Uncertainty of nitrate and sulphate measured by ion chromatography in wastewater samples

Brigita Tepuš[1*], Marjana Simonič[2†]

[1] *Komunalno podjetje Ptuj,
2250 Ptuj, Slovenia*

[2] *Faculty of Chemistry and Chemical Engineering,
2000 Maribor, Slovenia*

Abstract: This paper presents an evaluation of measurement uncertainty regarding the results of anion (nitrate and sulphate) concentrations in wastewater. Anions were determined by ion chromatography (EN ISO 10304-2, 1996). The major sources of uncertainty regarding the measurements' results were identified as contributions to linear least - square or weighted regression lines, precision, trueness, storage conditions, and sampling. Determination of anions in wastewater is very important for the purification procedure, especially the amount of nitrate in waste and potable waters.

The determined expanded uncertainty was 6.1 % for nitrate anions and 8.3 % for sulphate anions. The difference between measurement uncertainties determined by the two methods**,** the weighted and linear least - square methods, is negligible.

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Keywords: Nitrate, sulphate, measurement uncertainty

1   Introduction

The determination of nitrate and sulphate anions by ion chromatography plays a key role in assigning value to the purification process regarding wastewater. The non-linearity of the calibration curves could be an important source of error [1]. This paper demonstrates, that there is a very small difference between the measurement uncertainties determined by linear least - square and weighted regression, respectively.

The determination of nitrate and sulphate anions' content plays a key role in assigning

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*   E-mail: cistilna.lab@komunala-ptuj.si

†   E-mail: marjana.simonic@uni-mb.si

value to the purification process of wastewater or potable water. The purpose of this paper is to introduce a procedure for evaluating any uncertainty regarding the results for nitrate and sulphate concentration obtained by ion chromatography and to identify the steps in the analytical procedure which could be improved, the goal of which is the reduction of the overall measurement uncertainty.

The process to evaluate the uncertainty during the nitrate and sulphate anions determination is divided into the following components: description of the method, identification of uncertainty sources, quantification of uncertainty components, and calculation of combined and expanded uncertainty.

2   Experimentation

International Standard Water quality - Determination of dissolved anions by liquid chromatography of ions-Part 2 [2] provides guidance for the determination of nitrate and sulphate in wastewater samples. This standard applies to those water samples containing nitrate content ranging from 0.1 to 50 mg/L and sulphate from 0.1 to 100 mg/L, respectively.

In our experiments, the limits of detection (LOD) for nitrate and sulphate were determined at 1.2 mg/L. LOD was determined by means of standard addition (10 replicates were made for each solution).

The limits of quantification (LOQ) regarding nitrate and sulphate were determined at 1.7 mg/L. LOQ was calculated from 10 replicates made for a series of 5 different concentrations. Relative standard deviation (RSD) was determined to be 3 % for nitrate and 5% for sulphate ions. A range between 1.7 and 50 mg/L was applied for both anions due to the old type of IC and its poorer performance at lower concentrations. Higher concentration of nitrate (or sulphate) can be determined by appropriate dilution.

Selectivity was determined by the standard addition method. Certain concentrations of standard solutions of nitrate and sulphate were added to the distilled water. The recovery was between 93 and 105% for the determination of nitrate and between 102 and 108% for the sulphate determination.

Liquid chromatographic separation of ions was performed by means of a separating column instrument for ion chromatography (Dionex DX-100). Samples were cooled down to 2 - 5 °C and analyzed within 48 hours after sampling. Samples were filtered using black filter papers from Sartorius, Germany (pore size 0.45 μm) to prevent adsorption of the anions onto particulate matter or the conversion of anions by bacterial growth. Samples were then injected by syringe with cellulose acetate filter (pore size 0.2 μm) into the guard columns (IonPac AG12A, 4×50 mm, Dionex and IonPac AS12A, 4×200 mm, Dionex). A conductivity detector cell was used [3]. A solution of Na_2CO_3 (c = 0.0027 mol/L) and $NaHCO_3$ (c = 0.0003 mol/L) was used as eluent.

