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REQUIREMENTS FOR RADIOACTIVE EFFLUENTS SAMPLES SUBMITTED TO ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT

The current environmental Brazilian regulations access the parameters concerning on release of wastewater jointly with surface water quality and environmental radiological monitoring programs, considering the inherent dilution factor. Mainly, it does establish the legal and regulatory instruments that could contribute and improve the environmental management optimization practices carried out in effluents monitoring for nuclear and radioactive facilities. For this performance, it is necessary to understand the parameters involved in the dispersal of effluents released in the installation and internal locations near the release point, such as chemical and radioactive concentration. This paper discuss the assay protocols employed for the analysis of stable chemical species present in gross radioactive liquid effluents, which were released by the facilities of the Institute of Nuclear and Energy Research. Sampling, pretreatment and sample preparation were established. The geometry, chemical medium and range concentration were turned appropriate for measurement by flame atomic absorption spectrometry methodology. Standards were employed for calibration curves, has been also determined the minimum detectable concentration (MDC) and the selectivity of the methodology. The concentrations of the stable elements Ag, Cd, Cr, Fe, Mn, Ni, Pb e Zn were measured and validated.

1. INTRODUCTION

Monitoring and treatment of liquid effluents are required throughout the whole human production cycle. Effluents generated during mining, milling, processing, industrialization, health field and domestic uses contain radioactive isotopes and non-radioactive elements and compounds that, if not properly assessed, could contaminate drinking water resources or enter the food chain, potentially harming the environment and endangering the health and well being of human populations.

Accordingly, regulatory standards have been established that set maximum levels of contaminants that can be released to the environment. Initially, the objective of effluent monitoring program was to ensure that these limits were accomplished so that operations and releases do not endanger surrounding populations. As regulatory requirements become more rigorous, however, improved technologies were required. In addition to being driven by the regulatory environment, new technologies also focus on cost containment and water conservation. Radioactive and nuclear facilities takes place in a variety of physical and chemical conditions, which necessitate design of site specific effluent control, monitoring and treatment systems for radioactive and stable chemical species, under Brazilian laws [1, 2].

At the same time, the chemical and physical characteristics of the effluents from operation to operation are broadly similar, which means that production facilities worldwide share almost common monitoring and treatment requests. Therefore, the purpose of this study was to define a protocol for analyses of stable chemical elements in radioactive liquid effluents.

A wide range of metals have achieved significance as potential pollutant because of their toxic properties towards all forms of life. For this reason the dispersion of metal in the environment via sewage system is of considerable concern. Thus it is essential to understand fully the fate of the substantial quantities of metals entering sewage release and the consequences for human health and the environment.

The stable elements of major concern for liquid effluents include certain transition elements frequently referred to as the “heavy metals”. It is generally accepted that this term refers to chromium manganese, iron, cobalt, nickel, copper, zinc, molybdenum, silver, cadmium and mercury. Also of environmental importance are certain metals from groups IIIB, IVB and VB of the periodic table, in particular aluminum, tin, antimony, lead, bismuth and the metalloids arsenic and selenium. Boron although it is not a metal, is also toxic and frequently included with these elements. This group of elements was referred heavy metals in this paper, has been analyzed the elements Ag, Cd, Cr, Fe, Mn, Ni, Pb e Zn by flame Atomic Absorption Spectrometry Method (AAS).

A gross effluent sample contains significant concentrations of organic matter which are representative for present metals, remaining as complexes, co precipitated or for sorption chemical forms. When analyzing effluents samples by optical spectrometry, considerable sample pretreatment together with the selection of the correct calibration strategy are necessary to ensure accurate results. Flow injection techniques can be used to improve existing procedures and time-consumption and as the basis for new calibration methods.

Calorimetric methods are commonly recommended for the analysis of aluminum, calcium, cadmium, copper, chromium, iron, magnesium, molybdenum, nickel, lead and zinc in effluent samples with significant organic material. In recent years flame atomic absorption spectrometry has been extensively used for the analysis of metals in this kind of samples. Both calorimetric and atomic absorption spectrometry require the destruction of any organic matter present in the sample prior to analysis.

Organic and colloids destruction requires heating dissolution using drastic acid or basic medium, jointly with oxidizer and reducing chemical conditions. These steps are critical for retro contamination and loss of interest elements. This difficulty may be intensified by the sample size, concentration level, matrix composition and interferences, suspended solids content, organic matter and others.

