Original Paper

High Precision Titrimetry, Ion Chromatography and ICP-Optical Emission Spectrometry for the Estimation of Inhomogeneities in Aqueous Calibration Solutions for Metrological Purposes

Michael Weber[*], **Jürg Wüthrich,** and **Sergio Rezzonico**

Swiss Federal Laboratories for Materials Testing and Research (EMPA), CH-9014 St. Gallen, Switzerland

Abstract. The homogeneity of samples intended for metrological intercomparison studies must be granted without ambiguity. This holds equally true for aqueous solutions for which the determination of between-bottle variations requires measurement techniques with extremely high precision. Therefore measurement series were designed for automated analysis techniques such as titrimetry, optical emission spectrometry and ion chromatography which offer very high precision of results. Between-bottle relative standard deviations (RSD) of at best 0.008% were obtained with titrimetry. With optical emission spectrometry and ion chromatography, between-bottle RSD's of 0.02% and 0.05% were obtained. The contributions from these measurements were included in a conservative approach to the uncertainty budgets of the gravimetrical reference values for the analytes in the samples.

Key words: Metrology; ion analysis; homogeneity; calibration solution; precision; repeatability; uncertainty.

National metrological institutes (NMIs) compare their measurement results by participating in intercomparison studies at a metrological level, and this data represents the NMI's measurement capability [1, 2]. Since 1999 such intercomparisons were carried out using calibration solutions at the $1 \, g \, kg^{-1}$ level of the cations aluminium, copper, iron, magnesium and for the anions chloride and phosphate [3, 4]. The comparability of the NMI's results for such intercomparison studies with calibration solutions was very good, and deviation from the reference value of most results was less than 0.1% rel. [5]. Therefore it is of particular importance to know the exact value and uncertainty of the mass fraction of the analyte in these intercomparison samples provided by the piloting NMI. In the case of synthetic sample solutions, i.e. calibration solutions, the accuracy of the gravimetric reference value can be granted by using analyte materials of lowest uncertainty of mass fraction of main component on the one hand and performing all weighing operations in a weighing room on the other hand.

There are two types of calculable contributions for the determination of the uncertainty budget of the gravimetric reference value: the uncertainty of the mass value from weighing and the uncertainty of the purity of the reference material. Consideration of these uncertainty contributions only leads to combined uncertainties of the reference value of only 0.002% rel. [3, 6]. If the whole production procedure is taken into account, which includes the cleaning-up procedures (if possible), dissolution of the materials in acid or water, dilution, sample handling, homogenization and bottling – and if possible contamination and blanks are considered – an uncertainty budget of 0.002% is regarded as too optimistic.

* Author for correspondence. E-mail: michael.weber@empa.ch

This holds true if all operations are performed under controlled clean room conditions. Many other factors may affect the uncertainty of the analyte value, including inhomogenous dissolution or mixing of the starting material in the batch solution or different behavior of the individual sample solution in the PP bottles (adsorption on bottle surface, evaporation of liquids). Maybe nobody would expect significant inhomogeneities in a 20 L batch of a 1 g kg^{-1} single element solution after the FEP-coated container is tumbled overhead for 12 hours. Nevertheless, homogeneity of the analyte in the bottled samples is assumed but has not been established experimentally. As it is one of the main aims of the metrological community to elucidate unsolved questions and determine uncertainties from influence parameters, we decided to develop a novel approach to the conservative determination of between-bottle inhomogeneities of aqueous samples.

It goes without saying that only highly automated techniques with very low levels of uncertainty were considered. Therefore we compared the results from titrimetry, ion chromatography and ICP optical emission spectrometry in terms of best achievable repeatability. When assuming that within-bottle inhomogeneity in the 250 mL bottles is negligible (after shaking them very well), the between-bottle variability of the results as the relative standard deviation (RSD) of the mean values of all bottles can be taken as a rough and conservative estimation of the supposed between-bottle inhomogeneity. Because the repeatability of the measurement technique is included in this estimation, this approach represents a worst case scenario.

