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Quality of Water Quality Data — Consistency of the Results of Chemical Analyses and Sources of Uncertainty

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1. Introduction

Water quality has several aspects and brings together professionals with different backgrounds, which have diverse roles, participate and contribute in their own way and look at water quality issues from different perspectives. One of possible distinctions of roles is that on one side we have the providers of results of chemical analyses and on the other the users of these results. The providers, analytical chemists, have a good understanding of an analytical process, knowledge on the abilities and limitations of analytical methods and expertise in using them. The users of results, water quality experts and hydro-geologists have proficiency in analysing and explaining results within a wider context, drawing conclusions on the water quality, recognising trends and processes within a water body.

Chemical analyses can have different scopes and consequently different levels of complexity [1]. They can be either extended, tending to be as complete as possible, or partial, comprising only a selected number of chemical parameters, and scope or use orientated. Examples of the later are analyses intended for considerations of eutrophication processes in a water body, contamination of water with pesticides, or water suitability for irrigation or recreation.

The consistency and reliability of the results of chemical analyses are as essential for analytical chemists as they are for water experts. Analytical chemists on one side need to keep their professional reputation. Water experts on the other have to draw relevant conclusions from the provided results. Each side has different level of insight in to quality of the provided data, which they understand and treat differently. Water experts have rather limited options if an analysis is only partial and narrowly scoped. Their judgement is more or less limited to the consideration how likely the results seem to be within an established context, taking into account hypotheses, expectations and previous experiences. With an extended water analysis

the situation is very different and water experts have at their disposal several tests and miscellaneous checks on the consistency and coherency of analytical results [2].

In an extended water analysis a total ionic composition of a water sample comprising anions and cations is known. A consideration of a cation-anion balance is consequently the most basic test which can be applied. If an imbalance does not exceed 5 % it can be expected that an analysis as a whole comprises all main ions and contains no grave errors. Such consideration is in a way some sort of a top down approach telling nothing on the uncertainties of individual results nor taking them into account. The acceptable imbalance limit of 5 % is an agreed arbitrary value derived from experiences. Good agreement between anionic and cationic composition in terms of their balance may not be enough proof of the completeness of analysis and the calculated parameter (salinity×1000)/TDS seems to be a useful aid for reliable judgement for seawater and derived saline solutions as we demonstrated [3]. TDS stands for total dissolved solids usually expressed in mg/L. The judgement on the coherence of analytical results can be further supported by miscellaneous checks, considering additional parameters such as electric conductivity, pH, total dissolved solids, a dry residual and water density [2]. Evaluation of the proportions between concentrations of ions also applies. The judgement is based on a consideration if the established proportions are naturally possible and in a good agreement with what is known on the origin of water or its genesis.

An approach used by analytical chemists in evaluating the quality of analytical results is different. Analytical chemists limit errors in analytical results by gaining control over an analytical process. They can achieve this by having a system of quality assurance (QA) and quality control (QC) implemented into laboratory practice [4]. For an analytical chemist to choose an analytical method that is fit for purpose it is essential to understand the needs of a user of analytical results well. The method should be validated and under an internal and preferably also external quality control to produce reliable results. By considering critically all steps of an analytical process analytical chemists recognise sources of uncertainty and estimate a combined standard uncertainty of an analytical result by following the theory on the propagation of errors. By stating uncertainty they give to the user some additional insight into reliability of an analytical result. The approach described here is called a bottom-up approach in evaluating uncertainty. There are several papers and recommendations of official bodies which give guidance in evaluation of uncertainty of analytical results [5-8]. For a reader not specialised in analytical chemistry we give in next few paragraphs a brief account of the methodology used in quantifying uncertainty in analytical chemistry.

An uncertainty evaluation with a bottom-up approach is based on a detailed and comprehensive evaluation of a total analytical process. When considering the process a visualisation of its major steps in a form of a flow chart is usually helpful in recognising the sources of uncertainty. The next step is to write a mathematical equation, a model equation which defines the final result of an analysis y and relates this result to measured quantities x_i. By doing this we bring to light the uncertainty contributions, which we can further analyse in depth by drawing a cause and effect diagram, called also a fish bone diagram. The importance of this step is that it can prevent unjustifiable double counting of the same contribution. Another advantage is that it can lead to a simplification of a model and recognition that some uncer-

tainty sources in fact do not contribute and can be omitted. The model refined in such a way is a starting point for an estimation of the combined standard uncertainty $u_c(y)$ associated with the final result of an analysis. This estimation requires that all the uncertainty contributions are expressed as standard uncertainties $u(x_i)$ corresponding to standard deviations, and that they are combined by following the theory of propagation of errors.

If the uncertainties are primarily not given in such a way they should be recalculated into $u(x_i)$. Such examples are uncertainties which are expressed as a range ($\pm a$) or given in a form of tolerance limits. A range is converted into $u(x_i)$ by taking into account an appropriate distribution function. The distributions most frequently considered are a rectangular or a triangular distribution to which the equations $u(x_i)=a/\sqrt{3}$ or $u(x_i)=a/\sqrt{6}$ apply.

The theory on propagation of errors suggests how standard uncertainties should be combined considering mathematical operations used in a model equation. For the mathematical operations such as summation, subtraction, division and multiplication that are most frequently used in model equations we summarise the basic rules here. For more advanced cases guidance can be found in literature. In the theory on propagation of errors the mathematical operations of summation and subtraction are treated equally. The same is true for multiplication and division. With a model equation $y=x_1+x_2-x_3$ the equation for calculating the combined standard uncertainty of the result is $u_c(y)=(u(x_1)^2+u(x_2)^2+u(x_3)^2)^{1/2}$, and with a model equation $y=x_1 \times x_2 / x_3$ the equation for calculating the combined standard uncertainty reads $u_c(y)=y \times (u(x_1)^2/x_1^2+u(x_2)^2/x_2^2+u(x_3)^2/x_3^2)^{1/2}$. In different words in the first case the variances or the squares of standard uncertainties are combined; and in the second case the squares of relative standard uncertainties are combined.

It has to be noted that not all uncertainty sources necessarily directly reflect in a model equation. Such an example is inhomogeneity of a sample or uncertainty in concentration of a stock calibration standard solution. Such contributions are taken into account at the end and combined with the standard uncertainty obtained previously by combining the uncertainties related to the model equation. The law on propagation of errors for mathematical operations of summation is applied.

It is common practice that the final result y is stated with the expanded standard uncertainty $U(y)$, namely $y \pm U(y)$. The expanded uncertainty is calculated by the equation $U(y)=k \times u_c(y)$; and k stands for a coverage factor. The value of k should always be stated. It is usually between 2 and 3, but most frequently 2. With the k value 2 and a normal distribution of results it can be expected with approximately 95 % level of confidence that the measurand Y lies within the interval $y \pm U(y)$.

We briefly explained methodology for evaluating uncertainty of analytical results by using algebraic equations. But more in depth uncertainty evaluations tend not only to estimate the expanded uncertainty of the final result but to analyse the uncertainty contributions to the combined standard uncertainty. By doing this analytical chemists gain understanding of the major contributions to the combined standard uncertainty and can make effort in improving analytical process by reducing the major uncertainty sources. The results of such more in depth uncertainty evaluation are usually presented in a form of a bar graph in which the combined

standard uncertainty is presented in the comparison with the uncertainty contributions of measured quantities x_i. Such a graph can be obtained by a spreadsheet calculation method suggested by Kragten [7, 9] and easily performed with MS Excel software. Another numerical method which is gaining more and more attention in uncertainty evaluations is Monte Carlo simulation; and Chew demonstrated that a spreadsheet calculation method can also be applied to it [10].

For routine ion chromatographic analyses of drinking water of a low mineralisation a validation process is well established and sources of uncertainty well defined. For more versatile and highly mineralised water samples [11] with a complex matrix a situation is different and recognition and judgement of all uncertainty sources is far away from being trivial, well established and resolved. And this is the area where this chapter tends to make a contribution.

Ion chromatography is the most universal and the farthest reaching single method for determining the total ionic composition of natural waters [12-14]. Total ionic composition of a sample can be determined with ion chromatography at least predominantly if not completely, and this can usually be achieved within two separate runs, one for cations and another for anions, or recently even simultaneously. Concentrations of ions in a sample can differ for several orders of magnitude and ions which are targeted as analytes also define a matrix for the determinations of other ions. The requirement that major and minor ions in a sample should be determined simultaneously with ion chromatography as completely as possible adds an additional dimension to the considerations what is for a particular sample and under particular fitness for purpose requirements the limiting concentration of an ion that can still be successfully determined and how uncertain are concentrations of other ions determined above this limit.

This research is focused on the uncertainty sources and limitations in determining a total ionic composition of natural water with ion chromatography. The chapter is organised into sections corresponding to the steps performed during an analytical process. Each section is focused on a particular case study with the objective of recognising and evaluating uncertainty contributions with a bottom-up approach. Methodology necessary for these evaluations is described and applied to give answers on the importance of particular contributions. This chapter tends to develop guidance and strategies applicable to new complex cases.

Outline of content:

• Influence of impurities in chemicals on the uncertainty associated with a concentration of an ion in a stock combined standard solution

A case study is based on some selected central European brines of different types and provides an insight into influence that impurities in chemicals can have on the uncertainties associated with the concentrations of ions in a combined stock standard solution.

• Uncertainty associated with a concentration of an ion introduced into a final multi-ion calibration solution as a separate standard and combined there with a stock combined standard solution containing the same ion as an impurity

A case study is focused on magnesium ion introduced into the final set of calibration standards as a standard solution and combined there with a multi-ion stock standard solution containing other ions of interest and magnesium ion as an impurity originating from other chemicals.

• A Horwitz-like uncertainty function derived on a model of seawater analysed with ion chromatography

The uncertainty functions known by now either tend to be entirely general as it is the case with the Horwitz function [15, 16] or in contrast to this focus on a particular analyte determined in a particular matrix with a particular method. On the contrary this research is sample focused. We evaluate if an ion independent correlation can be recognised if relative fractions of ions in the total ionic composition of samples are related to the relative uncertainties in determining their concentrations with interpolation from calibration line equations. The results of ion chromatographic analyses of seawaters comprising 156 data serve as an appropriate model because of wide concentration ranges of ions in a sample.

• An uncertainty prediction tool for determining simultaneously minor and major ions with ion chromatography

For two different ways of expressing relative fractions of ions in a sample the meaningful ion independent relations in a form of the Horwitz-like uncertainty functions can be confirmed. The prediction tools established through this research enable recognition of ions for which it can be expected that they are determinable simultaneously with ion chromatography with acceptable uncertainties. By setting appropriate criteria the prediction tools can be accustomed to the user defined requirements.

2. Influence of impurities in chemicals on the uncertainty associated with a concentration of an ion in a stock combined standard solution

Among analytical methods relative methods which require calibration highly prevail, and ion chromatography is a relative method. A calibration procedure usually starts with a stock standard calibration solution from which a set of calibration standards with different concentrations is prepared. In techniques which enable a simultaneous determination of several analytes, as it is a case with ion chromatography, a combined standard solution comprising several ions is required. Some multi-ion stock standard calibration solutions which have concentrations of ions certified together with their combined standard uncertainties or expanded uncertainties are commercially available. Unfortunately they are of a limited usability when it comes to the analyses of natural waters with higher mineralisation. The concentrations of ions in commercial standards are usually far too similar to be applicable to analyses of waters in which concentrations of ions can extend over several orders of magnitude. Consequently a stock combined standard solution should be prepared from standard sub-stances in a laboratory in order to better reflect the composition of samples which one tends to analyse.

The most desirable in instrumental analyses are linear calibration functions. The ordinary least squares regression model (OLS) is most frequently used for fitting the straight line through calibration points. One of the requirements for applying the OLS regression model is that concentrations of calibration solutions bear a negligible standard error if compared with the standard error of a measured signal. Consequently the uncertainty in concentrations of calibration solutions is not considered in estimating a standard uncertainty of interpolation of a concentration of an ion in a sample from a calibration line equation. But anyway a concentration of a stock combined standard solution already is associated with a certain standard error or uncertainty which should be considered and taken into account. As it was already mentioned in introduction for cases similar to this when a particular uncertainty contribution does not reflect directly in a model equation, it is taken into account at the end of a process and combined with the standard uncertainty estimated previously from the model equation. The law on propagation of errors for the operations of summation is applied.

