Original Research

ICP-OES Determination of Select Metals in Surface Water – a Metrological Study

Aneta Chochorek[1], Andrzej Bobrowski[2]*, Zuzana Kiralyova[3], Jan Mocak[3,4]

[1]Inspectorate for Environmental Protection in Kraków, Poland
[2]Department of Building Materials, Faculty of Materials Science and Ceramics,
University of Mining and Metallurgy, Al. Mickiewicza 30, 30-059 Kraków, Poland
[3]Institute of Analytical Chemistry, Slovak University of Technology, Radlinskeho 9, SK-81237 Bratislava, Slovakia
[4]Department of Chemistry, University of St. Cyril and Methodius, Nam. J. Herdu 2, SK-91701 Trnava, Slovakia

Abstract

Ten selected metals, namely Zn, Cr, Cd, Cu, Ni, Pb, Fe, Mn, Mg and Ca, commonly present in surface waters were determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES). For all quantitative analyses, basic metrological characteristics were obtained, including estimation of combined and expanded uncertainties. Special attention was given to ascertaining which component of uncertainty plays a dominant role in the overall determination process (from sampling to final results), and particularly, in ICP-OES calibration and measurement. The largest contribution to the combined uncertainty of the final analytical determination of the element concentrations was due to sampling and calibration, as well as general imprecision of the whole analytical procedure.

Introduction

Analytical measurements do not truly reflect the actual concentration of the determined components in the analyzed sample. This is especially true in trace analysis, where the results always are more or less inaccurate and contain random and also systematic error components. On the other hand, contemporary analytical methods applied in environmental research should be at the same time accurate, i.e. precise and with the smallest bias, and should meet additional requirements of good laboratory practice in a quality system management.

The most crucial factor in evaluating analytical results is the uncertainty of measurement [1, 2], which reflects both the imprecision of the measurement and bias, and should be minimized. 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 confidence interval, even though they are related to the measurement uncertainties and used in the uncertainty estimation [2-5].

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 that characterizes the range on each side of the result, within which the true value is likely to occur with an assumed probability, e.g. 95%. Worldwide valid strict guidelines have been elaborated prescribing the way to assess the uncertainty for each source separately. They describe how

*e-mail: gcbobrow@cyf-kr.edu.pl

to include the contribution of each source of uncertainty in order to estimate the combined (total) uncertainty and the extended uncertainty of the result [2-4].

The assessment of uncertainty takes into account the influence of both random and systematic errors on the final result of the measurement, e.g. performed chemical analysis. It incorporates a classical statistical approach to estimate the type A standard uncertainty, which expresses the influence of random errors on analytical results and is given in terms of standard deviation or relative standard deviation. This classical approach to estimate the precision by repeated determinations unfortunately fails in the presence of systematic errors, which may occur in various steps of the analytical procedure and therefore they have to be evaluated by means of the type B standard uncertainty [6, 7].

This work deals with the ICP-OES determination of the selected metals, namely Zn, Cr, Cd, Cu, Ni, Pb. Fe, Mn, Mg and Ca, in surface water and estimation of the corresponding basic metrological characteristics. These investigations were performed in the framework of the environmental monitoring project in the Małopolska region [8]. A further 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 determination of individual elements depend on different sources of uncertainty, it was important to analyze, which partial uncertainties are the largest and most influence the final result. For this purpose several sources of information were collected, such as:

(a) results of analytical measurements related to the current quality control of analytical data, mainly control (Shewhart) charts and validation data,

(b) analyst knowledge and experience connected to the behaviour and properties of the investigated materials and the applied instrumentation,

(c) data provided by the supplier of analytical equipment,

(d) data from the certificates about instrument calibration and the specification of the employed standards.

Experimental Procedures

Reagents, Reference Materials and Sampling

Unless otherwise specified, all chemicals used were of Reagent Grade purity. Deionised water was purified with a cartridge system from MILLIPORE Milli-Q gradient. Tracepure 65% nitric acid, Multielement CertiPUR® Reference Material - ICP Standard Solution IV, and Reference Material Magnesium ICP Standard were produced by Merck. The multielement reference material contains nine metal elements with the following certified concentrations: 995 ± 5 mg/L Ca, 999 ± 5 mg/L Cd, 1,002 ± 5 mg/kg Cr, 1,000 ± 2 mg/L Cu, 1,000 ± 5mg/L Fe, 1,002 ± 5mg/L Mn, 1,003 ± 5mg/L Ni, 998 ± 5mg/L Pb, and 998 ± 5mg/L Zn. The magnesium reference material contains 1,004 ± 5 mg/L

Mg. Traceability of the mentioned ICP standards ensues from the high precision ICP measurements against the corresponding NIST SRM 3131a and SRM 3109a, respectively. In addition, the 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 now and then used to provide a double check of the obtained results. 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 levels.

