

Evaluation of a Brazilian ion chromatography interlaboratory study

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Received: 2 August 2012 / Accepted: 2 May 2013
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Abstract This paper describes a Brazilian interlaboratory program study on anion measurement in synthetic water. The program described is promoted regularly since 2007 and recommended the use of ion chromatography as analytical technique for all participant laboratories. Two samples (X and Y) with different anion (fluoride, chloride, nitrite-N, nitrate-N, sulfate and phosphate-P) concentration levels were twice distributed in 2011. Each sample on each round had the homogeneity, and the stability tested for a period of 15 days. Upon ensuring the homogeneity and stability, the samples were distributed to 39 laboratories located around the country. The aim of this study was to verify the laboratories' precision and to establish the measurement comparability among Brazilian laboratories that routinely use ion chromatography for water sample

analysis. It was also possible to identify the most frequent sources of systematic and random errors for each measured anion, related to the ion chromatography technique. Some specific metrological issues related to the geographical region are discussed.

Keywords Proficiency test · Ion chromatography · Brazilian metrological activities · Anion measurement

Introduction

An interlaboratory study intends to support the evaluation of the individual performance of each participant laboratory by studying the group precision, systematic errors or any particular limitation of the applied technique [1]. Proficiency tests (PTs) with a significant number of ion chromatography (IC) participants started in Europe in 1991 [2]. At that time, IC was already the most frequently used technique for anion determination. Only one decade later, a similar situation occurred in Brazil. Up to 2007, Rede Metrologica do Rio Grande do Sul offered an environmental PT for water and wastewater samples where several metals, anions and physicochemical parameters were included. No specific technique was recommended for any individual parameter in these previous programs. Significant operational differences related mainly to the anion measurement precision, working range and detection limit were observed by the authors when no specific analytical technique was used [3]. A similar observation was done by Marchetto et al. [4], comparing turbidimetric and spectrophotometric methods for chloride and sulfate measurements.

The Rede Metrologica do Rio Grande do Sul was requested to organize a specific program for anion

Presented at BERM-13, June 2012, Vienna, Austria.

Electronic supplementary material The online version of this article (doi:10.1007/s00769-013-0987-6) contains supplementary material, which is available to authorized users.

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measurements by ion chromatography in 2007. The pilot program dedicated to ion chromatography was launched in Brazil in that year [5]. The present paper discusses the results obtained in the 5-year program offered with the design dedicated to IC in Brazil. The usual precision associated with this technique and some operational failures that may impact an anion measurement will be discussed. Some corrective actions to help users to identify the most common source of systematic and random errors in IC applications will also be highlighted.

Setup of the program

PT organizers

Rede Metrologica do Rio Grande do Sul is one of the main interlaboratory providers in Brazil being certified by IN-METRO [6] since 2011 and has been listed in EPTIS (European Proficiency Testing Information System) [7] since 2006. The technical support to prepare, store and perform the stability and homogeneity tests came from the water supply company of the Rio Grande do Sul, CORSAN. The technical IC aspects observed in the PT were more recently evaluated by Ipen-CNEN/SP, one of the very first laboratories to use this technique in Brazil, with almost 30 years of IC experience. The personnel in charge of the fifth yearly version of the dedicated IC program were the same involved in all the previous editions.

Program general instructions

Each laboratory received by e-mail its confidential code, login and password that was later changed by the laboratory personal. That information was printed, folded, arranged randomly and then placed within the envelope already addressed to the laboratories to preserve confidentiality. No person in charge of that activity accessed the individual laboratory code during the program. The Rede Metrologica do Rio Grande do Sul's [8] Web site has a link that each laboratory could access to report the results. The program recommendation was that all participant laboratories had to apply ion chromatography as the analytical technique for fluoride, chloride, nitrite-N, nitrate-N, sulfate and phosphate-P determination. No particular manufacturer or operational conditions (such as column specifications, loop volume, detector, eluent type, concentration and suppressor) were recommended, nor were any of these data requested from users in order to assure confidentiality. Some laboratories informed about the dilution factor, specific assay date, official ion chromatography method or column used. None of that information could be used to identify the participants.

Sample preparation

The sample preparation was conducted under Rede Metrologica do Rio Grande do Sul responsibility at CORSAN Laboratory (Rio Grande do Sul States water supply company). All water samples were synthetically prepared by CORSAN with Specsol analytical grade inorganic standard solutions using NIST standard reference materials for calibration and direct comparison. The PT samples were homogenized, bottled and labeled under controlled conditions, according to ISO Guide 34 [9].

