxidized to $[IrCl_6]^{2-}$ by bubbling Cl_2 gas through the solution for 30 minutes. Excess Cl_2 gas was then removed by boiling the solution for 5 minutes after which the solution was cooled in an ice water bath. An excess of potassium iodide was added which reduced the iridium back to the trivalent state. The iodine liberated in the reaction was titrated with standard 0.01 N thiosulfate solution using starch solution as indicator. Special precautions for iodometric titration discussed by Vogel (55) were closely observed.

$$1.00 \text{ ml of } 0.01 \text{ N } [S_2O_3]^{2-} = 1.922 \text{ mg of Ir.} \qquad (7)$$

Reactions:

$$[IrCl_6]^{3-} + \frac{1}{2}\,Cl_2 \dashrightarrow [IrCl_6]^{2-} + Cl^- \qquad (8a)$$

$$[IrCl_6]^{2-} + I^- \dashrightarrow [IrCl_6]^{3-} + \frac{1}{2}\,I_2 \qquad (8b)$$

$$[S_2O_3]^{2-} + \frac{1}{2}\,I_2 \dashrightarrow \frac{1}{2}[S_4O_6]^{2-} + I^- \qquad (8c)$$

Palladium(II)

$PdCl_2$ powder was dissolved in water to make a solution containing ca. 5 mg of palladium per ml.

Standardization was accomplished by precipitation of palladium with dimethylglyoxime. Two-ml aliquots of the solution were taken and diluted to 100 ml in a 250-ml beaker. The resulting solution was acidified to contain 5% HCl and cooled in an ice water bath. An alcoholic solution of dimethylglyoxime was added dropwise to avoid a large excess of the reagent. The suspension of palladium dimethylglyxomate, $Pd(C_4H_7N_2O_2)_2$, was allowed to stand for 30 minutes while keeping the solution cool, then was filtered in a suction chimney filtration set-up onto a weighed piece of S & S No.

576 filter paper. The precipitate was washed with 2% HCl, rinsed first with water, then with 95% ethyl alcohol. The precipitate was next dried to constant weight at 110°C in a drying oven, cooled to room temperature in a desiccator, and weighed.

Silver(I)

A standard solution of 0.100 N $AgNO_3$ was prepared using the procedure by Vogel (55).

Platinum(IV)

Platinum carrier solution as $PtCl_6^{2-}$ was prepared by dissolving a weighed amount of high-purity platinum black powder in aqua regia, removing nitrate ion by repeated evaporation to dryness with concentrated HCl, dissolving the final residue in HCl and diluting with water to make a solution containing *ca.* 5 mg of platinum per ml.

Preliminary Studies

Previously discussed considerations of the nuclear properties of the elements involved in this investigation pointed out the need for the use of chemical separation procedures with high decontamination factors, particularly in the case of the analysis for palladium. Some preliminary experiments were therefore conducted mainly to develop a suitable radiochemical procedure for the isolation of palladium activity from a highly active platinum matrix.

One separation scheme which proved to be inadequate for the problem at hand was initially attempted. Briefly, the separation steps involved were the following: a 100-mg sample of platinum black powder was spiked with palladium and irradiated at the CP-5 reactor at Argonne National Laboratory for 24 hours with a thermal flux of ca. 10^{12} neutrons/cm^2-sec; the irradiated sample, received four days later at this laboratory, was dissolved in aqua regia and the nitrate ion was removed by repeatedly evaporating to dryness with concentrated HCl; the residue was redissolved in 6 N HCl and extracted three times with ethyl acetate that had been presaturated with 6 N HCl; palladium was then precipitated from the aqueous layer three times with dimethylglyoxime. The resulting palladium sample was counted and was found to be very badly contaminated with activities from the sample matrix. This sample was definitely unsuitable for gamma-ray spectrometry. Although this experiment was admittedly crudely performed, it could be generalized that the platinum radionuclides and Au^{199} could indeed be troublesome contaminants in a separation involving the precipitation of palladium dimethylglyoximate due to the fact that platinum and gold could be co-precipitated even under carefully controlled conditions. Furthermore, solvent extraction techniques seemed to be a hazardous radiochemical procedure for performance in a conventional laboratory where there are no sophisticated facilities for remote handling techniques.

The above separation scheme was therefore abandoned and the possibility of utilizing ion exchange methods was studied.

The elution behavior from a Dowex 1-X8 anion resin column of the chloro complexes of the elements involved in this work were observed using radioisotopic tracers. All the chloro complexes were adsorbed on the resin column from a dilute HCl medium. However, differences in the elution behavior were noted when the resin column was eluted with HCl solutions of varying concentrations. Iridium when present as $[IrCl_6]^{2-}$ was very strongly adsorbed by the resin and was not eluted out of the column with moderate amounts of concentrated HCl; but iridium when present as $[IrCl_6]^{3-}$ was easily desorbed and eluted out with 8 to 12 N HCl solution. Silver as $[AgCl_2]^-$ present in carrier-free concentration was also eluted out easily with 8 N HCl solution. Palladium, present as $[PdCl_4]^{2-}$, was strongly adsorbed by the resin but was eluted out of the column with moderate amounts of concentrated HCl. Both of platinum, as $[PtCl_6]^{2-}$, and gold, as $[AuCl_4]^-$, were very strongly adsorbed by the resin and were not at all eluted out of the column with moderate amounts of concentrated HCl. The adsorption bands of some of these ions were visible on the Dowex 1 resin column; iridium, present as $[IrCl_6]^{2-}$, gave a very dark red band; palladium, as $PdCl_4^{2-}$, a red band; platinum, as $[PtCl_6]^{2-}$, an orange band; and gold, as $[AuCl_4]^-$, an orange-red band. The observed elution curves for $[IrCl_6]^{3-}$ and $[PdCl_4]^{2-}$ are shown in Figure 6. A resin column 1.2 cm in diameter by 10 cm long was used. Elution was performed at a rate of 2 to 3 ml/min.

These differences in elution behavior of the anionic chloro complexes formed the basis for the ion exchange separation utilized in this analysis. Briefly, the separations described in the following sections essentially involved an initial qualitative separation by anion exchange of the activities of iridium, palladium and silver from those of the sample matrix, followed by more effective decontamination treatments for the individual radionuclides.

Preparation of Irradiation Samples

The platinum stock analyzed in this investigation was in the form of platinum black powder. Platinum samples, in 100-mg amounts, were weighed out and sealed in 5 mm ID silica ampoules.

Irradiation standards of iridium, palladium and silver were prepared by micropipetting aliquots of standard solutions of these elements into 5 mm ID silica ampoules and carefully evaporating them to dryness after which the ampoules were sealed.

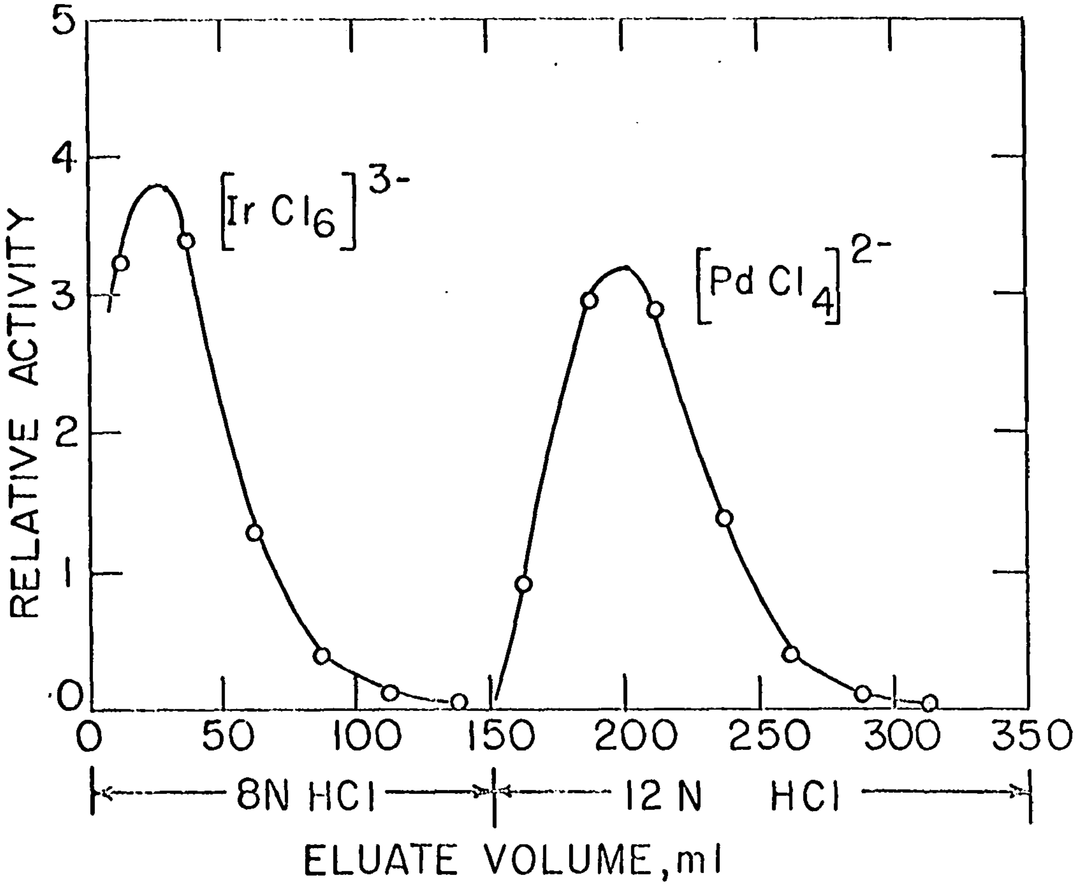


Figure 6. Elution curves of $[IrCl_6]^{3-}$ and $[PdCl_4]^{2-}$ from a 100-200 mesh Dowex 1-X8 anion resin column, 1.2 cm. dia. x 10 cm., at an elution rate of 2 to 3 ml/min.

