THE POTENTIAL OF NEUTRON SOURCES FOR THE IN-PLANT DETERMINATION OF MANGANESE AND CHROMIUM IN THE FERRO-ALLOY INDUSTRY

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ABSTRACT

A method and apparatus have been developed for the determination of manganese and chromium in ores,metals and slags by isotope source neutron activation analysis. The method was used for samples with masses of several kilograms with the minimum of sample preparation, namely a single pass through a jaw-crusher. An apparatus was constructed that made optimum use of the neutrons from a 370 GBq Am-Be source and provided an efficient counting geometry. The effect of neutron and gamma-ray absorption was considered, particularly in the case of the manganese samples for which there is strong neutron absorption in the manganese itself. A physical model was developed for this case in which the absorption is dominated by the element that is determined. It was however found that some of the samples contained boron, a strong neutron absorber that could not be directly determined, and a second method was therefore developed to measure the neutron absorption directly. By the use of these methods manganese was determined in a suite of samples of ores, metals and slags. The results were compared with X-ray fluorescence results and the root mean square deviation varied from 0,7% manganese, in the case of the slag,to 1,0% in the case of the silicon-manganese metal. The precision and accuracy obtained for the chromium determination were not as good and were limited to about 3% relative by the counting statistics. The latter results could be improved by the use of a larger neutron source, larger samples and multiple measurements. The apparatus is suitable for installation in a plant environment and the simplicity of the sample preparation makes it particularly useful as a method for in-situ or in-plant operation. With further development the method could be applied to on-line analysis on a moving belt.

INTRODUCTION

Neutrons and gamma-rays are both highly penetrating radiations and neutron activation analysis therefore is suitable for the analysis of the elemental composition of bulk samples with an absolute minimum of sample preparation. This gives it great potential in applications involving the analysis of raw materials particularly in process control applications.

One area of application is in the ferromanganese industry. In this industry the utilisation of very large furnaces with power levels of up to 40 MW has led to considerable economies of scale but it has also made control much more important as the economic penalties for malfunctions have risen sharply. It is thus necessary to analyse the raw material feed to the submerged arc furnaces. One of the most important parameters affecting this feed is the manganese content of the ore. Also of significance for optimum operation are the manganese contents of the ferromanganese metal product and of the slag.

Manganese has particularly favourable nuclear properties for neutron activation. The determination of manganese in bulk samples of ores, slags and metals therefore provides a promising field for the development and application of neutron activation methods.

Similar requirements are found in the ferrochromium industry and although the determination of chromium by neutron activation is not as sensitive as that of manganese, it offers the same advantages of bulk analysis, automation and a minimum of sample preparation.

Neutron activation has several advantages in comparison with conventional methods, such as X-ray fluorescence. Firstly, sample preparation in neutron activation does not require fine grinding. This is a slow and laborious process and although the measurement time in X-ray fluorescence is short, the total analytical process including the sample preparation is time consuming and difficult to automate.

Secondly, the final mass analysed by the X-ray beam is of the order of 100 mg. This must represent several tons of ore and the sampling and size reduction must be carried out in a carefully controlled procedure if the result is to be significant. In contrast, the isotope neutron source method described in this work is capable of analysing a sample of several kilograms. This is larger by a factor of some ten thousand. For example, consider the case where it is required to obtain a concentration figure representative of a ton of ore. In the case of the X-ray analysis, the sample analysed represents about one part in 10^7, whereas in the case of the neutron activation the factor is only one in 500, a considerably more advantageous situation. Finally, the apparatus required in conventional X-ray fluorescence is complex and sensitive to temperature and dust.

The concept of a large volume neutron activation analysis system is shown diagrammatically in Figure 1. The primary feed is sampled at A, passed through a jaw-crusher at B to reduce it to a particle size of say, 5mm, and a secondary sampling stage at C delivers the final sample directly into the container used for the analysis. This container is first inserted into the irradiator at D for activation and then transferred to the detector at E for the measurement of the gamma-ray spectrum. The total elapsed time from the sampling at A to the readout of the concentration could be of the order of five minutes or less, depend-

ing on the time constants for the crushing and sampling, and the analysis could be repeated at five minute intervals to give a precise and accurate picture of the variations in the material feed. The same apparatus could be used to analyse any other materials, such as the metal or the slag, simply by inserting a shovel-full of material at B and initiating the analytical cycle.

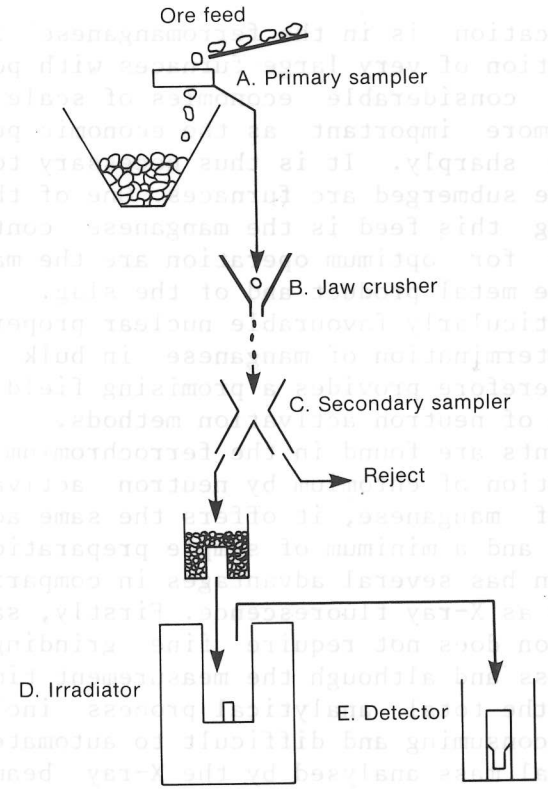

Figure 1: Schematic diagram of a system for the analysis, by neutron activation, of bulk samples.

