The Neutron Pile as a Tool in Quantitative Analysis; The Gallium and Palladium Content of Iron Meteorites

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THE SCIENCE OF METEORITICS has come to be looked upon in recent years as a science of increasing importance, largely because of its recognized bearing upon astrophysical problems. In particular, it now appears likely that an intensive study of the distribution of elements in meteorites will enable one to draw important conclusions concerning the structure of planets, the origin of our solar system, and the relative "cosmic" abundances of the chemical elements (*1, 2*).

Unfortunately, with the exception of a very few common elements such as oxygen, silicon, magnesium, iron, nickel, and calcium, elements are found in meteorites in quantities of only a few parts per million (*3, 4*). Assaying the concentration of these rarer constituents of meteorites with an accuracy of 10% or better, as we often wish to do, presents grave analytical problems. V. M. Goldschmidt (*4*), Hevesy (*6*), and the Noddacks (*11*), who did much of the excellent earlier work on assaying the rarer constituents of meteorites, used at one time or another straightforward quantitative chemical methods, X-ray spectroscopy, and chemical spectroscopy. While their work has been very useful, the difficulties inherent in such analytical work gave rise to errors which appear in many cases to be greater than factors of two, and in some cases as great as a factor of ten.

If marked progress is to be made in the application of meteorites to cosmological problems, it seems clear that analytical techniques are needed which will satisfy the following criteria: (1) The method must permit an accuracy of 10% or better in determining the concentration of a given element present in the concentration range of 0.01 ppm to 500 ppm; (2) there must be no interferences from other chemical elements; (3) there must be no danger of contamination during the analysis; (4) the method must be reasonably rapid. A survey of various possible analytical approaches to the problem led the authors to the conclusion that a radiochemical technique offered the most promise.

The General Method. The concept of utilizing neutron activation as an analytical tool is by no means new. As early as 1936 Hevesy and Levi (*7*) applied the neutron activation method of analysis to the rare earth elements. They were able to find the 2½-hr dysprosium period in a sample of yttrium, after activation with neutrons, and thus demonstrated the presence of dysprosium impurity to an extent of 1%. Using the same method, Hevesy and Levi were also able to detect small amounts of europium in gadolinium samples (*8*). Since that time, modifications of the method have been used for semiquantitative studies of elements possessing relatively high neutron activation cross sections.

Most elements when irradiated by slow neutrons give rise to radioactive species of the same atomic number. The specific activity produced in a given element by neutron irradiation depends upon the neutron capture cross section of the isotope giving rise to the activity when it captures a neutron, the abundance of the isotope, the neutron flux, the half-life of the radioactive species, and the length of the irradiation: $a = N\sigma f(1 - e^{-\lambda t})$ where a = activity (disintegrations/sec), N = number of atoms of the nuclear species giving rise to the activity, σ = neutron capture cross section of species per atom (cm^2), f = neutron flux (neutrons/cm^2/sec), λ = decay constant of radioactive product, t = length of irradiation.

With the advent of the neutron pile, neutron fluxes capable of producing very high specific activities have become available. For example, the flux of the order of 10^{12} neutrons/cm^2/sec available in the heavy water pile at the Argonne National Laboratory is capable

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of producing, in many elements, specific activities of the order of magnitude of 100,000–1,000,000 disintegrations/min/μg of element. Such specific activities make it possible to carry out the following general procedure: (1) A portion of the substance to be analyzed is irradiated in the pile, together with a standard consisting of a known weight of the element being determined; (2) the unknown is dissolved and a known weight of the element being determined is added to the solution; (3) the element added is chemically processed in order to free it from the activities associated with other elements present in the unknown; (4) the chemical yield of the procedure is determined; (5) the activity of the element in the unknown is compared with that of the standard; and (6) the purity of each activity is checked by measurements of half-lives and absorption spectra.