The nitrate and sulphate certified reference solutions (C_{CRM-NO_3}, C_{CRM-SO_4}) were purchased from Merck, Germany with the following concentrations (Eqs. 1 and 2):

$$C_{CRM-NO_3} = (0.997 \pm 0.005)\, g/L \tag{1}$$

$$C_{CRM-SO_4} = (1.000 \pm 0.002)\, g/L \qquad (2)$$

Working reference solutions $(C_{NO_3-SO_4})_{1-i}$ were prepared by dilution of the certified reference solution to 80 mg/L, 50 mg/L and 36 mg/L, respectively. By further dilution of the working reference solution of $\gamma = 80$ mg/L, working solutions $(C_{NO_3-SO_4})_{2-i}$ were prepared with mass concentrations of 2 mg/L, 4 mg/L, 8 mg/L, 16 mg/L and 24 mg/L (the same for both anions).

Adequate concentrations (C_i) for working reference solutions $(C_{NO_3-SO_4})_{1-i}$ and working solutions $(C_{NO_3-SO_4})_{2-i}$ were determined by (Eq. 3).

$$C_i = \frac{C_{CRM}}{f_{d-i}} = \frac{C_{CRM}V_{pipette}}{V_{100}} \qquad (3)$$

C_{CRM} –   g/L
V_{100} –   volume of one mark volumetric flask, L
$V_{pipette}$ –   volumes of pipettes, L
f_{d-i} –   dilution factor.

Thus, the calibration curve was established by measuring a series of nitrate and sulphate solutions mixed together, ranging from 2 mg/L to 50 mg/L (see above) of nitrate and sulphate ions, respectively.

The concentrations of each working reference solution and working solution were measured in three replicates. A new calibration curve was established every time new batches of reagents or columns were used. The solution with the same concentration of the nitrate and sulphate anions was always poured into the same lab-calibrated flask.

Control charts were created from the results obtained during the analysis of laboratory working reference standards. The laboratory participated in proficiency tests (Aqua check, UK) and a good performance for determination was obtained.

2.1   Identification of the uncertainty sources

Sources of uncertainty are:
- uncertainty of concentration of working reference solutions $(C_{NO_3-SO_4})_{1-i}$
- uncertainty of concentration of working solutions $(C_{NO_3-SO_4})_{2-i}$
- measurement uncertainty of area counts (A_i) from conductivity detector:
  - · flow of the effluent
  - · volume of the sample
  - · conductivity of the mobile phase
  - · pressure
  - · ambient and column temperature
- uncertainty of weighted or linear least - square regression (b_w, a_w, B_1, B_0)
  - · effluent preparation
  - · intercept of the calibration curve
  - · slope of the calibration curve

- measurement uncertainty of area counts (A) in sample
- dilution of the sample (F_d)
- repeatability (F_r)
- recovery (F_{re})
- storage conditions (F_h)
- sampling procedure (F_s)

The sources of uncertainty in nitrogen and sulphate ion determination are schematically presented in Figure 1.
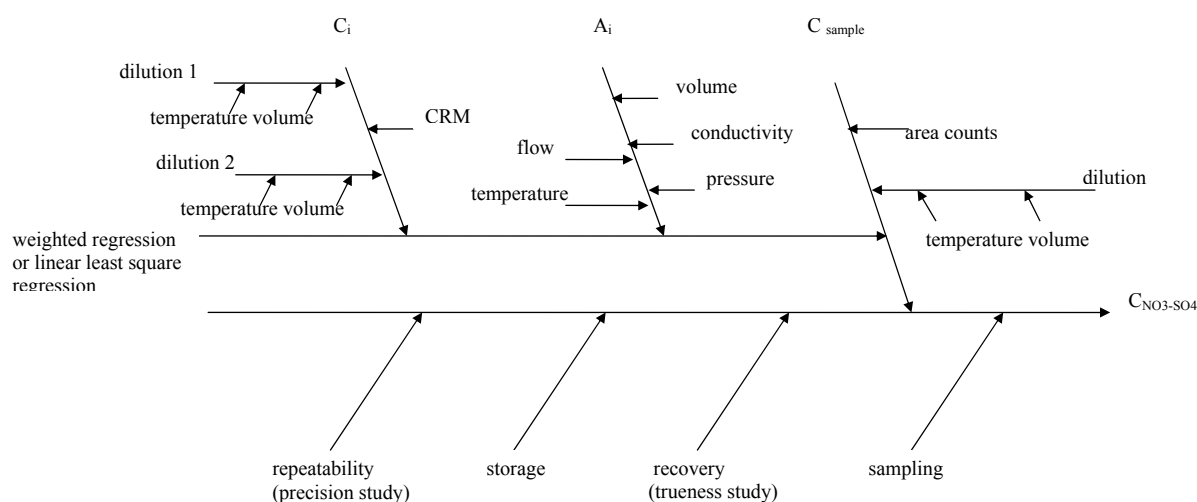
Fig. 1 Cause and effects diagram for the determination of nitrate and sulphate, using the ion chromatography method.