Table 1 shows the prepared concentrations and the expanded uncertainty values ($k = 2$) of the preparation. A spreadsheet with the first-round fluoride concentration planning and preparation, as well as the combined and expanded uncertainty calculations and standard uncertainty values, is available in the electronic supplementary material.

The Guide to the Expression of Uncertainty in Measurement (GUM) [10] was followed in order to calculate the uncertainty, and the procedures and spreadsheets provided by Konieczka et al. [1] were also applied.

Program schedule

Two samples (X and Y) containing six anions, fluoride, chloride, nitrite-N, nitrate-N, sulfate and phosphate-P, were distributed to 39 subscribed laboratories twice in 2011. The results were accepted on the RMRS Web site [8] up to 15 days after the samples were received. An e-mail was issued to all laboratories on the 14th day informing the laboratories that had not yet reported results. The laboratory was no longer able to access the result reporting area after the deadline. The individual report was sent to all laboratories with chemical and statistical evaluation before the second round in order to provide a tool for laboratory performance evaluation by its technical manager and analysts. This procedure was adopted to implement the corrective actions before laboratories received the second round of samples.

Assigned value, uncertainty u and $\hat{\sigma}$

The consensus values calculated from participants' results using the algorithm A in the Annex C of ISO/IEC 13528 [11] were used as assigned values and their standard uncertainties. This algorithm was also used to calculate the standard deviation for proficiency assessment ($\hat{\sigma}$) that derived from the results reported by all participants. The assigned values were compared with nominal concentrations in order to evaluate whether the consensus value was biased or not. Each anion concentration value and its uncertainty used as nominal value were calculated from the preparation plan following the GUM [10].

Table 1 Brazilian ion chromatography PT summary with concentration nominal and consensus values along with the standard deviation (*SD*), relative standard deviation (*SD*_{Rel}) and the number oflaboratories with satisfactory, questionable, unsatisfactory, underestimated, overestimated results and with individual *CV* higher than 5 %, in both rounds, to six measured anions

Anion	Round	Sample	Concentration (mg L ⁻¹)				Number of laboratories						
			Nominal value	Consensus value	<i>SD</i>	<i>SD</i> _{Rel} (%)	z ≤ 2	2 < z < 3	z ≥ 3	z ≥ 2	z ≤ -2	CV ≥ 5 %	
F ⁻	1	X	1.20 ± 0.03	1.20 ± 0.05	0.11	9.2	29	4	1	2	3	7	
		Y	0.74 ± 0.03	0.72 ± 0.03	0.07	10	26	2	4	5	1	3	
	2	X	0.33 ± 0.03	0.34 ± 0.02	0.05	15	30	3	1	1	3	4	
		Y	1.00 ± 0.03	1.08 ± 0.04	0.10	9.3	32	2	0	1	1	3	
	Cl ⁻	1	X	5.03 ± 0.06	4.82 ± 0.13	0.32	6.6	29	0	7	3	4	4
			Y	30.2 ± 0.3	31.93 ± 0.52	1.23	3.9	30	1	4	4	1	3
2		X	1.95 ± 0.03	1.90 ± 0.07	0.16	8.4	31	1	3	1	3	4	
		Y	20.1 ± 0.2	19.7 ± 0.5	1.1	5.6	31	1	3	1	3	3	
NO ₂ ⁻ as N		1	X	0.99 ± 0.01	1.00 ± 0.04	0.08	8.0	29	2	2	4	0	2
			Y	0.34 ± 0.01	0.31 ± 0.02	0.05	16	30	1	1	1	1	6
	2	X	0.34 ± 0.01	0.33 ± 0.01	0.03	9	29	1	1	1	1	1	
		Y	0.51 ± 0.01	0.50 ± 0.03	0.06	12	28	1	2	3	0	2	
	NO ₃ ⁻ as N	1	X	5.99 ± 0.07	6.02 ± 0.12	0.28	4.7	27	1	7	7	1	0
			Y	0.90 ± 0.01	0.90 ± 0.04	0.08	9	28	1	5	5	1	0
2		X	0.50 ± 0.01	0.50 ± 0.02	0.05	10	29	3	2	3	2	2	
		Y	3.99 ± 0.04	3.99 ± 0.06	0.14	3.5	23	4	5	5	4	1	
SO ₄ ²⁻		1	X	3.00 ± 0.06	2.89 ± 0.10	0.23	8.0	26	1	6	3	4	5
			Y	30.0 ± 0.3	30.1 ± 0.8	1.8	6.0	26	1	6	5	2	1
	2	X	5.00 ± 0.06	4.84 ± 0.15	0.37	7.6	30	0	5	2	3	2	
		Y	40.0 ± 0.5	40.5 ± 1.1	2.6	6.4	30	2	2	1	3	1	
	H ₂ PO ₄ ⁻ as P	1	X	1.01 ± 0.02	0.83 ± 0.04	0.09	11	26	0	4	2	2	2
			Y	0.35 ± 0.01	0.33 ± 0.02	0.05	15	23	1	4	3	2	4
2		X	0.50 ± 0.01	0.49 ± 0.05	0.11	22	25	1	2	2	1	3	
		Y	1.51 ± 0.02	1.44 ± 0.11	0.24	17	24	2	3	3	2	3	

