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REGULATORY QUALITY CONTROL IN THE METAL AND SEMI METAL ENVIRONMENTAL MONITORING PROGRAM AT IPEN/CNEN-SP

Mainara G. Faustino, Douglas Batista Silva, Lucilena R. Monteiro, Elizabeth S. K. Dantas, Maria Aparecida F. Pires, Marycel E. B. Cotrim.

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
lrmonteiro@ipen.br

ABSTRACT

The CONAMA's Resolution 430 recently published in May 13th of 2011, that completes and modifies the Resolution 357/2005, defined new quality standards to perform liquid effluent monitoring essays in order to allow the release in the public sewer system. This Resolution has established that the essay laboratories must be certified by Brazilian National Metrology, Normalization and Industrial Quality Institute – INMETRO and also count with an implemented quality control system. Thereby this publication affected directly IPEN´s Environmental Monitoring Program of Stables Chemical Compound (PMA-Q), performed since 2007. In this program, 20 parameters related to the metallic and non-metallic chemical elements content are monitored by using sensitive analytical techniques such as graphite furnace atomic absorption spectrometry – GF-AAS or inductively coupled plasma spectrometry – ICP-OES. Therefore this paper presents improvements to determine the laboratory individual performance performed by GF-AAS and ICP-OES. To achieve the legislation compliance for these parameters, the following actions were implemented: the construction of control charts (internal quality control) and the participation of the laboratory in interlaboratory proficiency tests (external quality control). These actions are presented and discussed with the results of elements such as Arsenic and Lead that are analyzed through GF-AAS as well as Chromium, Cooper, Zinc, Iron and Nickel, that are analyzed through ICP-OES. These actions of quality control allowed the continuous monitoring of laboratory performance, the identification and resolution of analytic problems and interlaboratory differences, provide additional confidence to monitoring program.

Keywords: Atomic Absorption Spectrometry, Inductively Coupled Plasma Spectrometry, Quality Control, Environmental Monitoring.

1. INTRODUCTION

This paper describes and establishes a quality control of the analytical laboratories for a variety of metals to meet institutional obligations regarding environmental licensing and nuclear.

The IAEA (International Atomic Energy Agency) uses nuclear techniques and complementary techniques to assess the environment, nuclear facilities, nuclear materials (IAEA-TEC DOC). As reporting and interpretation of the IAEA in many cases nuclear techniques might not be available or might not be sufficiently sensitive, other non-nuclear techniques, such as atomic absorption spectrophotometer (AAS), voltammetry or inductively coupled plasma atomic emission (ICP OES) or mass spectrometry (ICPMS) are also included in the discussion. The complexity of the problem requires full exploitation of the analytical armoury to obtain reliable and accurate results.

As an example, the IAEA considers: MESL Facilities Laboratories Inorganic: Inorganic Laboratories - Analysis of Trace Elements and Organometallic Species; Atomic

Absorption Spectrophotometry (AAS), Inductively Coupled Plasma - Mass Spectrometry (ICP-MS).

According to IPEN'S Environmental Monitoring Program of Stables Chemical Compound - PMA-Q, since 2007, have basics requirements for the life and propriety protection, because in your dependences are handled chemicals, biological and radioactive products e several equipments, all this have been reviewed annually (1).

Also this Environmental Program has a data base that shows a historical about all information that happens in the IPEN-CNEN-SP. In this data base beyond the continuous register of the activities effects performed in the installations, detections of eventual fails and scheduling correctives measures, evaluation of the environmental impact resulting of the IPEN'S activities, and we have the sewer evaluation that is originating from all IPEN-CNEN-SP'S institute (1).

The Environmental Monitoring Program of Stables Chemical Compound (PMA-Q) implanted in IPEN/CNEN- SP, has as an objective to attend the present laws environmental regulations. This program aimed to meet the requirements of CONAMA's Resolution 357/2005 that classifies water bodies and establishes fresh water environmental guidelines and establishes terms and standards to public sewer system release. (1). However, in 2011, CONAMA modified half of this resolution with the publication of a new Resolution 430/2011 (2). Its purpose was solely regulated terms and standards to public sewer releases.

CONAMA's Resolution 430/2011 established that the monitoring laboratories must have quality control system and the essays must be certified by Brazilian National Metrology, Normalization and Industrial Quality Institute – INMETRO. Due these recent changes in the Brazilian legislation, IPEN/CNEN-SP is doing adjustments to maintain its Environmental Monitoring Plan in accordance with the local legislation (2).

