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ANIONS ENVIRONMENTAL MONITORING CONTROL AT CNEN-IPEN/SP-BRAZIL

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ABSTRACT

The Nuclear and Energy Research Institute IPEN-CNEN/SP, to comply with guidelines and basic procedures to be observed by its installation regarding environmental control actions, related with conventional effluent release started in 2007 the Environmental Monitoring Program for stable chemical compounds (PMA-Q). This program includes, besides others parameters, ionic species such as Fluoride, Chloride, Nitrite-N, Nitrate-N and Sulfate, measured by Ion Chromatography. Among these compounds, Fluoride and Chloride are regulated in effluent discharges by CONAMA´s Resolution #430/2011 and the Sao Paulo State Decree 8468/76. Fluoride, Chloride, Nitrite-N, Nitrate-N in groundwater are regulated by CONAMA´s Resolution #396/2008. Considering the legal requirements, every year this program is revised and improvement actions are planned and implemented. The present paper will discuss these improvements to determine the individual performance of the laboratory related to those tests performed by ion chromatography. The adequacy actions performed were the construction of control charts (internal quality control) and the interlaboratory proficiency tests regular participation (external quality control). With these quality control actions it was possible to monitor continuously the laboratory performance, to identify and resolve analytical problems and also interlaboratory differences, to add value to the essay quality control and to provide additional confidence to the institutional program PMA-Q. The recent change in legislation by CONAMA Resolution #430/2011 and the requirements of Resolution CONAMA #396/2008 improvement requirements are also discussed in this work.

1. INTRODUCTION

In the Environmental Monitoring Program of chemical compound at IPEN (PMA-Q), anions are measured in groundwater and wastewater using ion chromatography system [1]. As Quality Control procedures, all data was evaluated regarding reproducibility, accuracy and sensitivity. This actions document the system behavior, in particular laboratory, become the operator familiar with the routine conditions, and become the operator able to evaluate correctly the results).

According to São Paulo State laws, the environmental monitoring must be performed with Quality Control (QC)or Good Laboratory Practices (GLP), from sampling up to the test report [2]. Without this QC actions results could be either an approximated value or even inaccurate. GLP describes and documents all procedures, equipment and analytical checks to assure good laboratory performances. It also assures continuous monitoring and sustained results reliability. So, as much as the accreditation criteria, as long as corrective actions attributions, must be clearly identified and established in the laboratory.

Since 1997, IPEN/ CNEN-SP´s Center for Chemical and Environmental Technology (CQMA) works under ISO9000 Quality Management System. As part of the accreditation procedure, this work presents internal and external QC results of ion chromatography essays in accordance with ISO 17025. The QC actions were also intended to meet the requirements of Sao Paulo State Environmental Resolution SMA90/2012 [2] and CONAMA´s Resolution 430/2011 [3] e 396/2008 [4].

2. MATERIAL AND METHODS

2.1. Instrumental

All of the anions essays were performed with DX120 Ion Chromatography system (DIONEX Corp.) accordingly with APHA Method 4110 [5], with auto regenerative suppressor, conductivity detection, with injection volume of 100µL, and data treatment Software Chromeleon 6.8.

The measured standards were prepared as listed in Table 1. The solutions were prepared by using the seven anions standard (Thermo Fisher, USA) traceable to NIST. The system baseline was collected for 15 minutes, before the blank and verification standard runs. The adopted normal operation condition established the blank values must be lower than the quantifications limit with ±10% of relative standard deviation.

Table 1: Concentration levels, in $mg.L^{-1}$ used in the analytical curve.

Anion	PD1 ($mg.L^{-1}$)	PD2 ($mg.L^{-1}$)	PD3 ($mg.L^{-1}$)	PD4 ($mg.L^{-1}$)	PD5 ($mg.L^{-1}$)
Fluoride	0.10	0.20	0.40	2.00	4.00
Chloride	0.50	1.00	2.00	10.00	20.00
Nitrite-N	0.50	1.00	2.00	10.00	20.00
Nitrate-N	0.50	1.00	2.00	10.00	20.00
Sulfate	0.50	1.00	2.00	10.00	20.00

2.2. Internal Quality Control

The analytical curve intermediary solution, named PD3 was prepared by dilution of a7Anion Standard (Thermo Fisher USA), and it was selected to be used in the internal quality control chart. This solution was measure monthly during the period between November 18th2010 and December 3rd2012. The control chart was constructed considering the average and a total of 46 control points were evaluated. The average and the standard deviation (σ) was calculated (n = 46) for each anion. The control charts were obtained in accordance with ISO 13528 [6] item 9.2. The operational limits adopted, also considered the normal operation the mean ± 1σ. Every value observed outside the mean ± 2σ was considered a warning value. Values over mean ± 3σ were considered out of the normal operation. If one value outside the mean ± 3σwas observed than a corrective action was required. Corrective actions were also programmed if it was observed two or three warning value in a role.