TABLE 1

SENSITIVITY OF PILE ANALYTICAL METHOD FOR CERTAIN ELEMENTS
(Argonne Heavy Water Pile, 7-hr bombardment at highest flux)

Element	Sensitivity (μg)	Element	Sensitivity (μg)
Na	0.01	Cu	0.004
Si	0.3	Ga	0.01
P	0.4	Ge	2.0
S	700.0	As	0.005
K	0.1	Rb	1.0
Ca	100.0	Sr	300.0
Sc	0.3	Y	0.05
Ti	400.0	Zr	2.0
Cr	1.0	Mo	0.7
Mn	0.003	Pd	0.005
Fe	700.0	Ag	5.0
Ni	0.1	Dy	0.00001

Table 1 gives examples of the estimated sensitivity of the neutron irradiation method for various elements in the Argonne heavy water pile. The term "sensitivity" is used here in a sense differing somewhat from its usual connotation in connection with analytical methods. In this paper the term is used to indicate the smallest quantity of an element that will give rise to an activity sufficiently intense to permit the measurement of half-life and absorption after the element has been exposed to the central pile flux for a period of 7 hr. Thus "sensitivity" here denotes the smallest quantity of an element that can be measured with a precision better than 10%, utilizing the central flux of the Argonne Pile for a time not unduly long.

It can be seen that the sensitivities obtainable are in general quite satisfactory, and in some cases are remarkable. The cases of manganese, copper, arsenic, palladium, and dysprosium, shown in Table 1, are particularly noteworthy. If one assumes that a half-life of 30 min represents the shortest life-time practicable for analytical determination, then the method is applicable to about 60 of the 75 stable elements existing in nature (excluding the rare gases). The method either cannot be applied or can be applied only with difficulty to hydrogen, lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, magnesium, aluminum, vanadium, cobalt, columbium, and rhodium. In general, the pile method of analysis is more sensitive for elements of odd atomic number than for elements of even atomic number, because nuclear species of odd mass number have larger activation cross sections and nuclear species giving rise to the activities in the even elements have generally low abundance.

Thus far the pile analysis method has been developed and tested for the elements gallium and palladium. The method has been applied extensively to the problem of analyzing iron meteorites for these elements. Gallium is present in iron meteorites to an extent of 10 to 100 ppm; palladium is present to an extent of 1 to 5 ppm.

The Method Applied to Gallium. Gallium is present in sufficient quantity in meteorites, and the activation cross section is sufficiently large, to permit the use of the more modest neutron fluxes obtainable some distance from the center of the Argonne pile.

Gallium has two stable isotopes (*10*), Ga^{69} (60.2%) and Ga^{71} (39.8%). The more abundant isotope captures a neutron to form 20-min Ga^{70}; the less abundant isotope captures a neutron to form 14.1-hr Ga^{72}:

$$Ga^{69} + n \rightarrow Ga^{70} \xrightarrow{20m} Ga^{70} + \beta^-$$

$$Ga^{71} + n \rightarrow Ga^{72} \xrightarrow{14.1h} Ga^{72} + \beta^-$$

The radiation characteristics of the radioactive products are described elsewhere (*13*).

The samples were transported to a position near the reactor tank of the pile and out again by means of an electronically controlled pneumatic tube device known as a "rabbit," which has been described elsewhere (*9, 15*). Samples ranging in weight between 0.3 and 0.5 g were cut from portions of meteorites free from discernible inclusions of troilite, silicate, or schreibersite. The samples were washed with 6*N* hydrochloric acid, distilled water, and alcohol to remove surface impurities. The samples were then placed in individual small plastic containers in the rabbit and irradiated for approximately 30 min. Standard samples of gallium 8-hydroxyquinolate were irradiated simultaneously. After removal from the pile, the samples were allowed to cool until the 20-min gallium activity had decayed. The unknowns and the standards were then chemically treated. In the case of the unknowns, the chemical procedure was designed to make use of the fact that gallium is ether-extractable, as the chloride (*5*), is amphoteric, and can be precipitated as the 8-

hydroxyquinolate. The combination of these chemical properties permits development of a procedure which successfully frees the gallium activity from other interfering activities.

TABLE 2

Summary of Results on Canyon Diablo

Run no.	Gallium content (ppm)	Δ Deviation from mean
6	77.4	0.0
7	76.0	1.6
10	76.2	1.2
12	74.6	2.8
13	84.2	6.8
14	78.0	0.6
17	70.0	7.4
18	76.2	1.2
19	79.2	1.8
20	82.0	4.6
21	80.4	3.0
149	76.8	0.6
152	75.2	2.2

Average: 77.4

Standard deviation $\sigma = \sqrt{\frac{\Sigma\Delta^2}{n-1}} = 3.4$ (4.4%)