Irradiation

Two platinum samples and one each of the irradiation standard samples were irradiated at a time. The ampoules containing the samples were wrapped in aluminum foil, placed inside an aluminum irradiation can, and irradiated in the vertical thimble, V-5, of the Ames Laboratory Research Reactor (ALRR) with a thermal flux of ca. 10^{13} neutrons/cm^2-sec for periods ranging from 9 to 30 hours. The irradiated samples were generally available for analysis in less than 12 hours after irradiation.

Sequence of Radiochemical Analyses

Inasmuch as the 14-hour Pd^{109} had the shortest half-life relative to the other radionuclides of interest, 74-day Ir^{192} and 253-day Ag^{110m}, the separation of palladium from the irradiated platinum samples and the subsequent measurement of its activity was performed first, followed by the measurement of the activity of the palladium irradiation standard. After completion of this radiochemistry for the palladium samples, the rest of the analytical steps followed in any arbitrary sequence since time pressure was no longer involved.

Radiochemical Analysis of the Platinum Samples

Sample dissolution and carrier addition

Each of the ampoules containing the irradiated platinum samples was washed thoroughly with warm HNO_3 solution to remove any extraneous contaminant. After rinsing with water and drying with acetone, the ampoule was broken and the contents were dissolved in a minimum volume of aqua regia. The solution was carefully evaporated to dryness several times with concentrated HCl to insure complete removal of the nitrate ion. The residue was then redissolved in 8 N HCl and Cl_2 gas was bubbled through the warm solution for 10 minutes. This treatment completely converted platinum to the $[PtCl_6]^{2-}$ form. After the removal of excess Cl_2 gas from the solution by boiling for 5 minutes, iridium carrier (9.66 mg iridium) as $[IrCl_6]^{3-}$ and palladium carrier (15.60 mg palladium) as $[PdCl_4]^{2-}$ were added. Special caution was exercised at this point. If any nitrate ion or Cl_2 gas were left in the solution, oxidation of $[IrCl_6]^{3-}$ to $[IrCl_6]^{2-}$ would occur, and the separation of iridium from the sample matrix by anion exchange would be impossible. A change in color of the solution from orange-red to dark red during the addition of the iridium carrier would indicate that oxidation had taken place.

After the addition of carriers the solution was evaporated to a volume of *ca.* 20 ml.

Ion exchange separation

A resin column, sketched below, was prepared. Dowex 1-X8 anion exchange resin 100-200 mesh, was slurried in water and poured into the column to a bed height of 9-11 cm. The resin column was then conditioned with 8 N HCl solution.

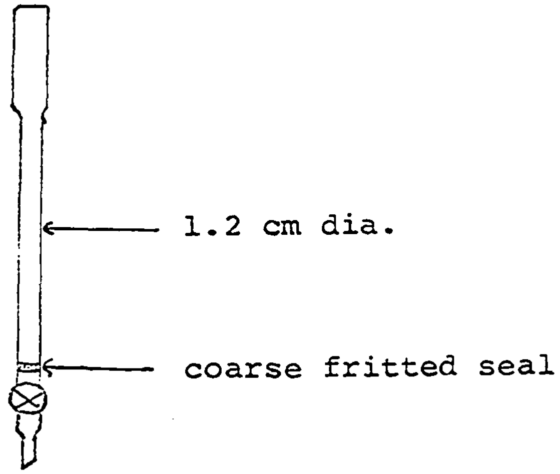


Figure 7. Resin column

The solution of the irradiated platinum and carriers was adsorbed in the resin column, leaving a column of liquid of about one-half cm above the resin bed. At this point, the $[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$ orange-red adsorption bands were clearly visible on top of the resin column.

Elution was performed at the rate of 2 to 3 ml/min. Iridium and carrier-free silver activity as $[IrCl_6]^{3-}$ and $[AgCl_2]^{-}$, respectively, were desorbed from the resin column with 120-150 ml of 8 N HCl solution. The eluate collected was set aside for future treatment. During this elution process, the red $[PdCl_4]^{2-}$ adsorption band was observed to diffuse slowly down the column.

Palladium as $[PdCl_4]^{2-}$ was eluted out with 150 ml of concentrated HCl. Completion of the elution was indicated by the removal of the red adsorption band from the column.

Palladium

The concentrated HCl eluate from the resin column was evaporated to a small volume and reconstituted with water to make a solution that was ca. 5% in HCl. Platinum carrier as $[PtCl_6]^{2-}$ was added at this point. The solution was cooled down in an ice water bath.

An alcoholic solution of dimethylglyoxime (6.73 mg DMG per ml) was added dropwise, avoiding a large excess. The resulting suspension of palladium dimethylglyoximate, $Pd(C_4H_7O_2N_2)_2$, was stirred in the ice water bath for 30 minutes. Filtration was then performed through S & S No. 576 filter paper using a suction chimney filtration set-up. The precipitate was washed thoroughly with 2% HCl, rinsed with water and dried with 95% ethyl alcohol.

The precipitate was peeled off the filter paper, transferred to a beaker, and decomposed with a few drops of concentrated HNO_3. Nitrate ion was removed by evaporating to dryness repeatedly with concentrated HCl and the final residue was redissolved in 5% HCl solution. Platinum carrier was added and after cooling the solution in an ice water bath, $Pd(C_4H_7O_2N_2)_2$ was reprecipitated.

A third precipitation was performed following the above procedure but without the platinum carrier. This treatment was performed purposely to insure that not too much platinum had co-precipitated with palladium dimethylglyoximate which could seriously affect the result of the gravimetric determination for palladium. A clear colorless filtrate was indicative of the absence of platinum, in contrast to a light yellow filtrate when platinum was present.

Finally, the third $Pd(C_4H_7O_2N_2)_2$ precipitate was dried to constant weight at 110°C, cooled in a desiccator and weighed to determine chemical yield. Experience had shown that a 20-minute drying time was sufficient to completely dry the precipitate to constant weight. Also, the dried precipitate was compact enough to enable peeling it off the filter paper; this fact made the chemical yield determination for palladium as the dimethylglyoximate precipitate convenient since it did away with the use of a weighed piece of filter paper.

After weighing, the precipitate was taped on an aluminum planchet for the measurement of activity.

Silver

The carrier-free silver activity was isolated by isotopic exchange with a freshly prepared silver chloride electrode. This procedure was essentially similar to that developed by Sunderman and Meinke (81) with some modifications to suit the conditions of this investigation.

The 8 N HCl eluate from the resin column was boiled down to almost dryness, then redissolved in water to make a dilute acid solution (less than 1% HCl).

A silver chloride electrode was prepared as follows. Approximately 50 mg of silver in Ag^+ carrier solution was added to 70 ml of plating bath made up of a mixture of 3 N NaCN and 0.5 N NaOH. With a 1.8 cm diameter x 4 cm circular platinum gauze cathode and a platinum wire anode, electrolysis was performed at 4 volts for 15 minutes. The resulting silver metal deposit on the cathode was rinsed with water and immersed in 100 ml of 0.1 N HCl solution and electrolyzed as the anode for 20 min. The silver chloride electrode thus formed was washed with 8 M HNO_3 solution.

The electrode was immersed in the solution containing the radioactive silver. The solution was stirred for 20 minutes.

The silver chloride electrode was then rinsed with water and redissolved in 70 ml of plating bath (3 N NaCN and 0.5 N NaOH). After dissolution was complete, silver metal was again plated out.

Finally, the silver metal electrode was washed with water and redissolved in concentrated HNO_3. The solution was transferred quantitatively to a polyethylene vial for the measurement of activity.

Iridium

After extraction of silver activity, the solution of $[IrCl_6]^{3-}$ was evaporated to a small volume and transferred to a polyethylene vial for the measurement of activity.

The determination of the chemical yield for iridium was performed after the measurement of its activity. An indirect iodometric titration method was used. The iridium sample was transferred quantitatively to Erlenmeyer flasks and diluted to 100 ml. The solution was warmed, and Cl_2 gas was bubbled through slowly for 30 minutes to oxidize $[IrCl_6]^{3-}$ to $[IrCl_6]^{2-}$. After removal of excess Cl_2 gas by boiling the solution for 5 minutes, the solution was cooled in an ice water bath. Excess potassium iodide was added which reduced iridium back to $[IrCl_6]^{3-}$. The iodine liberated from the reaction was titrated with a standard solution of 0.01 N thiosulfate using starch solution as indicator. Special precautions for iodometric titration discussed by Vogel (55) were closely observed.

To normalize the effect of any possible deterioration of the standard thiosulfate solution due to prolonged storage, a control solution of $[IrCl_6]^{3-}$ was prepared with an iridium content equal to the amount of iridium carrier added at the early stage of the analysis. This control solution was titrated simultaneously with the recovered iridium sample. The chemical yield was then calculated simply from the ratio of the volumes of thiosulfate solution used in the titration of each sample.

A schematic diagram of the radiochemical procedure for the analysis of the platinum samples is shown in Figure 8.

Radiochemical Analyses of the Irradiation Standards

Iridium

The ampoule containing the iridium irradiation standard was thoroughly cleaned after which it was broken and the contents were dissolved in aqua regia. Iridium carrier (9.66 mg iridium) as $[IrCl_6]^{3-}$ was added. Nitrate ion was removed from the solution by repeated evaporations to dryness with concentrated HCl. The final residue was redissolved in HCl solution and diluted to a measured volume in a volumetric flask.

Aliquots were taken and transferred to polyethylene vials for the measurement of activity.

The remaining solution was evaporated to a small volume. The chemical yield for iridium was determined by indirect iodometric titration as previously described.

