Quality Assessment of k_0-NAA by Statistical Evaluation of CRM Results

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Abstract

The k_0-based neutron activation analysis (k_0-NAA) is an analytical method based on nuclear properties of atoms. Since it is a multi-element technique, correlations among repeated measurement results for different elements can in principle be observed in case of certain systematic errors. For a deeper insight into potential sources of uncertainty and potential systematical errors of the analytical method, a set of measurement results for the Standard Reference Material (SRM) 2782 obtained from the National Institute for Standards and Technology (NIST) was analyzed using standard statistical approach. The measurements results were examined over an extended period of time to obtain reproducibility of the method. Correlations of repeated measurements among several elements, although dispersions are small, were indeed observed, and the origin of the correlations as the potential source of uncertainty is discussed. A comparison of the measurements with the NIST SRM 2782 reference values was made to benchmark the k_0–NAA setup at the TRIGA Mark II reactor of the Jožef Stefan Institute and proved the overall accuracy of the method. The article is focused on the possible sources of the correlations of the measurement results and not on the uncertainty of the method itself.

Keywords: NAA, QA, uncertainty, correlation, reproducibility, reference material.

1. Introduction

The k_0-NAA is an analytical method primarily intended for simultaneous determination of many elements in a sample. Consequently, it offers comprehensive insight into the sample composition. It is most frequently applied in "instrumental" mode, i.e. by analyzing the sample as it is, without any chemical treatment. In this case, the sample is just irradiated in a neutron flux and measured on a gamma spectrometer; under the given experimental conditions. In this case, the response signal cannot be intensified and the limit of detection cannot be altered.

In the simplified model based on the original approach developed by its founders[1], the mass fraction of an analyte (w_a) in a sample irradiated by whole spectrum reactor neutrons using the k_0 –NAA is calculated by[2]:

$$w_a = \frac{A_{sp,a}}{A_{sp,Au}} \frac{1}{k_{0,Au}(a)} \frac{f + Q_{0,Au}(\alpha)}{f + Q_{0,a}(\alpha)} \frac{\varepsilon_{p,Au}}{\varepsilon_{p,a}}, \quad (1)$$

where A_{sp} is specific count rate of the analyte (a) and co-irradiated gold monitor (Au), respectively, $k_{0,Au}$ (a) is the K_0 factor of the analyte (a) relative to gold, f is thermal-to-epithermal neutron flux ratio, ε_p is full-energy peak detection efficiency and

$$Q_0(\alpha) = (Q_0 - 0.429)\overline{E}_r^{-\alpha} + \frac{0.429}{(2\alpha + 1)0.55^\alpha}, \quad (2)$$

where $\overline{E}_r$ is the effective resonance energy, Q_0 is ratio of the resonance integral and thermal cross-section ($Q_0 = I_0/\sigma_0$), and α is the epithermal neutron spectrum shape factor.

As evident from Eq.1, there are three main sources of uncertainty: (1) specific count rates, depending mostly on amount of the analyte present in the sample, connected with counting statistics of the signal obtained as response to the activation following neutron irradiation, (2) irradiation conditions involving parameters f, α (both experimentally determined) and Q_0 (nuclear constant) and (3) detection efficiency including measurement geometry, represented primarily by ε_p. The prevailing uncertainty component in analyses of environmental samples is usually the counting statistics.[2] This uncertainty can partly be influenced by carefully selecting irradiation/counting conditions, but generally the sample should be treated as a whole and consequently compromises should be taken if panoramic analysis is in focus in order to extract as much as possible information from the analysis.

The purpose of this work was an attempt to reveal the latent information about the uncertainty sources other than the unavoidable and already well known ones by statistical analysis of the existing measurements results. The measurements can contain information other than just measurement result and the statistical analysis tools might be effective enough to disclose/reveal it. The statistical analysis was done posteriori, on already existing repetitive measurements of a certified reference material (CRM). For this purpose, the standard reference material of the National Institute of Science and Technology NIST SRM 2782 Industrial Sludge was used, measured within a framework of an international project SOILSAMP (Assessment of uncertainty associated with soil sampling in agricultural, semi-natural, urban and contaminated environment, during the years 2000–2006). The project was coordinated by APAT (Agencia per la protezione dell'ambiente e per servizi tecnici, Italy), involving national and international experts in the field of soil sampling and the analysis, uncertainty quantification and quality assurance[3].