The objective of this work is to increase the trustworthiness of the essays results issued in the PMA-Q regarding the sewer metal monitoring, to attend the CONAMA´s Resolution 430/2011; establish the quality control of the analytical laboratories of the metals and semi metals elements analyses, from statistical data jointly with the present environmental legislation.

2. MATERIALS AND METHODS

IPEN/CNEN-SP Quality control system follows ISO IEC 17025/2005 (3) that establishes the minimum quality requirements to essay laboratories. The construction of control charts with internal and external quality control data are some of its requirements. As internal quality control, the laboratory must keep the analytical instruments and the adopted reference standards calibrated, in order to avoid analytical errors and to ensure the analytical requirements will be stable in the laboratory. External quality control refers to the evaluation of the laboratory results in the interlaboratory programs participation (3).

Control charts are constructed from the data obtained during the analysis execution in the laboratory and by comparison with the interlaboratory program evaluation. The statistical data treatments referent of the participation in the interlaboratory program follows the ISO

13528/2005 (4), where the *Z*-score is obtained from each participant laboratory in each essays allows. These results can be evaluated as satisfactory, questionable or unsatisfactory. The individual laboratory performance depends on how many standards deviations the result differs from robust average. During Proficiency tests each participant laboratory has its results evaluated by the PT provider in accordance with these criteria.

Graphite furnace atomic absorption spectrometry – GF-AAS was used to perform the analysis of Arsenic and Lead. This technique requires fewer samples to the analysis; it can determine lows concentration (in order of $\mu g.L^{-1}$) and have more sensitivity (5).

Inductively coupled plasma spectrometry – ICP-OES, was applied to perform the analysis of Chromium, Cooper, Zinc, Iron and Nickel that is adequate to higher concentrations (in order of $mg.L^{-1}$) and with multi-elementary capacity (6) (7).

2.1 METALS ESSAYS

Sample aliquots of 45 mL were added to 1 mL of concentrated hydrochloric acid (MERCK) and 4 mL concentrated nitric acid (MERCK). All samples were digested by using microwave furnace MDS-2000 (CEM) with time and power program accordingly the EPA 3015 method (8). Each sample lot had quality control samples that were blank, standard addition and replicate. These samples evaluate the respectively environmental conditions and the reagent, the recuperation and the reproducibility of the essays. After the digestion the sample were analyzed through the GF-AAS (AAnalyst, Perkin Elmer) and ICP-OES (Spectraflame, Spectro).

The results were reported to Rede Metrologica do Rio Grande do Sul, in accordance with the Environmental proficiency test program. *Z*-score evaluation of each round was applied as external quality control charts.

2.2 STATISTICAL DATA

External Quality Control is performed by proficiency test programs by Rede Metrologica do Rio Grande do Sul, from 2010 until 2012. The evaluated data correspond to LAQA (Chemical Analysis Laboratory and Environmental) performance as per *Z*-score criteria. Z-score was calculated by interlaboratory program providers as stated in ISO / DIS 13528:2005 - *Statistical methods for use in proficiency testing by interlaboratory comparisons. Z*-score of each laboratory average (n = 3) was obtained by the equation 1:

$$Z = \frac{(x_i - x^{**})}{s^{**}} \quad (1)$$

Where: x_i = the arithmetic average of the results obtained by the participant;
x^{**} = the value average of the robust set of data;
s^{**} = the robust diversion.

Laboratories performances were classified as SATISFACTORY, QUESTIONABLE or UNSATISFACTORY, to each of the measure, considering the following criteria:

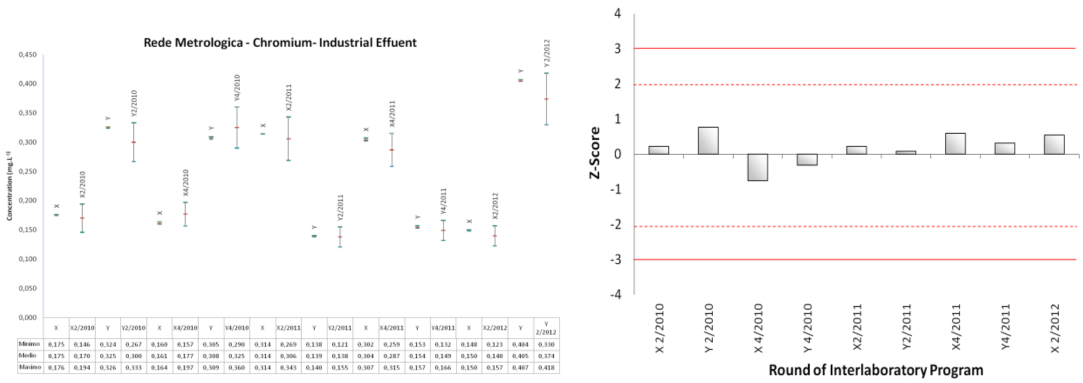
If:	$\lvert Z \rvert \leq 2$	Satisfactory results
	$2 < \lvert Z \rvert < 3$	Questionable results
	$\lvert Z \rvert \geq 3$	Unsatisfactory results

Internal Quality Control was accomplished by a control chart built with the measurement results of the reference material SRM 1643e, traceable to NIST (National Institute of Standards and Technology).

3. RESULTS AND DISCUSSION

The individual laboratory Proficiency performance obtained from 2010 to 2012, for Chromium, Copper and Lead are presented in Figures 1 to 3 respectively. The comparison between the individual laboratory results (mean and standard diversion) and the whole group of interlaboratory participants to Chromium, Copper and Lead are presented respectively in Figures 1a, 2a and 3a. Figures 1b, 2b and 3b presents the laboratory individual Z-score where 100 % of the results were satisfactory for these elements.

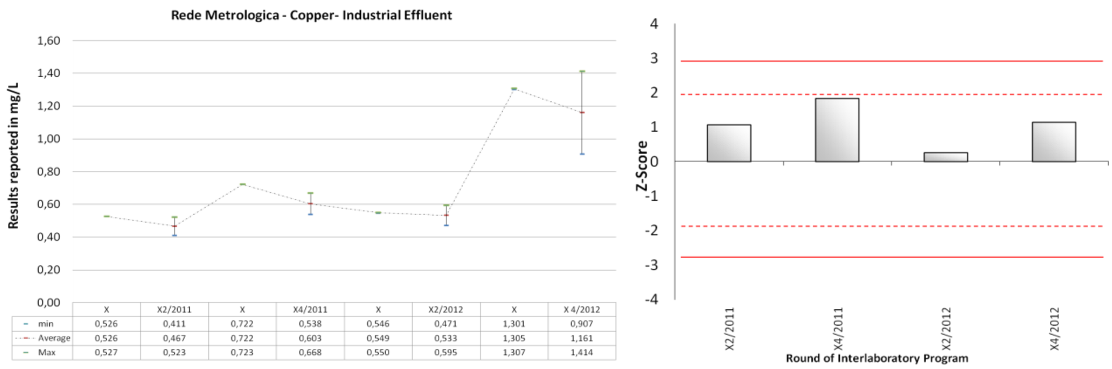
Since 2010 up to 2012, Chromium individual results showed the smallest dispersion being up to one standard deviation from the consensual average (Figure 1b) observed to the whole group of laboratory. Copper individual results were close to 2 *SD* (standard deviation) (Figure 2b). *Z*-score to Lead (Figure 3b), although satisfactory in all rounds, showed a decreasing trend to measured values in 2012 last two rounds (-2 < *Z* <-1). This behavior must be evaluated as an underestimation trend (-1 < *Z* <1) compared to lead consensus average results.



	X	X2/2010	Y	Y2/2010	X	X4/2010	Y	Y4/2010	X	X2/2011	Y	Y2/2011	X	X4/2011	Y	Y4/2011	X	X2/2012	Y	Y 2/2012
Minimo	0,175	0,146	0,324	0,267	0,160	0,157	0,305	0,290	0,314	0,269	0,138	0,121	0,302	0,259	0,153	0,132	0,148	0,123	0,404	0,330
Medio	0,175	0,170	0,325	0,300	0,161	0,177	0,308	0,325	0,314	0,306	0,139	0,138	0,304	0,287	0,154	0,149	0,150	0,140	0,405	0,374
Maximo	0,176	0,194	0,326	0,333	0,164	0,197	0,309	0,360	0,314	0,343	0,140	0,155	0,307	0,315	0,157	0,166	0,150	0,157	0,407	0,418