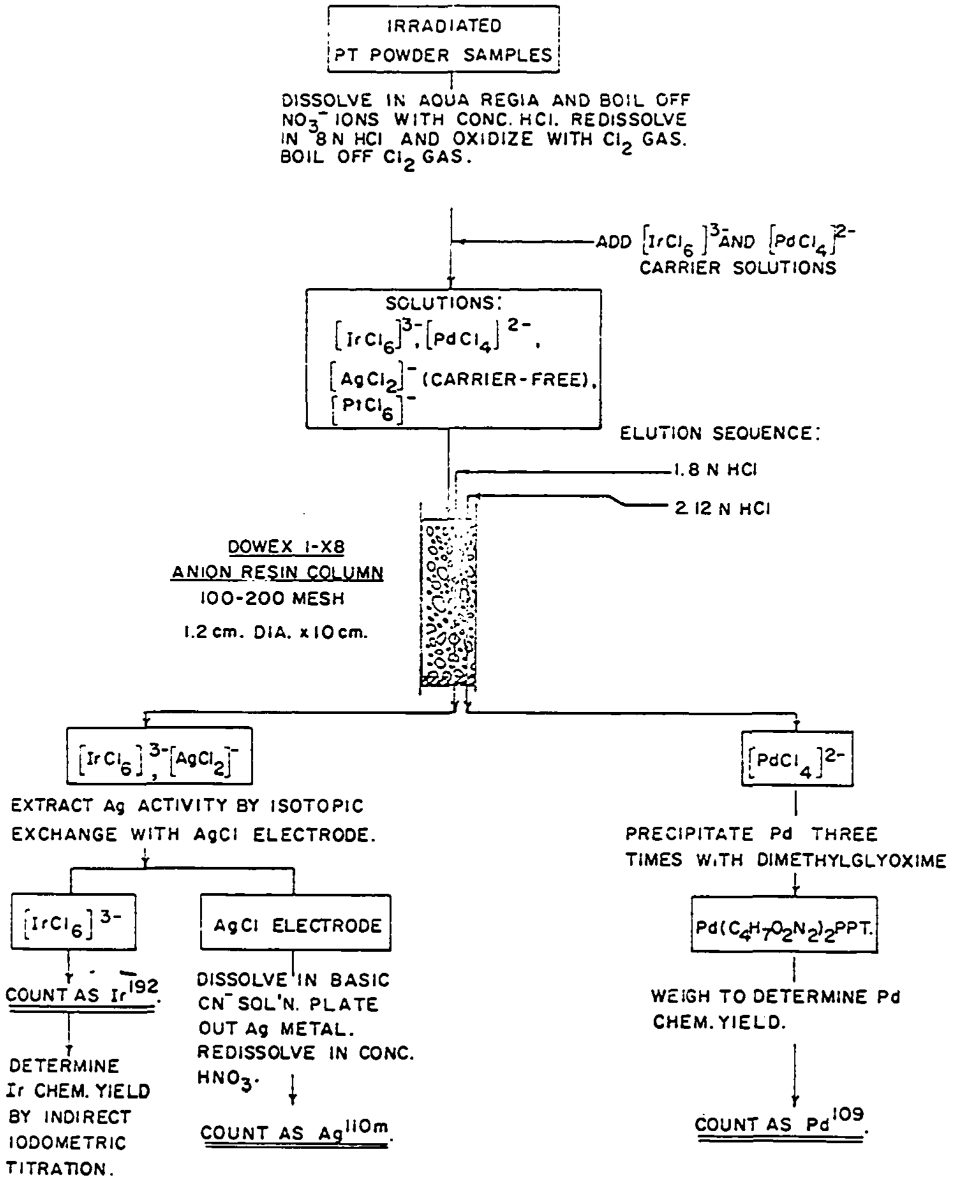


Figure 8. Radiochemical procedure for the analysis of the platinum samples

Palladium

The radiochemical procedure used for the analysis of the palladium irradiation standard was similar to that used for the analysis of the platinum samples. In one case, the probable iridium impurity in the palladium standard was also determined.

Silver

The silver irradiation standard was dissolved in basic cyanide solution. Silver carrier (ca. 10 mg of silver) as $AgNO_3$ was added and the solution was then diluted to a measured volume in a volumetric flask.

Aliquots were taken and transferred to polyethylene vials for the measurement of activity.

Gamma-ray Spectrometry

All radioactivities were measured by gamma-ray spectrometry. The counts were accumulated in a 400-channel Radiation Instrument Development Laboratory pulse height analyzer using a 3" diameter NaI(Tl) crystal detector.

The activity of the iridium sample was measured as 74-day Ir^{192} by integration of counts under the three prominent photopeaks in the gamma-ray energy spectrum corresponding principally to energies of 0.316, 0.469 and 0.605 Mev.

The activity of the palladium sample was monitored from the 0.022-Mev Ag K X-ray emission peak in the gamma-ray energy spectrum of 14-hour Pd^{109}.

The activity of the silver sample was measured as 253-day Ag^{110m} by integration of counts under the two photopeaks in the gamma-ray energy spectrum corresponding to energies of 0.656 and 0.885 Mev.

The radioactive decay of all samples were followed to ascertain their radiochemical purity. All counts were accumulated with the analyzer set on live time counting mode with automatic correction for dead time counting losses.

Both the iridium and the silver samples were counted in solution form. To normalize the effect of counting geometry, uniformly sized polyethylene vials with a diameter of 3" and the same volumes of solution were used throughout the activity measurement with the samples placed on top of the crystal detector.

The palladium samples were counted as the dimethylglyoximate precipitate mounted on an aluminum planchet and also placed on top of the crystal detector. Normalization of the effect of counting geometry was afforded by the use of the same amount of palladium carrier solution in the analysis of the platinum sample and of the palladium irradiation standard.

Evaluation of Counting Data

A number of factors were considered to minimize the errors in gamma-ray spectrometry as have been indicated below.

Background corrections

At least one background spectrum was taken daily, usually immediately before the samples were to be counted. The counts in the background spectrum corresponding to the energy range of interest were totalized and subtracted from the corresponding totalized counts in the gamma-ray spectrum of the sample.

Photopeak shift

Because of the inherent nature of electronic counting systems, the peak (the channel with the highest number of counts) in the gamma-ray energy spectrum of a specific radionuclide will sometimes drift by at least a fraction of a channel. Consequently, the energy corresponding to a particular channel number will also vary slightly and the integration of counts in a region of a set of gamma-ray spectra of a sample will not have a fixed energy range basis.

To minimize errors that may arise from this phenomenon, in this work the integration for a given set of spectra was performed over a constant number of channels with the integration range starting from a point located in terms of a fixed number of channels from the peak channel. Also, the integration range was chosen sufficiently wide in order to include the entire photopeak (or photopeaks) of interest.

Coincidence counting losses

An erroneous counting rate may be obtained upon counting samples of high activity because of coincidence counting losses. This error arises from the occurrence of two disintegration events within the resolving time of the gamma-ray energy analyzer, so a single high energy pulse is recorded instead of two low energy pulses.

Coincidence corrections in the gamma-ray spectrometry of palladium as Pd^{109} were determined. Samples of the metal of different weights were prepared from a pure palladium foil of uniform thickness and were simultaneously irradiated. The samples were arranged carefully during irradiation to prevent overlapping. The specific activity of each sample in terms of decay-corrected counts per minute per unit weight were then measured and the specific activity at zero weight was determined by extrapolation. A coincidence correction versus counting rate curve was constructed as shown in Figure 9.

An attempt was made to evaluate the coincidence corrections for the gamma-ray spectrometry of Ir^{192} by counting aliquots of 20, 50, 100, 200, 250 and 500 microliters of a radioactive solution of this nuclide. No definite decreasing trend in specific activity similar to that of Pd^{109} was obtained. It was believed that this observation was caused by the fact that the errors due to non-uniform micropipetting of the aliquots were at least of the same order of magnitude as those due to the coincidence losses. Moreover, the decreasing efficiency of photon detection by scintillation

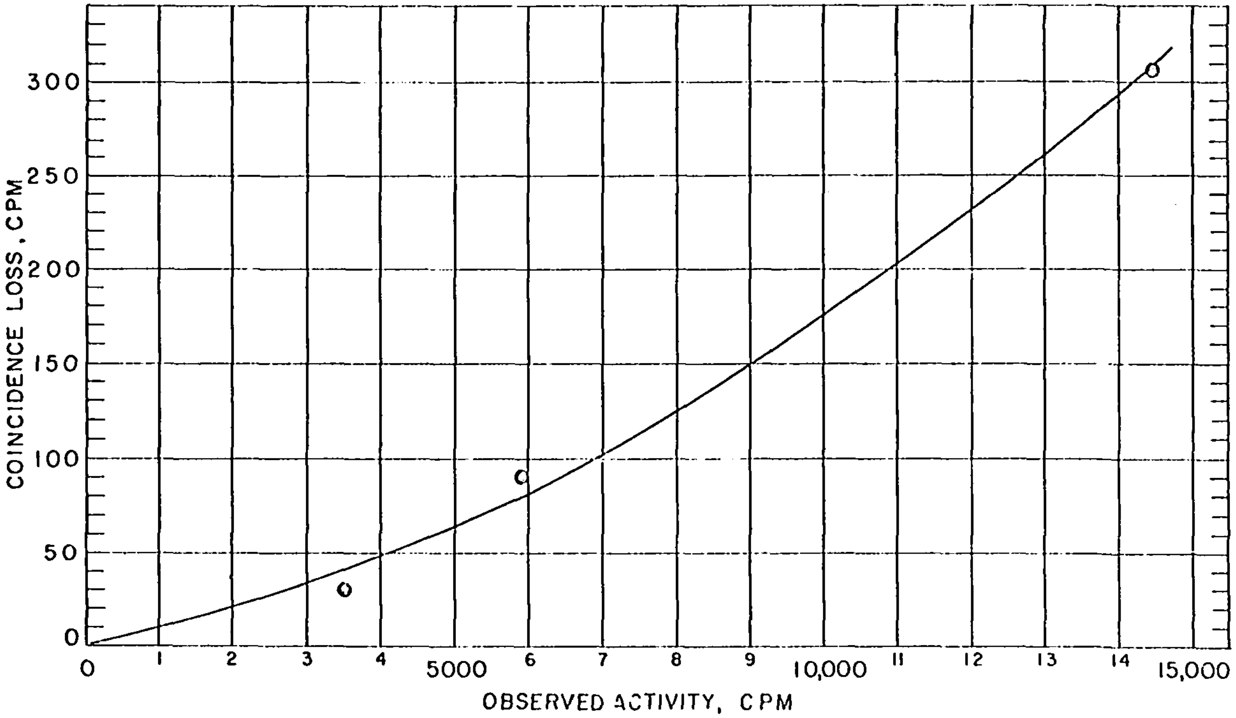


Figure 9. Coincidence correction curve for the gamma-ray activity measurement of Pd^{109} utilizing the 0.022-Mev Ag K X-ray emission peak

crystals with increasing gamma-ray energy and the wider integration range used in the evaluation of the activity would probably make coincidence losses for the spectrometry of Ir^{192} lower than the coincidence losses for the spectrometry of Pd^{109}. No further investigation on this aspect was done. The coincidence losses for Ag^{110m} were not evaluated since the same results as those for Ir^{192} were expected.