2. Experimental

About 0.1 g NIST SRM 2782 sample was sealed in a polyethylene ampoule (SPRONK system, Lexmond, The Netherlands). The sample and comparator (Al-0.1% Au IRMM-530 disc of 6 mm diameter and 0.2 mm high) were fixed together in the polyethylene ampoule and irradiated for about 20 hours in the carousel facility of the TRIGA Mark II reactor at the Jožef Stefan Institute (neutron thermal flux about 1.1×10^{12} n cm^{-2} s^{-1}). The flux parameters f and α were determined according to the multi monitor "Cd-ratio" method.[4,5] Each irradiated sample was counted two times, after 6 and 14 days cooling time, on one of four calibrated high purity Ge detectors (OR2 and OR4 from ORTEC and CA1 and CA5 from CANBERRA, USA) connected to a multichannel analyzer (CANBERRA Genie 2000 for CA1 detector, ORTEC DSPEC$^{PLUS™}$ for CA5 detector, G&G ORTEC Spectrum Master highrate MCA for OR2 detector and CANBERRA S100 MCA for OR4 detector). The software HYPERLAB[6,7] was used for the peak deconvolution. KAYZERO/SOLCOI$^{®8}$ was used for the calculation of the effective solid angle and elemental mass fractions. A total of 25 NIST SRM 2782 samples were irradiated and analyzed in the period from February 2004 to April 2005. The element content of the NIST SRM 2782 material is summarized in Table 1, along with our measurements results.

A NIST certified value is the value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST. Reference values are non-certified values that are the best estimate of the true value; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may

Table 1: Certificate of the NIST SRM 2782 and the values measured in our laboratory. All values are reported as mass fractions on a dry mass basis in [mg kg^{-1}].

Certified value					
element	x_{ref}	U_{ref} (k = 2)	x_{lab}	U_{lab} (k = 2)	ζ-score
As	166	20	173	12	0.57
Cr	109	6.0	99	9.1	−1.76
Hg	1.10	0.19	1.23	0.20	0.94
Mo	10.07	0.20	10.05	2.29	−0.02
Se	0.44	0.11	0.45	0.17	0.11
Zn	1254	196	1284	90	0.28

Reference value					
element	x_{ref}	U_{ref} (k = 2)	x_{lab}	U_{lab} (k = 2)	ζ-score
Ag	30.6	4.7	36.9	2.6	2.35
Ba	254	24	248	24	−0.35
Ca	6,700	600	6.753	2344	0.04
Ce	1240	110	1234	88	−0.08
Co	66.3	4.8	65.5	4.6	−0.24
Fe	269.000	7.000	262.466	18414	−0.66
In	238	70	283	20	1.22
K	3.200	100	3.249	1314	0.07
La	58.1	2.4	56.8	4.1	−0.54
Na	13.000	500	13.120	934	0.23

Information value			
element	x_{ref}	x_{lab}	U_{lab} (k = 2)
Au	2.2	2.5	0.2
Eu	0.34	0.33	0.09
Hf	0.77	0.76	0.08
Rb	23	18	4
Sb	2.0	2.0	0.2
Sc	3.4	2.7	0.2
Sm	1.3	1.2	0.1
Ta	0.73	0.68	0.06
Tb	0.48	0.48	0.04
Th	2.4	2.3	0.2
U	8.3	8.1	0.7
Yb	0.74	0.66	0.10

reflect only measurement precision and may not include all sources of uncertainty. For the information values insufficient information is available to adequately assess the uncertainty associated with these values.[9]

In the Table 1 our results are compared with the NIST assigned values by means of ζ-scores. The definition for ζ-score is $\zeta = \dfrac{x_{lab} - x_{ref}}{\sqrt{u^2(x_{lab}) + u^2(x_{ref})}}$ where $u(x)$ is standard uncertainty and results are assumed to be satisfactory if $|\zeta| \leq 2$ and questionable if $2 < |\zeta| < 3$. As evident from the Table 1, all our results are satisfactory according to this criterion, except for Ag with a questionable result.