Such an apparatus would be flexible and considerably less expensive than a full scale on-line analysis system. However the same principles, neutron activation and gamma-ray spectroscopy, could of course be used for the raw materials feed on a conveyor belt itself.

In 1964 Kusaka and Adachi[1] recorded the detection limits for a number of elements using a Ra-Be neutron source containing 49,3mg of radium and most recently, work by Alaerts et al[2] and by De Norre et al[3], has shown that precise and accurate measurements of manganese and fluorine can be made in samples with masses of ten to twenty grams. Beurton and Dugain[4] have described the determination of silicon in alloys with a sample masse of thirty grams.

In all these cases the samples have been fairly small, the methods developed were intended for use in a laboratory and no attempt was made to utilize the ability of neutron activation to analyse bulk samples. Bakes and Jeffrey[5] analysed samples with masses of up to 50 g using an

ingenious sample container that optimised the counting geometry as well as the irradiation geometry. They applied the method to the determination of fluorspar but they were unable to achieve good precisions in spite of an analytical cycle consisting of multiple irradiations and counts. This was probably because of the movement of the sample in the container during transfer. Lundan and Mattila[6] have described the use of a 185 GBq Am-Be source to determine chromium in one kilogram samples of chrome concentrate and they reported good results but with a highly non-linear calibration curve. Recently Borsaru and Eisler[7] have outlined a method for the determination of aluminium and silicon in samples of bauxite with a mass of 3,5kg. Their precision was good but they did not assess the accuracy of the method.

One of the main reasons that the use of neutrons for the analysis of materials in bulk has not been fully utilised, is the difficulty of making quantitative corrections for the absorption of the neutrons and gamma-rays. In the present work, a major object has been to deal with this problem and to provide a method that is suitable for the analysis of samples of ores, metals and slags with masses of several kilograms. This method has the additional advantage that it requires a minimum of sample preparation, namely a single pass through a jaw-crusher, and it is suitable for on-site or in-plant applications.

Two different problems were studied that are of direct interest to the ferro-alloy industry. The first was the determination of manganese in manganese ores, metals and slags, whereas the second was the determination of chromium in similar materials.

Manganese is an element with a large neutron cross-section and absorption is of great importance in this case, whereas chromium represents a case with very small absorption.

ACTIVATION ANALYSIS

The method depends on the activation of the material in a neutron flux and the detection of the gamma-rays emitted after the beta decay of the radioisotopes formed during the irradiation. The nuclear data for the neutron reactions with the important constitutents for the manganese and chromium ores, metals and slags are given in Table 1.

TABLE 1

NUCLEAR DATA

REACTION	THERMAL NEUTRON CROSS SECTION barns	ABUNDANCE OF TARGET %	HALF-LIFE OF PRODUCT	PRINCIPAL GAMMA ENERGIES AND INTENSITIES keV (%)
$^{55}Mn(n,\gamma)^{56}Mn$	13,3b†	100	2,58h	846,8 (98,9)
$^{56}Fe(n,p)^{56}Mn$	1,0mb*	91,7		1810,7 (27)
				2113,1 (14,5)
$^{52}Cr(n,p)^{52}V$	1,1mb*	100	3,76m	1434,1 (100)
$^{51}V\ (n,\gamma)^{52}V$	4,9b	99,8		
$^{55}Mn(n,\alpha)^{52}V$	0,1mb*	100		
$^{58}Fe(n,\gamma)^{59}Fe$	2,5b†	2,2	74d	1099,2 (56,5)
				1292,3 (43,5)
$^{28}Si(n,p)^{28}Al$	6,4mb*	92,2	2,24m	1778,7 (100)
$^{27}Al(n,\gamma)^{28}Al$	0,23b†	100		
$^{27}Al(n,p)^{27}Mg$	4,0mb*	100	9,4m	843,8 (72)
				1013,3 (28)
$^{10}B(n,\alpha)^{7}Li$	3837b†	19,8	-	-

† Thermal cross section * Fission spectrum cross section

Consider first the determination of manganese. In this case the reaction $^{55}Mn(n,\gamma)^{56}Mn$ is by far the most sensitive and the 845 keV gamma-ray from the decay of ^{56}Mn is at a very convenient energy for detection with a scintillation detector. An analysis of the data in Table 1 shows that the reaction $^{58}Fe(n,\gamma)^{59}Fe$, which is potentially of interest because of the importance of the iron to manganese ratio ,is too insensitive.For the same reason (lack of sensitivity) the reaction $^{56}Fe(n,p)^{56}Mn$, which is a potential source of interference, is not important. In fact, an examination of the nuclear data shows that the only other reactions of importance to the gamma-ray spectra are $^{28}Si(n,p)^{28}Al$ and, to a lesser extent, $^{27}Al(n,\gamma)^{28}Al$. This was confirmed by the spectra obtained.