In the measurement of the activities of the irradiation standards of iridium and silver, the effects of coincidence losses were minimized by taking convenient aliquots for counting. In the case of the palladium irradiation standards, the samples were allowed to decay until the specific activities were low enough for gamma-ray sepctrometry. Coincidence corrections read off from the plot in Figure 9 were applied.

Dead time corrections

The measurement of activity was performed using the live time mode of the gamma-ray analyzer with automatic correction of the counting rate for dead time losses.

RESULTS AND DISCUSSIONS

Irradiation Conditions

The conditions used for the irradiation of the samples analyzed are listed in Table 4. All the platinum samples were taken from a common laboratory stock.

Analysis for Iridium

The data and results of the determination of iridium are shown in Table 5.

All the samples for Ir^{192} were counted at least 16 days after irradiation, at which time the activity of 19-hour Ir^{194} had decayed out.

The gamma-ray energy spectra of some of the iridium counting samples isolated from the irradiated platinum exhibited slight contamination consisting mainly of Pt^{195m} activity. A typical contaminated spectrum is shown in Figure 10. In such cases, the samples were allowed to decay until the contaminant activity was sufficiently negligible to enable measurement of the Ir^{192} activity. The decay curve of a contaminated sample is shown in Figure 11. To ascertain the radiochemical purity of the samples, daily measurements were made for periods of 4 to 6 days after the contaminant activity had decayed out, and the integrated counts under the major photopeaks of the Ir^{192} gamma-ray energy spectra were then corrected for decay relative

Table 4. Irradiation conditions used in the thermal neutron activation of samples

Irradiation	I	II	III	IV	V	VI	VII
Time out of ALRR pile (hour, date)	0855, 6/21/66	0830, 8/18/66	0047, 11/9/66	1614, 11/23/66	0924, 12/7/66	1310, 1/4/67	1030, 1/27/67
ALRR irradiation position	V-5	V-5	V-5	V-5	V-5	V-5	V-5
ALRR power level (Mw)	5	4	5	5	5	5	5
Duration of irradiation (hours)	9	12	20	30	30	30	30
Integrated thermal flux (10^{18} n/cm^2)	0.97	1.0	2.2	3.2	3.2	3.2	3.2
Wt. of Pt samples (mg)	102.9 103.3	103.0 103.2	103.7 100.2	104.9 103.6	102.1 102.6	99.2 99.9	100.9 99.6
Wt. of irradiation stds.:							
Ir (mg)	0.0821	0.0821	0.0821	0.0821	0.0821	0.0821	0.0821
Pd (mg)	0.0586	0.1172	0.1172	0.1172	0.1172	0.1172	0.1172
Ag (mg)					0.5382	0.5382	0.5382

Table 5. Neutron activation analysis for iridium in platinum

Irradiation	I	II	IV	V	VI	VII
Reference time of activity measurement (days after irradiation)	22.17	26.07	22.89	16.07	19.45	17.56
Ir^{192} activity in Pt samples:						
Observed activity (c/m-100 mg Pt)	2115	1380	4724	4908	4992	6368
	1946	1382	7006	3501	4701	6190
Chemical yield factor (%)	95.0	88.2	84.5	85.1	87.6	88.4
	95.6	98.1	91.5	49.5	62.9	91.2
Activity 24 hours after irradiation (c/m-100 mg Pt)	2714	1980	6859	6644	6769	8414
	2481	1782	9394	8147	8879	7928
Ir^{192} activity in Ir irradiation standard (0.0821 mg Ir):						
Observed activity (10^6 c/m)	84.20	102.6	313.9	339.8	344.3	349.5
Chemical yield factor (%)	77.6	99.0	86.2	99.3	95.4	96.3
Activity 24 hours after irradiation (10^6 c/m)	132.2	131.1	446.9	394.2	428.7	424.5
Ir content of Pt samples (ppb)	17	12	13	14	13	16
	15	11	17	17	17	15

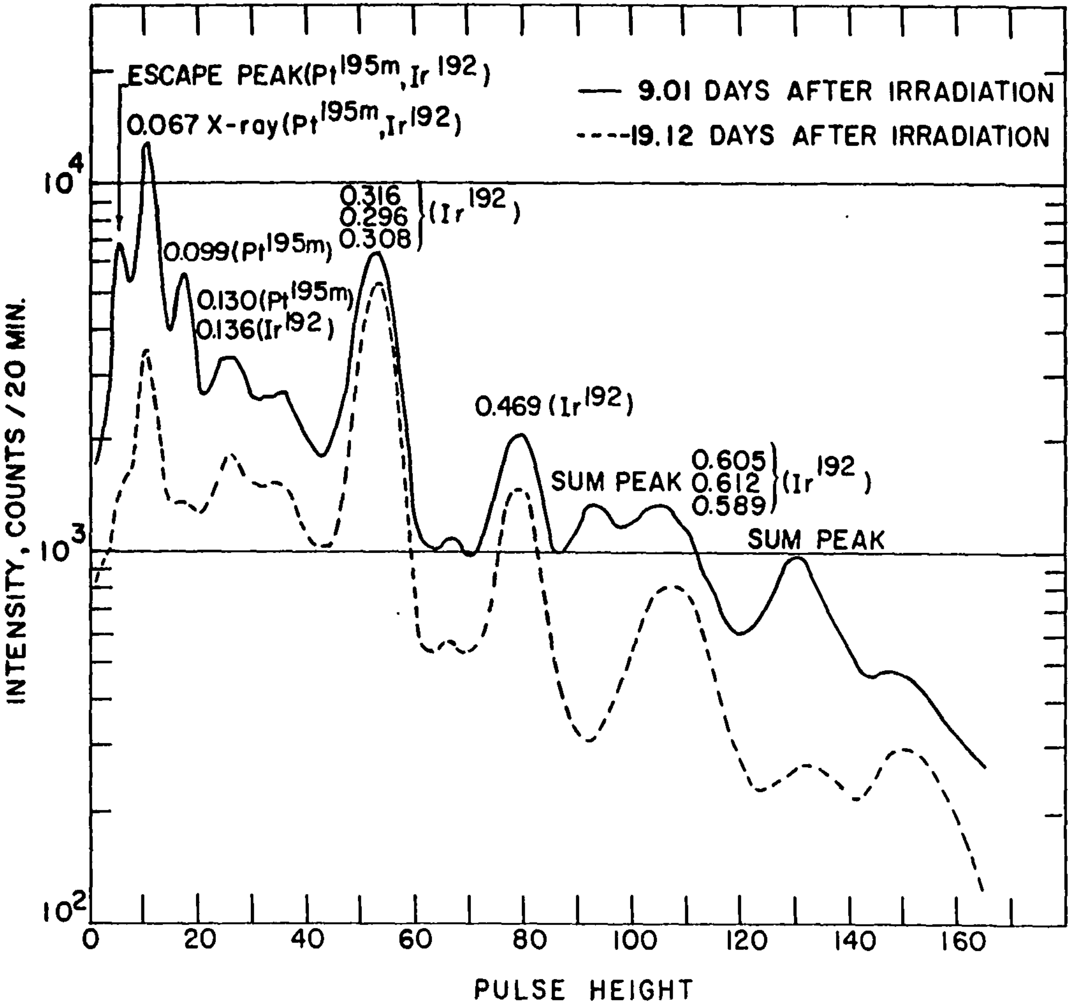


Figure 10. Gamma-ray energy spectra of Ir^{192} with Pt^{195m} contaminant

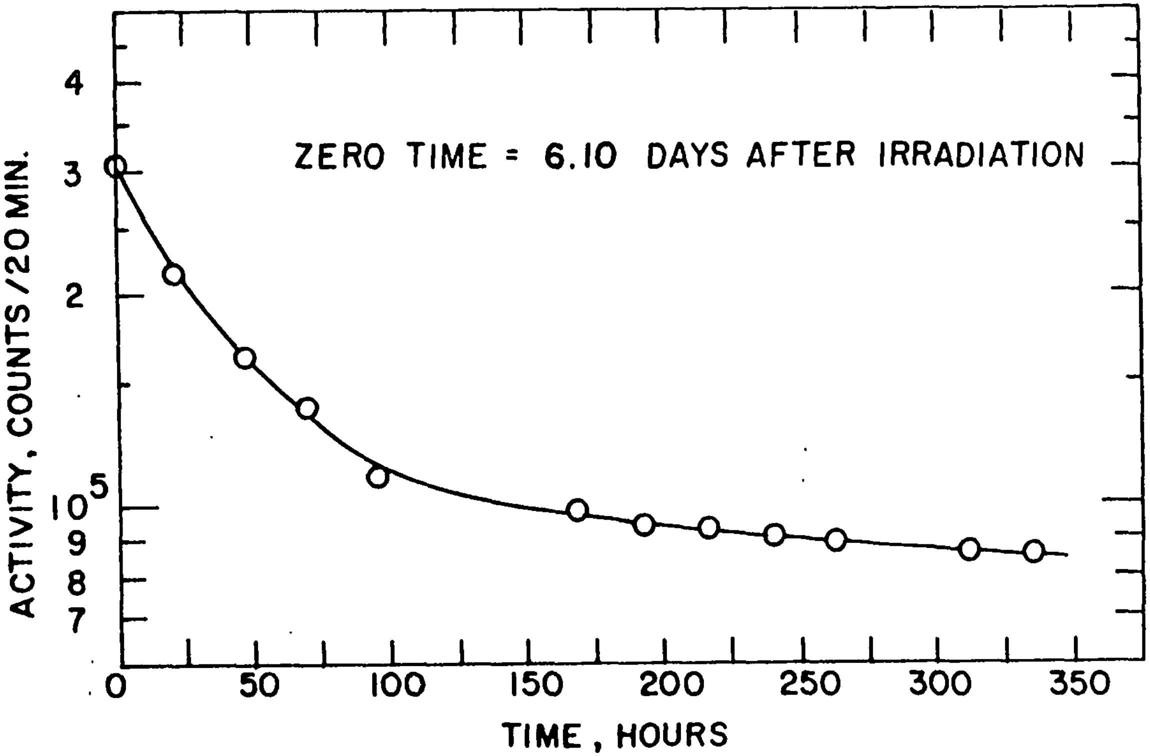


Figure 11. Decay curve of Ir^{192} sample contaminated with activities due to Pt radionuclides

