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Comparative performance of INAA and other spectroscopy techniques in the elemental analysis of stainless steel materials

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Samples of high alloy Stainless Steel SS 1 were analyzed by instrumental neutron activation analysis (INAA) at 5 research institutes in 4 European countries within the frame of an Inter-Laboratory Comparison (ILC) exercise aiming at checking if the results were independent of the standardization methods, and if INAA was accurate enough to contribute to certification. The mean element concentration values yielded by INAA were also compared with mean values obtained by atomic emission spectroscopy techniques at other laboratories that took part in the International Proficiency Testing organized by KIMAB Institute of Sweden, producer of the SS 1. The performances of the nuclear and atomic techniques were compared in terms of the *z*-score values calculated for 11 element concentrations evaluated by the two analytical ways. Finally, consideration is given to the ways in which highest accuracy and precision can be ensured for certifying stainless steels as CRMs.

Introduction

Neutron activation analysis (NAA) has long been known as a powerful analytical tool for determining the elemental composition of various types of materials and quantifying element concentrations at low (trace to ultratrace) levels in samples from almost every field of scientific or technical interest. Numerous papers have published in this field, including a whole new lot of communications (more than 280) presented at MTAA-11, the International Conference on Modern Trends in Activation Analysis held in Guildford, UK, in 2004. They all proved that NAA coupled with high resolution gamma-ray spectroscopy was and remained one of the most sensitive analytical techniques in material investigation and had a broad variety of applications. Moreover, it has been shown that instrumental NAA (INAA) due to its accuracy and reliability[1] matches the definition of what is called a primary ratio method of measurement.[2,3]

The analytical techniques most widespread for certification in the iron and steel industry are X-ray fluorescence spectrometry (XRF), arc/spark optical emission spectrometry (OES), and glow discharge – OE spectrometry (GDS-OES). They all are atomic emission spectroscopy (AES) techniques relying on the analysis of radiation emitted by atoms from the surface layers of an investigated material that is excited by specific procedures. By contrast, nuclear INAA investigates the whole sample, as its entire volume is irradiated in the thermal neutron field of a nuclear reactor without any physicochemical or microstructure alteration. For this reason and given the performance of INAA, we assumed its application could improve the elemental composition information usually obtained by AES techniques, especially in the case of minor and trace elements. INAA may therefore be useful for certifying stainless steel materials.

This work was aimed at checking this assumption on a certain type of stainless steel (SS) by using one of the most accurate ways of determining elemental compositions – Inter-Laboratory Comparisons (ILC) and/or Proficiency Tests (PT) performed by labs employing the same or/and different analytical techniques and provides evidence of the INAA performance, as established within a network of five INAA laboratories in four European countries: Romania (2), Belgium (1), Hungary (1), and Poland (1).

The analyzed material was a high alloy steel (SS 1) produced at the Swedish Institute for Corrosion & Metals Research, KIMAB, which launched an international PT exercise in 2004 to accurately evaluate its elemental composition. Eighteen out of 19 laboratories taking part in the PT employed the atomic spectrometry techniques mentioned above.

ACTIVA-N laboratory (IFIN-HH, Romania), which joined the KIMAB PT exercise in 2004, later developed a network collaboration with four other INAA laboratories in Belgium (SCK-CEN, Belgian Nuclear Research Centre, Mol), Hungary (INT, Budapest), Poland (INCT, Warsaw), and Romania (INR, Pitesti).

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Our objective was to check the reproducibility of INAA, the influence of the various standardization methods, the consensus of results, and the usefulness of our own network for analyzing and certifying stainless steels. The comparative performance of the nuclear and atomic emission spectroscopy techniques was evaluated using the Z-score criterion[5–7] calculated for the mean values of 11 element concentrations, as obtained in this work and given in the June 2005 KIMAB Report.[4]

Experimental

The high alloy Stainless Steel (SS 1) sample we received from KIMAB consisted of small chips of 2–3 mm each. To activate the nuclei of the elements in the sample matrix, amounts from 45 to 150 mg were irradiated by each laboratory in the specific conditions of its nuclear reactor. Each participant employed its own calibration and standardization procedures.

