

DETERMINATION OF RHODIUM BY THERMAL NEUTRON ACTIVATION ANALYSIS USING γ -RAY SPECTROMETRY

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INTRODUCTION

In a recent review article BEAMISH¹ pointed out the lack of satisfactory analytical methods for trace amounts of rhodium. Two colorimetric determinations² are applicable in the 25–200 μg region but these are complicated methods requiring detailed separation procedures. Thermal neutron activation with gross β -ray measurement has been used in this laboratory^{3,4} to determine trace rhodium content in samples such as meteorites. γ Spectrometry has also been attempted elsewhere⁵ but there was a need for a general evaluation of this method.

The concept of analysis by nuclear reaction is well established and was summarized a number of years ago by BOYD⁶. As applied to rhodium, the nuclear reactions, $^{103}\text{Rh}(p,n)^{103}\text{Pd}$, $^{103}\text{Rh}(n,\alpha)^{100}\text{Tc}$, and $^{103}\text{Rh}(n,\gamma)^{104}\text{Rh} + ^{104m}\text{Rh}$ are the principal reactions available to the analyst for qualitative and quantitative analysis. The (p,n) reaction requires a high-energy positive-ion accelerator and is relatively insensitive from a practical view because of the 17-day ^{103}Pd product. The (n,α) reaction is more adaptable from the product half-life consideration but presently available sources of the fast neutrons required for this reaction, limit the sensitivity to approximately 10 p.p.m. As neutron generators are improved, this reaction will become more important.

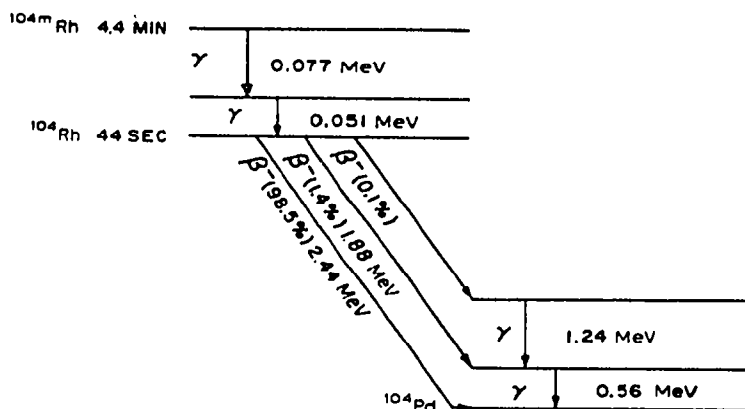


Fig. 1. Decay scheme of ^{104}Rh isomers⁸.

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At the present time, however, the (n,γ) reaction is the most important for activation analysis. This reaction has favorable cross-sections, produces radioactive products with convenient half-lives and can be run with any source of thermal neutrons⁷. Indeed rhodium is one of the elements for which thermal neutron activation is optimum.

When irradiated with thermal neutrons, the naturally-occurring mono-isotopic ^{103}Rh nuclei absorb neutrons to form an unstable configuration. Excess energy is emitted from this configuration mainly by the emission of prompt γ rays until the nuclei reach the ground state of ^{104}Rh or an isomeric state ^{104m}Rh . The probability is greater for the formation of ^{104}Rh than it is for ^{104m}Rh by a factor of 137.0 to 11.8 (*i.e.* the ratio of the reaction cross-sections). These isotopes are radioactive and decay to the ground state of ^{104}Pd by the emission of β and γ rays. The decay of these isomers is given in Fig. 1⁸.

The analyst can make use of the short-lived isomer (42- or 44-sec depending upon the reference^{8,9}) in a non-destructive method or can take advantage of the equilibrium between the two species (with an effective half-life of 4.4 min) to separate rhodium chemically from its matrix prior to measurement. This paper describes a procedure for sub-microgram quantities of rhodium based on each of these two approaches using the Ford Nuclear Reactor at the University of Michigan.

EXPERIMENTAL

Apparatus and reagents

Samples were irradiated in the Ford Nuclear Reactor of the Phoenix Memorial Laboratory at the University of Michigan. Use was made of the pneumatic tube system¹⁰ which permitted short and precisely-timed irradiations coupled with rapid delivery of the samples into and out of the neutron fields. Samples were delivered within 3 sec by this system to a hood in the neighboring radioisotope laboratory. Neutron fluxes, at the center of the irradiating positions, varied from $9.9 \cdot 10^{11}$ to $1.3 \cdot 10^{12}$ $n \text{ cm}^{-2} \text{ sec}^{-1}$. Relative values of neutron flux were determined for each sample by activation of gold foils. Measurement of these gold foils in a calibrated scintillation well counter permitted normalization of the results for all irradiations to a flux level of 10^{12} $n \text{ cm}^{-2} \text{ sec}^{-1}$.

