Activation Analysis of Manganese in Ferromanganese Alloy Using Radium-Beryllium Neutron Source

By Yuzuru KUSAKA

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The method of analysis using slow neutron activation was early suggested by Hevesy and Levi[1], who used a 200 to 300 mc radium-emanation beryllium source in their determination of certain rare-earth elements possessing high neutron activation cross sections. More recently Boyd etc.[2] have reviewed the principles of radioactivation analysis, and a large number of papers have been published on their applications to various problems.

In 1953 Meinke and Anderson[3] explored the possibility of using low level neutron sources, 25 mg. radium–beryllium source, for activation analysis of rhodium, silver and indium.

The thermal neutron activation with a low-level neutron source has one major advantage over activation with higher sources; only those isotopes with a very high activation cross section and a short half-life are detected after a short irradiation. The profusion of neutron-induced activity obtained when a mixture of elements is irradiated in a nuclear reactor is eliminated. Thus it is possible to perform activation analysis without subsequent chemical separation; therefore analysis for favorable elements can be completed rapidly. Morever the amount of activity formed in the irradiation is so small and decays out so rapidly that the sample used for the irradiations is unchanged at the end of the analysis.

Recently, the writer reported the fundamental studies on activation analysis of manganese[4]. This paper describes some results of activation analysis of manganese in ferromanganese alloy using a low-level neutron source, 50 mg. radium-beryllium with a thermal neutron flux of about 10^2—10^3 neutrons/cm^2/sec.

Nuclear Data for the Elements under Consideration

The radioactive isotopes and other nuclear data for the elements considered in this work are listed in Table I[5].

From Table I, one can expect that, an irradiation of eighteen hours will practically lead to the saturation activity of ^{56}Mn, whereas the activities of ^{55}Fe and ^{59}Fe will be negligible owing to their long half-lives, small cross sections and low abundance.

Experimental

The activation source consisted of a mixture of 84.2 mg. of radium bromide (49.3 mg. as radium element) with beryllium, which was sealed in a platinum tube, length 40.0 mm., diameter 5.0 mm., wall-thickness 0.5 mm., and certificated by the State Radiological Institute of the Czchoslovak Republic in 1938. The source was surrounded by paraffin to moderate the fast neutrons to thermal velocities. At the distance of 3.0 cm. around of the source, eight samples were arranged in the paraffin block of a 26.5×24.0×24.0 cm. cube; and the weight of each sample was 6.000 g. of granular powders (being sifted through a 100 mesh screen), which were put in the polyethylene tubes (inner diameter: 0.8 cm.,

1) G. V. Hevesy and H. Levi, *Kgl. Danske Videnskab. Math-Fys. Medd.*, **14**, 5 (1936); **15**, 11 (1938).
2) G. E. Boyd, *Anal. Chem.*, **21**, 335 (1949); J. V. Jakovlev, International Conference on Peaceful Uses of Atomic Energy, Geneva, Paper 632 (1955); A. A. Smales, ibid., Paper 770 (1955); M. P. Lévêque, ibid., paper 342 (1955): N. Saito, *Japan Analyst (Bunseki Kagaku)*, **4**, 254 (1955).
3) W. W. Meinke and R. E. Anderson, *Anal. Chem.*, **25**, 778 (1953).
4) Y. Kusaka., Radioisotopes, **6**, 1 (1957), (In Japanese).

height: 5.4 cm.) with cork stoppers. The standard samples were prepared by mixing metallic iron and manganese powders in an appropriate ratio.

The irradiated time was about eighteen hours. After irradiation, the specimens and the standards were spread into the copper counting cup (diameter: 2.9 cm., height: 0.6 cm.) and their induced radioactivities were directly measured for 5 minutes by means of an end window type G. M. tube (thickness of mica window: 1.96 mg./cm^2) in the same geometrical position. These measured values of radio-activity were corrected to the value at the end of the irradiation. A comparision of the activity of the unknown and the standard makes possible an estimate of the amount of manganese in the unknown sample.

Results and Discussion

Induced Radioactivity.—An example of the decay curve of the induced radioactivity of the ferromanganese sample (Mn content: 80.1%) is shown in Fig. 1. The measured value of half-life was 2.6 hours, being in good agreement with that of ^{56}Mn. The same results were obtained in every sample. From these results, it was recongnized that in those experiments all induced radioactivities were due to ^{56}Mn only.

Self-shadowing Effect for Neutrons.—The radioactivity strength produced by this method were approximately proportional to the manganese content in the samples. Concerning the specific activity of the samples of a higher manganese content, a significant decreasing effect was recognized, to a greater extent for 6 g. of the sample than for 1 g. of the sample, as shown in Fig. 2.

