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Precision and linearity of inorganic analyses by ion chromatography

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Abstract

The repeatability of the measurements of peak areas for calibration solutions and the precision of anion and cation determinations (3–600 μM) in freshwater are discussed on the basis of 2 years of measurements on calibration solutions and stabilized internal standards. Anion measurements show higher repeatability of the measurements of peak areas for calibration solutions (R.S.D. 2–5%) and precision (R.S.D. 2–8%) than those of cations (R.S.D. 2–10% and 2–15%, respectively). Results for the calibration technique show that multi-point (6–8 concentrations), quadratic or cubic regressions permit a correct quantification over a wide range (1.5–2 orders of magnitude) of concentrations. Thanks to the repeatability of the measurements of peak areas for calibration solutions, only two calibrations, at the beginning and end of a batch of 20–30 samples, are adequate. These conditions give better results than calibrations performed with 2–3 points and repeated every 8–10 samples.

1. Introduction

In the last decade, ion chromatography (IC) has become one of the most frequently used techniques for the determination of anions and, more recently, cations at low levels. Long-term quantitative reports of the performance of the method are required to estimate its precision and to allow method optimization.

In this work we used long-term (months or years) records of the peak areas for calibration solution and control charts to estimate the precision of the IC determination of inorganic ions. One of the major problems arising from routine analytical activity is the evaluation of the precision of chemical data, defined following the APHA as the measurement of the degree of agreement among replicate analyses of a sample with concentrations stable in time [1]. Leaving aside the problems related to sample representativeness, there are several manual and instrumental factors that contribute to precision, such as sample pretreatments, standard preparation and conservation, repeatability of the measurements of peak areas for calibration solutions and type of calibration [1–3].

This paper also aims to define an efficient calibration procedure, to assist those whose work involves routine analyses. In 5 years' operation as a reference laboratory in intercomparison exercises [4], we have found that most of the participating laboratories use one-point or multi-point linear calibration, repeated every batch of 5–20 samples. A different calibration function is

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generally required if the concentration of any sample lies out of the calibration range. To simplify this procedure, we investigated the reliability of a single calibration function over large ranges of concentration (1.5–2 order of magnitude, depending on the specific ion).

As our laboratory deals mainly with atmospheric deposition and surface water analysis (an average of 2000 samples per year), the application of our results to different media is not recommended.

2. Definitions

Response Factor (R.F.): ratio between the amount of the analyte (μmol) in the calibration solution and the detector signal (nS cm^{-1} s), expressed in μmol cm S^{-1} s^{-1}.

Repeatability of the measurements of peak areas for calibration solutions: relative standard deviation [R.S.D. (%)] of the peak areas of calibration solutions at different levels of concentrations, measured in 24–150 calibrations during 1 year. Of these, only complete multipoint calibrations (24–29 depending on the specific ion) were used to evaluate the reproducibility of whole calibration functions. It is assumed to be dependent on (a) preparation of standards (weighing, dissolution, volumetric dilution), (b) equipment repeatability of the measurements of peak areas for calibration solutions and (c) random, non-identifiable errors.

Precision: R.S.D. (%) of the measured concentrations of natural or artificial samples, stabilized with chloroform (control charts), analysed 1–2 times every batch of analyses. It is assumed to be dependent on (1) factors (a), (b) and (c) of repeatability of the measurements of peak areas for calibration solutions, (2) calibration (incorrect regression between concentration and instrument signals), (3) interferences among the ions present in the sample and (4) contamination or unrepeatability of the measurements of peak areas for calibration solutions of the natural or artificial samples used.

3. Experimental

3.1. Equipment for anions

A Dionex (Sunnyvale, CA, USA) Model 2010i ion chromatograph including analytical pump and CDM-1 conductivity detector, Spectra-Physics (San Jose, CA, USA) SP8780 autosampler with a Rheodyne Model 7010 injection valve and a 50-μl sample loop was used. The Dionex anion column consisted of an Ion Pac AG4A guard column, Ion Pac AS4A separation column and chemical suppression by an anion self-regenerating suppressor used in the autosuppression recycle mode. The eluent was 1.8 m*M* sodium carbonate–1.7 m*M* sodium hydrogencarbonate at a flow-rate of 2.0 ml min^{-1}, the system pressure was 650–750 p.s.i (1 p.s.i. = 6894.76 Pa) and the background conductivity was 14–15 μS cm^{-1}.