Precision $= \frac{\sigma}{\sqrt{n}} = \pm 0.9$

Final result for 13 runs: 77.4 ± 0.9 ppm

TABLE 3

Summary of Results on Henbury

Run no.	Gallium content (ppm)	Δ Deviation from mean
42	15.2	1.6
43	15.1	1.7
44	15.9	0.9
51	18.4	1.6
52	17.8	1.0
53	17.9	1.1
59	16.7	0.1
61	15.2	1.6
62	15.6	0.8
158	18.2	1.4
159	18.2	1.4

Average: 16.8

Standard deviation $\sigma = \sqrt{\frac{\Sigma\Delta^2}{n-1}} = 1.3$ (8.0%)

Precision $= \frac{\sigma}{\sqrt{n}} = \pm 0.4$

Final result for 11 runs: 16.8 ± 0.4 ppm

Chemical Procedure for Gallium in Iron Meteorites: 1) Dissolve sample in hot concentrated hydrochloric acid in 50-ml beaker. Add 4 to 5 mg of Ga^{+3} carrier. Decant solution from any insoluble residue present (seldom more than 0.1% by weight). 2) Make solution 5.5 to 6.5 M in hydrochloric acid. Extract gallium with an equal amount of ether saturated with hydrochloric acid. Extract gallium from ether phase with water. 3) Repeat step 2. Boil ether from water phase. 4) Add sodium hydroxide until solution possesses a hydroxide concentration of 1 to 2 M, precipitating all ferric ion present. This precipitate brings down with it residual interfering activities. Add one drop of aerosol, centrifuge, and discard the precipitate. Acidify the solution to a pH of 1.0 and heat to 60–70° C. 5) Add 5 ml of a 1% dilute acetic acid solution of 8-hydroxyquinoline. Add dropwise 3M ammonium acetate until the precipitation of yellow gallium 8-hydroxyquinolate is complete. 6) Filter and wash the precipitate with hot water, then ether. Determine the weight of the sample after heating at 110° C for 15 min. The sample is now ready to be counted.

TABLE 4

Summary of Results on Odessa

Run no.	Gallium content (ppm)	Δ Deviation from mean
24	67.8	1.5
25	66.0	3.3
40	68.2	1.1
48	72.6	3.3
49	72.4	3.1
50	67.8	1.5
58	63.8	5.5
65	72.6	3.3
66	71.0	1.7
163	70.4	1.1

Average: 69.3

Standard deviation $\sigma = \sqrt{\frac{\Sigma\Delta^2}{n-1}} = 3.0$ (4.3%)

Precision $= \frac{\sigma}{\sqrt{n}} = \pm 0.9$

Final result for 10 runs: 69.3 ± 0.9 ppm

TABLE 5

Summary of Results on Xiquipilco

Run no.	Gallium content (ppm)	Δ Deviation from mean
26	56.2	1.0
27	51.4	3.8
28	59.3	4.1
32	53.0	2.2
33	54.6	0.6
34	54.8	0.4
35	53.0	2.2
36	54.2	1.0
37	51.6	3.6
146	65.0	9.8
155	54.5	0.7

Average: 55.2

Standard deviation $\sigma = \sqrt{\frac{\Sigma\Delta^2}{n-1}} = 3.9$ (7.1%)