±*U* refers to nominal value, median ± *U* refers to consensus value

Homogeneity and stability studies

Samples were investigated in accordance with ISO/IEC 13528 [11] to evaluate the sample variability that could be caused by limited homogeneity or stability. Anion concentrations were measured in 10 randomly selected bottles from X and Y samples to evaluate whether that variability was significant or not among the total variability. The average concentration and the between-sample standard deviation (*S_s*) were calculated. *S_s* was compared with the standard deviation of the PT assessment ($\hat{\sigma}$). As per ISO/IEC 13528 [11] Annex B, the sample was considered adequately homogeneous if

$$s_s \leq 0.3 \hat{\sigma}$$

Three randomly selected bottles from the previous group of 10 bottles were analyzed in order to assess the stability test average over a period of 15 days. Also in accordance with ISO/IEC 13528 [11] Annex B, the stability criterion evaluated the concentration average (\bar{x}) and the stability

test average (\bar{y}). The samples were considered adequately stable if

$$|\bar{x} - \bar{y}| \leq 0.3 \hat{\sigma}$$

Interlaboratory study statistical and performance evaluation

The present PT was organized according to ISO/IEC 17043 [12], while the data were evaluated according to ISO/IEC 13528 [11] algorithm A of Annex C. The robust statistical evaluation was applied to each anion measurement. The consensus value was adopted and then compared with the nominal concentration. The laboratory *z*-score was calculated for each measurand as recommended by ISO/IEC 13528 [11]. Outliers were identified by computing a *z*-score based on the mean and the standard deviation (*SD*) of the laboratory averages. The criterion was that the absolute value of the *z*-score should not exceed 2, at a confidence level of 95 %.

Each laboratory was assigned to report three measurement values for each anion, and with these values, the

individual and the group coefficient of variation (*CV*) were calculated. Any laboratory that stated to use different analytical procedures than ion chromatography had its results excluded from the robust average and robust standard deviation calculations. Each laboratory performance was evaluated in accordance with the *z*-score criteria, as follows:

If $ z \leq 2$	Satisfactory result
$2 < z < 3$	Questionable result
$ z \geq 3$	Unsatisfactory result

Other evaluation criterion

A precision better than 5 % in the mg L^{-1} concentration range [2] is common to be obtained in IC measurements. The major manufacturers mention in their operation qualification procedures [13] that in a 10 injection sequence of the same solution, in that concentration range, a precision better than 1 % is obtained. Larger *CV* values indicate that the system may have a malfunction. So a *CV* larger than 5 % was adopted as an indicator of a possible malfunction or a warning sign.

Also, the PT evaluation intended to guide the IC user to solve the causes of questionable or unsatisfactory results. The authors have noticed that the simple *z*-score value observation was not enough to explain the error source. By that way, other criteria were applied where no discrimination was done between the probable causes of questionable ($2 < |z| < 3$) and unsatisfactory ($|z| \geq 3$) results. The second performance criterion was to evaluate questionable and unsatisfactory results if the *z*-score is higher than 2 over estimated concentration results or if *z*-score is smaller than -2 underestimated it. This criterion was also adopted to identify the error sources per measured anion.

The evaluation of random or systematic errors was performed by correlating results from samples X and Y. A group of experienced users commented the most probable causes of deviating results for each anion based on these criteria.

Results and discussion

Homogeneity and stability

The homogeneity test average considering the X sample to nitrite-N was 0.97 mg L^{-1} with the *SD* between samples of 0.01 mg L^{-1} and the *SD* within samples of 0.03 mg L^{-1} in the first round. The group robust standard deviation was 0.08 mg L^{-1} . So the stability criterion was achieved, and the samples were considered homogeneous. The nitrite-N average measured 15 days later was 0.94 mg L^{-1} , and the

difference between these two averages was larger than the stability criteria. So the sample was considered unstable what is frequently observed for nitrogen and phosphorous species solutions [14]. Similar results were observed for nitrite-N results of Y sample in the first round and with both X and Y samples in the second round. The stability component of the uncertainty was applied to the nitrite-N robust group deviation in order to evaluate the laboratories' performances. X and Y samples for other anions were considered stable in both rounds.