2.2   Quantification of components' uncertainty

The uncertainty associated with the volumetric flask's volume depends on the uncertainty regarding the volume of the volumetric flask itself, on the uncertainty associated with the use of volumetric equipment at a temperature different from that of calibration, and on the repeatability of volume delivery when preparing the working solutions (C_i).The accuracy limit of the volumetric flask's volume was indicated as type B uncertainty by the manufacturer, with no distribution data. Triangular distribution was assumed, therefore, the corresponding values were divided by $\sqrt{6}$. The uncertainty of the temperature effect was calculated using an estimate of the temperature range and the volume expansion coefficient. A temperature variation of $\pm$ 5 °C was taken as a reasonable estimate with 95% confidence. The volumetric expansion coefficient of the water was $2.1 \cdot 10^{-4}$ °C^{-1}. The repeatability of volume delivery during preparation of the stock reference solution was determined experimentally by a series of fill and weight experiments on a volumetric flask. All uncertainty contributions were then combined to obtain the volume uncertainty of the volumetric flask $u(V_{100})$.

The uncertainty sources for delivered volume from the pipettes are: the repeatability

of the delivered volume, the uncertainty of the calibration of that volume and the uncertainty resulting from the difference between the temperature in the laboratory and that of the calibration of the pipettes. Glass pipettes, class A were used.

The slope of the weighted regression line b_w and intercept a_w was calculated using the equations from 4 to 8. Data for nitrate and sulphate anions were determined to be heteroscedastic. The weighted regression line had to be calculated to give additional weight to those points where the error bars were the smallest: it is more important for the calculated line to approximate such points than to approximate the points representing higher concentrations with larger errors. This result is achieved by giving each point a weighting inversely proportional to the corresponding variance (s_i^2). Thus, if the individual points are denoted by $(x_1, y_1), (x_2, y_2)$ etc., then the individual weights, w_1, w_2, etc., are given by Eq. 4 [4].

$$w_i = \frac{s_i^{-2}}{\sum_i s_i^{-2}/n} \tag{4}$$

$$b_w = \frac{\sum_i w_i x_i y_i - n\bar{x}_w \bar{y}_w}{\sum_i w_i x_i^2 - n\bar{x}_w^2} \tag{5}$$

$$a_w = \bar{y}_w - b_w \times \bar{x}_w \tag{6}$$

w_i – weights

s_i^2 – variance

b_w – weighted slope of calibration curve

a_w – weighted intercept of calibration curve

n – number of calibration points

$\bar{x}_w$ and $\bar{y}_w$ represent the co-ordinates of the weighted centroid through which the weighted regression line must pass. These coordinates are given by Eqs. 7 and 8. The weighted centroid is much closer to the origin of the graph than the unweighted centroid, and the weighting given to the points nearer the origin ensures that the weighted regression line has an intercept very close to this point. Because of this, the weighted regression method provides more realistic results for error estimation, in theory. So we decided to determine the practical results.