to an arbitrary reference time; a standard deviation of the average of these decay-corrected activities of the same order of magnitude as that due to counting statistics was indicative of a radiochemically pure iridium sample. The observed counting rates shown in Table 5 are average values of the daily measurements taken over periods of 4 to 6 days.

A further test of the purity of the iridium counting samples was provided by the indirect iodometric method of titration used in the determination of the chemical yield of iridium. In this method, the iridium sample was oxidized to the $[IrCl_6]^{2-}$ form with Cl_2 gas. Any platinum impurity present in the sample would also be oxidized to $[PtCl_6]^{2-}$ by this treatment. After the removal of excess Cl_2 gas by boiling the solution for 5 minutes, followed by cooling in an ice water bath, iridium was again reduced to $[IrCl_6]^{3-}$ with excess potassium iodide. With this treatment, any platinum present in the solution would form the very dark red complex $[PtI_6]^{2-}$. With a molar absorptivity of <u>ca</u>. 1.2×10^4 in the visible range for $[PtI_6]^{2-}$, the presence of less than 0.5 micromoles of platinum in a 100-ml solution could change the transmittance of the $[IrCl_6]^{3-}$ solution by a factor of 2. A decontamination factor of at least 1000 would be required for the attainment of this platinum contaminant level. If occurring in extensive amounts, $[PtI_6]^{2-}$ could interfere with the endpoint detection during the subsequent titration of I_2

with thiosulfate solution using starch indicator. This interference was actually observed in some of the preliminary studies of this system.

Chemical yield factors obtained for iridium were generally better than 85%. In one case, an unusually low yield of 49.5% was obtained. This was caused by the incomplete removal of nitrate ions from the solution of the irradiated platinum sample resulting in partial oxidation of the iridium in the carrier solution to $[IrCl_6]^{2-}$.

An iridium standard sample containing 0.0821 mg of iridium was used in all the irradiations. The observed activities of the iridium irradiation standards shown in Table 5 are total activities calculated from the gamma-ray energy spectra of 1/5000 aliquots. To insure the accuracy of aliquot sampling, two equal aliquots were taken from the solution of the iridium irradiation standard in each analysis which showed activities different by less than 1%.

Table 5 also indicates that chemical yield factors less than 100% were obtained for the iridium irradiation standards although, as previously described in the experimental procedure, no actual radiochemical treatment was performed for these samples. These yield values are explained by the fact that, for these particular samples, no effort was made to recover the element quantitatively after the addition of iridium carrier to the solution of the irradiated samples, inasmuch as they had more than sufficient induced activity for gamma-ray spectrometry. The dissolution of the irradiated iridium compound, i.e., as $IrCl_3 \cdot xH_2O$ residue, involved breakage of the silica ampoule containing the sample inside a flexible polyethylene tube, after which the contents of the tube, including the pieces of broken glass, were quantitatively transferred to a beaker by rinsing repeatedly with aqua regia. After boiling off NO_3^- ions with concentrated HCl, iridium carrier was added and the solution was warmed for ca. 10 minutes to insure complete dissolution of the irradiated compound. The solution was then decanted only qualitatively into another beaker to separate it from the pieces of broken glass.

All the observed activities shown in Table 5 were corrected for background. A background activity of 300 counts/min was obtained in the region of the three photopeaks of the Ir^{192} gamma-ray energy spectrum. After the activities of the samples and the corresponding irradiation standard were corrected for decay relative to a common arbitrary reference time, the iridium impurity content of each platinum sample was calculated by the use of Equation 3. An average iridium content of 15 ppb was obtained in the analysis of 12 platinum samples with a standard deviation of the average value of ± 2.1 ppb or 14%.

As previously described, the radiochemical procedure used in the separation of iridium activity from the platinum matrix involved the addition of iridium carrier as $[IrCl_6]^{3-}$ and the subsequent separation of this anionic species by ion exchange. It is evident that the effectiveness of this method of separation depends on the rate of conversion of the radioactive iridium species, which are in the form of $[IrCl_6]^{2-}$ ions after dissolution of the irradiated platinum sample with aqua regia, to $[IrCl_6]^{3-}$ ions. This rate of conversion in turn depends on the kinetics of the electron exchange reaction in the system $[IrCl_6]^{3-}$-$[IrCl_6]^{2-}$. Sloth and Garner (82) reported that for this system the rate of electron exchange is immeasurably fast. Cotton and Wilkinson (83) theorized that the mechanism of electron exchange in the $[IrCl_6]^{3-}$-$[IrCl_6]^{2-}$ system involves the so-called outer-sphere process with a rate constant greater than 10^6 liters-mole^{-1}-sec^{-1} at 25°C. This high rate constant, and the time involved in the radiochemical separation of more than 10 minutes from iridium carrier addition to adsorption in the ion exchange resin column, would certainly insure the complete conversion of the radioactive iridium species to the $[IrCl_6]^{3-}$ form.

Analysis for Palladium

The data and results of the determination of palladium are listed in Table 6.

The radiochemistry involved in the determination enabled the measurement of Pd^{109} activity in no more than 26 hours

Table 6. Neutron activation analysis for palladium in platinum

Irradiation	III	IV	V	VII
Reference time of activity measurement (hours after irradiation)	25.13	14.77	22.60	13.50
Pd^{109} activity in Pt samples:				
Observed activity (c/m-100 mg Pt)	72.3 89.4	95.3 156	64.6 73.1	137 142
Chemical yield factor (%)	96.8 94.1	85.6 89.2	91.4 88.8	90.7 91.1
Activity at end of irradiation (c/m-100 mg Pt)	271 344	237 372	224 261	302 312
Pd^{109} activity in Pd irradiation standard (0.1172 mg Pd):				
Observed activity (10^6 c/m)	2.91	5.46	2.80	6.75
Chemical yield factor (%)	97.0	86.8	96.6	93.1
Activity at end of irradiation (10^6 c/m)	10.8	13.4	9.21	14.5
Pd content of Pt samples (ppb)	29 33	21 33	29 33	24 25

after irradiation of the samples, with the actual chemical separations taking approximately 10 hours.

In the 9- and 12-hour irradiations, the gamma-ray energy spectra of the palladium samples separated from the irradiated platinum did not show any of the characteristic peaks of Pd^{109}. Irradiation periods in the subsequent experiments were therefore increased, initially to 20 hours, and later to 30 hours. A saturation factor of 77% for the activation of palladium to 14-hour Pd^{109} was attained in the 30-hour irradiation periods.

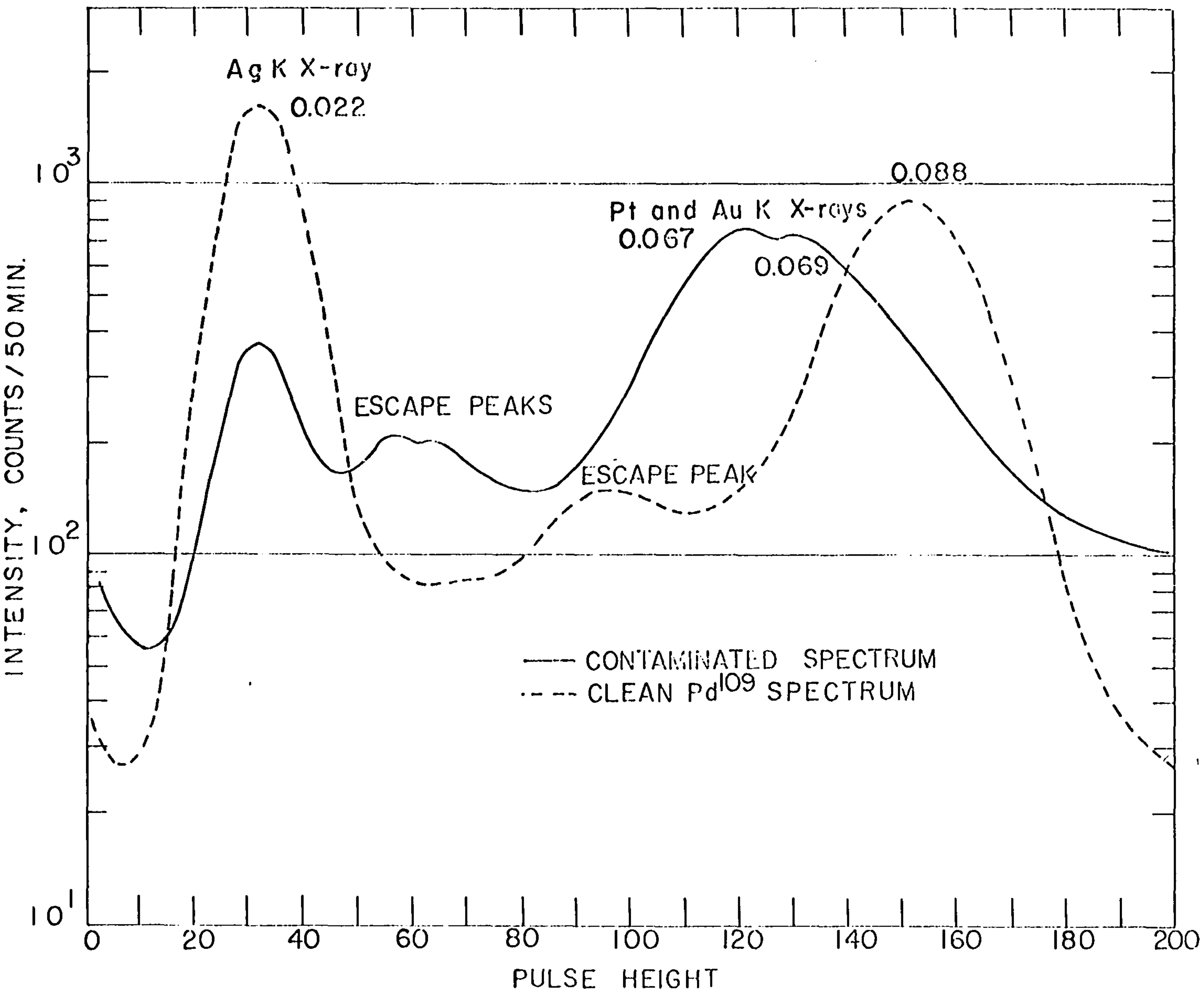
No interference from 4.4-minute Pd^{111} was expected. The time spent in the radiochemical separations insured the complete decay of Pd^{111} to 7.5-day Ag^{111} which in turn was eluted out of the resin column with 8 N HCl solution prior to the desorption of palladium. Moreover, as could be inferred from the nuclear properties in Table 1, the induced Pd^{111} activity was much less than Pd^{109} activity.

