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**A. Cardoso and F. W. Lima**

**COORDENADORIA DE RADIOQUÍMICA  
(CRQ)**

**INSTITUTO DE ENERGIA ATÔMICA  
SÃO PAULO - BRASIL**

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**Prof. Dr. Rômulo Ribeiro Pieroni**

**INSTITUTO DE ENERGIA ATÔMICA**  
Caixa Postal 11.049 (Pinheiros)  
Cidade Universitária "Armando de Salles Oliveira"  
SÃO PAULO - BRASIL

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# DETERMINATION OF MANGANESE IN ORES BY ACTIVATION ANALYSIS USING A CALIFORNIUM-252 NEUTRON SOURCE

A. Cardoso\* and F. W. Lima

## ABSTRACT

A  $^{252}\text{Cf}$  neutron source has been used to analyse manganese in ores such as pyrolusite, rochonite (manganese silicate) and blendings used in dry batteries

The californium source had a flux corresponding to about  $10^6 \text{ n/s cm}^2$  and was kept in the original shipping shield up to the moment of use. A cubic lucite tank with a volume corresponding to  $01 \text{ m}^3$  was mounted over the shield. A cylindrical plastic tube communicates the tank and the source shield. Every time the source had to be used it was pulled up into the tank which was filled with demineralized water. Cylindrical plastic tubes were used as irradiation facilities and were mounted around the tube through which the source was pulled up for irradiation. During irradiation source and samples stayed at about 0.5 m from the bottom of the tank.

Samples with about 150 mg and standards of manganese dioxide were irradiated for about 20 minutes, let to cool for 10 to 20 minutes and counted using a well type NaI(Tl) scintillator counter and scaler, with or without pulse height discriminator between the detector and the scaler. Counting time varied from 4 to 12 minutes.

The interferences of nuclear reactions  $^{56}\text{Fe}(n,p)^{56}\text{Mn}$  and  $^{59}\text{Co}(n,\alpha)^{56}\text{Mn}$  were studied, as well as problems in connection with neutron shadowing during irradiation, gamma-rays attenuation during counting and influence of granulometry of samples.

Some of the samples were also analysed by wet-chemical methods (sodium bismuthate) in order to compare results.

As a whole it was shown that the use of  $^{252}\text{Cf}$  neutron source is a very useful device for analysis of manganese ores by a method that is simple, rapid and with good precision and accuracy.

## INTRODUCTION

Manganese is an element of the iron group with a proportion corresponding to 0.09% in the earth composition. It occurs in nature as oxides, silicates, carbonates, sulphides, etc.. Its main use is in metallurgical industry (95%), being required about 30 Kg of manganese for the production of a ton of steel. 0.5% of the manganese world production is used in chemical industries, ceramic, electrical industries and fertilizers<sup>(1)</sup>.

Most of the analytical methods for manganese are volumetric ones and are based on the oxidation of manganese to permanganic acid followed by reduction with various reducing agents. Practically all chemical methods are lengthy requiring removal of interfering elements such as cerium, cobalt, chromium, vanadium and antimony<sup>(5)</sup>.

Smith<sup>(7)</sup> has developed an activation analysis method, associated with colorimetric measurements, using nuclear reactors for irradiation, for determination of traces of manganese in biological materials.

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Conrad and Kenna<sup>(3)</sup> have analysed manganese in polysulphides adhesives by activation analysis and using a nuclear reactor position where the thermal neutron flux was equal to  $2 \times 10^{10}$  n/cm<sup>2</sup> s. Samples with 2 to 3% of manganese were analysed with a precision corresponding to 2.9%.

Strain and Lyon<sup>(8)</sup> using "alpha-n" sources, i.e., <sup>210</sup>Po-Be, <sup>241</sup>Am-Be, analysed soil samples for manganese showing that as little as 6 mg of manganese could be determined with an accuracy of 20%.