Over the course of one year, 1,152 water samples were acquired from 96 sampling sites in Małopolska rivers according to the ISO recommendation [9] and collected in cleaned polypropylene bottles. They were immediately filtered through a 0.45 µm cellulose acetate membrane filter in a Sartorius device. Then they were acidified with conc. nitric acid to pH 2, transported to the laboratory and stored at 4°C. The ICP-OES determination [10] was performed within 24 h after sampling.

Instrumentation

The ICP-AES Optima 2000 DV spectrometer (Perkin Elmer) with an AS 93 autosampler and a scanning CCD detector (25600 pixels) were applied for the determination of metals using a standard calibration method. The wavelengths selected for the ICP-OES determination of the monitored elements are given in Table 1. The measured data were sampled and 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 [10]. Further details on 10 metal ions determined in Małopolska surface waters are introduced in Table 1 (although not all the data are shown due to their large size). The indicated analysis range is compatible with the linear range shown in Table 1; if the result for a particular element was larger than the upper limit of this range, the analysis was repeated after diluting the sample.

Results and Discussion

Basic Metrological Characteristics

The following metrological characteristics were calculated and summarized in Table 1: precision, trueness (expressed in two ways), linear response range, detection limit and quantification limit. These characteristics are well known, but it is worth defining at least some of them. Precision and trueness are components of accuracy, which expresses the closeness of a result to the true value [11] and is a combination of random error (precision) and systematic error (bias). Precision is the closeness of agreement between independent test results obtained under stipulated

Table 1. Metrological characteristics of the ICP-OES determination of metals in Małopolska surface waters.

Element	λ [a],	Precision [b],	Trueness [c],	Trueness by Prof. Test.[d],	Linear range [e],	LOD [f],	LOQ [g],
	nm	%	%	%	mg/L	mg/L	mg/L
Cadmium	214.438	4	101	93	0.001 - 0.10	0.00073	0.0024
Calcium	317.933 315.887	5	101	100	0.02 - 2.5 2.5 - 150	0.00022	0.00073
Chromium	267.716	4	101	94	0.002 - 0.10	0.00092	0.0031
Copper	324.754	5	102	100	0.002 - 0.20	0.00051	0.0017
Iron	259.940	2	101	98	0.005 - 0.20	0.00071	0.0024
Lead	220.353	4	100	100	0.005 - 0.10	0.0039	0.013
Magnesium	279.553 279.079	6	99	100	0.01 - 0.50 0.5 - 50	0.000063	0.00021
Manganese	257.610	5	101	98	0.001 - 0.20	0.000091	0.00030
Nickel	231.604	9	100	92	0.005 - 0.10	0.0012	0.0040
Zinc	213.856	3	102	103	0.007 - 0.50	0.0012	0.0040

[a] Selected wavelength.

[b] Precision is expressed as the RSD in % from a series of results plotted on the Shewhart control chart.

[c] Trueness was estimated by periodic analyses of the test samples prepared from the CRM.

[d] Trueness obtained from the analysis of the distributed samples of CRM during interlaboratory Proficiency Testing.

[e] Dynamic linear range; the determination coefficient, r^2, of the calibration lines in all investigated cases was larger than 0.999.

[f] The LOD was calculated as $3s_b$ of the measured blank signals divided by the slope of the calibration line.

[g] The LOQ was calculated as $10s_b$ of the measured blank signals divided by the slope of the calibration line.

conditions [12, 13]. Trueness [11, 13] expresses the closeness of agreement between the average value of the considered laboratory test obtained from a large set of test results and an accepted reference value; it is evaluated in terms of bias through the analysis of a reference sample [14].

In Table 1 the measurement wavelengths are specified in the second column. Overall precision (column 3) was expressed using the relative standard deviations (RSD) in %, which were calculated from a series of results plotted on the Shewhart control charts [15] serving for internal QC purposes. After 20 samples a new chart was made and a new test sample was measured. Intermediate precion was determined from three kinds of precision (repeatability, intermediate precision, reproducibility).

Proficiency Testing, used for estimating trueness from interlaboratory comparison, was based on the results of determination of the reference material analyzed during the European project "Screening methods for water data information in support of the implementation of the water framework directive", that closely depends on the quality of monitoring data and their comparability from the river basin. It required development, validation and dissemination of rapid, affordable and user-friendly measurement techniques. An important output was therefore the production of the quality control (QC) tools for the analytical methods applied for ecological, biological and chemical monitoring purposes. The results are assembled in the fourth column. Another way of trueness estimation (column 5) was obtained by periodic analysis of the test samples prepared from the certified reference material (CRM). In order to achieve a complete linear range (last column in Table 1) of the determination of calcium and magnesium, the measurement wavelength had to be changed.