A second pneumatic tube system was used to transfer the irradiated samples from the laboratory hood to the sodium iodide detector of the scintillation spectrometer. This system uses 0.5 in. i.d. aluminum tubing and a vacuum cleaner for suction. The sample is transported to the detector in 2 sec and there triggers circuits which are designed to start the analyzer when the sample is in position for counting.

Radioactivity assays were made by γ -ray spectrometry using a dual-memory, 100-channel, vacuum tube, Radiation Instruments Development Laboratory pulse height analyzer coupled with a 3 in. \times 3 in. NaI(Tl) detector. Resolution for this particular phototube and crystal was 10.8%. Dead time of the analyzer system varied with the strength of the samples and was recorded during the counting operation.

All reagents were C.P. or analyzed reagent grade and were used without further purification.

Non-destructive method using 44-sec ^{104}Rh

Samples containing varying amounts of rhodium (RhCl_3 in 1 *N* HCl) were sealed

in medical grade polyethylene tubing, enclosed in a 1 in. \times 3 in. polyethylene "rabbit" and irradiated in a thermal neutron flux of $\sim 10^{12}$ n cm $^{-2}$ sec $^{-1}$ for 42 sec. At the end of the irradiations, the samples were returned to the laboratory, repackaged, and sent to the scintillation detector. The elapsed time from the end of irradiation to the start of the counting period varied from 19 sec to 54 sec.

γ Radiations from the samples were detected, analyzed, and stored for 1 min in the memory of the analyzer. This information was then recorded both graphically on an X-Y recorder and in digital form by a Hewlett-Packard printer. The number of scintillation counts/min in the 0.56-MeV photopeak is proportional to the weight of rhodium present. All counts were normalized for decay (to the end of irradiation), for analyzer dead time (to 0%), and for neutron flux (to 10^{12} n cm $^{-2}$ sec $^{-1}$). Background radiations from other activities were eliminated by an extrapolation of the base line under the photopeak as illustrated in Fig. 2.

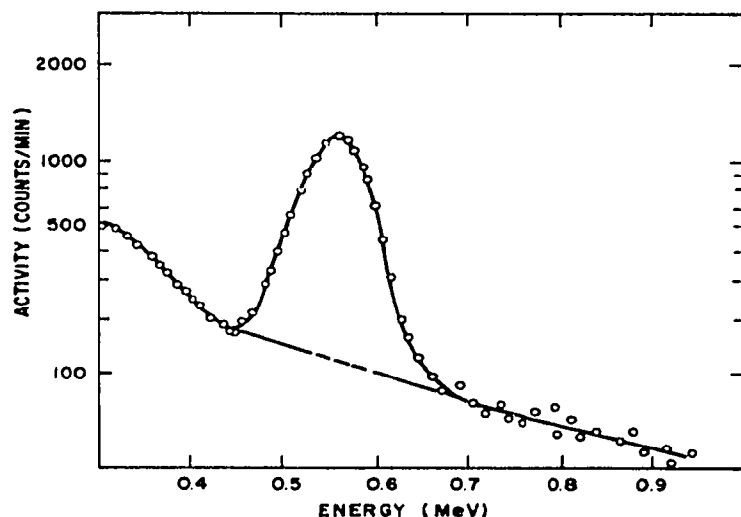


Fig. 2. γ -Ray spectrum of ^{104}Rh (from 0.3 to 1.0 MeV) showing extrapolation of base line under 0.56 MeV photopeak to eliminate contribution of other activities. Sample: 0.25 μg Rh as RhCl_3 in HCl; 42-sec irradiation; 23-sec transfer time; 1-min counting time; 7% dead time; 9,167 counts in peak; $A_0 = 13,398$ counts/min.

Destructive method using 4.4-min ^{104m}Rh

Rhodium samples, with and without other elements, were packaged as described above and irradiated for 5 min. When returned to the laboratory, they were cut open and cautiously added to ten times their weight of previously heated sodium peroxide. The melt was heated for 1 min, cooled by dipping the outside of the nickel crucible in cold water while rotating the crucible to coat the inside, and dissolved by cautiously adding 20 ml of concentrated hydrochloric acid.

5 ml of RhCl_3 carrier solution (1 mg/ml in 1 N HCl), 1 ml of 10% tartaric acid, and 8 ml of pyridine were added and the solution was filtered into a separatory funnel¹¹. An additional 5 ml of 6 N HCl was used to rinse the crucible and filter. The solution was then made basic with 15 ml of 12 N sodium hydroxide. After thorough mixing for 1 min the pyridine layer was separated. An aliquot was then measured by γ -ray spectrometry. The chemical yield of the separation procedure was determined by measuring the pyridine-rhodium complex absorbance at 440 $\mu\mu$. The counts in the 0.56-MeV photopeak were corrected for elapsed time, analyzer dead time, neutron flux variations, and for the chemical yields.