The decay behaviors of most of the palladium samples indicated some contamination by the activities from the platinum matrix. In some badly contaminated samples, the 0.088 Mev photopeak in the gamma-ray energy spectrum was totally masked by the K X-ray emission energy peaks of the platinum radionuclides, as shown in Figure 12. To evaluate the activity due to Pd^{109}, the decay curves of the integral counts under the 0.022 Mev Ag K X-ray emission peak were resolved, as depicted in Figure 13. The contaminant activity showed a half-life of approximately 70 hours, as was expected from the average half-life of the platinum radionuclides produced in the sample matrix. A background activity of 12 counts/min was observed in the energy region of the Ag K X-ray emission peak.

The activities of the palladium irradiation standards shown in Table 6 are decay-corrected activities based on the corresponding reference times indicated. The activities of these irradiation standards were measured only after the decay behaviors of the palladium samples from platinum were determined, *i.e.*, at least 3 days after irradiation. The observed activities of the palladium irradiation standards were therefore actually considerably lower than the values listed in Table 6.

In one case, the decay behavior of the Ag K X-ray emission peak of the gamma-ray energy spectrum of the palladium irradiation standard was observed for several days. A long-lived component was noted, as shown in the decay curve in Figure 14, with a half-life of 18.7 days. Also, after most of the Pd^{109} activity had decayed out, the X-ray peak shifted slightly to a lower channel number corresponding to an energy of *ca*. 0.020 Mev. It was suspected that this long-lived activity was due to the K X-ray emission peak of rhodium (0.0202 Mev) arising from the decay by EC of Pd^{103}. The half-life of Pd^{103} as listed in Table 1 is 17.0 days. Pd^{103} was

Figure 12. Gamma-ray energy spectrum of Pd^{109} contaminated with activities due to Pt radionuclides


Ag K X-ray
0.022
ESCAPE PEAKS
Pt and Au K X-rays
0.067
0.069
0.088
ESCAPE PEAK
CONTAMINATED SPECTRUM
CLEAN Pd^{109} SPECTRUM
INTENSITY, COUNTS / 50 MIN.
10^3
10^2
10^1
0
20
40
60
80
100
120
140
160
180
200
PULSE HEIGHT