The limit of detection (LOD) and the limit of quantification (LOQ) were obtained in the most common way (specified as the classical approach in the IUPAC recommendation paper [16]) using the standard deviation of the blank signal multiplied by 3 and 10, respectively; they are summarized in the last two columns.

Estimation of Uncertainties

Uncertainty estimation was performed in the following steps. At first all possible factors contributing to the measured analytical signal were specified. Then the sources of uncertainty were identified and their influence on the final result was judged. It included the following steps of the analytical process:

(a) sampling (sampling strategy and sample homogeneity, water flow rate, temperature, atmospheric pressure),

(b) sample storage and preparation (filtration, dilution errors, storage conditions, sample stability),

(c) calibration of the used solutions (uncertainties of the standard solutions in calibration, uncertainty of the ref-

Table 2. Combined and extended uncertainties of the ICP-OES 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)	5.0	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 ($\lambda_1 = 279.553$ nm)	6.0	9.5	19.0
Magnesium ($\lambda_2 = 279.079$ nm)	6.0	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 as type A uncertainty and was based on the sampling quality control according to ISO 8258 [15].

erence solution concentration, difference between the analyte and the standard solution compositions, instrumental precision, temperature, humidity),

(d) ICP-OES measurement (instrumental bias, choice of instrumental parameters, interferences from the sample matrix, impurities of nitric acid, imprecision of the performed measurements),

(e) data processing (rounding, fitting the calibration plot),

(f) presentation of final results (selection of confidence level α),

(g) additional unrecognized random effects.

After preliminary expression of all possible sources of uncertainty only those were taken into account which have a significant effect on the uncertainty of the final analytical result. It has to be emphasized that traceability of measurements was maintained throughout the whole study. It is noteworthy that traceability [1] is the ability to interrelate property of the measurement result or the value of a standard to stated references, usually national or international standards, through an unbroken chain of comparisons.

For determination of the combined uncertainty of every determined metal concentration it was necessary to combine all significant uncertainty contributions (partial uncertainties) occurring in individual stages of the analytical process. Assuming an additive model of the uncertainty sources and insignificant pair-wise correlations, the combined uncertainty of the determined concentration c for each metal element can be calculated according to the formula (1), which takes into account the standard uncertainties of all significant individual steps of the measurement process:

$$u_{comb}(c) = \sqrt{u_{samp}^2 + u_{ICP}^2 + u_{c0}^2 + u_{prec}^2 + u_{RM}^2 + u_{reff}^2} \quad (1)$$

...where:

u_{samp} – standard uncertainty of sampling,

u_{ICP} – standard uncertainty of the ICP-OES 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.

The standard uncertainty of sampling, "usamp", was repeatedly measured as type A uncertainty, evaluated on the basis of the sampling quality control by Shewhart charts [15]. The results are summarized in the second column of Table 2. It is obvious that the sampling uncertainty makes the main part of the combined uncertainty of the final result of analysis.

The uncertainty of the ICP-OES equipment, u_{ICP}, was calculated from 25 repetitive measurements of the standard solution of the corresponding element, from which Type A uncertainty $u_{ICP} = 1\%$ was found.

The standard uncertainty of the sample concentration c_0 was obtained from inverse calibration dependence:

$$\hat{y} = a + b c_0, \qquad c_0 = \frac{\hat{y} - a}{b} \qquad (2\ a,b)$$

...where $\hat{y}$ denotes the corresponding ICP-OES signal, and a and b are the regression parameters of the calibration line. The uncertainty $u(c_0)$ was calculated [7, 17] by the equation:

$$u(c_0) = \frac{s_y\, t_\alpha}{b}\sqrt{\frac{1}{n}+\frac{1}{m}+\frac{(\hat{y}-\overline{y})^2}{b^2\sum(c_i-\overline{c})^2}} \quad (3)$$

...where: s_y – residual standard deviation, $\hat{y}$ – the mean value of n ICP-OES signals of the standard solutions, $\overline{y}$ – the mean value of the ICP-OES analytical response for m replicates, c_i – the concentration of the i-th standard solution that was used for constructing the calibration plot, $\overline{c}$ – the mean concentration value of the standard solutions used in calibration, m – number of replicates of the sample measurements, n – number of calibration points, c_0 – concentration of the metal element in the investigated sample corresponding to the mean signal $\overline{y}$, and t_α – critical t-distribution value for n-2 degrees of freedom and confidence level α, a, b – regression coefficients of the calibration line. In the performed calibration studies, ten determinations were made ($n = 10$) for each element and three parallel determinations were made for the evaluation of the sample signal ($m = 3$); confidence level $\alpha = 0.05$ was used.