RESULTS AND DISCUSSION

Calibration data for the non-destructive analysis of rhodium were obtained by 42-sec irradiations of known amounts of the element and subsequent analysis of the γ -ray scintillation spectra. Part of such a γ -ray spectrum from 0.3 MeV to 1 MeV obtained with 0.25 μg of rhodium is shown in Fig. 2.

Table I gives the results of these calibrations. The method is probably accurate to within $\sim \pm 6\%$ over the weight range of 0.1 to 1 μg of rhodium. In the range of 0.01

TABLE I

CALIBRATION DATA FOR NON-DESTRUCTIVE RHODIUM ANALYSIS BY THERMAL NEUTRON ACTIVATION ANALYSIS ($10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$) USING 44-sec ^{104}Rh

Sample	Rhodium (μg)	Irrad. time (sec)	Transfer time (sec)	A_0 Photopeak ^a (counts min^{-1} at end of irradiation.)	Specific activity (counts $\text{min}^{-1} \mu\text{g}^{-1}$)
RhCl ₃ in 1 N HCl	0.01	42	19	575 ^b	57,500
RhCl ₃ in 1 N HCl	0.10	42	32	5,391	53,910
RhCl ₃ in 1 N HCl	0.25	42	23	13,398	53,592
RhCl ₃ in 1 N HCl	0.50	42	54	27,525	55,050
RhCl ₃ in 1 N HCl	0.75	42	25	41,340	55,120
RhCl ₃ in 1 N HCl	1.00	42	28	57,074	57,074
Average					55,374 \pm 2.6% ^c

^a Corrected for analyzer dead time and neutron flux variation.

^b Average of three determinations. All other values are from a single determination.

^c Error is "standard deviation" of the six values. Statistically the higher counting values of A_0 are more significant and hence some weighting factor should probably be used in determining the error. Such a procedure would tend to reduce the value of this error.

TABLE II

ANALYSIS OF STANDARD RHODIUM SAMPLES BY NEUTRON ACTIVATION ANALYSIS

Sample	Irradiation time	Matrix	Chemical separation	$\mu\text{g Rh}$	
				Added	Found
1	42 sec	H ₂ O-HCl	None	0.01	0.011 ^a
2	42 sec	H ₂ O-HCl	None	0.01	0.009 ^a
3	42 sec	H ₂ O-HCl	None	0.01	0.012 ^a
4	42 sec	H ₂ O-HCl	None	0.01	0.013 ^a
5	42 sec	H ₂ O-HCl	None	0.01	0.012 ^a
6	42 sec	H ₂ O-HCl	None	0.01	0.011 ^a
7	42 sec	H ₂ O-HCl	None	0.10	0.095 ^a
8	42 sec	Silica gel	None	0.50	0.53 ^a
9	42 sec	Silica gel	None	1.00	1.02 ^a
10	5 min	H ₂ O-HCl	Pyridine extraction	0.10	0.08 ^b
11	5 min	H ₂ O-HCl	Pyridine extraction	0.50	0.48 ^b
12	5 min	H ₂ O-HCl ^c	Pyridine extraction	1.00	1.10 ^b
13	5 min	H ₂ O-HCl ^c	Pyridine extraction	1.00	1.02 ^b
14	5 min	H ₂ O-HCl ^c	Pyridine extraction	1.00	1.08 ^b
15	5 min	Silica gel	Pyridine extraction	1.00	1.04 ^b

^a Based on 55,374 counts $\text{min}^{-1} \mu\text{g}^{-1} \text{ Rh}$ at $10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$

^b Based on 3,698 counts $\text{min}^{-1} \mu\text{g}^{-1} \text{ Rh}$ at $10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$

^c Contained approximately 100 p.p.m. K, Sr, Ce, Zr, Ru, Pd, Ag, Zn, In, Sb, and Re

to 0.1 μg , this accuracy is probably within $\sim \pm 20\%$. These data, along with the results of several standard sample analyses, are given in Table II. The average time per analysis is 7 min for this non-destructive method using the short-lived radioactive isomer.

It can be seen from Table II that at the 0.50- μg level of rhodium even such a "problem" matrix as silica gel offers little trouble in this non-destructive method since the 44-sec isomer has such a high sensitivity for activation analysis. One might, however, expect that elements such as silver, iodine, bromine, tungsten, arsenic, antimony, copper, zinc, and others with γ -ray peaks near 0.56 MeV might interfere if present in the matrix in much larger concentrations than the rhodium (see Fig. 27 of ref. ¹² for a graph of relative calculated sensitivities).

