ESTIMATION OF UNCERTAINITY OF THE ICP AES DETERMINATION OF SELECTED METALS IN INLAND WATERS[1]

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Determination of basic metrological characteristics and estimation of the combined uncertainty and expanded uncertainty of the results of the ICP AES determination of ten metals (Zn, Cr, Cd, Cu, Ni, Pb. Fe, Mn, Mg and Ca) commonly present in inland waters were performed. Special attention was given to the assessment, which uncertainty components play a dominant role in the overall determination process (from sampling up to the presentation of results), and particularly, in the ICP AES calibration and measurement. The largest contribution to the combined uncertainty of the final analytical result in all ten analytical determinations was found from the sampling procedure.

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[1] Presented at YISAC 2005 – 12th Young Investigator's Seminar on Analytical Chemistry held in Sarajevo (Bosnia and Hercegovina), July 5–10, 2005.

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Introduction and Theory

The results of analytical measurements never ideally reflect the actual concentration of the determined components in the analyzed sample. This experience is especially true for trace measurements where the results always tend to be more or less inaccurate and contain some errors, which are random ones but may contain also systematic error components. However, modern instrumental analytical methods applied in environmental research should be accurate and precise and at the same time they should meet further requirements of good laboratory practice in a quality system management.

Today the most crucial factor in evaluating analytical results is the *uncertainty of measurement*, which conveys both the accuracy and the precision of the measurement. This term is relatively new in the analytical terminology [1]. The measurement uncertainty is one of the more challenging concepts introduced into analytical quality assurance by official adoption of ISO standards, European standards and EUROCHEM recommendations and guides [2–4]. This approach goes beyond the well-known classical concept of standard deviation and confident interval. However, both mentioned statistical characteristics, together with the relative standard deviation (RSD) are more or less closely related to the measurement uncertainties and are used in the uncertainty computation [2–4].

The uncertainty of measurement (e.g. of an analytical determination) is a parameter pertaining to a given measurement result and describing the spread of the values, which can be ascribed to the measured quantity [1]. In other words, uncertainty is an estimate associated to a result, which characterizes the range on each side of the result, within which the true value is likely to occur with an assumed probability.

Strict guidelines, worldwide valid, have been elaborated, which prescribe the way of assessing the uncertainty for each uncertainty source separately. They describe how to include the contribution of each source of uncertainty in order to estimate the combined (total) uncertainty as well as the extended uncertainty of the result [2,3,5]. The recommended methods of assessing uncertainty take into account the influence of both random and systematic errors on the final result of the measurement, e.g. performed chemical analysis.

One way, in which uncertainty can be assessed, incorporates a classical statistical approach to estimate the so-called type A standard uncertainty, which expresses the influence of random errors on analytical results. This type of uncertainty is given in terms of the standard deviation or the relative standard deviation. Unfortunately, this classical approach to estimating the precision by performing repeated determinations fails in the presence of systematic errors, which may occur in various steps of the analytical procedure. However, they can be evaluated by means of the type B standard uncertainty.

In this work, the evaluation of individual standard uncertainties utilizes

several sources of information on the investigated problem collected by the laboratory staff, e.g.:

- results of earlier analytical measurements related to the current quality control of analytical data, like control charts (Shewhart charts) and validation data,
- analyst knowledge and experience connected to behaviour and properties of the investigated materials and the applied instrumentation,
- data provided by the supplier of analytical equipment,
- data from the certificates about the instrument calibration and found in the specification of standard solutions.

In analytical practice it is necessary, however, to combine different quantities or factors, grouped in individual stages of analytical process, and calculate the combined uncertainty for each group. Then the combined (total) uncertainty of an analytical result is the result of partial uncertainties and in simple cases can be calculated according to the error propagation theory [5,6]. When the result y is a function of n variables $x_1, x_2, \ldots x_n$, i.e.

$$y = f(x_1, x_2, x_3, \ldots, x_n) \tag{1}$$

then the combined uncertainty comes down according to the following general relation

$$u^2_{comb}(y) = \left(\frac{\partial y}{\partial x_1}\right)^2 [u(x_1)]^2 + \left(\frac{\partial y}{\partial x_2}\right)^2 [u(x_2)]^2 + \ldots +$$
$$+ \left(\frac{\partial y}{\partial x_1}\right)\left(\frac{\partial y}{\partial x_2}\right) u(x_1)u(x_2)r_{x_1 x_2} + \ldots \tag{2}$$

where $u_{comb}(y)$ – the combined uncertainty of the analytical result y; $x_1, x_2, \ldots x_n$ – the variables influencing the final result, $r_{x_1 x_2}$ – the pair correlation coefficient of the variables x_1, x_2. All pair correlations between the variables (e.g. p and q) are reflected in equation (2) by the corresponding mixed derivatives term multiplied by the corresponding $u(p)u(q)r_{pq}$ multiplier, which in fact expresses the covariance $cov(p, q)$ between the variables. Fortunately, in many practical occasions the correlation between the variables does not exist and the mixed derivatives term with the covariance is omitted.

