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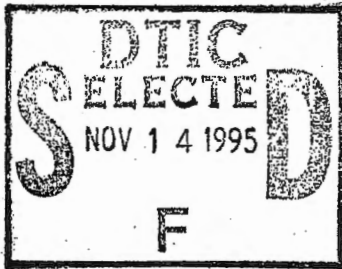
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THE NEUTRON PILE AS A TOOL IN QUANTITATIVE ANALYSIS; THE

GALLIUM AND PALLADIUM CONTENTS OF IRON METEORITES

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THE NEUTRON PILE AS A TOOL IN QUANTITATIVE ANALYSIS; THE

GALLIUM AND PALLADIUM CONTENTS OF IRON METEORITES

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INTRODUCTION

In recent years the science of meteoritics has come to be looked upon as a science of increasing importance, in large measure due to recognized bearing of meteorite information upon problems of astrophysical interest. 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, the large majority of the elements are present in meteorites to an extent of only a few parts per million.[3] As it is frequently desirable to assay the concentration of many of the rarer constituents of meteorites with an accuracy of 10 per cent or better, grave analytical problems are presented. V. M. Goldschmidt,[4] Hevesy,[5] and the Noddacks,[7] 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 2, and in some cases as great as a factor of 10.

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 the determination of the concentration of a given element when the element is present in the concentration range of 0.01 ppm to 500 ppm with an accuracy of 10 per cent or better.

  2. The method must be free from interferences from other chemical elements.

  3. The method must be free from the danger of contamination during the analysis.

  4. The method must be reasonably rapid.

A survey of the various possible analytical approaches to the problem led the authors to the conclusion that a radiochemical approach 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 2.5h dysprosium period in a sample of yttrium after activation with neutrons, thus demonstrating the presence of dysprosium impurity to an extent of 1 per cent. 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/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 have become available which are capable of producing very high specific activities. 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 of producing, in the cases of many elements, specific activities of the order of magnitude of 100,000 to 1,000,000 disintegrations/min/microgram of element. Such specific activities make it possible to carry out the following general procedure:

1. Irradiate a portion of the substance to be analyzed in the pile, together with a standard consisting of a known weight of the element being determined.

2. Dissolve the unknown and add to the solution a known weight of the element being determined.

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

3. Chemically process the element added in order to free it from the activities associated with other elements present in the unknown.

4. Determine the chemical yield of the procedure.

5. Compare the activity of the element in the unknown with that of the standard.

6. Check on the purity of each activity by measurements of half-lives and absorption spectra.

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. The term is used in this paper to indicate the smallest quantity of an element that will give rise to an activity of sufficient intensity to permit the taking of half-life and absorption measurements after the element has been exposed to the central pile flux for a period of seven hours. Thus "sensitivity" here denotes the smallest quantity of an element that can be measured with a precision of better than 10 per cent utilizing the central flux of the Argonne Pile for a length of time that is not unduly long.
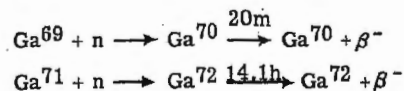
It can be seen that the sensitivities obtainable are in general quite satisfactory, and in some cases remarkable. The cases of manganese, copper, arsenic, palladium and dysprosium, shown in Table 1, are particularly noteworthy. If one assumes that a half-life of 30m represents the shortest lifetime with which one can conveniently work in an analytical determination, then the method is applicable to about 60 of the 75 stable elements existing in nature (excluding the rare gases). The elements to which the method is not applicable or applicable only with difficulty are: H, Li, Be, B, C, N, O, F, Mg, Al, V, Co, Cb, and Rh. In general the pile method of analysis is more sensitive for elements of odd atomic number than for elements of even atomic number due to the larger activation cross sections of nuclear species of odd mass number and the generally low abundance of the nuclear species giving rise to the activities in the even elements.

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 meteorities 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 possesses two stable isotopes, Ga^{69} (60.2 per cent) and Ga^{71} (39.8 per cent).[9] The more abundant isotope captures a neutron to form 20m Ga^{70}; the less abundant isotope captures a neutron to form 14.1h Ga^{71}:

$$Ga^{69} + n \longrightarrow Ga^{70} \xrightarrow{20m} Ga^{70} + \beta^-$$
$$Ga^{71} + n \longrightarrow Ga^{72} \xrightarrow{14.1h} Ga^{72} + \beta^-$$

The radiation characteristics of the radioactive products are described elsewhere.[10]

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.[11],[12] Samples of meteorites ranging in weight between 0.3 and 0.5 g were placed in individual small plastic containers in the rabbit and irradiated for approximately 30 minutes. Standard samples of gallium 8-hydroxyquinolate were irradiated simultaneously. After removal from the pile, the samples were allowed to cool until the 20m 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,[13] is amphoteric, and

can be precipitated as the 8-hydroxyquinolate. The combination of these chemical properties permits a procedure to be developed which successfully frees the gallium activity from other interfering activities.

Chemical Procedure for Gallium in Iron Meteorites

1. Dissolve sample in hot conc. HCl in 50 ml beaker. Add 4 to 5 mg of Ga^{+3} carrier.

2. Make solution 5.5 to 6.5M in HCl. Extract gallium with an equal amount of ether saturated with HCl. 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 2M, 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 and heat to 60 to 70°C.

5. Add 5 ml of a 1 per cent alcoholic solution of 8-hydroxyquinoline. Add drop-wise 3M ammonium acetate until the precipitation of yellow gallium 8-hydroxyquinolate is complete.

