MEASUREMENT UNCERTAINTY ASSESSMENT IN THE INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF CHROMIUM, MANGANESE, MOLYBDENUM AND NICKEL IN STEEL

Edson Gonçalves Moreira, Marina Beatriz Agostini Vasconcellos and Mitiko Saiki

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
emoreira@ipen.br

ABSTRACT

The establishment of measurement traceability and the use of internal quality control procedures and validated methods of analysis are requirements for accreditation under ISO/IEC 17025 international standard. Measurement uncertainty is one of the performance characteristics that are assessed in the validation process and its expression in a standardized form is a requirement for result reliability as it imposes implications to the interpretation of analytical results. In this work, sample mass, elemental standard mass, element decay constant and sample and elemental standard activities were identified as uncertainty sources for the relative method of instrumental neutron activation analysis. The contribution of these sources to the expanded standard uncertainty in the concentration of Cr, Mn, Mo, and Ni in steel was assessed and sample and elemental standard activities were identified as the major contributions.

1. INTRODUCTION

Reliable analytical methods are required for compliance with national and international regulations in every analytical field. Chemical analysis laboratories must ensure that their results are fit for purpose, i.e., that their results are produced with the required quality. The ISO/IEC 17025 international standard specifically addresses the establishment of the measurement traceability, only achievable if measurements are performed using internal quality control procedures and validated methods of analysis [1].

The validation of a method of analysis makes use of a set of tests to establish and document the performance characteristics of the method, in order to demonstrate that it is fit for a particular purpose. Typical performance characteristics are: applicability, selectivity, calibration, accuracy, precision, recovery, operating range, limit of detection, limit of quantification, sensitivity, ruggedness and uncertainty [2].

Instrumental Neutron Activation Analysis, INAA, is a mature technique for multielement analysis, suitable for diverse matrix materials. The Neutron Activation Laboratory, LAN, of Nuclear and Energy Research Institute, IPEN/CNEN-SP, has been using INAA successfully in studies ranging from environment monitoring and reference material certification to food bulk analysis and archeology, as confirmed by frequent interlaboratory and proficiency trials.

The process of uncertainty assessment includes the specification of the measurand, the identification of uncertainty sources, the quantification of the individual standard uncertainties, the calculation of the combined standard uncertainty, and the presentation of the combined expanded uncertainty [2]. In this work, the uncertainty sources for the relative method of INAA applied to steel samples were identified according to international accepted instructions, as part of the Quality Assurance System implementation at LAN [3]. The identified uncertainty sources were sample mass, elemental standard mass, element decay constant and sample and elemental standard activities [4, 5, 6]. In this last case, the various uncertainty sources for the irradiation step and for the gamma-ray spectrometry measurement were considered and finally, the contribution of the uncertainty sources to the expanded standard uncertainty in the concentration of Cr, Mn, Mo and Ni in steel was assessed.

An alloy steel sample from the CCQM-K33 Key Comparison (Consultative Committee for Amount of Substance – Metrology in Chemistry) of the International Bureau of Weights and Measures, BIPM, was used for the uncertainty assessment. As the participants of the CCQM Key Comparisons are the designed National Metrology Institutes in the field of application, LAN analyzed the same steel sample in the CCQM-P56 Pilot Study, where other laboratories may participate.

1.1. Specification of the Measurand

The measurand is the concentration in mass fraction (% w/w) of Cr, Mn, Mo and Ni in a low alloy steel (CCQM-P56, sample bottle No. 190) by the relative method of INAA.

In the relative method of INAA, where the unknown sample is irradiated simultaneously with standards of the elements of interest, the concentration C is determined by means of the following equation:

$$C \quad = \quad \frac{m \, A_u \, e^{\lambda(t_u - t_s)}}{M \, A_s} \tag{1}$$

where:
m = mass of the element to be determined in the standard;
M = mass of the sample;
A_u = activity of the unknown sample;
A_s = activity of the elemental standard;
t_u = unknown sample decay time;
t_s = elemental standard decay time;
λ = decay constant, where $\lambda = \dfrac{\ln 2}{t_{1/2}}$ and $t_{1/2}$ is the element half life;

1.2. Identification of Uncertainty Sources

Various contributions to the uncertainty in sample mass, elemental standard mass, sample and elemental standard decay correction and sample and elemental standard activities were considered and are treated in the discussion section of this paper.