In most simple case when using uncorrelated variables and an additive model for the variables combination, the combined uncertainty is given by

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equation

$$u_{comb}(y) = \sqrt{u(x_1)^2 + u(x_2)^2 + ... + u(x_n)^2} \qquad (3)$$

Having calculated the combined uncertainty, the expanded uncertainty, U, can be estimated. It allows for the assessment of the uncertainty for a *defined* function of the measurement results distribution (e.g. normal distribution) and an appropriate choice of probability $P = 100(1 - \alpha)\%$ or corresponding significance level α (preferably $P = 95\%$ or $P = 99\%$, which corresponds to $\alpha = 0.05$ or $\alpha = 0.01$).

This work deals with the estimation of the uncertainties of the determination of the selected metals (Zn, Cr, Cd, Cu, Ni, Pb. Fe, Mn, Mg and Ca) in surface waters by inductively coupled plasma atomic emission spectrometry (ICP AES). The investigations were performed in the framework of an environmental monitoring project in the Malopolska shire [7]. Another aim of this work is to show the variability of uncertainties of the determined elements corresponding to their real concentration in the river water samples. Since the final uncertainties of the elements determination depend on different sources of uncertainty, it was important to analyze, which partial uncertainties are the largest and most influencing the final result of analysis.

Experimental

Reagents and Reference Materials

All the chemicals used, if it is not particularly specified, were of Reagent Grade purity. Nitric acid 65 %, Tracepure, was produced by Merck. The purity of the used argon gas was 99.99 % (V:V). Deionised water was purified with a cartridge system from MILLIPORE Milli-Q gradient.

Reference Material Magnesium ICP Standard and Multielement CertiPUR® Reference Material, ICP Standard Solution IV, were purchased from Merck. The mentioned magnesium reference material contains 1004 ± 5 mg l^{-1} Mg. The multielement reference material contains nine metal elements with the following certified concentrations: 995 ± 5 mg l^{-1} Ca, 999 ± 5 mg l^{-1} Cd, 1002 ± 5 mg l^{-1} Cr, 1000 ± 2 mg l^{-1} Cu, 1000 ± 5 mg l^{-1} Fe, 1002 ± 5 mg l^{-1} Mn, 1003 ± 5 mg l^{-1} Ni, 998 ± 5 mg l^{-1} Pb, and 998 ± 5 mg l^{-1} Zn. Traceability of the mentioned ICP standards ensues from high precision ICP measurements against the corresponding NIST SRM 3131a and SRM 3109a, respectively. In addition to the mentioned CRM another CRM (SPS-SW2, Batch 112, Reference Material for Measurement of Elements in Surface Waters, produced by Spectrapure Standards, Manglerud,

Oslo, Norway, and containing 45 elements) was used from time to time in order to make a double check of the results obtained.

For Proficiency Testing, described in further text, four test reference materials with a set of suitable calibrants were used. Two test materials were determined for major component analysis and two test materials contained metals — one at natural and one at fortified concentration level.

Instrumentation

The ICP-AES Optima 2000 DV spectrometer (Perkin Elmer) with the Autosampler AS 93 plus and a scanning CCD detector (with 25600 pixels) was applied for the metals determination using a standard calibration graph method. The measurement wavelengths for the ICP AES determination of the monitored elements are given in Table I. The sampled data were processed using the WinLab32ICP computer program. All determinations were performed in accordance with the ISO standard applied to the water quality determination by inductively coupled plasma atomic emission spectroscopy [8].

Table I   Metrological characteristics of the ICP AES determination of metals in inland waters of Malopolska shire

Element	λ[a] nm	LOD[b] mg l^{-1}	LOQ[c] mg l^{-1}	Interlaboratory accuracy[d], %	Accuracy[e] %	Precision[f] %	Linear range[g] mg l^{-1}
Cadmium	214.438	0.00073	0.0015	93	101	4	0.001 – 0.10
Calcium	317.933 315.887	0.00022	0.020	100	101	5	0.02 – 2.5 2.5 – 150
Chromium	267.716	0.00092	0.0030	94	101	4	0.002 – 0.10
Copper	324.754	0.00051	0.0025	100	102	5	0.002 – 0.20
Iron	259.940	0.00071	0.0060	98	101	2	0.005 – 0.20
Lead	220.353	0.0039	0.0050	100	100	4	0.005 – 0.10
Magnesium	279.553 279.079	0.000063	38625	100	99	6	0.01 – 0.50 0.5 – 50
Manganese	257.610	0.000091	0.0025	98	101	5	0.001 – 0.20
Nickel	231.604	0.0012	0.0060	92	100	9	0.005 – 0.10
Zinc	213.856	0.0012	0.0075	103	102	3	0.007 – 0.50