Precision was calculated as the relative standard deviation of 60 determinations performed with the reference material samples and expressed as type A uncertainty. Its value reflect the overall precision of the determined concentration and is influenced by all steps of the analytical process, like sample preparation, calibration, ICP measurement, and personal factors.

Recovery is defined as the proportion of the amount of analyte, present or added to the analytical portion of test material, which is extracted and presented for measurement [17]. The term "recovery" is used in two different contexts [18]:
(1) To express the yield of an analyte in a preconcentration or extraction stage in an analytical method.
(2) To denote the ratio of the concentration c obtained from an analytical process via a calibration graph compared to the reference value c_{ref}, i.e. $R = c/c_{ref}$.
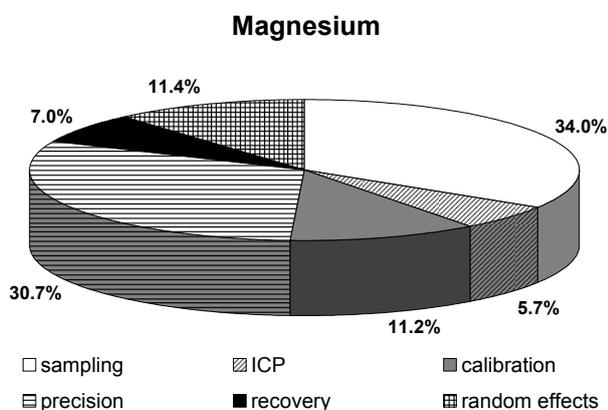In this work the second meaning is valid.

The uncertainty of recovery was calculated from the following equation using the type A uncertainty evaluation [19]:

$$u(R_M) = R_M \cdot \sqrt{\left(\frac{s_{obs}}{\sqrt{n}\cdot\overline{c}_{obs}}\right)^2 + \left(\frac{u(c_{CRM})}{c_{CRM}}\right)^2} \quad (4)$$

...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 standard deviation of the mean when divided by $\sqrt{n}$), n – number of measurements, $\overline{c}_{obs}$ – 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. For $u(R_M)$ calculation the number of measurements $n = 10$ was used for all investigated elements.

The uncertainty of unrecognized random effects, u_{ref}, was estimated at 2% using the type B evaluation and involving random errors in measurement as well as in results interpretation. It was made as a qualified estimate based on the analyst's experience. Utilization of the B type uncertainty used in addition to the random effects expressed by the A type uncertainty is justified, e.g. in the NIST Technical Note [20].

The calculation of the expanded uncertainty is the ultimate step in expressing the uncertainties. It was calculated by multiplying the combined standard uncertainty by the coverage factor $k = 2$ (corresponding to the significance level $\alpha = 0.05$ and referred to the 95% probability) according to the formula [2, 3, 19, 21]:

$$U = k\, u_{comb} \quad (5)$$

After calculation of the combined uncertainty, the expanded uncertainty, U, can be estimated. It allows for the assessment of the uncertainty considering normal distribution of the measurement result distribution and a chosen

Magnesium

Fig. 1. Contribution of the uncertainty components to the final combined uncertainty for the ICP-OES determination of magnesium in surface waters.
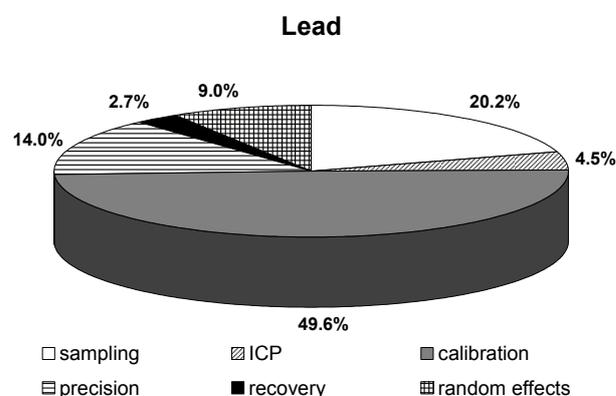
Lead

Fig. 2. Contribution of the uncertainty components to the final combined uncertainty for the ICP-OES determination of lead in surface waters.

probability $P = 100\,(1 - \alpha)\%$ or corresponding significance level α; preferably $P = 95\%$ (which corresponds to $\alpha = 0.05$) [7]. Table 2 presents all values of the combined and expanded uncertainties calculated for the monitored elements. A detailed study of all contributions to the combined uncertainty revealed that the largest uncertainty contribution for most elements is the sampling uncertainty. For illustration, Figs. 1 and 2 depict the individual standard uncertainty contributions to the combined uncertainty of the final analytical result for magnesium and lead.