$$\bar{x}_w = \frac{\sum_i w_i x_i}{n} \tag{7}$$

$$\bar{y}_w = \frac{\sum_i w_i y_i}{n} \tag{8}$$

$\bar{x}_w, \bar{y}_w$ – co-ordinates of the weighted centroid

n – number of calibration point

The slope of the linear least - square calibration curve B_1 and calculated blank B_0

were calculated using Eqs. 9 to 12.

$$B_1 = \frac{\sum\limits_{i} (C_i - \overline{C_i}) \times (A_i - \overline{A_i})}{\sum\limits_{i} (C_i - \bar{C_i})^2} \tag{9}$$

$$B_0 = A - B_1 \times C \tag{10}$$

$$\overline{A_i} = \frac{1}{n} \sum_i A_i \tag{11}$$

$$\overline{C_i} = \frac{1}{n} \sum_i C_i \tag{12}$$

C_i – concentration of individual points

C – concentration of sample

A_i – area counts of individual points

A – area counts of the sample

n – number of calibration point

The concentration of nitrate or sulphate ($C_{NO_3-SO_4}$) was calculated from Eq. 13 for weighted regression and from Eq. 14 for linear least - square regression.

$$C_{NO_3-SO_4} = \frac{A - a_w}{b_w} \times F_d \times F_r \times F_{re} \times F_h \times F_s \tag{13}$$

$$C_{NO_3-SO_4} = \frac{A - B_0}{B_1} \times F_d \times F_r \times F_{re} \times F_h \times F_s \tag{14}$$

B_1 – slope of calibration curve

B_0 – intercept of calibration curve

F_d – dilution factor of sample

F_r – repeatability factor (precision study)

F_h – storage factor

F_{re} – recovery factor (trueness study)

F_s – factor for sampling procedure

3   Results and discussion

3.1   Quantification of the components' uncertainty

Concentration uncertainty of working reference solutions $(C_{NO_3-SO_4})_{1-i}$

The concentrations of nitrate and sulphate ions for working reference solutions were calculated using Eqs. 1 to 3. The values were as follows: 0.0798 g/L, 0.0499 g/L and 0.0359 g/L for nitrate and 0.0800 g/L, 0.0500 g/L and 0.0360 g/L for sulphate, respectively. The concentration uncertainty of the working reference solution is associated with

the uncertainty of the certified reference solution, the volume of the volumetric flask for the preparation of the working reference solution, and the volumes of pipettes (3.6 mL, 5 mL and 8 mL). The rectangular distribution was assumed for the certified reference solution. For calculating the concentration uncertainty of the working reference solutions, the data presented in Table 1 for nitrate were used, plus those presented in Table 2 for sulphate.

Table 1 Uncertainty components and their relative standard uncertainty of nitrate working reference solutions.

	Unit	Value	Uncertainty u	Uncertainty $(RSD=u/Value)$
C_{NO3}	g/L	0.997	0.002890	0.002899
V_8	L	0.008	0.000005	0.000640
V_5	L	0.005	0.000003	0.000655
$V_{3.6}$	L	0.0036	0.000003	0.000696
V_{100}	L	0.1	0.000061	0.000609

Table 2 Uncertainty components and their relative standard uncertainty of sulphate working reference solutions.

	Unit	Value	Uncertainty u	Uncertainty $(RSD=u/Value)$
C_{SO4}	g/L	1	0.001160	0.001160
V_8	L	0.008	0.000005	0.000640
V_5	L	0.005	0.000003	0.000655
$V_{3.6}$	L	0.0036	0.000003	0.000696
V_{100}	L	0.1	0.000061	0.000609

The concentration uncertainty of working reference solutions $(C_{NO_3-SO_4})_{1-i}$ were calculated using Eq. 15 and were determined to be 0.000242 g/L for C_{NO_3-80}, 0.000151 g/L for C_{NO_3-50}, 0.000109 g/L for C_{NO_3-36}, 0.000117 g/L for C_{SO_4-80}, 0.000073 g/L for C_{SO_4-50} and 0.000053 g/L for C_{SO_4-36}.