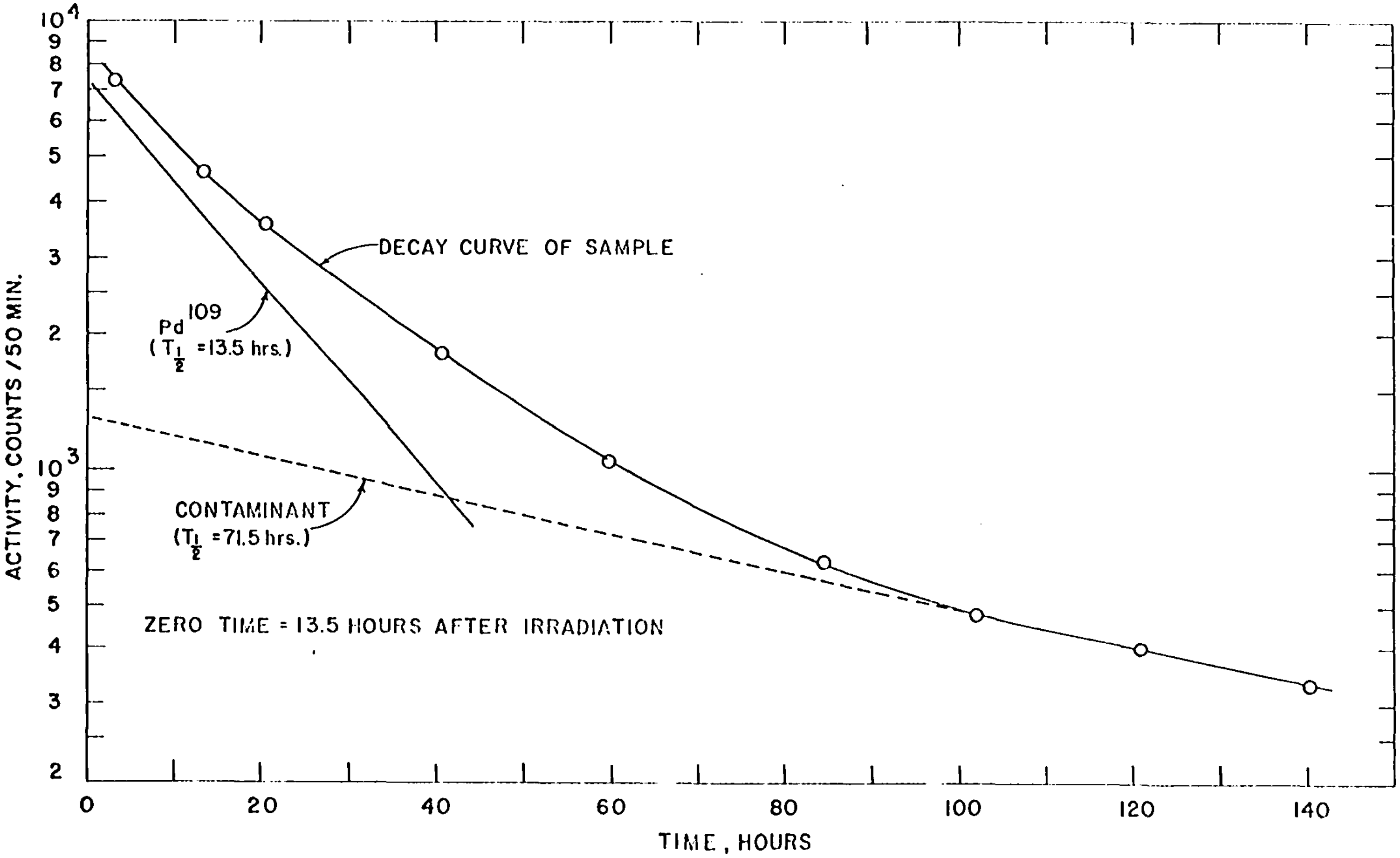


Figure 13. Decay curve resolution of a contaminated Pd^{109} sample

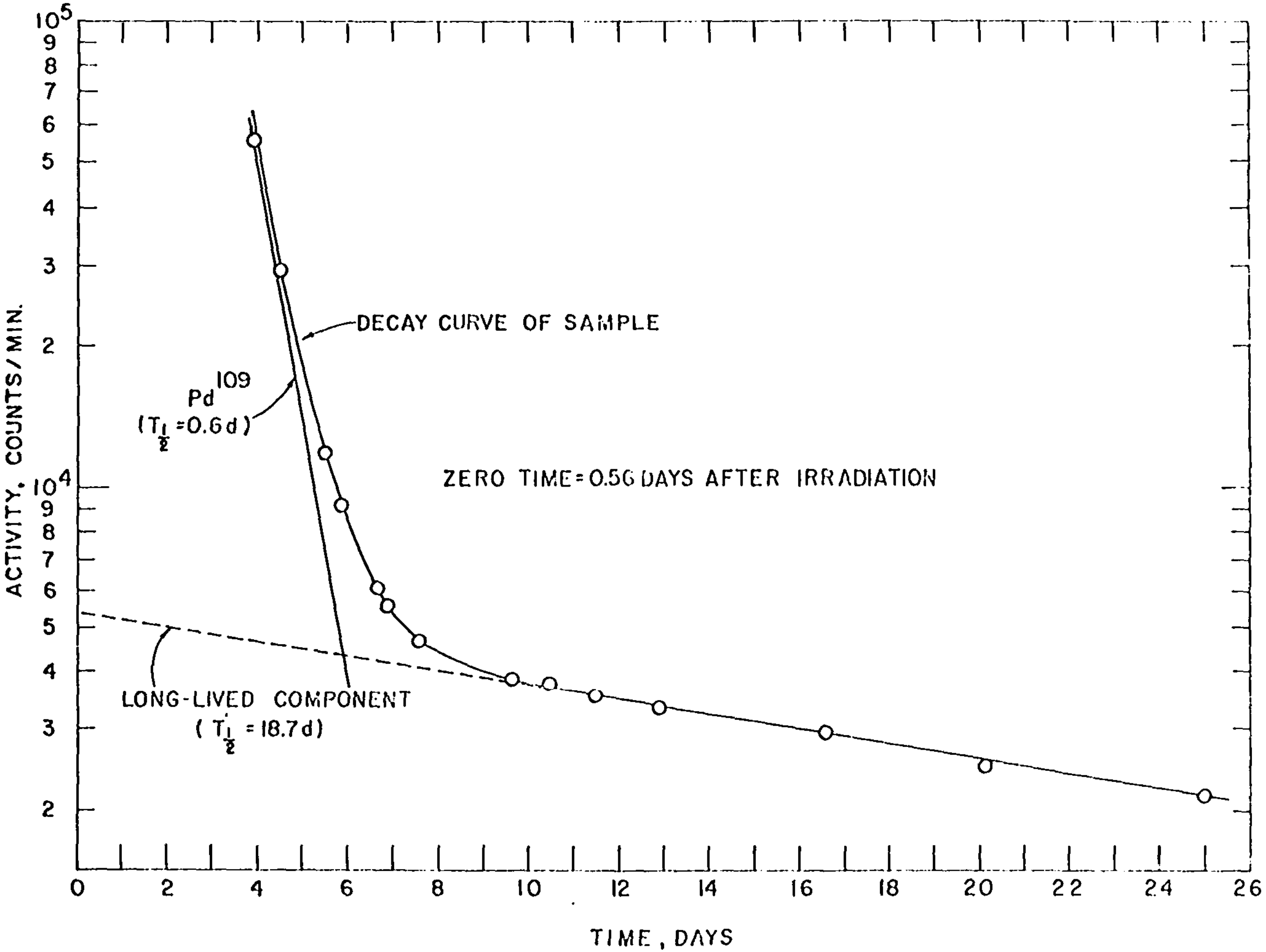


Figure 14. Decay curve of a pure Pd^{109} sample showing a long-lived component activity

produced by (n,γ) reaction of Pd^{102} (natural abundance = 0.96%). Fortunately, as can be deduced from Figure 14, this long-lived component had a negligibly small activity compared to that due to the Ag K X-ray of Pd^{109} when the sample was counted within 4 days after irradiation. Its presence in the sample had therefore no effect on the results of the analysis for palladium.

From the data shown in Table 6, an average palladium content of 28 ppb was obtained in the analysis of 8 platinum samples. The standard deviation of the average value is ± 4.3 ppb or 15%.

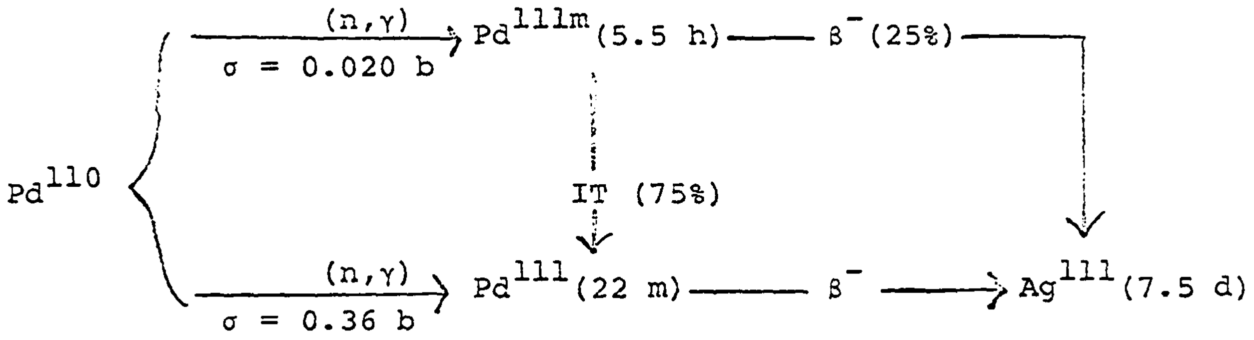
Analysis for Silver

The data and results of the determination of silver are listed in Table 7.

The analysis for silver was done only in the last three irradiations after the radiochemical separation procedure for the determination of iridium and palladium had been established.

As previously described, Ag^{110m} activity was isolated from the platinum sample matrix on a carrier-free basis by isotopic exchange with a freshly prepared silver chloride electrode. In work previously reported which utilized this method (81), silver recovery factors of better than 99% were claimed.

The efficiency of the isotopic exchange method under the conditions of this investigation was tested indirectly. A radioactive solution containing carrier-free Ag^{111} (β^--emitter with a half-life of 7.5 days) was prepared from the 8 N HCl solution eluate obtained during the ion exchange purification of the palladium irradiation standard. Ag^{111} was produced during thermal neutron irradiation of palladium by the neutron activation and decay sequence shown below. By following the



procedure for isotopic exchange described previously, Ag^{111} activity was totally extracted from the solution, as confirmed by subsequent gamma-ray spectrometric measurements of the dissolved silver chloride electrode and the solution originally containing the Ag^{111} activity.

In the analysis for silver in the irradiated platinum samples, further confirmation of the complete extraction of Ag^{110m} was afforded by the absence of the characteristic photopeaks of this radionuclide from the gamma-ray energy spectra

Table 7. Neutron activation analysis for silver in platinum

Irradiation	V	VI	VII
Reference time of activity measurement (days after irradiation)	15.18	5.83	7.50
Ag^{110m} activity in Pt samples:			
Observed activity (c/m-100 mg Pt)	1914 1940	1616 1631	1496 1846
Activity 24 hours after irradiation	1995 2022	1642 1657	1524 1883
Ag^{110m} activity in Ag irradiation standard (0.5382 mg Ag):			
Observed activity (10^6 c/m)	4.313	4.204	3.407
Activity 24 hours after irradiation (10^6 c/m)	4.496	4.272	3.476
Ag content of Pt samples (ppm)	2.4 2.4	2.1 2.1	2.4 2.9

of the iridium samples. In view of these considerations, a 100% chemical yield factor was therefore assumed in the calculation of the silver content of the platinum samples. In the determination of silver, sufficient care was exercised to make the radiochemical analysis quantitative up to the ion exchange separation of the carrier-free silver activity.

The decay behaviors of the silver samples did not indicate the presence of Ag^{111} activity that could come from the palladium impurity of the platinum sample. As in the case of the iridium samples, the activity measurements for silver were performed daily for periods of 4 to 6 days and the integrated counts under the two major photopeaks of the Ag^{110m} gamma-ray energy spectra were then corrected for decay relative to an arbitrary reference time; a standard deviation of the average of these decay-corrected activities of the same order of magnitude as that due to counting statistics was indicative of a radiochemically pure sample. The activities listed in Table 7 are average values of the daily measurements.

The activities of the silver irradiation standards shown in the table are total activities calculated from the observed activities of 1/200 aliquots. The accuracy of aliquot sampling was ascertained by taking two equal aliquots from the solution of the irradiation standard in each analysis which showed activities different by less than 1%.

Radiochemically clean gamma-ray energy spectra of Ag^{110m}

were obtained in all experiments. An average silver content of 2.4 ppm was obtained in the analysis of 6 platinum samples with a standard deviation of the average value of ± 0.27 ppm or 11%.

Sensitivities of the Analysis

The results of the analysis for iridium and silver indicate that these two elements can be detected in the platinum matrix even when present in concentration levels much lower than the values obtained in this investigation. For instance, it can be deduced from Table 5 that a 30-hour irradiation at 5 Mw in ALRR would induce an Ir^{192} activity of approximately 300 counts/min in a 100-mg sample of platinum containing 1 ppb of iridium; likewise, a Ag^{110m} activity of approximately 60 counts/min would be induced in a 100-mg sample of platinum containing 0.1 ppm of silver. The detection sensitivities of iridium and silver could also be considerably enhanced by using longer irradiation periods, considering the fact that for the 30-hour irradiations used in this work, saturation factors of only 0.012 for the activation of iridium to Ir^{192} and 0.0034 for the activation of silver to Ag^{110m} were attained. For instance, these saturation factors could be approximately doubled by using a 60-hour irradiation period.

The high activity induced in the sample matrix did not seem to be a limiting factor in the chemical separations used in this analysis. After irradiation for 30 hours at a power level of 5 Mw in ALRR, each ampoule containing 100 mg of platinum showed a dosage reading of approximately 5 roentgens/hour of β^-- and gamma-radiation at a point one-half inch from the sample. This dosage reading was taken after cooling the sample for 4 hours. Although this was indeed a dangerously high activity level to work with, in the radiochemical method used in this work close proximity with the sample was experienced for no more than one minute when the silica ampoules containing the irradiated samples were being broken. This part of the analysis was done inside a glove box provided with a body shield of lead bricks. After the dissolution of the sample and the ion exchange separation, most of the matrix activities were left adsorbed in the resin column, and the rest of the chemical separation steps could be performed much more conveniently.

The results of the analysis for palladium indicate that the palladium concentration level in the platinum matrix obtained in this investigation is approaching the limit of detection of this element in the particular sample matrix, at least, on the basis of the decontamination technique used. It can be predicted from the data in Table 6 that an activity less than 50 counts/min above background would be obtained from a 100-mg sample of platinum containing 10 ppb of palladium with the irradiation conditions used in this work. A sample of this low specific activity would certainly require long counting times to obtain results of sufficient statistical accuracy. Moreover, such a sample could not tolerate too much contaminant activity, and its isolation from the matrix would therefore entail more tedious chemical separation procedures. A longer irradiation time would not increase the induced Pd^{109} activity considerably inasmuch as a 77% saturation factor is already attained with a 30-hour irradiation. Furthermore, it is rather unlikely that the 10-hour radiochemical separation time involved in this work could be significantly reduced, due to the high decontamination factor required in the analysis and the closely similar chemical behaviors of palladium and platinum.

Error Considerations

Preparation of irradiation samples

The 100-mg samples of platinum were weighed to an accuracy of 0.1 mg. Since the concentration levels of the impurities calculated from the analysis were rounded off to two significant figures due to other error considerations, the uncertainty in the weight of the platinum sample did not have any considerable influence on the experimental results.