3.2. Equipment for cations

A Dionex Model 4000 ion chromatograph including an analytical gradient pump and CDM-2 conductivity detector, Spectra-Physics AS3500 autosampler with a Rheodyne Model 9010 injection valve and a 100-μl sample loop was used. The Dionex cation column consisted of an Ion Pac CG12 guard column, Ion Pac CS12 separation column and chemical suppression by a cation self-regenerating suppressor used in the autosuppression recycle mode. The eluent was 20 m*M* methansulfonic acid at a flow-rate of 1.0 ml min^{-1}, the system pressure was 1000–1100 p.s.i. and the background conductivity was 0.6–1.0 μS cm^{-1}.

Both the cation and anion columns were changed during the study period, without any noticeable effect on the response factors.

3.3. Integration

A Dionex Model III advanced computer interface with AI-450 program release 3.31 was used. Peak-area integration using external standards was applied.

3.4. Reagents

Eluents and combined standards were prepared fresh weekly using ultra-pure water (resistivity 18 MΩ cm, filtered through a 0.2-μm membrane filter), analytical-reagent grade chemicals for chloride, nitrate, sulphate and ammonium and ready-for-use standard solutions (1 mg ml^{-1}) for sodium, potassium, calcium and magnesium. Standards were kept at room temperature, stored in polycarbonate bottles.

3.5. Analyses

The equipment was equilibrated for at least 1 h before starting the analyses. All the analyses were performed as a single measurement. Up to now calibration was performed using three external standards, with concentrations including those of the samples, and it was repeated every 8–12 sample measurements. Calibration was done on the basis of peak areas, using linear regressions in the case of cations and linear or quadratic regressions, depending on the range of concentrations, in the case of anions. All the area signals of the calibration solutions in the period August 1993–July 1994 were recorded and are used in this paper to evaluate the repeatability of the measurements of peak areas for calibration solutions and mean response factor.

Control charts [1] were obtained from the analyses of natural and artificial samples of 2-l volume, filtered and stabilized with chloroform (0.2% v/v), with 2–4 concentration levels for each ion in the range of those normally used. Two different types of stabilized, multi-variable samples were used: the first analysed routinely 3–5 times per week, covering the whole range of concentrations, preserved for 6 months–1 year, the second analysed monthly, with a narrow range of variation in the concentrations, and preserved for 2–3 years. Precision values presented in this paper were obtained from both types of stabilized samples, while the examples of control charts refer to the second type.

4. Results and discussion

The repeatability of the measurements of peak areas for calibration solution values for all anions (Fig. 1a), obtained from the signals of the calibration solutions, is between 2 and 3% for concentrations higher than 10 μM, increasing to 5% for the lowest concentration of 3 μM. The repeatability of the measurements of peak areas for calibration solution values for cations (Fig. 1c) is 2–5% for concentrations lower than 100 μM, slightly higher than those for anions; the highest values of 5–10% were calculated for concentrations lower than 10 μM.

For every batch of analyses, natural and artificial stabilized samples were analysed as internal quality controls. Chloroform (0.2%, v/v) was sufficient to stabilize the solutions for a period of years in the case of calcium, magnesium, potassium, sulphate and nitrate. Examples of the control charts obtained are shown in Fig. 2. Magnesium is an example of a stable analyte, whereas in the case of ammonium a statistically significant decrease in concentration was observed after 3 years, probably due to the evaporation of chloroform and the consequent bacterial oxidation of the ammonium. A slight increase in the concentrations of chloride and sodium was observed, probably because of contamination during manipulation.

As in the case of repeatability of the measurements of peak areas for calibration solutions, precision values, obtained from the R.S.D.s for stabilized samples used for the control charts, are lower for anions then for cations (Fig. 1b and d, respectively). Sodium, potassium and magnesium show the highest R.S.D.s for concentrations lower than 10 μM; several factors may contribute, including sample contamination and release from the glass vials used for the autosampler. As expected, the precisions are worse than the repeatability of the measurements of peak areas for calibration solution values.