Ataerts et al<sup>(2)</sup> used a radium-beryllium source with activity corresponding to 1 Ci for activation analysis of manganese ores and ferromanganese alloys. Pyrolusite ores, with a manganese content of 30 to 50%, and ferromanganese alloy, with a manganese content of 80%, were analysed with a precision corresponding to 0.1%. Irradiation times used were of 20 minutes, followed by 20 minutes cooling time and counting for 20 minutes using NaI(Tl) scintillation counters and single channel analysers, for samples of about 4 grams of pyrolusite and 3 grams of ferromanganese.

The availability of californium 252 neutron sources and the importance of developing simple analytical methods for manganese, suggest the study of the determination of manganese in various materials, using a Cf-252 source containing 352 µg of Cf-252 (September, 1972) and with a thermal neutron flux of about  $10^{10}$  n/s cm<sup>2</sup>. The method developed is purely instrumental, involving no chemical separations for the materials studied (manganese silicate and manganese oxides ores and blending of ores used for dry batteries).

## EXPERIMENTAL

### Samples

Ore I – Manganese silicate, rodonite type, from Lafayette, Minas Gerais

Blending II – Blending of various ores used for dry batteries manufacture.

Ore III – Manganese silicate, from Uruaçu, Goiás.

Ore IV – Manganese oxide, from Igarapé Azul, Pará

Ore V – Manganese oxide, from Serra do Navio, Amapá

### Irradiation and Counting

All samples were crushed in a agate mortar and classified in granules from 60 to 80 mesh and smaller than 80 mesh. Samples were put in 1 cm by 1 cm polyethylene envelopes and irradiated in polystyrene tubes, 12 cm height by 1.4 cm internal diameter. Standards of about 40 mg in Mn of MnO<sub>2</sub> (J. T. Baker Chemical Co.) were irradiated together with the samples. These standards were reused after one week cooling.

Irradiation of the samples and standards, placed in the polystyrene tubes, were made using a cylindrical graphite tube, Figure 1. At the moment of irradiation the californium source was pulled up from the shielding, using remote control, into a water tank 1 m x 1 m x 1 m placed on top of the shielding. The irradiation tube, with sample and standard, was lowered at the side of the source using the irradiation facility tubes (polyethylene, 4 cm diameter) placed around the source position. Counting was carried out using a single channel analyser and a well type NaI(Tl) scintillation counter 2 x 1 3/4 inches. The analyser was used in integral counting mode with a discriminator level placed at 700 keV.

To check eventual interferences from other radioisotopes present in the samples, half-lives determinations were made of the irradiated samples. Spectra of samples were also registered and are presented in Figures 2, 3, 4, 5 and 6. Half-lives values of samples and MnO<sub>2</sub> standards are presented in Table I.

