

# DETERMINATION OF TRACE ELEMENTS IN WATER SAMPLES BY $k_0$ BASED INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS USING SODIUM AS COMPARATOR

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## ABSTRACT

Neutron Activation Analysis in liquid samples has been a challenge for our laboratory due to the following difficulties: i) to irradiate samples in the polyethylene vials avoiding pressure build up ii) to get an appropriate geometry for irradiation and measurement of liquid samples, and iii) to avoid excessive manipulation of samples. This work shows the development of the method for multi-element trace determination in water samples using  $k_0$  based instrumental neutron activation analysis using sodium as comparator. Samples are concentrated by evaporation in a microwave oven under controlled temperature and irradiated in aqueous solution for short lived radionuclides determination and in pellets for medium and long lived radionuclides determination. The sodium standard was prepared either liquid or solid for the corresponding analysis. After certain decay time it is possible to quantify a group of elements with sufficient sensitivity and accuracy as shown by the analysis of the standard reference material NRCC SLRS-2. This method has been satisfactorily applied for monitoring natural water samples from Lima city and other locations in Peru.

## 1. INTRODUCTION

There is a global interest to improve the water resources management due to an increasing global demand for water which is higher than the current available supplies and to the low quality of water which could be unsafe for human consumption [1].

Human activities pollute the rain water, river water, lake and even the groundwater. The last one, provides drinking water to large part of the population. Most of the time, contamination of surface- and groundwater is caused by chemicals used in agriculture as well as organic compounds

and by heavy metals produced and used by the industry. This chemical waste causes damage to the ecosystem and affects the human health.

The quantitative analysis of trace elements in water samples provides important information for environmental decisions, is very important to making decisions. Water samples are suited ideal to be analysed using spectrometric techniques such as ICP-MS, ICP-ES and AAS; since previous treatment of samples is not required. Trace element determination in water samples by NAA as an alternative certified quantitative analysis is a challenge.

In the case of NAA, liquid sample irradiation have some difficulties because of the production of gas by radiolysis that can leak, in such case it is necessary to use quartz ampoules; the irradiation time should be very well established, limiting long irradiation time which also limit the possibility to increase sensitivity. We should also achieve a homogeneous irradiation and measurement geometry. Other groups treated the samples before irradiation with processes such as; pre-concentration using inorganic adsorbents [2], sulphur co-precipitation [3], evaporation under infrared lamp [4], or ten days pre-concentration in quartz ampoules [5]. These treatments increase the risk of contaminating the samples, which is critical as the amount of the element in samples is small.

In the present work a sensitive, simple and alternative procedure is presented using  $k_0$  based instrumental neutron activation analysis method and using sodium as comparator, in order to avoid dependence on the alpha parameter variation [6]. Sample preparation is performed by evaporating, in a microwave oven, under controlled temperature.. The content of short radionuclides in the samples is determined directly by irradiating a volume of evaporated water sample, while the

content of medium and long live radionuclides is determined by placing a volume of evaporated sample in small discs of filter paper dried under infrared lamp and then pressure to form pellets. The SLRS-2 reference material has been used as an internal control.

This procedure is been applied for the analysis of groundwater coming from wells located near a river that supplies drinking water to a small Peruvian town.

## 2. EXPERIMENTAL

### Sample preparation

NRCC SLRS-2 reference material has been used to test the method according to the following procedure: Approximately, 100 mL sample is weighed in a Pyrex glass vessel, cleaned previously with 5 % neutral extran® and nitric acid 1:1 and then evaporated in the microwave oven MARS-5, under controlled temperature of 85°C, open vessel, during 6 h. When a volume of approximately 10 mL is reached, the vessel is weighed again and the concentration factor determined.

For medium and long lived radionuclides, an aliquot of 600 µL of pre-concentrated sample is deposited on a disc of 70 mm of Whatman 42 filter paper and dried under infrared lamp. The drying distance is 30 cm, so that the temperature received by the sample is less than 60 °C. Using a hydraulic press, pellets of 13 mm of diameter and 2 mm of thick are formed. These pellets are packed into small cleaned polyethylene bags and enveloped in pieces of aluminium foil to be labelled.