An additional reaction shown in Table 1 is $^{10}B(n,\alpha)^{7}Li$. The importance of this reaction was not initially apparent since it was not appreciated that the manganese ore could contain appreciable amounts of boron. This reaction has an extremely large cross-section and although ^{7}Li does not emit a gamma-ray and contributes no interference to the gamma-ray spectrum, the presence of boron can significantly affect the results obtained by its contribution to neutron self-shielding in the sample.

In the case of a chromium ore the important reactions are $^{52}Cr(n,p)^{52}V$ and $^{28}Si(n,p)^{28}Al$. These are both fast neutron reactions, and since the cross-sections for neutrons in this energy range are much smaller than in the case of thermal neutrons, the effects of neutron absorption are much less important. The reaction $^{51}V(n,\gamma)^{52}V$ is important as a source reference.

These two analytical applications of neutron source activation thus have very different sensitivities and behaviour as regards the effect of absorption. The determination of manganese is the most sensitive, and also the analysis in which self absorption is very important. In particular the effect of neutron self-shielding must be taken into account.

EFFECT OF SELF ABSORPTION

Although neutrons and gamma-rays are highly penetrating, they do undergo absorption in the sample and in any quantitative analysis this must be taken into account. Table 2 gives typical compositions for a manganese ore, a slag and a metal together with the macroscopic neutron absorption cross-section and the gamma-ray mass absorption coefficients for these elements. The calculated thermal neutron diffusion length and the linear gamma-ray absorption coefficients for these materials are also given.

The general treatment of neutron absorption is complicated and it is best treated by a multi-group[8] or Monte Carlo[9] method. Some insight into this process can however be obtained by making some severely simplifying assumptions.

Since manganese is a strong absorber with a large thermal neutron cross-section and a small resonance integral, the activation is effectively all produced by the thermal neutrons. The neutron flux can then be considered in a first approximation to consist of two groups, a thermal group that produces the activation and that is strongly absorbed by the manganese (and by any boron that may be present) and a fast group that is weakly absorbed and that is moderated in energy by elastic and inelastic scattering to provide a source of thermal neutrons.

Consider first the thermal flux. In a spherical absorber surrounding a point source of neutrons the thermal neutron flux will vary as[10]

$$\phi = \frac{k.\exp(-r/L)}{r} \qquad (1)$$

at a distance r in a medium with diffusion length:

$$L = \frac{1}{\sqrt{3.Ea.(Etr + Ea)}} \qquad (2)$$

where Ea and Etr are the macroscopic absorption and transport cross-sections respectively. In the case of a strongly absorbing medium, as is the case for a substance with a large concentration of manganese:

$$L = \frac{1}{\sqrt{3.Ea}} \qquad (3)$$

For a manganese ore with 45% manganese, a density of 2,2 and the composition shown in Table 2, L = 38mm.

TABLE 2

NEUTRON AND GAMMA-RAY ABSORPTION DATA FOR MANGANESE SAMPLES

ELEMENT	NEUTRON ABSORPTION CROSS SECTION barns	GAMMA-RAY MASS ABSORPTION COEFFICIENTS cms 9	TYPICAL ELEMENT CONCENTRATIONS ORE %	METAL %	SLAG %
Mn	13,3	0,065	45	77	20
Fe	2,55	0,065	8	14	-
Si	0,16	0,069	2	-	16
Ca	0,43	0,069	5	-	25
O	0,00027	0,069	40	-	39
C	0,0034	0,069	-	9	-
B	759	0,061	-	-	-

With the cylindrical geometry of the sample holders developed for the present project, the number of counts detected from a thin circular element of width dr at a radial distance r will be given by:

$$Y.dr = \frac{\exp(-(r-ro)/L).\exp(-\mu.(r-ro)).2.\pi.r.dr}{r^2} \qquad (4)$$

where μ is the linear gamma-ray absorption coefficient as is given in Table 2 and ro is the inner radius of the sample container. In this instance, the sample holder has an inner diameter of 45mm and an outer diameter of 67mm and Figure 2 shows the variation of Y, which could be termed the radial sensitivity function, across the sample container for the typical ore of Table 2.

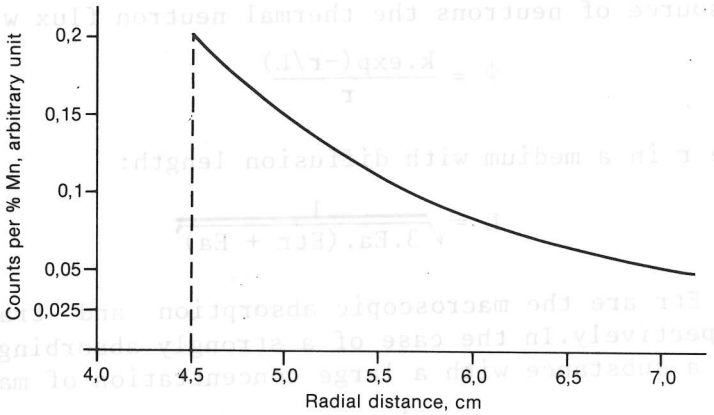

Figure 2: Plot of radial-sensitivity function.