Uncertainty of a concentration of a single component stock calibration standard solution depends on a procedure and quality of equipment used in a preparation of a solution, and also on purity of a chemical. The most usual way of preparing a stock combined standard solution is by weighing. An adequate mass of a chemical is weighed on an analytical balance; the chemical is transferred quantitatively into a volumetric flask, dissolved and diluted with a solvent to a final volume. Evaluation of uncertainty of a single component stock calibration solution concentration in such a case is straight forward taking into account the three main uncertainty contributions, namely uncertainty in measuring mass and volume and uncertainty associated with the purity of a chemical. Several easy to follow examples of such evaluations can be found in literature [7, 17].

But when it comes to stock combined standard solutions with concentrations of components extending over a wide concentration range a situation is more complicated. In such a case the presence of other chemicals in the same solution brings in another uncertainty contribution originating from the impurities present in other chemicals. We developed methodology for evaluating uncertainties associated with mass concentrations of ions in stock combined standard solution and proved that ion originating as an impurity from other chemicals can represent an important contribution to the combined standard uncertainty associated with the concentration of this ion primarily originating from its mother salt; and that this aspect was previously overlooked as we pointed out [18]. Here we apply this methodology to a case study relevant for water quality data evaluation with an objective of learning lessons on the importance of particular uncertainty contributions under different circumstances and with the objective of refining and simplifying the methodology for a further intended use.

2.1. A case study outline

A case study focuses on real central European brines of different types with different concentration proportions of chloride and sulfate. We intentionally limit ourselves on only two ions because in practice it is less likely that an additional ion has an impact as important as the previous one already influencing the uncertainty budget of the primary ion. We examine the influence of the presence of another chemical in a combined standard solution on the uncer-

tainty associated with a concentration of the ion originating from a chemical of its prime origin and consider different purities of a prime chemical and different mass fractions of the ion present as an impurity in another chemical, and give answers on the importance of particular uncertainty contributions.

2.2. A choice of water samples for a study and characteristics of water samples

Data on a composition of natural waters, which we use in this study, originate from an extensive compilation of water analyses of the Central European mineral and thermal waters, which was prepared by Carlé [19]. In order to make these data manageable and to be able to exploit their full potential we prepared an electronic database comprising all essential information on more than 700 water samples. From this database we selected ten water samples with different proportions of mass concentrations of sulfate and chloride ions. The requirement was to include samples with a proportion of the two ions extending over a range as wide as possible but at the same time not allowing that mass concentration of any of the two ions becomes so low that uncertainty in weighing the chemical from which the ion originates becomes an essential influential factor in the uncertainty budget associated with the concentration of this ion. We ensured that the uncertainty in weighing a chemical was in the worst case below 40 % of the magnitude of the contribution of the most influential factor. Another requirement which we set was that at least one of the two ions determines a water type, meaning that it represents a major component.

A water type describes a water sample in terms of the most prevailing ions and can indicate to some extent a water genesis or a hydrogeological origin. A water type is determined by naming the major ions in a sequence corresponding to their decreasing concentration. The cations are named before the anions. An ion qualifies to be named in a water type by at least reaching by its concentration a limit of 20 milliequivalent percent. A judgement in this non SI unit is made possible by converting the results of an analysis from mass concentrations, usually expressed in mg/L, into milliequivalent (meq) concentrations. Mass concentration of an ion is divided by its molar mass and multiplied by the charge number of the ion under consideration. Anions and cations are treated separately. A total milliequivalent concentration of cations is calculated by a summation of milliequivalent concentrations of all catons. A milliequivalent percent of a cation is calculated as a fraction of the total milliequivalent concentration and expressed in percent. The same procedure is applied to anions. An example is a Ca-Mg-HCO3-SO4 type of water; or in words calcium, magnesium, hydrogen carbonate, sulfate type. The presence of dissolved CO_2 can also be indicated in a water type. The criterion which applies in such cases is that CO_2 concentration should at least reach a limit 200 mg/L. An example is a water of a Na-HCO3-CO2 type.

The waters, which qualified for a study, are summarised in table 1. They are identified by their place and state of origin and classified by a water type and further defined by mass concentrations of chloride and sulfate ions. Mass concentrations of ions under consideration are indicated in bold. Another ion defines a matrix. A concentration proportion of the matrix ion and ion under consideration is also given and marked in bold, either sulfate and chloride ratio or chloride and sulfate ratio.

Place	State	Water type	$\gamma(Cl^-)$ / mgL^{-1}	$\gamma(SO_4^{2-})$ / mgL^{-1}	SO_4^{2-}/ Cl$^-$	Cl$^-$/ SO_4^{2-}
Budapest	Hungary	Mg-Na-SO4	**49.7**	11982.9	**241.1046**	0.004148
Forste	Deutschland	Na-Cl-SO4	**36.5**	4360.4	**119.463**	0.008371
Nateln	Deutschland	Na-Cl-CO2	**22.4**	1589	**70.9375**	0.014097
Leer	Deutschland	Na-Ca-Cl	**580**	27728.16	**47.80717**	0.020917
Laa an der Thaya	Austria	Mg-Ca-SO4	**2515.9**	12270.2	**4.877062**	0.205041
Grunewald	Deutschland	Na-Cl	4204	**1577**	0.375119	**2.665821**
Buggingen	Deutschland	Na-Cl	50200	**2400**	0.047809	**20.91667**
Purbach	Austria	Mg-Na-SO4-Cl	197426.5	**1016.4**	0.005148	**194.2409**
Winzlar	Deutschland	Ca-Mg-SO4	153727	**335.7**	0.002184	**457.9297**
Bad Niedernau	Deutschland	Mg-Na-SO4-CO2	145386	**202**	0.001389	**719.7327**

Table 1. Characteristics of water samples selected for a study [19]

A water type gives a first impression on the composition of a water sample. A more comprehensive presentation of the characteristics of natural water is in a Piper diagram. Equally as for a water type the composition of a water sample has to be expressed in milliequivalent percent in order to be represented in a Piper Diagram. A Piper diagram has three sections; a triangular one on the left for a representation of a cationic composition, a triangular section on the right for an anionic composition, and a diamond on the top to represent a water sample as a whole in terms of anionic and cationic composition. A pair of dots in the two triangles of which one represents the cationic composition and another the anionic composition of the same water sample is transferred into a diamond section by drawing two lines and finding the intersection between them and representing the intersection by a dot. The procedure is that each line is drawn though one of the points parallel to the external edge of a triangle to which the dot pertains. A Piper diagram demonstrates that the dots distribute nearly evenly along the whole extent of the left upper edge of a diamond. Waters which position themselves into left corner of a diamond are brines and those in the upper corner of a diamond are characterised by high permanent water hardness. A distribution of the dots in a diagram confirms that the choice of the ten water samples was reasonable also in terms of the diversity in their composition.

The data summarised in table 1 represent models for preparations of stock combined calibration standard solutions. The lowest concentration of an ion under consideration is 22.4 mg/L and the highest 2515.9 g/L. The lowest concentration of a matrix ion is 1.589 g/L and the highest 197.4 g/L. Nine different water types are included. Proportions of mass concentrations of the matrix ion and the ion under consideration extend over three orders of magnitude. These water samples are so different that for a preparation of calibration solutions with appropriate concentrations of the two ions each of the samples would require its own stock combined calibration standard solution similar to it in its composition. By a choice of these ten water samples there are two sets of five uncertainty cases to be considered. In the first five cases,
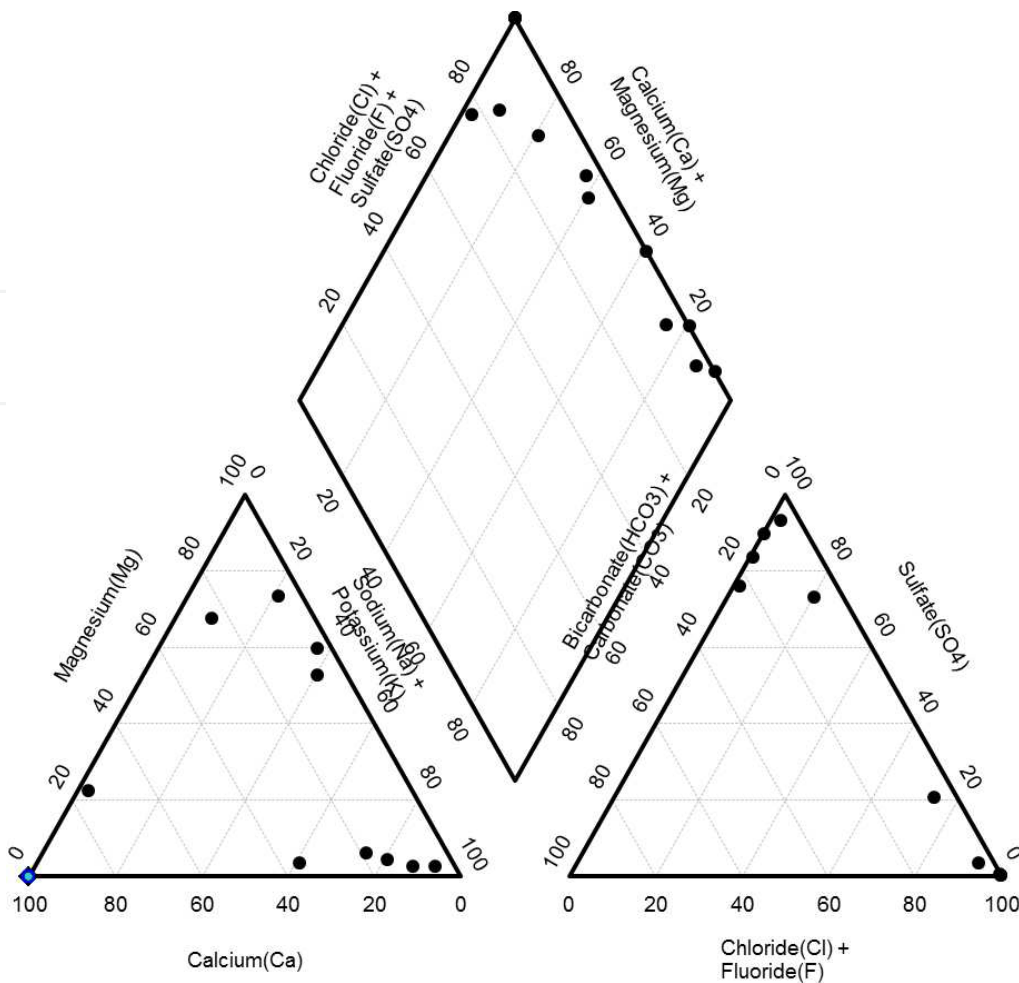
Figure 1. Ionic composition of ten central European water samples selected for evaluation of the influence of impurities in chemicals on the uncertainty associated with a concentration of an ion in a stock combined calibration standard

which are defined by a mass ration of sufate and chloride ion extending between 241 and 4.88, the chloride ion present as an impurity in a sodium sulphate chemical contributes to the uncertainty associated with the chloride concentration primarily originating from a sodium chloride chemical. In the second five cases, which are defined by a mass ratio of chloride and sufate ion between 2.67 and 720, the sulfate ion present as an impurity in a sodium chloride chemical contributes to the uncertainty associated with the sulfate concentration primarily originating from a sodium sulfate chemical.

2.3. A choice of chemicals for a study

For evaluating uncertainty associated with a concentration of a stock combined calibration standard solution apart from selecting the composition of model solutions in terms of their chloride and sulfate concentrations other parameters had to be defined. A decision was that a class A, 500 mL volumetric flask, provides a good compromise between a volume of a solution and masses of chemicals required for a preparation of a stock combined calibration standard solutions. The lowest mass of a chemical weighed under these circumstances is 18.5 mg of

sodium chloride required for a preparation of a solution, which models a composition of water from Nateln, Deutschland.