Sodium comparators are prepared in the same way, depositing 500 µg of sodium standard solution. Flux monitors are prepared depositing 150 µg and 0.4 µg of standard solutions of zirconium and gold, respectively. Samples, sodium comparators and flux monitors are packed into aluminium can, to be irradiated.

For short lived radionuclides, 1 mL of pre-concentrated sample is deposited in a polyethylene container of 1.25 mL of capacity, previously cleaned with HNO<sub>3</sub> 1:1 and bidistilled water. Sodium comparator is prepared depositing an aliquot of 1 mL of 1000 µg.mL<sup>-1</sup> sodium standard solution,

reproducing sample geometry. Each polyethylene vial containing sample and sodium comparator is packed independently, into a rabbit container. A 500 µg sodium flux monitor is evaporated on a filter paper and attached to each vial. Water samples were prepared in the same way as mentioned above but filtering and acidifying previous to evaporation.

### Irradiation and Measurement

The aluminium can is irradiated 6 hours, in a position of the reactor core; the thermal neutron flux at this position is  $4 \cdot 10^{13} \text{ n.cm}^{-2} \cdot \text{s}^{-1}$ . After two days decay a 10 000 s first counting is performed and a 20 000 s counting after twenty days decay. Flux monitors are count after two days decay for 2 000 s and sodium comparators are counted after 6 days decay for 600 s. The  $f(\alpha)$  and  $(\alpha)$  values are 32 and 0.15 respectively.

The irradiation capsule with the sample and sodium comparator in liquid form, are pneumatically transported and irradiated at a thermal flux of  $2.6 \cdot 10^{13} \text{ n.cm}^{-2} \cdot \text{s}^{-1}$ . These samples are irradiated in a sequential form for 5 min each one.

After a 5 min of decay time, the liquid content of sample and comparator is transferred into a 20 mm diameter polyethylene container, weighed them and completed with deionised water to a volume of 1.5 mL. The counting times are 1200 s and 600 s respectively.

The induced activities of samples, sodium comparators and flux monitors are measured at 60 mm distance from the detector with a less that 5% dead time using a Ge HP CANBERRA GC 1518 detector of 70 cm<sup>3</sup> and 1.9 keV resolution for the 1408 keV <sup>152</sup>Eu peak. The evaluation of gamma spectra was performed using the interactive option of the DBGamma Programme V5.0® program [7]. The photopeaks of Al and V have been evaluated using the Covell integration method [8]. Concentration calculation was determined using the  $k_0$  method, Högdahl convention [9,10]. The nuclear constant was taken from Blaauw [11].

### 3. RESULTS AND DISCUSSION

The results obtained for the reference material SLRS-2 are presented in table 1. The first eight values correspond to the analysis of sample in liquid form and the remainder correspond to the analysis of samples in pellet form

**Table 1.** Elements concentration in SLRS-2 Riverine Water.

Element	Experimental Value (n=10) ( $\mu\text{g.L}^{-1}$ )	Certified Value ( $\mu\text{g.L}^{-1}$ )	Agreement
Al <sup>a</sup>	89 ± 13	84.4 ± 3.4	1.05
Ba	14.9 ± 3.4	13.8 ± 0.3	1.08
Ca <sup>b</sup>	5.63 ± 0.16	5.70 ± 0.13	0.99
Mg <sup>b</sup>	1.59 ± 0.04	1.51 ± 0.13	1.05
Mn	10.5 ± 0.2	10.1 ± 0.3	1.04
Na <sup>b</sup>	2.05 ± 0.04	1.86 ± 0.11	1.10
Sr	32 ± 5	27.3 ± 0.4	1.17
V <sup>a</sup>	0.21 ± 0.08	0.25 ± 0.06	0.84
As	1.11 ± 0.08	0.77 ± 0.09	1.44
Cr	< 20	0.45 ± 0.07	
K <sup>b</sup>	0.81 ± 0.04	0.69 ± 0.09	1.17
Fe	< 300	129 ± 7	
Sb	0.21 ± 0.05	0.26 ± 0.05	0.81
Zn	< 10	3.33 ± 0.15	

<sup>a</sup> Elements evaluated using Covell method

<sup>b</sup> Concentrations expressed in  $\text{mg.L}^{-1}$  uncertainty express as  $\pm U$  (95%)

All the results were corrected by blank contribution and coincidence effect. In general, good agreement is observed from the results. The high discrepancy shown in the potassium result may be explained by the unfavourable nuclear constants ( $\theta = 6.73\%$ ,  $t_{1/2} = 12.36\text{ h}$ ,  $\gamma = 18.8\%$ ) that made difficult the right evaluation of small peaks in presence of high content of sodium ( $>100\text{ mg.L}^{-1}$ ).