Experimental

Apparatus

Titrations were performed under argon atmosphere on a modular automatic system from Metrohm (Herisau, Switzerland) with a 730 sample changer with 2 working stations, a 662 Photometer including a glass fiber light guide with a mirror with a $2 \times 10 = 20$ mm light path; wavelength range 400 to 700 nm, dispensing unit 700 Dosino with 796 Titroprocessor, 722 propeller rod stirrer, titration software Metrodata "TiNet$^{©}$ 2.4" and thermostat with heating finger. For end point detection of copper measurements, an ion selective electrode (Cu-ISE, Metrohm, no. 6.0502.140) with Ag/AgCl double junction reference electrode (Metrohm, no. 6.0726.100) was used. For magnesium and chloride titrations, end point detections were performed with an Ag-rod electrode (Ag-Titrode, Metrohm, no. 6.0430.100) and Ag/AgCl double junction reference electrode (Metrohm, no. 6.0726.100).

Inductively coupled plasma optical emission spectrometry (ICP-OES) data was measured on a radial-view Optima 3000 instrument (PerkinElmer) with auto sampler AS-90, 40 MHz RF generator, optical system with Echelle polychromator, segmented-array charge-coupled device detector (SCD) and a concentric glass nebuliser Conikal (Glass Expansion SARL, Switzerland). Ion chromatography measurements were performed on an IC system from Metrohm with chemical suppression and conductivity detection consisting of the modules 762 IC Interface, 733 IC Separation Center, 709 IC Pump (double piston pump), 752 IC Pump Unit, 766 IC Sample Processor (injection loop 20 µL), and 732 IC Detector. The anions were separated on a METROSEP A SUPP 5 column (4.0×150 mm, Metrohm) with a CO_3^{2-}/HCO_3^- eluent (3.2 mM Na_2CO_3/1.0 mM $NaHCO_3$, flow 0.7 mL min^{-1}).

Reagents

All aqueous solutions were prepared with helium and subsequently ultrasonic bath degassed water (18 MOhm, 0.2 µm filtered). The following solutions were prepared using reagents of the highest quality available (analytical or high-purity grade) from Fluka GmbH, Buchs (Switzerand) or Merck AG, Dietikon (Switzerland): 0.01 M Na_2EDTA (from disodium dihydrate salt of the compound), 0.01 M zinc sulfate (from 0.1 M Titrisol$^{®}$ solution), Chromazurol S indicator solution (from 50 mg Chromazurol S in 100 mL of water), Dithizon indicator solution (freshly prepared from 125 mg Dithizon in 250 mL of ethanol), 0.0004 M silver nitrate solution (from 1 mL of a 0.1 M silver nitrate solution in 250 mL of 0.01 M nitric acid, protected from light), 0.1 M borate buffer solution (from disodium tetraborate in water), acetate buffer solution with pH 4.66 (prepared by mixing the same volumes of 2 M sodium acetate solution and 2 M acetic acid), 2 M ammonia buffer solution (prepared by dissolving 80.0 g ammonia nitrate and 75 mL ammonia solution (25%) in 1000 mL water).

1000 mg kg^{-1} phosphate reference solution (gravimetrically prepared by dissolving 374 mg di-sodium hydrogenphosphate in water to a total of 250 g solution) and 2000 mg kg^{-1} sulfate internal standard solution (gravimetrically prepared by dissolving 740 mg sodium sulfate in water to a total of 250 g of solution).

Procedures

General Procedure for Titration

A lot of 8 out of 50 samples was investigated (regular sampling) in all cases. Each of the eight samples S_i was titrated 10 times under controlled climatic conditions (50% $\pm$ 2% relative humidity, 23.0 °C $\pm$ 0.5 °C) giving the following measurement sequence (sample S_i with i = 1 to 8, replicate number in parentheses): $S_1(1)$, $S_1(2),\ldots, S_1(10),\ldots, S_8(1),\ldots, S_8(10)$. Due to the fact that under these conditions drift effects are negligible, the measurement sequence for titrimetry is less important than in the case of ICP-OES and IC measurements.

Titration of Iron(III) Solution (1000 mg kg^{-1}) [7]

A mixture of 4.75 mL iron(III) sample solution in 80 mL of water was treated with 1 mL Chromazurol S indicator solution. After heating to 50 °C, titrations were performed at a pH of 2–3 with a 0.01 M Na_2-EDTA solution followed by photometric detection at 615 nm and end point determination by intersection of tangents on titration curve.

Titration of Aluminum(III) Solution (1000 mg kg^{-1}) [8, 9]

A mixture of 2.00 mL of aluminum(III) sample solution in 40 mL of ethanol, 15 mL of water, 10 mL acetate buffer and 1 mL Dithizon

indicator solution was treated with 18 mL excess of 0.01 M Na$_2$-EDTA solution. After heating to 50 °C, back titration with a 0.01 M zinc sulfate solution was performed at pH 2–3 (photometric detection at 515 nm and tangent intersection method for end point calculation).