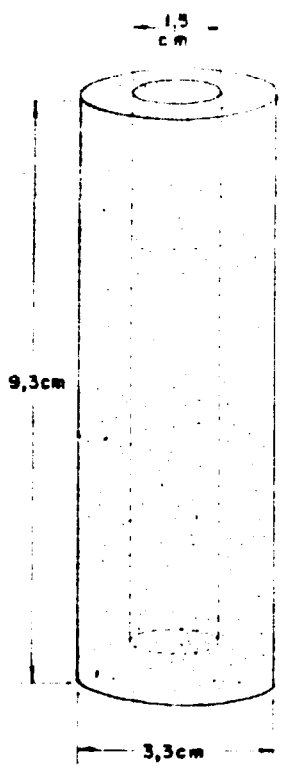


Figure 1 - Graphite Tube Used for Irradiation on the <sup>252</sup>Cf - Source

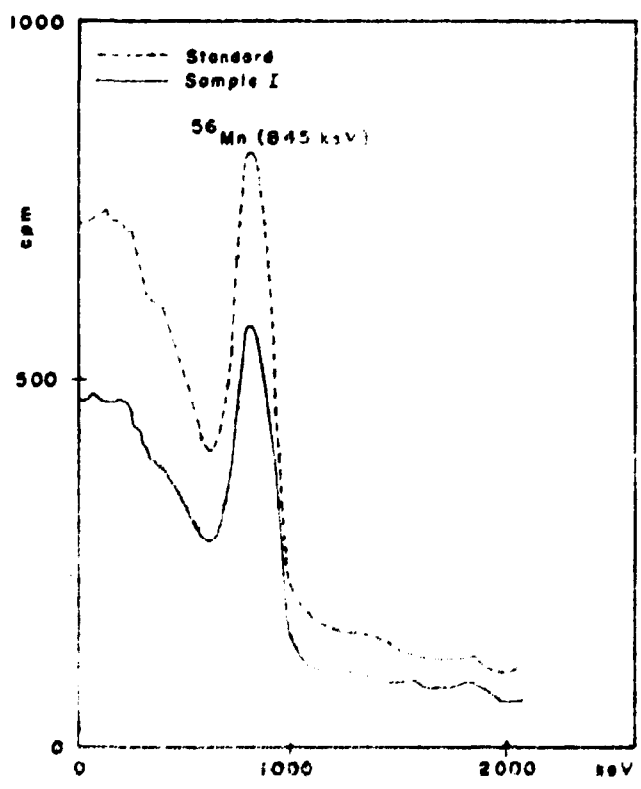


Figure 2 - Comparison of Gamma Ray Spectra of Sample I and MnO<sub>2</sub> Standard

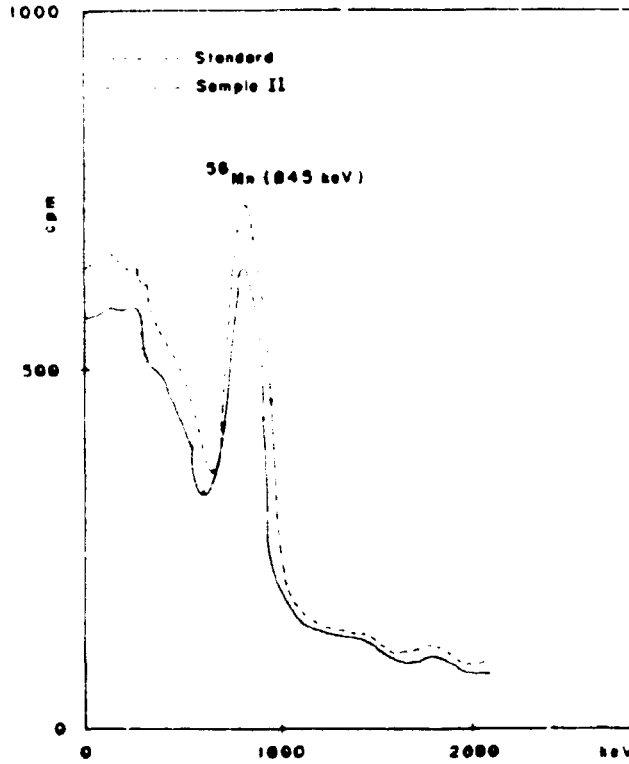


Figure 3 - Comparison of Gamma Ray Spectra of Sample II and MnO<sub>2</sub> Standard