Arsenic is other element that shows high discrepancy however it should be taken into account the low concentration of this element. In the case of iron the detection limit is  $300\text{ }\mu\text{g.L}^{-1}$  the same value reported by WHO (1996) as the maximum level contaminant, the sensitivity is not good enough to take decisions. The contribution of zinc in the polyethylene bag hindered to reach a good precision for this element.

**Table 2.** Element concentration in pellets and polyethylene blanks (n = 10).

Element	Polyethylene bag ( $\mu\text{g}$ )	Paper filter pellet and bag ( $\mu\text{g}$ )
As	0.0003 ± 0.0001	
Cr		0.19 ± 0.05
Sb	0.002 ± 0.001	
Zn	0.47 ± 0.02	0.56 ± 0.05

Table 3. Shows the concentration obtained in the evaluation of peaks following the methods mentioned, the evaluation of the emergent area is better for the Covell method.

**Table 3.** Element concentration according evaluation method.

Element	Total Peak Area $\mu\text{g.L}^{-1} \pm U$ (95%) 0.81	Covell Method $\mu\text{g.L}^{-1} \pm U$ (95%)
Al	103 ± 6	89 ± 13
V	0.31 ± 0.04	0.21 ± 0.08

In the case of the irradiation in the pneumatic system the flux variation effect was studied, it was obtained an average relative variation of 5%. Due to the fact that samples and comparators are not irradiated at the same time, a sodium flux monitor was used each time in order to take into account flux variations and a  $C_f$  factor was defined and used for this purpose. This factor is defined as:

$$C_f = \frac{(A_{sp}Na)_c}{(A_{sp}Na)_x}$$

where  
 $A_{sp}, Na$

Counting specific rate of sodium monitor (counts  $\text{s}^{-1}\mu\text{g}^{-1}$ )

$c$  Comparator  
 $x$  sample

By multiplying  $C_f$  by the concentration value determined in  $k_0$  calculation, it is possible to minimize the flux variation error allowing to

irradiate, independently, samples and standards.

**Table 4.** Detection Limits vs. Maximum Contaminant Level (MCL).

Element	Detection Limits ( $\mu\text{g.L}^{-1}$ )	MCL [12] ( $\mu\text{g.L}^{-1}$ )
Al	5	200
Ba	10	700
Ca	100	-----
Mg	50	-----
Mn	0.1	500
Na	10	200 000
Sr	20	-----
V	0.1	-----
As	0.2	10
Cr	20	50
K	300	-----
Fe	300	300
Sb	0.2	5
Zn	10	300

**Table 5.** Water samples analysed following the described method (n = 5).

Element	Concentration $\mu\text{g.L}^{-1}$	Element	Concentrat. $\mu\text{g.L}^{-1}$
Al*	$0.85 \pm 0.02$	Fe*	$3.9 \pm 0.6$
As	$12.0 \pm 1.3$	Mg*	$9.70 \pm 1.4$
Ca*	$68.9 \pm 1.1$	Mn*	$1.36 \pm 0.02$
Cd	$29.6 \pm 5.7$	Na*	$1.46 \pm 0.04$
Co	$5.2 \pm 0.6$	Sb	$0.8 \pm 0.1$
K*	$1.45 \pm 0.5$	Zn*	$4.8 \pm 1.9$

\* Concentrations express in  $\text{mg.L}^{-1}$   
uncertainty express as  $\pm U(95\%)$

As shown in table 4 the detection limits vs. maximum contaminant level adopted by the Peruvian government and in table 5 the typical values analysed in a sample, the

method is suitable to be applied to water analysis.

#### 4. CONCLUSIONS

Results show that the method is appropriate for a complete view of trace element by  $k_0$  Based INAA.

The sensitivity for Fe and Cr are not good for the INAA, so it is recommended the use of radiochemical separation.

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