

*Original Paper*

## **Ion Analysis at the Highest Stage – The Metrological Approach by National Metrological Institutes**

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**Abstract.** National Metrological Institutes (NMI's) from fifteen different countries participated in interlaboratory comparisons where concentrations of about  $1 \text{ g kg}^{-1}$  in solutions of aluminium, copper, iron, magnesium, chloride and phosphate were measured. A very high comparability of the results irrespective of the analyte and the applied measurement technique was observed. The relative in-between laboratory standard deviations of the results as reported by the participating laboratories were between 0.13% for copper and chloride up to 0.33% for aluminium, and all of the 81 results were found in the range of  $\pm 1\%$  with respect to the reference value. Due to the gravimetric preparation of the samples, a conventional true reference value was calculated, and no significant deviations of the reference values and the means of all results reported by the institutes were found.

**Key words:** Metrology; ion analysis; calibration solution; interlaboratory comparison; key comparison; uncertainty.

The global market provides a strong driving force for the mutual recognition of measurement results. On a formal basis this was established by the mutual recognition arrangement (MRA, [1]) that was signed some years ago by the National Metrology Institutes (NMI) of the participating countries all over the world. The MRA is based on a huge data base which is managed

by the International Metrology Institute (BIPM) in Paris [2]. The BIPM operates under the exclusive supervision of the International Committee for Weight and Measures (CIPM). Different Consultative Committees have been set up by the CIPM to provide it with information on matters it submits to them for study and advice. For chemistry, the Consultative Committee for Amount of Substance (CCQM) was set up in 1993 by the CIPM.

The data base contains several appendices dedicated to the measurement capabilities and the national standards provided by the NMI. In order to prove its declared competence, each NMI has to participate in international comparisons at the highest level of measurement. The results of these key comparisons as well as the resulting degree of equivalence are also reported in the data base and thus available to the public.

As most results from ion analysis refer to a calibration solution containing the determined ion in a defined concentration, the quality of these solutions is a decisive factor in the reliability of the measurement result and thus in its acceptance. However, for many of these solutions, which are available from several commercial producers, an unrealistically low uncertainty is declared on the label. The given uncertainties do not comprise all uncertainty sources, i.e. the uncertainty of the purity of the starting material, contaminations, evaporation and other possible

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changes of the declared value during storage. Some market overviews have shown that not only the declared value is sometimes incorrect but also that the quoted uncertainty is often too low. Values for certified calibration solutions are supposed to be traceable by an unbroken chain of comparisons to the international system of units (SI). This traceability chain always starts with values for pure and well characterised substances or values for the analyte amount contents of solutions thereof or a value obtained by a primary method of measurement [3]. Due to the relevance of these calibration solutions, several intercomparison studies have been carried out by the NMI of fifteen countries, applying a wide range of different ion analysis techniques such as ion chromatography, titrimetry, ICP-OES, ICP-MS, coulometry and gravimetry [4, 5]. The cations of aluminium, copper, iron and magnesium as well as the anions chloride and phosphate, each in aqueous solution, were measured at a typical concentration level of  $1 \text{ g kg}^{-1}$ . These ions were chosen due to their relevance for the analytical community (analyses for environment and health) and according to the availability of stable and well characterised substances as starting material. All solutions were prepared under controlled conditions from sufficiently pure metals or well characterised salts, respectively. Thus a highly reliable and precise gravimetric reference value with a defined combined uncertainty value was available.