2. EXPERIMENTAL

2.1. Sample and Elemental Standard Preparation

About 0.050 g of low alloy steel sample was weighed in a properly cleaned polyethylene vial using a Shimadzu AEM-5200 analytical balance. Elemental standards were prepared by pipetting standard element solutions (Spex) onto Whatman paper filters, using a Jencons variable volume pipettor. For Mo, the original solution (NIST SRM 3134 Mo standard solution) was diluted prior to pipetting and pipettor and volumetric flask contributions to the uncertainty assessment were considered. After drying, paper filters were kept in polyethylene vials with the same geometry of the sample. Six replicate results were obtained in this study.

2.2. Irradiation and Element Determination

Two series of irradiation were used, according to the half lives of the radionuclides to be determined. Sample aliquots were simultaneously irradiated with elemental standards. For Mn determination, a 15-s irradiation at the Pneumatic Station of IEA-R1 Nuclear Research Reactor at IPEN under 10^{11} n cm^{-2} s^{-1} thermal neutron flux was used. ^{56}Mn was measured for a 30-min period, 1 hour after irradiation. For determination of the other elements, a 30-min irradiation at 10^{12} n cm^{-2} s^{-1} thermal neutron flux was used. ^{99}Mo was measured for 1 hour, after a 2-day decay period, while the long lived ^{51}Cr and ^{58}Co (for Ni determination) radionuclides were measured also for 1 hour, after a decay period of one month. Samples and standards were measured using a CANBERRA GX 2020 HPGe detector (coupled to a CANBERRA multi-channel system and electronics) with a 1.70 keV resolution for 1332 keV gamma ray peak of ^{60}Co. Analysis of gamma ray spectra and element concentration was calculated applying in-house software.

3. RESULTS AND DISCUSSION

3.1. Quantification of Uncertainty Components

3.1.1. Sample mass

In Table 1 the contributions for sample mass combined standard uncertainty (u_M) are summarized. The repeatability contribution, a Type A uncertainty, was taken from a control chart for the measurements of a 0.5 g standard weight, with n = 60. The other contributions were taken from the balance calibration certificate.

Table 1. Contributions for sample mass combined standard uncertainty, u_M

Uncertainty source	Uncertainty, g	Probability distribution	Factor	Standard uncertainty, g
Repeatability	0.00003	Normal	1	3.0×10^{-5}
Readability	0.00001	Rectangular	$1/2\sqrt{3}$	2.89×10^{-6}
Calibration	0.00000^a	Normal	2	0
Eccentricity	0.00002	Rectangular	$1/2\sqrt{3}$	5.77×10^{-6}
Combined uncertainty				3.07×10^{-5}

a. expanded uncertainty, k = 2.

3.1.2. Elemental standard mass

The uncertainty in the element mass in the elemental standards depends on the certified concentration values for the standard solutions (taken from the solution certificates), and on the volume of the solution pipetted onto paper filters. Volume repeatability was achieved by a series of weightings of the pipettor dispensed water volume (V = (98,47 ± 0,16) μL, n = 10). The pipettor producer states that, for a 50 μL volume, the imprecision is 0,11 % of the volume. This was taken as the uncertainty for the 100 μL used. In the estimation of the uncertainty from volume expansion due to differences in the temperature of the laboratory and the temperature at the time of the pipettor calibration, a 4 °C difference and a liquid expansion coefficient of 2.1 x 10^{-4} °C^{-1} were taken. In Table 2 the combined standard uncertainties for element mass in elemental standards (u_m) are summarized, with contributions of pipetted volume and concentration uncertainties.

Table 2. Contributions to the combined standard uncertainty of element mass in elemental standards, u_m

Element	Concentration[a], mg L^{-1}	Pipetted volume, μL	Element mass, μg
Cr	1002.5 ± 3	98.47 ± 0.095	98.72 ± 0.18
Mn	1004 ± 3	(98.47 ± 0.095) x 2	197.73 ± 0.33
Mo	1261 ± 4.14	98.47 ± 0.095	124.16 ± 0.24
Ni	10039.5 ± 30	98.47 ± 0.095	988.59 ± 1.76

a. Expanded uncertainty, k= 2;   Mo expanded uncertainty estimated after original solution dilution.