The data on a quality of commercial chemicals, sodium chloride and sodium sulfate were collected. The specifications on their purity and presence of another ion as an impurity are summarised in table 2. A code for a level of purity and level of impurity was assigned to each chemical for easy marking. H stands for higher and L for lower level of purity. The level of impurity is graded with numbers from one to six, one indicating the lowest level of impurity, and six the highest. The symbol w_{salt} stands for a mass fraction of a salt e.g. NaCl or Na$_2$SO$_4$, which is assigned to a chemical on the basis of a specification given by a producer. This value is used in calculations and uncertainty evaluations. It is calculated as a middle of a range between the lowest expected purity specified by a producer and the highest possible purity, 100 %, and divided by 100 so that it is expressed as a fraction of one, instead of percent. A mass fraction of an impurity indicated by $w_{impurity}$ is obtained similarly as a middle of the range, but in this case the specified value represents the highest expected impurity and the lowest possible is 0 %.

Chemical	NaCl	NaCl	Na$_2$SO$_4$	NaCl	Na$_2$SO$_4$	Na$_2$SO$_4$	NaCl	NaCl
Specified purity (%)	>99.5	>99.5	>99.5	>99.5	>99.0	>99.0	>99.0	>99.0
Purity code	H	H	H	H	L	L	L	L
w_{salt}	0.9975	0.9975	0.9975	0.9975	0.995	0.995	0.995	0.995
Impurity	SO$_4$ $^{2-}$	SO$_4$ $^{2-}$	Cl$^-$	SO$_4$ $^{2-}$	Cl$^-$	Cl$^-$	SO$_4$ $^{2-}$	SO$_4$ $^{2-}$
Specified impurity (%)	<0,001	<0,01	<0.02	<0.05	<0.0005	<0.001	<0.004	<0.02
Impurity code	2	4	5	6	1	2	3	5
$w_{impurity}$	0.000005	0.00005	0.0001	0.00025	0.0000025	0.000005	0.00002	0.0001

Table 2. The characteristics of chemicals selected for a study

Eight combinations of sodium chloride and sodium sulfate chemicals were selected for a study. The combinations were generalised irrespective of a role of a particular chemical and coded in accordance with the purity level of prime chemical and impurity level of the ion under consideration in the secondary chemical. The codes were: L6, L2s, L2c, L1, H1, H2, H4 and H5. The first two and the seventh combination are dedicated to the consideration of the uncertainty associated with the concentration of sulfate ion. All others pertain to the considerations of chloride ion concentration and its uncertainty. In the first four cases the chemicals which are the prime source of an ion are of a lower purity, L. In the remaining four cases the chemicals were of a higher purity, H. A number as indicated in table 2 gives information on the impurity level in the secondary chemical. A stock combined standard solution corresponding to H5 and dedicated to a consideration of uncertainty associated with the chloride ion concentration could have been prepared from any sodium chloride chemical with purity higher than 99.5 % and the sodium sulfate chemical containing chloride ions in a mass fraction lower than 0.02

%. The combinations L2 are indistinguishable in terms of the quality of the two chemicals used for a preparation of each solution. The difference is in the ion under consideration. Hence an additional letter is assigned to these two combinations; a letter s stands for sulfate and c for chloride.

2.4. Uncertainty evaluation and uncertainty budget

Uncertainty evaluations were performed with a spreadsheet method. Each combination of chemicals which is dedicated to evaluation of the uncertainty associated with a concentration of chloride ion in a stock combined standard solution, namely L2c, L1, H1, H2 and H5 was considered for a preparation of five stock combined standard solutions, corresponding in their composition to first five examples of water samples listed in table 1. The remaining five water compositions were considered in relation to the sulfate ion uncertainty budget and combinations of chemicals L6, L2s and H4. Consequently 40 cases were evaluated altogether.

An uncertainty evaluation starts with an analysis of a process or procedure, which is in this case simple enough and does not require a presentation in a form of a flowchart. The two chemicals are weighed and transferred quantitatively into a 500 mL, class A volumetric flask. The solution is diluted with purified water to its final volume.

Model equation 1 which is commonly used in literature for calculation of a mass concentration obtained by a preparation of a solution by weighing takes into account only a direct source of an ion in a chemical of its prime origin. The symbols γ_{ion}, $m_{ion—due\_to\_source}$ and $V_{solution}$ stand for a mass concentration and mass of the ion in a solution and volume of a solution, respectively. Mass of a salt weighed for a preparation of a solution is indicated by m_{salt}. The symbols M_{ion} and M_{salt} stand for molar mass of an ion or salt, respectively. It is necessary mentioning that in all the cases considered here a stoichiometric relation between an ion and the salt of its origin is one. If this is not the case a stoichiometric factor has to be introduced into equation.

$$\gamma_{ion} = \frac{m_{ion\_due\_to\_source}}{V_{solution}} = \frac{m_{salt} \cdot w_{salt} \cdot M_{ion}}{M_{salt} \cdot V_{solution}} \tag{1}$$

If other chemicals which contain the same ion as an impurity are present in a solution in concentrations higher than the ion under consideration additional parameters should be included and taken into account (18). Consequently equation 1 should be rewritten to give equation 2.

$$\gamma_{ion} = \frac{m_{ion\_due\_to\_source} + m_{ion\_from\_another\_chemical}}{V_{solution}} = \frac{\dfrac{m_{salt} \cdot w_{salt} \cdot M_{ion}}{M_{salt}} + m_{other\_salt} \cdot w_{impurity}}{V_{solution}} \tag{2}$$

A cause and effect diagram indicating all uncertainty sources associated with a preparation of a stock combined standard solution and pertaining to equation 2 is presented in figure 2 (left)

and compared to a diagram usually used (right). What distinguishes the diagram on the left from the one usually drawn is a branch in its lower part indicated with $m_{\text{ion\_from\_another\_chemical}}$ and corresponding to a mass of an ion originating as an impurity from another chemical.
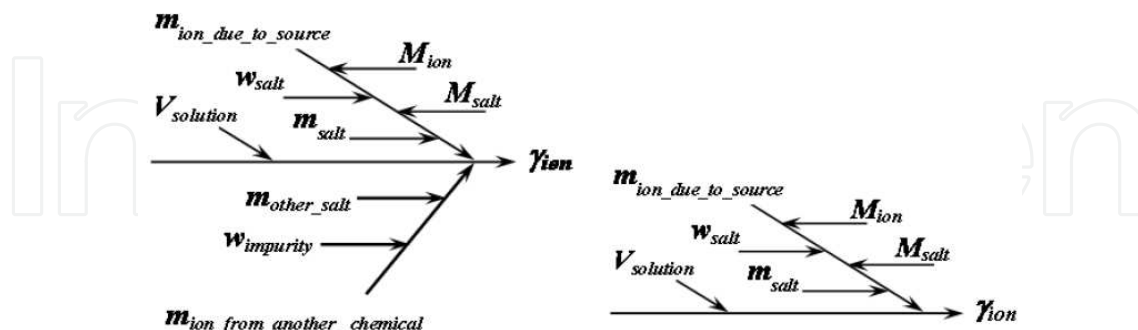
Figure 2. A cause and effect diagrams identifying contributions to the uncertainty associated with a mass concentration of an ion in a stock combined calibration standard; left pertaining to equation 2; right pertaining to equation 1.

In the continuation we outline the main steps undertaken during the uncertainty evaluation, more details can be found elsewhere [8]. An uncertainty statement relating to equation 2 is given by equation 3.

$$u(\gamma_{\text{ion}}) = \frac{m_{\text{ion\_due\_to\_source}} + m_{\text{ion\_from\_another\_chemical}}}{V_{\text{solution}}} \sqrt{\left(\frac{u\left(m_{\text{ion\_due\_to\_source}} + m_{\text{ion\_from\_another\_chemical}}\right)}{m_{\text{ion\_due\_to\_source}} + m_{\text{ion\_from\_another\_chemical}}}\right)^2 + \left(\frac{u(V_{\text{solution}})}{V_{\text{solution}}}\right)^2} \quad (3)$$

Equation 4 combines uncertainty sources contributing to the uncertainty associated with a mass of an ion originating directly from a chemical of its prime origin.

$$u(m_{\text{ion\_due\_to\_source}}) = m_{\text{ion\_due\_to\_source}} \sqrt{\left(\frac{u(m_{\text{salt}})}{m_{\text{salt}}}\right)^2 + \left(\frac{u(M_{\text{salt}})}{M_{\text{salt}}}\right)^2 + \left(\frac{u(M_{\text{ion}})}{M_{\text{ion}}}\right)^2 + \left(\frac{u(w_{\text{salt}})}{w_{\text{salt}}}\right)^2} \quad (4)$$

For the quantification of the measurement uncertainty associated with weighing by difference, equation 5 derived from the calibration certificate following the DKD-R 7-1 calibration procedure was used:

$$u(m_{\text{salt}}) = 0.0105 \cdot \text{mg} + 1.7 \cdot 10^{-6} \, m_{\text{salt}} \quad (5)$$

The standard uncertainty associated with the purity of a chemical is derived from a half of the purity range by taking into account appropriate probability function. A half of the purity range is defined by a difference between 1 corresponding to 100 % purity, and w_{salt}, which is a mass fraction of the salt in a chemical which corresponds to the middle of the purity range specified by a producer. A rectangular distribution is most frequently used assuming that all values within a specified range are of equal probability. The rectangular probability function is taken

into account by dividing a half of the range by a square root of three. We used this approach in equation 6, even though some authors claim that different probability functions should be applied to the purities determined by different analytical methods, recognising that the rectangular distribution is only fit for purpose if purities were determined by titrimetry. If chromatographic methods were used a triangular-ramp probability function is more relevant [20]. We did not distinguish these two cases due to lack of information on the testing methods used by a producer of a chemical.

$$u(w_{salt}) = \frac{1 - w_{salt}}{\sqrt{3}} \tag{6}$$

Uncertainty associated with a mass of an ion originating from another chemical has two contributions, uncertainty in measuring a mass of this chemical indicated by m_{other_salt} and uncertainty in the mass fraction of the impurity in a chemical. As equation 7 demonstrates the second term under a square root simplifies into an inversion of a square root of three. The reason is that $w_{impurity}$ indicates two parameters which are numericaly equal. Firstly it indicates the middle of the impurity interval defined by the maximal expected impurity level declared by a producer and the lowest theoretically possible, zero impurity. Secondly it also represents the half width of this interval, which is transformed into a standard uncertainty by dividing by a square route of three.

$$u(m_{ion\_from\_another\_chemical}) = m_{other\_salt} \cdot w_{impurity} \sqrt{\left(\frac{u(m_{other\_salt})}{m_{other\_salt}}\right)^2 + \left(\frac{w_{impurity}}{w_{impurity}\sqrt{3}}\right)^2} \tag{7}$$

If it is proved that uncertainty contribution associated with the weighing is negligible if compared with the impurity contribution, equation 7 can be simplified into equation 8.

$$u(m_{ion\_from\_another\_chemical}) = \frac{m_{other\_salt} \cdot w_{impurity}}{\sqrt{3}} \tag{8}$$

Uncertainty associate with the volume measurement is estimated as specified by equation 9. The symbols $V_{toler\_as\_\pm}$, $u(V_{rep})$ and $T_{variability\_as\_\pm}$ stand for tolerance of a calibration volume, uncertainty due repeatability of filing a volumetric flask and expected temperature variations around the temperature of calibration.

$$u(V_{solution}) = \sqrt{\left(\frac{V_{toler\_as\_\pm}}{\sqrt{6}}\right)^2 + \left(u(V_{rep})\right)^2 + \left(\frac{V_{soluton} \cdot 2.1 \cdot 10^{-4} \cdot {}^{\circ}C^{-1} \cdot T_{variability\_as\_\pm}}{\sqrt{3}}\right)^2} \tag{9}$$