## Experimental

### Gravimetric Preparation of Solutions

For each element a 10L batch of a solution of a mass fraction of about  $1 \text{ g kg}^{-1}$  was gravimetrically prepared using the best available high purity metal (primary material) and both high purity nitric acid (sub-boiled) and water (from a Milli-Q Element system, Millipore AG). In the case of aluminium, the dissolution reaction had to started off by adding concentrated hydrochloric acid. The purity of all of the six starting materials was determined elaborately and reported in a certificate, and in all cases a detailed uncertainty budget for the purity calculation was attached by the providing NMI. Aluminium and magnesium were provided by NIST U.S.A. (SRM 3101a and NP-Mg-1). Copper was provided by BAM, Germany (A-Primary-Cu 1). Iron was provided by LNE, France (B.N.M. 001). The anion solutions were prepared by dissolving high purity KCl (NIST SRM 999a) and  $\text{Na}_2\text{HPO}_4$  (EMPA ARF-005) in ultrapure water. All weighings were performed in a weighing room fulfilling the requirements of OIML Class E2 [6]. The solutions were homogenised in an FEP-coated mixing tank by tumbling them for 12 hours, and the solutions were filled into 250 mL PP bottles using a closed loop system to minimise evaporation and contamination. An intensive between-bottle inhomogeneity study was performed in every case [7]. The stability of the packed samples in

terms of evaporation was investigated by exposing the closed bottles to air at a temperature of 295 K and 50% rel. humidity during 120 days. No significant evaporation was observed when the bottles were welded into mylar bags [7]. The final mass fractions of the analyte in the sample solutions shipped were in the range of  $0.988 \text{ g kg}^{-1}$  up to  $1.020 \text{ g kg}^{-1}$  with respect to the corresponding ion. The relative combined uncertainty of the assigned gravimetric value (GV) was less than 0.045% (95% confidence) for all six solutions. In this publication the individual reference values are normalised to  $1 \text{ g kg}^{-1}$  to simplify the graphical presentation.

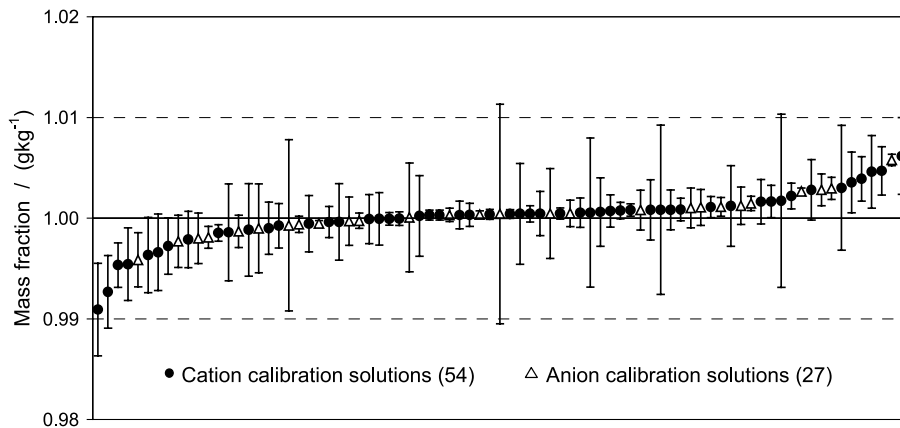
### Analytical Techniques Applied by the NMIs

The technique most often applied in the measurement of mass fractions of the ions in the solutions was titrimetry (28 results), followed by ICP-OES (20 results), coulometry (10 results), ion chromatography (IC) and mass spectrometry (ID-TI-MS, ID-ICP-MS and ICP-MS, 9 results each) and gravimetry (5 results). Titrimetry was applied in cation analysis either by direct titration with EDTA or using back titration techniques (mostly with Zn solution as the back titrant). Titrimetry in anion determination was applied argentometrically for  $\text{Cl}^-$ , whereas for the phosphate solution two NMIs performed acidimetric titration of  $\text{HPO}_4^{2-}$  to  $\text{H}_2\text{PO}_4^-$ . ICP-OES with standard calibration using an internal standard was applied to all of the four cation solutions. In addition, two NMIs used ICP-OES for indirect determination of  $\text{PO}_4^{3-}$  via measurement of total phosphorus. Different experimental designs were applied in coulometric determination of  $\text{Cl}^-$ , i.e. direct precipitation titration with electrogenerated silver ions or indirect coulometric titration of the  $\text{H}^+$  generated by passing the solution through a cation exchange resin. This indirect method was also applied by one NMI to determine the  $\text{PO}_4^{3-}$  concentration using coulometry. In addition, controlled potential coulometry was applied in the determination of copper and iron in one case. Ion chromatography was only used to determine anions and in no case cation determination was performed by IC. By contrast, mass spectrometry (ID-TI-MS and ID-ICP-MS) was used for cation determination only. In all cases except for monoisotopic aluminium, isotope dilution techniques were applied in element determination.