Titration of Copper(II) Solution (1000 mg kg^{-1}) [10]

A mixture of 4.75 mL copper(II) solution in 60 mL water, 10 mL acetate buffer solution and 2 mL of a 1 M sodium hydroxide solution was titrated at pH 9.0 ± 0.5 with a 0.01 M Na$_2$-EDTA solution. Potentiometric end point indication was applied.

Titration of Magnesium Solution (1000 mg kg^{-1}) [11]

A mixture of 4.00 mL magnesium sample solution in 20 mL water, 0.1 mL 0.0004 M silver nitrate solution and 40 mL of 0.1 M borate buffer was titrated at pH 9.0–9.2 with a 0.01 M Na$_2$-EDTA solution. Potentiometric end point indication was applied.

Titration of Chloride Solution (1000 mg kg^{-1})

A mixture of 3.0 g chloride sample solution in 30 mL water and 30 mL acetone was titrated with a 0.005 M silver nitrate solution. Potentiometric end point indication was applied.

Experimental Design of Phosphorus Determination with ICP OES

A lot of 5 out of a total of 30 produced samples (regular sampling) was investigated. To minimize drift effects in signal intensity during the measurement series, the internal standard (IS) technique with sulfur (as sulfate) as the IS was applied, and the ratio of the P and S signals was recorded. The instrument was preconditioned for a minimum of 12 hours (see Results and Discussion). Drift correction was made by measuring a reference solution before and after each sample solution. Sample and reference solutions were prepared with almost similar concentrations (<1% rel. difference) and identical matrices (same stoichiometry of materials).

ICP OES Determination of Phosphate Solution (1000 mg kg^{-1})

The operating conditions are listed in Table 1. 6 g of sulfur IS solution were gravimetrically added to 6 g from each of the 5 sample solutions and filled up to 50 g with water in a polypropylene vial. Each sample solution S$_i$ was divided into 2 sub-samples (S$_i$A and

S$_i$B) and measured between two reference solutions in one set. This set of 20 measurements in total was repeated 7 times so that 14 individual values for each sample solution were obtained. This leads to the following schematic measurement sequence (sample S$_i$ with i = 1 to 5, R = reference, replicate number in parentheses): S$_1$A(1), R, S$_1$B(1), R, S$_2$A(1), R, S$_2$B(1), ..., S$_5$B(1), ..., S$_1$A(7), R, S$_1$B(7), ..., S$_5$B(7).

IC Analysis of Chloride Solution (1000 mg kg^{-1})

A lot of 5 out of a total of 30 produced samples (regular sampling) was investigated under controlled climatic conditions (50% ± 2% relative humidity, 23.0 °C ± 0.5 °C). 10.0 g of sample solution and 10.0 g of sulfate IS solution (1600 mg kg^{-1}) were gravimetrically mixed. Each of the 5 sample solutions S$_i$ was divided into two sub-samples (S$_i$A and S$_i$B), and the set of 10 sub-samples was measured 7 times giving 14 results for each of the 5 sample solutions. The ''response factors'' were recorded (product of chloride signal and chloride sub-sample mass divided by the product of sulfate signal and sulfate sub-sample mass) as results. This leads to the following schematic measurement sequence (sample S$_i$ with i = 1 to 5, replicate number in parentheses): S$_1$A(1), S$_1$B(1), S$_2$A(1), S$_2$B(1), ..., S$_5$B(1), S$_1$A(7), S$_1$B(7), ..., S$_5$B(7).

Results and Discussion

Preconditioning and Equilibration of Instruments

To obtain best repeatabilities it was necessary to bring all the instruments into equilibration while performing a series of pre-measurements. In the case of titrimetry, a test series with 5 measurements led to adequate repeatability, and no significant drift at the level of <0.01% RSD was observed during this conditioning time. With the IC instrument, about 10 to 15 pre-measurements were necessary until the signals showed acceptable repeatability due to conditioning of the column. Both the titrimetry and IC apparatuses were located in a climatized laboratory, and only as little changes in temperature as possible were allowed during the measurement series. Switching off the lights or

Table 1. ICP-OES operating conditions for high precision determination of phosphorus

ICP Source operating parameters		Spectrometer operating parameters	
Plasma flow Ar	15 L min^{-1}	Signal measurement mode	peak integration,
Auxiliary flow Ar	0.5 L min^{-1}		low-res. readout
Nebuliser flow Ar	0.8 L min^{-1}	Background correction	manually selected,
Sample uptake rate	1.5 mL min^{-1}		2-point interpolation
RF-power	1300 W	Measurement time	10 s
Probe rinse	90 s	Integration time	0.05
		Read delay time	120 s
		Replicate measurement	10
		Wavelength analyte	P at 213.618 nm
		Wavelength internal standard	S at 180.669 nm

activating the sleep mode of the monitors during the measurements led to small changes in the room temperature, resulting in a significant effect on the end point detection of the titration curves.