$$u(C_{NO_3-SO_4})_{1-i} = (C_{NO_3-SO_4})_{1-i} \times \sqrt{\frac{u(C_{CRM-NO_3, CRM-SO_4})^2}{C_{CRM-NO_3, CRM-SO_4}^2} + \frac{u(V_{pipette})^2}{V_{pipette}^2} + \frac{u(V_{100})^2}{V_{100}^2}}$$
(15)

Concentration of working solutions $(C_{NO_3-SO_4})_{2-i}$

The calculated values obtained from Eq. 3 were 1.99 mg/L, 3.99 mg/L, 7.98 mg/L, 15.95 mg/L and 23.93 mg/L for nitrate, and 2 mg/L, 4 mg/L, 8 mg/L, 16 mg/L and 24 mg/L for sulphate, respectively. The uncertainties of the concentrations of the working calibration solutions for curves were associated with the uncertainty of the concentration of working reference solutions of nitrate or sulphate (80 mg/L), the volume of pipette

(2.5 mL, 5 mL, 10 mL, 20 mL or 30 mL) and volume of the 100 mL volumetric flask for preparation of working solutions (see Tables 3, 4).

Table 3 Uncertainty components and their relative standard uncertainty of nitrate working solution.

	Unit	Value	Uncertainty u	Uncertainty ($RSD=u/Value$)
V_2	L	0.00199	0.000002	0.000978
V_4	L	0.00399	0.000003	0.000820
V_8	L	0.00798	0.000006	0.000787
V_{16}	L	0.01595	0.000012	0.000777
V_{24}	L	0.02393	0.000018	0.000771
C_{NO3-80}	g/L	0.07976	0.000242	0.003034
$V_{flask100}$	L	0.1	0.000061	0.000607

The concentration uncertainties of the working reference solutions were calculated using Eq. 16. They were 0.000006 g/L for C_{NO_3-2}, 0.000013 g/L for C_{NO_3-4}, 0.000067 g/L for C_{NO_3-8}, 0.000051 g/L for C_{NO_3-16} and 0.000076 g/L for C_{NO_3-24}.

$$u(C_{NO_3-SO_4})_{2-i} = (C_{NO_3-SO_4})_{2-i} \times \sqrt{\frac{u(C_{NO_3-80,\,SO_4-80})^2}{C_{NO_3-80,\,SO_4-80}^2} + \frac{u(V_{pipette})^2}{V_{pipette}^2} + \frac{u(V_{100})^2}{V_{100}^2}} \quad (16)$$

Table 4 Uncertainty components and their relative standard uncertainty of sulphate working solution.

	Unit	Value	Uncertainty u	Uncertainty ($RSD=u/Value$)
V_2	L	0.00199	0.000002	0.000978
V_4	L	0.00399	0.000003	0.000820
V_8	L	0.00798	0.000006	0.000787
V_{16}	L	0.01595	0.000012	0.000777
V_{24}	L	0.02393	0.000018	0.000771
C_{SO4-80}	g/L	0.07976	0.000117	0.001467
$V_{flask100}$	L	0.1	0.000061	0.000607

The concentration uncertainties of the working reference solutions were calculated using Eq. 16 and were 0.000004 g/L for C_{SO_4-2}, 0.000007 g/L for C_{SO_4-4}, 0.000014 g/L for C_{SO_4-8}, 0.000028 g/L for C_{SO_4-16} and 0.000042 g/L for C_{SO_4-24}.

The measurement uncertainty of area counts (A_i, A) from conductivity detector:

The standard measurement uncertainty of area count from the conductivity detector of solutions (A_i) and of the sample (A) were estimated as the standard deviations of the mean of four replicate determinations of each conductivity measurement, and contributed to the combined and expanded uncertainties in Tables 5 and 6.

The measurement uncertainty due to the dilution of the sample

The standard uncertainty of the sample dilution factor (F_d) was estimated from the uncertainty of the volumetric equipment and the uncertainty associated with the temperatures different from those for calibration, similar to those described above, and contributed to the combined and expanded uncertainties in Tables 5 and 6.