When such interferences are found in samples, a chemical separation is necessary before a radioactive assay can be made. A calibration curve for rhodium analysis was prepared using the separation techniques of sodium peroxide fusion and pyridine extraction to isolate the 4.4-min $^{104\text{m}}\text{Rh}$ pure enough for γ -ray spectroscopy. These calibration data are given in Table III and the results for several standard samples analyzed by this method are included in Table II. The method is probably accurate to within $\sim \pm 20\%$ over the range of 0.10 to 1 μg of rhodium. The average time per analysis using the 4.4-min isomer is 20 min including 5 min for the irradiation.

TABLE III

CALIBRATION DATA FOR RHODIUM ANALYSIS BY THE PYRIDINE EXTRACTION METHOD USING THE 4.4-min $^{104\text{m}}\text{Rh}$ FOR THERMAL NEUTRON ACTIVATION ANALYSIS ($10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$)

Sample	Rhodium (μg)	Irrad. time (min)	Time for chemistry (min)	A_0 Photoppeak* (counts min^{-1} at end of irrad.)	Specific activity (counts $\text{min}^{-1} \mu\text{g}^{-1}$)
RhCl ₃ in 1 N HCl	0.10	5	8.3	3.43 ^b	3.43 ⁰
RhCl ₃ in 1 N HCl	0.50	5	7.1	1,880	3.76 ⁰
RhCl ₃ in 1 N HCl	1.00	5	7.8	3,903	3.903
					Average 3.698 \pm 5.4% ^c

* Corrected for analyzer dead time, neutron flux variation, and chemical yield.

^b Average of three determinations. Other values are from a single determination.

^c Error is "standard deviation" (see note c, Table I)

The short-lived ^{104}Rh also has a γ -ray peak at 1.24 MeV. In this region of the γ spectrum there are fewer potential interferences (indium, silicon, argon, and cadmium being the principal ones¹².) However, since the sensitivity of the peak is less than that of the 0.56-MeV peak by a factor of ~ 20 , the lower-energy peak will probably be used for most non-destructive analyses.

A glance at the decay scheme of these rhodium isomers (Fig. 1) shows that a large percentage (98.5%) of the decay is by β emission directly to the ground state rather than through the 0.56-(1.4%) or 1.24-(0.1%) MeV γ rays. Thus, activation analysis of rhodium by measuring the high-energy β ray of ^{104}Rh should give considerably higher sensitivities¹³ than reported above. Unfortunately β -ray measurement cannot be made as discriminating as γ -ray spectrometry and hence samples with few other activating impurities would probably be required to utilize the very high sensitivity of the 44-sec ^{104}Rh . Suitable designs of regular or low-background β counting equipment could, however, be used with good radiochemical separations

(as developed above or adapted from ref. 14) to lower the limit to at least 10^{-9} g with thermal neutron fluxes of 10^{12} n cm^{-2} sec^{-1} . Similar procedures should give sensitivities approaching μ g levels of rhodium with low cost neutron generators such as are now available^{12,15}.

For most practical situations requiring high sensitivity, however, it would appear that at present the non-destructive method using a reactor and γ -ray spectrometry will be of most importance because of its simplicity.

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SUMMARY

Trace amounts of rhodium have been determined by thermal neutron activation analysis using both destructive and non-destructive methods. With a neutron flux of 10^{12} n cm^{-2} sec^{-1} the lower limits of detection are about 0.1 μ g and 0.01 μ g, respectively. A rapid sodium-peroxide fusion followed by a pyridine extraction was used in the destructive method to separate the 4.4-min 104m Rh from its matrix. The 4.4-sec 104 Rh was used in the non-destructive method. Both radioactive isomers were measured by γ -ray spectrometry with a multichannel pulse height analyzer. The average time required per non-destructive analysis was 7 min while the chemical method averaged 20 min.

RÉSUMÉ

Des traces de rhodium ont pu être analysées par activation au moyen de neutrons thermiques, en utilisant soit une méthode destructive (fusion avec peroxyde de sodium et extraction dans la pyridine pour séparer 104m Rh (4.4 min), soit une méthode non-destructive (utilisant 104 Rh (4.4 sec)). Ces deux isomères radioactifs ont été mesurés au moyen d'un spectromètre γ à plusieurs canaux.

ZUSAMMENFASSUNG

Spurenmengen von Rhodium können durch Aktivierung mit thermischen Neutronen bestimmt werden unter Anwendung von destruktiven (Aufschluss mit Natriumperoxyd und Isolierung des 4.4-Min 104m -Rh) oder nicht destruktiven Verfahren durch Verwendung von 4.4-sec 104 -Rh. Die beiden radioaktiven Isomere werden mit einem Mehrkanal-Gammastrahlen Spektrometer gemessen.

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