As regards the signal response to different analyte concentrations, apart from ammonium, it was apparently linear up to 0.6–2 μM (Fig. 3). However, a more accurate evaluation (restricted

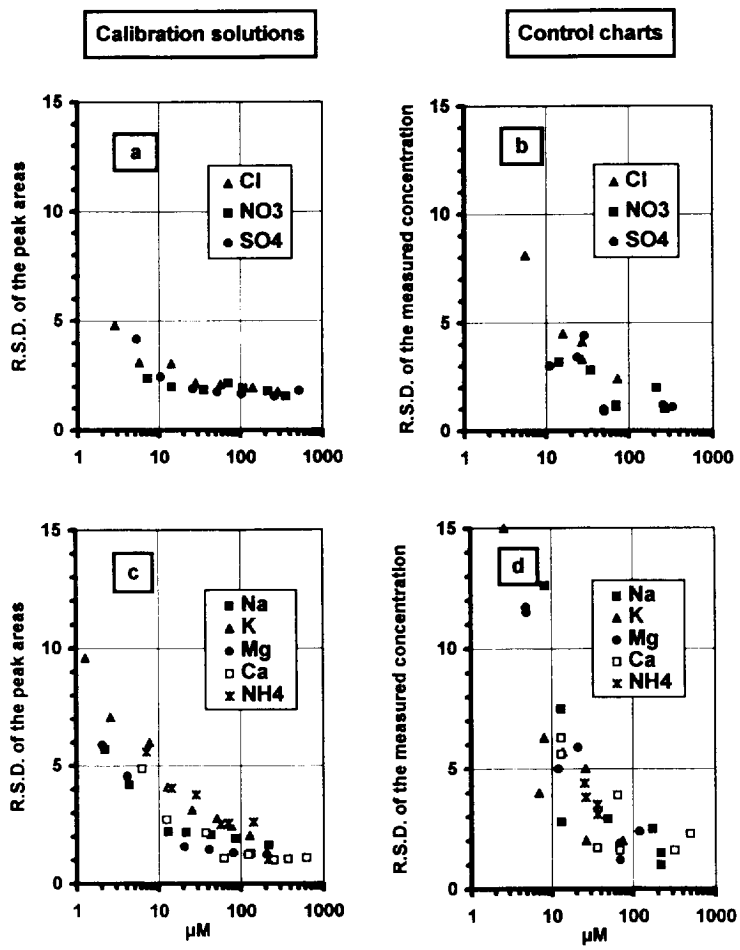

Fig. 1. Repeatability of the measurements of peak areas for calibration solutions and precision on control charts of anions and cations.

to the most common calibration ranges) showed that anions, base cations and ammonium have different patterns: in the case of anions, linear regression overestimates the lowest and highest concentrations and underestimates the values in the central part of the calibration range (Table 1). The residual of the regression is very large, up to 150–300%, in the case of the lowest concentrations of the anions, whereas in the central part the underestimation may account for 10%. The residuals decrease using the quadratic regression, and are least with the cubic regression. It must be stressed that in all cases the correlation coefficient was very close to unity. In the case of cations, excluding ammonium, the signal response is more linear, but even in this case the residual is large in the lowest range of concentrations. In the case of ammonium the signal response is the opposite of that of anions: linear regression greatly underestimates the lowest and highest concentrations and overestimates concentrations in the middle of the calibration range. The use of quadratic or cubic regressions significantly improves the results (Table 1).

The goodness of fit of the calibration models was compared by the analysis of variance. The F-test was used to evaluate the significance of the cubic versus the quadratic, the quadratic versus the linear, and the linear versus the constant-response model. The linear model was