Brazilian proficiency test evaluation

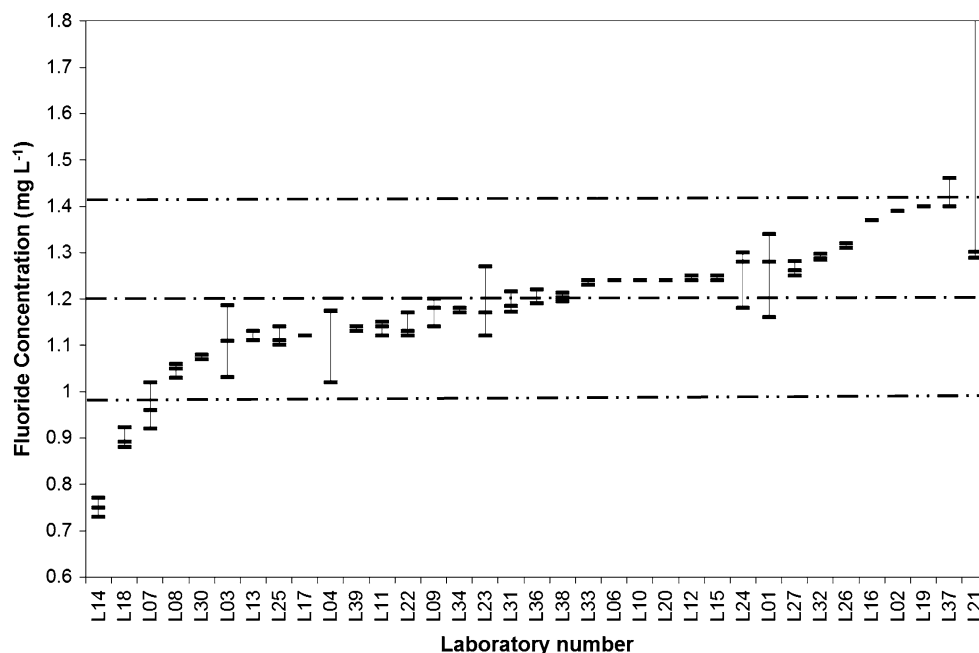
The assigned value was obtained by consensus means and compared with the nominal content, and the conclusion was that the assigned value was not biased for most anions (Table 1). Assigned value and consensus means did not agree for chloride (Y sample) and phosphate-P (X sample) results, both in the first round (see bold values in Table 1).

Group *CV* values varied from 3.85 % for chloride at $(31.93 \pm 0.52) \text{ mg L}^{-1}$ (median $\pm U$, $k = 2$) up to 17.10 % for nitrite-N at $(0.31 \pm 0.02) \text{ mg L}^{-1}$, in the first round. Similar values were observed in the second round, with a *CV* of 3.63 % for nitrate-N at $(3.99 \pm 0.06) \text{ mg L}^{-1}$ up to 21.99 % for phosphate-P at $(0.49 \pm 0.05) \text{ mg L}^{-1}$. Also, these values of *CV* and *U* presented in Table 1 were similar to other ion chromatography PTs in Europe and compatible with the performance of industrialized countries [15]. Considering the group *CV* and *U* values, the ion chromatography PT was considered satisfactory.

The number of laboratories that had satisfactory, questionable and unsatisfactory results, respectively, as well as the number of laboratories that over- ($z \geq 2$) or underestimated ($z \leq -2$) the consensus value is presented in Table 1. The percentage of unsatisfactory results varied from 3 to 20 % in the first round, and from 0 to 16 % in the second round, with fewer laboratories reporting unsatisfactory results in the second round. The percentage of questionable results varied from 0 % observed for chloride, sulfate and phosphate-P to 13 % observed for nitrate-N. Also, there was a reduction in the number of the laboratories that reported questionable results for fluoride, nitrite-N and sulfate and an increase for chloride, nitrate-N and phosphate-P.

The number of laboratories that had $CV \geq 5\%$ is presented in Table 1. Figure 1 shows three fluoride values reported for each laboratory in the first round. In Fig. 1, at least six laboratories exhibit large *CV* while most of the laboratories present *CV* that agrees with major manufacturer's specification [13]. Usually, a *CV*-based lack of performance is related to some operational failure of the IC system, because a repeatability performance better than 1 % is achieved in many commercial systems. A

Fig. 1 Fluoride reported values per laboratory (first round, X sample). -●- Consensus value, -••- satisfactory results limits



correlation was observed between few laboratories that presented questionable or unsatisfactory results and also presented a *CV* larger than 5 %. Laboratories that presented at least one anion measurement with a *CV* larger than 5 % (Fig. 1) also had at least one questionable or unsatisfactory result. Few laboratories presented more than one questionable or unsatisfactory result. If a laboratory had *CV* values larger than 5 %, in the mg L^{-1} concentration range, it was recommended to users to perform a system maintenance, to double check the environmental conditions (water, flask, auto sampler vials, etc.) and even in the event of a persistent fail, to replace the equipment.

