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Precision of ion chromatographic analyses compared with that of other analytical techniques through intercomparison exercises

Aldo Marchetto[a], Rosario Mosello[a,*] Gabriele A. Tartari[a], Herbert Muntau[b], Michele Bianchi[b], Helga Geiss[b], Giorgio Serrini[b], Gianna Serrini Lanza[b]

[a]*CNR Istituto Italiano di Idrobiologia, I-28048 Verbania Pallanza, Italy*

[b]*JRC Environmental Institute, Ispra (VA), Italy*

Abstract

Three intercomparison exercises on simulated rainwater were held in 1991–1993 involving 72–98 laboratories in Europe and South America. Ion chromatography was used for the determination of anions (chloride, nitrate and sulphate) by 59–72% of the participating laboratories and for the determination of cations (Na, K, Mg and Ca) by 14–22% of them. The concentration of the single ions ranged between 5 and 150 μmol l^{-1}. The results were used to evaluate the precision of the method, and showed that it was comparable to that of spectrophotometric methods. For ammonium ion, ion chromatography was used by only 4–14% of the laboratories and the results depended on the calibration technique adopted. A general improvement in precision was observed in the course of the exercises.

1. Introduction

The authors have been involved since 1984 in intercomparison exercises for inorganic ions, in the framework of limnological research in Italy [1] and the Italian network for the study of atmospheric deposition chemistry (RIDEP) [2]. Since 1991, intercomparison exercises have been carried out every year, involving laboratories participating in, besides RIDEP, also the EEC projects "AQUACON–MedBas" and "AL:PE, acidification of mountain lakes: paleolimnology and ecology", or working with the International Commission for the Protection of Lake Leman, or requesting participation, such as laboratories in South America and in the former Eastern Europe. The number of participating laboratories was 72 in 1991, 78 in 1992 and 99 in 1993. Full data and the list of participating laboratories have been published elsewhere [3–5].

The aim of the work described in this paper was to obtain general information on the precision of ion chromatography (IC), one of the methods most widely used by the participating laboratories for the determination of inorganic ions (Table 1). The exercises and the range of application of the results are aimed at the analysis of freshwater and atmospheric deposition.

2. Experimental

For each exercise, two solutions were prepared starting from water of the highest quality

* Corresponding author.

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Table 1
Number of laboratories participating in the three intercomparison exercises and percentage of laboratories using ion chromatography for the determination of each ion

Exercise	1991	1992	1993
No. of participating laboratories	72	77	99
Ion	Laboratories using IC (%)		
Anions			
Cl^-	72	68	64
NO_3^-	69	66	59
SO_4^{2-}	72	73	65
Cations			
Na^+	14	23	22
NH_4^+	4	14	14
K^+	15	22	21
Mg^{2+}	15	21	21
Ca^{2+}	15	21	21

(Nanopure UWS, Barnstead) and the purest chemicals available. The carefully weighed chemicals were dissolved and water was added to prepare a stock standard solution (1 l), which was then checked analytically for correctness of the envisaged analyte concentrations. The stock standard solution was added to approximately 20 l of Nanopure water in a 50-l polyethylene container, previously conditioned with the same quality of water for 2 weeks. The calculated amount of Suprapur HCl required to reach the previously fixed pH value of the final solution was added and the solution was made up to a total of 50 l. The solution was mixed by rolling the container. Bottling was performed by hand, rinsing the previously conditioned 0.5-l polypropylene bottles (2 weeks with Nanopure water) with the samples and then filling them up to the top.

Samples were sent to the participating laboratories by mail, and the stability of the samples was checked by analysing samples kept in the dark at room temperature over the period allowed for the exercise [3–5]. Participating laboratories were only requested to perform a single analysis for each sample.

Target values were calculated as the mean of the values obtained by the organizing laboratories, using IC for anions, the salicylate spectrophotometric method for ammonium and atomic absorption spectrometry for the other cations.