2.3. External quality control

As external quality control, it was considered the laboratory results in Proficiency tests provided by Rede Metrologica do Rio Grande do Sul from 2011 and 2012 [7,8]. These Proficiency tests adopted the Z-score criteria calculated in accordance with ISO 13528 [6] Annex B that considered the laboratory result as following:

If: $|Z| \leq 2$ Satisfactory Results
$2 < |Z| < 3$ Questionable Results
$|Z| \geq 3$ Unsatisfactory Results

The regular participation in interlaboratory programs and the Z-score results evaluation enables the laboratory to:

- Evaluate the individual performance of the proposed essay;
- Monitor continuously the laboratory performance;
- Identify results *Bias* in the measurement process;
- Allow analytical problem identification and resolution;
- Identify interlaboratory diferences.

Corrective actions were planned in the case of Questionable or unsatisfactory results occur, to solve any laboratory performance deviation. Any bias, identified by more than three positive (Z>0) or negative (Z<0) z-score values in a role, it was also evaluated and discussed below.

3. RESULTS

3.1. Internal Quality control

Anions nominal concentrations that are the planned and prepared concentration are shown in Table 2. The two year average, standard deviation and relative standard deviation (n=46) are also presented in table 2.

Table 2: Nominal and average concentrations comparison observed from 2010 to 2012.

Anion	Nominal Amount $mg.L^{-1}$	Mean $mg.L^{-1}$	Standard Deviation (n=46)	RSD	Normal Operation Limit(8)	*Bias* $mg.L^{-1}$	*Bias* %	Normal Operation Limit(8)	Result evaluation
Fluorite	0.400	0.397	0.048	12%	15%	-0.003	-0.75%	10%	Satisfactory
Chlorite	2.000	1.855	0.269	13%		-0.145	-7.25%		Satisfactory
Nitrite-N	0.608	0.604	0.013	2%		-0.004	-0.66%		Satisfactory
Nitrate-N	0.452	0.446	0.013	3%		-0.006	-1.33%		Satisfactory
Sulfate	2.000	1.944	0.278	14%		-0.056	-2.80%		Satisfactory

Bias is the difference between the nominal average and the planned concentrations on every anion. That corresponds to how far is the planned value from the real measured values and as smaller is the observed bias better the measurement accuracy. Fluoride, Nitrite-N, Nitrate-N and Sulfate concentrations agreed with the nominal concentrations. Chloride bias was the largest one and corresponded to 7.25 % and Nitrite-N bias was the smallest one 0.66 %. The two years relative standard deviation (N=46) was considered acceptable, in the range of 2% for Nitrite-N up to a 14% maximum value for Sulfate. These values were considered satisfactory in the evaluated concentration range.