The first round of results was reported to all laboratories before the samples of the second round were shipped. This was intentional to help laboratories with questionable or unsatisfactory results to perform the result evaluation and to correct the possible causes of error. It can be assumed that some recommendations presented in the first-round report were useful to help laboratories to identify analytical problems. Considering the number of laboratories that had satisfactory results in the first round (see fluoride results in Fig. 2) and presented questionable results in the second round (see fluoride results in Fig. 3), it is clear that their systems were not under internal quality control and presented performance degradation. Users must be aware that good results rely on continuous user surveillance by internal quality control to check the IC performance. Only the implementation of internal quality control actions [1] such as control charts will assure good operational conditions continuously and not only in specific events. So, a PT can and will identify operational problems, but continuous

internal quality control actions must be implemented to avoid any performance degradation.

The last scenario corresponds to those laboratories with questionable and unsatisfactory results in both rounds. For those who tried to solve the problems identified in the first round and failed in the second round, the best action could be to contact the instrument manufacturer to perform a system re-qualification and, if required, a user retraining. That could be followed by quality control implementation and training.

Standard and expanded uncertainty evaluation

The preparation uncertainty (u) and the expanded uncertainty (U) [10, 16, 17] were calculated considering the uncertainty contributions in the standard solution preparation by simple dilution. The uncertainty calculation used the contributions of pipette and tank volumes, temperature, repeatability ($n = 10$) and standard concentration uncertainties (see supplementary material). Stability and homogeneity uncertainty components were also combined. The assigned value and its uncertainty were calculated as described item 5.6 of ISO/IEC 13528 [11]. No further components were considered in the present PT uncertainty budget. However, when for the present IC PT, the uncertainties for nitrate-N measurement results are compared with those from similar instruments, procedures and concentration range by IC, in a much more detailed uncertainty budget calculation [16] performed in accordance with EN/ISO 10304-1 [18], u and U seem to be in accordance with each other. As pointed out by Tomić et al. [16] for high-

Fig. 2 z-Score for each laboratory considering fluoride results (first round, X sample)

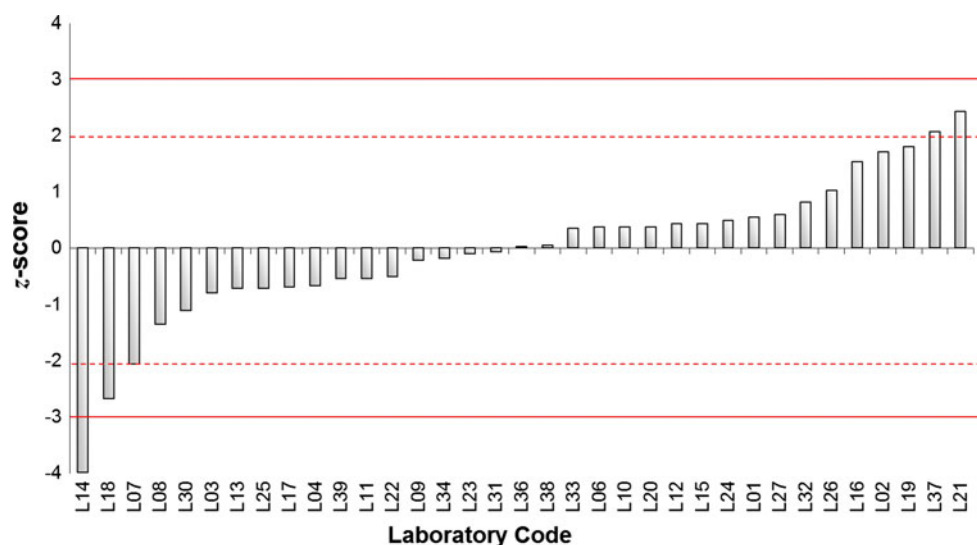
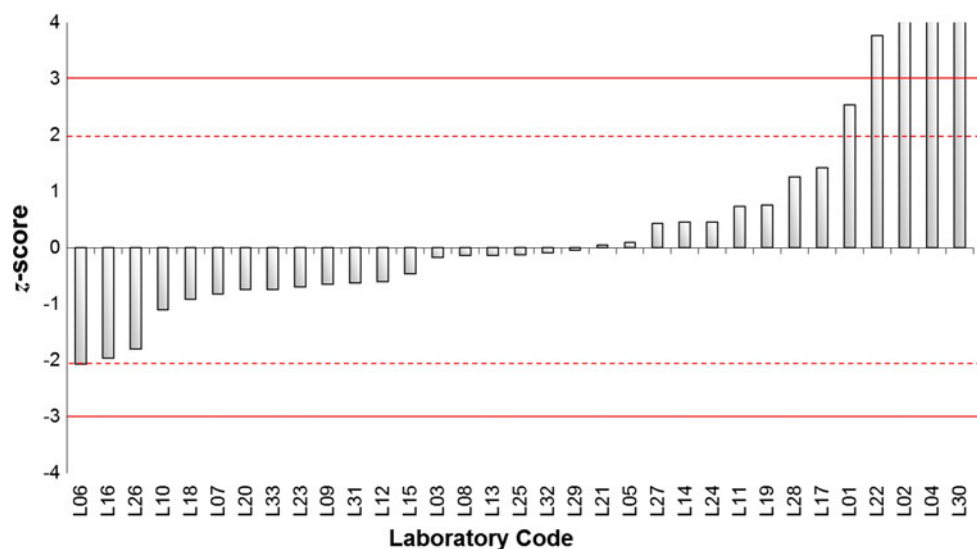