The relatively large set of collected data (25 measurements) allowed for the relevant statistical analysis. The set was tested for normal distribution and the dispersion of measurements was examined over time and among diffe-

rent detectors. Since measurements were performed over a long period of time, the closeness of the agreement between the results of measurements of the same measurand is represented as reproducibility[7]. Other conditions besides time of irradiation and measurement were unchanged. For the quantitative expression of the reproducibility in terms of the dispersion characteristics of the results the standard deviation of all measurements over the observed period of time is used. Since mass fractions of many elements in each sample were determined, correlations between different elements were evaluated.

4. Results and Discussion

4. 1. Reproducibility

The reproducibility for the determination of each element on each detector was determined and examined in terms of the nominal mass fraction of the element. The changed condition for the reproducibility is a relatively long period of time for the successive measurements. Fig.1 shows no considerable reproducibility dependence on the mass fraction. For most of the measurement results the reproducibility standard deviation is less than 10%, for some of them up to 15% and only four of them more than 20% (Se up to 45%, K up to 40%, Hg up to 25%, Rb around 20%, and Ca up to 22%).

The higher measurement reproducibility standard deviations are due to measurements of the mass fractions close to the detection limit for that elements under given irradiation and measurement conditions. Consequently, the specific count rates for that elements were low and the related counting statistics, contributing the most to overall measurement uncertainty, relatively poor.

4. 2. Accuracy

Measured mass fractions of the elements in the sample are compared with reference values from the certificate (Table 1) in Fig.2. Dashed error bars of reference values in Fig.2 represent 95% confidence intervals for uncertainty stated in the certificate. Solid error bars for measurement values represent the combined uncertainty of the weighted averages of the measurements with coverage factor 2. For most of the elements having stated certified and reference mass fractions, the measured values agree with the mass fractions reported in the certificate and accuracy of the method used is satisfactory. The comparison confirmed the reliability of the k_0–NAA measurement results obtained during the SOILSAMP project and of the method itself. The results are questionable only for Ag (Table 1), whose mass fraction determined is about 20% higher than the reference value. The reason for the deviation is for the time being unknown. However, it should be noted that the Ag value is not a certified value and does therefore not meet NIST criteria for certification.

The relatively high ζ-score (1.76) is also for Cr (Table 1), where the determined mass fraction is about 10% lower than the reference value, although the value for ζ-score is satisfactory. The reason for the lower chromium value can be attributed to two sources; (1) erroneous blank correction and (2) erroneous correction for an interfering nuclear reaction. The samples were measured in the irradiated polyethylene vials. It was found that the vials contain some chromium. Although this blank value was corrected for, it might have happened that the correction was not appropriate, since it was based on another experiment. It is estimated that an erroneous correction might have contributed up to 3% of the total Cr content. Furthermore, chromium was determined via the ^{50}Cr (n, γ) ^{51}Cr reac-
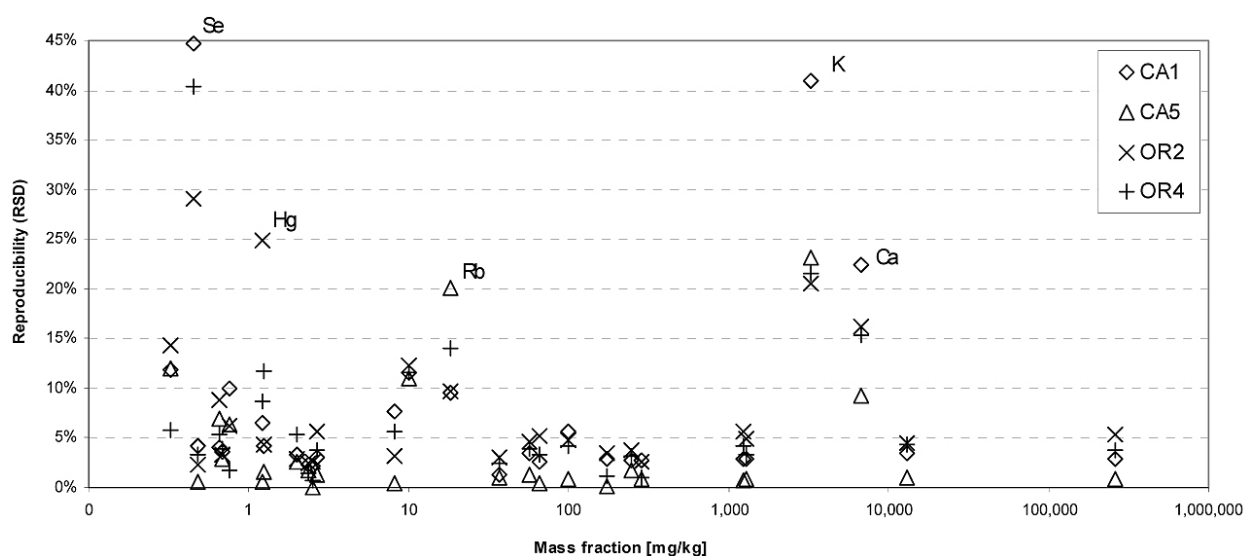