This behaviour will be somewhat modified by the fact that the thermal neutron flux is being supplemented by the slowing down of the fast neutrons. This will have the effect of extending the region of activation further into the sample.

The degree of self absorption will depend on the concentration of the manganese and other absorbers as well as on the bulk density of the sample. This means that the calibration factor will not be a constant but will also be dependent on these factors and they must be taken into account in the quantification of the method.

This can be done in one of two ways. In the first method the assumption is made that the manganese itself dominates the absorption effect. In this case the total gamma activity will be given by the integral of the radial sensitivity function of expression (4).

Although this treatment is based on the idealized case of an infinite neutron source and detector it indicates that the quantitative analysis of bulk samples is practicable when the absorption behaviour of the samples is dominated by the manganese content of the samples provided that the bulk density terms of a non-linear calibration that depends on the total mass per unit volume of the manganese.

When the absorption behaviour of the samples cannot be predicted from the elements determined, it is necessary to measure the neutron absorption directly and this was done in a specially constructed apparatus as described in the next section.

The cross-section for the fast neutron reaction $^{52}Cr(n,p)^{52}V$ is very much lower than that of the thermal neutron reaction $^{55}Mn(n,\gamma)^{56}Mn$. The value for a fission spectrum flux is given in Table 2 and this yields a mean free path of some 240mm. The gamma-ray from ^{52}V also has a significantly higher energy and in this case absorption is much less serious. On the other hand the sensitivity in terms of counts per gram of the element is much lower.

APPARATUS

The apparatus that was used for this work consisted of four main items, the irradiator, the detector, the neutron absorption apparatus and the electronics system. A block diagram of the apparatus is shown in Figure 3.

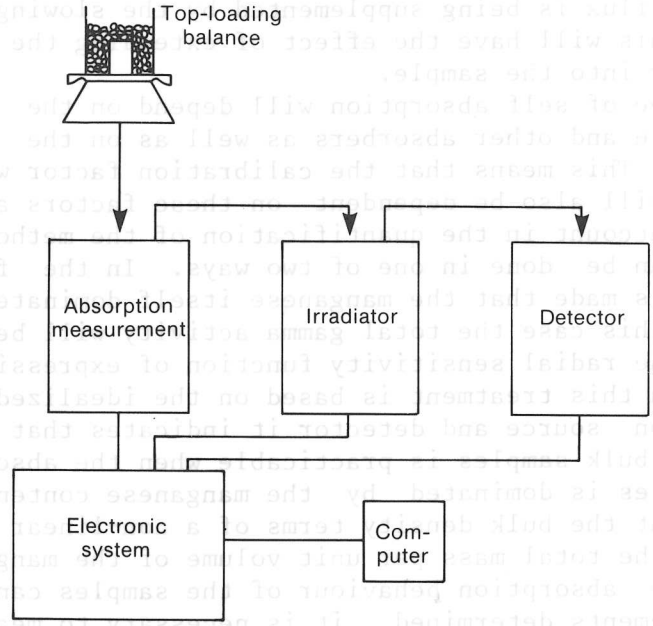

Figure 3: Block diagram of the apparatus for irradiation and counting.

The efficient use of the neutrons was an important consideration and the sample holder was designed accordingly. It was made large enough to hold several kilograms of ore, slag or metal samples with particle sizes of up to several millimeters in accordance with the idea of using only a jaw-crusher for sample preparation. A 75mm x 75mm NaI(T1) detector equipped with an Am-241 alpha particle source for gain stabilization, was used for the measurement of the gamma-ray activity of the sample. A second neutron source consisting of 3 Ci (111 GBq) of Am-Be was used in a separate apparatus for the direct determination of the neutron absorption of the material. Ideally this measurement would be combined with the irradiation step by installing neutron detectors in the irradiator.

The electronic system for these experiments was based on the modular Nuclear Instruments Module system. This had the great advantage of flexibility for the experimental stage of the project described here.

The accurate timing of the irradiation, decay and counting sequence was central to the method. A three stage timer was developed for this application in a single width N.I.M. module. Each of the three timers could be pre-set with a precision of 0,1s.

Three single channel analysers and three scalers were used so that three sections of the gamma-ray spectrum could be monitored independently.These scalers were started and stopped by the three stage timer mentioned above.

When the neutron absorption apparatus was used there were five time periods that were monitored. Three of these were fixed and two were variable.

The data from the four scalers and the five timers, as well as the time of day and the sample mass, were printed out at the end of each analysis.

EXPERIMENTAL PROCEDURE

The procedure for the neutron activation analysis was very simple. The sample holder was filled to a constant height and the mass of this sample was determined on a top-loading balance.

Where the neutron transmission was not measured, the sample was irradiated for a pre-set time, typically 90s in the case of the manganese and 15 minutes in the case of the chromium. After the irradiation the sample was removed from the irradiator and transferred to the detector. In the case of the manganese, the count was started after an elapsed time of 30s, while in the case of the chromium a time of 100s was allowed in order to reduce the activity from ^{28}Al.