The precision determination of phosphorus measurement in the phosphate solution with ICP-OES proved to be more difficult. In contrast to the prevalently used internal standards, such as manganese or scandium [12], sulfur was chosen (as sulfate salt) in this experiment to be the IS having the development of a high performance OES analysis technique for sulfur determination with phosphorus as internal standard in mind.

Figure 1 shows the response factors of the first measurement series after switching on the instrument. A nonlinear drift of about 40% increase was observed during a time period of 12 hours. A closer look at the signal intensities of S and P revealed that only the signals of S are responsible for this effect (Fig. 2). It is assumed that traces of oxygen in the optical path of the spectrometer may be the reason for this drift because molecular oxygen absorbs UV light below 200 nm where the wavelength of the sulfur spectral line used is located. Therefore, with this experimental setup and sulfur as the internal standard, this drift becomes less significant and almost linear only after a purging and operating time of more than 12 hours, enabling the high precision measurement series to be started. A more favorable IS would allow reducin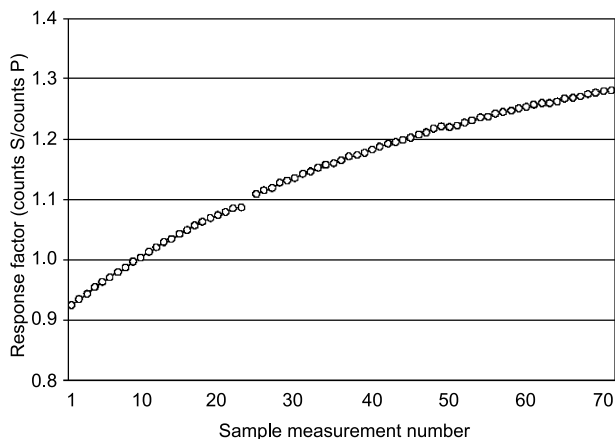g the stabilization time and at the same time similar or better precision are achievable for phosphorus solutions [12]. Nevertheless, it could be demonstrated that sulfur is an adequate IS when the instrument is properly conditioned.

Fig. 2. Highly significant drift in the signals of sulfur used as internal standard led to a nonlinear 40% drift in the phosphorus measurement series

Precision Measurement Series Results

Table 2 shows the measured RSD results obtained in this repeatability study of the ion calibration solutions investigated. Graphical presentations of all data are given in Fig. 3 (cation solutions) and Fig. 4 (anion solutions). Assuming that inhomogeneity within the 250 mL samples is negligible, the average within-bottle RSD is defined as s_{meas} representing the relative measurement precision. The experimental relative variability between bottles s_{bb} is expressed as RSD of the individual within-bottle mean values. Therefore s_{bb} represents the RSD of the sample and not the RSD of the sample mean. With regard to measurement precision, titrimetry led to the best results with s_{meas} for the copper solution of 0.004%. As expected, the within-bottle RSD s_{meas} of IC measurements are found to be less precise by almost up to two orders of magnitude compared to titrimetry measurements (Table 2). The differences between IC and titrimetry measurements are less distinctive when looking at the between-bottle RSD s_{bb}. Values for s_{bb} from 0.008% to 0.0038% are found for titrimetry measurement, whereas the IC measurements lead to s_{bb} of 0.053%. This is the consequence of the fact that s_{meas} is not included in s_{bb}.

