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Instrumental neutron activation analysis (INAA) for steel analysis and certification

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Abstract. Instrumental neutron activation analysis (INAA) procedure of elemental steel analysis has been elaborated. The reliability of results obtained by the described procedure has been proved in the frame of different proficiency testing/interlaboratory comparison (PT/ILC) programmes, in which the Institute of Nuclear Chemistry and Technology (INCT, Warsaw) took part since 2005. This work summarizes participation of INCT in these exercises and demonstrates the usefulness of INAA to the certification of steel reference materials.

Key words: steel analysis • neutron activation analysis (NAA) • proficiency testing/interlaboratory comparison (PT/ILC) • certification of steel reference materials

Introduction

Addition of trace elements (intended or as impurities) in steel or alloys can completely change the properties of materials; thus, there is a necessity to have reliable analytical techniques to determine major and trace components in this type of material. Also, to solving problems with quality control/quality assurance (QC/QA) in this subject, appropriate certified reference materials should be available in the wide range.

Several methods have been proposed for quantitative analysis of steel samples: inductively coupled plasma (ICP-OES) [1, 4], inductively coupled plasma mass spectrometry (ICP-MS) [5, 8], atomic absorption spectrometry (AAS) [11], X-ray fluorescence (XRF) [1, 6], and neutron activation analysis (NAA) [1, 2, 7, 10]. As a rule, all of these techniques possess some limitation like required sample dissolution or appropriate sample mass. These requirements like preliminary separation get worse the accuracy. For accuracy reason, it is advisable to apply more than one method for analysis.

INAA is one of the preferred methods because it provides information on a large number of elements simultaneously. Another important feature of INAA is that it is free from the problems connected with digestion of difficult matrices and potential contamination of a sample from reagents. Moreover, by changing irradiation and cooling parameters as well as measurement time, the effect of the interfering radionuclides on the results of analysis of particular elements can

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be decreased. Because of these advantages, INAA is used as a microanalytical method in metallic material analysis [1, 2, 16].

The position of NAA among the analytical techniques is still strong despite some weaknesses like the necessity of having access to a nuclear reactor, long analysis time, etc. and NAA is, with no doubt, a valuable method in inorganic trace analysis, especially important in certification of reference materials [9, 12]. During recent years, it has been proved that instrumental NAA (INAA), because of its unique possibilities, can meet Consultative Committee for Amount of Substance (CCQM) criteria for a primary method of measurement (PMM) [14–17].

INAA procedure including irradiation conditions, decay and measurement times, interpretation of the results for the elemental analysis of metallurgical samples has been described. Elaborated procedure gives accurate results for several elements in a different concentration range with very low combined uncertainty, what has been confirmed by participation in proficiency testing/interlaboratory comparison (PT/ILC) exercises concerning elemental analysis of steel material by neutron activation analysis.

Experimental

Sample irradiation

Different certified steel reference materials were applied for analysis. All used stock standards solutions were obtained from appropriate amounts of special purity elements or oxides by weighing an appropriate amount, dissolving in aqua regia or nitric acid, and weighing the solution obtained. Standard solutions for irradiation were prepared by weighing aliquots of a standard solution in a polyethylene (PE) capsule and air dried in a laminar flow box before encapsulation. The package containing samples sandwiched between standards, certified reference materials (CRMs) and blanks, was irradiated in the reactor MARIA (Otwock/Świerk, Poland) for 5 min at a thermal neutron flux density of 2×10^{13} cm^2·s^{-1}. The irradiation, cooling and counting times were chosen according to half-lives of the determined elements. Table 1 presents irradiation and measurements details.

Apparatus

To prepare samples, CRMs and standards for irradiation, calibrated analytical and micro-analytical balances Sartorius MC5 and Sartorius BP221S were used. To perform gamma-ray spectroscopic measurements the following spectrometer was used: a 255 cm^3 high purity germanium (HPGe) well type detector (Canberra) with associated electronics (resolution 2.15 keV for 1332 keV ^{60}Co line, efficiency ca. 55%), coupled to a multichannel analyzer and spectroscopy software Gennie-2000 (Canberra).

Results and discussion

In the INCT instrumental neutron activation analysis is mostly used for the elemental analysis of various unique types of materials like tissues, meteorites etc. Due to lack of access to a pneumatic transfer system (rabbit) in the nuclear reactor, elements forming short-lived isotopes like: Al, Ti, V have not been determined.

To show usefulness of INAA in steel analysis, the INCT took part in interlaboratory comparisons (ILC) and proficiency tests (PT) in the frame of INAA European Laboratories Network [2].

The first exercise was conducted in 2004 by the Swedish Institute for Corrosion and Metals Research (SIMR), where five INAA laboratories from four European countries: Poland, Romania, Belgium and Hungary participated in the evaluation of elemental composition of high alloy steel (SS1) [1, 2, 13]. Figure 1 illustrates the results obtained in the INCT in comparison to the assigned values calculated by the providers from results obtained by atomic spectrometry techniques, and to the arithmetic mean of all INAA results.

As can be seen, results obtained in the INCT are in good agreement with both values, however a higher difference between the Laboratory results and the assigned value is observed.

Only the difference in antimony determination by atomic techniques and NAA is observed. INAA demonstrates a very good sensitivity and selectivity for antimony and it is often required for measuring Sb in materials in which the antimony level is very low. Non-destructive methods are not only advantageous because of reduced sample handling, but also because they are independent of the efficiency of the digestion or extraction procedure. Hence, it can be assumed that the results provided by NAA laboratories are more accurate than those obtained by other methods.

The second exercise was performed in 2008 by the "Horia Hulubei" National Institute for Physics and Nuclear Engineering, Romania. The analysed material was EURONORM-CRM no. 297-1 High Alloy Stainless Steel HAAS-1. Table 2 demonstrates the results obtained by the INCT in comparison with the assigned value. For all elements, the results agree very well, however INAA assures the lower relative standard uncertainty u (k = 1) for all the determined elements. In this type of material, due to a high content of boron in the matrix (mean B concentration was 1.146 ± 0.0045%) correction for neutron self-absorption has been made.

Table 1. Irradiation and measurements details for stainless steel analysis by INAA

Nuclide used	Thermal neutron flux, irradiation time	Cooling time	Measurement time
^{56}Mn	2×10^{13} cm$^{-2} \cdot$ s^{-1}, 5 min	24 h	100 s
^{76}As, ^{64}Cu, ^{187}W		48–72 h	1500–2000 s
^{51}Cr, ^{59}Fe, ^{60}Co, ^{122}Sb, ^{124}Sb, ^{99}Mo, ^{58}Ni (via ^{58}Co)		2 weeks	2000 s

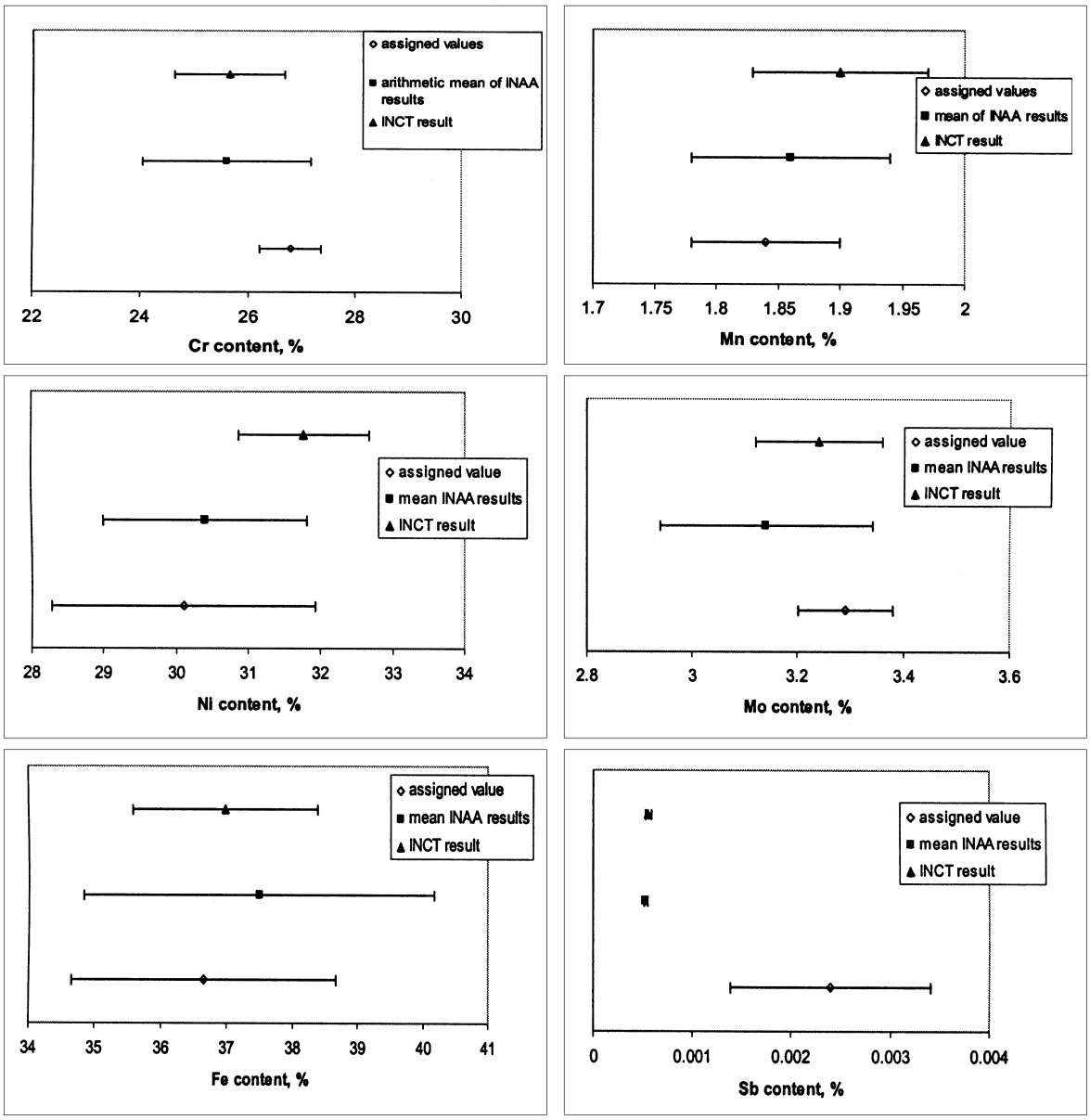

Fig. 1. Comparison of the results obtained by the INCT with the assigned values calculated by the providers from results obtained by atomic spectrometry techniques, and with the arithmetic mean of all INAA results.

In PT exercise conducted in the frame of "NAA Euro-Network", six NAA laboratories from Europe participated in 2010. As test material EURONORM--CRM no. 298-1 Duplex Stainless Steel was chosen. The NAA spectrum of a steel sample after 4 days cooling is presented in Fig. 2. In Table 3 the certified and information values for CRM no. 298-1 [3] are compared to the results obtained in the INCT. As can be seen,

Table 2. Results of analysis of High Alloy Stainless Steel HAAS-1 by INCT

Element	High Alloy Stainless Steel HAAS-1			
	Assigned value		INCT results by INAA	
	Wt.%	u (k = 1)%	Wt.%	u (k = 1)%
As	0.00418	0.00006	0.0040	0.0003
Co	0.039	0.001	0.0413	0.0003
Cr	17.89	1.470	18.37	0.02
Cu	0.191	0.005	0.204	0.002
Mn	0.832	0.107	0.8970	0.0035
Mo	0.292	0.011	0.290	0.003
Ni	12.40	0.170	12.33	0.01
Sb	0.00066	0.00005	0.00075	0.00007
W	–	–	0.00423	0.00022

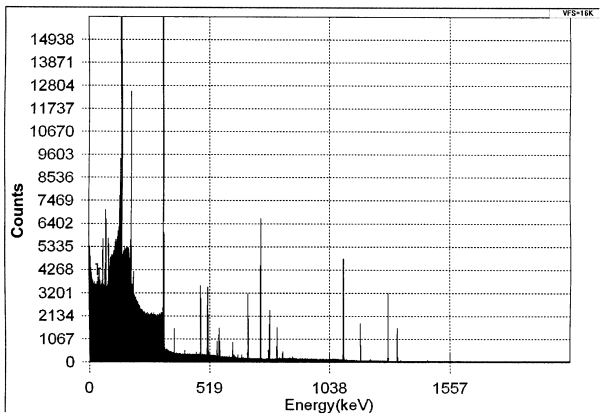

Fig. 2. The NAA spectrum of a steel sample 4 days after cooling, measurement time: 1500 s.

the INAA values were near the center of the certified values. On the basis of the INCT results and estimated standard uncertainties, *zeta*-score was calculated (Fig. 3). All the obtained values are in the range $-1 < zeta < 1$ and this means that the procedure applied in the INCT for standard uncertainty evaluation is correct. The mean values of the experimental data given by all participants using the INAA method were as follows (Cx ± SD), (%, w/w): As: 0.0350 ± 0.0002, Co: 0.056 ± 0.005, Cr: 24.2 ± 1.2, Cu: 0.191 ± 0.025, Fe: 63.59 ± 3.96, Mn: 0.39 ± 0.02, Mo: 3.68 ± 0.30, Ni: 7.35 ± 0.33, Sb: 0.00081 ± 0.00004, W: 0.017 ± 0.0033. *Zeta*-score calculated for all the above-mentioned values is between – 1.0 and 1.0 (Fig. 4). This range delivers proof that the neutron activation analysis gives accurate results. Also, looking at the antimony determination, the delivered data (mean Sb concentration for five laboratories 8.1 ± 0.4 $mg \cdot kg^{-1}$) are in excellent agreement with data listed in the Certificate (mean value: 7.4 ± 0.8 $mg \cdot kg^{-1}$). This confirms that the previous analysis of Sb in SS1 steel were carried out correctly by NAA laboratories.

Looking at the obtained INAA data for steel certified reference materials analysis, it can be noted that this method gives accurate results for the major and trace elements. A comparison of the results from NAA method with the certified/assigned values gives an independent proof that the applied certification/assignment procedure is properly performed. In the case of some elements like antimony, when atomic spectroscopic reference methods [2, 13] give questionable results, INAA can meet requirements of the reference method.

Conclusions

The elaborated INAA procedure has proved its reliability for steel analysis. This can be stated on the basis of results of the participation of INCT in proficiency tests dedicated for European NAA Laboratories. It can be emphasized that INAA results obtained by INCT in the frames of PT/ILC exercises in the years

Table 3. Results of analysis of ECISS[a] for CRM no. 298-1 Duplex Stainless Steel

Element	298-1 Duplex Stainless Steel			
	ECISS Certificate		INCT results by INAA	
	Wt.%	u (k = 1)	Wt.%	u (k = 1)
As	0.0034[c]	–	0.0036	0.0002
Co	0.055	0.001	0.0553	0.0011
Cr	24.72	0.02	24.81	0.58
Cu	0.201	0.002	0.217	0.013
Fe	63.38	0.06	65.97	1.54
Mn	0.398	0.003	0.395	0.009
Mo	3.799	0.013	3.85	0.05
Ni	7.056	0.009	7.19	0.14
Sb	0.00077[b]	–	0.00075	0.00003
W	0.0180[c]	–	0.017	0.002

[a] ECISS – European Committee for Iron and Steel Standardization.
[b] The mean concentration for Sb calculated from the data in the Certificate [3].
[c] Information value.

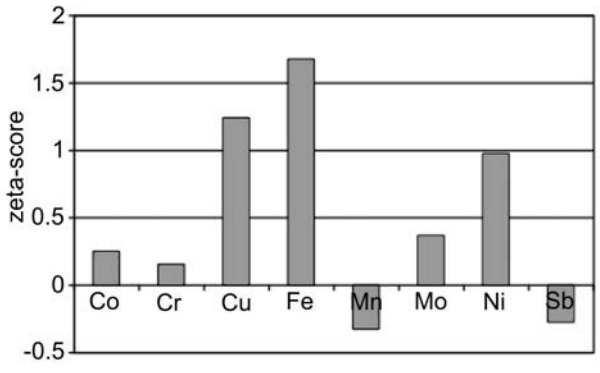

Fig. 3. *Zeta*-score for INCT results for Duplex Stainless Steel.

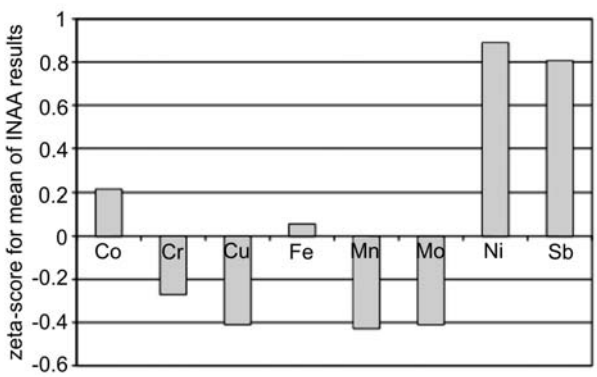

Fig. 4. *Zeta*-score calculated for the arithmetic mean of INAA results delivered by participant laboratories.

2005–2010 agree very well with the consensus/certified values of the investigated steel test materials. In the case of this type of material, INAA can be used for the determination of both major and trace elements which are determined with similar relative standard uncertainty. Obviously, in this type of materials (metal, steel, alloy), characterized by relatively high density or addition elements with high absorption cross sections, the gamma-ray self-absorption occurs and appropriate corrections should be calculated [14, 15]. Nevertheless, INAA is one of the preferred multi-elemental methods for "difficult" samples analysis, because it is free from problems connected with digestion of difficult matrices and potential contamination of a sample from reagents. Unique properties of NAA, i.e. the fact that this is a method based on nuclear properties of individual isotopes of an element and good accuracy at low concentration levels, are the explanation why this technique is often used for certification of the candidate reference materials. For some "difficult" elements, NAA should be taken into consideration as an alternative reference technique instead of atomic spectrometry techniques for certification of CRMs.

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References

1. Cincu E, Craciun L, Manera-Grigore I *et al*. (2009) Application of the INAA technique for elemental analysis of metallic biomaterials used in dentistry. Appl Radiat Isot 67:2133–2136
2. Cincu E, Manera I, Manu V *et al*. (2007) Comparative performance of INAA and other spectroscopy techniques in the elemental analysis of stainless steel materials. J Radioanal Nucl Chem 274:199–205
3. European Committee for Iron and Steel Standardization (2002) Certificate of chemical analysis EURONORM--CRM no. 298-1 Duplex Stainless Steel. Swedish Institute for Metals Research, Stockholm
4. Gervasio APG, Luca GC, Menegario AA, Reis BF, Filho HB (2000) On-line electrolytic dissolution of alloys in flow injection analysis: determination of iron, tungsten, molybdenum, vanadium and chromium in tool steels by inductively coupled plasma atomic emission spectrometry. Anal Chim Acta 405:213–219
5. Granfors M, Gustavsson I (2001) Determination of trace and ultra-trace elements in wet-digested steel using inductively coupled plasma time of flight mass spectrometry (ICP-TOFMS). J Anal At Spectrom 16:1439–1941
6. Ida H, Kawai J (2005) An X-ray fluorescence spectrometer with X-ray generator and a secondary target for the determination of Cr in steel. Spectrochim Acta B 60:89–93
7. Kimura A, Toh Y, Oshima M, Hatsukawa Y, Goto J (2007) Determination of As and Sb in iron and steel by neutron activation analysis with multiple gamma-ray detection. J Radioanal Nucl Chem 271:323–327
8. Liu H, Jiang SJ (2003) Dynamic reaction cell inductively coupled plasma mass spectrometry for determination of silicon in steel. Spectrochim Acta Part B 58:153–157
9. Mackey EA, Becker DA, Spatz RO *et al*. (2004) Certification of NIST Standard Reference Material 1575a Pine Needles and Results of an International Laboratory Comparison. NIST Special Publication 260-156. NIST, Washington
10. Moreira EG, Vasconcellos MBA, Saiki M (2005) Instrumental neutron activation analysis applied to the determination of the chemical composition of metallic materials with study of interferences. J Radioanal Nucl Chem 264:45–50
11. Oss Giacomelli MB, Borba da Silva JB, Curtius AJ (1998) Determination of Mo and Bi in steels by electrothermal atomic absorption spectrometry after complexation and sorption on activated carbon. Talanta 47:877–881
12. Polkowska-Motrenko H, Dybczyński RS, Chajduk E (2010) Certification of reference materials for inorganic trace analysis: the INCT approach. Accredit Qual Assur 15:245–250
13. SIMR (2005) Report on Interlaboratory Comparison of elemental composition in Stainless Steel SS1 determined by laboratories from Belgium, Hungary, Poland and Romania using the INAA analytical technique on the Stainless Steel SS1 received from SIMR within the PT Exercise 2004–2005. Swedish Institute for Corrosion and Metals Research, Stockholm
14. Tian W, Ni B, Wang P, Cao L, Zhang Y (2001) Metrological role of neutron activation analysis. IA. Inherent characteristics of relative INAA as a primary ratio method of measurement. Accredit Qual Assur 6:488–492
15. Tian W, Ni B, Wang P, Cao L, Zhang Y (2002) Metrological role of neutron activation analysis. IB. Inherent characteristics of relative INAA as a primary ratio method of measurement. Accredit Qual Assur 7:7–12
16. Zeisler R, Greenberg RR, Mackey EA, Murphy KE, Spatz RO, Tomlin BE (2009) Challenges and success in the use of neutron activation analysis procedures for value assignment of animal serum and bovine liver Standard Reference Materials. J Radioanal Nucl Chem 281:11–15
17. Zeisler R, Lindstrom RM, Greenberg RR (2005) Instrumental neutron activation analysis: a valuable link in chemical metrology. J Radioanal Nucl Chem 263:315–319