Precision $= \frac{\sigma}{\sqrt{n}} = \pm 1.2$

Final result for 11 runs: 55.2 ± 1.2 ppm

Treatment of Gallium Standard. Samples contain-

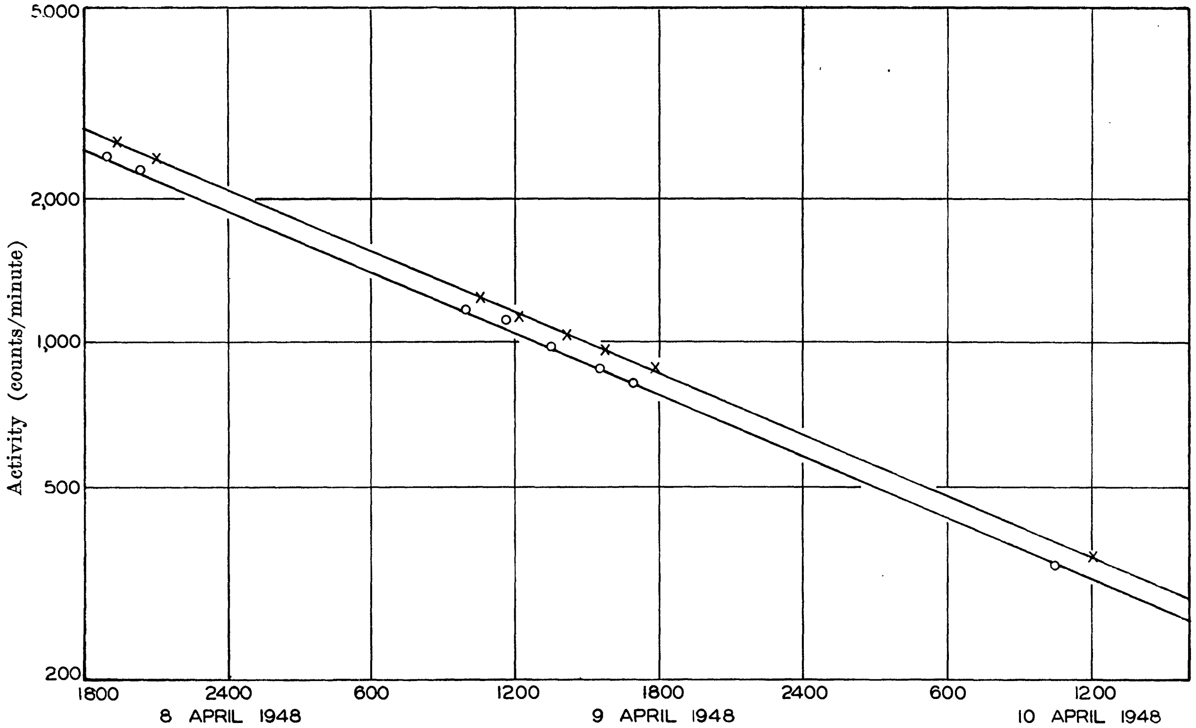

FIG. 1. Typical gallium decay curves. o Iron meteorite. x Standard.

ing approximately 10 mg of gallium 8-hydroxyquinolate were irradiated in containers identical with those used for samples of meteorites. The standards were dissolved in hot concentrated hydrochloric acid and diluted to 50 ml such that a 0.5-ml aliquot precipitated with gallium carrier as in the procedure above gave a dilution factor of 100 and the resulting precipitate had approximately the same counting rate as the gallium precipitate in the meteorite procedure.

Results. Extensive runs were made on four meteorites in order to ascertain the precision of the method. The results are shown in Tables 2, 3, 4, and 5. It will be noted that the standard deviation varies from 4.3% in the case of Odessa, where the gallium content is 69.3 ppm, to 8.0% in the case of Henbury, where the gallium content is 16.8 ppm. Such a drift of standard deviation with gallium content is to be expected under the conditions used, as all runs were made under nearly identical conditions of flux and irradiation time. Under such circumstances the counting rates for samples with low gallium content are lower than those with high gallium content. A marked increase of flux, irradiation time, or counting time would lower the standard deviation.

Figs. 1 and 2 show typical decay curves and aluminum absorption curves of standards and unknowns normalized to each other. Such data show that only gallium is being counted.

The results on Canyon Diablo, Henbury, Odessa, and Xiquipilco serve to show that the statistical errors involved in such a method of analysis are not prohibitively large. Runs were made on different days,

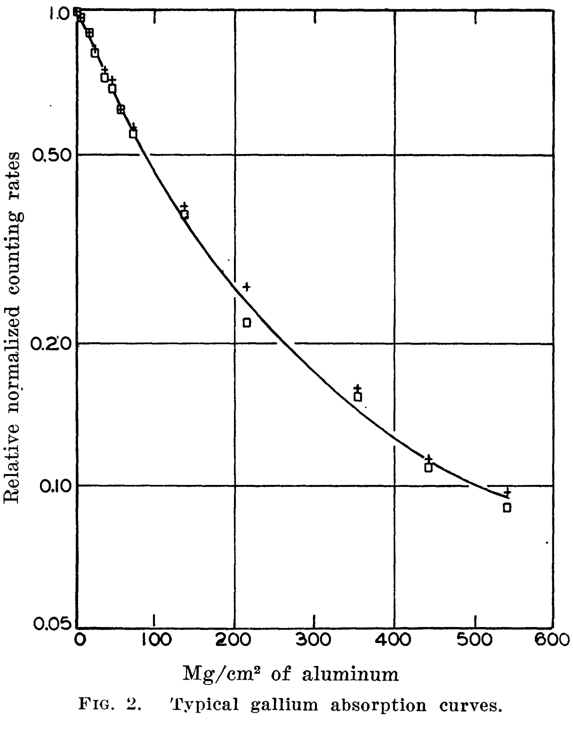

FIG. 2. Typical gallium absorption curves.