3.1.3. Decay constant

The contribution of the decay constant (u_d) depends on the uncertainty of the half lives of the elements [7, 8]. Half lives were converted to minutes and uncertainties in decay constant were propagated as exponential uncertainties. Uncertainties due to the decay time of sample and elemental standards may be neglected for the radionuclides under consideration.

3.1.4. Sample and elemental standard activities

There are various sources of uncertainty in sample and elemental standard activities, some are due to the irradiation process and others due to gamma-ray spectrometry measurement:

3.1.4.1. Irradiation

- **Irradiation geometry differences**
This contribution is due to neutron flux differences inside the irradiation capsule. From a flux density calibration certificate [9], this contribution was estimated as 0.18 % of sample and elemental standards activities, for the irradiation site and geometry used in this work.

- **Nuclear reaction interferences**
In the analysis of metallic materials by INAA, nuclear reaction interferences may present an important contribution. In the case of steel, Mn may suffer interference from fast neutron

reactions from Fe and Co. In previous studies, it was observed that a second order interference of Cr in Mn determination and a primary interference of Fe in Cr were negligible [10]. For the 846 keV energy of ^{56}Mn, the apparent mass of Mn formed from the irradiation of 1 g of Fe and Co are (27.6 ± 1.7) µg g^{-1} and (4.7 ± 1.2) µg g^{-1}, respectively. From the mass sample of 0.050 g and considering a 90% mass fraction of Fe and a 0.05 % mass fraction of Co in a low alloy steel, the uncertainty in activity from the interference of Fe in Mn was estimated as 0.846 cps and the interference of Co in Mn as 1.78 x 10^{-4} cps.

Other sources or uncertainty in the irradiation as neutron self shielding and scattering differences, neutron spectrum variations in time and space, volatilization losses during irradiation and the duration of irradiation may be considered negligible for the elements under investigation, the matrix and irradiation scheme used.

3.1.4.2. Gamma-ray spectrometry measurement

- **Counting statistics**

The counting statistics component to uncertainty is available from the measurement result as the square root of the measured activity, as it follows the Poisson distribution. Usually, this is the most important contribution to activity uncertainty in INAA.

- **Gamma-ray self shielding**

Gamma-ray self shielding is negligible in most cases, but in steel analysis, it might play an important role. Scattering differences may be important for low Z elements and can be considered negligible for the elements under investigation. In a gamma-ray self shielding study, using europium as gamma-ray source and a metallic material as shielding, it was observed that the shielding is higher for lower gamma ray energies. For the samples under investigation, the uncertainty in the activities were estimated as 0.37 % for 140 keV (Mo); 0.28 % for 320 keV (Cr); and 0.37 % for 810 keV (Ni) and 0.24 % for 846 keV (Mn).

Other sources of uncertainty in the gamma-ray spectrometry as counting geometry differences, gamma-ray interferences, pulse pile-up losses, duration of counting and dead time effects were kept to a minimum or are irrelevant for the elements under investigation and were neglected in this study.

The contributions to the combined standard uncertainties of sample and elemental standards activities (u_{A1} and u_{A2}, respectively) are presented in Fig. 1 as percentage of the total activity. Counting statistics was the major contribution for the activities of sample and elemental standards. For Mo, gamma-ray self shielding contribution is comparatively more important than the observed for the other elements due to the lower energy of the analytical peak used.