Fig. 3 z-Score for each laboratory considering fluoride results (first round, Y sample)



performance liquid chromatography (HPLC) and IC measurements: “The uncertainty originating from sample and standard preparation was small because it contains only standard purity, weighting, and volume measurement.” The same behavior was observed when the uncertainty values for preparations were compared with the consensus uncertainty values. The same authors [16] stated that “...uncertainty associated with calibration was significant.” Considering chloride and sulfate measurements, a larger uncertainty related to higher concentration levels was observed; the curve fitting was noticed as the error source for results on these two anions that clearly increased significantly the measurement uncertainty. At last, it was also stated that “the contribution of repeatability component gives a large contribution to the combined uncertainty...,” so this component was related to the larger

CV results presented by some laboratories with questionable and unsatisfactory results that did not report their measurement uncertainties. The uncertainty and expanded uncertainty obtained by the present PT were well adjusted to the IC measurement purpose in the studied concentration range. However, considering the concentration range of satisfactory values (see Fig. 1) in this PT in comparison with measurement uncertainties, $\hat{\sigma}$ could be determined by perception with reduced values in future PTs.

Guideline to laboratory work

The identification of random and systematic errors was made by evaluating Youden plots on each round, as presented in Figs. 4 and 5. This information was used to identify some of the main analytical problems that affected

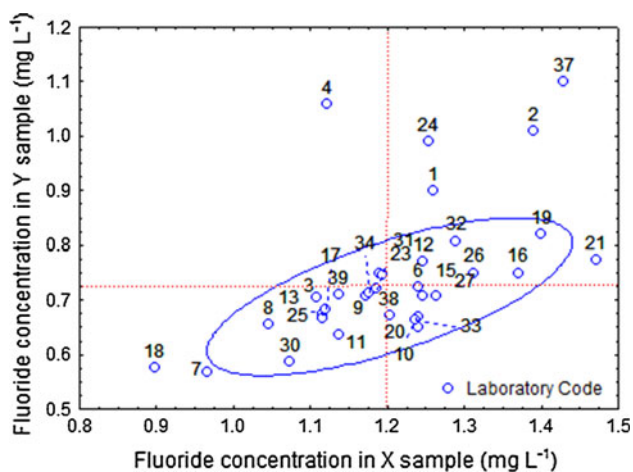


Fig. 4 First round, fluoride Youden plot, with assigned values (*dotted line*) and 95 % confidence ellipse

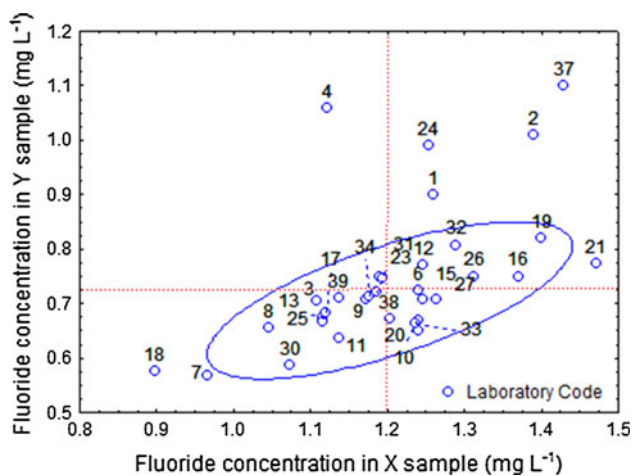


Fig. 5 Second round, fluoride Youden plot, with assigned values (*dotted line*) and 95 % confidence ellipse

each anion measurement. The source of these errors could serve as a guideline to laboratories working in this field.