Uncertainty evaluations were performed with a spreadsheet method in order to gain understanding on the importance of the particular uncertainty contributions under different circumstances. For each of 40 cases a bar diagram on uncertainty contributions was drawn. We are not going to give a detailed account of the spreadsheet method which we used at this stage, due to a fact that some contributions as we explain later can be omitted and a model simplified. Four examples of the results of uncertainty evaluations are presented in figures 3 and 4 in a form of bar graphs. The bar graphs in figure 3 correspond to the evaluation of the uncertainty associated with a chloride ion concentration. The graph on the left was obtained for the L2c case evaluated at a sulfate-chloride mass ratio 4.88. The graph on the right relates to the H1 case evaluated at a sulfate-chloride mass ratio 70.9. The bar graphs in figure 4 correspond to the uncertainty evaluation associated with the sulfate ion concentration, the L6 and H4 cases and chloride-sulfate mass fractions 2.67 and 194 apply, respectively. Full details are given in text accompanying the figures. The expression $u(\gamma)/\gamma$ indicates a relative combined standard uncertainty in mass concentration of an ion. Text on the ordinate corresponds to $u(w_{impurity})$, $u(m_{other\_salt})$, $u(V_{solution})$, $u(M_{salt})$, $u(M_{ion})$, $u(w_{salt})$, $u(m_{salt})$ and $u(\gamma)$ if read from top to bottom.
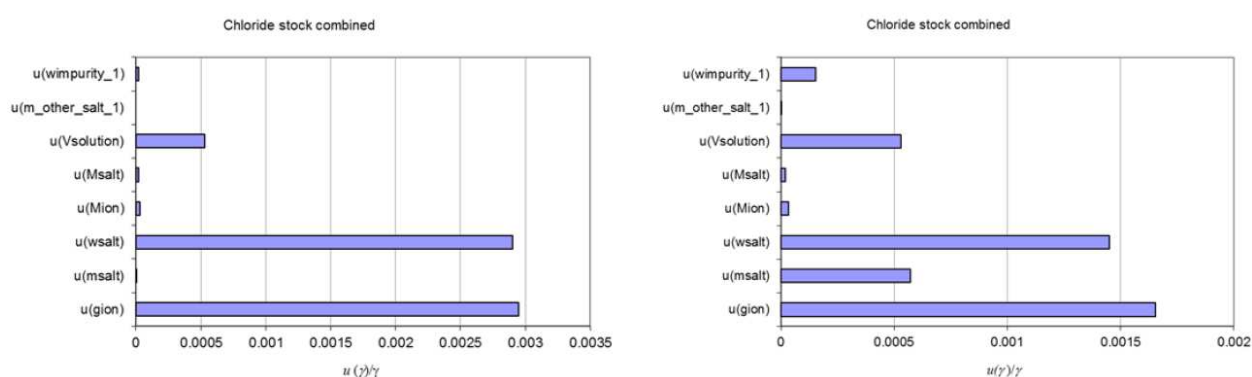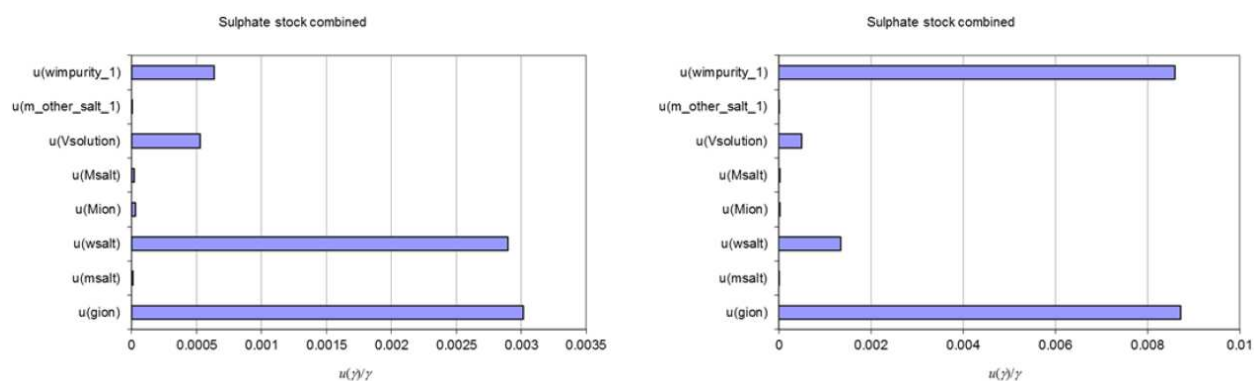

Figure 3. Uncertainty contributions associate with relative standard uncertainty of chloride concentration in a stock combined standard solution. The L2c example on the left: a sulfate-chloride mass ratio 4.88, sodium chloride purity 99.5 % and chloride impurity in sodium sulfate 0.001 %. Composition corresponds to a water of a Mg-Ca-SO4 type from Laa an der Thaya, Austria. The H1 example on the right: a sulfate-chloride mass ratio 70.9, sodium chloride purity 99.75 % and chloride impurity in sodium sulfate 0.0005 %. Composition corresponds to a water of a Na-Cl-CO2 type from Nateln, Deutschland.

A similarity between the two cases in figure 3 is that the impurity levels, which are indicated by a number in a code, are the lowest two of all. Far the greatest contribution to the combined standard uncertainty in both cases is due to uncertainty associated with the purity of a prime chemical. Consequently the relative combined standard uncertainty is in the first case slightly below 0.003 or 0.3 % and in the second case close to 0.0017 or 0.17 %. The distinction between these two cases is that uncertainty in measuring a mass of the prime chemical contributes to the combined standard uncertainty in the second case even to a slightly higher extent than uncertainty in a volume measurement which is similar in both cases. The reason is that a mass of sodium chloride measured for a preparation of the stock combined standard solution that corresponds to a composition of a water from Nateln, Deutschland was the lowest of all, only

18.5 mg. Even though the impurity level was the lowest of all in the H1 example and a sulfate-chloride mass ratio with its value 70.9 was moderate, a mass fraction of impurity in another chemical starts to indicate a contribution.

The L6 example in figure 4, left, which corresponds to the highest impurity level, indicates that uncertainty in a mass fraction of the impurity in another chemical contributes to the standard combined uncertainty already as the second major factor exceeding the uncertainty contribution associated with a volume measurement, even though the chloride-sulfate mass ratio is by 2.67 the lowest of all examined. A bar graph on the right side of figure 4, which corresponds to the H4 example, shows a graphical pattern that differs from all previous cases. In spite of the fact that the impurity level is only third the highest and the chloride-sulfate mass fraction is by 194 far away from the highest examine 720; uncertainty associated with the mass fraction of the impurity in a chemical is the major factor contributing to the relative combined standard uncertainty associated with the concentration of sulfate ion in a solution. The influence of the uncertainty in a purity of a prime chemical is small and uncertainty in volume measurement becomes negligible under such circumstances.

These four examples demonstrate that different combinations of experimental conditions lead to uncertainty budgets with very different profiles. In the continuation we are going to focus on the lessons that can be learned from all the 40 uncertainty evaluations performed.


Figure 4. Uncertainty contributions associated with relative standard uncertainty of sulfate concentration in a stock combined standard solution. The L6 example on the left: chloride-sulfate mass ratio 2.67, sodium sulfate purity 99.5 % and sulfate impurity in sodium chloride 0.05 %. Composition corresponds to a water of a Na-Cl type from Grunewald, Deutschland. The H4 example on the right: chloride-sulfate mass ratio 194, sodium sulfate purity 99.75 % and sulfate impurity in sodium chloride 0.01 %. Composition corresponds to a water of a Mg-Na-SO4-Cl type from Purbach, Austria.

2.5. Lessons learned

Figure 5 demonstrates the influence that a mass ratio of the matrix ion and the ion under consideration has on the combined relative standard uncertainty associated with a mass concentration of the ion under consideration. Different combinations of a mass fraction of a salt in a prime chemical and a mass fraction of the ion under consideration present as an impurity in another chemical were considered. Each curve pertains to a particular combination

of the source and matrix ion chemicals indicated by a code in a legend. Different scales are used in graphs on the left and right.
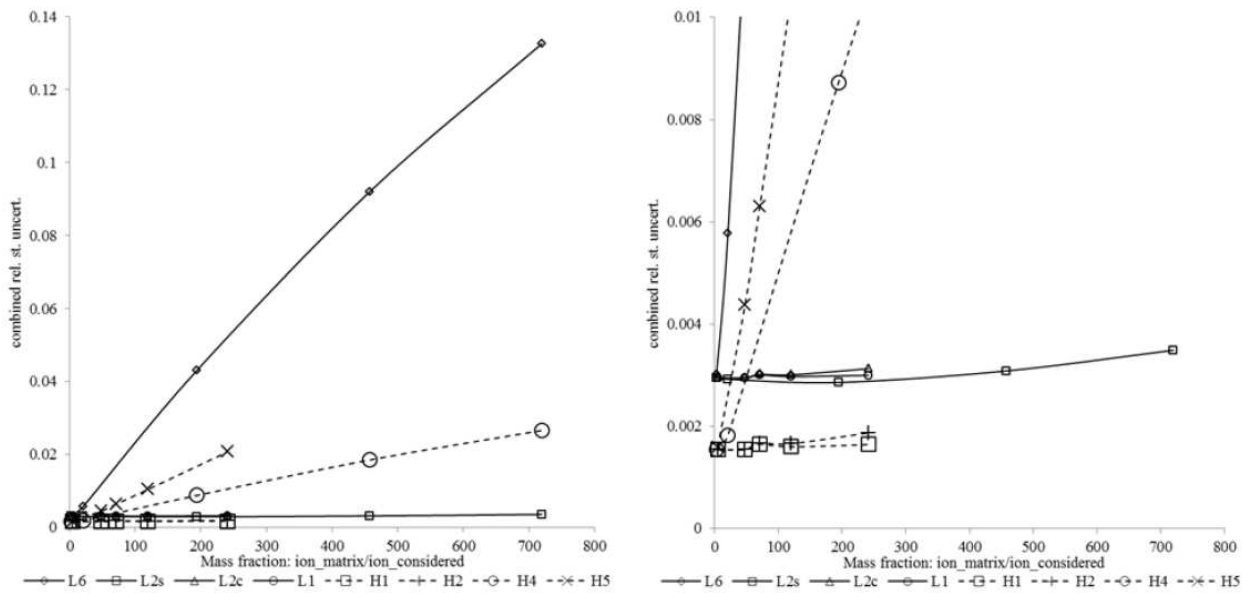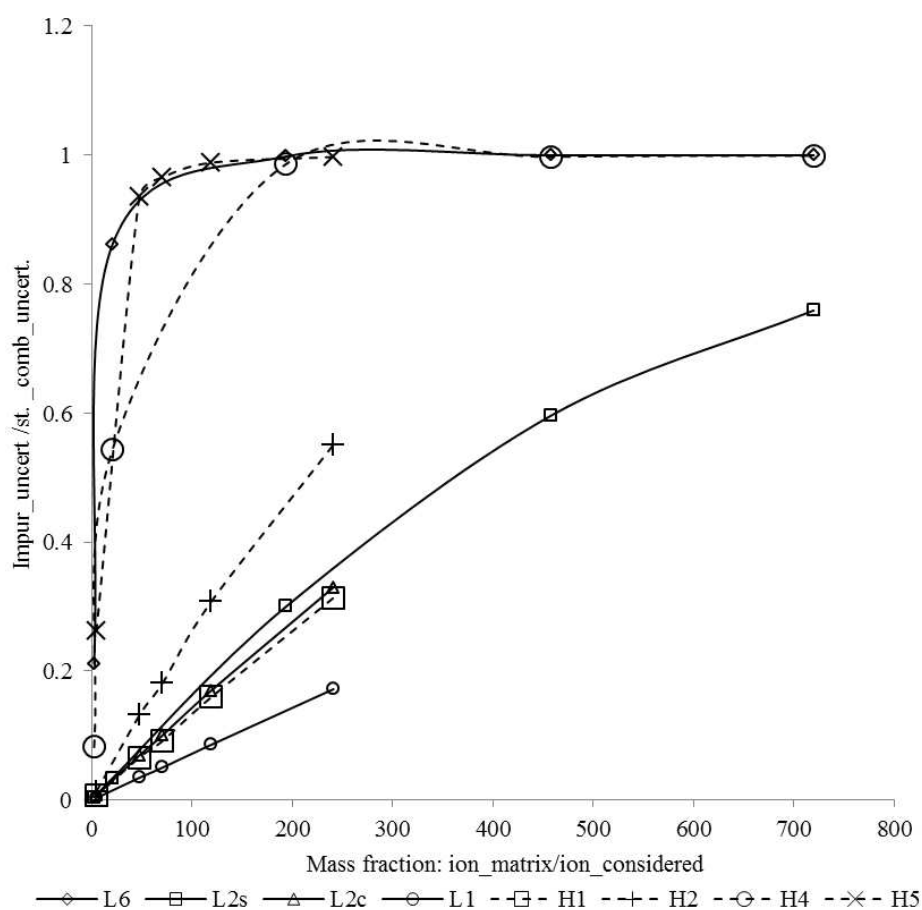

Figure 5. Influence of a mass ratio of a matrix ion and an ion of interest on a relative standard uncertainty associated with a concentration of the ion of interest at different purities of the ion source chemical and different impurity levels of this ion in another chemical.