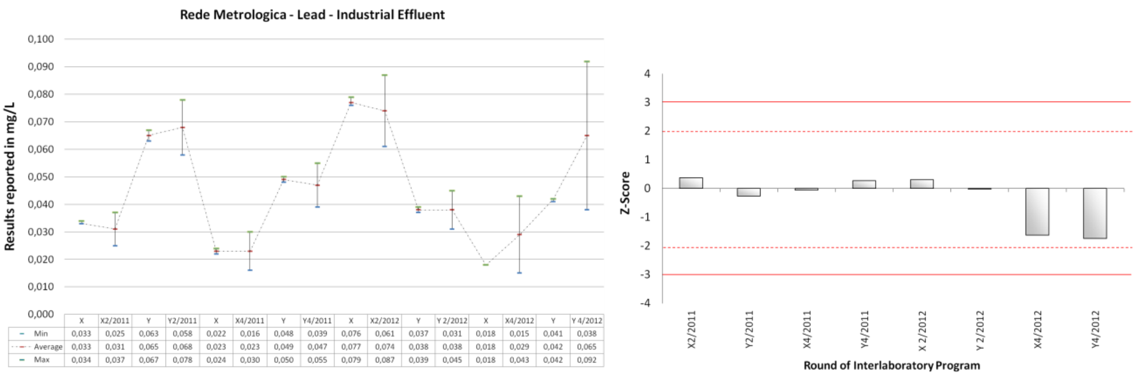
(a) **(b)**

Figure 1: Comparison between individual and LAQA average consensus Interlaboratory Program (a) and the history of Z-score (b) between 2010 and 2012 for Chromium.



(a) **(b)**

Figure 2: Comparison between Copper and issued by LAQA average consensus Interlaboratory Program (a) and the history of Z-score (b) between 2011 and 2012.



(a) **(b)**

Figure 3: Comparison between LAQA results for Lead and the consensus average of each PT round (a) and the correspondent Z-score (b) from 2011 and 2012.

Similar evaluations, as presented in Figures 1 to 3, were performed to iron, arsenic, nickel and zinc. Table 1 shows results summary for these elements. Questionable and unsatisfactory results were observed to some of these elements. After critical analysis of results, the error source of non-compliant values was found. The evaluation was performed by using the Ishikawa diagram (see Figure 5). The unsatisfactory or questionable results main causes were identified as following:

- Reagents contamination;
- Incorrect results expression, such as incorrect chemical form or incorrect measurements unity;
- Test condition degradation, such as standards and analytical curve.

These problems were identified also in the internal quality control so corrective measures were taken to ensured satisfactory values in the following interlaboratory programs rounds.

Table 1: Summary of interlaboratory programs results to Iron, Nickel, Arsenic, and Zinc, from 2010 to 2012.

Elements	Total number of	Number of	Number of	Number of	Tendency

	rounds between 2010 and 2012	Satisfactory results $\|Z\| \leq 2$	Questionable results $2 < \|Z\| < 3$	Unsatisfactory results $\|Z\| \geq 3$	
Iron	10	8	1	1	Z>0
Nickel	10	8	0	2	Z>0
Arsenic	8	7	1	0	Z<0
Zinc	4	4	0	0	-

3.1 INTERNAL QUALITY CONTROL

Every sample batch had as internal quality control blank, standard addition, reference material and replicate samples for every metal. As reference material for recovery evaluation, it was used the NIST – SRM 1643e. This reference material was used to evaluate the reproducibility and the element recovery by comparison with its certificated and reference values. Figure 4 presents some of the arsenic measured values from 2010 to 2012 that were measured together with the PT´s rounds. In this paper only the arsenic values are presented and compared with the certificates values (60.45 ± 0.72 µg/L). Arsenic recovery is presented in Figure 4.

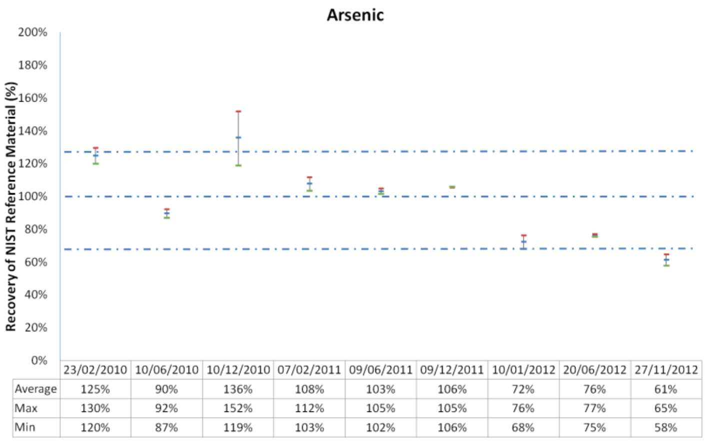


Figure 4: Some Arsenic recovery values of SRM 1643 from 2010 and 2012.