The main stages for gross effluent sample metals monitoring by AAS are described [3].
a) Planning. Prepare the strategies that consider the objective compliance. Generally, should begin with a preliminary evaluation of sample composition and physical characterization, for pretreatment steps, method development or selection, error acceptance, calculation and data assessment.

b) Sample Collection and Storage. Ideally the analyst is involved in this stage, but if not, the analyst should be informed of the sampling procedure at the very least. Sample representation and contamination issues must be considered for recognized and standard methodology

c) Laboratorial Sub Sample and Sample Preparation. The homogeneity of sample must be secured. Cross contamination issues are a major concern during this stage, but not the only false risk result. Pre treatment by physical and chemical steps is truly important. This study put emphasis in techniques for homogenization, sub sampling and chemical treatment by several chemical medium, acid and basics condition.

d) Sample Measurement. The main concerns during this stage are:

d.1)- Availability of Certified Reference Materials. These are essential for method validation, plus stable and accurate calibration standards, interference standards, and quality control standards.

d.2)- Achieving the Required Precision. It serves no purpose in acquiring a precision that has been reduced to less than one-third of the sampling error. In situations where the sampling error is small and the highest level of precision is required, the analyst faces a difficult task in acquiring precision equivalent to classical wet chemical techniques.

d.3)- Required Sensitivity and Concentration Minimal Detectable Determination. Baseline preparation of standard curves need describe the components and appropriate settings of the instrument and provide a list of which metals will be studied in the current laboratory session. Metal absorption wavelength (nm), optimal spectral bandpass (nm), flame stoichiometry, lamp current (mA), optimal working range (ppm) and required stock solutions. It provides relevant information for each chemical element to be quantitatively analised with AAS and atomization by an air-acetylene flame. One of the difficulties encounter in the data interpretation is the quantification of trends, such as calculation of slope and demonstration that this estimation of trend is statistically different from zero.

d.4)- Overcoming Interferences. It include matrix differences between standards and samples; spectral interferences, chemical enhancement of atom lines by high matrix element compositions; and drift due to nebulizer plugging, changes in sample gases, power supply instability, or room temperature changes.

d.5)- Confidence Interval. The range of values which span from the Lower Confidence Limit to the Upper Confidence Limit, which encompass the population parameter of interest, such as the population mean, with a degree of certainty which we specify up front.

e) Calculating and Reporting the Data. Working with error budgets and calculating the uncertainty is integrating part of this stage.

f) Validation. Using statistical tools and participating in run intercomparison program, this step is accomplished.

The main stages summarized above are also presented in the Figure 1.

2. METHODS AND RESULTS

Radioactive liquid effluents typically contain both radioactive contaminants from natural series or artificial way and non-radioactive contaminants. Thus, these contain isotopes, anionic and cationic forms. Because of the diversity of operating environments and potential contaminating elements and compounds, a single matrix treatment technology may not work for all potential contaminants. Therefore, different combinations of treatment strategies may be required depending on the matrix chemical characteristics.

Detection of chemical concentration in effluents contaminants is a critical step in assessing the operational condition of a given system. While a variety of methods exist for the destruction of suspended solids in liquid effluents. These solids are composed by inorganic and organic matter with colloidal forms, being interference for all chemical or physical analyses method. Considering the techniques for solids elimination most are time consuming and few are appropriate pretreatments for all of the common determinands species.

For determination of soluble and insoluble stable analyte in gross radioactive effluent, the chemical attack by using a stronger reagents and temperature variation was evaluated. Its offers the opportunity to solids destruction, avoid time consuming pretreatment procedures and duplication of analyses, for soluble and insoluble forms. The Fig. 1 represents the procedure for complete assay. This paper emphasizes the steps in gray color.