## Results and Discussion

All reported uncertainty budgets are given as expanded uncertainty  $U$  with the coverage factor  $k = 2$  (95% confidence intervals). Due to inexplicable large biases in all results of one NMI, the data from this laboratory was neglected.

The remaining total of 81 results reflect a normal distribution with a relative between-laboratory standard deviation of  $s_L = 0.24\%$  and average relative expanded uncertainties of  $\bar{U}_{\text{rel}} = 0.26\%$ . All data is distributed in the range of  $\pm 1\%$  with respect to the GV (Fig. 1). Comparability among the results of anion solutions  $s_L = 0.19\%$  was slightly better than that for cation solutions with  $s_L = 0.26\%$ . This trend becomes clearer when the highest and the lowest values are omitted in both data sets (Table 1). With regard to the analyte, the chloride and copper measurement



**Fig. 1.** Reported values and expanded uncertainties ( $U=2$ ) of metrological intercomparisons of all cation and anion calibration solutions independent of applied analysis method and analyte (normalized to the gravimetric values GV)

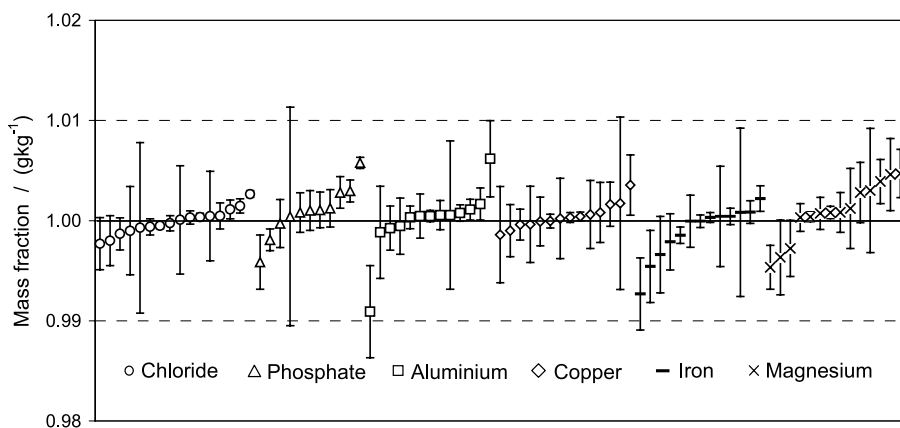
**Table 1.** Comparability of ion analysis in terms of the nature of the analyte given by relative between-lab deviation  $s_L$ . The mean values  $\bar{U}_{rel}$  of relative expanded uncertainties  $U_{rel}$  reported by the laboratories do not show significant differences with respect to the analyte ('mean' stands for the mean value of the laboratory means; GV represents the gravimetric value; values for anions and cations are given as the mean of the corresponding individual values)

Analyte (results)	$s_L$ (%)	$\bar{U}_{rel}$ (%)	$s_L$ without highest and lowest value (%)	(GV-mean)/GV*100 (%)
Chloride (16)	0.13	0.22	0.09	+0.011
Phosphate (11)	0.26	0.25	0.15	-0.089
Aluminium (13)	0.33	0.26	0.08	-0.004
Copper (14)	0.13	0.29	0.08	-0.043
Iron (13)	0.27	0.27	0.18	+0.107
Magnesium (14)	0.29	0.26	0.24	-0.087
Anions	0.19	0.24	0.14	-
Cations	0.26	0.27	0.26	-
All ions	0.24	0.26	0.24	-