3.1.1 Precision study

The precision was investigated at concentrations covering the full range specified in the method range [5]. Four concentrations were chosen for investigation (0.90 mg/L, 3.06 mg/L, 15.10 mg/L and 40.50 mg/L for NO_3^- , but 1.05 mg/L, 2.68 mg/L, 34.70 mg/L and 50.10 mg/L for SO_4^{2-}) with 6 replicates at each concentration level (relative standard deviations (RSD) were 0.023, 0.013, 0.016, 0.016 for nitrate and 0.030, 0.037, 0.012, 0.011 for sulphate, respectively). It was found that there is no significant difference between the relative standard deviations for each sample. This indicates that the precision is proportional to the analyte concentration. The relative standard deviations were pooled to give a single estimate which can be applied to the concentration range covered by the precision study (Eq. 17).

$$RSD_{pool-NO_3-SO_4} = \sqrt{\frac{(n_1 - 1)\,.RSD_1^2 + (n_2 - 1)\,.RSD_2^2 + ...}{(n_1 - 1) + (n_2 - 1) + ...}} \tag{17}$$

It was discovered, that the RSD_{pool} for nitrate is 1.73% and for sulphate 2.52%. 1, 2...RSD are relatively standard deviations calculated for a sample at concentration level 1, 2, ..., and 1, 2...n are the number of replicates for these samples.

The results calculated with the linear least - square and with weighted regression were combined into one calculation because four determinations in the precision study were not enough to calculate the uncertainty measurement of each anion, separately.

3.1.2 Trueness study

Trueness is estimated in terms of overall recovery [6, 7], i.e., the ratio of the observed value to the expected value. Recovery can be evaluated in a number of ways, in our case from the results of interlaboratory tests (Eqs. 18, 19 and 20).

$$RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{n}} \tag{18}$$

$$u(C_{ref}) = \frac{S_R}{\sqrt{n}} \tag{19}$$

$$u_{(bias)} = \sqrt{RMS_{bias}^2 + u(C_{ref})^2} \tag{20}$$

$bias_i$ – the sum of the squares for all biases between the referenced and analyzed samples during interlaboratory tests,

n – average number of participated laboratories, and

S_R – interlaboratory standard deviation.

An uncertainty of 1.97% was determined for nitrate and 3.23% for sulphate over nine interlaboratory tests (nine different samples, each with three replicates - Eq. 20).

3.1.3   Uncertainty associated with storage conditions

The standard uncertainty associated with the effect of storage conditions on the results was determined experimentally. The samples which were analyzed within a two-week time period, were filtered and stored in the dark at temperatures between 2 °C and 5 °C. It was discovered, that the uncertainty for nitrate was 1.24% and for sulphate, 0.55% (samples were analyzed in ten replicates each week).

3.1.4   Uncertainty due to sampling

The variance [8, 9] (replicate analyses of the same sample prepared in laboratory), sub - sampling transport variance (analyses of replicate samples taken in the field from the bulk sample) and total sampling variance (analysis of bulk samples obtained by separate application of the sampling procedure) was determined. The comparison between the different estimates of variance described above can be used to identify the most important sources of measurement uncertainty. After combining all contributions, the determined uncertainties were 0.61% for nitrate anions and 0.19% for sulphate anions..

3.2   Calculation of combined and expanded uncertainty

The standard uncertainty of input parameters for different anions is presented in Tables 5 and 6.

The uncertainty of nitrate and sulphate were determined by combining the standard uncertainties of $A_i, C_i, F_d, F_r, F_{re}, F_h, F_s$. Uncertainties were combined by using the rule of error propagation. To calculate the expanded uncertainty of measurement results at the 95% confidence level, the result for the combined uncertainty (U) was multiplied by a coverage factor k of 2.

