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Instrumental neutron activation analysis applied to the determination of the chemical composition of metallic materials with study of interferences

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Instrumental neutron activation analysis was applied to evaluate the chemical composition of metallic materials, namely iron, steel, silicon and ferrosilicon certified reference materials. As, Co, Cr, Mn, Mo, Ni, V and W concentrations were analyzed in the iron and steel samples whereas 21 elements were determined in silicon and ferrosilicon samples. Accuracy and precision results of about 10% were achieved for most elements, indicating that the technique is suitable for the analysis of metallic materials. Interferences of Cr and Mn in V; Fe and Co in Mn; Co in Fe and Cr in Ti were quantified and only the last one was critical to the analysis of the materials employed in this work.

Introduction

Various analytical techniques have been used in the characterization of the chemical composition of metallic materials.[1] However, nuclear techniques including instrumental neutron activation analysis (INAA) have been scarcely used in the analysis of such materials. This fact can be explained by the difficulty of access to nuclear facilities and the great development, in the last few years, of less expensive techniques like ICP-MS, AAS and XRF.[2]

INAA was used in the characterization of metallic ores,[3] metals, and other materials of interest in the metallurgical and semiconductor industries.[4,5] The technique was successfully used for high purity materials, like high purity nickel[6] and iron.[7] Metallic silicon matrices are very favorable to INAA as the ^{31}Si formed during irradiation has a short half-life. This allows the analysis of a large number of elements after its decay and longer irradiation periods which provide better sensitivities and detection limits. This feature makes INAA a technique of choice for the microelectronic industry.[8] However, consistent analytical problems due to the high amounts of interfering elements present in some metallic matrices can arise.[9] The following potentially significant interferences were selected in the analysis of steel, iron and silicon matrices among the various possible interferences present in INAA.[10–12]

Gamma-ray spectral interference

In this kind of interference two radionuclides have gamma-ray peaks of the same energy, and hence, one may interfere in the detection of the other. In this work, the ^{51}Cr interference in Ti determination via ^{51}Ti radionuclide, using 320 keV peak (common to both radionuclides) was investigated.

Primary interference reactions

The indicator radionuclide is produced by other reaction than the analytical reaction. The following cases were investigated:

Cr and Mn in V determination:
Main reaction: ^{51}V (n, γ) ^{52}V.
Interference reactions: ^{52}Cr (n, p) ^{52}V and ^{55}Mn (n, α) ^{52}V

Fe and Co in Mn determination:
Main reaction: ^{55}Mn (n, γ) ^{56}Mn
Interference reactions: ^{56}Fe (n, p) ^{56}Mn and ^{59}Co (n, α) ^{56}Mn

Fe in Cr determination:
Main reaction: ^{50}Cr (n, γ) ^{51}Cr
Interference reaction: ^{54}Fe (n, α) ^{51}Cr

Co in Fe determination:
Main reaction: ^{58}Fe (n, γ) ^{59}Fe
Interference reaction: ^{59}Co (n, p) ^{59}Fe

Second order interference reactions

Rare situation in which a nuclear reaction or some element in the matrix produces a measurable amount of the analyte radionuclide. The following possibilities were studied:

Cr in Mn determination:
Main reaction: ^{55}Mn (n, γ) ^{56}Mn
Interference reaction:
^{54}Cr (n, γ) ^{55}Cr $\xrightarrow{\beta^-}$ ^{55}Mn (n, γ) ^{56}Mn

Fe in Co determination:
Main reaction: ^{59}Co (n, γ) ^{60}Co
Interference reaction:
^{58}Fe (n, γ) ^{59}Fe $\xrightarrow{\beta^-}$ ^{59}Co (n, γ) ^{60}Co

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The aim of this work was to apply INAA in the study of the chemical composition of metallic materials. For this purpose, the technique was applied to certified reference materials (CRMs) of iron, steel, silicon and ferrosilicon. Possible INAA interferences in the analyses of these materials are also investigated.