This phenomenon will be based upon the self-shadowing effect for the neutrons used for activation of manganese. The

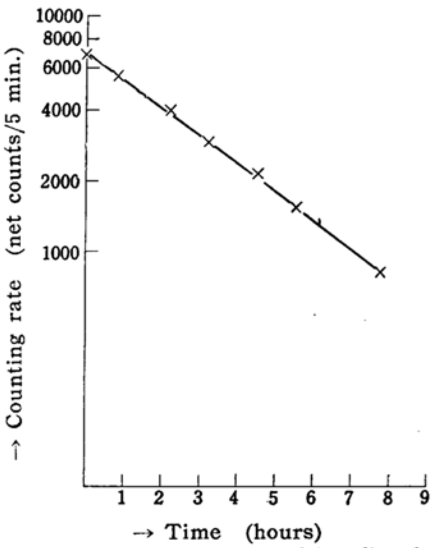

Fig. 1. Decay curve of irradiated ferromanganese.

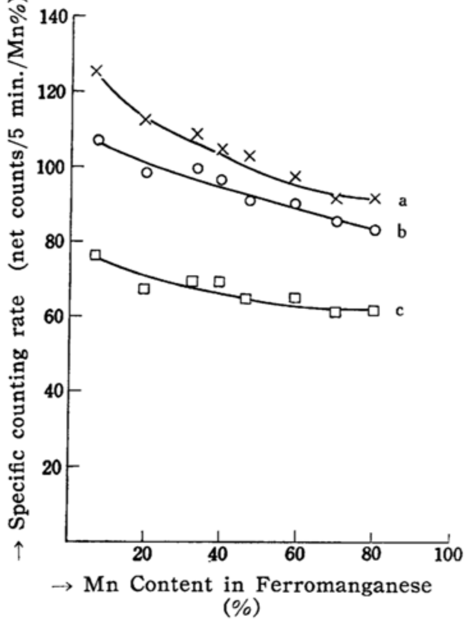

Fig. 2. Specific counting rate formed as a function of Mn content of ferromanganese.
(a)……sample weights 6 g.
(b)……sample weights 3 g.
(c)……sample weights 1 g.

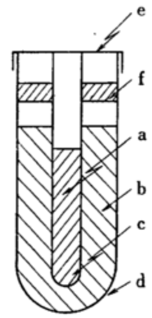

Fig. 3. Irradiation sample for self-shadowing experiments.
(a): manganese powder (2 g.)
(b): ferromanganese powder (15 g.)
(c): glass tube (inner diameter: 0.5 cm., thickness: 0.1 cm, height: 5.0 cm.)
(d): polyethylene tube (inner diameter: 1.7 cm., thickness: 0.1 cm., height: 5.4 cm.)
(e): polyethylene cup
(f): cork stopper

5) D. J. Hughes and J. A. Harvey, "Neutron Cross Sections", BNL 325 (1955).

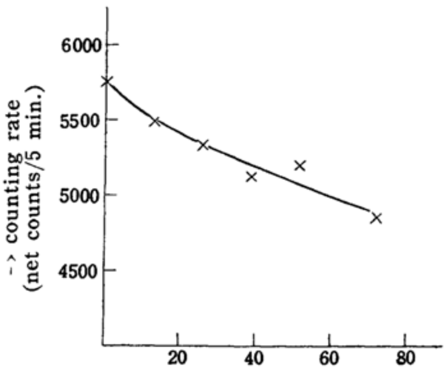

Fig. 4. Radioactivity formed in manganese powders.

manganese atoms in the samples did not encounter identical neutron flux during the irradiation, —that is, the flux for the inner part of the sample may be entirely different from that for the skin of the specimen. The next experiment was designed to investigate the flux depression caused by increasing manganese content. Two grams of manganese powder and 15 g. of ferromanganese powder of various manganese contents were separately put in a polyethylene tube as shown in Fig. 3 and irradiated in the paraffin block, at a distance of 3.0 cm. from the source. After irrradiation under the same condition, the radioactivity induced in 2 g. manganese powder was measured. In Fig. 4 the radioactivity strength was plotted against the content of manganese in ferromanganese.

Fig. 4 shows that under the experimental conditions the flux at the center of the 80% ferromanganese is about 0.85 of the flux without manganese and with iron.