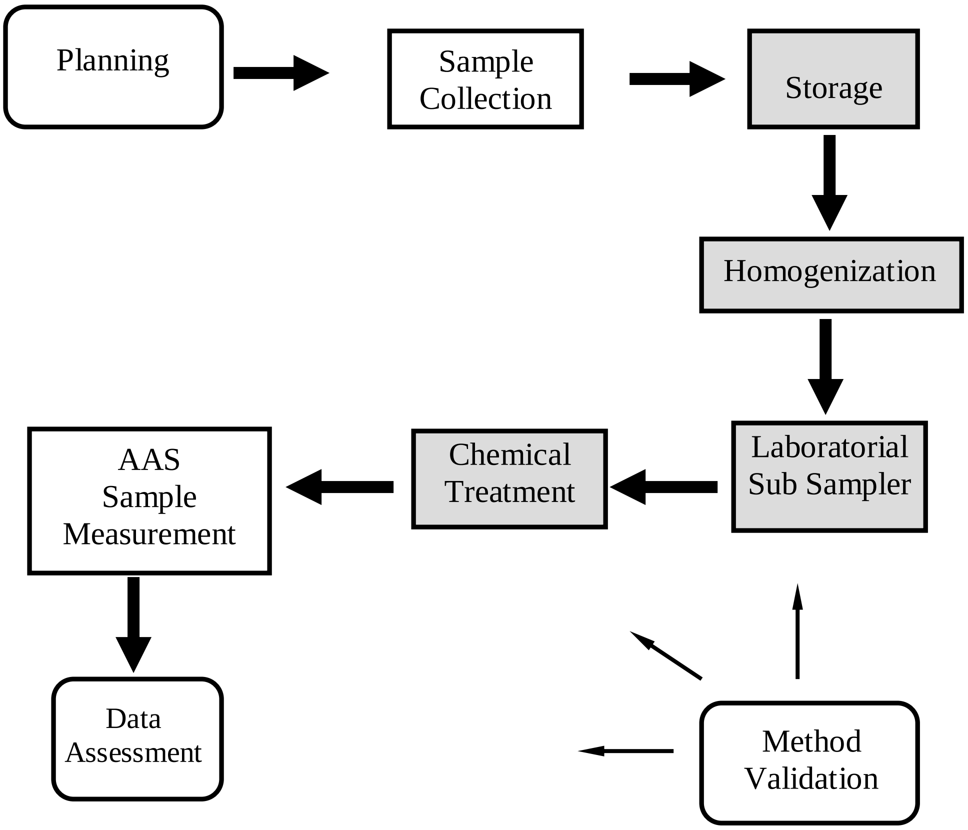

Figure 1. Procedure for total metals analysis in gross liquid radioactive effluent.

2.1. Principles of Atomic Absorption Spectroscopy (AAS)

The flame atomic absorption spectrometry (AAS) is a widely used spectroanalytical procedure for the quantitative determination of a large number of metals concentration, employing the absorption of optical radiation by free atoms in the gaseous state. Electrothermal AAS (EAAS) using graphite tube atomizers has a wide variety of graphite tube designs, being used over the last years, consisting of stages, such as drying, pyrolysis, atomization and cleaning.

An aqueous sample containing the metal is aspirated into an air-acetylene flame, causing evaporation of the solvent and vaporization of the free metal atoms. This process is called atomization. A line source, hollow cathode lamp operating in the UV-visible spectral region, is focused on the atomic vapor in flame or an eletrothermal atomizer. Its promotes the electrons of the atoms to higher orbitals, remaining in excitation for a short period of time, by absorbing a defined energy quantity. This amount of energy is specific to a specific electron transition in a particular element. In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few picometers, giving to technique its elemental selectivity.

The absorbance is measured with a conventional UV-visible dispersive spectrometer with photomultiplier detector. The radiation flux without a sample and with a sample in the atomizer is measured and the ratio between the two absorbance values is converted to analyte concentration. The very narrow spectral lines of atoms, about 0.02 Å, necessitate the use of a line source as well as a high-resolution monochromator. This prevents interference from adjacent spectral lines of other atomic species present in the sample matrix [4]. The Fig. 2 presents the operational sequence for AAS methodology.