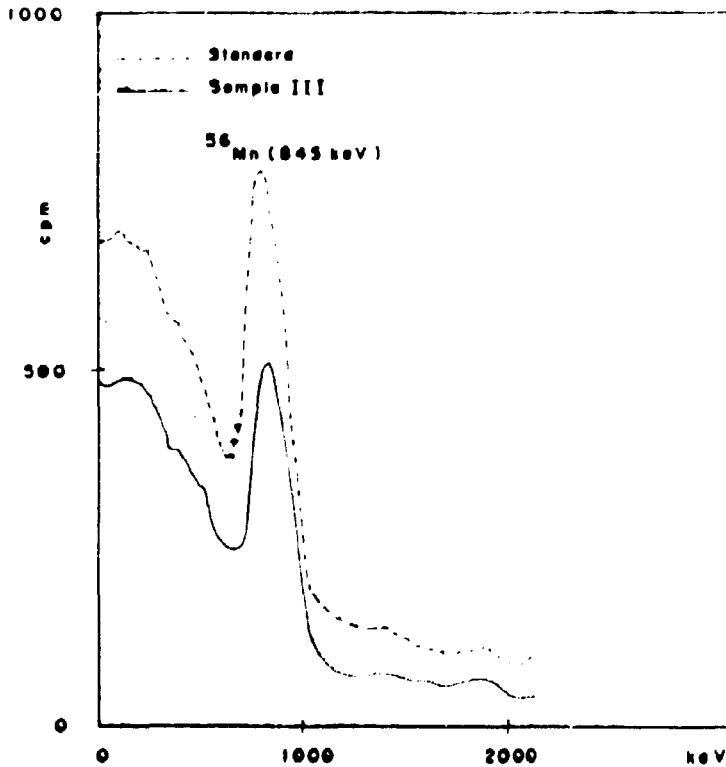


Figure 4 - Comparison of Gamma Ray of Sample III and MnO<sub>2</sub> Standard

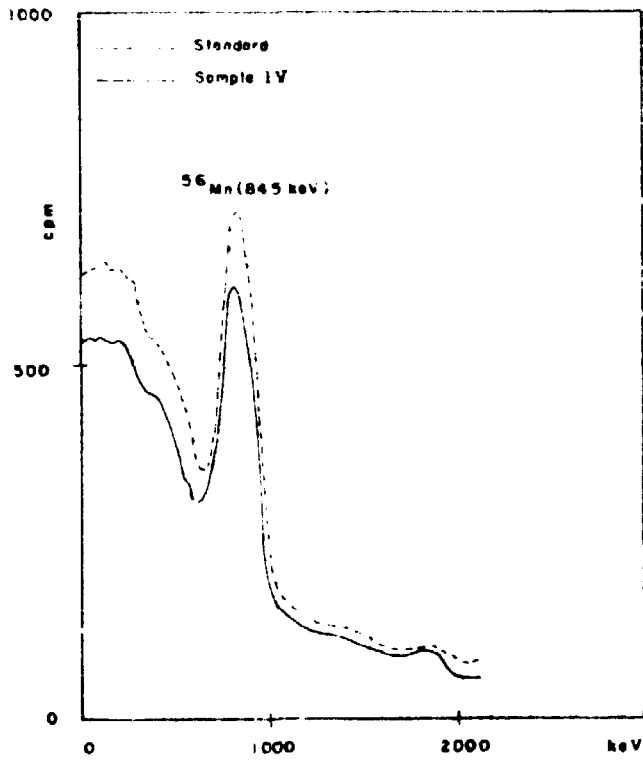


Figure 5 - Comparison of Gamma Ray Spectra of Sample IV and  $\text{MnO}_2$  Standard

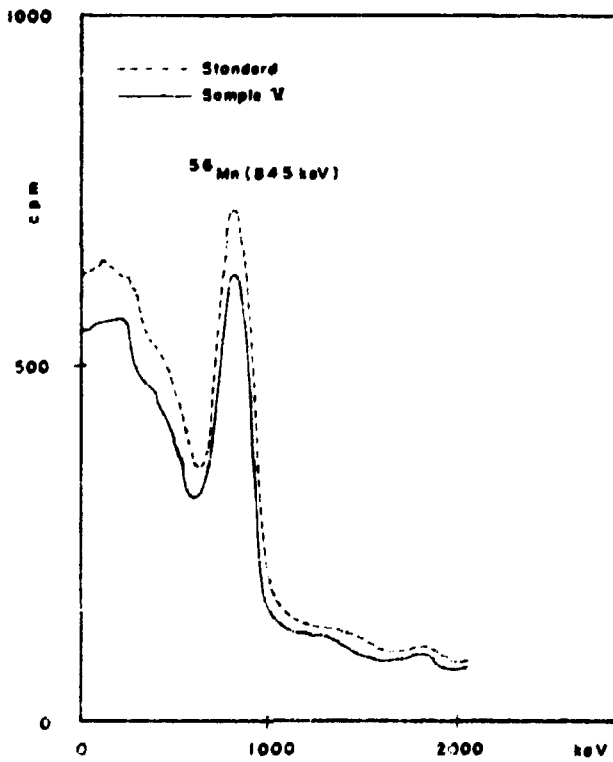


Figure 6 - Comparison of Gamma Ray Spectra of Sample V and  $\text{MnO}_2$  Standard