Making a statement about whether or not there are significant between-bottle inhomogeneities requires a closer look at the ratio of $s_{bb}/(s_{meas}/\sqrt{n})$ whereby n is

Fig. 1. Intensity ratio of spectral line intensities of sulfur to phosphorous ("response factors") of all 70 phosphate sample measurements after switching on the instrument (reference measurements omitted) showing an increase drift of about 40% with a tendency to slowly decrease (No. 24 is ignored due to instrument failure)
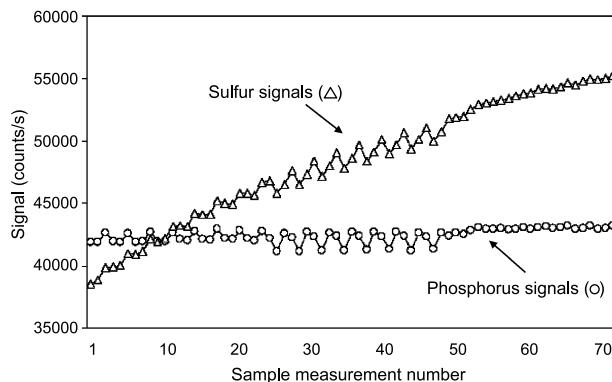
Table 2. Summary of all precision measurements including estimates for uncertainty contribution assumed to be due to between-sample inhomogeneity ($^{*}u_{inhom} = s_{bb}$, $u_{inhom} = s_{meas}/\sqrt{n}$)

Analyte	Technique	n	s_{bb} %	s_{meas} %	$s_{meas}/\sqrt{n}$ %	$s_{bb}/(s_{meas}/\sqrt{n})$	u_{inhom} %
Aluminium	Titration	10	0.025	0.036	0.011	2.2	0.025*
Copper	Titration	10	0.008	0.004	0.001	5.4	0.008*
Iron	Titration	10	0.038	0.049	0.015	2.4	0.038*
Magnesium	Titration	10	0.019	0.016	0.005	3.7	0.019*
Chloride	Titration	10	0.017	0.053	0.017	1.0	0.017**
Chloride	IC	14	0.053	0.345	0.092	0.6	0.092**
Phosphate	ICP-OES	14	0.020	0.088	0.024	0.8	0.024**
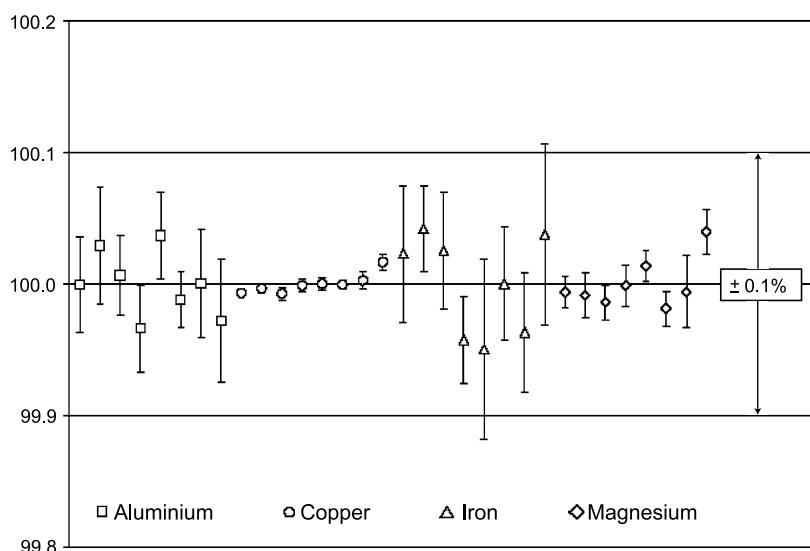
Fig. 3. Results (normalized to 100) from repeatability titrimetry measurements of aqueous $1\,g\,kg^{-1}$ cation calibration solutions showing between bottle variations of 0.008% for copper to 0.38% for iron (the bars illustrate the individual $s_{i,meas}$ for bottle i)
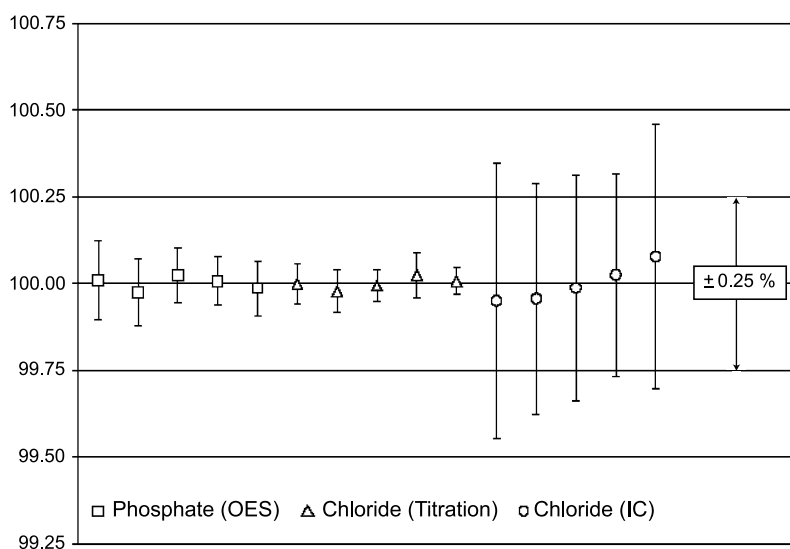
Fig. 4. Results (normalized to 100) from repeatability measurements of aqueous $1\,g\,kg^{-1}$ anion calibration solutions with different analysis techniques (cf. Fig. 3)