Laboratory 1 used a complex procedure involving chemical treatment: the elemental standards were prepared from appropriate amounts of spectral purity elements or oxides by dissolving them in aqua regia or nitric acid of high purity and weighing the obtained solutions. Aliquots of (10 to 50) μg of the standard solutions were weighed in polyethylene vials and air-dried in a laminar flow box; the irradiated package contained samples sandwiched between standards, CRMs, and blanks.

Laboratory 2 used an in-house developed standardization method similar to the $k_{0,\mathrm{Au}}$ one,[8] but using Zr instead of Au.

Laboratories 3 and 4 used external standards of certified stainless steel materials that were irradiated together with the samples (packed as sandwiches) and analyzed identically.

Laboratory 5 used INAA based on single element solution standards traceable to NIST, and a SMELS sample to check and validate the experimental protocols.

The neutron flux in each reactor ranged between 10^{12} and 10^{13} $\mathrm{n \cdot cm^{-2} \cdot s^{-1}}$, and the analyses of the gamma-ray spectra of the radioactive samples and standards were carried out using high resolution HPGe spectrometers according to the routine practice of each laboratory. Details on the procedures employed by each participant for sample preparation, irradiation, gamma-ray spectroscopy analysis, and result processing may be found in other works.[9–14]

Results

The INAA method mainly relied on the spectrometric analysis of delayed gamma-rays from medium and long half-life nuclides ($T_{1/2}$>2 h), but some short-lived nuclides (^{52}V, $T_{1/2} = 3.74$ min) were also analyzed at some participant laboratories. Finally, 11 elements – $_{23}$V, $_{24}$Cr, $_{25}$Mn, $_{26}$Fe, $_{27}$Co, $_{28}$Ni, $_{29}$Cu, $_{33}$As, $_{42}$Mo, $_{51}$Sb, and $_{74}$W – were identified, and their concentrations were evaluated. Thermal neutron activation (n_{th}, γ) reactions were studied in almost every case, but the fast neutron activation reaction ^{58}Ni(n_f, p)^{58}Co was also used to evaluate Ni concentration at Labs 2 and 4. The number of replicates varied from 3 (Lab 2) to 4 (Labs 1, 3, 4, 5), and each replicate was measured 3 to 5 times. The radioisotopes generated by the above elements emitted a number of γ-rays, 1 (^{52}V, ^{51}Cr, ^{58}Ni, ^{64}Cu, ^{122}Sb) to 5 (^{187}W) of which were intense enough to be analyzed. The same number of measurements of the same γ-rays was performed on the reference standards at each laboratory. To evaluate the concentration of each element, we analyzed the γ-rays specific of its corresponding radioisotope; their total number (as given by: No. of labs × No. of replicates × No. of measurements per replicate × No. γ-rays analyzed per measurement) varied from 32 (for V) to over 100, thus giving enough consistency to every assignment.

The element concentration values obtained at the INAA laboratories are shown in Table 1 together with the calculated standard deviation S_{n-1} values (for $k = 1$), a parameter which best reveals the spread of the results.

For the sake of comparison, we also showed in Table 1 the mean concentrations values of the same elements and their associated absolute uncertainties (for $k = 1$), as established by KIMAB from the results of some PT participant laboratories[4] that used Other (atomic) Techniques (OT).

The values corresponding to the empty places were not taken into account in calculating the mean concentration values as they were found as outliers when applying the Dixon test.

Figure 1 illustrates the elemental analysis performance of the nuclear technique and the 3 atomic emission ones; the element concentration values determined by the two analytical approaches are represented on the same scale, except for Sb. The uncertainty limits (s, 2s, 3s) are indicated by ‘error bars’ added to the INAA results; the limits given by (u, 2u, 3u) are marked by ‘error bars’ added to the KIMAB values. Where the maximum range corresponding to the 3u limit was too large, only the limit given by u was represented.