Generally, the measurement result is determined from other quantities, and the relationship between result y and the values of the input parameters can be expressed by a model of Eq. 21, where x represents model input parameters $(A_i, C_i, F_d, F_r, F_{re}, F_h, F_s)$. The uncertainty of the result $u(y)$ depends on the uncertainty of the input parameters (x_i) and is described by Eq. 22 (variables are independent). $\partial y/\partial x_i$ is a sensitivity coefficient; the partial differential of y with respect to x_i and $u(x_i)$ denotes the uncertainty in y arising from the uncertainty in x_i. These sensitivity coefficients describe how the value of y varies with changes of the parameter x_i.

$$y = f(x_1, ...x_n) \tag{21}$$

$$u(y) = \sqrt{\sum_i \left(\frac{\partial y}{\partial x_i}\right)^2 \times u(x_i)^2} \tag{22}$$

Table 5 Uncertainty components and their relative standard uncertainty regarding nitrate anion.

	Unit	Value	Uncertainty u	Uncertainty $(RSD=u/Value)$
A	no unit	4.99E+08	3.21E+06	6.43E-03
A_2	no unit	3.77E+07	8.06E+05	2.14E-02
A_4	no unit	7.24E+07	7.92E+05	1.09E-02
A_8	no unit	1.46E+08	2.20E+06	1.51E-02
A_{16}	no unit	3.04E+08	1.64E+06	5.39E-03
A_{24}	no unit	4.68E+08	3.20E+06	6.84E-03
A_{36}	no unit	7.22E+08	1.81E+06	2.51E-03
A_{50}	no unit	1.04E+09	6.25E+06	6.01E-03
C_2	g/L	1.99E-03	6.00E-06	3.01E-03
C_4	g/L	3.99E-03	1.30E-04	3.26E-02
C_8	g/L	7.98E-03	6.70E-05	8.40E-03
C_{16}	g/L	1.60E-02	5.10E-05	3.20E-03
C_{24}	g/L	2.39E-02	7.60E-05	3.18E-03
C_{36}	g/L	3.59E-02	1.09E-04	3.04E-03
C_{50}	g/L	4.99E-02	1.51E-04	3.03E-03
F_d	no unit	1	6.10E-05	6.10E-05
F_r	no unit	1	1.97E-02	1.97E-02
F_{re}	no unit	1	1.73E-02	1.73E-02
F_h	no unit	1	1.24E-02	1.24E-02
F_s	no unit	1	6.10E-03	6.10E-03

3.3 Expanded measurement uncertainty of nitrate

The evaluation of measurement uncertainty is one of the requirements of the standard EN ISO/IEC 17025 [10] which must be completed by laboratories to obtain accreditation.

The result of the measurement was 25.1 mg/L for the nitrate and the evaluated combined uncertainty was 0.75 mg/L. To obtain an expanded uncertainty at the 95% confidence level, the combined uncertainty was multiplied by the coverage factor k of 2. Therefore, the expanded measurement uncertainty of nitrate ions was 25.1 ± 1.5 mg/L (5.95%) when applying weighted regression, and 24.7 ± 1.5 mg/L (6.09%) when applying the linear least - square regression.

3.4 Expanded measurement uncertainty of sulphate

The result of the measurement was 25.1 mg/L for sulphate and the evaluated combined uncertainty was 1.0387 mg/L. To obtain an expanded uncertainty at the 95% confidence level, the combined uncertainty was multiplied by the coverage factor k of 2. Therefore,

Table 6 Uncertainty components and their relative standard uncertainty regarding sulphate anion.