Figure 1: Reproducibility of measured mass fractions for different elements in dependence of mass fraction. The relative standard deviation of all measurements of mass fraction for certain element on one detector is plotted as a single point. Four vertical points correspond to four relative standard deviations for the same element, measured on four different detectors.
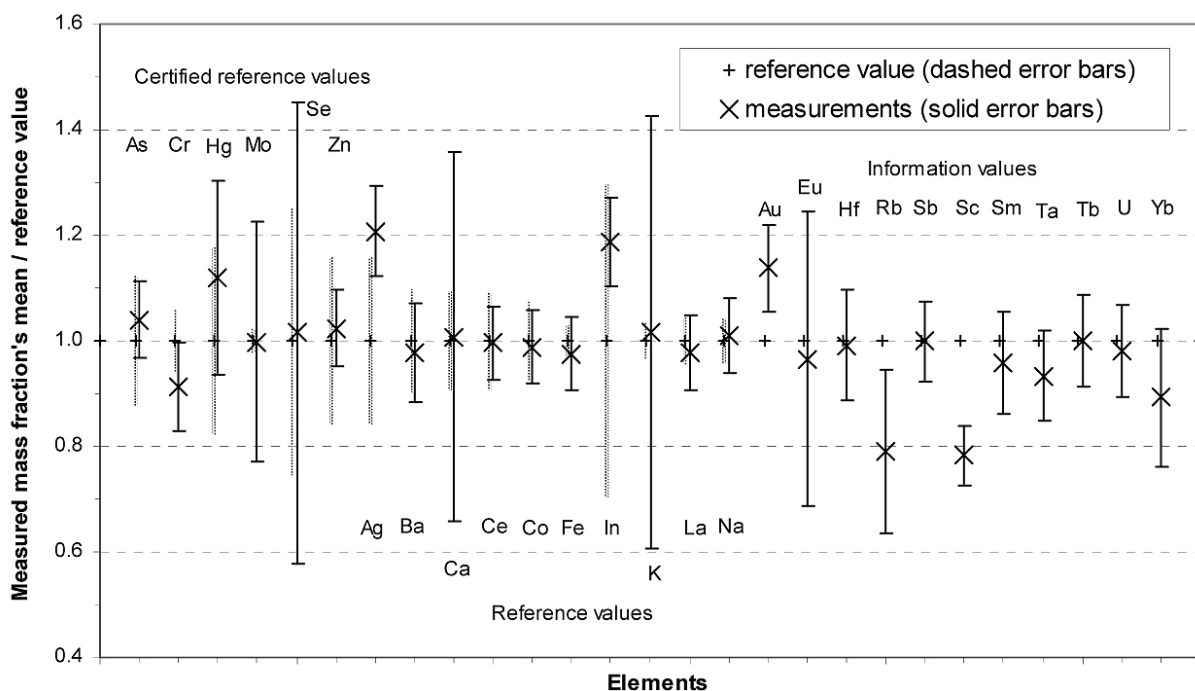
Figure 2: Measured mass fractions normalized on certified, reference or information values for different elements, compared with the certified, reference or information value of mass fraction as stated in certificate. Uncertainties of certificate values (k = 2) are presented with dashed error bars and uncertainties of measurement averages (k = 2) with solid error bars.