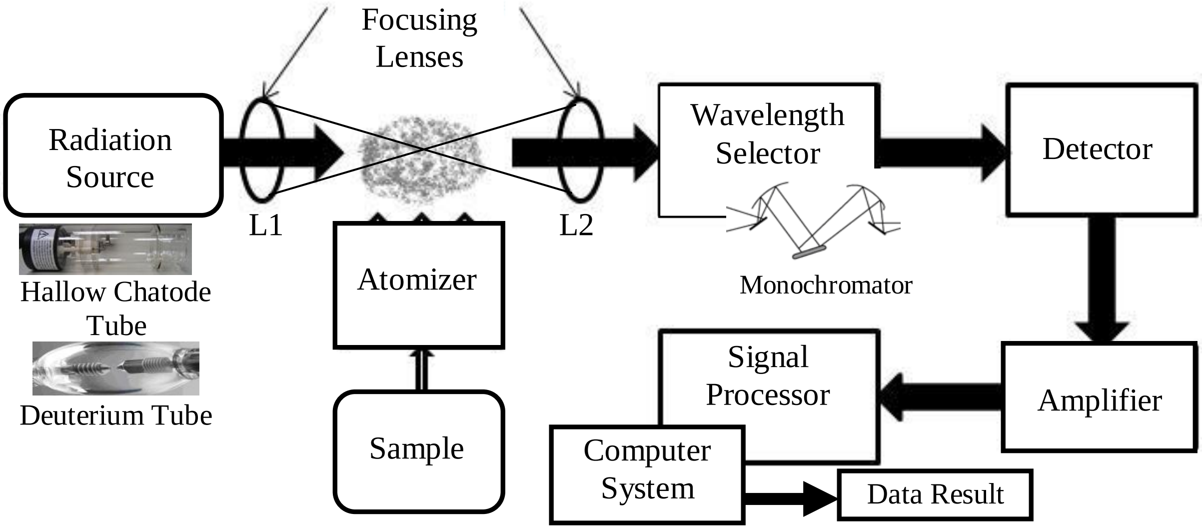

Figure 2. Block diagram of atomic absorption spectrometry method.

For the background, the relatively small number of atomic absorption lines, when compared to atomic emission lines for chemical elements and their narrow width of a few pm make spectral overlap rare occurrence. There are only very few examples known that an absorption line from one element will overlap with another. Molecular absorption, in contrast, is much broader, so that it is more likely that some molecular absorption band will overlap with an atomic line. Another source of background absorption, particularly in EAAS, is scattering of the primary radiation at particles that are generated in the atomization stage, when the matrix could not be removed sufficiently in the pyrolysis stage. These phenomena, molecular absorption and radiation scattering, can result in artificially high absorption and an improperly high calculation for the concentration or mass of the analyte in the sample. The technique available to correct the background absorption was considered.

In analytical chemistry, the use of absorption spectrometry to assess the concentration of an analyte in a sample, requires standards with much known metal content to establish the relation between the measured absorbance and the element concentration and relies therefore on Lambert–Beer law.

In optics, the Lambert–Beer law relates the absorption of light to the properties of the material through which the light is traveling. The transmissivity is expressed in terms of an absorbance, which, for liquids, is defined as equation 1 [4].

$$\mathbf{A = -\log (I/I_0)} \tag{1}$$

Where:
A: absorbance;
$I_{0:}$ intensity of the incident light and;
I: intensity of the transmitted light,

2.2. Evaluation for Solid Destruction

Atomic spectrometric techniques almost need a continuous sample supply, being well suited for on-line connection through flow injection arrangements. For the determination of elements at lower concentrations, electrothermal atomization is often needed owing to the requirement for better detection limits. However, connecting a batch technique such as electrothermal atomic absorption spectrometry to a continuous flow or a flow injection system presents some fundamental difficulties. There are different ways of interfacing the systems to each other; the available versions utilize either on-line sample treatment with off-line measurement or are completely on-line arrangements.

Matrix preparation can be achieved on-line through solvent and sorbent extraction, precipitation and coprecipitation, volatile compound generation and liquid chromatography. Moreover, transformation of the sample and its fractions into a form that can be analyzed in a graphite furnace often requires time-consuming and high risk procedures. Microwave heating has emerged as a means of dramatically improving leaching, mineralization or digestion processes and has frequently been used with in-batch or on-line systems.

Complex samples cannot be directly processed by this technique owing to severe matrix interferences, which have not been minimized despite the development of efficient background correction devices. Making it a real challenge, the establishment of a technique for total dissolution and sample homogenization is fundamental. This paper outlines the development of digestion-dissolution technique for gross effluent samples and also describes the sample pre-treatment system samples before flame atomic absorption detection.

Gross effluent chemical digestion was carried out for five different techniques: sodium hydroxide, nitric acid – hydrogen peroxide, nitric acid – hydrochloric acid, nitric acid concentrated and nitric acid – sulfuric acid. The systems were evaluated for controlled heating, using the same range of 80-90 °C. In optimal determination condition for sample transparency, the five different digestion results of analysis, obtained satisfactory determination result. By comparison besides, nitric acid concentrate effect was a better technique for colloids destruction. This proved a feasibility of acid digestion in nitric medium, had been adopted for gross effluent preparation.