under varying conditions of neutron flux, location of samples in the rabbit, and irradiation time, and no constant drift of the results could be detected. However, if gallium in the form of room dust were being measured in addition to meteoritic gallium, a constant error would result. Consequently a number of substances were analyzed in order to ascertain whether or not the natural gallium contamination level was introducing errors. A sample of electrolytic iron, in which gallium could not be detected spectroscopically, was analyzed and found to contain 0.08 ppm of gallium. A sample of commercial aluminum was analyzed and found to contain less than 0.01 ppm of gallium. On the basis of these results, it seems safe to assume that no appreciable constant error due to gallium contamination was introduced in the measurements. The errors contributing to the standard deviation represent the sum of three effects: counting errors, actual deviations in gallium content from sample to sample (within a given meteorite), and actual errors involved in the chemical procedure.

TABLE 6

GALLIUM CONTENT OF VARIOUS IRON METEORITES

Name	Number of runs	Average gallium content (ppm)
Arispe	5	64.1
Canyon Diablo	13	77.4
Canyon Diablo #2	5	85.0
Carleton	3	11.2
Deport	8	61.4
Henbury	11	16.8
Mount Joy	4	47.5
Odessa	10	69.3
Sandia Mountains	6	53.2
Spearman	6	21.4
Tlaxcala	2	20.8
Xiquipilco	11	55.2
Institute of Meteoritics #2	3	21.1
“ “ “ #6	3	90.5

A total of 14 iron meteorites were analyzed for gallium content. The results of the analyses are given in Table 6.

TABLE 8

SUMMARY OF PALLADIUM RESULTS ON HENBURY

Run no.	Palladium content (ppm)	Δ Deviation from mean
11	2.29	0.27
12	1.77	0.25
99	1.71	0.31
100	1.96	0.06
101	1.88	0.14
102	1.81	0.21
107	2.31	0.29
108	2.14	0.12
109	2.18	0.16
110	2.16	0.14
	Average: 2.02	

Standard deviation $\sigma = \sqrt{\frac{\Sigma\Delta^2}{n-1}} = 0.22$ (10.9%)

Precision $= \frac{\sigma}{\sqrt{n}} = \pm 0.07$

Final result for 10 runs: 2.02 ± 0.07 ppm

The Method Applied to Palladium. Palladium exists in iron meteorites to an extent of about 1 to 5 ppm. Activities obtainable in the rabbit were too low to permit the accumulation of precise enough data, and so all runs were made in the center of the pile, using irradiation times of approximately 1 hr. The element yields two prominent activities upon irradiation with slow neutrons, one of half-life 13 hr produced from Pd^{108} and one of half-life 26 min produced from Pd^{110}. The two isotopes giving rise to the activities have abundances of 26.8% and 13.5% re-

TABLE 7

SUMMARY OF PALLADIUM RESULTS ON CANYON DIABLO

Run no.	Palladium content (ppm)	Δ Deviation from mean
9	3.03	0.95
10	3.85	0.13
52	3.85	0.13
53	3.64	0.34
54	4.21	0.23
75	4.79	0.81
76	4.30	0.32
77	3.91	0.07
78	3.91	0.07
98	4.35	0.37
	Average: 3.98	

Standard deviation $\sigma = \sqrt{\frac{\Sigma\Delta^2}{n-1}} = 0.47$ (11.9%)

Precision $= \frac{\sigma}{\sqrt{n}} = \pm 0.15$

Final result for 10 runs: 3.98 ± 0.15

TABLE 9

SUMMARY OF PALLADIUM RESULTS ON ODESSA

Run no.	Palladium content (ppm)	Δ Deviation from mean
95	4.16	0.01
96	4.01	0.14
97	3.52	0.63
103	4.06	0.09
104	3.64	0.49
111	4.12	0.03
112	4.06	0.09
113	4.22	0.07
114	5.04	0.89
115	4.64	0.49
	Average: 4.15	

Standard deviation $\sigma = \sqrt{\frac{\Sigma\Delta^2}{n-1}} = 0.45$ (10.81%)

Precision $= \frac{\sigma}{\sqrt{n}} = \pm 0.14$

Final result for 10 runs: 4.15 ± 0.14

spectively (*13*). The radiation characteristics of the two activities are discussed elsewhere (*13*).