In the preparation of the irradiation standards, 50- and 100-microliter "Pyrex" brand pipettes were used in the introduction of the standard solutions into the silica ampoules.

These pipettes were calibrated to a tolerance of ± 0.3%.

Neutron irradiation

No considerable self-shielding effects during the irradiation of the samples were expected.

The irradiation standards used were in submilligram amounts prepared by careful evaporation of standard solutions inside the silica ampoules. The resulting samples were in the form of thin layers of residues deposited on the inside surfaces of the hemispherical tips of the silica ampoules. Neutron attenuation of samples of these thicknesses would certainly be nil.

The attenuation of neutrons by 100 mg of the platinum sample was estimated in the extreme case where irradiation was performed for a sufficiently long duration to cause the attainment of saturation activities of all the platinum radionuclides in the matrix. The fraction of neutrons absorbed by the sample matrix under these irradiation conditions, assuming that there is no "overlapping" of the target nuclei, would simply be $N\sigma_{abs}$, where N is the number of target nuclei and σ_{abs} is the absorption cross section. Since the average absorption cross section of the platinum nuclides is 8.8×10^{-24} cm^2 (84), the fraction of neutrons absorbed by 100 mg of the element is only 0.0027.

The flux gradients during irradiation were also deemed negligible. The silica ampoules containing the two platinum samples and the irradiation standards included with each irradiation were arranged in a bundle which was positioned vertically during irradiation. The platinum powder samples and the irradiation standards were located at one end of the silica ampoules.

Counting statistics

Due to the random nature of radioactive decay processes, the relative statistical standard error, σ_R, for a given number of accumulated counts, C, of a radioactive sample is given by the equation

$$\sigma_R = \frac{\sqrt{C}}{C} .$$

At least 10^5 counts in the determination of iridium, and 3×10^4 counts in the determination of silver, were accumulated for each sample, to give a statistical standard error of about 0.3% and 0.6%, respectively.

A higher statistical standard error was obtained in the determination of palladium due to the low specific activities of the palladium counting samples isolated from platinum. As shown in Table 6, background-corrected rates generally less than 150 counts/min were obtained even with the chemical yields of better than 85%. The palladium samples were counted for 50 minutes live time to give a standard error of less than 2% initially to about 5% after the samples had decayed for two or three half-lives of Pd^{109}.

Determination of chemical yield factors

The uncertainty in the chemical yield factor for the determination of iridium was largely dependent on the accuracy of the thiosulfate titration. An error of not more than 0.3% was expected for the titration. Additional errors due to aliquot sampling by volumetric pipets could have caused an error of about 0.2%.

In the gravimetric determination of the chemical yield factor for palladium, the palladium dimethylglyoximate precipitates weighed were generally more than 40 mg. An error of less than 0.3% due to weighing was expected.

Gamma-ray spectrometry

Comparative measurements made by comparing the areas of corresponding photopeaks in two gamma-ray energy spectra are also subject to uncertainties, particularly when the peak or peaks of interest are located in a region of the spectra having a Compton or bremsstrahlung continuum. This is true in the spectra of Ir^{192}, Pd^{109} and Ag^{110m}. Although the Compton and bremsstrahlung background can be subtracted from the peak area by creating a base across the minima on either side of the peak, this method also leads to subjective errors. In this work, the determination of the peak area was done simply by summing the individual channel counts over the photopeak region.

Even with the use of computer techniques, it is now normally accepted by activation analysts that gamma-ray spectrometry gives an inherent error of 5-15% (85).

Decay curve resolutions

A considerable uncertainty was introduced by decay curve resolution on the results of the determination of palladium. The error arising from this treatment was aggravated by two factors. First, the Pd^{109} activity induced in the platinum sample was rather low and the statistical errors of counting were therefore consequently large, especially after the sample had decayed to almost background. Secondly, the palladium sample in itself was actually a multicomponent mixture of Pd^{109} and the contaminant radionuclides of platinum; consequently, the amount of Pd^{109} activity was resolved from the decay curve of the sample by assuming an average half-life of the contaminant activities.

It is generally accepted that the measurement of a decay curve is often not accurate enough to show up an interference of 10% from another isotope, especially when made on a logarithmic plot (85).

In light of the above error considerations, it is apparent that the uncertainties in the results of this activation analysis are caused mainly by unavoidable factors inherent in the method. Whereas the errors due to chemical manipulations like sample weighing, aliquot sampling and volumetric titration were never more than 0.3%, the error contribution of gamma-ray spectrometry alone was at least 5%. In the particular case of the determination of palladium, the statistical errors of counting and the uncertainties in the decay curve resolutions also contributed significantly to the over-all error of the results.

In addition to all of the above uncertainty factors, further explanation must be sought for the apparently large variations in the results of this work. A possible cause of these variations could well be the inhomogeneity of distribution of the elemental impurities in the platinum matrix. In general, activation analysis requires the use of small samples due to the very high sensitivity of this method and the limitations of space during irradiation. Consequently, errors that may arise during the process of sampling, such as the effects of any inhomogeneities in the sample, are magnified. These effects could indeed be considerable particularly in the analysis for trace impurities.

Implications

This investigation demonstrated among others the practical advantages of anion exchange columnar separation methods in the neutron activation analysis for trace impurities in a platinum matrix. The very high matrix activity level did not at all limit the performance of the necessary chemical manipulations since most of the matrix activities were adsorbed by the anion resin. Au^{199}, which had been a troublesome contaminant in previously reported works on activation analysis of platinum matrices, was totally adsorbed by the strongly basic resin. Although in this work only a qualitative separation of iridium from platinum and palladium from platinum was attained, more carefully controlled experimental conditions and the proper choice of eluting solutions could certainly improve the degree of separation. Further work on this particular aspect of the analysis is recommended.

The radiochemical separation method by anion exchange can also be easily utilized in the activation analysis for other elemental impurities in a platinum matrix. Indeed, in some of the platinum samples irradiated in this work, cobalt as Co^{60}, which later proved to be an extraneous contaminant, was quantitatively separated from the matrix by elution of the anion resin column with dilute (less than 1 N) HCl solution.

The activation analysis for impurities in an iridium matrix or a palladium matrix can likewise be performed with a separation scheme similar to that utilized in this investigation. For instance, the analysis for palladium in an iridium matrix would involve adsorbing a solution of $[PdCl_4]^{2-}$ and $[IrCl_6]^{2-}$ in the anion resin column, followed by elution of $[PdCl_4]^{2-}$ with concentrated HCl; $[IrCl_6]^{2-}$ would remain adsorbed on the resin. Conversely, the analysis for iridium in a palladium matrix could be done by performing the same procedure utilized in this work. One determination, actually performed in the course of this investigation, yielded the presence of 22 ppm of iridium impurity in the palladium irradiation standard.

SUMMARY

Trace amounts of iridium, palladium and silver in a platinum stock were simultaneously determined by thermal neutron activation analysis utilizing gamma-ray spectrometry.

One hundred milligram samples of platinum metal in powder form and irradiation standards consisting of submilligram amounts of the elements to be determined were each sealed in 5 mm ID silica ampoules and irradiated for 9 to 30 hours with a thermal flux of *ca*. 3×10^{13} neutrons/cm^2-sec.

A radiochemical separation scheme was developed, involving selective elution of the chloro complexes of the elements of interest through a strongly basic anion exchange resin column, followed by further decontamination methods. Iridium and palladium carriers were used while silver activity was separated from the matrix on a carrier-free basis. $[IrCl_6]^{3-}$ and carrier-free $[AgCl_2]^-$ were eluted out of the resin column with 8 N HCl, after which $[PdCl_4]^{2-}$ was eluted out with 12 N HCl. $[PtCl_6]^{2-}$ and Au^{199} as $[AuCl_4]^-$ remained adsorbed on the resin after the sequential elution. Palladium was precipitated three times with dimethylglyoxime, after which the precipitate was dried, weighed and mounted on an aluminum planchet for activity measurement. Silver activity was extracted from the $[IrCl_6]^{3-}$ solution by isotopic exchange with a freshly prepared silver chloride electrode; the electrode was dissolved in a basic cyanide bath and silver was plated

out as the metal; the silver metal electrode was dissolved in concentrated HNO_3 in a polyethylene vial for activity measurement. The $[IrCl_6]^{3-}$ solution was evaporated to a small volume and transferred to a polyethylene vial for activity measurement; the chemical yield of iridium was then determined by an indirect iodometric titration method.

All activity measurements were performed by accumulation of counts in a 400-channel pulse height analyzer using a 3"- diameter NaI(Tl) crystal detector. The activities of 14-hour Pd^{109}, 74-day Ir^{192} and 253-day Ag^{110m} were monitored to represent the corresponding elements of interest. Dead time losses during counting were automatically compensated by the pulse height analyzer. Consistent geometry was maintained throughout the activity measurements. The channel counts in selected photopeak regions of the gamma-ray energy spectra were integrated, and corrected for coincidence losses where applicable, background, decay and chemical yield. Impurity calculations were then performed by a comparison of the corrected activities isolated from the platinum matrix with those of the corresponding irradiation standards.

Average impurity contents of 15 ± 2.1 ppb of iridium in 12 analyses, 28 ± 4.3 ppb of palladium in 8 analyses and 2.4 ± 0.27 ppm of silver in 6 analyses, were obtained.

The purity of all the counting samples were ascertained by observation of their radioactive decay behaviours. In some of the palladium samples which were slightly contaminated with the matrix activities, the activity of Pd^{109} was evaluated by resolution of the decay curves.

The concentration level of palladium obtained in this work seemed to approach the limit of detection of this element in a platinum matrix, on the basis of the radiochemical separation and instrumentation used.

The over-all errors in the results appeared to be mostly due to uncertainties inherent in gamma-ray spectrometry. The errors due to self-shielding during irradiation, and the interferences arising from secondary neutron reactions and threshold reactions, were deemed insignificant.

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