tion that might be interfered by the ^{54}Fe (n, α) ^{51}Cr reaction. Due to the very high Fe content in this particular sample (Table 1), this interference took place in relatively high amount and it might have happened that the correction made to compensate for this contribution was overestimated, resulting in lower Cr value determined. For particular irradiation channel the experimental estimated interference correction is about 2% based on experiment with 99.9% Fe wire irradiated under the Cd cover.

The uncertainties of some elements (Se, K, Ca) are extremely high due to the measurements close to the detection limit, which is confirmed by the high value of relative standard deviation data for those elements (Fig. 1), that indicate high dispersion of the measured data.

There are several other elements that appear not to be in accordance with the information value. However, it should be considered that there are no uncertainties stated in the certificate for the information values of mass fractions. Therefore, only error bars for the measured uncertainty are given in Fig. 2. The measurement results are an additional characterisation of the NIST SRM 2782, especially for gold, which is accurately determined by k0-NAA.

4. 3. Correlations

Correlation is the relationship between two or several random variables within a distribution of two or more random variables. The degree of correlation between x_j in x_j is characterized by the estimated correlation coefficient:

$$r = \frac{u(x_i, x_j)}{u(x_i)u(x_j)}$$. The correlation coefficient is a measure of the relative mutual dependence of two variables, equal to the ratio of their covariances to the positive square root of the product of their variances. The correlation coefficient is a pure number such that $-1 \leq r \leq 1$[10]. For each pair of elements correlations among measurement results obtained at different times were calculated. Since amount of the elements present in the sample is constant, the successive measurement results should vary randomly for approximately up to two standard deviations. For most of the elements determined indeed no correlations were found indicating absence of systematic errors in the measurements. The results for those elements do not follow each other through the repeated measurements. However, for some elements correlations were established and the elements with the highest (≥ 0.7) mutual correlation factors are shown in Table 2.

All significant correlation factors are positive; when the value for the mass fraction of one element increases, the value for the mass fraction of correlated element increases as well. The origin of such correlations is usually in a common mechanism/influence that forces both measurement results into the same direction. There are several elements that are by pairs correlated among each other, but a group of elements is observable. Those are the elements, where measurement results are consistently correlated among each other with an absolute value of correlation factor between 0.9 and 1. The strongly correlated group of elements consists of Ce, Co, Fe, Sc and Zn. The correlations are observed among the measurements on all

Table 2: Elements having absolute correlation factors higher than or equal to 0.7. The elements having extremely high correlation factors are located on the top left side and marked with a rectangle.