TABLE 10

SUMMARY OF PALLADIUM RESULTS ON XIQUIPILCO

Run no.	Palladium content (ppm)	Δ Deviation from mean
36	4.52	0.20
37	4.18	0.56
38	4.14	0.58
49	5.37	0.35
50	4.59	0.13
51	4.74	0.02
86	5.21	0.49
87	4.85	0.13
88	4.87	0.15
89	4.73	0.01

Average: 4.72

Standard deviation $\sigma = \sqrt{\frac{\Sigma\Delta^2}{n-1}} = 0.31$ (6.6%)

Precision $= \frac{\sigma}{\sqrt{n}} = \pm 0.10$

Final result for 10 runs: 4.72 ± 0.10

Samples of iron meteorite each weighing approximately 0.3–0.5 g were irradiated in soft glass vials, together with a standard of palladium dimethyl glyoxime. After irradiation the samples were permitted to cool until the 26-min activity had died away. The samples were then chemically processed. The chemical procedure used for the isolation of the palladium activity was a modification of a procedure developed by Seiler (*14*). Use was made of the fact that palladium can be precipitated as the dimethyl glyoxime, and that it also forms a complex in excess ammonium hydroxide.

TABLE 11

PALLADIUM CONTENT OF VARIOUS IRON METEORITES

Name	Number of runs	Average palladium content (ppm)
Arispe	4	2.69
Canyon Diablo	10	3.98
Canyon Diablo #2	3	5,30
Carleton	4	6.52
Deport	3	4.45
Henbury	10	2.02
Institute of Meteoritics #2	3	2.82
" " " #6	5	4.46
Mount Joy	3	3.30
Odessa	10	4.15
Sandia Mountains	3	2.24
Spearman	3	3.67
Tlaxcala	4	2.29
Willow Creek	3	3.70
Xiquipilco	10	4.72

Chemical Procedure for Palladium in Iron Meteorites: 1) Dissolve the sample of irradiated meteorite in hot concentrated hydrochloric acid in a 50-ml centrifuge tube covered with a watch glass. Add 10 mg of Pd^{+2} carrier. Keep tube in ice bath in order to inhibit oxidation of Fe^{+2}. (Palladium dimethyl glyoxime will not precipitate easily in the presence of Fe^{+3}.) 2) Add ammonium hydroxide until solution is 0.4 M in acid. Add 3–5 ml of 1% dimethyl glyoxime solution. Allow solution to stand 40 min.