3. Data analysis

3.1. Sample homogeneity

The total variance measured at the JRC laboratory on ten randomly selected samples (representing about 3% of the whole population) is assumed to be equal to the sum of the variances resulting from the analytical method used, the non-homogeneity of the samples and other random errors:

$$(\mathrm{S.D.}_{\mathrm{tot}})^2 = (\mathrm{S.D.}_{\mathrm{method}})^2 + (\mathrm{S.D.}_{\mathrm{heterog.}})^2 + (\mathrm{S.D.}_{\mathrm{random}})^2$$

The variance due to the analytical method for each ion was estimated by repeating the measurement ten times on the same bottle of each sample. All the measurements were performed in one laboratory by the same analyst using the same analytical method for each variable. Heterogeneity of the variables in the solutions was then estimated as the square root of the difference of the squares of the standard deviations of samples and methods.

3.2. Outlier detection

In intercomparison exercises it often happens that some laboratories obtain results which stand out from the rest, either because of some error in calibration, or unreliable laboratory practice, mistakes in recording the results, contamination of the samples or of the standard solutions used for calibration, and so on. The effect of these outliers is to increase the estimate of the variance of the results, which would then show a wide deviation from the normal distribution. For these reasons, it is common practice to discard outliers before statistical treatment of the data. In this paper, outlier rejection was performed by excluding data out of the range of ±50% of the

Table 2
Selected statistical parameters of the values obtained using ion chromatography for each ion and sample

Ion	Parameter	Sample					
		1991A	1992A	1993A	1991B	1992B	1993B
Sulphate	No. of data	52	56	64	52	57	66
	Target concentration (μM)	24.6	27.1	36.1	121.3	124.9	150.9
	Heterogeneity (%)	0.4	0.5	0.8	0.6	0.5	0.4
	Parametric estimate of R.S.D. (%)	8.6	6.9	12.2	8.3	8.4	10.7
	Robust estimate of R.S.D. (%)	6.5	6.1	5.0	6.4	6.2	4.3
	No. of outliers	1	1	3	1	1	3
	R.S.D. after outliers rejection (%)	7.6	6.0	6.6	6.6	7.1	4.9
Nitrate	No. of data	50	51	58	50	52	61
	Target concentration (μM)	7.9	9.3	8.6	56.4	74.3	69.3
	Heterogeneity (%)	0.5	0.3	0.5	0.6	0.1	0.7
	Parametric estimate of R.S.D. (%)	67.6	42.8	11.2	63.4	17.5	36.6
	Robust estimate of R.S.D. (%)	17.5	16.7	9.7	7.7	4.2	4.0
	No. of outliers	7	4	0	5	4	2
	R.S.D. after outliers rejection (%)	14.2	14.9	11.2	7.7	4.4	5.7
Chloride	No. of data	52	52	63	52	56	65
	Target concentration (μM)	5.1	4.5	24.5	57.5	33.6	53.9
	Heterogeneity (%)	1.4	1.4	0.3	1.1	0.6	0.2
	Parametric estimate of R.S.D. (%)	221.8	59.5	21.0	53.9	18.8	12.6
	Robust estimate of R.S.D. (%)	45.9	16.7	12.3	11.3	10.3	8.9
	No. of outliers	16	11	2	3	2	1
	R.S.D. after outliers rejection (%)	21.7	21.5	15.3	15.2	11.2	11.2
Sodium	No. of data	10	18	22	10	18	24
	Target concentration (μM)	7.4	8.7	7.4	52.2	64.3	30.4
	Heterogeneity (%)	1.4	1.5	1.4	0.5	0.2	0.6
	Parametric estimate of R.S.D. (%)	65.0	114.1	22.5	25.4	18.6	28.0
	Robust estimate of R.S.D. (%)	38.5	26.2	16.3	25.4	6.8	13.8
	No. of outliers	2	2	2	0	0	1
	R.S.D. after outliers rejection (%)	24.0	21.9	14.9	25.4	18.6	13.6
Ammonium	No. of data	3	11	14	3	11	15
	Target concentration (μM)	22.9	27.1	27.1	90.0	83.6	100.0
	Heterogeneity (%)	1.3	1.1	0.8	0.6	0.4	0.1
	Parametric estimate of R.S.D. (%)	103.5	55.5	50.3	69.2	24.8	18.3
	Robust estimate of R.S.D. (%)	103.3	48.2	16.8	69.1	12.7	14.5
	No. of outliers	2	4	1	1	1	0
	R.S.D. after outliers rejection (%)		15.5	14.8	4.6	14.4	18.3
Potassium	No. of data	11	17	21	10	17	24
	Target concentration (μM)	5.9	7.4	5.1	8.2	11.0	11.5
	Heterogeneity (%)	1.5	1.2	1.3	1.4	0.6	0.5
	Parametric estimate of R.S.D. (%)	187.2	31.8	81.0	40.1	43.5	29.6
	Robust estimate of R.S.D. (%)	69.6	31.5	8.2	35.2	19.0	10.8
	No. of outliers	4	2	1	3	3	1
	R.S.D. after outliers rejection (%)	15.0	22.7	7.2	12.9	12.7	11.3