Table 1. Element concentrations in the High Alloy Stainless Steel SS 1 (sample *x*) determined by INAA and by other analytical techniques*

Crt. No. (*i*)	Element	Other techniques (mean values)[4]	u_i^{Kimab} (abs) ($k = 1$)	Concentrations C_i^x of the elements *i* determined by INAA in the sample *x* by the laboratories [1–5] participating in the ILC Exercise						
		C_i^{Kimab}, %		C_i^x, % [1]	C_i^x, % [2]	C_i^x, % [3]	C_i^x, % [4]	C_i^x, % [5]	$C_{i_{\text{mean}}}^x$, %	Std. Dev. s_{n-1} (abs) ($k = 1$)
1	Fe	36.66	2.01	37.00	–	37.5	36.71	35.89	36.78	0.67
2	Mn	1.84	0.06	1.90	1.817	1.88	1.825	1.78	1.840	0.045
3	Cr	26.80	0.57	25.67	26.19	25.6	26.84	26.69	26.2	0.6
4	Co	0.035	0.011	0.038	0.039	0.0398	0.0387	0.040	0.0391	0.0008
5	Cu	0.940	0.079	Not identified	0.945	1.08	0.924	0.99	0.985	0.069
6	W	0.025	0.017	0.011	0.013	0.0081	0.012	0.0089	0.0106	0.002
7	As	0.002	0.002	0.00273	–	0.00258	0.00328	0.0030	0.0029	0.0003
8	Mo	3.29	0.09	3.24	–	3.24	3.33	3.24	3.263	0.045
9	Ni	30.10	1.83	31.76	31.11	29.4	29.19	30.34	30.36	1.10
10	Sb	0.0024	0.001	0.00056	0.000547	0.00052	0.00054	0.00056	$54.5 \cdot 10^{-5}$	$1.7 \cdot 10^{-5}$
11	V	0.064	0.007	Not identified	Not identified	0.0704	Not identified	0.0634	0.067	0.005

* The element concentrations determined by other analytical techniques (XRF, OES, GDS) are taken from the Report published by the KIMAB Institute.[4]
The empty places correspond to values found as outliers (see the text).