the number of independent replicates per sample. The term $\sqrt{n}$ takes into consideration that the RSD of the mean is smaller than the RSD of the individual mea- surements following ISO 35. Because the reduction of s_{meas} by $\sqrt{n}$ is only allowed for independent measure- ments, the replicates should be considered indepen-

dent if they show no trend or pattern [13]. This is the case for all of the measurement series in this study, as can be seen in Figs. 3 and 4, except for the IC measurement series of chloride solution where a slight tendency of increased values is obtained (see Fig. 4). Due to the IC measurement sequence described in the experimental section, an instrumental drift can not be the reason for this trend because the within-bottle data was not acquired time-correlated. Moreover, a real trend of detected inhomogeneity among the chloride samples may also be unlikely due to the fact that the titrimetry data which is much more significant does not show any trend for the same samples.

If the ratio $s_{bb}/(s_{meas}/\sqrt{n})$ gives a value >1, then the between-bottle variation s_{bb} is a good but conservative estimate for between-bottle inhomogeneity. When $s_{bb} = u_{inhom}$, in this case u_{inhom} is independent of the number of replicates n. In this study this is only true for the titrimetry measurement series of the four cation solutions leading to the values for u_{inhom} given in Table 2. Splitting up s_{bb} into a term consisting of s_{meas} and the term describing effective between-bottle variability caused by inhomogeneity $s_{inhom} = u_{inhom}$ is a less conservative approach to the estimation of u_{inhom} in accordance to the GUM [14]. With this approach it is assumed that a measured between-bottle variation s_{bb} always contains contributions from the measurement itself:

$$s_{bb}^2 = u_{inhom}^2 + \frac{s_{meas}^2}{n} \qquad (1)$$

which implies

$$u_{inhom} = \sqrt{\left(s_{bb}^2 - \frac{s_{meas}^2}{n}\right)} \qquad (2)$$

If we calculate u_{inhom} following Eq. (2) for the four titrimetry results of the cation solutions where $s_{bb}/(s_{meas}/\sqrt{n}) > 1$, this leads to slightly decreased values for u_{inhom} ($u_{inhom} = 0.022\%$ for Al, 0.008% for Cu, 0.035% for Fe, 0.018% for Mg solutions). A disadvantage of this approach is that when the values of s_{bb} and $(s_{meas}/\sqrt{n})$ are almost equal, the values for u_{inhom} become very small, implying that the approach tends to towards optimistic estimates for the between-bottle inhomogeneity. In other words, the discriminatory power of this statistical test depends on the precision of the analytical measurements s_{meas}.

Hence, for data sets with a ratio of $s_{bb}/(s_{meas}/\sqrt{n}) < 1$, no statistically significant statement can be made about s_{bb} in terms of inhomogeneity. In this study this is the case for the IC, ICP-OES and chloride titration measurement series. In such cases it is recommended that u_{inhom} is set to $u_{inhom} = s_{meas}/\sqrt{n}$, leading to the values given in Table 2 which are labeled with a double asterisk [15–18]. In these cases u_{inhom} is dependent on n. Note that in [15–18] a different notation for s_{bb} and u_{inhom} is used.

With the exception of the IC data, all estimates of relative values of u_{inhom} in this study were in the range of 0.008% (copper titration) and 0.038% (iron titration). For the IC series with $u_{inhom} = 0.092\%$ it would be possible to decrease the measurement variability by increasing of the number of replicates. However, more than 40 measurement replicates per sample would be necessary to bring the term $s_{meas}/\sqrt{n}$ to an equal value as the one for s_{bb} (0.053% in this case). Nevertheless, it has been demonstrated that when using IC it is possible to detect between-sample inhomogeneities in aqueous solution in the range of 0.1%.

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