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Boron Determination in Polyethylene by EDXRF

M. O. Scapin[1], M. A. Scapin[2] and M. E. B. Cotrim[2]

[1] *marianedeoliveirascapin@gmail.com, Faculdades Oswaldo Cruz (FOC) - CEP 01151-000, São Paulo – SP - Brasil*
[2] *mascapin@ipen.br, Instituto de Pesquisas Energéticas e Nucleares IPEN-CNEN - CEP 05508-000, São Paulo – SP - Brasil*

1. