

방사화 분석에 의한 고순도 팔라듐 금속중의 미량 루테튬에 관한 새로운 정량법

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A New Method of Determination for the Trace Ruthenium in High Purity Palladium by Neutron Activation Analysis

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요약 고 순도 팔라듐 금속(99.9%)에 함유된 루테튬 함량을 $^{104}\text{Ru}(n, \gamma; \beta^-)^{105}\text{Rh}$ 의 핵반응에 의하여 생성된 ^{105}Rh 의 방사능을 측정함으로써 결정하였다.

원자로에서 조사된 팔라듐 시료와 루테튬 표준시료를 각각 왕수 처리 및 과산화나트륨으로 용융시킨 다음 ^{105}Rh 을 음이온 및 양이온 교환수지로 분리하였다.

팔라듐 시료로부터 얻은 ^{105}Rh 의 방사능을 루테튬 표준시료로부터 얻은 ^{105}Rh 의 방사능과 비교함으로써 루테튬의 함량을 결정하였다.

본 방법으로 구한 루테튬의 검출한계는 팔라듐 10 mg을 시료로 하였을 때 약 1 ppm이었으며 이 검출 감도는 $^{102}\text{Ru}(n, \gamma)^{103}\text{Ru}$ 의 핵반응을 사용한 종래의 방사화 분석에 비해 약 40배 더 예민하였다.

Abstract Ruthenium content in highly purified palladium metal (99.9%) was determined by counting ^{105}Rh nuclide which was produced by $^{104}\text{Ru}(n, \gamma; \beta^-)^{105}\text{Rh}$ nuclear reaction.

Palladium sample and ruthenium standard were irradiated by neutron with the Pneumatic Transfer System of TRIGA MARK II reactor. Palladium and ruthenium were dissolved by treating with aqua-regia and by fusing with sodium peroxide flux respectively. ^{105}Rh was separated through anion and cation exchange resin columns.

The ruthenium content was determined by comparing the ^{105}Rh activities, obtained from the palladium sample, with that from pure ruthenium standard.

The detection limit of ruthenium by the present method is about 1 ppm of ruthenium in 10 mg of palladium, which is approximately 40 times more sensitive than that of the conventional radio-activation method which employs $^{102}\text{Ru}(n, \gamma)^{103}\text{Ru}$ nuclear reaction.

Introduction

Due to the lack of sensitive method for ruthenium, the direct determination of trace impurities of this metal in highly purified platinum metals and ores, without previous concentration, has not been accomplished by conventional method. Recently neutron activation procedure has been developed for this purpose, e. g., for the determination of trace amounts of ruthenium in platinum¹, osmium² and ores^{3,4}.

However, these methods require delicate distillation for the quantitative separation of ruthenium. After distillation, these methods often require the use of multichannel analyzer in order to eliminate interferences of other nuclides. Moreover the sample has to be irradiated for several days at a neutron flux of $3-5 \times 10^{12}$ neutrons per $\text{cm}^2\text{-sec}$. in order to obtain sufficient activities of ^{103}Ru . This paper describes a simple and more sensitive method of neutron activation analysis for the determination of ruthenium using $^{104}\text{Ru}(n, \gamma; \beta^-)^{105}\text{Rh}$ reaction.

For the present work, it seemed that the anionic exchange separation, developed by Berman and McBryde⁷, is most suitable for the separation of rhodium from other platinum metals because the distribution coefficient of rhodium (III)^{8,9} is the smallest among the

platinum metals in hydrochloric acid medium.

The radiochemical purity of ^{105}Rh after the separation from the irradiated ruthenium by anion exchange resin was confirmed by multi-channel analyzer. However, it was found that copper and other trace elements interfered with the counting of ^{105}Rh after anion exchange separation of this nuclide from the irradiated palladium, i. e., the activities of the interfering nuclides were usually as high as that of ^{105}Rh . In order to eliminate these interfering ions as well as cerium, which was used as oxidant in Berman's method, cation exchange separation was also employed in addition to anion exchange separation. Strelow's data¹⁰ on distribution coefficients were used for the cation exchange separation. The elimination of cerium was necessary because the cerium activity will seriously interfere with the chemical yield which, at later stage, is determined non-destructively, using $^{103}\text{Rh}(n, \gamma)^{104}\text{Rh}$ reaction.

The present method consists of the following four steps: irradiation and fusion, anion and cation exchange separation, γ -ray counting and finally the yield determination. The last step was carried out by non-destructive neutron activation using $^{108}\text{Rh}(n, \gamma)^{104}\text{Rh}$ reaction. By the present method ruthenium could be determined with 95% confidence down to 30 ppm and the

Table I. Principal radionuclides of ruthenium and rhodium

Stable Isotope	Abundance (%)	Activation Cross-section (barn)	Nuclear reaction	Half life of radionuclide	Radiation (Kev)
^{96}Ru	5.7	0.21 ± 0.02	$^{96}\text{Ru}(n, \gamma)^{97}\text{Ru}$	2.88 d.	E. C. γ 's(216)
^{102}Ru	31.3	1.44 ± 0.16	$^{102}\text{Ru}(n, \gamma)^{103}\text{Ru}$	39.8 d.	β^- 's(220) γ 's(498, 610)
^{104}Ru	18.3	0.7 ± 0.2	$^{104}\text{Ru}(n, \gamma)^{105}\text{Ru}$ $^{104}\text{Ru}(n, \gamma; \beta^-)^{105}\text{Ru}$	4.5 h 36 h	β^- 's(1150) γ 's(726) γ 's(310, 320)
^{103}Rh		12	$^{103}\text{Rh}(n, \gamma)^{104}\text{Rh}$	4.4 m	I. T., (21, 53)
^{105}Rh		140	$^{105}\text{Rh}(n, \gamma)^{106}\text{Rh}$	43 sec	γ 's(560)

detection limit was found to be 1 ppm of ruthenium in 10 mg of palladium.

Nuclear data The nuclear data pertinent to the present work are shown in Table I. In the nuclear reaction of $^{104}\text{Ru}(n, \gamma; \beta^-)^{105}\text{Rh}$ which was used for this work, the decay constant (λ_1) of ^{105}Ru is larger than decay constant (λ_2) of ^{105}Rh , i. e., $\lambda_1 > \lambda_2$. The calculated time for the daughter (^{105}Rh) to reach its maximum activity is 17.6 hours.

Experimental

Apparatus and reagents A well type scintillation counter (Tracerlab, Versa/Matic V Scaler) was used. A 100 channel analyzer (TMC model 102) was used in conjunction with $2'' \times 2''$ NaI (TI) detector.

Dowex 1, X 8 (50-100 mesh, Cl^- form) anion exchange resin and Dowex 50, X 8 (50-100 mesh, H^+ form) cation exchange resin were washed in the following sequence, i. e., first with 6N ammonium hydroxide, distilled water, 6N hydrochloric acid and finally with distilled water.

The internal diameter of both cation and anion resin columns were 5 mm and the heights of both columns were about 12 cm. The flow rates of eluant in both columns were 50 ml per hour. The oxidizing solution was prepared by adding 1 ml of 0.1 M cerium(IV) sulfate to 100 ml of 0.8 M hydrochloric acid. The carrier solution of rhodium was prepared by dissolving the chlorosalt of high purity rhodium which was obtained from Kishida Chem. Co., Japan, in 0.1 M hydrochloric acid (1 mg of Rh/ml).

Ruthenium sponge, Johnson and Matthey Co., spectrographic purity, was used as ruthenium standard. The palladium sample was high purity metal sheet (99.9%) which was obtained from Kishida Chem. Co., Japan. Hydrochloric acid

and all the other chemicals were reagent grade.

Irradiation About 10 mg of ruthenium sponge were added to a polyethylene vial of 1 ml capacity and 10.0 mg of iron wire was attached to the outer surface of the vial as a thermal neutron flux monitor. The use of iron wire containing manganese as flux monitor in activation analysis was previously reported⁶.

After irradiation for 1 hour in the Pneumatic Tube of TRIGA MARK I reactor, where the thermal neutron flux is approximately 3.0×10^{12} neutrons per $\text{cm}^2 \cdot \text{sec.}$, the ruthenium was treated by the method as described below. Iron wire was counted for the activity of 845 Kev. γ -ray of ^{55}Mn with multichannel analyzer after 1 hour cooling.

Fusion and dissolution of ruthenium sponge In general, the following procedure for fusion and dissolution are similar to the recent works of Chung and Beamish³.

The irradiated polyethylene vial was opened after 1 day cooling and the contents were transferred to the nickel crucible by gentle tapping. To eliminate the possibility of loss, the irradiated materials were reweighed. One ml of rhodium carrier solution was added to the crucible and dried under an infrared lamp.

Sodium peroxide (ca. 1.5 gr.) was added, and the sample and flux were mixed thoroughly with a thin glass rod. The moist material adhered to glass rod was carefully scraped with another glass rod. The crucible was covered with a lid and the low temperature flame of a Meker burner was applied for about 2 min. until mixture was just melted. The heat was gradually raised, using a medium flame, for about a further 2 min., when the bottom of the nickel crucible became a dull red colour.

The molten mass was cooled by rotating the

crucible so that mass solidified in a layer on the wall. About 10 ml of water were carefully added through a dropper to disintegrate the melt, the crucible being covered with a lid to avoid the loss by spurting. By repeating this procedure with the total 20 ml of water, the disintegrated melt was transferred to a 100 ml beaker. About 10 ml of 6 N hydrochloric acid were added dropwise to dissolve the remaining residue. Finally the solution was transferred to a 50 ml measuring flask and diluted with water. The activity of the irradiated material remaining in the crucible was found to be negligible.

Anion exchange separation Five ml of the standard sample solution in 50 ml measuring flask were taken into a 20 ml beaker and evaporated under infrared lamp. The residue was evaporated to near dryness on hot plate after the addition of 2 ml of concentrated nitric acid. The evaporation was repeated twice in order to oxidize iridium to tetravalent state. About 2 ml of concentrated hydrochloric acid and 6 mg of sodium chloride were added and evaporated to dryness. The residue was dissolved in about 2 ml of 0.8 M hydrochloric acid and fed with a dropper onto 10 cm bed of anion exchange column which had been previously washed with 10 ml water and 10 ml of the oxidizing solution.

The beaker was twice rinsed with 2 ml of the acid solution and the rinsed solutions were fed onto the bed, which was then eluted with 90 ml of the oxidizing solution. All the effluents were collected together and evaporated to near dryness.

Cation exchange separation The residue was dissolved by adding 2 ml of 0.1 N hydrochloric acid and fed with a dropper onto 10 cm bed of cation exchange column which had been previously washed with 10 ml of 0.1 N hydro-

chloric acid solution. The beaker was twice rinsed with 2 ml of 0.1 N hydrochloric acid and the rinsed solutions were fed onto the bed, which was then eluted with 30 ml of the 0.1 N hydrochloric acid.

The effluents were collected together into a 100 ml beaker and evaporated on a hot plate to near dryness. The residue was dissolved with 2 ml of 0.1 N nitric acid and transferred to a 15 ml centrifuge tube.

Preparation of the sample for counting

^{105}Rh One ml of ferric chloride solution (10 ml of Fe) was added to the centrifuge tube. ^{105}Rh ions in the solution were coprecipitated with ferric ions by adding 6 N ammonium hydroxide solution dropwise. After centrifuge, the residue was dissolved with 5 ml of 1 N nitric acid and ferric hydroxide was precipitated with 5 ml of 2 N ammonium hydroxide solution. The precipitate was washed with 5 ml of 0.1 N ammonium hydroxide and dissolved with about 1.2 ml of 6 N nitric acid. 1.00 ml of this solution was pipetted into a ca. 1 ml polyethylene vial, which was finally sealed with flame. The exact volume of the final solution, 1.00 ml, was necessary because of the counting geometry. The sample solution in the vial was counted by the well type scintillation counter.

Procedures for the determination of ruthenium in palladium sheet About 10 mg of palladium sheet were accurately weighed and irradiated in the Pneumatic Tube along with iron wire as described above under the section of irradiation. After 24 hours' cooling the palladium sheet was dissolved with 5 ml of aqua regia, 100 λ of rhodium carrier solution were added and the solution was evaporated to near dryness. In order to isolate ^{105}Rh , the evaporated residue was treated with the same proce-

ture as described above, i. e., through the cation and anion exchange separation. The final solution for counting ^{106}Rh was prepared as mentioned above under the section of preparation of sample for counting ^{105}Rh . 1.00 ml of this solution pipetted into a ca. 1 ml vial was counted for 40 min. with the well type scintillation counter.

Chemical yield determination After 40 min. counting, both solutions each in 1 ml vial, i. e., one obtained from the irradiated ruthenium sponge and another from the irradiated palladium sample solution, were reirradiated for 1 min. in the Pneumatic Tube. After reirradiation, the samples were cooled for 30 seconds and transferred to the $2' \times 2'$ NaI(Tl) detector. The samples were counted for 0.1 min. with the multichannel analyzer. The reirradiation and the counting were repeated several times for each vial and the mean value was calculated from the counts of gamma activities of ^{104}Rh (43 sec.) at 560 Kev.

The ratio of the chemical yields for rhodium in each vial was determined by comparing the gamma activities of ^{104}Rh at 560 Kev. Using this ratio, a correction was made for the difference of chemical yields.

Results

Although it can be estimated by the equation¹⁴ that the disintegration rate of ^{105}Rh , produced from the $^{104}\text{Ru} (n, \gamma; \beta^-)^{105}\text{Rh}$ reaction, would be about five times as much as that of ^{103}Ru , produced from the $^{102}\text{Ru} (n, \gamma)^{103}\text{Ru}$ reaction, this high rate of disintegration of ^{105}Rh can not be the case if the activity is measured with multichannel analyzer because of the low intensity of γ -ray of ^{105}Rh ; i. e., the total γ -ray intensity of ^{105}Rh in the range of 306-319 Kev. is 24%,⁵ which is much less intense as compared with

that of ^{103}Rh which is 95% in the range of 497-610 Kev.

In the present work, because of the low counting efficiency of multichannel analyzer, the measurement of ^{105}Rh activity was performed with a well type scintillation counter so as to improve the counting efficiency. The results, which are described below, indicate a significant improvement upon the efficiency for the counting of ^{105}Rh by the present method.

The number of counts per μg of ruthenium per min. is shown in Table II, which are the corrected value to the condition of 48 hours' cooling from the end of irradiation. The correction for the chemical yield was also incorporated in calculations of these number of counts. In order to compare the sensitivity of the present method with that of ^{103}Ru method^{2,3}, the number of counts expected to obtain by the latter method was determined as follows; i. e., 2 ml of the standard ruthenium solution, which has been prepared after irradiation as described above under the section of Fusion and Dissolution etc., were transferred to a 25 ml volumetric flask, diluted with distilled water. The volumetric flask was placed in close contact with the NaI crystal, and counted with analyzer. These values are shown in the last column of Table II.

Table II. Number of counts of ^{105}Rh and ^{103}Ru per μg of Ru per min.

Exp. No.	^{105}Rh counted with well type scintillation counter	^{105}Rh counted with multichannel analyzer	^{103}Ru counted with multichannel analyzer
1	163	23.2	7.9
2	159	22.5	7.7
3	149	25.3	
4	155		
Average	157±6 (s. d. = 3.82%)	23.7±1.5 (s. d. = 6.32%)	7.8±0.2

Table III. Quantitative detection limit for ruthenium in terms of ruthenium amount, μg

By counting ^{105}Rh with well type scintillation counter	By counting ^{105}Rh with multichannel analyzer	By counting ^{103}Ru with multichannel analyzer
0.3	13	4.3

The calculated value for the determination limits¹² are shown in Table III. In this calculations, the background was assumed to be well known for the scintillation counting. The background was taken to be zero in the case of the analyzer since it was subtracted automatically.

It can be seen from Table III that by the present work, in which ruthenium is determined by counting the ^{105}Rh activity with well type scintillation counter, the determination limit for ruthenium can be improved about 40 times as compared to the other method, in which the ^{103}Ru activity is counted with multichannel analyzer.

The activity of ^{105}Rh per g. of palladium per min. are shown in Table IV after correction to the same condition as described for Table II. From Table II and IV, the ruthenium contents are calculated as follows, i. e., ruthenium content, ppm = counts of ^{105}Rh per g of Pd / counts of ^{105}Rh per μg Ru = $(13,690 \pm 750) / (157 \pm 6) = 87.8 \pm 5.8$ (s. d. = 6.7%) ppm.

Table IV. Number of counts of ^{105}Rh per g of Pd per min.

Ex. No.	cpm
1	14,610
2	112,830
3	14,040
4	13,621
Average	$13,690 \pm 750$ (s. d. = 5.5%)

Discussion

The main source of error seems to be the variation in neutron flux during the reirradiation of each sample for the determination of chemical yield. In order to reduce this error, the reirradiation of each sample was repeated several times after the decay of ^{104}Rh (43sec.). Each activities of ^{105}Rh thus obtained were averaged and the mean value was used for the correction of the chemical yield on rhodium.

Neutron shielding effects on 10 mg of ruthenium sponge and palladium sheet can be considered as negligible because thermal total absorption cross sections for each metal are less than 15 barns^{2,13}.

The radiochemical purity of the separated ^{105}Rh from palladium was confirmed by determining the half life (Fig. 1). The half life showed a good agreement with the data (35.9 hours) from literature.

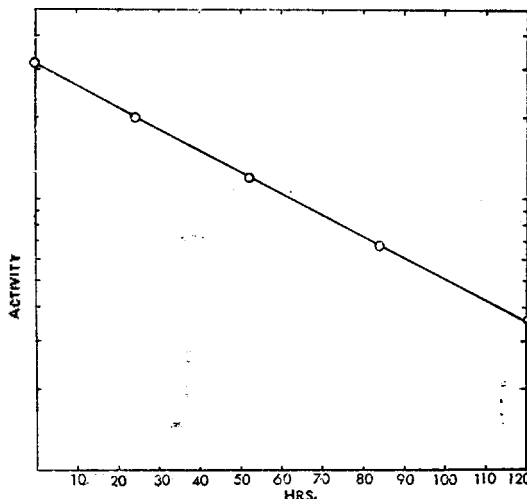


Fig. 1. Radiochemical purity of ^{105}Rh from palladium

The chemical recovery of rhodium was in the range of 70~80%, which was found by the tracer work using ^{105}Rh . This loss of rhodium was found to occur in anion exchange separation and also in pipetting 1.00 ml of

ferric hydroxide solution from the centrifuge tube.

The efficiency of the coprecipitation of ^{105}Rh with ferric hydroxide and the radiochemical purity of ^{104}Rh after the coprecipitation with ferric hydroxide has been reported to be satisfactory.¹¹

The half-life of ^{103}Rh was determined to be 42 seconds, which agreed well with the reported value. It was suspected that ^{104}Rh might also be formed from ruthenium or palladium metal. Such possibility was found to be non-existent. This was confirmed by examining the gamma spectra of the reirradiated solution, in 1 ml vial, of ruthenium and palladium. This solution to be irradiated was prepared, without adding rhodium carrier, by following the whole procedure as described above for ruthenium standard (or palladium sample).

The time taken to separate ^{105}Rh from palladium sample was about three hours.

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