**Table I**  
**Half-Life Determination for the Various**  
**Samples and a MnO<sub>2</sub> Standard**

Samples	Half-Life (hours)
I	2,62
II	2,58
III	2,58
IV	2,56
V	2,60
Standard	2,60

Literature half-life: 2,58 hours

Irradiation time: 20 minutes

Cooling time: 15 minutes

Counting time: 10 minutes

Sample I – Manganese silicate type (rodonite)

Sample II – Blending of ores

Sample III – Manganese silicate

Sample IV – Manganese oxide

Sample V – Manganese oxide (pyrolusite)

Standard – MnO<sub>2</sub>

## INTERFERENCES

Main nuclear interferences in instrumental determination of manganese are the reactions



To check these interferences, standards of iron and cobalt were irradiated with standards of manganese in the same irradiation position. Irradiations were made with and without cadmium shielding. After 20 to 40 minutes irradiation the spectra of the iron and cobalt standards were registered using NaI(Tl) scintillation detector or Ge-Li counter and in no case the 845 keV photopeak of <sup>56</sup>Mn showed in a significant manner in the spectra. Total gamma counting gave only background value, within counting standards deviation.

## Neutron Self-Shielding and Gamma-Rays Attenuation

Although the amounts of material irradiated were not large, it was necessary to verify the effect of neutron self shielding and attenuation of gamma-rays during counting. Samples and standards, with masses from 15 to 270 mg, were irradiated for 40 minutes in the californium source. A ten minutes counting time was carried out after a cooling time corresponding to three minutes. Results are presented in Table II and Figure 7, showing no effect of self-shielding or gamma-rays attenuation for samples and standards with masses up to 270 mg.

**Table II**

**Data to Verify Self Shielding and Gama Attenuation**

Standard		Sample I		Sample II		Sample III		Sample IV		Sample V	
mass (mg)	cpm	mass (mg)	cpm	mass (mg)	cpm	mass (mg)	cpm	mass (mg)	cpm	mass (mg)	cpm
15,35	1852	30,95	1670	46,55	5506	51,70	1882	18,95	1593	33,40	3990
25,95	3170	43,40	2473	30,05	3603	88,80	3098	34,55	3014	38,35	4615
46,30	5757	50,50	2841	42,25	4935	107,55	3879	62,75	5035	57,30	6860
57,50	7178	58,55	3358	61,45	7152	115,05	4106	100,90	8043	68,75	8240
76,00	9517	72,20	3993	102,90	12404	141,15	4843	142,45	11130	76,00	9154
128,50	15869	81,45	4501	122,90	13913	186,15	6546	152,35	12301	88,35	10680
-	-	87,90	5008	149,45	17623	220,20	7761	175,00	13935	100,80	12168
-	-	107,30	6027	-	-	263,80	9186	-	-	103,65	12560
-	-	115,00	6208	-	-	272,20	9601	-	-	-	-
-	-	126,25	6745	-	-	-	-	-	-	-	-

