

IMPORTANCE OF THE NEUTRON ACTIVATION ANALYSIS FOR THE DETERMINATION OF ELEMENTS IN DIFFERENT ORGANIC MATERIALS

Maria J. A. Armelin¹ and Edson G. Moreira¹

¹Instituto de Pesquisas Energéticas e Nucleares (IPEN - CNEN/SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
marmelin@ipen.br
emoreira@ipen.br

ABSTRACT

Instrumental Neutron Activation Analysis (INAA) was the analytical technique used to determine the concentrations of As, Ba, Br, Ca, Ce, Cl, Co, Cr, Fe, La, K, Mg, Mn, Pr, Sb, Sm, V and Zn in the following materials: petroleum, rubber, plastics and petroleum coke. The precision of the results were mostly between 1 and 20%. The technique is non-destructive and fast for Cl, Cu, Mg and V analyses. For this reason, INAA showed to be a good option to be applied in organic matrices.

1. INTRODUCTION

The knowledge of element composition in materials such as petroleum and its derivatives is important, depending on where these materials will be used.

The term petroleum is used to describe a fossil fuel consisting of a mixture of organic chemical compounds such as saturated and aromatic hydrocarbons, polycyclic compounds and trace elements of inorganic origin that have been accumulated in underground reservoirs for thousands of years [1-3].

Due to the complexity of their composition there is no identical petroleum. Such differences in composition have influence on the properties of the refining technique and hence on the products that can be obtained. The percentage of inorganic salts in petroleum must be kept bellow certain limits for both production and refineries, so petroleum is subjected to dehydration and desalination processes [4].

In refineries, petroleum with excess salt affects distillation units, heaters and exchanges, leading to more frequent equipment replacement, due to corrosion, reduction in the efficiency of the catalysts and formation of deposits [3-4]. In this step, the analysis of the concentrations of the inorganic constituents present in petroleum samples can be important, since metal composition and content vary with the geographical location of the producing field [5].

Petroleum refining is done by distillation. According to the distillation temperatures, the different petroleum products are separated by means of openings made in the distillation tower. Some derivatives such as gas, gasoline, kerosene and others, leave the refinery ready to be marketed, going directly to distributors and consumers. Others derivatives such as naphtha, propene, lubricating oils and others, are raw materials for petrochemical industries,

responsible for the manufacture of thousands of products of daily consumption. For instance, naphtha gives rise to monomers and polymers which give origin to the most diverse plastic materials [6].

Since these obtained products will be used in different areas, with different specifications as to the purity of inorganic constituents, monitoring of the concentration of these elements in these materials is a necessary step to attest to their quality. Instrumental Neutron Activation Analysis (INAA) followed by gamma-ray spectrometry is an analytical method which may be advantageous in this monitoring step. This analytical method is non-destructive, so the analysis requires minimal sample handling and it is very sensitive to several elements [7-8].

In this case, it was proposed to study the best experimental conditions using INAA, to determine the concentrations of number of elements present in petroleum samples and some samples of petroleum sub-products such as: rubber, plastics and petroleum coke.

2. EXPERIMENTAL

2.1 Samples and treatment for the experiment

Samples were transferred to the laboratory, coming from different places. This study was not concerned with sampling because the main objective was to show the performance of the method for these types of matrices.

The following samples were considered: 1) two distinct samples of petroleum, liquid – aqueous petroleum extract; 2) a sample of pulverized petroleum coke; 3) two separate samples of “rubber”, derived from petroleum, as a pasty solid; 4) three distinct plastic samples in the form of granules.

Samples were weighed into polyethylene bags suitable for irradiation. In the case of liquid petroleum, a strip of Whatman filter paper was inserted into the bag as a support for the sample. Two aliquots were weighed, and the masses were approximately 500 mg. All other samples were weighed directly into the bag and the aliquots ranged from 80 to 200 mg. The “blank” were prepared: 1) polyethylene bag with filter paper strip; 2) only the polyethylene bag. Aliquots of the IAEA Soil 7 reference material, of the order of 60 mg, were also weighed.