Experimental

Sample preparation

The following CRMs were used in this study: Stainless Steel 316 (IPT 24), Stainless Steel (NIST SRM 442), Cu-Ni-Cr-Mo Molten Gray Iron (IPT 75), Pure Iron (IPT 73), Ferrosilicon-75% Si (IPT 56), Ferrosilicon-45% Si (IPT 70), Ferrosilicon-73% Si (NIST SRM 58), Ferrosilicon (NIST SRM 59a) and Refined Silicon (NIST SRM 57). About 0.050 g of CRM fillings/powder were weighed in properly cleaned polyethylene vials and irradiated with elemental standards. Standards were prepared by pipetting element solutions of known concentration onto Whatman paper filters, which, after drying, were kept in polyethylene vials with the same geometry of the samples. When suitable, multielement standards were prepared for silicon and ferrosilicon CRMs. Most of the samples were prepared in four replicates.

Irradiation and element determination

Two series of irradiation were used, according to the half-lives of the radionuclides to be analyzed.[13] For Mn and V determination, samples and standards were irradiated for 30 seconds at the Pneumatic Station of IEA-R1 Nuclear Research Reactor at IPEN with 10^{11} n·cm^{-2}·s^{-1} thermal neutron flux. ^{52}V was measured for a 5-minute period, immediately after irradiation and ^{56}Mn was measured for a 20-minute period, 30 minutes after irradiation. For determination of the other elements, a 30-minute (iron and steel matrices) or 8-hour (silicon and ferrosilicon matrices) irradiation at 10^{12} n·cm^{-2}·s^{-1} thermal neutron flux was used. Intermediate lived radionuclides were measured for 1 hour, after a 2-day decay while long lived ones were measured also for 1 hour, after a month decay period. Samples and standards were measured using a Canberra GX 2020 HPGe detector (coupled to a Canberra multichannel system and electronics) with a 1.70 keV resolution for 1332 keV gamma-ray peak of ^{60}Co. Analysis of gamma-ray spectra was carried out using the software developed by Dr. D. PICCOT (Saclay, France).[14] Element concentration was calculated applying in-house software.

Interference evaluation

For INAA interference evaluation, increasing masses of pure element or oxides of interest or standards (prepared from element solutions) were irradiated and measured in the same conditions that of the CRM samples. Counting rates were corrected to initial decay time and the results were used to determine the specific activities of each radionuclide. The specific activities were applied in the evaluation of possible interferences in the CRMs used in this work. Due to the high counting rates obtained in the irradiation of Mn and Co, it is not possible to measure the induced radioactivity from radionuclides generated in the interference reactions. To avoid this problem, epithermal neutrons were used in the irradiation of samples of these elements. This allows the measurement of the induced radiation from radionuclides generated in reactions other than the thermal neutron flux induced reactions.

Results and discussion

Interferences in INAA

By means of irradiation of different masses of the various elements under investigation, it was possible to plot graphs for specific sensitivity of the elements obtained in the irradiation and measurement conditions used in this work. As an example, Fig. 1 shows the graphs obtained for the counting rates of the two peaks of ^{56}Mn obtained from the irradiation of different masses of Mn, Fe and Co. The graphs presented good correlation coefficient, most of them about 0.99. It was possible to detect all the interference reactions but it was impossible to quantify the specific sensitivity for the second peak in the Co standard due to the high counting statistics uncertainty obtained for this element at this energy 1811 keV.

From the sensitivity graphs, apparent analyte masses were calculated for each interference, as presented in Table 1. These results may be used in our laboratory, independent of the matrix under investigation, once the same irradiation and measurement conditions are employed.

Although detected, the interferences of Fe in Cr, Cr in Mn and Fe in Co were not quantified due to very low values and were not taken into account in this study.