3.2. Determination of Combined Standard Uncertainty and Expanded Uncertainty for Mass Content in Steel by INAA.

The standard uncertainties from the relevant sources of uncertainty were combined, using the relative method, yielding the combined standard uncertainty, u_c, for the concentration of Cr, Mn, Mo and Ni in steel. The contributions to the combined standard uncertainties are summarized as a percentage of the concentration in Fig. 2. Sample and elemental standard
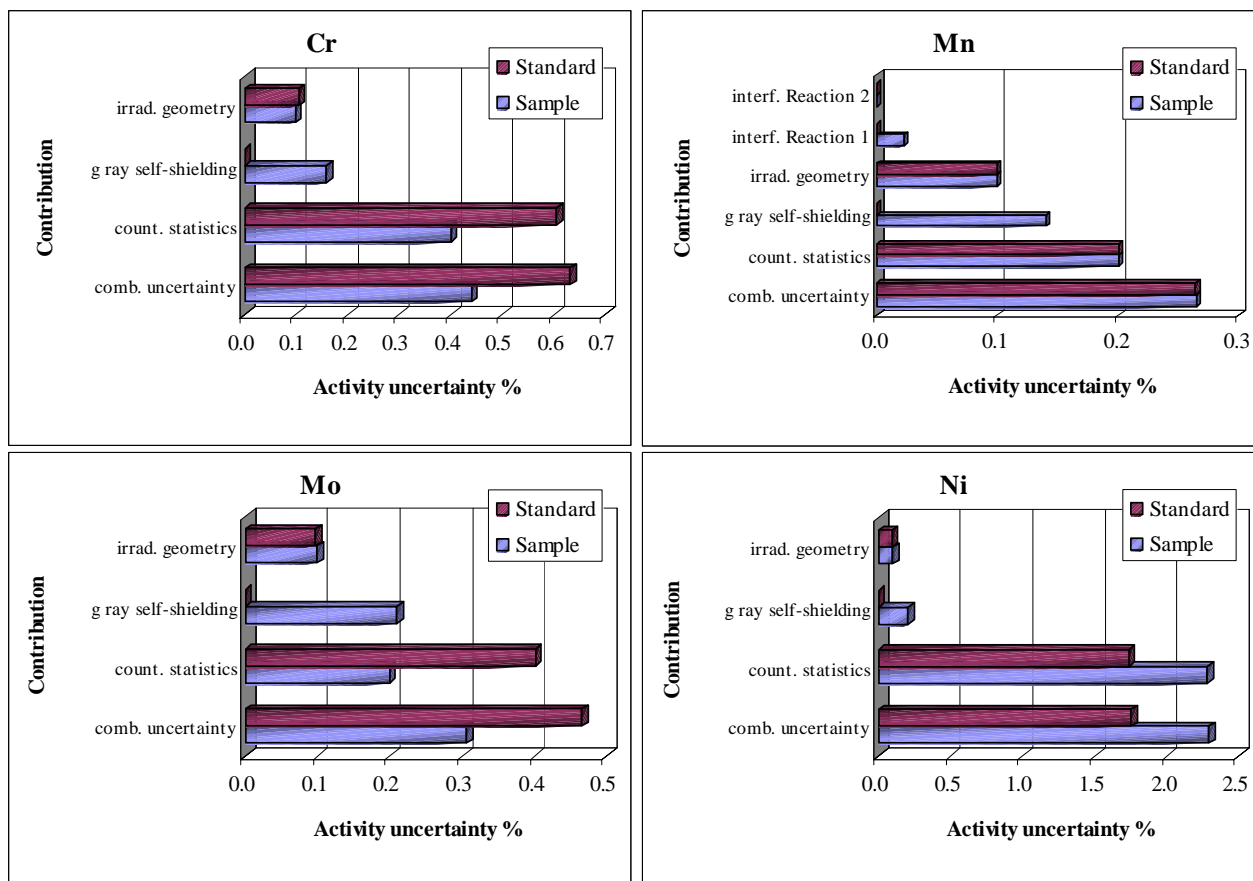
Figure 1. Contributions to the combined standard uncertainty in sample and elemental standards activities.

activities were the major contributions to the combined standard uncertainty in the concentration of Cr, Mo and Ni. In the case of Mn, due to the high counting rates of ^{56}Mn that are obtained in the shorter irradiation procedure, the concentration of the element in the Mn standard was the major contribution to the uncertainty in the concentration.