The advantage is that, the nitric medium is the ideal condition for AAS assay measurement. The total dissolution was investigated by turbidity. The processes were carried out in each individual sample: carefully virgin flask beacker was used, serious tempearature interval control and analytical grade reagents.

The Table 1 summarizes various techniques for sample total dissolution using different reagents and chemical conditions.

Table 1. Several chemical medium for digestion were evaluated

Assays for Total Dissolution		
Chemical Medium	Turbidity	Time spent (h)
NaOH – 1.0M	good	good
HNO_3 37% -H_2O_2 40V	good	good
HNO_3 37%-HCl	good	good
HNO_3 37%	excellent	excellent
HNO_3 37% -H_2SO_4	good	excellent

2.3. Gross Radioactive Effluent Preparation and Results

Radioactive effluents from several IPEN-CNEN/SP installations are under responsibility of radioprotection supervision area. In a four years period, a set of 48 representative sample of 1.0 ± 0.1L volume each were collected, transferred to glass bottles and stored. The matrix effluent physical proprieties were done by measuring the parameters pH, temperature, conductivity and turbidity.

Samples were carefully prepared in order to avoid chemical and physical interferences. For laboratorial sub sample the effluents matrix were submitted to homogenization as following. An intense initial mixing by magnetic agitation was applied, for 30 minutes at least. Soon afterwards an aliquot of 50 mL was taken using a volumetric glass pipette, it was transferred for a virgin borosilicate glass beacker cup.

Each sub sample was submitted to hot-plate heating, under controlled temperature interval 80 to 90^{o}C, by 30 minutes. After, was added 5 mL of HNO_3 37%, by using a calibrated micropet Gilson P1000. The system was carefully maintained under magnetic agitation even total particulate material dissolution. The obtained final solution was transferred for a HDPE flask and stored. The sub samples, free any solids and colloids, were analyzed by flame absorption atomic spectrometry technique for metals determination Ag, Cd, Cr, Fe, Mn, Ni, Pb e Zn [5].

The radioactive liquid effluents stable elements concentrations were determined by using a flame way atomic absorption spectrometer, Spectra AA-220, Sequential Fast (Varian), associate to the software SpectrAA, version 5.01. The total analysis scheme is presented in the Fig. 1 and 2.

The methodology calibration was accomplished using certified material solution, containing Ag, Cd, Cr, Fe, Mn, Ni, Pb, and Zn (Merck and Spex Plasma). The concentrations of 0.1, 0.2, 0.5, 1, 1.25, 1.6, and 2 ppm (parts per million) were prepared, in the same conditions used for the samples preparing. Three different patterns solutions were prepared, being one multi-elementary containing the metals Cd, Fe, Mn, Ni, Pb and Zn, and separate solution for Cr and Ag each one. The separation of the Chrome and of the Silver of the other elements in the standard calibration solution became necessary, due to the precipitation occurrence after the mixture of those two elements with the others one [3,5,6].

The reference stock solutions were prepared by gravimetric technique in analytical balance AL500C (Marte), being used micropet RBC 7993/07 P100 [3].

Results presented have been statistically analysed and shows that the solid and colloids dissolution with nitric acid treatment accomplished the sample preparation for flame atomic absorption procedure.

A digestion procedure based upon the use of nitric acid and heating in conjunction with flame atomic absorption analysis gave results comparable to those of the rapid eletrothermal atomic absorption method for determinands metals in gross effluent sample.

3. CONCLUSIONS

The correct homogenisation ensure that the solids are uniformly dispersed permitting representative sub-sampling, has been evaluated by comparison with standard and recommended methods of analysis

The purpose of acid and basic tested digestion was the removal of insoluble and colloidal organics and inorganic suspended solids present in the gross radioactive liquid effluent sub-sample. This was done through chemical dissolution processes by using drastic continuous attack.

Each technique for solids dissolution has advantages and disadvantages, which should be taken to choice case to case. Carefully must be examined the kind and composition of gross effluent and subsequent analysis method. Several characteristics, such as baseline, present elements, solids and colloids must be considered.

Selection of the appropriate conditions for the digestion stage and the use of heating could avoid "non atomic" interferences in AAS method. It eliminates the need for complex and time consuming pretreatment. The flame atomic absorption technique, in conjunction with sub sample nitric acid sample preparation, ensures good time analysis for the metals Ag, Cd, Cr, Fe, Mn, Ni, Pb e Zn.

The dissolution technique could be applied to gross effluents samples with similar composition for solids suspended and colloids particles, in conventional or nuclear field.

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