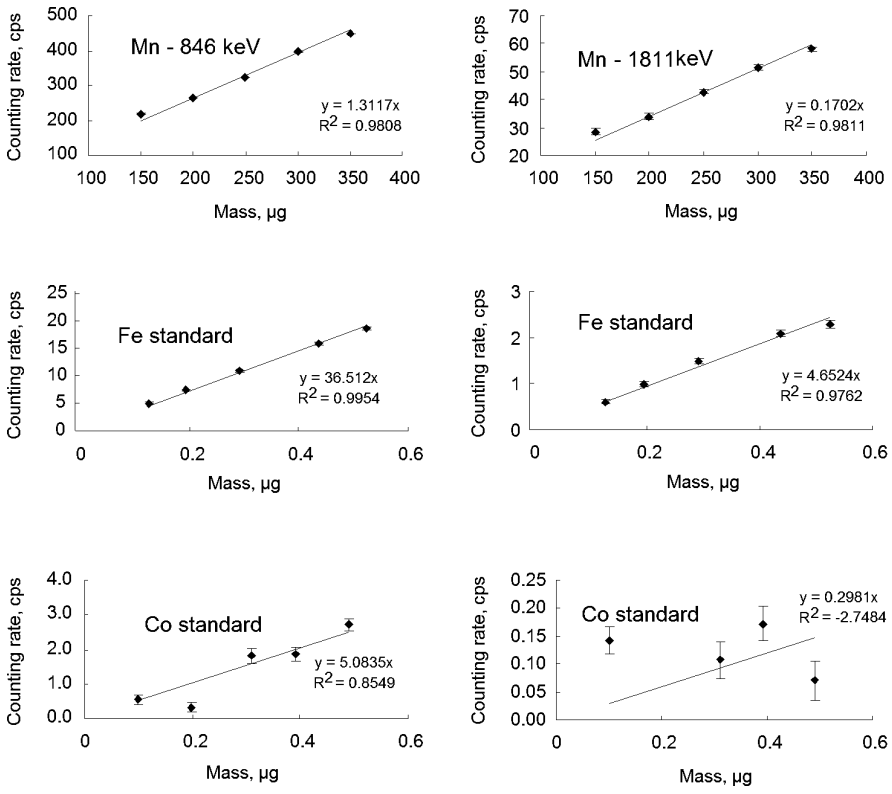

Fig. 1. Counting rate for ^{56}Mn obtained by INAA using Mn, Fe and Co standards

The apparent mass results obtained are in good agreement with the nuclear characteristics of the investigated radionuclides as cross sections and isotope abundances. In Ti analysis, ^{50}Cr has thermal neutron cross section much higher than ^{50}Ti, thus, even for very short irradiation periods, Cr may interfere in Ti determination. The small cross sections for the (n,p) and (n,α) reactions, described in the Introduction of this paper, account for the very small contribution of these reactions for the primary interferences observed. The exception goes to the interference of Co in Fe, which radinuclide cross sections are 1.42 and 1.31 barns, respectively.[12] In addition, isotope abundance for the Co radionuclide is much higher than for the Fe radionuclide. The quantification of the second order interferences was unfeasible, not only by virtue of unfavorable cross sections of the (n,γ) reactions, but also because connected β-decays are necessary for the second order interference to occur.

In Table 2 are presented the errors in element determination in the various CRMs due to INAA interferences under the conditions used in this work. At higher interferent/analyte ratio, a higher interference occurs. It can be noticed that with the exception of the spectral interference of Cr in Ti, for high Cr/Ti ratio, the other interferences may be neglected in the analysis of the CRMs used in this work. In the cases of the interferences of Cr in V and Fe in Mn, according to the type of samples and/or high interferent/analyte ratio, corrections should be considered. For the interference of Co in Fe, even though the apparent mass of Fe due to Co interference is significant, the ratio of these two elements is very small in the CRMs used in this work and, hence, the interference may be ignored. Since ^{56}Mn has very high activities in these samples and longer half-life than ^{51}Ti, it was not possible to determine Ti in the analyzed samples due to the high ^{56}Mn activities. Nevertheless, in cases when it is possible to determine Ti, it is mandatory to consider the correction due to the Cr interference.

Table 1. Analyte apparent mass formed by INAA interference in the irradiation and measurement conditions of this work

Interference type	Interferent	Analyte	Apparent mass,[a] g
Spectral	Cr	Ti	0.00103
Primary	Cr	V	$6.0 \cdot 10^{-5}$
Primary	Mn	V	$4.6 \cdot 10^{-6}$
Primary	Fe	Mn	$2.9 \cdot 10^{-5}$
Primary	Co	Mn	$4.7 \cdot 10^{-6}$
Primary	Fe	Cr	ND[b]
Primary	Co	Fe	0.12361
2nd order	Cr	Mn	ND
2nd order	Fe	Co	ND

[a] Mass of analyte formed during irradiation, considering one gram of interferent.
[b] Not detected.