The expanded uncertainty, U, was determined from the combined standard uncertainties using the expression U = k u_c, with a coverage factor k = 2, which gives a level of confidence of approximately 95 %. Expanded uncertainties were lower than 1 % for Cr, Mn and Mo concentration, showing the suitability of the used method for steel bulk analysis. For Ni, the relative expanded uncertainty is lower than 3 %, as Ni is not a very favorable element to be determined by INAA due to the lower neutron capture cross section for the (n, p) reaction used.
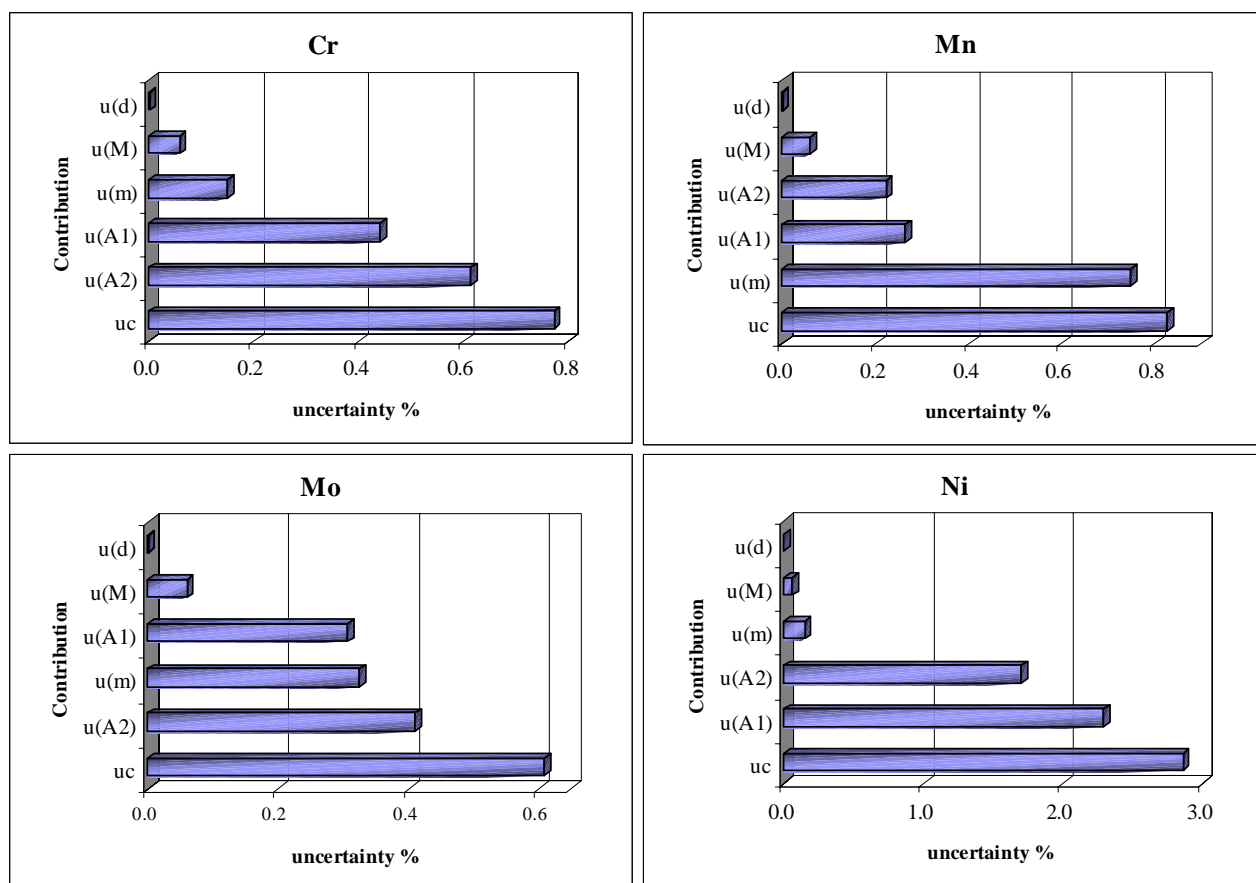
Figure 2. Sample mass (u_M), elemental standard mass (u_m), decay constant (u_d), sample activity (u_{A1}) and elemental standard activity (u_{A2}) contributions to the combined standard uncertainty (u_c) in the concentration of Cr, Mn, Mo and Ni in steel sample by INAA.