Considering the measurement of lower ug.L^{-1} concentrations, a recovery from 70 up to 130 % for arsenic was considered acceptable. From 2010 up to 2012 only two result were outside this range. The non-compliant value observed in December 2010 overestimated the arsenic measurement. Higher blank values were observed and the usual decontamination procedure was repeated and revised. More recently, a decreasing trend was observed in 2012. Due the smaller values recovery required was made the corrective maintenance of the equipment.

3.2 CRITICAL ANALYSIS

Ishikawa diagram was used as process control. This is also known as a fishbone diagram or cause-effect diagram. This diagram is a well-known tool to determine problem causes in the process analysis or to evaluate the necessary improvements (9).

In the effluent Environmental Monitoring Program of metals with the Interlaboratory Program, it was possible to determine questionable and unsatisfactory results causes. By using this kind of diagram, it was also possible to solve non-compliant results. The used diagram is shown in Figure 5.

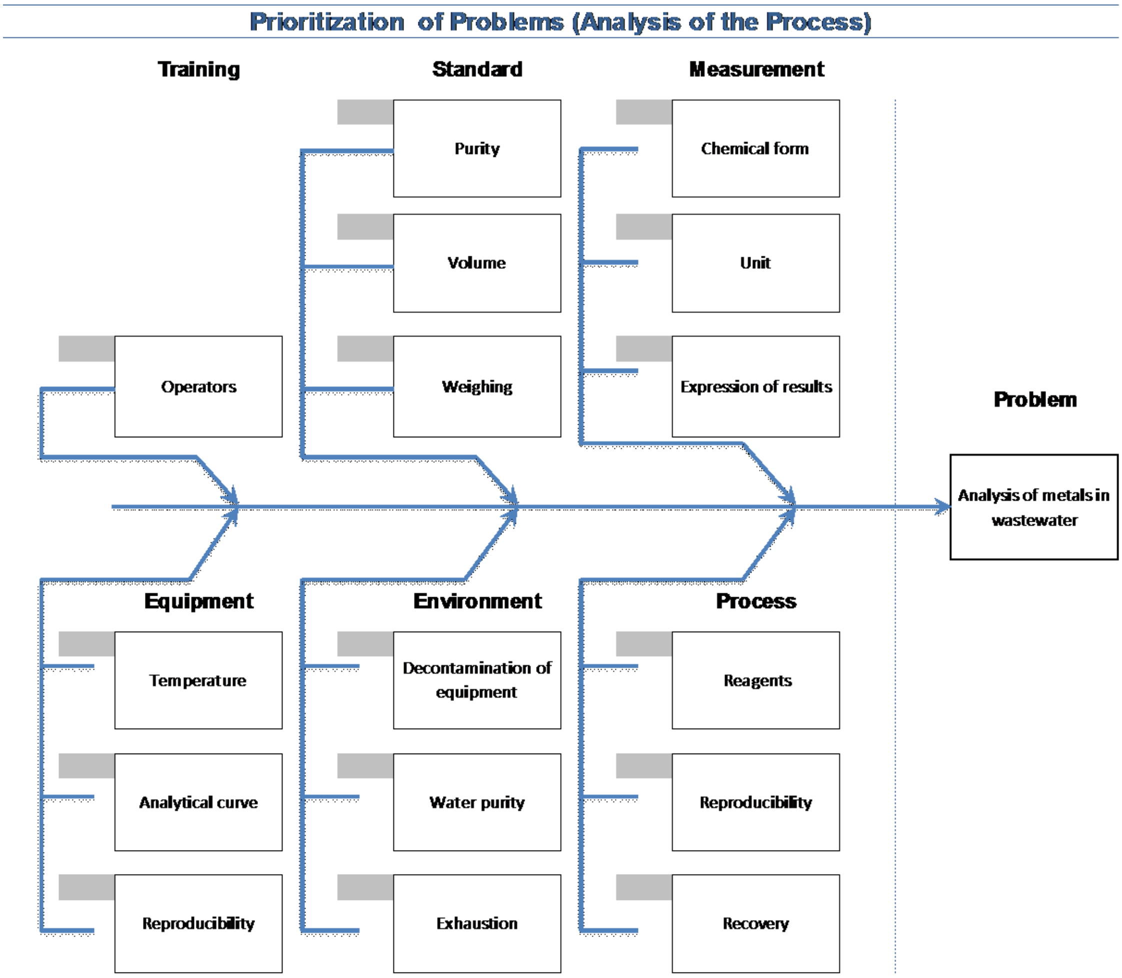


Figure 5: **Process control diagram on metal measurement in effluents.**

4. CONCLUSIONS

Quality control charts, such as internal and external QC charts, are very important to assure long-term analytical consistency in to low concentration metal measurement in effluents. Proficiency Test results issued in IPEN´s laboratory and internal QC data treatment allowed the identification of the main analytical error sources, related with the metal measurement in effluents. From 2010 to 2012, to the studied elements it was observed only 5.7 % of unsatisfactory and questionable results of the measurements total in proficiency tests. Due the large number of samples, the low concentration range and the analytical procedure complexity that figure was considered acceptable to these elements measurement in the yearly Environmental Monitoring Program.

The identification and correction of these error sources, contributed directly to improve the results reliability issued by IPEN/CNEN-SP´s Environmental Monitoring Program of Chemical Compounds Stable (PMA-Q). It also meets the requirements of the most recent environmental standards in Brazil that corresponds to CONAMA´s Resolution 430/11.