Conclusions

In this work, metrological characteristics of the determination of ten metal elements in surface waters by ICP-OES measurements are reported. The uncertainties of sampling, the ICP-OES measurement, calibration, precision, recovery, and random effects have significant influence on the combined standard uncertainty of the finally determined concentration of the monitored metal elements. As documented in Table 2 and by Figs.1 and 2, sampling, calibration and imprecision of the whole analytical procedure are the most critical step in surface water monitoring.

The combined and expanded uncertainties representing the final results decrease with the increase of the concentration of the determined element. For example, the uncertainty for magnesium and calcium (Table 2) present in higher content in surface water is lower than that of other investigated elements whose concentrations are lower.

In general, the ICP-OES was found as the method with satisfactory good trueness and precision, sufficiently large linear range and sensitivity enabling to reach low limits of quantification of the determined metals in the water matrix. Therefore it is fully suitable for routine analysis of metals in surface waters.

Acknowledgements

References

1. BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML. International vocabulary of basic and general terms in metrology. 2nd Ed. ISO, Geneva, **1993**.

2. EURACHEM/CITAC. Quantifying uncertainty in analytical measurement. 2nd ed. EURACHEM/CITAC, Teddington, Middlesex, **2000**.

3. ISO, OIML, IEC, BIM. Guide to the expression of uncertainty in measurement. 1st ed. ISO, Geneve, Paris, 1993. Corrected and printed **1995**.

4. EAL-R2. Expression of the uncertainty of measurement in calibration. Draft EAL/6A/96, European cooperation for accreditation of laboratories, **1996**.

5. HULANICKI A. Modern analytical chemistry. Wydaw. Naukowe, Warszawa, **2001** [In Polish].

6. CROSBY N.T., DAY J.A., HARDCASTLE W.A., HOLCOMBE D.G., TREBLE R.C., PRICHARD F.E. Quality in the analytical chemistry laboratory. J. Wiley, Chichester, **6**, **1995**.

7. MOCAK J. Evaluation procedures and uncertainties. Open and distance learning study - quality of chemical measurements and chemical metrology. European training foundation, Torino, Charter **5** and **6**, **1999**.

8. Report on the environmental conditions in Małopolska shire in 2002 Biblioteka Monitoringu Srodowiska, Kraków, **2003** [In Polish].

9. ISO 5667-6. Water quality sampling: Guidance on sampling of rivers and streams. ISO, Geneva, 1990. Revised **2005**.

10. ISO 11885. Water Quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy. ISO, Geneva, 1996. Revised as ISO 11885:2007, **2007**.

11. ISO Guide 5725. Accuracy (Trueness and Precision) of measurement methods and results. ISO, Geneva, **1994**.

12. ISO 3534-1. Statistics, vocabulary and symbols. ISO, Geneva, **1993**.

13. MENDITTO A., PATRIARCA M., MAGNUSSON B. Understanding the meaning of accuracy, trueness and precision. Accred. Quality Assurance, **12**, 45, **2007**.

14. BOQUE R., MAROTO A., RIU J., RIUS F.X. Grasas y Aceites **53**, 128, **2002**.

15. ISO 8258. Shewhart control charts. Geneva, 1991. Corrigendum: ISO 8258/Cor1, **1993**.

16. MOCAK J., BOND A.M., MITCHELL S., SCHOLLARY G. A statistical overviewof standard and new procedures for determining the limits of detection and quantification. Pure & Appl. Chem. **69**, 297, **1997**.

17. IUPAC. Harmonised Guidelines for In-House Validation of Methods of Analysis. Technical Report, http://www.iupac.Org/projects/1997/501_8_97.html. **1997**.

18. IUPAC. Harmonised guidelines for the use of recovery information in analytical measurement. Pure Appl. Chem. **71**, 337, **1999**.

19. SIERZPUTOWSKI A. Uncertainty of measurement procedures. AQUA LAB, Gdańska Fundacja Wody, Gdańsk, **2003** [In Polish].

20. TAYLOR B.N., KUYATT C.E. Guidelines for evaluating and expressing the uncertainty of NIST measurement results. NIST TN-1297. Appendix D. NIST, Gaithersburg, MD, **1994**.

21. Information Bulletin No. 1/39/2003. Uncertainty of laboratory measurement. Warszawa, **2003** [In Polish].