2.2 Preparation of standards

Certified standard solutions (Spex Certiprep) of As, Ba, Br, Ca, Ce, Cl, Cr, Co, Cu, Fe, K, La, Mg, Mn, Pr, Sb, Sm, V and Zn were used to prepare elemental synthetic standards. Aliquots (50 – 100 µL) were pipetted onto small sheets of analytical filter paper (Whatman N° 42) for irradiation. After drying, these filter papers were placed into polyethylene bags.

2.3 Irradiation and counting

Two types of irradiation were carried out at the IEA-R1 nuclear research reactor. In one case, the sample, IAEA Soil 7 and standards (Ba, Cl, Cu, Mg, Mn and V) were irradiated together in Nylon container for 30 s and after a decay time of 2 min the ^{38}Cl , ^{66}Cu , ^{27}Mg and ^{52}V

radionuclides (1642, 1039, 1013 and 1434 keV, respectively) were measured in sample, IAEA Soil 7 and in standards. ^{139}Ba and ^{56}Mn radionuclides (166 and 846 keV, respectively) were measured after 90 min of decay time. In the second irradiation, the samples, IAEA Soil 7 and standards (As, Br, Ca, Ce, Cr, Co, K, La, Pr, Sb, Sm, and Zn) were irradiated together in an aluminum container for 8 h. The ^{76}As , ^{82}Br , ^{42}K , ^{140}La , ^{142}Pr and ^{153}Sm (559, 776, 1525, 1596, 1575 and 103 keV, respectively) were measured after 3 days of decay time, while ^{47}Ca , ^{141}Ce , ^{60}Co , ^{122}Sb and ^{65}Zn (1298, 145, 1332, 564 and 1115 keV, respectively) were measured after, at least, 7 days of decay time. The IAEA Soil 7 was always irradiated along samples and standards to monitor the quality of the synthetic standards.

The equipment used to measure the gamma-radiation was a Canberra model GX2020 high purity Ge detector, coupled to a model 1510 Integrated Signal Processor and MCA System 100, both from Canberra. The detector used had a resolution (FWHM) of 1.1 keV for the 122 keV gamma rays of ^{57}Co and 2,2 keV for 1332 keV gamma-ray of ^{60}Co .

2.4 Detection Limit

The limits of detection (LD) were determined according to IUPAC [9]. For the calculation of the LDs the following expression was used:

$$LD = \frac{3\sqrt{BG}}{LT} \quad (1)$$

Where, BG is the background radiation and LT is the live counting time.

Background radiation (BG) values were obtained directly from the data emitted in the gamma radiation spectrum of the sample, for the photopic of the element of interest. The LD value represents the counting rate corresponding to the minimum detectable mass.

In INAA, the irradiation, decay and measurement conditions as well as the interference situation, including background radiation and the Compton effect can influence the values of the detection limits.

3. RESULTS AND DISCUSSION

The results for the concentration of elements were calculated using the comparative method. Table 1 shows the results obtained for the concentrations of the elements in the petroleum samples, with the uncertainty resulting from count statistics. In cases where the element could not be detected, the Detection Limit (LD) was calculated for that sample under the experimental conditions in which the analysis occurred.

Table 1: Results of the element concentrations in the petroleum samples with the uncertainties resulting from the counting statistics.