Figure 6 gives an insight into influence that uncertainty associated with a mass fraction of the ion present as an impurity in another chemical has on the final combined standard uncertainty associated with the concentration of this ion in a stock combined standard solution. The results of the uncertainty estimations are expressed relatively on the ordinate axis. A contribution of the uncertainty associated with a mass fraction of the ion present as an impurity in another salt to the final combined standard uncertainty was divided with the final combined standard uncertainty. The meaning of abscise is the same as in figure 5. The curves for all eight combinations of the source and matrix ion chemicals which were considered are presented. The codes of the combinations are given in a legend. As figure 6 demonstrates if the ion under consideration is present in another salt as an impurity in a mass fraction not exceeding 0.01 % or 0.02 % or 0.05 % and a mass ratio of the matrix ion and an ion under consideration is higher than 200 than the uncertainty associated with a mass fraction of the impurity contributes by being close to 1 nearly 100 % to the standard combined uncertainty associated with a mass concentration of the ion.

Lessons learned from figures 5 and 6:

• The uncertainty budget of the stock combined standard solutions, which imitate the composition of natural waters, changes significantly with the change in the mass ratio of the matrix ion and ion under consideration and in relation to the mass fraction of a salt in a prime chemical.

Figure 6. Influence of a mass ratio of a matrix ion and an ion of interest on a relative contribution of the uncertainty associated with the impurity mass fraction to the combined standard uncertainty in concentration of the ion of interest at different purities of the ion source chemical and different impurity levels of this ion in another chemical

- Mass fraction of an ion present as an impurity in another chemical should be taken into account in uncertainty evaluations; otherwise the combined standard uncertainty associated with the concentration of an ion in a stock combined standard solution can be underestimated.

- A mass fraction of a salt in a prime chemical is a decisive factor determining the relative combined standard uncertainty at low mass ratios of the matrix ion and ion under consideration.

- If a purity of the prime chemical is not lower than 99.0 % and an ion under consideration is present in another chemical as an impurity in a mass fraction lower than 0.001 % a relative combined standard uncertainty lower than 0.4 % can be expected for a mass concentration of an ion in a combined standard solution even in the most unfavourable cases in which another ion strongly prevails, as it is the case with sulfate ion in a solution with a chloride-sulfate mass ratio 720. At lower matrix ion and ion under consideration ratios relative combined standard uncertainties around 0.3 % can be expected.

- If a prime chemical is of a higher, at least 99.5 % purity and an ion under consideration is present in another chemical as an impurity in a mass fraction lower than 0.001 % a relative combined standard uncertainty lower than 0.2 % can be expected for mass ratios of the matrix ion and ion under consideration lower than 250.

- At higher mass fractions of impurities than previously stated the relative combined standard uncertainty starts to rise rapidly with a mass ratio of the matrix ion and ion under consideration.

- With a mass fraction of the impurity in a secondary chemical up to 0.01 % or 0.02 % or 0.05 % a relative standard combined uncertainty associated with a mass concentration of the ion under consideration remains below 0.4 % only if a mass ratio of the matrix ion and ion under consideration does not exceed 80 or 40 or 10, respectively.

- The relative standard uncertainty associated with the concentration of an ion in a stock combined standard solution is hardly acceptable if its magnitude reaches 1 %. With a mass fraction of the impurity in a secondary chemical not exceeding 0.01 % or 0.02 % or 0.05 % a relative standard combined uncertainty associated with the mass concentration of the ion under consideration exceeds 1 % if the mass ratios of the matrix ion and an ion under consideration exceeds 220 or 120 or 40, respectively.

- With a mass fraction of the impurity in a secondary chemical up to 0.05 % a relative standard combined uncertainty associated with the mass concentration of the ion under consideration can exceed 13 % in the most unfavourable cases in which another ion strongly prevails, as it is the case with sulfate ion in a solution with a chloride-sulfate mass ratio 720.

- If any of the uncertainty contributions in the uncertainty budget exceeds 30 % of the combined standard uncertainty it cannot be considered negligible. Impurity of the secondary chemical has larger effect on the uncertainty budget associated with the concentration of an ion in a stock combined standard solution if the prime chemical is of higher purity.

- If the mass ratio of the matrix ion and ion under consideration exceeds 240 and the purity of the prime chemical exceeds 99.5 % it can even be expected for the secondary chemical with the lowest mass fraction of the ion present as an impurity, lower than 0.0005 %, that the impurity contribution exceeds 30 % of the combined standard uncertainty in the uncertainty budget. With a chemical with a mass fraction of an impurity not exceeding 0.001 % a 30 % contribution to the uncertainty budget is reached at the mass ratio 120. With a chemical with a mass fraction of an impurity not exceeding 0.01 % this happens already at the mass ratio 5.

- With a mass fraction of the impurity in a secondary chemical up to 0.01 % or 0.02 % or 0.05 % the uncertainty associated with the impurity of a chemical exceeds 80 % of the combined standard uncertainty associated with the mass concentration of an ion in a stock combined standard solution if the mass ratio of the matrix ion and ion under consideration exceeds 10 or 45 or 100, respectively.

2.6. Refined methodology for uncertainty evaluations in prospect complex cases

Critical evaluation of all 40 bar graphs lead to a conclusion that only uncertainties associated with the mass fraction of an ion present as an impurity in another chemical, mass fraction of a salt in a prime chemical, mass of the prime chemical and volume of solution should really be taken into account. A refined cause and effect diagram which we suggest for prospect use is presented in figure 7, left. A mass of the prime chemical, although negligible in most cases, is not left out. When it comes to solutions with a high ration of matrix ion an ion under consideration a compromise between the volume of the solution not being too high and a mass of the prime chemical not being too low has to be found. This leads to masses which are below a limit recommended for a reliable weighing. Even though as solid bars in figure 7, right, demonstrate, the uncertainty contribution associated with weighing does not reach 40 % of the major uncertainty contribution and it is comparable in magnitude to the uncertainty contribution of the volume measurement, it cannot be considered non-existent. The bars with a pattern confirm that further simplification of a model not taking into account this contribution would have led to an underestimation of the combined standard uncertainty associated with a concentration of an ion in a stock combined standard solution.
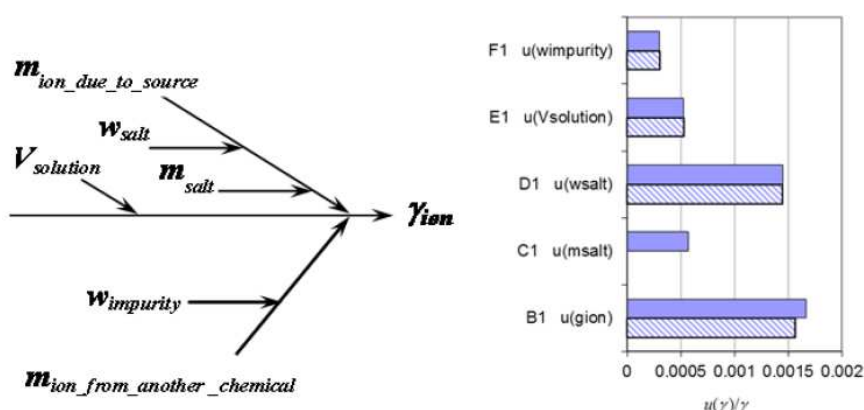
Figure 7. A refined cause and effect diagram, left, and uncertainty budget associated with it, right. Solid bars correspond to a cause and effect diagram on the left, bars with a pattern demonstrate the influence of a further simplification of a model by omitting the uncertainty associated with a mass of the prime chemical

A spreadsheet method which we suggest for evaluation of combined standard uncertainty in prospect cases is presented in table 3. Shaded cells are intended for input. Formulas in line 12 are not all fully visible but they are all similar to a formula in a cell B12, apart from a difference in a letter. Cells with frames indicate the main results of an uncertainty evaluation, namely a mass concentration of the ion under consideration in the stock combined standard solution, a standard uncertainty associated with it and a relative standard uncertainty pertaining to it. Data in line 16 or 17 can be used for a bar graph representation of the uncertainty contributions of particular parameters to the combined standard uncertainty. Numerical results are given below. Calculations were performed for H2 example and mass ratio 70.9 corresponding to a

A1	B1 $u(\gamma \text{ion})$	C1 $u(m\,\text{salt})$	D1 $u(w\,\text{salt})$	E1 $u(V\,\text{solution})$	F1 $u(w\,\text{impurity}$
		=0.0105+0.0000017*B4	=(1-B5)/(3^0.5)	0.26392738900440	=B10/3^0.5
A3 a ion/compound	1	1	1	1	1
A4 m salt (mg)	1165.90875381845	**=B4+C2**	=B4	=B4	=B4
A5 w salt	0.995	=B5	**=B5+D2**	=B5	=B5
A6 M ion (g/mol)	96.0626	=B6	=B6	=B6	=B6
A7 M salt (g/mol)	142.04213856	=B7	=B7	=B7	=B7
A8 V solution (mL)	500	=B8	=B8	**=B8+E2**	=B8
A9 m another_salt (mg)	3465.05799302062	=B9	=B9	=B9	=B9
A10 w impurity_1	0.00025	=B10	=B10	=B10	**=B10+F2**
A12 γ ion (g/L)	=(B3*B4*B5*B6/B7+B9*B10)/B8	=(C3*C4*C5*C6/C7+C9	=(D3*D4*D5*D6/	=(E3*E4*E5*E6/E	=(F3*F4*F5*F6/
A13 $u(\gamma \text{ion,xi})$		=C12-B12	=D12-B12	=E12-B12	=F12-B12
A14 $u(\gamma \text{ion})$	=(C14+D14+E14+F14)^0.5	=C13^2	=D13^2	=E13^2	=F13^2
A16 ABS($u(\gamma \text{ion,xi})$)	=B14	=ABS(C13)	=ABS(D13)	=ABS(E13)	=ABS(F13)
A17 $u(\gamma \text{ion,xi})/\gamma \text{ion}$	=B16/B12	=C16/$B12	=D16/$B12	=E16/$B12	=F16/$B12
γ ion (g/L)	1.57084752899651				
ABS($u(\gamma \text{ion,xi})$)	0.0047341372961131	0.0000167987106964862	0.00455240687256(	0.00082874191832	0.0010002760ε
$u(\gamma \text{ion,xi})/\gamma \text{ion}$	0.00301374717069922	0.0000106940427930759	0.002898057760875	0.00052757629434	0.0006367747;

Table 3. A spreadsheet method suggested for prospect evaluations of uncertainty associated with a concentration of an ion in a stock combined standard solution

preparation of a stock combined standard solution simulating a composition of water from Nateln, Deutschland, table 1. The final result would have been written $\gamma(\text{Cl}^-) \pm U = (1.571 \pm 0.009)$ g/L; k=2.

## 3. Uncertainty associated with a concentration of an ion introduced into a final multi-ion calibration solution as a separate standard and combined there with a stock combined standard solution containing the same ion as an impurity

Another case, which requires consideration of the influence of impurities present in other chemicals on the uncertainty associated with a concentration of this ion appears when a stock combined standard solution has to be combined with a separate standard solution of this particular ion. Such cases materialise when a standard substance which would have allowed for a direct introduction of this particular ion into sock combined standard solution is not available and a commercial standard solution should be used instead, but is not available in a concentration high enough to be introduced into the stock combed standard solution directly, for a reason that a volume grater then a volume of a volumetric flask would have been required. Consequently this ion can be added only at the final stage when series of standard calibration solutions are prepared.