Counting times were typically 200s for the manganese and 900s for the chromium. At the end of the counting time, the results from the three scalers were used as input to a computer programme that made the appropriate corrections according to the activation analysis equation and also made the appropriate interference corrections. When the neutron transmission was measured, a total of five different timed steps were necessary and the computer programme was modified accordingly.

RESULTS

A gamma-ray spectrum obtained with a NaI(T1) detector from a typical manganese ore is shown in Figure 4. The spectra obtained from typical manganese metal and slag samples were qualitatively similar. In order to identify all the gamma-rays present, the spectra from these samples were also measured on a high resolution Ge(Li) detector under the same conditions, and the corresponding spectrum for an ore is also shown in Figure 4.

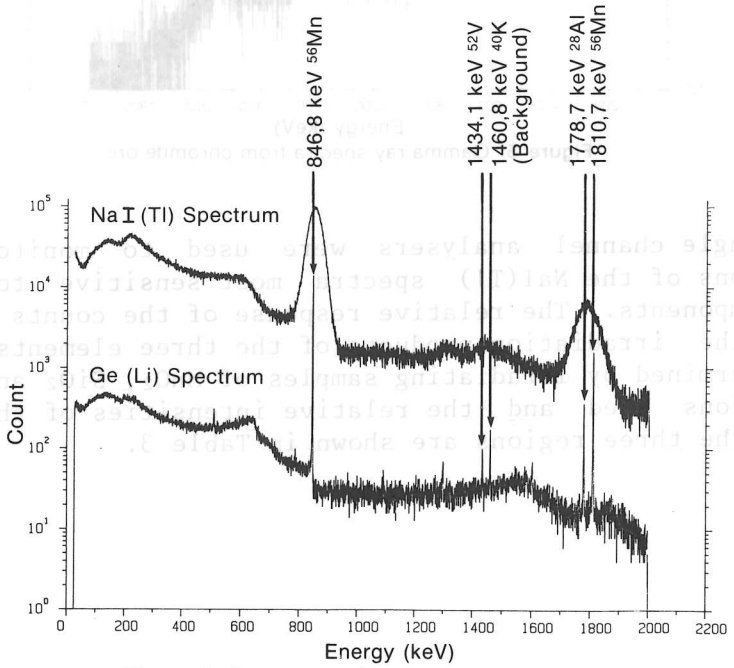

Figure 4: Gamma ray spectra from manganese ore.

A typical NaI(T1) spectrum from a chromite ore and the corresponding spectrum obtained with a Ge(Li) detector are shown in Figure 5.

The possible modes of formation for the isotopes producing the peaks shown in these figures are all given in Table 1.

The direct interference of the reaction $^{56}Fe(n,p)^{56}Mn$ with the determination of manganese was expected to be negligible because of its extremely low cross-section and this was confirmed experimentally. The reaction that made the dominant contribution to the spectra was $^{55}Mn(n,\gamma)^{56}Mn$ in the case of the manganese, but under the conditions used there was an appreciable component from the isotope ^{28}Al and a small contribution from the isotope ^{27}Mg. These two isotopes are both formed by neutron reactions with the elements silicon and aluminium, but in different ratios.

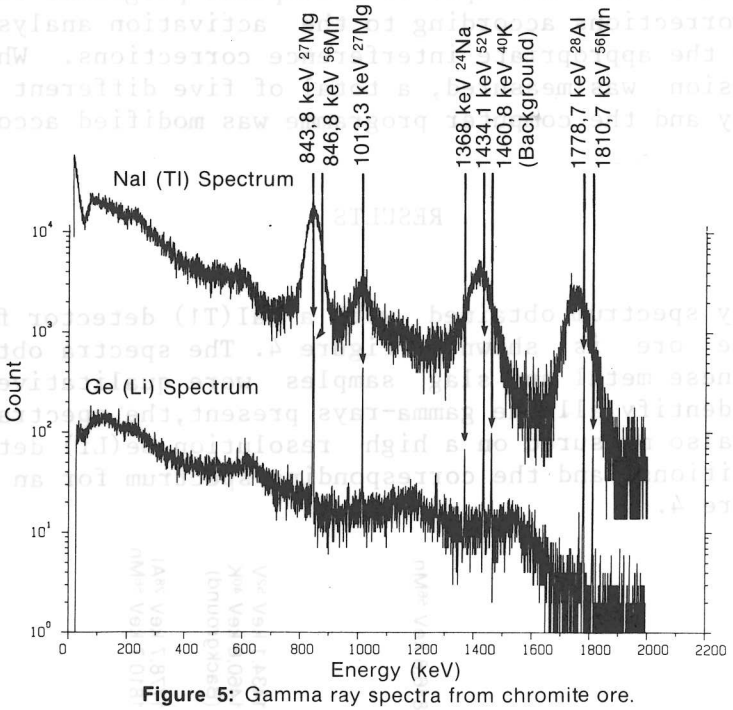

Figure 5: Gamma ray spectra from chromite ore.