[a] Selected wavelengths. [b] The LOD was calculated as $3s_b$ of the measured blank signals divided by the slope of the calibration line. [c] The LOQ was calculated as the concentration of the control sample for which the relative standard deviation amounts to 10 %. [d] Interlaboratory accuracy was estimated from the analysis of the CRM (semiblind samples) obtained during Proficiency Testing. [e] Laboratory accuracy was estimated by periodic analysis of the test samples prepared from the CRM. [f] Precision is expressed as the RSD in % from a series of results plotted on the Shewhart control charts. [g] Dynamic linear range. Determination coefficient, r^2, of the calibration lines in all investigated cases was larger than 0.999

Sampling and Sample Treatment

The investigated water samples were sampled from the selected sampling sites of the rivers of Malopolska shire according to the ISO recommendation [9]. The water samples were collected in cleaned polypropylene bottles and immediately filtered through a 0.45 mm cellulose acetate membrane filter in the Sartorius device. The samples were then acidified with conc. nitric acid to pH 2, transported to the laboratory and stored at 4 °C in a refrigerator. The ICP AES determination [8] was performed within 24 h after sampling.

Results and Discussion

Basic Metrological Characteristics

Basic metrological characteristics of the investigated method applied to ten determined metal elements are summarized in Table I. The metrological quantities summarized in columns 3 – 8 correspond to the ICP AES measurements of the respective metals at the wavelengths specified in column 2. The limit of detection (LOD) was derived in a common way — from the triplicate of the standard deviation of the blank signal. The *limit of quantification* (LOQ) was evaluated according to the concentration at which the relative standard deviation is 10 % [10,11] — using interpolation of the RSD values of the control samples prepared with appropriate concentrations. This way of the LOQ expressing, which gives slightly larger values, is common in water laboratories in Poland.

Proficiency Testing, used for estimating *interlaboratory accuracy*, was based on determination of the reference material analyzed during the SWIFT-WFD European project Screening methods for Water data Information in support of the implementation of the Water Framework Directive (WFD). The main objective of this project was to support successful implementation of the WFD, which closely depends on the quality of monitoring data and their comparability from river basin. This objective required development, validation and dissemination of rapid, affordable and user-friendly measurement techniques. One of the main outputs of the project was the production of the Quality Control (QC) tools for the analytical methods applied for ecological/biological and chemical monitoring purposes. The results obtained at the Dukedom Inspectorate for Environmental Protection in Krakow, which took part in Proficiency Testing, are assembled in the fifth column of Table I. *Laboratory accuracy* (sixth column of Table I) was estimated by periodic analysis of the test samples prepared from the CRM.

Precision (column 7, Table I) was expressed using the RSD values in %. They were calculated from a series of results plotted on the Shewhart control charts [12] serving for internal QC purposes. After 20 samples a new chart was

made and a new test sample was measured. In order to achieve a *linear range* (last column in Table I) in some cases (determination of calcium and magnesium) the measurement wavelength should be changed.

Estimation of Uncertainty

After preliminary expression of the possible sources of uncertainty only those were taken into account which have a significant effect on the uncertainty of the final analytical results. It has to be emphasized that traceability of measurements was maintained throughout the whole study. Uncertainty estimation was performed in the following steps:

1. Specification of possible measurands and assessment of factors contributing to the measured analytical signal.
2. Identification of the sources of uncertainty including (a) sampling (choice of the sampling strategy, sample homogeneity, the water flow rate, temperature, atmospheric pressure), (b) sample storage and preparation (filtration, splitting the sample bulk solution into smaller samples, storage conditions, sample stability, dilution errors), (c) calibration of the apparatus (uncertainties of the standard solutions in calibration, uncertainty of the reference solution concentration, the extent to which the analyte composition matches the standard solution composition, instrumental precision, temperature, humidity), (d) ICP AES measurement (instrumental bias, appropriate choice of instrumental parameters — like integration time, interferences from the sample matrix, nitric acid purity, precision of performed measurements), (e) data processing (averaging, rounding, statistical evaluation of the results, appropriate choice of algorithm — e.g. fitting the calibration plot), (f) presentation of final results (e.g. confidence level), (g) random effects.
3. Calculation of the standard uncertainty for each particular source of uncertainty calculated according to the type A uncertainty evaluation (by statistical analysis of the observation series) and type B uncertainty evaluation.