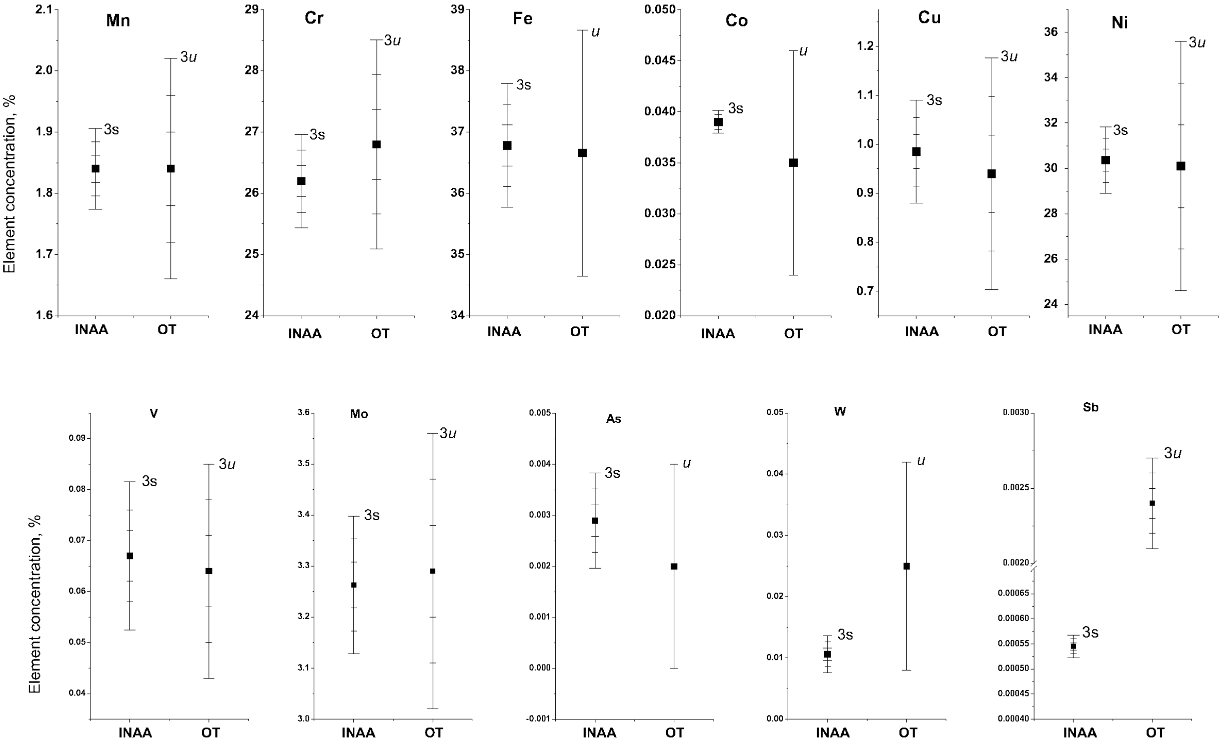

Fig. 1. Mean values of the element concentrations determined by 5 INAA laboratories from 4 European countries (this work) compared with mean values determined by laboratories that employed Other (atomic) Techniques (OT).[4] The associated uncertainty values corresponding to each case (standard deviation *s* – in case of INAA, and *u* –values in case of OT data) are also shown. When the maximum limit (3*u*) was too large, only the value *u* for $k = 1$ was indicated

For Sb, there was a broad discrepancy between the results yielded by the nuclear technique and the atomic ones. We had to break the ordinate scale in order to compare both results on the same graph.

The data in Fig. 1 show that the range of maximum uncertainty (3s) of the mean INAA values is generally lower than the range of maximum uncertainty (3*u*) associated to the results obtained by OT, even considerably lower in the cases of Co, Sb, and W.

Although the number of laboratories was not high, the *z*-score parameter is appropriate for evaluating and comparing the analytical performance of the nuclear and non-nuclear approaches. The expression of the *z*-score parameter, according to the reference standards[5,6] and documents,[7] is the following:

$$z = (X_{\text{Lab}} - X_{\text{Ref. assigned}})/s \qquad (1)$$

where X_{Lab} is the element concentration value provided by each INAA laboratory; $X_{\text{Ref.assigned}}$ is the value assigned as 'Reference', and *s* is the 'fitness-for-purpose' standard deviation,[6,7] the expression of which was established in this work as s_{n-1}, as this is the most relevant parameter with regard to the spread of the experimental results.

The s_{n-1} values were calculated for each element from the data provided by the INAA laboratories (Table 1). The *z*-score values were then calculated for each element concentration in two cases: (a) where the mean values of the element concentrations obtained by the atomic (OT) techniques were assigned as 'Reference values' in the *z*-formula [Eq. (1)]; (b) where the mean concentration values obtained by INAA (values of $C^{x}_{i_{\text{mean}}}$ in Table 1) were assigned as 'Reference values' in Eq. (1).

Figure 2 is a representation of the *z*-score values for each of the earlier mentioned variants: the *z*-score values corresponding to case (a) are represented by stars (∗), and those corresponding to case (b) are represented by dots (•). The dashed line in each graph indicates the average value of the *z*-scores for each element (labeled $z_{\text{OT-Av}}$) calculated in the case (a); it illustrates the discrepancy between the INAA value and the 'Reference' value; $z_{\text{OT-Av}}$ is ≅0 where there is no discrepancy.

Significant discrepancies of ($z_{\text{OT-Av}}$) were found for the low-level concentration elements: Co ($z_{\text{OT-Av}} = 5.0$), As ($z_{\text{OT-Av}} = 3.6$), W ($z_{\text{OT-Av}} = -8.1$), and Sb ($z_{\text{OT-Av}} = -111.7$).