Fe	Zn	Co	Sc	Ce	Na	La	Th	Au	Cr	Br	As	In	Ag	Se	U
Fe	1	0.99	0.99	0.98	0.97	0.82	0.71	0.68	0.60	0.57	0.05	0.07	0.23	0.08	−0.11	0.01
Zn	0.99	1	0.98	0.98	0.97	0.79	0.67	0.67	0.63	0.58	0.08	0.08	0.29	0.09	−0.06	0.05
Co	0.99	0.98	1	0.97	0.95	0.79	0.68	0.74	0.66	0.60	0.09	0.10	0.30	0.08	−0.08	0.05
Sc	0.98	0.98	0.97	1	0.93	0.79	0.68	0.68	0.59	0.59	0.07	0.08	0.22	0.09	−0.12	0.01
Ce	0.97	0.97	0.95	0.93	1	0.80	0.73	0.55	0.53	0.43	−0.01	0.03	0.20	0.02	−0.08	−0.02
Na	0.82	0.79	0.79	0.79	0.80	1	0.95	0.54	0.51	0.47	0.32	0.30	0.01	0.01	−0.21	0.05
La	0.71	0.67	0.68	0.68	0.73	0.95	1	0.40	0.39	0.34	0.33	0.36	−0.08	−0.01	−0.28	−0.07
Th	0.68	0.67	0.74	0.68	0.55	0.54	0.40	1	0.79	0.70	0.44	0.39	0.62	0.29	0.25	0.35
Au	0.60	0.63	0.66	0.59	0.53	0.51	0.39	0.79	1	0.75	0.63	0.63	0.78	0.09	0.10	0.39
Cr	0.57	0.58	0.60	0.59	0.43	0.47	0.34	0.70	0.75	1	0.53	0.48	0.58	0.08	0.18	0.36
Br	0.05	0.08	0.09	0.07	−0.01	0.32	0.33	0.44	0.63	0.53	1	0.86	0.52	−0.06	0.13	0.38
As	0.07	0.08	0.10	0.08	0.03	0.30	0.36	0.39	0.63	0.48	0.86	1	0.57	0.10	0.16	0.41
In	0.23	0.29	0.30	0.22	0.20	0.01	−0.08	0.62	0.78	0.58	0.52	0.57	1	0.12	0.55	0.57
Ag	0.59	0.59	0.62	0.59	0.52	0.33	0.31	0.70	0.59	0.45	0.22	0.33	0.54	1	0.19	0.26
Se	−0.11	−0.06	−0.08	−0.12	−0.08	−0.21	−0.28	0.25	0.10	0.18	0.13	0.16	0.55	0.06	1	0.70
U	0.01	0.05	0.05	0.01	−0.02	0.05	−0.07	0.35	0.39	0.36	0.38	0.41	0.57	0.26	0.70	1

detectors and among isolated measurements on a single detector as well. All correlation factors are close to 1, which indicate extremely strong correlations.

Given the fact that the correlations were observed for the measurements carried out on all detectors, systematic error due to detection efficiency including measurement geometry (ε_p) could be eliminated. Each of the four detectors was calibrated independently and particular nuclides emit gamma rays at different energy having different efficiency, so any systematic uncertainty would be detectable.

It was observed that all the correlated measured radionuclides had relatively high specific count rates and consequently relatively low statistical uncertainty in their peak areas. Therefore, it can be assumed that in these cases other sources of uncertainty might be revealed.

The correlated elements all have low Q_0 factors and consequently also low $Q_0(\alpha)$, since α has low impact on $Q_0(\alpha)$ in this case. As presented in Eq.1, the Q_0 factor enters the equation in form of expression $\frac{f + Q_{0,Au}(\alpha)}{f + Q_{0,a}(\alpha)}$. Since the numerator is a constant for the given irradiation channel ($Q_{0,Au}(\alpha)$ is constant for the gold monitor irrespective of the analyte element), the only variable factor for a different radionuclide is the denominator. The factor f and its fluctuations around the constant value used in the calculations are properties common to all correlated and non-correlated elements. It can be assumed that f varies among different irradiations for the amount comparable to its uncertainty ($f \approx 28 \pm 1$)[11]. For the nuclides with larger values of Q_0, the variation of f does not have observable influence on the denominator sum.

For the nuclides with low Q_0 factor (Q_0 around 1), on the contrary, Q_0 is negligible compared with f and f remains the only term in the denominator that defines the behavior of the whole expression. When f is a major part of the sum, the sum fluctuates simultaneously with f and the fluctuations of f are seen in the result as correlation.