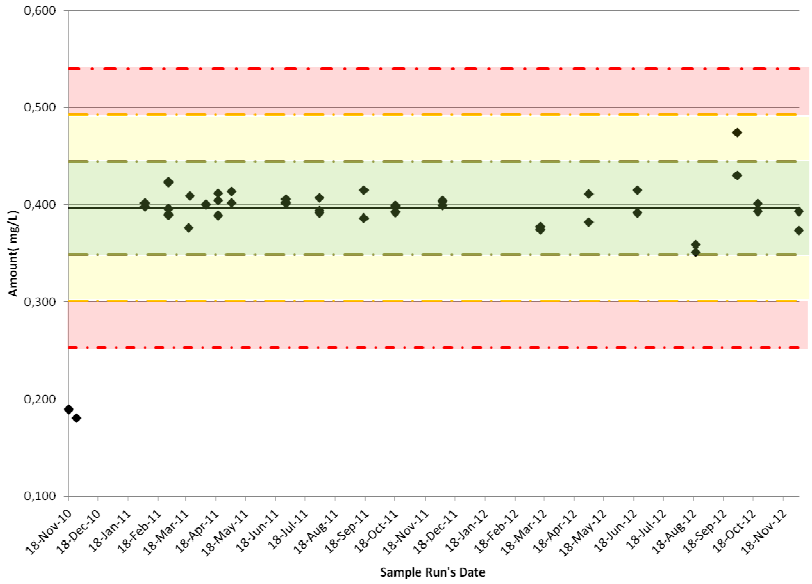

Figure 1a - Internal Quality Control Charts for fluoride

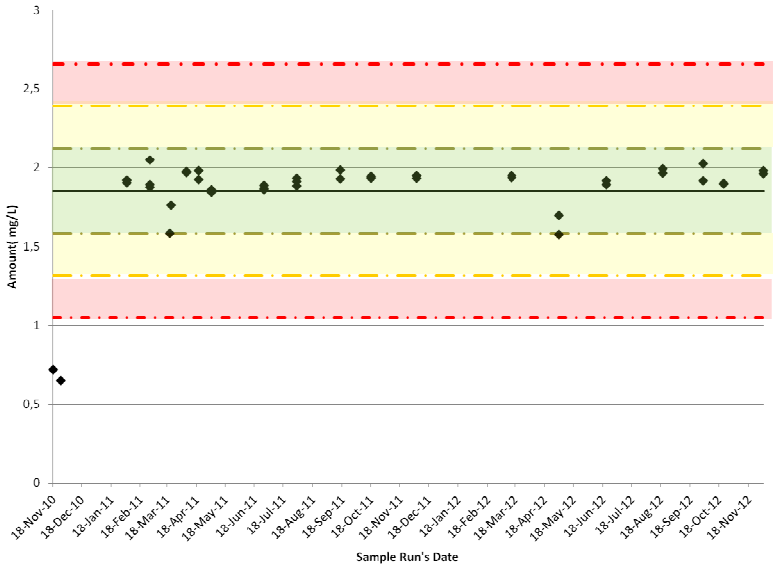

Figure 1b - Internal Quality Control Charts for chloride

In the considered period, no more than two values outside of normal condition of operation were observed (See Figures 1). When the occurrence of values outside of normal operation limit was identified, the corrective maintenance was performed. The corrective action consisted in to the system clean-up procedure column filters or even guard or analytical column replacement and the system recalibration (new solutions were prepared from the same standard lot or from a different one).