	Unit	Value	Uncertainty u	Uncertainty $(RSD=u/Value)$
A	no unit	6.69E+08	2.57E+06	3.84E-03
A_2	no unit	5.33E+07	1.64E+06	3.08E-02
A_4	no unit	9.87E+07	1.15E+06	1.17E-02
A_8	no unit	1.96E+08	1.58E+06	8.06E-03
A_{16}	no unit	4.03E+08	2.08E+06	5.16E-03
A_{24}	no unit	6.21E+08	2.70E+06	4.35E-03
A_{36}	no unit	9.76E+08	2.20E+06	2.25E-03
A_{50}	no unit	1.38E+09	9.57E+06	6.93E-03
C_2	g/L	2.00E-03	4.00E-06	2.00E-03
C_4	g/L	4.00E-03	7.00E-06	1.75E-03
C_8	g/L	8.00E-03	1.40E-05	1.75E-03
C_{16}	g/L	1.60E-02	2.80E-05	1.75E-03
C_{24}	g/L	2.40E-02	4.20E-05	1.75E-03
C_{36}	g/L	3.60E-02	5.30E-05	1.47E-03
C_{50}	g/L	5.00E-02	7.30E-05	1.46E-03
F_d	no unit	1	6.10E-05	6.10E-05
F_r	no unit	1	3.23E-02	3.23E-02
F_{re}	no unit	1	2.52E-02	2.52E-02
F_h	no unit	1	5.50E-03	5.50E-03
F_s	no unit	1	1.90E-03	1.90E-03

the expanded measurement uncertainty of sulphate ions was 25.1 ± 2.1 mg/L (8.29%) when applying the weighted regression method, and 24.9 ± 2.1 mg/L (8.34%) when applying linear least - square regression method.

The following data contribute to the uncertainty: precision, trueness, storage conditions, sampling data, concentration data, and area counts. The equations for calculating curves were different (weighted and linear least - square). The results for measurement uncertainties differ very little in both cases, so we can conclude, that the measurement uncertainties of nitrate and sulphate by ion chromatography can be very well determined by applying the linear least - square method, which is less complicated compared to weighted regression. The largest contribution to measurement uncertainty was precision and trueness for both anions.

4   Conclusions

Measurement uncertainties for nitrate and sulphate anions were estimated. Two different statistical methods, the weighted and the linear least - square method, were applied

to calculate the measurement uncertainties. Combined and expanded uncertainties were determined. The largest contribution regarding the measurement uncertainty was precision and trueness regarding both anions. The expanded uncertainty for nitrate anion measurements was determined to be approximately 6.1% and apprixomiately 8.3% for sulphate anions. It was established that the difference between measurement uncertainties determined by two applied statistical methods (the weighted and linear least - square method), is negligible.

Acknowledgment

References

[1] R. Mosello, G.A. Tartari, A. Marchetto, S. Polesello, M. Bianchi and H. Muntau: "Ion chromatography performances evaluated from the third AQUACON freshwater analysis interlaboratory exercise", *Accred. Qual. Assur.*, (2004), Vol. 9(4-5), pp. 242–246.

[2] European Standard EN ISO 10304-2: 1996, *Water quality- Determination of dissolved anions by liquid chromatography of ions- Part 2: Determination of bromide, chloride, nitrate, nitrite, orthophosphate and sulphate in waste water* (ISO 10304- 2: 1995), International Organization for Standardization, Geneve.

[3] Dionex: DX-100 Ion Chromatograph with SRS Control Operators Manual, 1996.

[4] J.N. Miller and J.C. Miller: *Statistics and Chemometrics for Analytical Chemistry*, Pearson, England, 2000.

[5] G.A. Tartari, A. Marchetto and R. Mosello: "Precision and linearrity of inorganic analyses by ion chromatography", *J. Chromatogr. A*, Vol. 706, (1995), pp. 21–29.

[6] V.J. Barwick, S.L.R. Ellison: VAM project 3.2.1, *Development and Harmonisation of Measurement Uncertainty Principles, Part (d): Protocol for uncertainty evaluation from validation data*, 2000.

[7] S.L.R. Ellison, M. Rosslein and A. Williams: *Quantifying Uncertainty in Analytical Measurement; EURACHEM/CITAC*, 2000.

[8] *EUROLAB Technical Secretariat, Measurement Uncertainty in Testing*, Technical Report No. 1/2002, Germany, 2002.

[9] International Standard ISO 5667-14:1999, *Water quality-Sampling-Part 14: Guidance on quality assurance of environmental water sampling and handling*, International Organization for Standardization, Geneve.

[10] European Standard EN ISO/IEC 17025: 2005, *General requirements for the competence of testing and calibration laboratories*, European Committee for Standardization, Brussels.