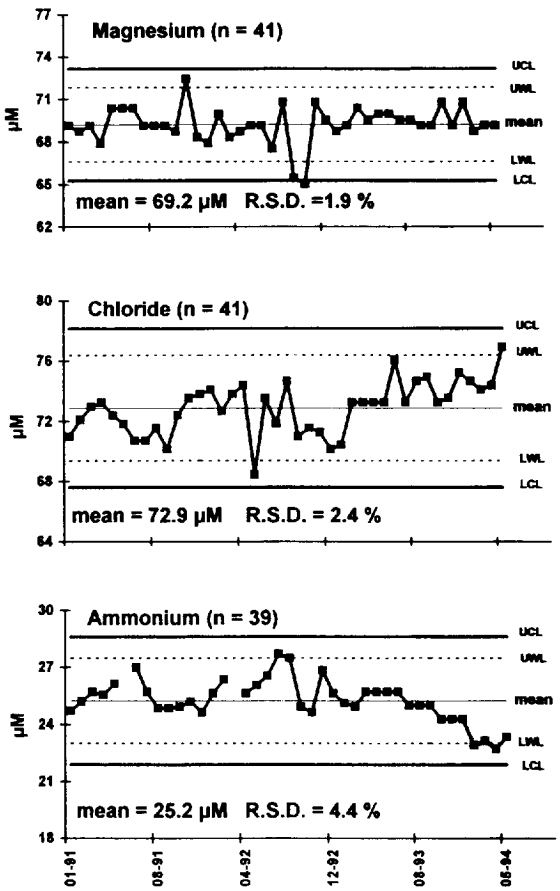

Fig. 2. Examples of control charts. UCL and LCL = upper and lower control limits (±3 S.D.); UWL and LWL = upper and lower warning limits (±2 S.D.).

obviously significantly different from the null model in all cases. The quadratic model was significantly better than the linear model for ammonium, sodium and all the anions. Only for sulphate did the introduction of the cubic term lead to a significant improvement in the goodness of fit of the model.

These different patterns may be due to the type of signal response (R.F.) of the conductivity detector to different concentrations of anions, cations and ammonium (Fig. 4). In the case of anions there is evident overlapping of chloride and nitrate, both monovalent ions, and roughly halved values for sulphate, a bivalent ion. All three anions show a decrease in R.F. with increasing concentration. The standard deviations relative to each concentration, calculated from 24–150 measurements on calibration solutions over about 1 year, are very low, if compared with the variations in R.F. as a function of concentration. In the case of cations (ammonium excluded), the R.F. values show no significant variations with concentration; further, there is a clear difference between mono- and bivalent ions. The ammonium R.F. increases with increasing concentration, even in the absence of sodium and potassium, whose peaks are close to that of ammonium. Also for cations and ammonium, the standard deviations are small compared with the variations of R.F. with concentration (Fig. 4).

The reasons for these differences are not known; however, we can assess that the background signal is 14–15 μS cm^{-1} for anions (suppressed eluent, carbon dioxide and water), whereas it is only 0.6–1.0 μS cm^{-1} for cations (suppressed eluent, water after the exchange of methanesulphonate). Finally, for ammonium, a partial conversion into non-ionized ammonia as a function of pH must be expected. In the absence of other buffering ions, as is the case with the ammonium solution after suppression, the pH of solutions in the range 7–215 μM ammonia solution, is between 8.73 and 9.72. At these pH values, at a temperature of about 25°C, the percentage of non-ionized ammonia is 24 and 75% [5] of the total ammonium, respectively, with a corresponding decrease in conductivity.

5. Conclusions

Ion chromatography is one of the most widely used techniques for inorganic analyses of natural waters. The equipment gives very good repeatability of the measurements of peak areas for calibration solutions, permitting a high analytical precision. A strict program of both internal and external quality controls is essential, however, to ensure accuracy. In particular, critical aspects are the preparation of calibration solutions and the use of control charts for every analyte, at different levels of concentration. Of