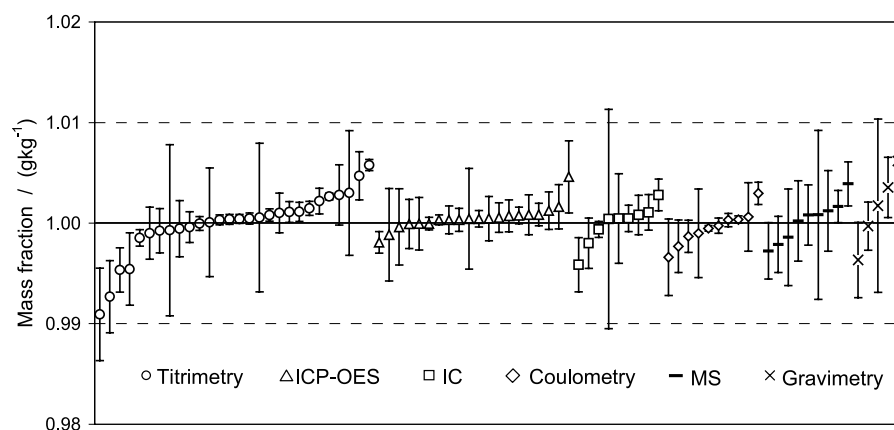
results are slightly more comparable ( $s_L=0.13\%$ ) than the results of other analytes. Results of aluminium measurements show the highest between-laboratory variability with  $s_L=0.33\%$ . Figure 2 illustrates the results arranged by nature of the analyte.

Due to the generally small deviations of the individual results from the GV, in some cases the comparability

of results is significantly decreased by one or two results showing elevated deviations. This is especially true in the case of aluminium and phosphate. Therefore, for all data sets the  $s_L$  values calculated without the highest and lowest results are given as well. This leads to the best comparability with  $s_L=0.08\%$  for aluminium and copper solutions mea-



**Fig. 2.** Analysis of intercomparison data in terms of the nature of the analyte reveals best comparability for chloride and copper measurements



**Fig. 3.** Comparability of metrological intercomparison results arranged by analysis method

**Table 2.** Comparability of ion analysis in terms of the analysis method applied

Method (results)	$s_L$ (%)	$\bar{U}_{rel}$ (%)	$\bar{U}_{rel}/s_L$	$s_L$ without highest and lowest value (%)
ICP-OES (20)	0.12	0.20	1.67	0.06
Coulometry (10)	0.17	0.19	1.12	0.10
Ion chromatography (9)	0.20	0.31	1.55	0.11
Mass spectrometry (9)	0.21	0.37	1.76	0.14
Titrimetry (28)	0.32	0.24	0.75	0.25
Gravimetry (5)	0.37	0.43	1.16	–

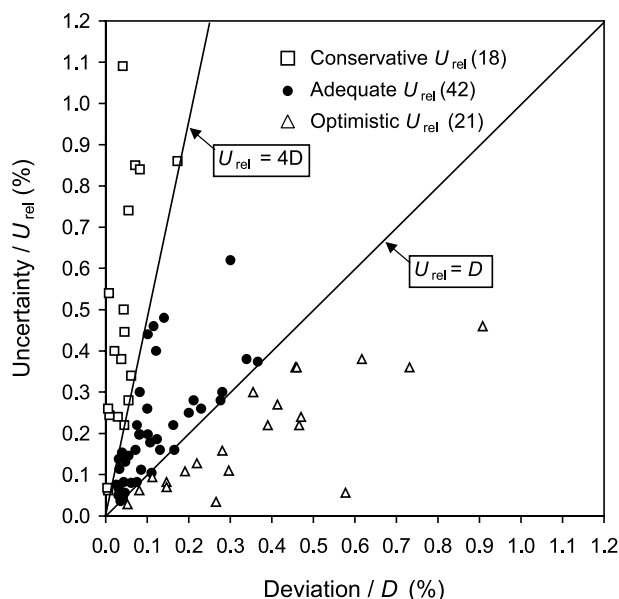
surements. No significant differences in the uncertainty budgets are found with respect to the analyte, and no significant bias between the means and the GV was found either.