Uncertainty of a certain factor in the Eq.1 propagates to the final result with the uncertainty propagation factors, dependent on other quantities[10]. Uncertainty propagation factor for A_{sp} of the analyte is 1, but the uncertainty propagation factor of f is $Z(f) = f\dfrac{Q_{0,a}(\alpha) - Q_{0,Au}(\alpha)}{(f + Q_{0,a}(\alpha))(f + Q_{0,Au}(\alpha))}$. Using the numerical values for our measurements and for elements with low Q_0 factors, the uncertainty propagation factor of A_{sp} is found to be three times higher than the uncertainty propagation factor for f. In case that the uncertainty of f is three times higher than those of A_{sp}, both would contribute about equally to the final uncertainty and the correlations would not be observable. However, in case of the correlated elements, the uncertainties of A_{sp} are in the range of 0.5% or lower due to high specific count rates, whilst the uncertainty in experimental determination of f is estimated to be approximately 3%[11]. In that case the uncertainty contribution of f prevails over the contribution of A_{sp} more than six times and the correlations could be revealed. In the calculations f is usually treated as a constant and the corresponding fluctuations are not accounted for. It is assumed that the observed correlations might arose from this unaccounted fluctuations. The small systematic uncertainty belonging to the fluctuations of f, detected in the above correlation analysis, is obviously a part of every k_0–NAA measurement uncertainty, but is usually not observable.

There are several other elements that are correlated, but the correlation factors are lower, correlations differ from detector to detector and there is no evident pattern that would lead to straightforward conclusions on origin of those almost negligible variations.

5. Conclusions

The set of 25 NIST SRM 2782 measurement results was posteriori analyzed using standard statistical approach. Reproducibility of the measurements using the k_0–NAA was calculated and the long term stability of the results was proved. The quality performance of the k_0–NAA measurements was reconfirmed and accuracy of the results evidenced by comparing measurement results with the reference values. Particular deviations existed but can reasonably be explained by the expertise and knowledge of the method.

The correlations between measurement results of mass fraction of different elements found in successive measurements were calculated. The systematic uncertainties could be identified for the elements with the highest correlation factors, Fe, Zn, Co, Sc, Ce.

It was shown that the small counting statistic uncertainty is the primary condition for the other uncertainties to become visible. In case of a nuclide having the Q_0 value negligible in comparison to f, the influence of fluctuations in f on the measurement result could be observed.

The effect was observed for the above-mentioned elements in case of NIST SRM 2782 analysis. The counting uncertainty was small enough and the Q_0 factors for the nuclides measured low, so that the measurement results were dependent on the fluctuations of factor f, which in equation is a constant. The observations indicated that calculated mass fractions varied proportionally with variations in f, which was demonstrated as correlations, since f was held constant in calculations.

For further uncertainty reduction of k_0–NAA measurement results, i.e. below the generally proposed level of $3.5\%^2$, research into more accurate determination of the thermal-to-epithermal neutron flux ratio f is needed. If assumed that the observed correlations are based mostly on f, it should be possible to determine the deviation of parameter f from its mean value by observing deviation of measurement results of mass fraction and knowing the sensitivity coefficient $\frac{\partial w_a}{\partial f}$. This approach would reveal

uncertainty of f from the observed correlated variations of experimental result. By knowing its deviation, f can be corrected for each individual irradiation session and the result could be re-calculated using the corrected value. Such approach that would yield lower variations of the measurement results and hence lower uncertainty, will be further investigated.

6. Acknowledgment

7. References

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Povzetek

S pomočjo standardnih statističnih orodij smo ovrednotili merilne rezultate, ugotovljene s k_0-metodo nevtronske aktivacijske analize (k_0-NAA), za standardni referenčni material NIST 2782 Industrijsko blato. Pri tem so nas zanimali predvsem potencialni viri negotovosti in potencialne sistematske napake uporabljene analizne metode. Pregledali smo merilne rezultate, dobljene v daljšem časovnem obdobju in ugotovili korelacije med vsebnostmi nekaterih elementov (Fe, Zn, Co, Sc in Ce). Ugotovljene korelacije smo lahko pripisali fluktuaciji razmerja med hitrostma fluenc termičnih in epitermičnih nevtronov (parameter f) od običajno uporabljene povprečne vrednosti. Z opazovanjem odmika merilnih rezultatov za masno frakcijo izbranega elementa in poznavanjem faktorja širjenja negotovosti parametra f lahko zanesljeveje izračunamo njegovo pravilno vrednost za posamezno obsevanje z nevtroni in s tem zmanjšamo skupno negotovost merilnega rezultata.