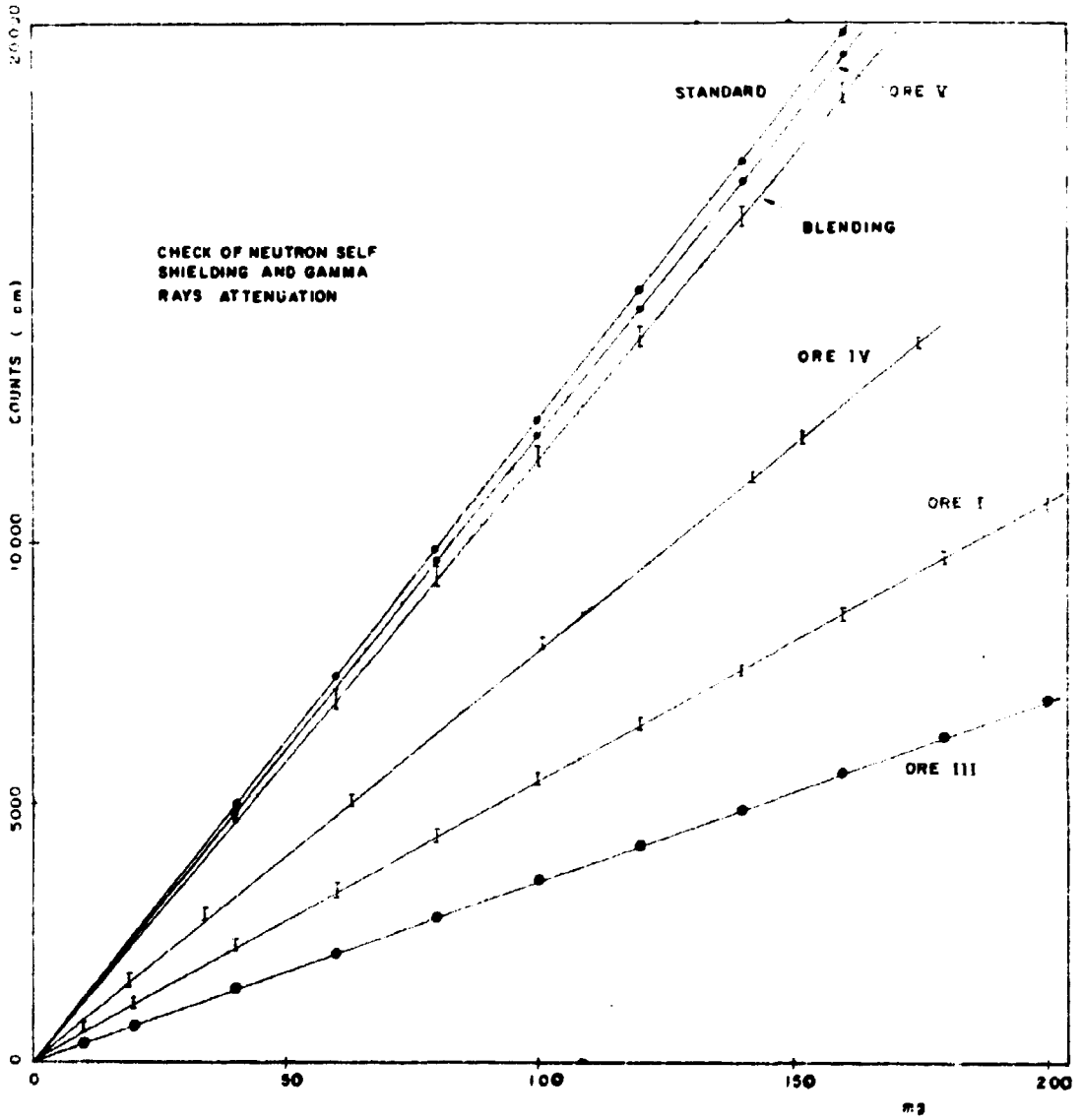


Figure 7

**Table III**  
**Data to Verify Influence of Granulometry (Sample I)**

Run n°	Percentage of Manganese	
	60 – 80 mesh	< 80 mesh
1	31,92	30,13
2	31,08	31,23
3	31,09	32,26
4	34,02	31,15
5	30,76	29,80
6	29,28	30,23
7	31,37	30,60
8	32,46	32,34
9	32,94	33,59
10	31,26	31,02
Mean	31,62	31,24
Standard Deviation	1,30	1,18

Average Sample Mass: 122, 82 mg

## RESULTS

Results for the manganese content for the various samples are presented in Table III, IV, V, VI, and VII.