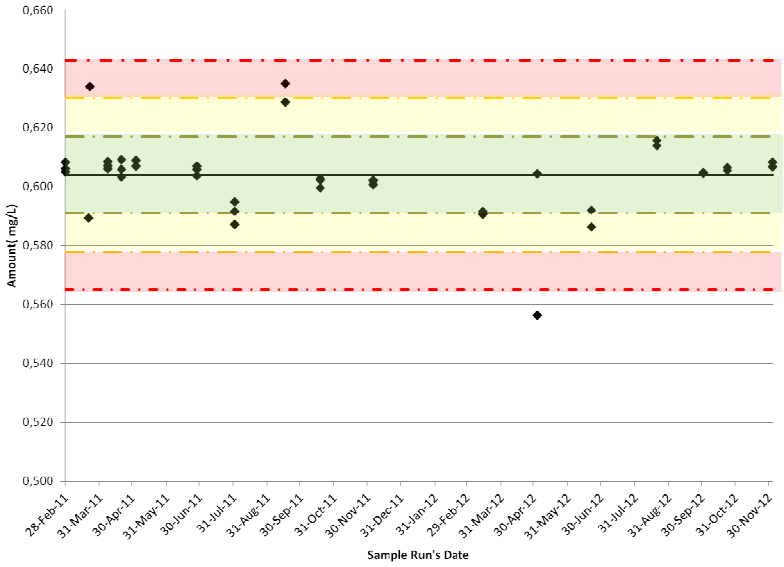

Figure 1c - Internal Quality Control Charts for nitrite-N

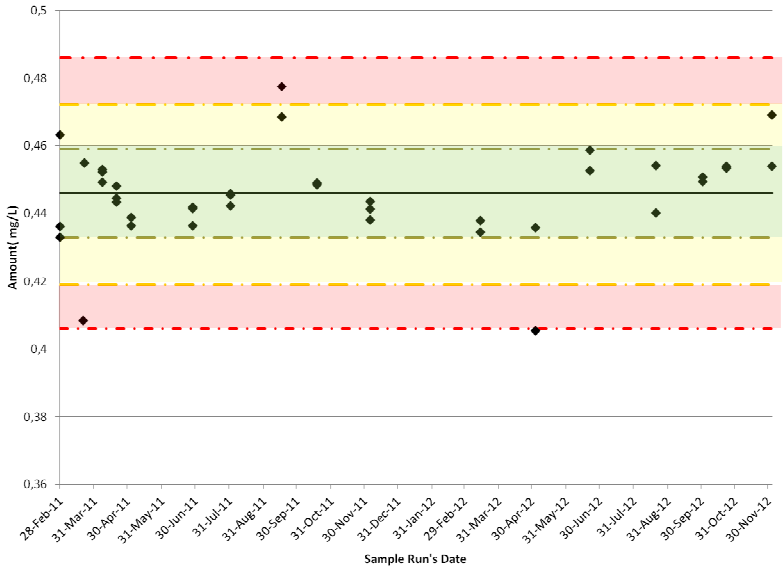

Figure 1d - Internal Quality Control Charts for nitrate-N

For Fluorite (Figure 1a), Chloride (Figure 1b) and Sulfate (Figure 1e) the values out of the operations conditions was observed in the beginning of method development when the system was not in the daily basis operation. Once the control limits were established, no values outside normal operational condition was observed for these anions.

For Nitrite-N (Figure 1c) and Nitrate-N (Figure 1d), values outside the normal operation condition were observed that deriving from solution degradation. These species are nutrients consumed in the microorganism growth. Nitrite-N also could be oxidized converting in Nitrate-N. To run recently prepared solutions allowed the system to return to the normal operational limits. No value outside the normal operation limit was observed for phosphate-P (Figure 1f).