A case study focusses on magnesium ion introduced into the final set of calibration standards as a stock standard solution and combined there with a stock multi-ion combined standard

solution containing other ions of interest. Even though not added in a form of magnesium salt the magnesium ion is present in the combined stock standard solution as an impurity origi‐ nating from other chemicals. Example is taken from the analyses of sea water, more precisely determination of cations with ion chromatography. Only the influence of magnesium ion present as an impurity in sodium chloride is considered for the reason that sodium is the only cation in sea water with a concentration higher than the concentration of magnesium ion. The sodium and magnesium mass ratio is 8.4.

A procedure carried out for a preparation of a final multi ion combined standard solution, and a cause and effect diagram pertaining to it, are presented in figure 8, left/right. A symbol γ_{ion} previously used in relation to the stock combined standard solution was replaced with $\gamma_{another\_sol}$ in order to enable a clear distinction of the two sources of magnesium ions originating from two solutions. Magnesium ions in a combined multi-ion calibration standard solution have two contributions $m_{ion\_st\_sol}$ originating from a magnesium ion commercial stock standard solution and $m_{another\_sol}$ originating from the stock combined standard solution. The symbols γ_{st_sol} and $\gamma_{another\_sol}$ and V_{st_sol} and $V_{another\_sol}$ stand for mass concentrations of magnesium ions in the two solutions and volumes of the two solutions measured with a piston micropipette. A mass concentration of magnesium ion in a final multi-ion calibration standard is indicated by $\gamma_{ion\_dil\_total}$ and a volume of this solution by V_{final}.
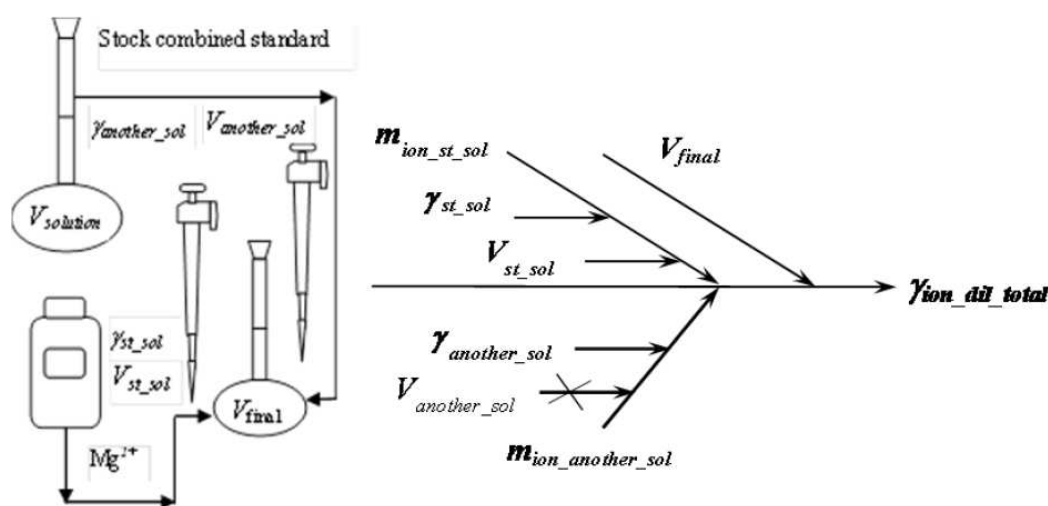
Figure 8. Influence of magnesium ion present as an impurity in a stock combined standard solution on the final con‐ centration of magnesium ion and its uncertainty; a flow chart for a preparation of the final combined calibration solu‐ tion and a cause and effect diagram, left/right

A model equation 10 defining a mass concentration of an ion in a solution prepared by a dilution of a stock standard solution, which is usually used and does not take into account the influence of ions present as impurities in another solution, has to be amended and rewritten to give a model equation 11.

$$\gamma_{ion\_dil\_total} = \frac{\gamma_{st\_sol} \cdot V_{st\_sol}}{V_{final}} \tag{10}$$

$$\gamma_{ion\_dil\_total} = \frac{\gamma_{st\_sol} \cdot V_{st\_sol} + \gamma_{another\_sol} \cdot V_{another\_sol}}{V_{final}} \tag{11}$$

Uncertainty contributions appearing in figure 8 and associated with volumetric operations are treated by following equation 9 but by omitting the last term associated with the deviation of the ambient temperature from the temperature of calibration. The reason is that all volumetric operations are performed during a short period of time, during which the ambient temperature is not expected to change, therefore it affects all the measurements proportionally.

Uncertainty associated with a mass concentration of magnesium ion in a commercial stock standard solution is declared by a producer as a range of a possible variation and transformed into standard uncertainty by dividing by a square root of three.

The only contribution requiring explanation is uncertainty associated with a mass concentration of magnesium ion in another solution, namely the stock combined standard solution containing sodium chloride. An expression for a mass concentration of an ion present as an impurity in another solution and originating from another salt is derived from equation 2 and reduced to equation 12 by taking into account that m_{salt} equals zero.
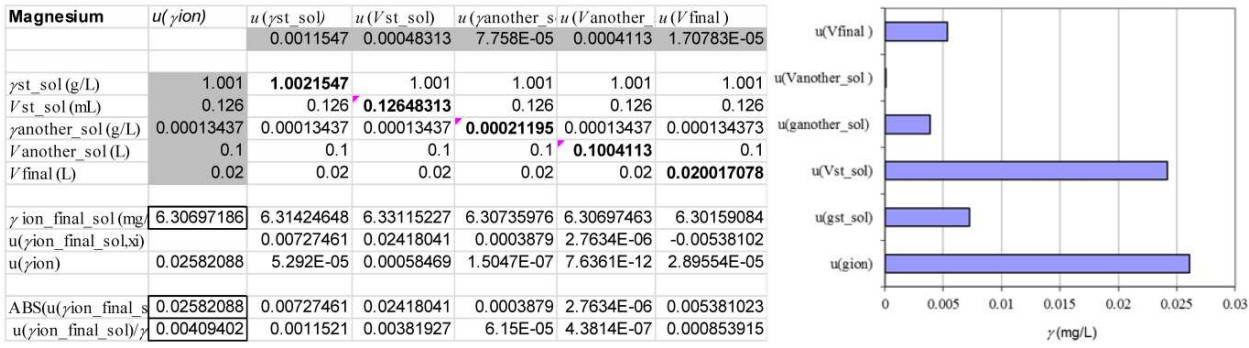
$$\gamma_{another\_sol} = \frac{w_{impur} \cdot m_{other\_salt}}{V_{solution}} \tag{12}$$

The uncertainty contribution associated with $\gamma_{another\_sol}$ can be evaluated using a spreadsheet method presented in table 3 by substituting input data in cells B4 to B7 by zero, zero, one and one, respectively and providing relevant input data for cells B8 to B7, and E1, namely 100 mL, 2687.45 mg, 0.000005 and 0.0643402 mL for a preparation of a solution in 100 mL volumetric flask from 2687.45 mg of sodium chloride with magnesium ion impurity content lower than 0.001 %. This procedure gives results for $\gamma_{another\_sol}$ and $u(\gamma_{another\_sol})$ $1.3437 \cdot 10^{-04}$ and $7.758 \cdot 10^{-05}$ expressed in g/L, respectively. It turns out that the uncertainty contribution associated with the volume of a solution is negligible by being three orders of magnitude smaller than the contribution of w_{impur}. Consequently the uncertainty evaluation can be simplified as declared by equation 13. It was confirmed that the uncertainty estimation obtained by this equation is numerically equal to the one obtained by a spreadsheet method.

$$u(\gamma_{another\_sol}) = \frac{w_{impur} \cdot m_{other\_salt}}{V_{solution} \cdot \sqrt{3}} \tag{13}$$

A combined standard uncertainty associated with a concentration of magnesium ions in a final combined calibration standard solution can be evaluated by using a spreadsheet method as indicated in figure 9, left. In the example given here the final solution is prepared in a 20 mL volumetric flask by measuring 126 µL of the commercial magnesium stock standard solution with a concentration (1.001±0.002) g/L, and 100 µL of the stock combined standard solution containing magnesium ion as an impurity in concentration $1.3437 \cdot 10^{-04}$ g/L, as realised in the previous step.

Magnesium	$u(\gamma ion)$	$u(\gamma st\_sol)$	$u(V st\_sol)$	$u(\gamma another\_s$	$u(V another$	$u(V final)$
		0.0011547	0.00048313	7.758E-05	0.0004113	1.70783E-05
γst_sol (g/L)	1.001	1.0021547	1.001	1.001	1.001	1.001
Vst_sol (mL)	0.126	0.126	0.12648313	0.126	0.126	0.126
γanother_sol (g/L)	0.00013437	0.00013437	0.00013437	0.00021195	0.00013437	0.000134373
Vanother_sol (L)	0.1	0.1	0.1	0.1	0.1004113	0.1
Vfinal (L)	0.02	0.02	0.02	0.02	0.02	0.020017078
γ ion_final_sol (mg/	6.30697186	6.31424648	6.33115227	6.30735976	6.30697463	6.30159084
$u(\gamma$ion_final_sol,xi)		0.00727461	0.02418041	0.0003879	2.7634E-06	-0.00538102
$u(\gamma$ion)	0.02582088	5.292E-05	0.00058469	1.5047E-07	7.6361E-12	2.89554E-05
ABS($u(\gamma$ion_final_s	0.02582088	0.00727461	0.02418041	0.0003879	2.7634E-06	0.005381023
$u(\gamma$ion_final_sol)/γ	0.00409402	0.0011521	0.00381927	6.15E-05	4.3814E-07	0.000853915

Figure 9. A spreadsheet method for evaluating the uncertainty associated with a concentration of an ion in a final combined calibration standard solution prepared by combining the ion stock standard solution and stock combined standard solution which contains the ion under consideration as an impurity (left), and the results obtained for magnesium ion and presented in a form of a bar graph (right)

As a bar graph in figure 9 demonstrates the uncertainty associated with the mass concentration of the magnesium ion present as an impurity in another solution, u(ganother_sol), contributes to the final combined standard uncertainty in spite of the fact that in the example which we considered the sodium ion mass concentration was only 8.4 times higher than magnesium ion concentration. This leads to a conclusion that in calculating the concentration and its uncertainty the influence of impurities should be taken into account when another ion is present in higher concentration than the ion under consideration and a multi-ion solution is prepared by combining the ion stock standard solution and the stock combined standard solution.

4. A Horwitz-like uncertainty function derived on a model of seawater

Total ionic composition of a sample can be determined with ion chromatography at least predominantly if not completely, and this can usually be achieved within two separate runs, one for cations and another for anions, or recently even simultaneously [3, 13, 21-23]. Concentrations of ions in a sample can differ for several orders of magnitude and ions which are targeted as analytes also define a matrix for the determinations of other ions. The requirement that major and minor ions in a sample should be determined simultaneously with ion chromatography as completely as possible adds an additional dimension to the considerations what is for a particular sample and under particular fitness for purpose requirements the limiting concentration of an ion that can still be successfully determined and how uncertain are concentrations of other ions determined above this limit.

Samples can be recognised as similar for ion chromatographic analyses not on the bases of concentration levels but on the bases of their relative proportions [24]. For the highest simultaneity of ion chromatographic determination of ions a sample dilution should be selected so that it prevents the major ions from overloading the column, and keeps their chromatographic peak areas linearly related to concentration, but at the same time lowers the concentrations of minor ions as little as possible. Hence sample dilutions reduce the number of distinctive analytical cases and set the ground for consideration if any general ion independent relation

between the relative uncertainty of interpolation of concentrations from calibration lines, and fractions of ions in a sample can be recognised.

Every analytical result should be given together with the standard uncertainty assigned to it. Below a certain concentration limit the uncertainty of the result obtained with an analytical method becomes too high to be acceptable or tolerable and fit for purpose. Trying to determine the concentration at this limit is not feasible from the economical point of view. A prediction tool that could help making a correct consideration in advance could prevent such cases.