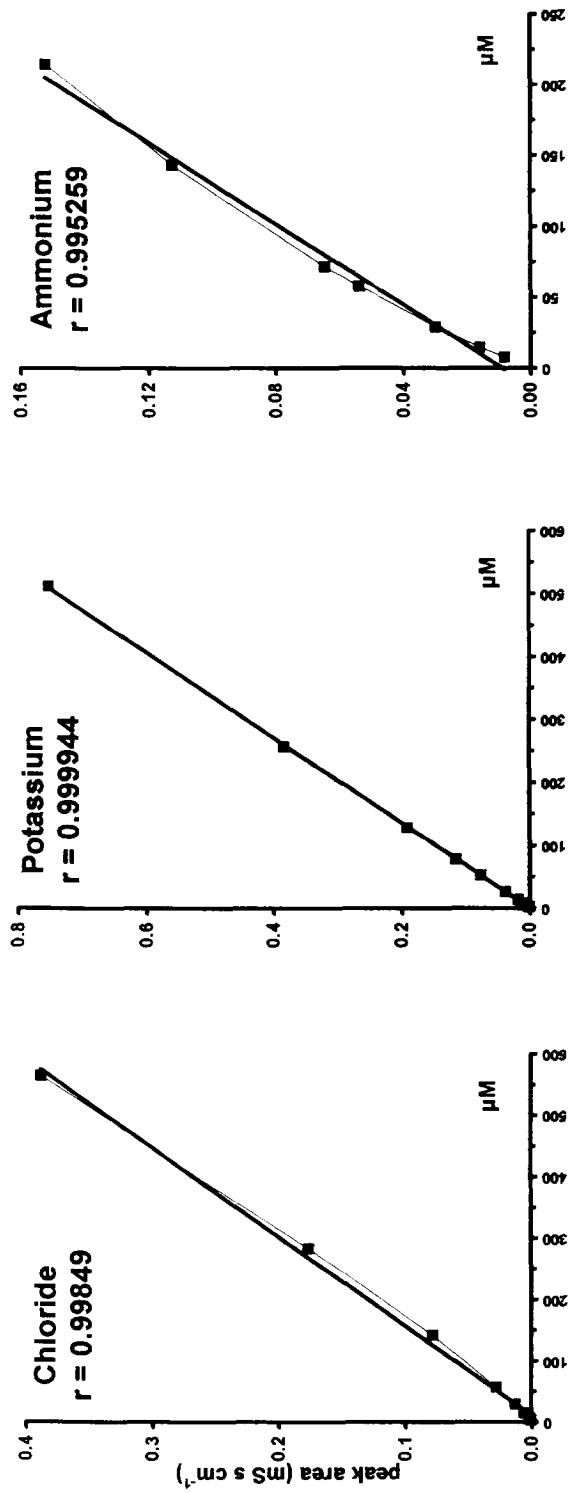

Fig. 3. Examples of calibration graphs for anions, cations and ammonium. ■ = Measured values; straight lines = linear regression.

Table 1
Mean and S.D. of the expected concentrations for the calibration concentrations (Cal.) obtained by repeating the application of different calibration functions 24–28 times

Sodium (μM) (n = 24)

Cal	Linear	Quadratic	Cubic
2.2	2.6 ± 0.4	2.1 ± 0.3	2.1 ± 0.3
4.3	4.8 ± 0.4	4.3 ± 0.2	4.3 ± 0.2
13.0	13.3 ± 0.4	13.3 ± 0.2	13.0 ± 0.3
21.7	21.9 ± 0.4	21.9 ± 0.4	21.9 ± 0.5
43.5	43.1 ± 0.6	43.5 ± 0.6	43.5 ± 0.4
87.0	86.0 ± 1.2	86.8 ± 0.8	86.8 ± 0.7
130.5	129.9 ± 1.5	130.6 ± 0.9	130.6 ± 0.4
217.5	218.3 ± 1.0	217.5 ± 0.2	217.47 ± 0.04
r^2	0.99978 ± 0.00033	0.999937 ± 0.0000049	0.999963 ± 0.0000025
s_y	1.01 ± 0.54	0.61 ± 0.23	0.51 ± 0.19
m_0	0.33 ± 0.42	−0.21 ± 0.27	−0.25 ± 0.35
m_1	$6.82 \cdot 10^{-4} \pm 9.39 \cdot 10^{-6}$	$7.00 \cdot 10^{-4} \pm 1.71 \cdot 10^{-5}$	$7.03 \cdot 10^{-4} \pm 3.44 \cdot 10^{-5}$
m_2		$5.85 \cdot 10^{-11} \pm 6.81 \cdot 10^{-11}$	$8.55 \cdot 10^{-11} \pm 2.78 \cdot 10^{-10}$
m_3			$6.25 \cdot 10^{-17} \pm 6.25 \cdot 10^{-16}$
F	92819 $p < 0.001$	144.6 $p < 0.001$	0.049 n.s.

Potassium (μM) (n = 27)