Table 3. Concentration of Cr, Mn, Mo and Ni in steel sample obtained in this work by INAA and from CCQM-K33 Key Comparison [11]

Element	Concentration, % (w/w)		Relative Error, %
	This work, INAA[a]	CCQM-K33	
Cr	0.5276 ± 0.0083	0.5091 ± 0.0030	3,7
Mn	0.5121 ± 0.0085	0.5063 ± 0.0016	1,5
Mo	1.029 ± 0.013	1.0393 ± 0.0058	-1,0
Ni	2.63 ± 0.15	2.5490 ± 0.0123	3,2

a. Reported uncertainties are expanded uncertainties, calculated using a coverage factor of 2, which gives a level of confidence of approximately 95 %.

3.3. Element Concentration in the Steel Sample by INAA

The results obtained in this work for the concentration of Cr, Mn, Mo and Ni in steel are presented in Table 3, with their expanded uncertainties, as well as the results from the CCQM-K33 Key Comparison Report [11]. Relative errors lower than 4 % were obtained, demonstrating the accuracy of the INAA technique used. In the participation of LAN in the CCQM-P56 Pilot Study, gamma-ray self shielding and irradiation geometry contributions to the expanded uncertainty were overestimated. Using an improved experimental design for the assessment of these contributions, the uncertainty results reported in this paper were assessed. Estimated uncertainties are still higher than those reported in the key comparison. However, they are similar to uncertainties reported by individual CCQM-K33 participating laboratories and to the uncertainties reported by the other CCQM-P56 Pilot Study participant, which also used an INAA technique.

3. CONCLUSIONS

This paper shows the steps involved in the expanded uncertainty assessment for the concentration of various elements in steel obtained by the INAA relative method. With a better understanding of the various sources of uncertainty, it is possible to address the most important ones in order to minimize their contributions and to improve the quality and confidence on the analytical results.

ACKNOWLEDGMENTS

REFERENCES

1. International Standard Organization, "General Requirements for the Competence of Testing and Calibration Laboratories," ISO/IEC 17025:1999.
2. M. Thompson, R. Ellison, R. Wood, "Harmonized Guidelines for Single-laboratory Validation of Validation of Methods of Analysis (IUPAC Technical Report)," *Pure Appl. Chem.*, **74-5** pp.835-855 (2002).
3. Eurachem/Citac, "Guide on Quantifying Uncertainty in Analytical Measurement" (2002).
4. J. Kucera, P. Bode, V. Stepanek, *Uncertainty Evaluation in Instrumental and Radiochemical Neutron Activation Analysis, in: IAEA, Quantifying Uncertainty in Nuclear Analytical Measurements*, TECDOC-1401, Vienna, Austria (2004).
5. T. Weizhi, N. Bangfa, W. Pingsheng, C. Lei, Z. Yangmei, "Metrological Role of Neutron Activation Analysis, 1A. Inherent Characteristics of Relative INAA as a Primary Ratio Method of Measurement," *Accred. Qual. Assur.* **6** pp. 488-492 (2001).
6. R. R. Greenberg, R. M. Lindstrom, D. S. Simons, "Instrumental Neutron Activation Analysis for Certification of Ion-implanted Arsenic in Silicon," *J. Radioal. Nucl. Chem.*, **245** pp. 57-63 (2000).

7. IAEA, *Practical Aspects of Operating an Activation Analysis Laboratory*, TECDOC-564, Vienna, Austria (1984).
8. J. K. Tulli, *Nuclear Wallet Cards*, 6th ed. (2000).
9. IPEN, *Neutron Flux Density Calibration Certificate*, F-001/2004. (Internal Communication).
10. E. G. Moreira, M. B. A. Vasconcellos, M. Saiki, "Instrumental Neutron Activation Analysis Applied to the Determination of the Chemical Composition of Metallic Materials with Study of Interferences." *J. Radioal. Nucl. Chem.,* **264** pp. 45-50 (2005).
11. A. Hioki, M. Kurahashi, G. Turk, R. Matschat, S. Recknagel, *Report of the Pilot Study CCQM-P56 – Determination of Minor Elements in Steel (Final Report),* Tsukuba, Japan (2005).