**Table IV**  
**Results for Manganese Determination on Sample II**

Run n°	% of Mn
1	38,87
2	37,34
3	38,02
4	38,35
6	38,29
6	36,88
7	39,62
8	38,85
9	38,97
Mean	38,35
Standard Deviation	0,85

Average Sample Mass: 101,33 mg

**Table V**  
**Influence of Granulometry (Sample III)**

Run n°	Percentage of Manganese	
	60 – 80 mesh	< 80 mesh
1	10,88	10,08
2	9,70	10,26
3	9,92	9,79
4	9,65	10,00
5	10,95	9,68
6	9,40	9,42
7	10,66	9,45
8	10,56	10,12
9	10,51	10,15
10	9,53	9,04
Mean	10,18	9,80
Standard Deviation	0,594	0,396

Average Sample Mass: 254,10 mg.

**Table VI**  
**Influence of Granulometry (Sample IV)**

Run n°	Percentage of Manganese	
	60 – 80 mesh	< 80 mesh
1	47,63	44,84
2	47,08	47,14
3	47,17	48,30
4	47,84	46,80
5	46,77	47,69
6	48,67	46,62
7	46,48	47,49
8	–	46,51
9	–	44,58
10	–	45,45
Mean	47,38	46,54
Standard Deviation	0,682	1,233

Average Sample Mass: 92,35 mg.

**Table VII**  
**Influence of Granulometry (Sample V)**

Run nº	Percentage of Manganese	
	60 – 80 mesh	< 80 mesh
1	54,57	55,69
2	53,56	52,09
3	55,41	54,41
4	54,69	55,85
5	55,55	55,26
6	54,31	52,00
7	54,90	54,04
8	54,06	53,02
9	54,56	53,90
10	54,28	53,91
Mean	54,59	54,02
Standard Deviation	0,598	1,36

Average Sample Mass: 102,34 mg.

Effect of granulometry of samples was studied by applying "R" test for verification of homogeneity of results as well as Student "t" test<sup>(6)</sup> for data obtained with samples with granules from 60 mesh to 80 mesh and granules smaller than 80 mesh. No such effect was shown on the results, Tables III, V, VI, VII.

In order to compare results of activation analysis with wet chemical method, sample number V was analysed by the method of sodium bismuthate<sup>(4)</sup>.

This method is based on the oxidation of Mn(II) to permanganic acid by means of sodium bismuthate, followed by the addition of excess of ferrous sulphate in ammonium hydroxide solution and titration of the excess of ferrous sulphate with  $\text{KMnO}_4$ . Results of such comparison are presented in Table VIII. A "t" and "F" test were applied to such results showing that at a confidence level of 95% no difference of results exists and that both methods have the same precision.

**Table VIII**  
**Comparison of Wet Chemistry and Activation**  
**Analysis Methods (Sample V)**

Percentage of Manganese	
Activation Analysis	Bismuthate
*54,02 ± 1,36	**53,55 ± 1,35

(\* ) Mean of ten analysis.

(\*\* ) Mean of seven analysis.

## DISCUSSION

From the linearity of the results presented in Table II and Figure 7, and from the simple steps required for a complete analysis of manganese in the samples studied in this paper, it is seen that the method is very simple and rapid. Precision and accuracy are very good, what can be observed from the small standard deviation values for the analysed samples as well as by linearity of results (Figure 7), when increasing masses of samples were used. Also, results obtained by applying the well known bismuthate method and activation analysis showed that precision and accuracy of both methods are the same. The bismuthate method is described in the literature as the most accurate chemical method available<sup>(4)</sup>. However, the activation analysis method, using a  $^{252}\text{Cf}$  neutron source, is much simpler and rapid and a much larger number of samples can be analysed by activation analysis during the same time a single analysis is run by wet chemistry. The wet chemistry method takes about 4 hours for one single sample. During this time about 6 samples can be analysed by activation.