More results with $z \geq 2$ for fluoride results (Figs. 2, 3, 4) in the first round could be related to unresolved peaks from organic acids at the same retention time as fluoride. In the second round, more questionable and unsatisfactory results were associated with fluoride sub-quantification (Fig. 5). This may be related to iron and aluminum interferences, causing contamination on column filters or suppressor membranes/beds [19]. These cations are among the major ions present in natural waters and can be precipitated with fluoride and phosphate, decreasing the anion concentrations in the soluble phase of water samples. It was recommended to those laboratories with $z < -2$ to proceed with the usual maintenance suggested by manufacturers that may include exchange of column bed supports and

cleanup of suppressors membranes [19] or replacement of suppressors beds.

Chloride is not a difficult species to analyze by ion chromatography. The usual laboratory environmental controls are enough to prevent chloride cross-contamination that could cause random errors. If the laboratories eliminate the environmental contamination from its list of problems, the second most probable cause of “good X-, bad Y-results” or vice versa is the curve fitting. Usually, the lack of accuracy is associated with a bad fit of the analytical curve and/or the selection of the proper analytical range. Due to the difference of one order of magnitude in concentration between X and Y samples in both rounds, it seems that some laboratories had the sample X in an adequate fit of the analytical curve, but the Y sample was probably out of this range [16]. Other laboratories may have the proper adjustment on the Y range instead of the X range. The deviation from the ionic equilibrium could be the cause of this already well-documented effect on anion measurements by IC [4, 20]. This deviation causes a non-linear conductivity response. In this case, a multi-point quadratic adjustment presents a much smaller deviation than a linear fitting.

In both rounds, at least one laboratory presented results based on nitrite- NO_2^- instead of N as requested. Almost all questionable or unsatisfactory results were related to positive deviations ($z \geq 2$) that could be caused by nitrite-N degradation in calibration solutions. The sample results are amplified with lower measurement results in calibration solutions. The validity of the calibration solution and the last calibration run must be checked in that event.

Many sources of error were related to nitrate-N measurements. In some cases, results were reported as nitrate- NO_3^- instead of nitrate-N. These errors are likely presented by the laboratories with less than 1 year of operation time or that participated in a PT for the first time. This type of error almost disappeared in the second round. Nitrate-N variations could be associated with environmental contamination. Some participant laboratories also perform elemental analysis by AAS or ICP-OES and those techniques use diluted HNO_3 as washing solution. This could be the cause of this frequent random error, if no clear glassware segregation was applied.

The calibration solution degradation could affect sample quantification considering nitrate-N and phosphate-P species as nutrients for microorganisms. All these error sources could explain the large number of unsatisfactory and questionable results in both rounds.

Overestimated questionable or unsatisfactory sulfate results ($z > 2$) in both rounds were frequently observed. This could be caused by environmental contamination (glassware, flasks, etc.). Analysis of method blanks could monitor this false-positive contribution. Underestimated

results could be caused by errors in analytical curve fitting. Usually, the IC analytical range was lower than the highest sulfate concentration in both rounds. That could lead to a dilution procedure or the analyst could simply extrapolate the value under the available curve.

Negative deviations ($z < -2$) were frequently presented in phosphate-P results for both rounds. That could be caused by iron and aluminum contaminations in columns and bed supports, as already mentioned. Positive deviations ($z > 2$) could be caused by environmental contamination, especially by detergents containing phosphates. The stoichiometric correction from phosphate to P could be also one of the reasons for one laboratory unsatisfactory result. On the other hand, this correction would not be sufficient to justify such a large deviation to others.

One laboratory even presented questionable results that presented an individual CV of 20.8 % (see Fig. 1) that was larger to the fluoride whole group CV of 9.38 % reported to participants as a clear warning signal of an instrumental lack of performance. Considering that in the first round the chloride sample Y had a group average of 31.93 mg L⁻¹ and a total CV of 3.85 %, it is clear that those laboratories presented an abnormal instrumental behavior.

Conclusions

Interlaboratory studies are an external quality control procedure intended to evaluate a laboratory performance under normal operating conditions and under internal quality control condition. That is also a fundamental criterion for obtaining an accreditation status. The group precision was assessed by a Rede Metrologica do Rio Grande do Sul ion chromatography PT at lower concentration levels than with a broader environmental PT. The precision observed in this Brazilian program is compatible with the precision observed in similar European PTs.