In the case (b), the *z*-score values are distributed around the 'concentration 0' for every element, and the average $z_{\text{OT-Av}}$ values were found ≡0, as expected.

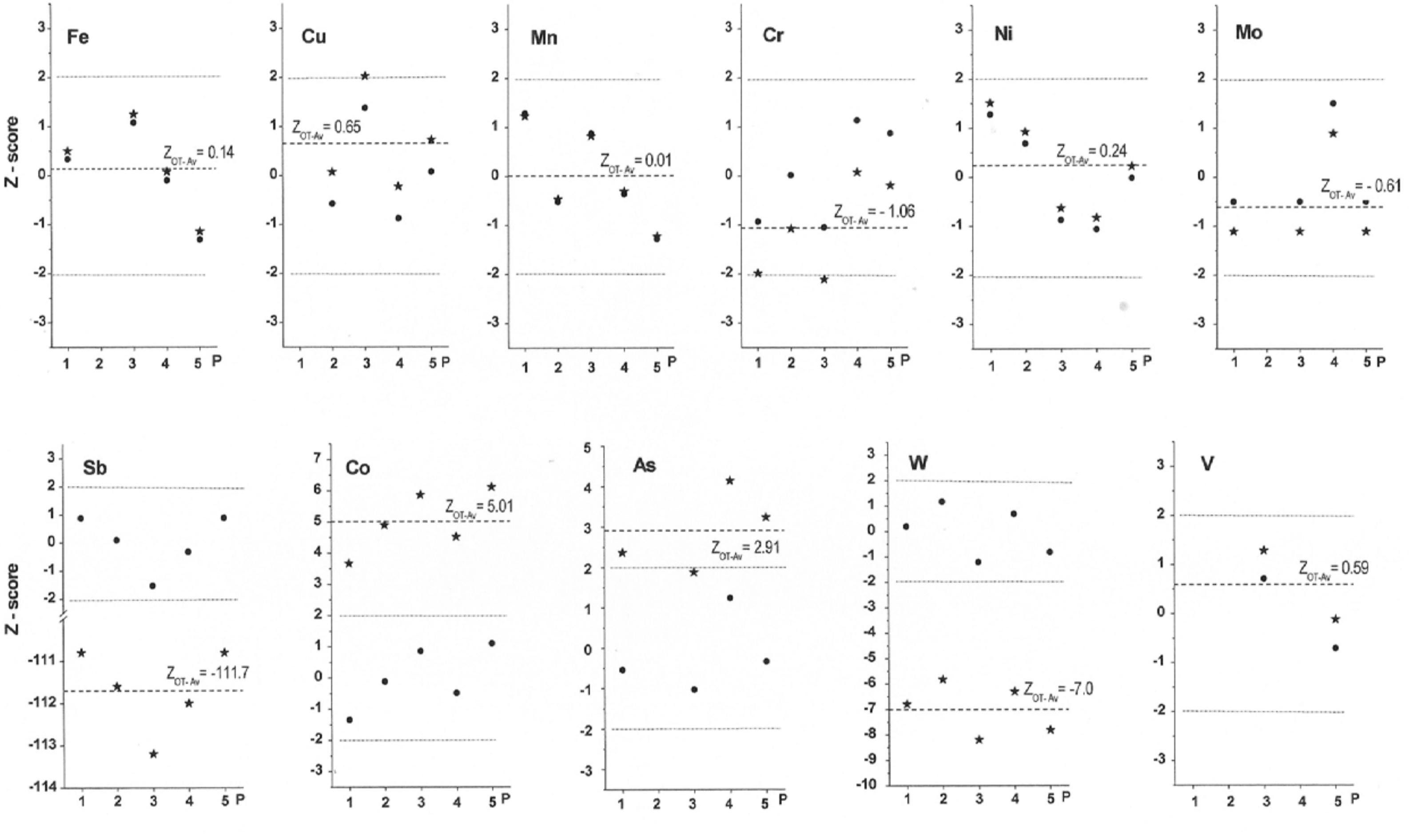

Fig. 2. *Z*-score values of the mean element concentration data determined by INAA laboratories, calculated when the reference values correspond: (a) to the atomic (OT) techniques[4] (*), and (b) to the average values of the INAA results (•). The range of accepted limits ($-2 \leq z \leq 2$), as well as the average *z*-score values $\{z_{OT-Av}\}$ in case (a) are also shown; in case (b) $z_{OT-Av} \cong 0$. P is the participant code number