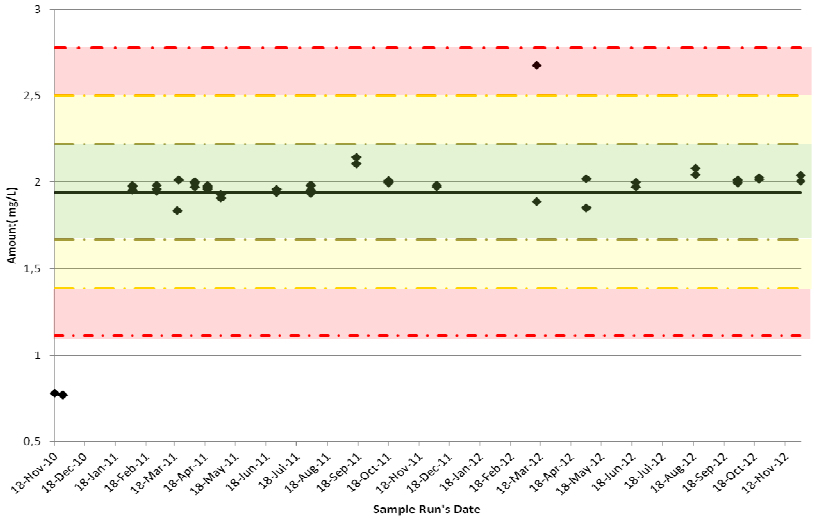

Figure 1e - Internal Quality Control Charts for sulfate

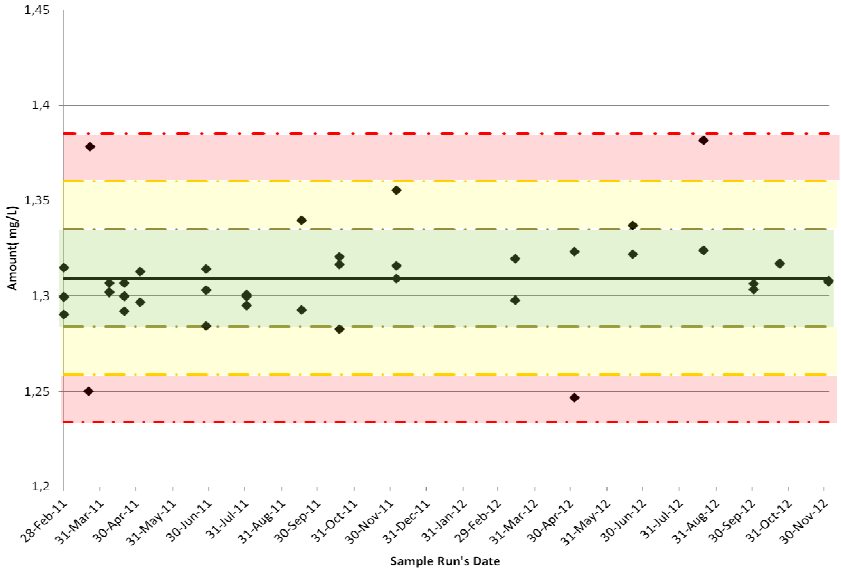

Figure 1f - Internal Quality Control Charts for phosphate-P

Warning values were individual observed, returning later to normal operation values to almost all anions. Not once it was observed two warning values subsequently, that could be considered the system was outside the normal operation condition, as stated by ISO13528 [6]. So it was not required corrective actions in this case.

3.2. External Quality Control

The external quality control was performed by the laboratory performance in interlaboratory proficiency tests [8] and available through the laboratory Z-score evaluation, to each anion, in the two year period. The external quality control is presented to each anion in Figures 2a to2e.

In 2011, it was observed 100% of satisfactory results in the dedicated ion chromatography interlaboratory programs. In 2012, only one questionable result was observed for chloride, in the first round of the dedicated ion chromatography program. To all other anions, in all other anion proficiency tests and in all rounds, the results were considered satisfactory.

The evaluation of anions Z-score allows the identification of the laboratory relative performance in comparison with proficiency program. So successive positive Z-score (Z>0) could be a laboratory overestimation trend, or negative Z-score (Z<0), could identify underestimation laboratory trends. Considering this trend, fluoride (see Figure 2a) had positive Z-score values in to all rounds even with satisfactory results. To other anions alternated Z-score values were observed. Neither positive nor negative trend was identified to other anions as presented in Figure 2b to 2e.

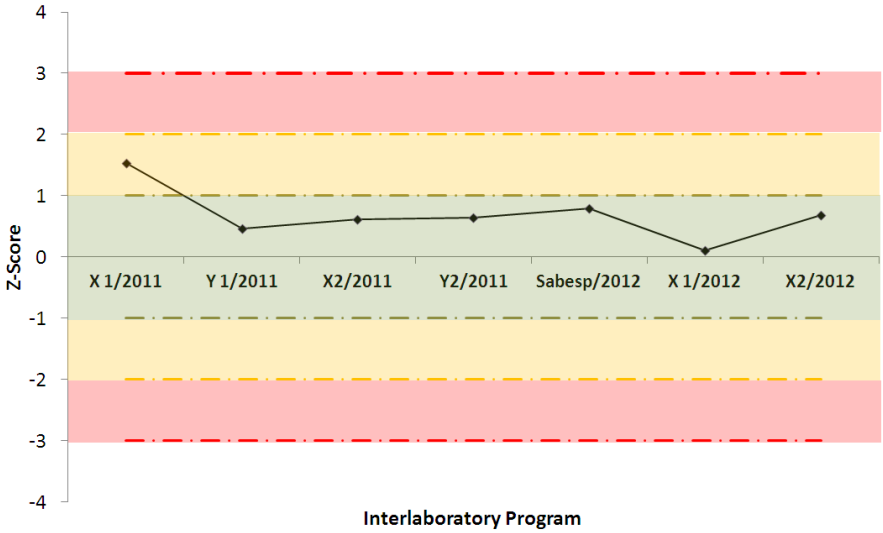

Figure 2a - External Quality Control evaluation by z-score in two years interlaboratory programs for flouride