With regard to the method of measurement, there are significant differences in terms of comparability of measurement results. Figure 3 shows the results arranged by analytical methods applied and Table 2 gives the  $s_L$  values relating to the applied method. Results by ICP-OES and coulometry revealed to be comparable with the smallest spread ( $s_L = 0.12\%$  and  $0.17\%$ ), followed by IC and MS measurement results ( $s_L = 0.20\%$  and  $0.21\%$ ). Variabilities within the titrimetry ( $s_L = 0.32\%$ ) and gravimetry ( $s_L = 0.37\%$ ) data are found to be significantly higher compared to the other methods. This is surprising considering that titrimetry and gravimetry are primary methods from a metrological point of view [3]. Furthermore, although ICP-OES is not a primary method, the ICP-OES results reported by the NMIs showed the best comparability. The order of the measurement methods in terms of  $s_L$  is consistent even when the highest and lowest results are omitted (Table 2). It should be noted that within the same analysis method, totally different analysis techniques (and performance of individual

measurement procedure) were applied, and the comparability of these results might therefore be restricted.

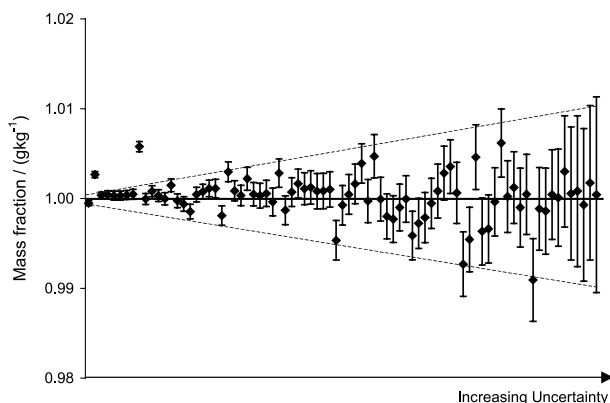
#### Discussion of Uncertainties Reported by the NMIs

The determination of measurement uncertainty is a difficult task although there are guides stating the principle of and instructions on how to evaluate and determine a correct uncertainty budget [8, 9]. Even within the metrological community there are still open questions concerning this issue, and not all NMIs use the same approach to work out the uncertainty budgets of their measurement results. In addition, many different measurement techniques and procedures are applied by the NMIs for the same analytical problem. This leads to a wide spread in the size of uncertainty statements. For values from titrimetry, combined uncertainty budgets from  $0.03\%$  relative up to  $0.85\%$  relative are reported. Even though different performances of measurement procedures lead to different uncertainties, the big spread of uncertainty budgets indicates that there is a need for further harmonisation of uncertainty determination. Table 2 uses the term  $\bar{U}_{rel}/s_L$  in order to reflect



**Fig. 4.** Correlation of deviation from reference “accuracy” (given as deviation of result from gravimetric value) and reported relative uncertainty. Three quarters of the results were reported to have adequate or conservative uncertainty budgets

whether the uncertainty reported tends to be too optimistic (small  $\bar{U}_{rel}/s_L$  ratio) or too conservative (high value of  $\bar{U}_{rel}/s_L$  ratio). The results from the three so-called primary methods – titrimetry, coulometry and gravimetry – show more optimistic uncertainty budgets than the values resulting from non-primary methods which are reported with relatively higher uncertainties. This might provoke the question of whether there is overconfidence concerning primary methods of measurement when uncertainties are evaluated for the results. Figure 4 shows the correlation between deviation  $D$  (reported value minus gravimetric value) and the accompanying uncertainty of the results. Approximately half of the results (42 out of 81) are reported with adequate uncertainty budgets, whereas about a quarter of the results reported were too optimistic (21 of 81) or too conservative (18 of 81). Nevertheless, the intensive discussions about this issue within the metrological community has led to improvements in uncertainty evaluation. Figure 5 illustrates that the results with the smallest uncertainty budgets are also those with the smallest deviations from the reference (with few exceptions). Finally, it can be stated that comparability of ion analysis results at the metrological level is good. The metrological approach of the NMI’s permits excellent comparability of the results far below one percent relative. In contrast, field



**Fig. 5.** All data arranged according to increasing uncertainty budgets. With few exceptions, the results with the least deviation from the reference value are also the results with the smallest uncertainties reported

laboratories which can generally put much less effort into measurement tasks show results of questionable comparability [10]. This study shows that comparability in chemical measurement at such a high level is possible despite the multiplicity of different analysis methods and techniques applied by the NMI’s.

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