In the results of several independent inter-laboratory collaborative studies, in which different analytes in different matrices were targeted by different analytical techniques, William Horwitz recognised a general rule that the mean percent standard deviation $s_r(\%)$ as a measure of reproducibility of results, and concentration level of an analyte expressed relatively as a mass fraction (w), are related (equation 14). As follows from the equation each decrease in a concentration level of two orders of magnitude doubles $s_r(\%)$ [15, 25].

$$s_r(\%) = 2^{(1-0.5 \times \log w)} \tag{14}$$

The graphical representation of this relation is known as the Horwitz function and together with the Horwitz ratio [16] became a guidance for a judgement on the achievable and acceptable performance of an analytical method [26-28]. Horwitz estimated that a within laboratory $s_r(\%)$ ordinarily accounts for one-half to two-thirds of the total between-laboratory $s_r(\%)$, which comprises the within and between-laboratory variability contribution [15, 29].

Albert and Horwitz demonstrated that the Horwitz function can be rewritten in a slightly different form (equation 15) and assumed that the interlaboratory limit of quantitation corresponds to w of the order of magnitude 1×10^{-9} [30].

$$s_r(\%) = 2\ w^{-0.1505} \tag{15}$$

It was recognised that a Horwitz-like function holds for the results of proficiency tests [31, 32]. Thompson and Lowthian confirmed that experimental data follow the Horwitz function well down to w of 1×10^{-8} and that at the $s_r(\%)$ greater than 33 % the judgement on the presence of an analyte in the absence of other information is questionable [33].

Thompson later evaluated the results of more recent collaborative trials concerning analytes in sub 100 ppb concentration levels and observed greater deviations from the Horwitz function than previously observed, and suggested three different expressions for reproducibility standard deviation (s) for different concentration ranges (equation 16) [34].

$$s = \begin{cases} 0.22\ w & \text{if } w < 1.2 \times 10^{-7} \\ 0.02\ w^{0.8495} & \text{if } 1.2 \times 10^{-7} \le w \le 0.138 \\ 0.01\ w^{0.5} & \text{if } w > 0.138 \end{cases} \tag{16}$$

Linsinger and Josephs questioned the applicability of the Horwitz equation as a performance criterion for analytical methods [35]. Thompson objected the methodology they used and opposed a generalisation of their conclusions [36]. He suggested the uncertainty characteristic function as a tool for summarising or specifying the behaviour of an analytical system [37] and as a method-specific alternative to the Horwitz function [38] (equation 17). The relative standard deviation is denoted by s_r.

$$s=\sqrt{\alpha^2 + (\beta \times w)^2} \ or \ s_r=\sqrt{\frac{\alpha^2}{w^2} + \beta^2} \tag{17}$$

In contrast to the Horwitz function the characteristic function follows the principles of error propagation theory and can therefore represent adequately the standard uncertainty of the final result obtained by an analytical method and apart from this also accommodates a detection limit, that can be derived from α. A form of the function is general but parameters α and β should be determined for each method separately through a method validation.

Côté et *al* applied the Horwitz equation and the uncertainty function suggested by Thompson to the data derived from the proficiency testing schemes aiming at the quantification of cadmium, lead and mercury in blood and urine and confirmed that the uncertainty function describes well the dependence of the reproducibility standard deviation on the mass fraction of an analyte [39]. In accordance with already stated it comes with no surprise that the limits of detection which they derived from the uncertainty function defined by the reproducibility data were twenty-times higher than those determined under the within laboratory circumstances as a part of a method validation process.

4.1. A case study outline

The uncertainty functions known by now either tend to be entirely general and analyte, sample and analytical method independent, or in contrast to this focus on a particular analyte determined in a particular matrix with a particular method or predominantly so in the cases of proficiency trials.

In contrast to the cases which defined the Horwitz function and in which different analytes of different concentrations were determined in different matrices this research is sample orientated and tends towards the simultaneous ion chromatographic determination of the total ionic composition of a sample as completely as possible and with acceptable uncertainties. In the uncertainty budgets of analytical results obtained by the bottom-up approach the uncertainty associated with the interpolation of concentration from a calibration function equation can represent the major or one of the major contributions and this holds also for ion chromatography [7, 40].

The results of ion chromatographic analyses of seawaters and related samples can because of their wide concentration ranges between the minor and major ions provide an appropriate model for the consideration and evaluation if any general ion independent Horwitz-like prediction tool can be developed for the uncertainty of interpolation of concentrations from

calibration lines under the conditions of determining simultaneously very different concentrations, and this was the objective of this research.

4.2. Materials and methods

The data set comprised 156 data points originating from the results of analyses of 25 natural and artificial sea waters, estuary waters and control standards. Fluoride, chloride, bromide, nitrate, sulfate, sodium, potassium, magnesium, calcium and strontium were determined simultaneously within two separate runs, one for anions and another for cations. Two different models of ion chromatographs were used. The factor of dilution for determination of anions was 16.7 for the estuary waters and 41.7 or 44.4 or 50.0 for all other samples. The factor of dilution for determination of cations was 50.0 for estuary water and 125 or 133 or 154 or 182 for other samples.

Anions were determined with a DIONEX DX-300 Gradient Chromatography System comprising: the Conductivity detector II, a 25 μL injection loop, an IonPac AS9-HC separation column with an AG9-HC pre-column and an ASRS-ultra II 4 mm suppressor used in a chemical mode of operation. The 9 mmol/L sodium carbonate eluent was used at the flow rate 1 mL/minute. The flow rate of the 25 mmol/L sulphuric acid regenerant solution was 7 mL/minute. ChromJet Integrator Spectra Physics Analytical was used for data acquisition.

Cations were determined with a DIONEX 500 chromatography system consisting of the IP 20 isocratic pump, the CD 20 conductivity detector, a 25 μL injection loop, an IonPac CS12A separation column with a CG12A pre-column and a CSRS-ultra II 4 mm suppressor used in a closed loop mode of operation at the 100 mA current setting. The eluent was 20 mmol/L methane sulphonic acid with flow rate 1 mL/minute. Data acquisition was performed with the PeakNet software.

A combined stock calibration standard with fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate concentrations 2.00 mg/L, 19.0 g/L, 15.6 mg/L, 140 mg/L, 15.2 mg/L, 83.0 mg/L and 2.65 g/L respectively was prepared from the corresponding sodium salts, which were all p.a. grade chemicals dried for two hours at 110 C. Commercial 1 g/L phosphate ion standard solution purchased from Merck-Darmstadt (Germany) was used as a source of this ion. Five calibration solutions were prepared daily from the combined stock calibration standard. Calibration ranges for simultaneous determination of fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate were: 0.01-0.08, 95-759, 0.078-0.624, 0.7-5.6, 0.076-0.608, 0.415-3.32, and 13.2-106 mg/L, respectively. Each calibration standard was injected once.

A combined stock calibration standard solution for the determination of cations was prepared from p.a. grade sodium chloride and strontium chloride dried for two hours at 110 C; sources of all other cations were commercial 1 g/L single cation standard solutions purchased from Merck-Darmstadt (Germany). The combined stock calibration standard solution contained sodium, potassium, calcium and strontium in concentrations 10.55 g/L, 382.1 mg/L, 400.3 mg/L, 13.00 mg/L respectively. Five calibration solutions were prepared daily from the combined stock calibration standard. The commercial 1 g/L magnesium ion standard solution was introduced directly into calibration solutions at this stage. Calibration ranges for simultaneous

determination of sodium, potassium, magnesium, calcium and strontium were: 26.4-132, 0.96-4.78, 3.15-15.8, 1.00-5.00 and 0.033-0.163 mg/L.

All solutions were prepared with distilled water additionally purified through the Milli-Q Academic system (Millipore, Billerica, MA, USA).

4.3. Results and discussion

Concentrations of ions (x_0) were obtained by interpolations from calibration functions using peak area as a measured variable (y_0) and by employing the ordinary least squares (OLS) linear regression model (equation 18). An intercept and a slope are denoted by a and b, respectively. The uncertainties (s_{x0}) associated with x_0 were calculated from equation 19. The symbols $s_{y/x}$, n, $\bar{y}$ and $\bar{x}$ stand for: a standard error of estimate, a number of calibration points, a mean of peak areas and a mean of concentrations of calibration solutions, respectively.

$$x_0 = (y_0 - a) / b \tag{18}$$

$$s_{x0} = \frac{s_{y/x}}{b}\sqrt{1 + \frac{1}{n} + \frac{(y_0 - \bar{y})^2}{b^2 \sum_i (x_i - \bar{x})^2}} \tag{19}$$

An appropriate way of expressing concentrations of ions relatively was necessary in order to test if any general ion independent Horwitz-like prediction tool can be developed. Expressing analytical results as mass fractions as it is usual in uncertainty functions is not appropriate for determinations of a total ionic composition.

A measure of the completeness of analysis in determining a total ionic composition of a sample is a cation-anion balance, requiring that the sums of equivalent concentrations of cations and anions are very similar (equation 20). An equivalent concentration c_{e_i}, (equation 21) takes into account the charge number of an ion z_i; nevertheless it is calculated from a mass concentration γ_i and a molar mass of an ion M_i similarly as amount concentration.

$$c_{e\_cation\_total} = \sum_{i=1}^{n} c_{e\_cation\_i} \quad c_{e\_anion\_total} = \sum_{i=1}^{n} c_{e\_anion_i} \tag{20}$$

$$c_{e\_i} = \frac{\gamma_i \times z_i}{M_i} \tag{21}$$

An established way of expressing ionic composition relatively is by using milliequivalent percent, meq% as a unit. Samples with similar meq% composition are analysed under similar experimental conditions. Results expressed in meq% for example help recognise a water type, a potential use, a hydrogeological origin, and processes in a water body. A fraction of an ion in a total cationic or anionic composition denoted by fraction_meq and expressed in meq% is obtained by applying equation 22.

$$\text{fraction\_meq} = \frac{c_{e\_cation}}{c_{e\_cation\_total}} \times 100 = \frac{c_{e\_anion}}{c_{e\_anion\_total}} \times 100 \tag{22}$$

Another widely used parameter related to determinations of ionic compositions of samples is TDS, total dissolved solids, calculated as a sum of mass concentrations (γ_i) of anions, cations and weak electrolytes; usually expressed in mg/L (equation 23). Mass concentrations of weak electrolytes usually contribute negligibly to TDS.

$$TDS = \sum_{i=1}^{n} \gamma_i \qquad (23)$$

We used this parameter as a ground for an alternative way of expressing ionic composition relatively and introduced fraction_TDS expressed in percent in order to have a parameter expressed similarly as fraction_meq (equation 24).