Petroleum 1		Petroleum 2	
Element (unit)	Concentration \pm uncertainty	Element (unit)	Concentration \pm uncertainty
Br ($\mu\text{g}/\text{kg}$)	724 ± 13	Br (mg/kg)	79.7 ± 0.2
Cl (mg/kg)	101 ± 9	Cl (g/kg)	19.1 ± 0.5
Cu (mg/kg)	< 5	Cu, (mg/kg)	< 57
Fe (mg/kg)	18.9 ± 0.6	Fe (mg/kg)	< 13
K (mg/kg)	4.6 ± 1.6	K (mg/kg)	< 323
Mg (mg/kg)	< 119	Mg (mg/kg)	< 645
Mn ($\mu\text{g}/\text{kg}$)	69 ± 9	Mn ($\mu\text{g}/\text{kg}$)	277 ± 75
Na (g/kg)	12.5 ± 0.7	Na, (mg/kg)	177 ± 10
V (mg/kg)	30.3 ± 0.7	V (mg/kg)	20.1 ± 0.6
Zn (mg/kg)	4.9 ± 0.7	Zn (mg/kg)	15 ± 2

< indicates less than the Detection Limit

The elements: Br, Cl and Mn were found in the “blank”. In these cases, the concentrations of these elements were subtracted to obtain the real concentration in the sample.

The determination of Cu and Mg in Petroleum 1 was influenced by the high concentration of Na present in the sample, whereas in Petroleum 2 the high concentrations of Cl and Zn present in this sample interfered in the determinations of Cu, Fe, K and Mg. According to Speight [1], the elements V, Ni, Fe and Cu, if present in petroleum, even in trace amounts, can be deleterious to refining processes, especially processes in which catalysts are used. INAA is a very sensitive method for the determination of V, Cl and Cu, in addition, it is quite fast for these elements, the result can be obtained in about 15 min.

The results of the element concentrations present on the rubber samples, plastic samples and petroleum coke sample, with uncertainties resulting from the counting statistic, are shown in Tables 2, 3 and 4, respectively.

Table 2: Results of the element concentrations in the rubber samples with the uncertainties resulting from the counting statistics.

Element (unity)	Concentration \pm uncertainty	
	Rubber 1	Rubber 2
Ba (mg/kg)	3.7 ± 0.7	161 ± 2
Br ($\mu\text{g}/\text{kg}$)	377 ± 21	1186 ± 100
Cl (mg/kg)	10.8 ± 0.7	126 ± 6
Cr ($\mu\text{g}/\text{kg}$)	995 ± 169	1124 ± 105
Fe (mg/kg)	33 ± 11	3022 ± 102
K (mg/kg)	< 3	9 ± 3
Mn (mg/kg)	0.47 ± 0.01	19.7 ± 0.2
Sb ($\mu\text{g}/\text{kg}$)	17 ± 3	42 ± 5
Zn (mg/kg)	36 ± 2	4.3 ± 0.5

< indicates less than the Detection Limit

Table 3: Results of the element concentrations in the plastic samples with the uncertainty resulting from the counting statistics.

Element (mg/kg)	Concentration \pm uncertainty		
	Plastic 1	Plastic 2	Plastic 3
Ba	0.9 ± 0.3	2820 ± 93	< 2
Br	1.64 ± 0.08	1696 ± 161	18.8 ± 0.9
Cl	52 ± 2	< 85	35 ± 4
Cr	0.83 ± 0.07	122 ± 4	8.2 ± 0.3
Fe	15 ± 4	589 ± 35	48 ± 5
K	6.2 ± 0.6	233 ± 85	5 ± 2
Mn	0.80 ± 0.01	27.9 ± 0.5	933 ± 14
Sb	0.113 ± 0.002	360 ± 3	6.80 ± 0.04
Zn	91 ± 19	2148 ± 68	81 ± 3

< indicates less than the Detection Limit

In the case of petroleum coke, it was considered important to determine the lanthanide elements. For the results presented in Tables 2, 3, and 4, the “blank” was not discounted because these values were insignificant when compared to the concentrations present in the samples.

Table 4: Results of the element concentrations in the petroleum coke with the uncertainties resulting from the counting statistics.