Discussion

The INAA results obtained at five laboratories in four countries showed very good general consistency with one another (Fig. 2 dots), as the *z*-score values of 7 elements (V, Cr, Mn, Fe, Ni, As, W) were ≤ 1.3, and those of Co, Cu, Mo, Sb were <1.55, lower than the limit of accepted results ($z=2$). Agreement between the INAA results was remarkable for Fe, Mn, Cr, Co, Mo, Ni, and Sb and quite good for V, Cu, As, and W**.** The fact that each laboratory has the Quality Management System implemented in its activity, and that four of them have already got accreditation according to the EN ISO/IEC Standard of Competence[15] accounts for this good performance.

One should also notice that the INAA data are quite consistent with those obtained by the atomic spectrometry techniques (Figs 1, 2). This agreement is particularly evident for Fe, Cu, Mn, Cr, Ni, Mo, and V where the *z*-scores of both types of data (stars and dots) are ≤ 2 (Fig. 2).

The differences only appear in the case of the low-level elements: Co, As, Sb, and W; the broadest discrepancy ($z_{\text{OT-Av}}=-111.7$) was found for Sb. Taking into account the low content of Sb, but also the good agreement in the concentration range of 10^{-5} g/g (Table 1) between results provided by the INAA laboratories, one may conclude the INAA results are more reliable, as the detection limit is much more favorable to INAA than to the atomic techniques.

In all cases the INAA data are similarly distributed (higher or lower) as compared with the atomic OT data, but no systematic deviation (of the same sign and with close values of the *z*-scores for all elements) was noticeable.

Such results may lead us to assume that the discrepancies originate in either the atomic techniques, since they opera s_{n-1}te in the surface layers of the investigated sample and therefore, are more or less dependent on its physico-chemical characteristics and treatment, or in the standardization procedures.

All the aspects discussed above* support the conclusion that INAA results obtained at different laboratories can agree very well with one another, although the labs themselves differ in terms of irradiation and γ-ray analysis conditions, standardization methods used for element concentration, and uncertainty evaluation procedures. At the same time, the results (Fig. 1) clearly show that INAA uncertainty values for the low-level elements are lower than those obtained by the atomic spectrometry techniques; this is important for a highly accurate determination of all element concentrations in stainless steels, including those of the low-level elements. The atomic analytical spectrometry techniques (XRF, Arc/Spark OES, GDS-OES) instead have the major advantage of yielding results much more rapidly than INAA.

Conclusions

The above results add ‘fresh’ evidence to the known literature[17] proving that INAA is a high-performance analytical technique that can provide reliable information on the elemental composition of materials, including stainless steels. Compared with the atomic spectrometry techniques, the INAA results demonstrated a very high accuracy for both major and trace elements in the SS 1 material, and superior performance, with lower detection limits and lower uncertainty, for the trace elements. The remarkable consistency of the experimental results obtained at five laboratories in four different countries proves the particular usefulness of analytical networks in the analysis and certification of materials by Inter-Comparison Exercises, especially of those materials that are of interest in industry and medicine.

However, the best way to ensure top accuracy and precision in determining the elemental composition of stainless steels, especially in certifying such materials as CRMs, is to use all results provided by INAA and the atomic spectrometry techniques, in order to increase the statistic relevance of the experimental data; the only condition is that each Laboratory should ensure measurement traceability and apply an internal selection of intermediary results based on statistical criteria.

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* Preliminary results of this work were discussed at the International Workshop on “Applications of the Ionizing Radiation in Industry, Health and Environment, IWIRAD–2005”, June 20–21, Bucharest, Romania.[16]

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