The standard uncertainty of sampling, u_{samp}, was determined using the type A uncertainty evaluation on the basis of data from the sampling quality control by Shewhart control charts [12]. The results are summarized in Table II. It is clearly demonstrated that the sampling uncertainty makes the main part of the combined uncertainty of the final result of analysis.

The uncertainty of the ICP AES equipment, u_{ICP}, was repeatedly measured as the Type A uncertainty and $u_{ICP} = 1$ % was found.

For the standard uncertainty of the sample concentration c_0, obtained from the calibration plot, the transformed (inverse) calibration equation was used

Table II Combined and extended uncertainties of the ICP AES determination of the monitored elements in inland waters

Determined element	Sampling uncertainty[a] u_{samp}, %	Combined uncertainty u_{comb}, %	Expanded uncertainty $(k = 2)$ U, %
Calcium ($\lambda_1 = 317.933$ nm)	5.0	9.6	19.2
Calcium ($\lambda_2 = 315.887$ nm)		6.0	12.0
Cadmium	3.0	13.0	26.0
Chromium	5.0	12.0	24.0
Copper	3.0	9.9	19.8
Iron	1.0	12.0	24.0
Lead	4.5	12.5	25.0
Magnesium ($\lambda_1 = 279.553$)	6.0	9.5	19.0
Magnesium ($\lambda_2 = 279.079$)		7.7	15.4
Manganese	1.0	11.6	23.2
Nickel	5.0	12.1	24.2
Zinc	4.0	13.4	26.8

[a] The standard uncertainty of sampling was determined using the type A evaluation, based on data from the sampling quality control according to ISO 8258 "Shewhart control charts"

$$\hat{y} = a + bc_0 \qquad c_0 = \frac{\hat{y} - a}{b} \tag{4}$$

The corresponding uncertainty $u(c_0)$ was calculated [13] by the following equation

$$u(c_0) = \frac{s_y t_\alpha}{b} \sqrt{\frac{1}{n} + \frac{1}{m} \frac{(\hat{y} - \bar{y})^2}{b^2 \sum (x_i - \bar{x})^2}} \tag{5}$$

where s_y – residual standard deviation, $\hat{y}$ – the mean value of the ICP AES analytical response for m replicates, $\bar{y}$ – the mean value of n ICP AES signals of the standard solutions, x_i – the concentration of the i-th standard solution that was used for constructing the calibration plot, $\bar{x}$ – the mean concentration value of the used standard solutions in calibration, m – number of the sample replicates, n – number of calibration points, c_0 – concentration of the metal element in the investigated sample corresponding to the mean signal , t_α – critical t-distribution value for $n - 2$ degrees of freedom and confidence level α, a, b – regression coefficients of the calibration line.

Precision was expressed as the relative standard deviation of 60 determinations performed on the reference material samples. For the corresponding uncertainty the type A uncertainty evaluation was used. This value is influenced by all steps of analytical process — sample preparation, calibration, ICP measurement, as well as personal factors.

The uncertainty of recovery was calculated from the following equation (6), using the type A uncertainty evaluation [13]

$$u(R_M) = R_M \sqrt{\left(\frac{s_{obs}}{\sqrt{n}\,\bar{c}_{obs}}\right)^2 + \left(\frac{u(c_{CRM})}{c_{CRM}}\right)^2} \qquad (6)$$

where R_M – the mean value of recovery (based on the certified concentration of the metal component), s_{obs} – the standard deviation (it gives the mean standard deviation when divided by $\sqrt{n}$), n – number of measurements, $\bar{c}_{obs}$ – found mean concentration of the determined element, c_{CRM} – concentration of the particular element in the certified reference material, $u(c_{CRM})$ – uncertainty of the element concentration in the certified reference material declared by the supplier.

The uncertainty of random effects, u_{reff}, was estimated at 2 % using type B evaluation, with consideration of random errors as well as presentation and interpretation of results. It was made as a qualified estimate based on the analyst experience.