Cal	Linear	Quadratic	Cubic
1.3	1.3 ± 0.3	1.5 ± 0.3	1.1 ± 0.3
2.6	2.7 ± 0.3	2.9 ± 0.2	2.6 ± 0.3
7.7	7.6 ± 0.4	7.7 ± 0.4	7.8 ± 0.4
12.8	12.6 ± 0.4	12.6 ± 0.4	12.9 ± 0.6
25.6	25.2 ± 0.7	25.1 ± 0.8	25.6 ± 0.8
51.1	51.1 ± 1.3	50.8 ± 1.4	51.0 ± 1.2
76.7	77.8 ± 1.8	77.5 ± 1.3	76.8 ± 0.6
127.9	127.3 ± 1.0	127.6 ± 0.3	127.85 ± 0.07
r^2	0.99938 ± 0.00061	0.99954 ± 0.00084	0.99975 ± 0.00028
s_y	1.02 ± 0.48	0.90 ± 0.54	0.73 ± 0.41
m_0	0.06 ± 0.29	0.27 ± 0.30	−0.21 ± 0.40
m_1	$6.59 \cdot 10^{-4} \pm 1.15 \cdot 10^{-5}$	$6.47 \cdot 10^{-4} \pm 2.51 \cdot 10^{-5}$	$7.01 \cdot 10^{-4} \pm 4.89 \cdot 10^{-5}$
m_2		$6.88 \cdot 10^{-11} \pm 1.52 \cdot 10^{-10}$	$7.43 \cdot 10^{-10} \pm 8.45 \cdot 10^{-10}$
m_3			$2.86 \cdot 10^{-15} \pm 3.33 \cdot 10^{-15}$
F	54328 $p < 0.001$	1.58 n.s.	1.76 n.s.

Magnesium (μM) (n = 29)

Cal	Linear	Quadratic	Cubic
2.1	2.3 ± 0.3	2.2 ± 0.2	2.0 ± 0.2
4.1	4.4 ± 0.3	4.3 ± 0.2	4.1 ± 0.1
12.3	12.4 ± 0.3	12.3 ± 0.2	12.3 ± 0.2
20.6	20.4 ± 0.2	20.4 ± 0.2	20.6 ± 0.3
41.1	40.8 ± 0.4	40.9 ± 0.4	41.2 ± 0.4
82.3	81.9 ± 0.8	82.1 ± 0.7	82.2 ± 0.6
123.4	123.7 ± 1.2	123.9 ± 0.7	123.5 ± 0.3
205.7	205.8 ± 0.8	205.6 ± 0.2	205.71 ± 0.04
r^2	0.99988 ± 0.00015	0.999947 ± 0.0000064	0.999970 ± 0.0000042
s_y	0.67 ± 0.41	0.49 ± 0.29	0.39 ± 0.26
m_0	0.13 ± 0.33	0.02 ± 0.23	−0.24 ± 0.26
m_1	$3.44 \cdot 10^{-4} \pm 3.62 \cdot 10^{-6}$	$3.46 \cdot 10^{-4} \pm 7.48 \cdot 10^{-6}$	$3.56 \cdot 10^{-4} \pm 8.83 \cdot 10^{-6}$
m_2		$3.09 \cdot 10^{-12} \pm 1.50 \cdot 10^{-11}$	$-5.04 \cdot 10^{-11} \pm 5.08 \cdot 10^{-11}$
m_3			$5.37 \cdot 10^{-17} \pm 6.90 \cdot 10^{-17}$
F	476889 $p < 0.001$	0.31 n.s.	0.57 n.s.

Calcium (μM) (n = 28)

Cal	Linear	Quadratic	Cubic
6.2	6.8 ± 0.6	6.9 ± 0.5	6.2 ± 0.5
12.5	12.7 ± 0.7	12.8 ± 0.4	12.3 ± 0.3
37.4	37.4 ± 0.8	37.5 ± 0.5	37.6 ± 0.6
62.4	61.9 ± 0.5	61.9 ± 0.5	62.4 ± 0.6
124.8	124.0 ± 1.1	123.9 ± 1.2	125.0 ± 1.1
249.5	249.0 ± 2.2	248.8 ± 1.9	249.1 ± 1.6
374.3	375.8 ± 2.8	375.7 ± 1.8	374.4 ± 0.8
623.8	623.2 ± 1.9	623.4 ± 0.4	623.73 ± 0.09
r^2	0.999926 ± 0.000072	0.999957 ± 0.0000046	0.999979 ± 0.0000027
s_y	1.70 ± 0.81	1.38 ± 0.72	1.05 ± 0.59
m_0	0.12 ± 0.63	0.25 ± 0.60	−0.63 ± 0.65
m_1	$3.37 \cdot 10^{-4} \pm 3.40 \cdot 10^{-6}$	$3.37 \cdot 10^{-4} \pm 5.59 \cdot 10^{-6}$	$3.47 \cdot 10^{-4} \pm 7.10 \cdot 10^{-6}$
m_2		$4.63 \cdot 10^{-13} \pm 3.61 \cdot 10^{-12}$	$1.59 \cdot 10^{-11} \pm 1.38 \cdot 10^{-11}$
m_3			$5.99 \cdot 10^{-18} \pm 5.78 \cdot 10^{-18}$
F	474455 $p < 0.001$	0.18 n.s.	0.29 n.s.