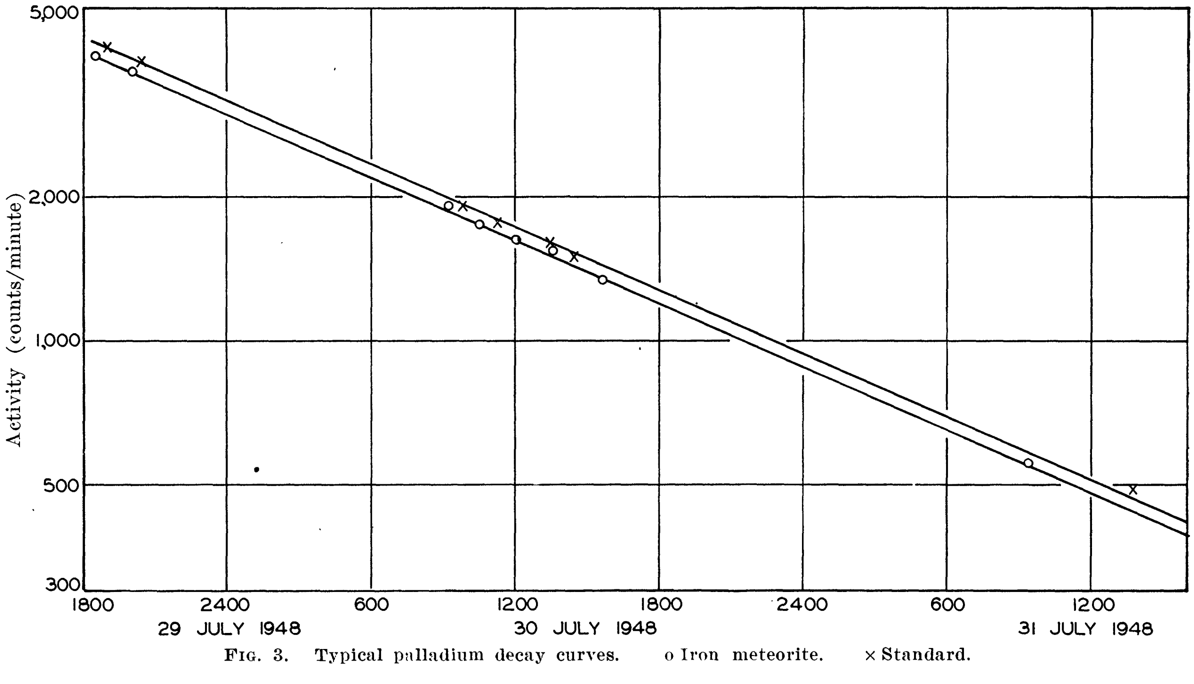

FIG. 3. Typical palladium decay curves. o Iron meteorite. × Standard.

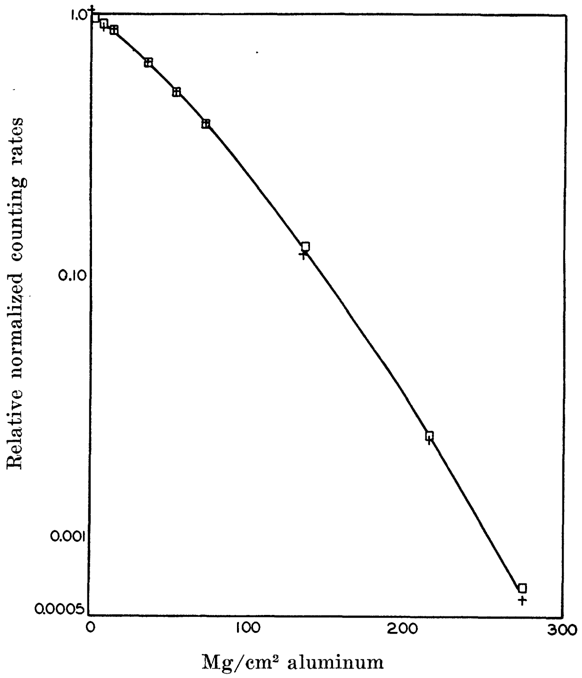

FIG. 4. Typical palladium absorption curves. ☐Iron meteorite. + Standard.

Centrifuge. 3) Dissolve precipitate in 1 ml of hot concentrated nitric acid. Cool and dilute with 10 ml of water. Add 5 mg of Fe^{+3} carrier. Add excess ammonium hydroxide to precipitate iron. (This step removes a number of extraneous activities.) Add 10 mg of Ag^{+} carrier and enough iodide to precipitate all silver. (This step removes any silver activity present.) 4) Centrifuge and discard the precipitate. 5) Repeat steps 3 and 4. 6) Adjust acidity to 0.4 M. Centrifuge solution to remove any silver chloride precipitate formed. 7) Add 3–5 ml of 1% dimethyl glyoxime solution and allow solution to stand 40 min. Filter. 8) Wash the precipitate with first hot and then cold water and ethyl alcohol. Determine the weight of the sample after heating at 110° C for 10 min. The sample is now ready to count.

Treatment of Palladium Standard. Samples containing approximately 10 mg each of palladium dimethyl glyoxime were irradiated in containers identical with those used for meteorite samples. Each standard was then dissolved in hot concentrated nitric acid and diluted to 500 ml such that a 0.5-ml aliquot, when precipitated with the standard carrier aliquot, gave a dilution factor of 1 part per 1,000 and approximately the same counting rate as the palladium from the meteorite.

Results. In order to estimate the reproducibility and precision of the palladium procedure, as in the case of gallium, a number of runs were made on four meteorites. The results are shown in Tables 7, 8, 9, and 10. It will be noted that the standard deviations obtained are quite satisfactory. Table 11 gives the palladium contents of 15 iron meteorites. Figs. 3 and 4 show typical palladium decay curves and aluminum absorption curves.

Thus, the neutron pile as a tool in quantitative analysis is quite generally applicable and is particularly useful in analyzing unknowns for minor constituents. In applying the method to the problem of analyzing for minute concentrations of gallium and palladium in iron meteorites we found that the procedures gave consistent results, with low standard deviations from the mean. The procedures are not complicated, are free from interferences from other elements, and are also free from the danger of contamination during the course of the analysis.

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