6. Filter, wash the precipitate with hot water, then ether. Determine the weight of the sample after heating at 110°C for 15 minutes. The sample is now ready to be counted.

Treatment of Gallium Standard

Samples containing 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 HCl 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 possessed 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 deviations vary from 4.3 per cent in the case of Odessa where the gallium content is 69.3 ppm, to 8.0 per cent 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 deviations.

Figure 1 and 2 show typical decay curves and aluminum absorption curves of standards and unknowns normalized to each other. Such data insure one that only gallium is being counted. Copies of the figures were not furnished with the manuscript.

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, under conditions of varying neutron flux, locations 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 was being measured in addition to meteoritic gallium, a constant error would result. Consequently a number of substances were analyzed in order to ascertain that the natural gallium contamination level was not 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.

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	2.6
21	80.4	3.0
149	76.8	0.4
152	75.2	2.2

Average 77.4

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

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

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

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

Final result for 11 runs: 16.8 $\pm$ 0.4 ppm

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

Precision $= \dfrac{\sigma}{\sqrt{n}} = 0.9$

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	0.8
28	59.3	4.1
32	53.0	2.2
33	54.6	0.6
34	54.8	0.4
35	53.0	1.8
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 $\sigma = \sqrt{\dfrac{\Sigma \Delta^2}{n-1}} = 3.7 \ (6.7\%)$

Precision $= \dfrac{\sigma}{\sqrt{n}} = \pm 1.1$

Final result for 11 runs: 55.2 ± 1.1 ppm

Table 6. Gallium contents of various iron meteorites.

Name	Number of runs	Average gallium content (ppm)
Arispe	5	64.1
Canyon Diablo	13	77.4
Canyon Diablo No. 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
Saudia Mts.	6	53.2
Spearman	6	21.4
Tlaxcala	2	20.8
Willow Creek	3	19.4
Xiquipilco	11	55.2
I. M. No. 2	3	21.1
I. M. No. 6	3	90.5

A total of 15 iron meteorites was analyzed for gallium content. The results of the analyses are given in Table 6.

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 data possessing adequate precision, so all runs were made in the center of the pile, using irradiation times of approximately 1 hour. The element yields two prominent activities upon irradiation with slow neutrons, one of half-life 13h produced from Pd^{108} and one of half-life 26m produced from Pd^{110}. The two isotopes giving rise to the activities possess abundances of 26.8 and 13.5 per cent respectively.[10] The radiation characteristics of the two activities are discussed elsewhere.[10]

Approximately 0.3 to 0.5 g of iron meteorite were irradiated in a given run, together with a standard of palladium dimethyl glyoxime. After irradiation the samples were permitted to cool until the 26m 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 in addition forms a complex in excess ammonium hydroxide.

Chemical Procedure for Palladium in Iron Meteorites.

1. Dissolve the sample of irradiated meteorite in hot conc. HCl 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 will not precipitate easily in the presence of Fe^{+3}.)

2. Add ammonium hydroxide until solution is 0.4M in acid. Add 3 to 5 ml of per cent dimethyl glyoxime solution. Allow solution to stand for 40 minutes. Centrifuge.

3. Dissolve precipitate in 1 ml of hot conc. HNO_3. 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 0.4M. Centrifuge solution to remove any AgCl precipitate formed.

7. Add 3 to 5 ml of 1 per cent dimethyl glyoxime solution and allow solution to stand for 40 minutes. Filter.

8. Wash the precipitate with hot, then cold, water and ethyl alcohol. Determine the weight of the sample after heating at 110°C for 10 minutes. 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 conc. HNO_3 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.

SUMMARY

The possibilities of using the neutron pile as a tool in quantitative analysis have been investigated. The method is quite generally applicable and is particularly useful in analyzing unknowns for minor constituents. The method has been applied to the problem of analyzing for minute concentrations of gallium and palladium in iron meteorites. The procedures were found to give consistent results, with standard deviations never exceeding 12 per cent. The procedures are not complicated, are free from interferences from other elements, and are free from the danger of contamination during the course of the analysis.

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	<u>4.35</u>	0.37

Average 3.98

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

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

Final result for 10 runs: 3.98 ± 0.15

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	0.05
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	<u>2.16</u>	0.14

Average 2.02

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

Precision $= \dfrac{\sigma}{\sqrt{n}} = 0.07$

Final result for 10 runs: 2.02 ± 0.07 ppm

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	0.03
104	3.64	0.59
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 $\sigma = \sqrt{\dfrac{\Sigma \Delta^2}{n-1}} = 0.449 \ (10.81\%)$

Precision $= \dfrac{\sigma}{\sqrt{n}} = 0.142$

Final result for 10 runs: 4.15 ± 0.14

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	0.46
38	4.14	0.42
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 $\sigma = \sqrt{\dfrac{\Sigma \Delta^2}{n-1}} = 0.31 \ (6.6\%)$

Precision $= \dfrac{\sigma}{\sqrt{n}} = 0.10$

Final result for 10 runs: 4.72 ± 0.10

Table 11. Palladium contents of 15 iron meteorites.

Meteorite	Number of Runs	Average Palladium Content (ppm)
Arispe	4	2.69
Canyon Diablo	10	3.98
Canyon Diablo No. 2	3	5.30
Carleton	4	6.52
Deport	3	4.45
Henbury	10	2.02
I. M. No.2	3	2.82
I. M. No. 6	5	4.46
Mount Joy	3	3.30
Odessa	10	4.15
Sandia Mts.	3	2.24
Spearman	3	3.67
Tlaxcala	4	2.29
Willow Creek	3	3.70
Xiquipilco	10	4.72

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