Element (unity)	Concentration \pm uncertainty
As ($\mu\text{g}/\text{kg}$)	138 ± 4
Ba (mg/kg)	2.1 ± 0.7
Br ($\mu\text{g}/\text{kg}$)	1108 ± 23
Ca (mg/kg)	< 218
Ce ($\mu\text{g}/\text{kg}$)	< 51
Cl (mg/kg)	54 ± 3
Co (mg/kg)	8.7 ± 0.2
Cr ($\mu\text{g}/\text{kg}$)	356 ± 43
Fe (mg/kg)	14 ± 5
La ($\mu\text{g}/\text{kg}$)	217 ± 5
Mg (mg/kg)	< 131
Mn ($\mu\text{g}/\text{kg}$)	183 ± 16
Pr ($\mu\text{g}/\text{kg}$)	< 105
Sb ($\mu\text{g}/\text{kg}$)	72 ± 6
Sm ($\mu\text{g}/\text{kg}$)	0.8 ± 0.2
V (mg/kg)	176 ± 7
Zn (mg/kg)	5 ± 1

< indicates less than the Detection Limit

Based on the results, the precision of the method for most elements was between 1 and 20%, except for Fe and Ba in some samples. This precision performance is quite acceptable. The sensitivity of the method to Fe and Ba is relatively low; in addition to that the concentration of these elements in some sample was low. It was possible to determine elements in very low concentrations in petroleum coke, such as: As, Sb and some lanthanides.

4. CONCLUSIONS

INAA showed to be a good option for the quantitative analysis of several elements of industrial concern present in organic matrices. The method is non-destructive, i.e. for its application it is not required complex sample preparations such as digestion. This fact is important because if sample preparation is required, significant losses of organometallic complexes may occur, as well as contamination of the sample caused by the environment or reagents used.

ACKNOWLEDGMENTS

The authors wish to thank the companies that provided the samples and Brazilian National Energy Commission (CNEN).

REFERENCES

1. J. G. SPEIGHT, *Handbook of Petroleum Analysis*, John Wiley and Sons, New Jersey, 2001.
2. R. Q. F. CHIMIN, “*Estudo da Evolução de Cloretos no Processo de Destilação de Petróleo*”, Dissertação de Mestrado, Universidade Federal do Espírito Santo, Brasil, 2013.
3. M. O. Souza, K. P. RAINHA, E. V. R. CASTRO, M. T. W. D. CARNEIRO, R. Q. FERREIRA, “Análise exploratória das concentrações dos metais Na, Ca, Mg, Sr e Fe em extrato aquoso de petróleo, determinados por ICP OES, após otimização empregando planejamento de experimentos”, *Química Nova* Vol. **38-7**, pp. 980-986 (2015).
4. M. K. MORIGAKI, R. Q. F. CHIMIN, C. M. S. SAD, P. R. FILGUEIRAS, E. V. R. CASTRO, J. C. M. DIAS, “Salinidade em petróleo bruto: otimização de metodologia e proposta de um novo método para extração de sais de petróleo”, *Química Nova* Vol. **33-3**, pp. 607-612 (2010).
5. L. D. LACERDA, R. V. MARINS, “Geoquímica de sedimentos e o monitoramento de metais na plataforma continental nordeste oriental do Brasil”, *Geochimica Brasiliensis*, Vol. **20 -1**, pp. 123-132 (2006).
6. “Petróleo e seus derivados” (<https://www.ebah.com.br/content/ABAAAAX-QAC/petroleo-seusderivados>), Accessed on 07/02/2019.
7. D. DE SOETE, R. GIJBELS, J. HOSTE, J., *Neutron Activation Analysis*, John Wiley and Sons, New York, 1972
8. M. J. A. ARMELIN, M. SAIKI, “INAA applied to the multielemental characterization of a sedimentary column: a contribution to oceanographic studies”, *Journal of Radioanalytical and Nuclear Chemistry*, Vol. **28-2** pp. 91-94 (2009).

9. L. A. Currie, “Nomenclature in evaluation of analytical methods including detection and quantification capabilities – International Union of Pure and Applied chemistry (IUPAC Recommendations 1995)”, *Pure and Applied Chemistry*, Vol. **67-10** pp. 1669-1723 (1995).