(*Continued on page 28*)

Table 1 (*Continued*)

Chloride (μM) (n = 28)

Cal.	Linear	Quadratic	Cubic
2.8	7.5 ± 1.1	4.0 ± 0.4	2.9 ± 0.2
5.6	9.6 ± 0.9	6.5 ± 0.4	5.6 ± 0.2
14.1	16.0 ± 0.6	14.2 ± 0.3	14.1 ± 0.4
28.2	27.1 ± 0.5	27.2 ± 0.5	28.2 ± 0.5
56.4	50.6 ± 1.3	54.1 ± 1.2	56.4 ± 0.3
141.0	132.9 ± 3.4	142.5 ± 0.7	141.03 ± 0.03
282.1	286.5 ± 1.5	281.8 ± 0.1	282.064 ± 0.002
r^2	0.9950 ± 0.0015	0.9996 ± 0.0003	0.999986 ± 0.0000009
s_y	7.22 ± 1.10	2.10 ± 0.69	0.45 ± 0.16
m_0	5.64 ± 0.63	1.84 ± 0.49	−0.38 ± 0.26
m_1	$1.62 \cdot 10^{-3} + 3.66 \cdot 10^{-5}$	$1.93 \cdot 10^{-3} + 6.41 \cdot 10^{-5}$	$2.18 \cdot 10^{-3} + 6.49 \cdot 10^{-5}$
m_2		$1.83 \cdot 10^{-9} + 4.52 \cdot 10^{-10}$	$-6.46 \cdot 10^{-9} + 1.55 \cdot 10^{-9}$
m_3			$1.88 \cdot 10^{-14} + 7.82 \cdot 10^{-15}$
F	1956 $p < 0.001$	57.2 $p < 0.01$	270 $p < 0.01$

Sulphate (μM) (n = 26)

Cal.	Linear	Quadratic	Cubic
5.2	13.4 ± 1.9	7.3 ± 0.6	5.3 ± 0.3
10.4	17.3 ± 1.6	11.9 ± 0.5	10.4 ± 0.2
26.0	29.3 ± 0.9	26.0 ± 0.3	25.9 ± 0.3
52.1	50.0 ± 0.8	50.1 ± 0.8	51.9 ± 0.8
104.1	94.1 ± 2.3	100.4 ± 1.4	104.2 ± 0.5
260.3	245.8 ± 4.8	262.7 ± 0.8	260.24 ± 0.06
520.5	528.5 ± 2.2	520.1 ± 0.1	520.520 ± 0.004
r^2	0.9954 ± 0.0013	0.99969 ± 0.00012	0.999988 ± 0.0000017
s_y	12.69 ± 1.81	3.60 ± 0.68	0.72 ± 0.37
m_0	10.02 ± 1.05	3.26 ± 0.48	0.82 ± 0.37
m_1	$8.11 \cdot 10^{-4} + 2.11 \cdot 10^{-5}$	$9.62 \cdot 10^{-4} + 1.77 \cdot 10^{-5}$	$1.07 \cdot 10^{-3} + 2.49 \cdot 10^{-5}$
m_2		$2.39 \cdot 10^{-10} + 4.02 \cdot 10^{-11}$	$-8.07 \cdot 10^{-10} + 1.31 \cdot 10^{-10}$
m_3			$6.26 \cdot 10^{-16} + 1.78 \cdot 10^{-16}$
F	2127 $p < 0.001$	64.6 $p < 0.01$	0.57 n.s.