Radioactivation Analysis of Manganese in Ferromanganese.—Manganese content of ferromanganese alloy is in 70—80% as manganese metal. In this region of

TABLE I

NUCLEAR CHARACTERISTICS OF THE ELEMENTS DETERMINED

Element	Isotope	Abundance (%)	Thermal Neutron Cross Section (barn) σ abs.	σ act.	Radioactive Nuclide Formed	Half -life	Radiations (Energy, Mev)
Mn	^{55}Mn	100	13.2 ±0.4	13.4±0.3	^{56}Mn	2.58 hr.	β^-(2.81), γ
Fe			2.53±0.06				
	^{54}Fe	5.84	2.2 ±0.2	2.2±0.5	^{55}Fe	3.0 yr.	k
	^{56}Fe	91.68	2.6 ±0.2				
	^{57}Fe	2.17	2.4 ±0.2				
	^{58}Fe	0.31	2.5 ±2.0	0.9±0.2	^{59}Fe	45.1 d	β^-(0.46), γ

TABLE II

ONE EXAMPLE OF EXPERIMENTAL RESULTS

Sample	Mn Content (%)	Measurment Time* (minutes)	Counting rate (net counts/5 min.) Obtained	St. Dev. (%)	Activity at the end of irradiation	Mean
ferromanganese	unknown	43— 48	5013	1.4	6157	6137
		67— 72	4484	1.5	6117	
ferromanganese	unknown	19— 24	5624	1.3	6193	6136
		92— 97	3982	1.6	6079	
standard	78.7	7— 12	6301	1.3	6577	6240
		105—110	3648	1.8	5903	
standard	78.7	31— 36	5497	1.3	6384	6331
		80— 85	4338	1.5	6278	
standard	73.8	37— 42	5046	1.4	6036	5983
		73— 78	4228	1.5	5930	
standard	73.8	25— 30	5171	1.4	5850	5874
		86— 91	3970	1.6	5899	
standard	68.9	13— 18	5383	1.4	5770	5576
		98—103	3434	1.7	5382	
standard	68.9	49— 54	4395	1.5	5535	5519
		61— 66	4144	1.5	5503	

* The time after the end of irradiation.

TABLE III

EXPERIMENTAL RESULTS OF MANGANESE ANALYSIS IN FERROMANGANESE

Exp. No.	Manganese Content (%) Radioactivation Method						Mean	Chemical Method
1.	78.4	78.1	76.1	77.9	77.8		77.7	77.4
2.	76.6	76.6	74.6	74.2	79.5	76.6	76.5	78.7
	77.1	77.8	77.3	76.7	74.0			
3.	74.0	74.6	78.0	76.3			75.7	78.2
4.	75.0	75.3	77.3	71.1	73.2	72.3	74.0	77.1

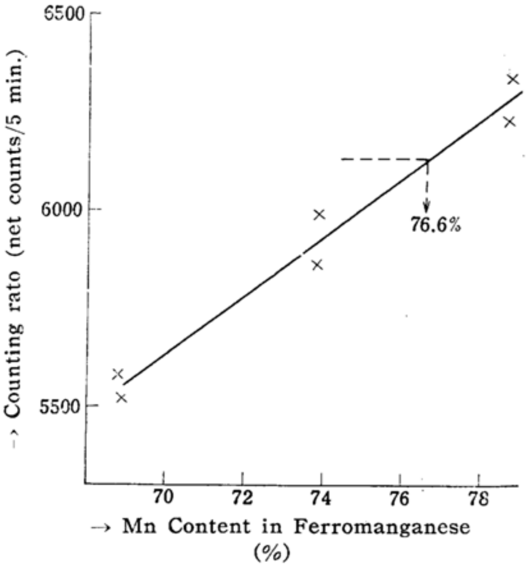

Fig. 5. Calibration curve in radioactivation analysis of Mn in ferromanganese.

manganese content, within experimental error it is possible to assume that the specific counting rate has a definite value. In these experiments, the manganese contents of the standard samples were 68.9%, 73.8% and 78.7%. A pair of samples, one a standard sample and the other, an unknown sample, were irradiated at the same time. One example of experimental results is shown in Table II.

From Table II, the manganese content of an unknown sample was graphically determined as shown in Fig. 5.

The experimental results of manganese analysis in various ferromanganese alloys by this method and comparison with the chemical analysis by the bismuthate method[6] are summarized in Table III.

Summary

A method was developed to determine macro-amounts of manganese in ferromanganese by radioactivation, using 50 mg. radium-beryllium as thermal neutron source. By activation of a sample (6 g.) for 18 hours and directly counting the activity with an end-window G. M. counter, the induced radioactivity was found to be entirely due to the 154.8 min. ^{56}Mn radioisotope. The amount of radioactivity was approximately proportional to the manganese content, but with samples of higher manganese content the self-shadowing phenomenon was recognized. By this method, it was possible to determine the manganese content in ferromanganese with a mean error of 2.5% without chemical procedures.

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Department of Chemistry, Faculty of Science, Konan University Higashinada-ku, Kobe

6) Treadwell-Hall, "Analytical Chemistry", Vol. II, p. 551 (ninth edition).