Three single channel analysers were used to monitor the three energy regions of the NaI(T1) spectra most sensitive to these three spectral components. The relative response of the counts in the three regions to the irradiation products of the three elements: Mn, Si and Al were determined by irradiating samples of MnO_2, SiO_2 and Al_2O_3. The energy regions used and the relative intensities of the gamma-ray spectra in the three regions are shown in Table 3.

TABLE 3

Settings for single channel analysers for manganese

SCA No	Energy region L.B. KeV	R.B. KeV	Relative spectral intensities Mn	Si	Al
1	773	938	1,00	0,30	0,35
2	941	1103	0,080	0,30	0,31
3	1679	1975	0,18	1,00	1,00

These values were used to correct the manganese counts for possible interference from the other spectral components. It should be noted that the correction for example for the ^{28}Al, was necessary because, although the ^{28}Al does not have a peak in the window centred on the 846keV peak that was used for the determination of manganese, the Compton continuum from the 1778keV peak does extend across this region.

A computer programme was written to make the corrections. It solved three simultaneous equations to obtain the contributions to the spectrum from the manganese, silicon and aluminium respectively. If any of the components were not statistically significant or were less than zero, then the component was eliminated and the three equations were solved again for the two remaining components by a least squares method. If either of these two components was insignificant or negative then the three equations were solved for the remaining component.

In general, the amount of interference found varied from less than one percent relative in the case of several of the ores to about seven percent relative in the case of the slags.

The accuracy and precision of any nuclear method is limited by the statistics of the counting process. This follows a Poisson distribution and for measurements yielding more than about 100 counts the standard deviation is the square root of the count.

Under the experimental conditions described previously, i.e. with an irradiation time of 90s, a decay time of 30s, a measurement time of 200s and a sample mass of 3000g, a typical ore containing about 45% manganese gave over 100 000 counts in the manganese channel with a background of 300 counts. The limiting precision from the counting statistics was thus of the order of 0,3% relative and more than adequate for this application. In the case of the metals this figure was even better, whereas in a typical slag with a content of 25% manganese in a mass of 2000g the number of counts was in the region of 30 000 yielding a limiting precision of 0,6% relative.

On this basis of the counting statistics the limit of determination of this method is about 0,02% manganese in a 2000g sample and by extending the irradiation and counting time to 10 minutes and half an hour respectively, this could be reduced to below 0,01%. These figures correspond to a standard deviation from the counting statistics of about 20% relative at this level of concentration.

Under the experimental conditions used for the chromium the limiting precision from the counting statistics for an ore containing about 32% chromium was 0,9% in a sample of 500g and the limit of determination is 1% chromium. This limiting precision could be further improved by using a larger sample. It could also be improved by the use of a more intense neutron source.

In this case the isotopes ^{27}Mg and ^{28}Al were also present in the spectra and corrections were made for the contribution from ^{28}Al in the same way as was outlined above. The isotope, ^{52}V, was also formed from the reaction $^{51}V(n,\gamma)^{52}V$ as well as from the reaction $^{52}Cr(n,p)^{52}V$. The former reaction has a very much greater intrinsic sensitivity than the latter and the interference from minor amounts of vanadium in the samples was reduced by the use of cadmium shielding.

Measurements were made on a number of different manganese ores and it was found that the specific counts did not vary smoothly with the manganese content for all the ores. This is shown in Figure 6. A direct measurement of the absorption was effective, the apparatus described previously was constructed and the calibration factor was found directly as a function of the neutron absorption.

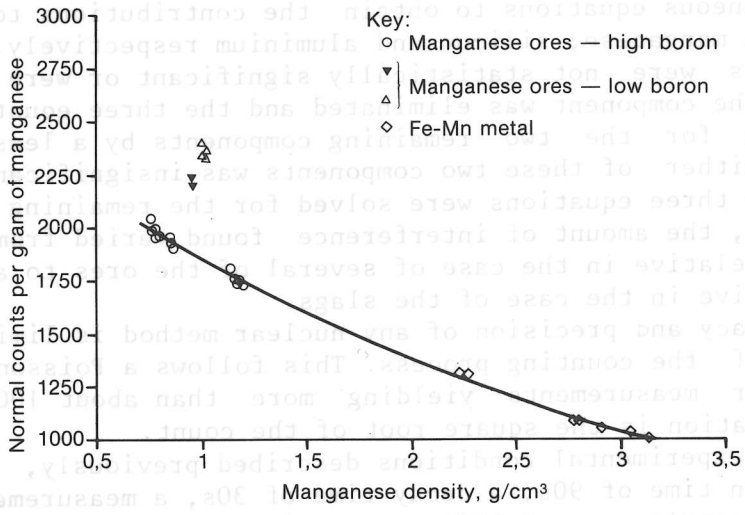

Figure 6: Variation of specific count with manganese content in ore and metal samples.

The reason for this anomalous behaviour is important. It was found to be produced by the presence of boron in some of the manganese ores. Since boron has an extremely high neutron absorption cross-section, this provided an explanation for the anomalous absorption.

Although these results demonstrated that the simple model and measurement could not be used for all the manganese ore samples because of the presence of boron in some of them, it is still possible to apply the simple method to the ores from one source provided that the boron level is relatively constant.