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REFERENCES

1. **IPEN-CNEN-SP.** *RELATÓRIO DE AVALIAÇÃO DO PROGRAMA DE MONITORAMENTO AMBIENTAL (PMA-Q) ATENDENDO AOS COMPOSTOS QUÍMICOS ESTÁVEIS DO IPEN – 2011.* CNEN - COMISSÃO NACIONAL DE ENERGIA NUCLEAR/IPEN – INSTITUTO DE PESQUISAS ENERGÉTICAS E NUCLEARES. SÃO PAULO : s.n., 2012.

2. **BRASIL.** CONAMA 357/2005. *Ministério do Meio Ambiente* . [Online] 17 de Março de 2005. [Citado em: 15 de Janeiro de 2013.] http://www.mma.gov.br/port/conama/res/res05/res35705.pdf.

3. —. CONAMA 430/2011. *Ministério do Meio Ambiente* . [Online] 13 de Março de 2011. [Citado em: 2013 de Janeiro de 15.] http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=646.

4. —. Acreditação de Laboratórios (ABNT NBR ISO/IEC 17025:2005). *INMETRO.* [Online] 2005. [Citado em: 2013 de Fevereiro de 06.] http://www.inmetro.gov.br/credenciamento/acre_lab.asp#info.

5. **ISO.** 13528:2005 - Statistical methods for use in proficiency testing by interlaboratory comparisons. *ISO - International Organization for Standardization.* [Online] 09 de 01 de 2005. [Citado em: 21 de 03 de 2013.] http://www.iso.org/iso/catalogue_detail.htm?csnumber=35664.

6. **HARRIS, Daniel C.** *Análise Química Quantitativa.* Rio de Janeiro : LTC, 2001.

7. **GINÉ, Maria Fernanda.** Espectroscopia de Emissão Atômica com Plasma Acoplado Indutivamente - ICP-AES. *Centro de Energia Nuclear na Agricultura - CENA/USP.* [Online] 09 de 1988. [Citado em: 15 de 04 de 2013.] http://apostilas.cena.usp.br/Fernanda/Livro%20ICP%20OES.pdf.

8. **UFSCAR.** Espectrometria de emissão óptica com plasma acoplado indutivamente (ICP OES). [Online] UFSCAR, c.2013. [Citado em: 15 de 04 de 2013.] http://www.ufscar.br/dq-gaia/images_2007/ICPOES_Parte1.pdf.

9. **3015, EPA.** [Online]

10. **ESALQ- USP.** DIAGRAMA DE ISHIKAWA. *Escola Superior de Agricultura "Luiz de Queiroz".* [Online] c2013. [Citado em: 25 de 04 de 2013.] http://www.esalq.usp.br/qualidade/ishikawa/pag1.htm.

11. **BENNETT, P. A. e ROTHERY, E.** *Introducing Atomic Absorption Analysis.* Australia : Varian Techtron Pty Limited , 1983.