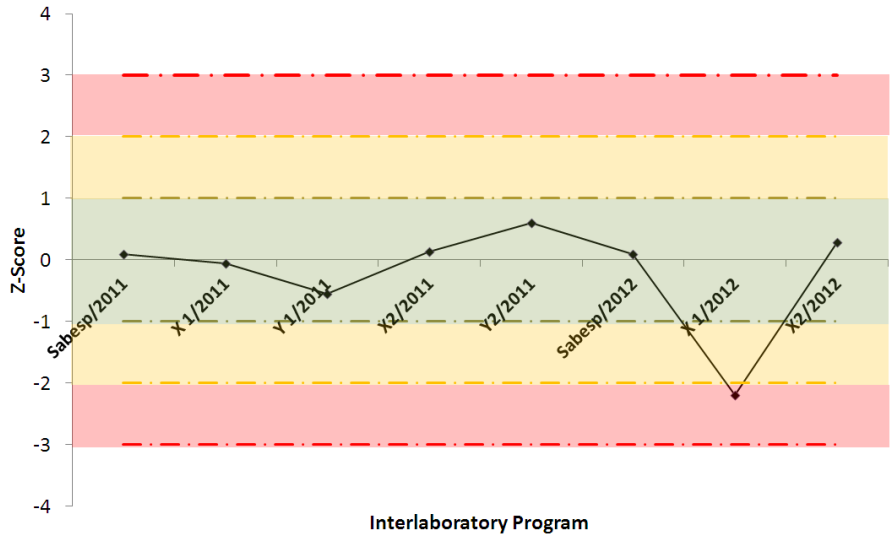

Figure 2b - External Quality Control evaluation by z-score in two years interlaboratory programs for chloride

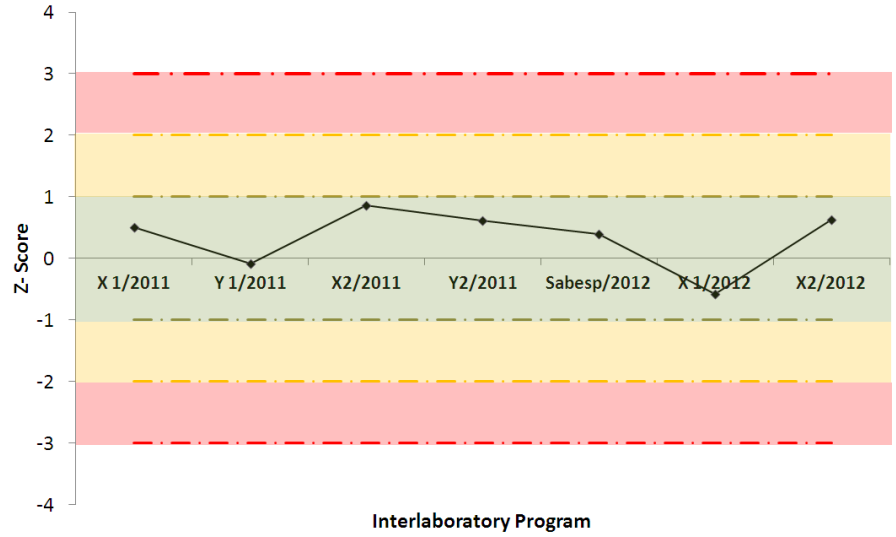

Figure 2c - External Quality Control evaluation by z-score in two years interlaboratory programs for nitrite-N

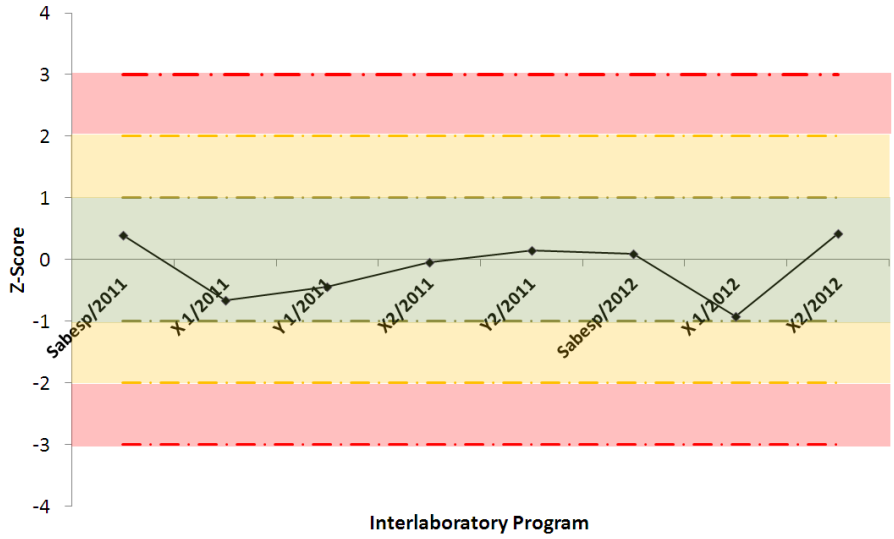

Figure 2d - External Quality Control evaluation by z-score in two years interlaboratory programs for nitrate-N