(*Continued on page 16*)

Table 2 (*continued*)

Ion	Parameter	Sample					
		1991A	1992A	1993A	1991B	1992B	1993B
Magnesium	No. of data	11	16	21	11	17	23
	Target concentration (μM)	4.1	4.1	5.8	8.6	13.2	14.0
	Heterogeneity (%)	0.4	0.4	0.4	0.5	0.5	0.4
	Parametric estimate of R.S.D. (%)	56.0	27.0	32.8	38.1	137.8	36.6
	Robust estimate of R.S.D. (%)	23.8	17.1	10.6	18.4	13.9	8.9
	No. of outliers	2	1	1	2	1	1
	R.S.D. after outliers rejection (%)	15.6	17.0	12.7	12.6	13.3	13.9
Calcium	No. of data	11	16	21	11	17	23
	Target concentration (μM)	5.2	5.0	9.0	20.2	31.4	26.9
	Heterogeneity (%)	1.0	1.1	1.1	0.6	0.1	0.3
	Parametric estimate of R.S.D. (%)	68.0	32.1	15.3	38.4	14.4	20.4
	Robust estimate of R.S.D. (%)	49.8	26.3	10.6	30.5	9.6	11.7
	No. of outliers	5	1	0	1	0	1
	R.S.D. after outliers rejection (%)	29.2	22.7	15.3	25.1	14.4	13.6

expected values. The mean and standard deviation of the remaining results were then calculated and values out of the range of ±3 S.D. iteratively excluded [6].

3.3. Robust estimate of the S.D.

Outlier rejection is not correct practice when included in the evaluation and comparison of the

Table 3
Summary of the results of the *F*-test to compare the variance obtained using ion chromatography and that obtained using more common concurrent methods

Ion	Method[a]	Sample[b]					
		1991A	1991B	1992A	1992B	1993A	1993B
Chloride	MAS	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
Nitrate	MAS	n.s.	n.s.	n.s.	n.s.	S	S
Sulphate	Turb.	S	S	S	S	S	S
Sodium	AAS	L	n.s.	n.s.	n.s.	n.s.	n.s.
	AES	L	n.s.	n.s.	S	S	n.s.
Ammonium	MAS: Nessler	n.s.	n.s.	n.s.	S	n.s.	n.s.
	MAS: indophenol	L	L	L	L	L	L
Potassium	AAS	L	n.s.	n.s.	L	n.s.	n.s.
	ICP	n.s.	n.s.	n.s.	L	S	n.s.
Magnesium	AAS	L	L	L	L	n.s.	n.s.
	ICP	L	L	L	L	n.s.	n.s.
Calcium	AAS	L	n.s.	n.s.	n.s.	S	n.s.
	ICP	L	n.s.	n.s.	n.s.	n.s.	n.s.