Where this is not the case the direct absorption method must be applied. In this case the neutron absorption was expressed in terms of the absorption ratio. This is the ratio of the transmitted flux with an absorber to that without an absorber. It would be zero if the absorption were that of boric acid and one, if there were no absorption at all. It was found that the relative statistical uncertainty in this ratio was about 0,34%. Figure 7 shows the variation of the specific counts from the manganese ores with the absorption ratio.

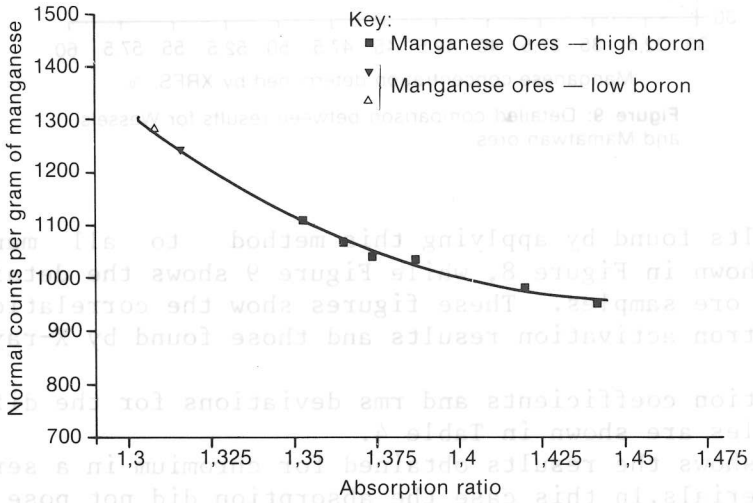

Figure 7: Variation of specific count with absorption ratio.

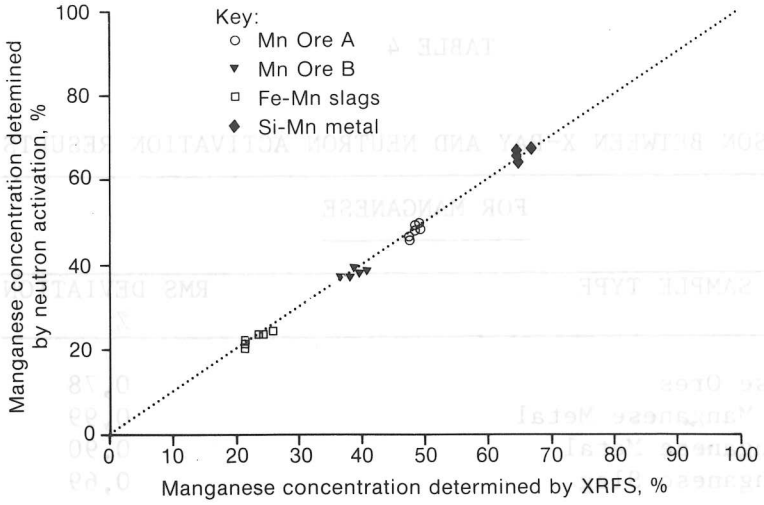

Figure 8: Correlation between neutron-activiation and X-ray-fluorescence results for ores, metals, and slags.

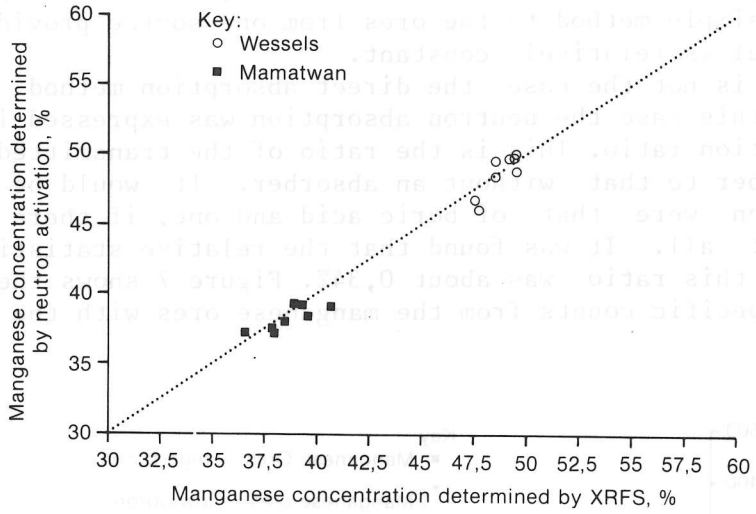

Figure 9: Detailed comparison between results for Wessels and Mamatwan ores.

The results found by applying this method to all manganese samples are shown in Figure 8, while Figure 9 shows the detailed results for the ore samples. These figures show the correlation between the neutron activation results and those found by X-ray fluorescence.

The correlation coefficients and rms deviations for the different types of samples are shown in Table 4.

Figure 10 shows the results obtained for chromium in a series of reference materials. In this case the absorption did not pose a problem and the deviations from the straight line are due to counting statistics and to the corrections for vanadium intereference.