Nitrate (μM) (n = 26)

Cal.	Linear	Quadratic	Cubic
7.1	12.2 ± 1.4	8.3 ± 0.8	7.3 ± 0.3
14.3	18.1 ± 1.2	14.9 ± 0.6	14.3 ± 0.3
35.7	36.3 ± 0.6	35.2 ± 0.4	35.6 ± 0.6
71.4	67.9 ± 1.3	69.9 ± 1.5	71.2 ± 1.2
107.1	101.4 ± 2.2	105.9 ± 1.9	107.3 ± 1.1
214.2	209.2 ± 3.6	216.0 ± 1.7	214.13 ± 0.22
357.0	361.6 ± 2.1	356.5 ± 0.4	356.978 ± 0.024
r^2	0.9967 ± 0.0014	0.99970 ± 0.00024	0.999958 ± 0.0000035
s_y	7.23 ± 1.50	2.23 ± 0.96	0.93 ± 0.41
m_0	6.63 ± 1.08	1.99 ± 0.89	0.47 ± 0.61
m_1	$1.79 \cdot 10^{-3} + 3.79 \cdot 10^{-5}$	$2.02 \cdot 10^{-3} \pm 5.92 \cdot 10^{-5}$	$2.17 \cdot 10^{-3} \pm 9.72 \cdot 10^{-5}$
m_2		$-1.19 \cdot 10^{-9} \pm 3.63 \cdot 10^{-10}$	$-3.38 \cdot 10^{-9} \pm 1.70 \cdot 10^{-9}$
m_3			$7.49 \cdot 10^{-15} + 6.50 \cdot 10^{-15}$
F	3705 $p < 0.001$	56.4 $p < 0.01$	248 n.s.

Ammonium (μM) (n = 27)

Cal.	Linear	Quadratic	Cubic
7.1	0.7 ± 0.6	6.5 ± 1.1	7.1 ± 0.7
14.3	10.3 ± 0.8	14.4 ± 0.5	14.4 ± 0.4
28.6	29.7 ± 1.1	29.0 ± 0.9	28.5 ± 1.4
57.1	64.5 ± 1.5	58.2 ± 2.2	57.6 ± 1.4
71.4	78.8 ± 1.9	71.3 ± 2.0	71.0 ± 1.7
142.8	146.6 ± 3.8	141.7 ± 3.7	142.8 ± 0.6
214.2	206.2 ± 2.6	214.5 ± 1.4	214.16 ± 0.15
r^2	0.9791 ± 0.0031	0.9990 ± 0.0012	0.99967 ± 0.00029
s_y	10.97 ± 0.83	2.26 ± 1.48	1.51 ± 0.77
m_0	12.65 ± 1.03	−1.62 ± 1.94	−0.05 ± 2.45
m_1	$1.43 \cdot 10^{-3} \pm 1.62 \cdot 10^{-5}$	$9.43 \cdot 10^{-4} \pm 9.42 \cdot 10^{-5}$	$8.18 \cdot 10^{-4} \pm 2.50 \cdot 10^{-4}$
m_2		$3.07 \cdot 10^{-9} + 5.62 \cdot 10^{-10}$	$5.11 \cdot 10^{-9} + 5.03 \cdot 10^{-9}$
m_3			$-8.46 \cdot 10^{-15} + 2.32 \cdot 10^{-14}$
F	645 $p < 0.001$	312 $p < 0.01$	0.61 n.s.

r^2 = Correlation coefficient squared; s_y = standard error; m_i = regression coefficient of ith order; F = F ratio and significance level (p) for the introduction into the model of the higher degree term (see text); n.s. = Not significant.

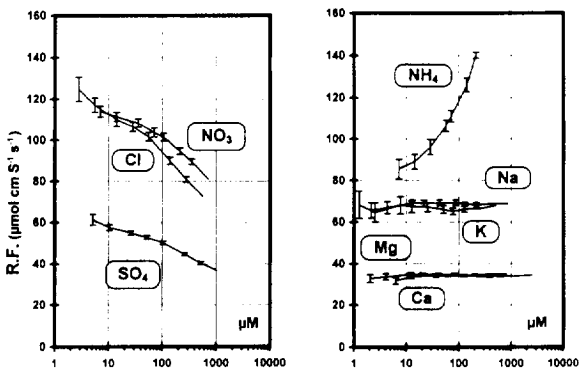

Fig. 4. Response factors in relation to concentrations. Bars indicate S.D.s obtained from 24–150 measurements.

the many aspects related to instrument calibration, this paper highlights the importance of the type of regression and frequency of calibration used. The results show that multi-point (6–8 concentrations), non-linear regression permits a correct quantification over a wide range of concentrations of anions and cations. Because of the repeatability of the measurements of peak areas for calibration solutions, two calibrations, at the beginning and end of the batch of 20–30 samples, are adequate. These conditions give better results than calibrations performed with 2–3 points and repeated every 8–10 samples.

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