The most frequent error sources of IC measurements were identified. Nitrite-NO₂, nitrate-NO₃ and phosphate-PO₄ results were reported instead of nitrite-N, nitrate-N and phosphate-P that led to unsatisfactory performance in the first round. This was the most easily corrected error because it requires only a simple stoichiometric conversion. Instrumental contamination on column bed supports and on suppressors affected fluoride and phosphate-P results. The quantification method was affected by analytical curve fitting for chloride and sulfate. This effect caused a significant increase in the expanded uncertainty for chloride and sulfate when compared with the remaining anions. Cross-contamination effects were observed in chloride, nitrate-N and phosphate-P measurements. The standard instability could affect the nitrite-N, nitrate-N and phosphate-P quantification once these species could be

modified by the action of microorganisms. Therefore, the continuous participation in this sort of program is an important tool for identifying failures in IC methods and in taking the appropriate corrective actions to improve confidence levels of anion measurements in water samples.

The authors believe that further metrological actions should be implemented in Brazil, such as PTs with assigned values by nominal content instead of consensus means. There is still a long way to go. Only larger multinational companies (in the fuel, steel, pulp and paper market), a few water supply companies, analytical and academic laboratories are currently embracing this kind of PT. This type of PT, presently with around 30 participant laboratories, covers a small fraction of the metrological activities expected in Brazil considering that

- Anion measurement is one of the most frequently demanded tests;
- the number of IC systems already installed is between 500 and 700 in Brazil
- and 20 to 50 new unities are installed every year in Brazil.

Many and much more detailed metrological actions should be implemented in Brazil, especially by health, environmental and export regulatory organizations.

Acknowledgments The authors would like to thank to the reviewers that patiently helped us to improve this text. We have learned a lot with your comments and that will help us mainly in future PTs.

References

1. Konieczka P, Namiesnik J (2009) Quality assurance and quality control in the analytical chemical laboratory—a practical approach. CRC Press, Boca Raton
2. Tartari GA, Marchetto A, Mosello R (1995) J Chromatogr A 706:21–29
3. RMRS Programa Ambiental (2012) <http://www.redemetrologica.com.br/2010/>. Accessed 3 Dec 2012
4. Marchetto A, Mosello R, Tartari GA, Muntau H, Bianchi M, Geiss H, Serrini G, Lanza GS (1995) J Chromatogr A 706:13–19
5. Rede Metrologica do Rio Grande do Sul (2007) Programa Piloto de Ensaio de Proficiencia em Cromatografia Iônica- Relatório Final 15
6. INMETRO RMRS Accreditation Certificate (2012) <http://www.inmetro.gov.br/credenciamento/pdf/PEP0002.pdf>. Accessed 3 Dec 2012
7. European PT Information System (2012) <http://www.eptis.org>. Accessed 3 Dec 2012
8. RMRS Interlaboratory Results (2012) <http://www.redemetrologica.com.br/programainterlaboratorial/>. Accessed 3 Dec 2012
9. ISO/IEC Guide 34 (2009) General requirements for the competence of reference material producers
10. BIPM, IEC, IFCC, ILAC, IUPAC, ISO, OIML (2008) Evaluation of measurement data—guide for the expression of uncertainty in measurement. JCGM 100, <http://www.bipm.org/en/publications/guides/gum.html>
11. ISO/IEC 13528 (2005) Statistical methods for use in proficiency testing by interlaboratory comparisons

12. ISO/IEC 17043 (2010) Conformity assessment—general requirements for proficiency testing
13. Dionex Qualification operation manual (2012) http://www.dionex.com/en-us/webdocs/64696-31726-15_OQ_PQ_Rev5.11_V30.pdf. Accessed 3 Dec 2012
14. Alkema H, Simser J, Hjelm L (1998) *Fresenius J Anal Chem* 360:339–343
15. International Vocabulary of Metrology (2008) Basic and general concepts and associated terms VIM, 3rd edition, JCGM 200
16. Tomić T, Nasipak NU, Babić S (2012) *Accred Qual Assur* 17:291–300. doi:[10.1007/s00769-011-0872-0](https://doi.org/10.1007/s00769-011-0872-0)
17. EN/ISO 10304-1(2009) Water Quality. Determination of dissolved anion by liquid chromatography of ions. Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate
18. DIONEX. Product Manual for AS18 (2012) <http://www.dionex.com/en-us/products/columns/ic-rfic/hydroxide-selective-packed/ionpac-as18/lp-73261.html>. Accessed 3 Dec 2012
19. Mosello R, Tartari GA, Marchetto A, Polesello S, Bianchi M, Muntau H (2004) *Accred Qual Assur* 9:242–246
20. Doury-Berthod M, Giampaoli P, Fitsh H, Seila C (1985) *Poitre-naud. Anal Chem* 57:2257–2263