Table 2. Element determination error due to INAA interferences for 0.050 g of CRM

Interferent	Analyte	CRM	$R_{i/a}$[a]	Error,[b] %
Cr	Ti	NIST SRM 442	8050	830
		IPT 75	22	2.3
		IPT 56	0.6	0.1
		IPT 70	2.6	0.3
		NIST SRM 58	0.4	0.04
		NIST SRM 57	0.3	0.03
Cr	V	NIST SRM 442	503	3.0
		IPT 75	16.2	0.1
Mn	V	NIST SRM 442	90	0.04
		IPT 75	24	0.01
Fe	Mn	NIST SRM 442	20	0.07
		IPT 75	123	0.36
		IPT 73	2270	6.6
		IPT 56	831	2.4
		IPT 70	191	0.6
		NIST SRM 58	158	0.5
		NIST SRM 59a	67	0.2
		NIST SRM 57	18	0.05
Co	Mn	NIST SRM 442	0.05	$2.1 \cdot 10^{-5}$
		IPT 73	0.91	$4.3 \cdot 10^{-4}$
Co	Fe	NIST SRM 442	0.0018	0.02
		IPT 73	0.0004	0.005

[a] Mass ratio between interferent and analyte in the CRM.
[b] Positive error in the concentration obtained by INAA due to interference.

Element determination

The results obtained by INAA of elements in iron and steel, and in silicon and ferrosilicon CRMs are given in Tables 3 and 4, respectively. All results are presented at 95% confidence interval. Using INAA, it was possible to obtain results for non certified elements such as As, V and W in the iron and steel CRM and many other elements in the silicon and ferrosilicon CRM.

For most of the elements determined in the iron and steel samples, the results were obtained with relative standard deviations and relative errors lower than 10%.

Although it was not possible to determine the concentration of some elements of interest by INAA such as Al, C, Cu or Ti in silicon and ferrosilicon CRMs, the concentration of elements which are hardly determinable by other techniques, such as U, Th and rare earths, could be determined. In the analysis of these CRMs, most of the results were obtained with relative standard deviation lower than 15% with a relative error of about 12% in respect to the certified values.

In Figs 2 and 3 are shown the graphical representations of the results as normalized concentration in respect to the certified values for some CRMs studied in this work. The accuracy is measured by deviation from unit whereas precision is measured by dispersion of the obtained values. The z score of the results also shows that most figures are within the expected $\pm 3z$ score in INAA.[15]

Table 3. Element concentrations in steel and iron CRMs obtained in this work by INAA at 95% confidence interval

Element, $\mu g \cdot g^{-1}$	IPT 24	NIST SRM 442	IPT 75	IPT 73
As	83 ± 5	76 ± 10	35 ± 2	29 ± 2
Co	417 ± 14	1256 ± 36	46 ± 2	29 ± 2
	(450 ± 30)[c]	(1300)		(40 ± 10)
Cr[a]	18 ± 1	15 ± 1	0.47 ± 0.03	0.034 ± 0.003
	(17.81 ± 0.05)	(16.1)	(0.487 ± 0.006)	(0.030 ± 0.003)
Cu	346 ± 283	1022 ± 235	0.46 ± 0.06[a]	783 ± 94
	(390 ± 20)	(1100)	(0.433 ± 0.004)	(760 ± 30)
Mn[a]	1.34 ± 0.04	2.6 ± 0.1	0.75 ± 0.04	0.053 ± 0.003
	(1.50 ± 0.02)	(2.88)	(0.722 ± 0.005)	(0.044 ± 0.003)
Mo	2.6 ± 0.2[a]	1176 ± 148	0.42 ± 0.05[a]	47 ± 4
	(2.54 ± 0.03)	(1200)	(0.439 ± 0.005)	(49 ± 4)
Ni[a]	10 ± 1	9.5 ± 0.8	0.48 ± 0.05	NO
	(9.93 ± 0.05)	(9.9)	(0.425 ± 0.004)	
V	310 ± 70	336 ± 92	289 ± 39	NO
		(320)	(300 ± 20)	
W	6.4 ± 0.4	721 ± 50	12.2 ± 0.8	3.1 ± 0.2
		(800)		

[a] Concentration in mass percentage.
[b] NO: Not obtained.
[c] Certified values in parenthesis.