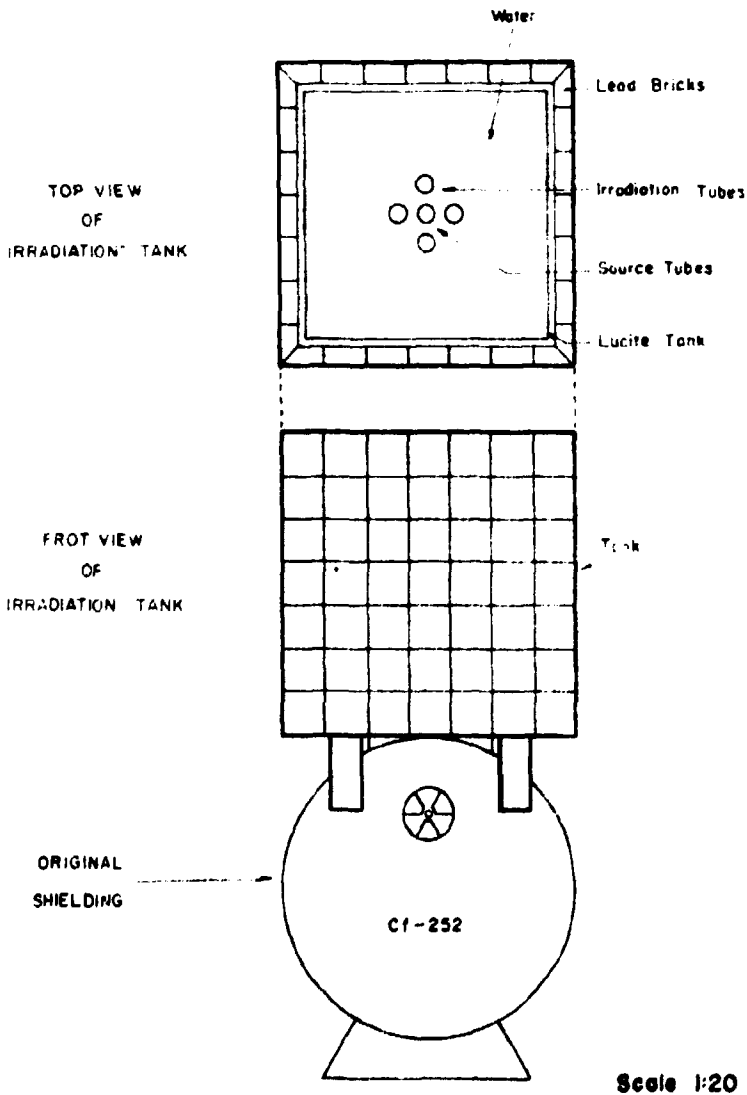


Figure 8 -  $^{252}\text{Cf}$  Irradiation Facility

## RESUMO

Estudou-se neste trabalho, um método analítico, por ativação com nêutrons térmicos de uma amostra de Califórnio 252 para a determinação de manganês em minérios e "blendas" usado em pilhas secas.

Devido as condições favoráveis como alta seção de choque para a reação  $^{55}\text{Mn}(n,\gamma)\text{Mn}^{56}$ , elevada concentração de manganês na amostra e meia vida relativamente curta do manganês 56, pôde-se analisar vários minérios de manganês, de diferentes localidades através de análise puramente instrumental, sem processamento químico.

Após 20 minutos de irradiação simultânea de amostra e padrão, e de 4 a 15 minutos de decaimento, foi determinada a atividade do Mn 56 utilizando-se analisador de raios gama mono canal e cristal de cintilação de NaI(Tl).

As interferências devidas as reações nucleares  $^{59}\text{Fe}(n,p)^{59}\text{Mn}$  e  $^{54}\text{Cr}(n,\alpha)^{56}\text{Mn}$  foram estudadas, bem como os problemas de depressão do fluxo de nêutrons durante a irradiação, atenuação dos raios gama durante as contagens e influência da granulometria das amostras.

O método do presente trabalho foi examinado comparativamente com o método químico do bismutato de sódio.

Em conjunto foi demonstrado ser o método estudado muito vantajoso para análises de minérios de manganês devido a sua simplicidade, rapidez e boa precisão e exatidão.

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