[a] AAS = atomic absorption spectrometry; AES = atomic emission spectrometry; ICP = inductively coupled plasma spectrometry; MAS = molecular absorption spectrometry; Turb = turbidimetry.

[b] L, variance of ion chromatography significantly ($p < 0.01$) larger than that of concurrent method; S, variance of ion chromatography significantly ($p < 0.01$) smaller than that of concurrent method; n.s., no significant difference.

precision of analytical methods, as it can produce a smaller S.D. for methods producing a larger number of outliers. An alternative approach is robust statistics (e.g., Ref. [7]), which shifts from outliers rejection to outlier accommodation: extreme values are downweighted and that downweighting is compensated for. In this paper we used the iterative technique known as H15, assuming a value of 1.5 for the constant c [8].

The procedure begins by assigning to the estimated robust mean (m_0) the median of the sample values (x_i) and to the estimated robust S.D. (s_0) the median absolute deviation (MAD), that is the median of the quantities ($|x_i - m_0|$)/0.6745. Then, at each nth iteration, all values higher than $m_{n-1} + cs_{n-1}$ or lower than $m_{n-1} - cs_{n-1}$ are replaced by the pseudo-values $m_{n-1} + cs_{n-1}$ and $m_{n-1} - cs_{n-1}$, respectively, while the pseudo-values for the remaining values are the values themselves. The new estimate of the robust mean m_n will be the mean of the pseudo-values, while the new estimate of the robust S.D. (s_n) will be their S.D. divided by the square root of the constant β, which compensates for the downweighting of the extreme values. At $c = 1.5$, $\beta = 0.736$ [8]. The estimated parameters rapidly converge to the robust mean and S.D.

4. Results

The results for the three intercomparison exercises are summarized in Table 2. For all the ions, the number of laboratories using IC increased during the period of the exercises.

As expected, for more dilute solutions, higher RSDs were observed. The contribution of sample heterogeneity to the final data dispersion was not significant in all instances.

As the first exercises contributed to stimulating the analysts to solve technical problems and improve laboratory practice, the dispersion of the values and the number of outliers generally decreased from the first to the last exercise. Apart from ammonium, the robust S.D. obtained for the last exercise can be considered to be a good estimate of the precision of the method. However, in the case of ammonium, the number of laboratories using IC was too small for such an estimate.

5. Discussion

The relative performance of IC compared with the more widely used concurrent methods was evaluated by comparing the robust estimates of the averages and variances by means of Student's t- and the F-tests. No significant difference was obtained for the means, whereas for the vari-

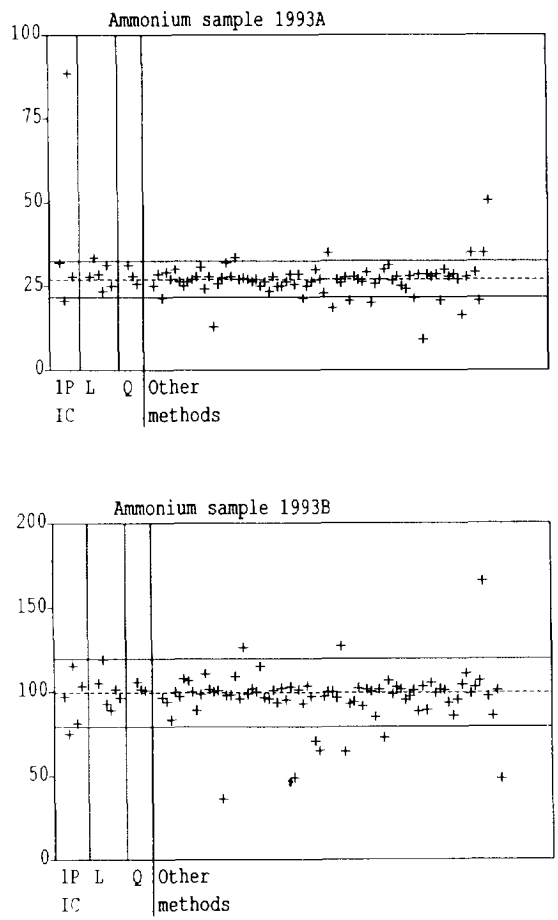

Fig. 1. Distribution plot of the values obtained for ammonium using ion chromatography and other methods in the third intercomparison exercise. Note the different dispersion of the values obtained using different calibration techniques (1P = single point; L = multi-point linear; Q = multi-point quadratic). Units: μmol l^{-1}.