Table 4. Elements concentration in silicon and ferrosilicon CRMs obtained in this work by INAA, at 95% confidence interval

Element, $\mu g \cdot g^{-1}$	IPT 56	IPT 70	NIST SRM 58	NIST SRM 59a	NIST SRM 57
As	1.2 ± 1.3	18 ± 2	4.7 ± 3.7	37 ± 4	1.0 ± 0.2
Br	0.15 ± 0.4	NO[b]	0.48 ± 0.44	0.5 ± 0.1	0.5 ± 0.1
Co	4.6 ± 0.3	23.9 ± 0.9	25 ± 2	40 ± 3	3.2 ± 0.6
Cr	112 ± 25	415 ± 34	182 ± 19	785 ± 59	241 ± 24
	(110 ± 20)	(460 ± 40)	(200 ± 10)	(800 ± 30)	(250 ± 10)
K	NO	NO	NO	27 ± 2	78 ± 12
Eu	0.15 ± 0.04	0.12 ± 0.04	0.5 ± 0.1	NO	0.8 ± 0.1
Fe[a]	24 ± 1	48 ± 2	27 ± 1	48 ± 2	0.63 ± 0.03
	(24.1 ± 0.3)	(54.1 ± 0.2)	(25.23 ± 0.03)	(50.05 ± 0.04)	(0.65 ± 0.02)
La	5.3 ± 0.1	28 ± 2	14.4 ± 0.2	3.3 ± 0.1	26.5 ± 0.7
Mn	276 ± 28	2572 ± 239	1558 ± 92	7646 ± 400	332 ± 39
	(290 ± 20)	(2830 ± 50)	(1600 ± 100)	(7500 ± 100)	(360 ± 40)
Mo	6 ± 3	28 ± 2	27.6 ± 0.6	192 ± 56	56 ± 13
Na	14 ± 2	16 ± 29	14 ± 3	21 ± 7	38 ± 11
Nd	5 ± 3	18 ± 3	NO	NO	27 ± 3
Sb	0.3 ± 0.1	6.7 ± 0.6	2.1 ± 0.3	66 ± 43	0.75 ± 0.03
Sc	0.9 ± 0.4	0.6 ± 0.1	3.2 ± 0.3	0.9 ± 0.1	1.27 ± 0.03
Sm	0.9 ± 0.1	3.3 ± 0.9	2.7 ± 0.5	0.63 ± 0.05	4.2 ± 0.6
Tb	NO	NO	NO	NO	0.4 ± 0.1
Th	0.8 ± 0.4	1.0 ± 1.3	NO	1.2 ± 0.1	6.9 ± 0.8
U	0.9 ± 0.1	1.2 ± 0.1	1.1 ± 0.4	0.5 ± 0.1	2.1 ± 0.2
V	19.2 ± 1.9	22 ± 11	33 ± 5	25 ± 4	23 ± 3
W	0.35 ± 0.05	5.7 ± 0.5	5.1 ± 0.2	28 ± 4	NO
Yb	0.2 ± 0.1	NO	2.2 ± 0.2	NO	1.2 ± 0.1

[a] Concentration in mass percentage.
[b] NO: Not obtained.
[c] Certified values in parenthesis.