$$fraction\_TDS = \gamma_{ion} / TDS \times 100 \qquad (24)$$

Relative uncertainties of interpolations of concentrations of different ions from calibration lines related to their fractions in samples expressed in meq% are presented in figure 10. An unusual pattern was observed for calcium already when calibrations have been performed. The repeatability of the areas of chromatographic peaks obtained for calibration solution with the intermediate concentration was the worst and the least comparable between days, contributing to unequal uncertainties of interpolation assigned to similar concentrations of calcium in samples determined on different days. No obvious technical reason for these observations was recognised. A possible explanation lies in chemical equilibrium at the presence of sulfate in exceeding concentrations. Due to these observations calcium was excluded from further data evaluations.
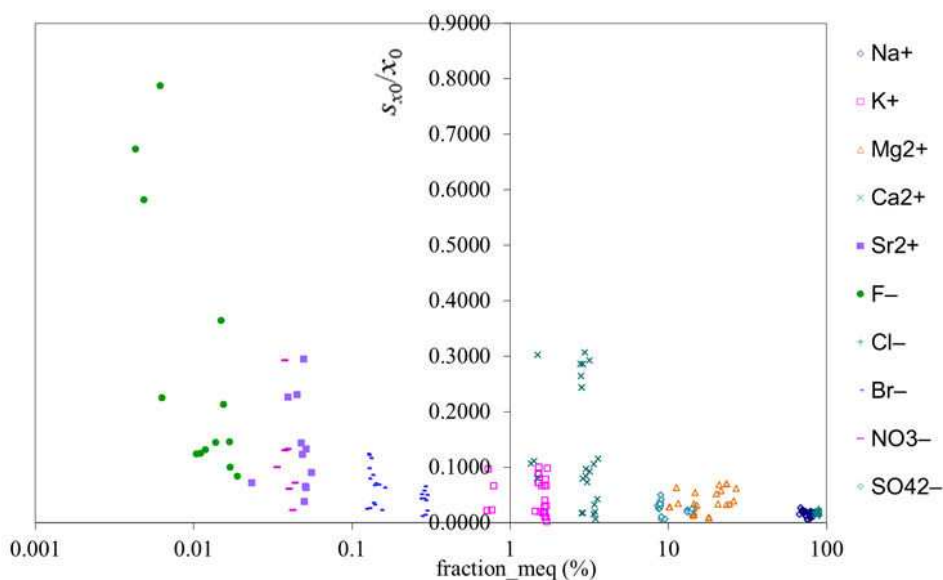
Figure 10. Relative standard uncertainties with which the mass concentrations of individual ions were determined from calibration lines, related to a fraction of an ion in the anionic or cationic composition of a sample, expressed in meq%
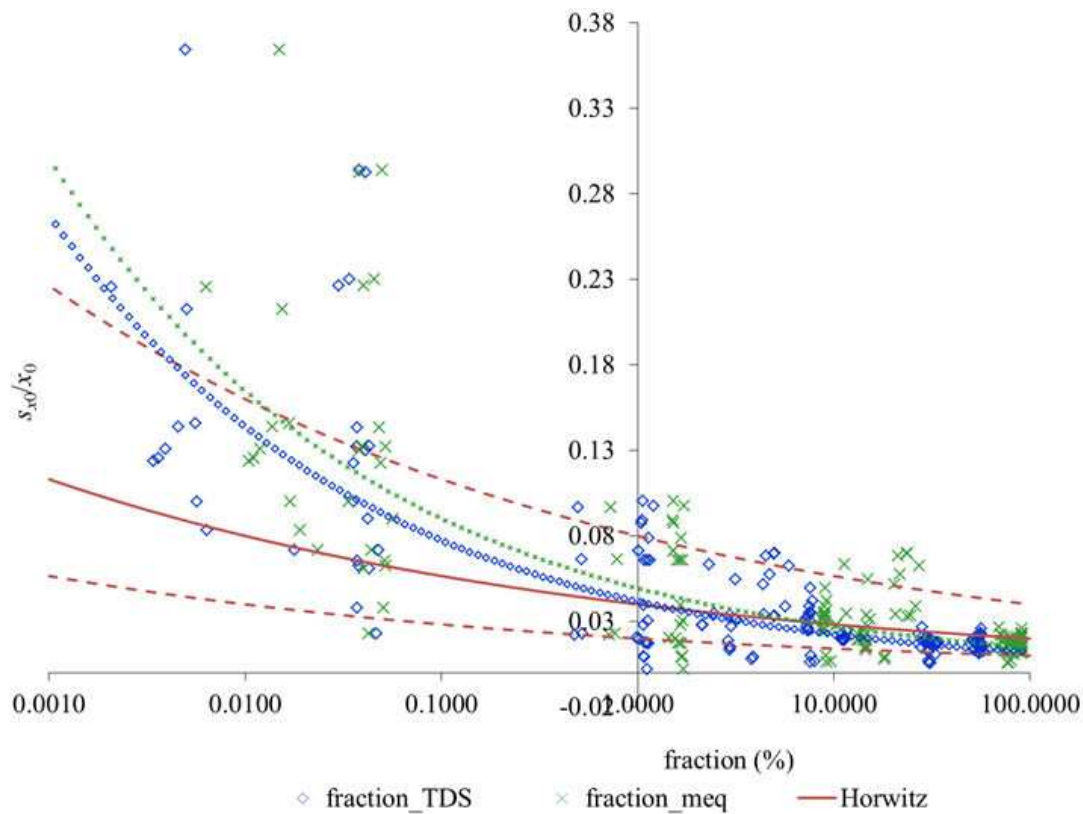
Figure 11. The Horwitz-like functions derived from the experimental results, and expressed either as a fraction of TDS (diamonds) or as a fraction of meq of anions or cations, meq% (crosses), compared with the Horwitz function (solid line) and its two-times and 0.5-times range (dashed lines)

The experimentally obtained data were linearized by applying logarithms to s_{x0}/x_0, fraction_TDS and fraction_meq. The OLS regression line equations 25 and 26 with the correlation coefficients, r 0.7875 and 0.7740 were derived, respectively. The rearrangements of these equations resulted in the Horwitz-like equations 27 and 28 and the corresponding curves are in figure 11 indicated with small size diamonds or crosses, respectively.

$$\log_{10}\left(\frac{s_{x0}}{x_0}\right) = -0.27002 \times \log_{10}\left(\text{fraction\_TDS}\right) - 1.38204 \tag{25}$$

$$\log_{10}\left(\frac{s_{x0}}{x_0}\right) = -0.26200 \times \log_{10}\left(\text{fraction\_meq}\right) - 1.30732 \tag{26}$$

$$\frac{s_{x0}}{x_0} = 0.041492 \times \left(\text{fraction\_TDS}\right)^{-0.27002} \tag{27}$$

$$\frac{s_{x0}}{x_0} = 0.049281 \times \left(\text{fraction\_meq}\right)^{-0.26200} \tag{28}$$

In order to enable the comparison of the experimentally obtained data with the equation of the Horwitz curve [15], which relates a percent relative standard deviation, $s_r(\%)$ and mass

fraction, w (equation 15); we transformed this equation into equation 29, which relates the relative standard deviation, s_r and $w_{(\%)}$, which denotes a mass fraction of an analyte expressed in percent. The resulting curve is indicated in figure 11 with a solid line. Dashed lines indicate two-times and 0.5-times range of the Horwitz function.

$$s_r = 0.04 \; w_{(\%)}^{-0.1505} \tag{29}$$

4.4. Lessons learned

In contrast to the observations derived from the data of interlaboratory comparisons that the Horwitz function holds well for mass fractions between 1.2×10^{-5} % and 13.8 % (equation 16) [34], the Horwitz-like curves are in the best agreement with the Horwitz function for fractions of ions between 1 % and 100 %, but deflect towards higher s_0/x_0 below 1 % as figure 11 demonstrates. This comes with no surprise since if a single minor component is targeted as it is usually a case with the interlaboratory comparisons a matrix elimination and pre-concentration are possible, in contrast to the ion chromatographic determination of the total ionic composition requiring that the minor and major ions are determined simultaneously what is a more demanding case.

5. An uncertainty prediction tool for determining simultaneously minor and major ions with ion chromatography

The results of ion chromatographic analyses of seawaters comprising 156 data serve as an appropriate model because of wide concentration ranges of ions. For two different ways of expressing relative fractions of ions in a sample the meaningful ion independent relations in a form of the Horwitz-like uncertainty functions can be confirmed. The prediction tools established through this research enable recognition of ions for which it can be expected that they are determinable simultaneously with ion chromatography with acceptable uncertainties. By setting appropriate criteria the prediction tools can be accustomed to the user defined requirements.

The meaningful ion independent curves in a form of Horwitz-like functions are presented in figure 12 for the entire data range together with their 0.5-times to two-times, and 0.33-times to three-times ranges which are indicated with dashed lines. In both figures nearly all data points lie in the 0.33-times to three-times range, with the fraction_TDS representation having fewer points outside this range.

These figures can in association with equations 27 and 28 serve as prediction tools. If for example we set a criterion that for any single determination of a concentration the relative uncertainty of interpolation of a concentration from a calibration line equation greater than 0.33 is considered unacceptable ions present in a sample in a fraction_TDS below 0.027 % or in a fraction_meq below 0.046 % cannot be successfully determined simultaneously with the others, as vertical solid lines in figure 12 indicate. In prospective considerations different
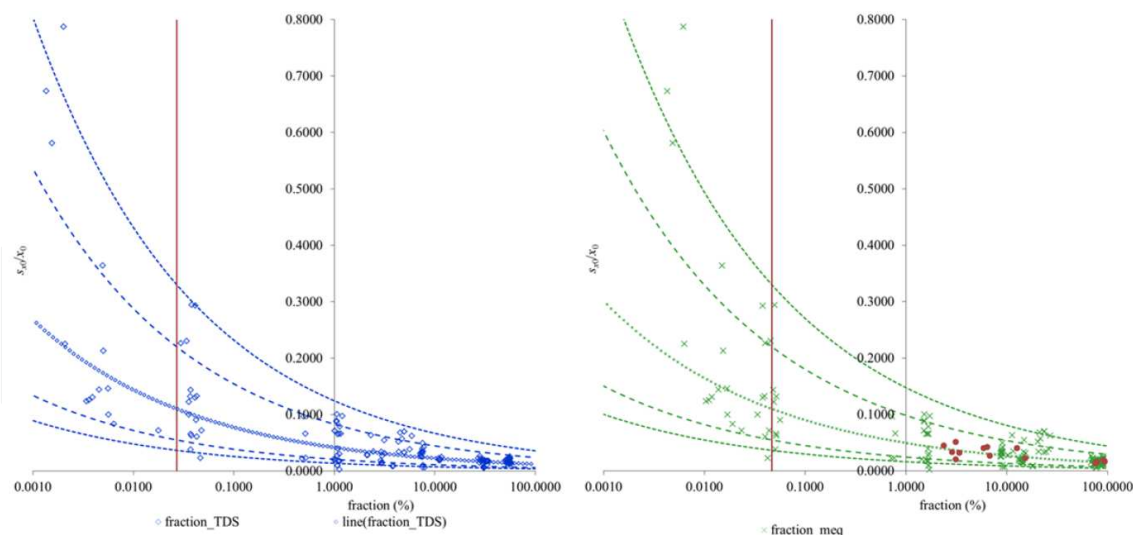
Figure 12. A Horwitz-like function for the results expressed as a TDS fraction, left or in meq%. right, and a three-times, two-times, 0.5-times and 0.33-times ranges (dashed lines)

criteria can be set for the relative uncertainty of interpolation of a concentration from a calibration line equation and decisions made if it is reasonable trying to determine a particular ion in a sample simultaneously with the others.

An independent confirmation of the prediction tools presented here is not an easy task, firstly due to a lack of studies comprising determinations of the total ionic composition of samples in such a wide concentration range, and secondly if this first condition is fulfilled at least for a narrower concentration range extending over two to three orders of magnitude, the uncertainty values are seldom given or evaluated in a way that would allow for a comparison.

To the best of our knowledge the research of Mosello *et al* comes the closest to fulfilling both criteria [41]. For the AQUACON interlaboratory exercise, which evaluated the ion chromatographic performance, the expected values and uncertainties were determined by two reference laboratories and given for determination of the main anions and cations in two freshwater samples. The data, which are presented in figure 12, right, with dots, are in a good agreement with the Horwitz-like function. All data points are within a 0.5-times to two-times range.

6. Conclusions

Determination of total ionic composition of water samples is an important aspect of water quality evaluation. The ordinary least squares linear regression method is most frequently used in instrumental analysis. In spite of the fact that uncertainty associated with the concentration of ions in calibration solutions is considered negligible if compared with the uncertainty associated with a measured quantity, the uncertainty associated with an analytical result obtained with interpolation from a calibration line equation and taking into account the uncertainty originating from a dilution of a sample has to be combined at the end also with the uncertainty associated with the concentration of the ion in a stock calibration standard solution.

This research confirmed that in preparation of multi-ion standard solutions that are intended for analyses of water sample in which concentrations of ions extend over wider concentration ranges the impurities originating from other chemical have to be taken into account in evaluations of concentrations of ions and standard uncertainties associated with them. Otherwise standard uncertainties can be underestimated. This is of special importance when it comes to high purity of a prime chemical from which the ion under consideration originates, higher mass fraction of this ion present as an impurity in another chemical and higher mass ratios of the matrix ion and ion under consideration. A refined and simplified methodology for further evaluations is suggested.

The Horwitz-like functions established through this research enable recognition of ions for which it can be expected that they are determinable simultaneously with ion chromatography with an acceptable uncertainty if their approximate relative fractions in a sample were previously estimated. The prediction tools suggested here in spite of the fact of being derived from the experimental data using a particular calibration scheme and data treatment can serve as a useful guide which can be adapted to user defined requirements by setting appropriate criteria.

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