The *combined uncertainty* of the final result (for each metal element) was calculated according to the formula (7), assuming the additive model of the uncertainty sources. It takes into account the standard uncertainty of all significant individual steps of the measurement process

$$u_{comb}(y) = \sqrt{u_{samp}^2 + u_{ICP}^2 + u_{c0}^2 + u_{prec}^2 + u_{RM}^2 + u_{reff}^2} \qquad (7)$$

where u_{samp} – standard uncertainty of sampling, u_{ICP} – standard uncertainty of the ICP AES equipment, u_{c0} – standard uncertainty of calibration, u_{prec} – standard uncertainty of precision (from Shewhart charts), u_{RM} – standard uncertainty of recovery, u_{reff} – standard uncertainty of random effects.

Calculation of Expanded Uncertainty

The *expanded uncertainty* was calculated by multiplying the combined standard uncertainty by the coverage factor $k = 2$ (using confidence level 95 %) according to the formula [2–5,13]

$$U = k u_{comb} \qquad (8)$$

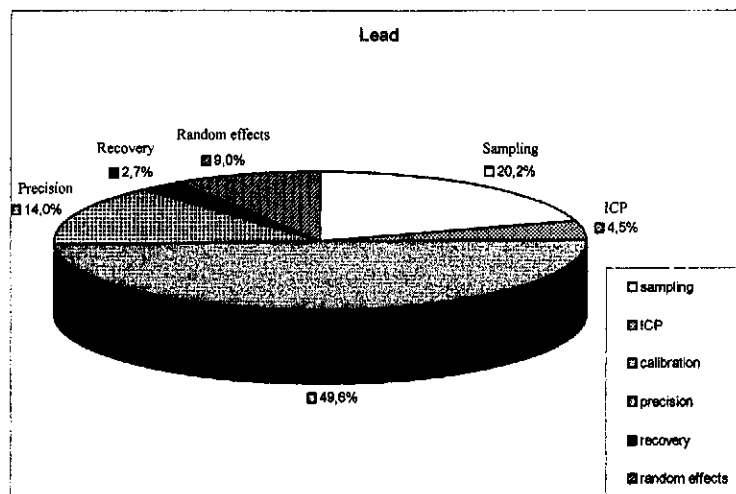Chochorek A. *et al.*/Sci. Pap. Univ. Pardubice Ser. A 11 (2005) 331–342

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Fig. 1. Contribution of the uncertainty components to the final combined uncertainty for the ICP AES determination of lead in surface waters
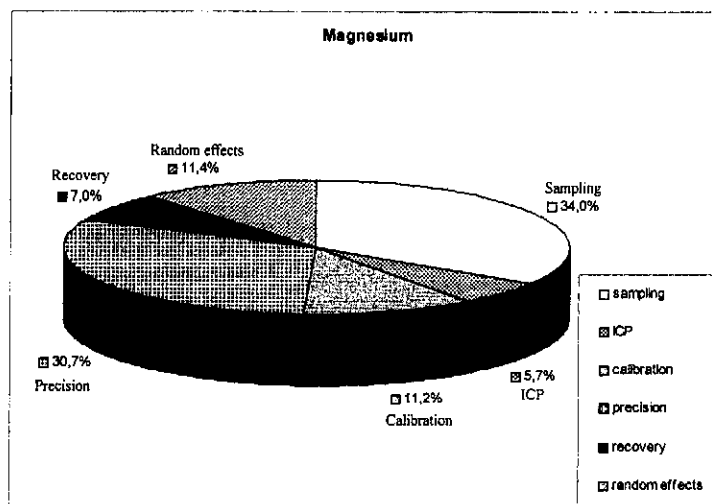

Fig. 2. Contribution of the uncertainty components to the final combined uncertainty for the ICP AES determination of magnesium in surface waters

The values of the combined and expanded uncertainties calculated for monitored elements are presented in Table II. A detailed study of all combined uncertainty contributing uncertainties for all monitored metal elements revealed that the largest contribution comes from the sampling uncertainty. As an example, Fig. 1 and Fig. 2 depict the individual standard uncertainty contributions to the combined uncertainty of the final analytical result for lead and magnesium.

Conclusion

Basic metrological characteristics, the combined and expanded uncertainties of the determination of ten metal elements in surface waters by ICP AES measurements was given in this work.

It was found that the uncertainty of sampling, measurement by the ICP AES equipment, calibration, precision, recovery, and potential random effects have significant influence on the combined *standard* uncertainty of the final determined concentration of the monitored metal elements in inland waters. As documented by Fig. 1 and Fig. 2, sampling is the most critical step in surface water monitoring. Surprisingly, the calibration procedure influences combined uncertainty of the ICP AES determination to a relatively small extent.

The uncertainty of the final results of analytical determinations decreases with the increase of the concentration of the determined element. For example, the uncertainty is lower for magnesium and calcium (Table II), which are present in higher content in surface waters, than that of other investigated elements.

Acknowledgements

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