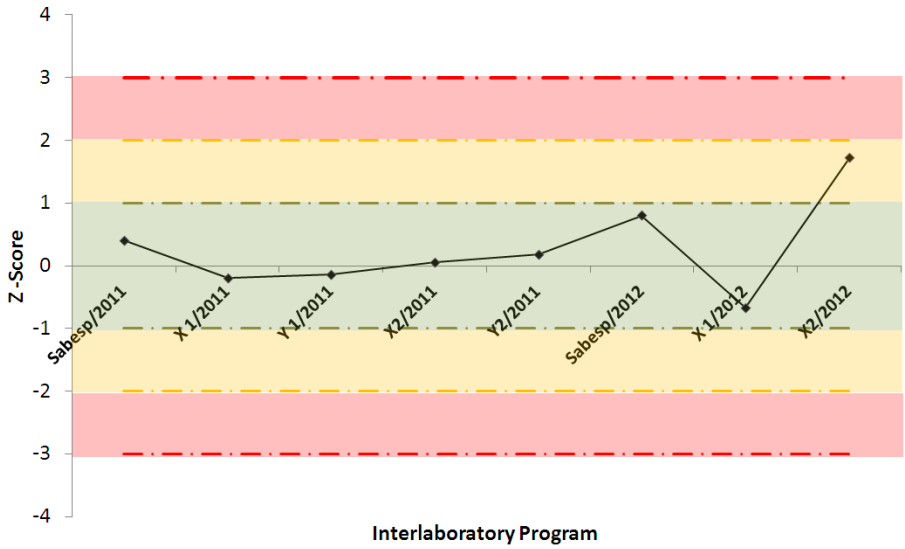

Figure 2d - External Quality Control evaluation by z-score in two years interlaboratory programs for sulfate

3.3. Brazilian Environmental Legislation Requirements

The anion working range by ion chromatography is compared with Brazilian legislation in Table 3. The anion legal limits are established in to liquid effluent release in public sewer systems [3,11], in to groundwater guideline values [9], in to potable water [10]. These values are also presented in Table 3. CONAMA Resolution #420/2009 [9] establishes guideline values to groundwater environmental monitoring. CONAMA's resolution #430/2011 [3] presents limits and conditions to liquid effluent release in public sewer systems. Health

Ministry presents anion limits in to potable water. The São Paulo state decree 8468/76 [10] establishes limits to prevent and to control environmental pollution, with much more restrictive limits to liquid effluent release in public sewer systems.
Considering Sao Paulo state and country legislation (Table 3), the anion working range and quantification limits performed by ion chromatography at IPEN facility are Satisfactory to environmental monitoring activities. IPEN monitored concentration are in the same range or smaller than the concentrations established in Brazilian legislation. When the measured concentrations exceed the legislated working range, the samples are diluted to the appropriate working range. However, in most of the measurements values observed both in the effluent and in the groundwater are within the usual working range and thus below the maximum limit established by law. Therefore measurements are made within the limits laid down as normal operation condition and meet the environmental laws requirements concerning the effluents discharge and groundwater monitoring.

Table 3: Working range compared with Brazilian environmental regulations.

Parameter	Working Range ($mg.L^{-1}$)	Resolution n°420 ($mg.L^{-1}$)	Resolution n°430 ($mg.L^{-1}$)	Health Ministry 2914 ($mg.L^{-1}$)	State Decree 8468 ($mg.L^{-1}$)
F	0.02–2.00	-	10	1.5	10
Cl	0.1-20.00	-	-	250	-
NO_3-N	0.03–3.04	10	-	10	10
NO_2-N	0.02–4.50	-	-	1.0	1.0
SO_4	0.1-20.00	-	-	250	1000

4. CONCLUSION

The latest environmental laws require that tests for monitoring purposes must comply with quality control operation and that all performed test must be conducted under quality management systems. Thus internal and external quality control of anion measurement in groundwater and effluent performed at IPEN in the last two years (2011 and 2012) meet the both ISO 17025 and ISO 13528 standards and Brazilian legislation requirements. With the internal quality control was also possible to prove that the tests conducted in this period were under controlled operating conditions, without significant variation in test conditions. With external quality control, it was possible to state that the results issued during the reporting period, are comparable to the average consensus held by other laboratories employing the same assay technique. In conjunction with these assessments, the working range meets the concentration range required by Brazilian environmental regulations.

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