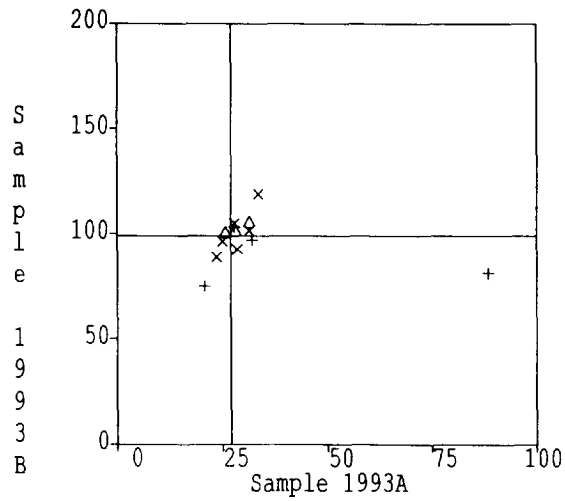

Fig. 2. Youden plot of the values obtained in the third intercomparison exercise for ammonium using ion chromatography and different calibration techniques (+ = single point; × = multi-point linear; △ = multi-point quadratic). Units: μmol l^{-1}.

ances the results of the tests were as summarized in Table 3.

From the first to the last exercise, as the analysts' practice improved, the precision of the chromatographic method increased. In the last exercise, IC performed better than turbidimetric and spectrophotometric methods for sulphate and chloride, respectively, whereas for metals, the differences with respect to the common spectrophotometric methods were not generally significant. It seems that, at low levels, IC would perform better than atomic emission spectrometry for Na and K and than atomic absorption spectrometry for Ca. For ammonium, the dispersion of the values obtained by IC is significantly higher than that of values obtained by molecular absorption spectrometry. As the detector did not show a linear response for ammonium in this range of concentration (e.g., [9]), the results were divided on the basis of the calibration technique used (Fig. 1). The exercise for ammonium focused on such low concentration levels as are typically encountered during monitoring. Although the number of the data is too small for a statistical comparison, it is evident that values obtained using multi-point quadratic calibration have a smaller dispersion around the target values.

The Youden plot [10] presented in Fig. 2 shows the scatter of the data relative to both samples, analysed by each laboratory using IC. It allows for the distinction between random and systematic errors: if analyses were only affected by random errors, the results would be spread over the whole diagram. In this case, the results obtained by multi-point linear calibration are mainly located along the line passing through the origin and the expected values. This clearly shows the presence of systematic errors which underestimate or overestimate the concentration in both samples. Values obtained with single-point calibration generally stand out from the rest, and the better performance of multi-point quadratic calibration is also evident.

6. Conclusions

The importance of repeated intercomparison exercises for rainwater analysis, aimed at better performance from an analytical method, finds further confirmation in the case of IC. From the first to the third exercise the dispersion of the data decreased. The values obtained in the last exercise, apart from those for ammonium, can be used to estimate the precision of the method: the R.S.D. ranges from 4–5% for sulphate (24–151 μmol l^{-1}) to 13–16% for sodium (7.4–64 μmol l^{-1}), depending on the sample concentration. For ammonium (23–100 μmol^{-1}), the number of laboratories using IC was too small for such an estimate, but it was clear that the tendency for systematic errors is related to an unreliable calibration technique; multi-point non-linear calibration at very low concentration is required.

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