TABLE 4

COMPARISON BETWEEN X-RAY AND NEUTRON ACTIVATION RESULTS FOR MANGANESE

SAMPLE TYPE	RMS DEVIATION %
Manganese Ores	0,78
Silicon Manganese Metal	0,99
Ferromanganese Metal	0,90
Ferromanganese Slag	0,69

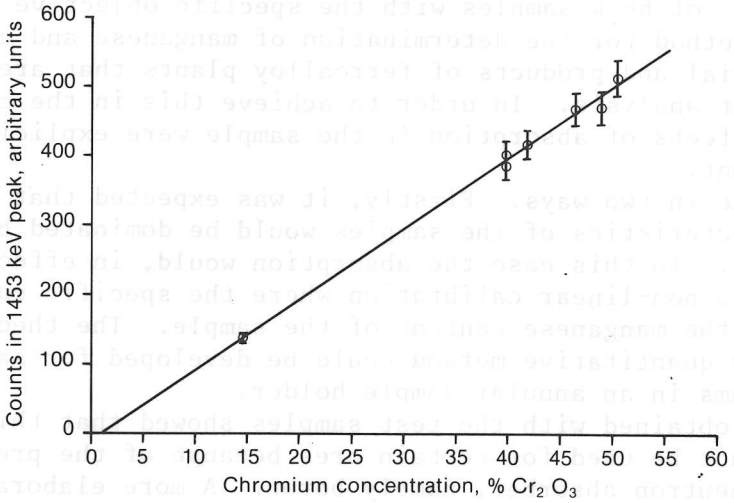

Figure 10: Counts in 1453 keV peak as a function of chromium concentration.

DISCUSSION AND CONCLUSIONS

Neutrons and gamma-rays provide a unique method for the analysis of materials in the bulk with a minimum of sample preparation. With the use of isotopic neutron sources they can also provide a relatively inexpensive method that is simple to use and that can analyse ore samples in mineral processing plants or on mines or in the field during exploration. This is particularly attractive if the only sample preparation that is required is a single pass through a jaw-crusher, eliminating the need for grinding which is a time consuming process. An additional important advantage of such a system is that if the final sample analysed has a mass of a few kilograms, then the gross inaccuracies, that are often present because of sampling problems in conventional analytical procedures, could be greatly reduced.

It is somewhat surprising that the development of such systems is not more widespread. One of the reasons for this is the relative insensitivity of the isotope source activation method. With the use of readily available sources there has always been a problem in obtaining adequate counting statistics. However this problem can be lare overcome by the use of the large sample sizes that are central to the idea of bulk analysis. The availability of spontaneous fission neutron sources in recent years also provides a significant contribution to the solution of this problem.

The other important reason is that although neutrons and gamma-rays are not absorbed as much as most other radiations, nevertheless absorption does occur and most methods have been concerned with the elimination or minimization of this effect rather than with the development of techniques for compensating for it. A knowledge of

these techniques is of course essential for the analysis of materials in bulk.

In this work the method of neutron activation has been developed for the analysis of bulk samples with the specific objective of establishing a method for the determination of manganese and chromium in the raw material and products of ferroalloy plants that are suitable for in-plant analysis. In order to achieve this in the case of manganese the effects of absorption in the sample were explicitly taken into account.

This was done in two ways. Firstly, it was expected that the absorption characteristics of the samples would be dominated by the manganese itself. In this case the absorption would, in effect, merely lead to a non-linear calibration where the specific count would depend on the manganese content of the sample. The theory indicated that a quantitative method could be developed for samples of a few kilograms in an annular sample holder.

The results obtained with the test samples showed that this approach could not be used for certain ores because of the presence of another strong neutron absorber, namely boron. A more elaborate experimental procedure was then devised in order to measure the neutron absorption directly. This procedure involved a separate measurement of the neutron transmission of the sample in a spearate neutron source.

With this procedure the differing neutron absorption characteristics of the samples could be taken into account and all of the samples, ores, slags and metals, were analysed. The rms deviations between the neutron activation and the X-ray results then varied from 0,7% manganese for the ores to 1% manganese for the silicon manganese metal. These results showed that this method is capable of determining manganese with a high degree of precision and accuracy in a variety of materials and with the minimal sample preparation described above. The procedure was rapid and the full cycle of filling the sample container determining the mass, irradiating and counting the sample, and calculating the results, could be accomplished in less than ten minutes. This time could be further reduced by the use of additional sample containers and a shorter counting period.

With additional development the whole procedure could be automated and in this case a goal of one analysis every few minutes would be attainable.

The absorption measurement will be incorporated in the irradiator and this will improve the precision of the method by eliminating the additional timing steps that were performed manually in the above work.

The method can be extended to the determination of certain other elements, such as fluorine, antimony, vanadium, copper, silicon and aluminium in ores, slags and mineral processing products. In its higher concentrations, gold could be determined. The determination of rhodium in platinum ores, and mineral processing is feasible. The method involving the measurement of the neutron transmission can be developed to provide for the determination of boron as well. In all of these applications the use of more efficient detectors and stronger neutron sources will be extremely important.

It is clear that neutrons and gammarays have unique properties to offer in the fields of in-plant and on-line analysis in mineral pro-

cessing. This project has shown that they can be used for the accurate analysis of manganese and chromium in an instrument that is suitable for use on a plant and the same techniques can be used for the on-line analysis of manganese ores.

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