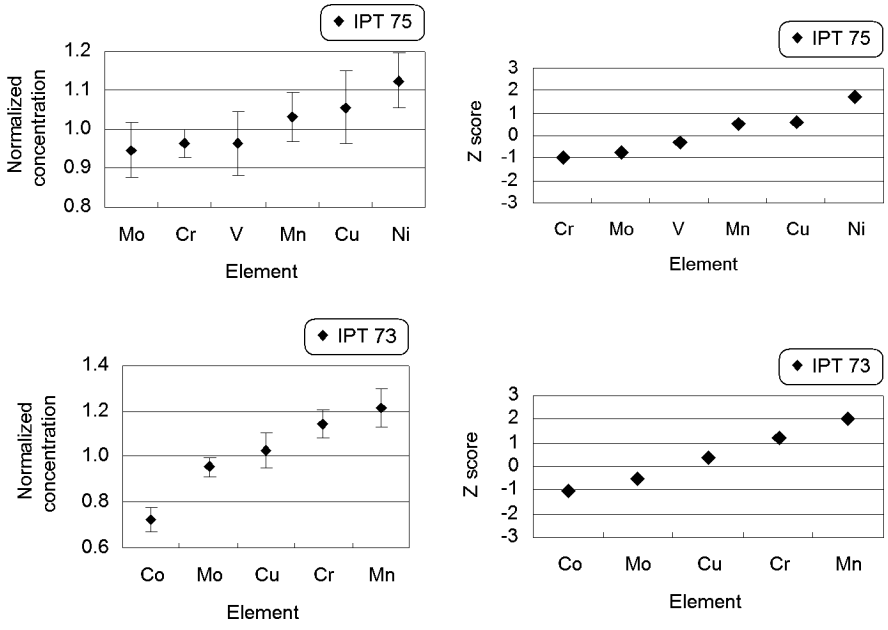

Fig. 2. Normalized concentration as a function of certified value and *z* score for iron CRMs

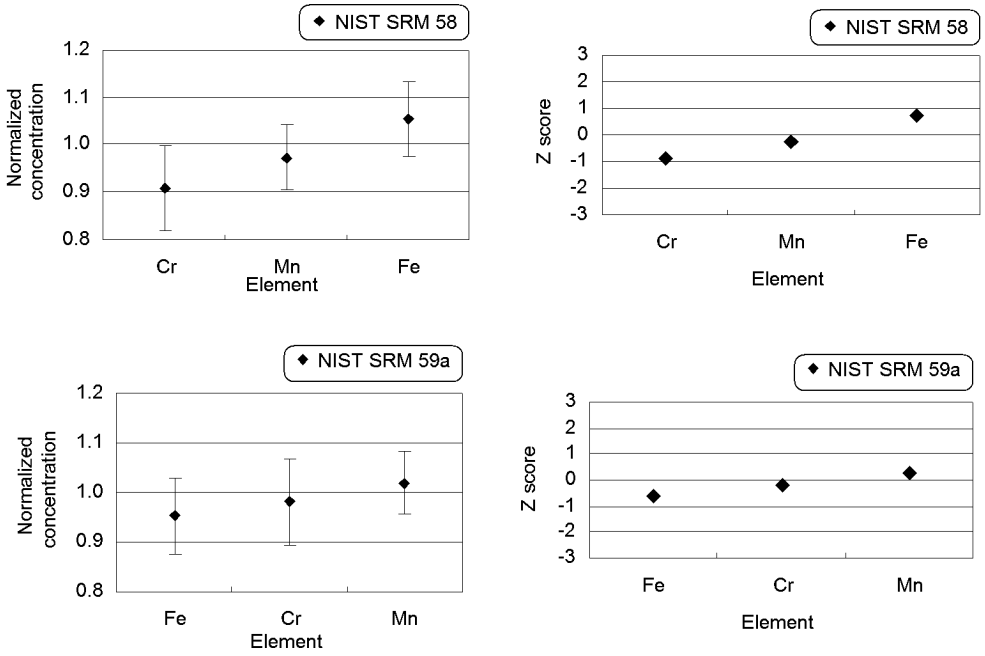

Fig. 3. Normalized concentration as a function of certified value and *z* score for ferrosilicon CRMs

Conclusions

The results showed that INAA may be used successfully in the determination of various elements in iron and steel and 21 elements in silicon and ferrosilicon. Precision and accuracy of about 10% indicate that INAA is a suitable alternative technique for element determination in metallic samples.

From the interference study, it was possible to quantify Cr interference in Ti and V, Mn interference in V and Fe and Co interferences in Mn. Only the Cr interference in Ti could impose corrections for the samples analyzed.

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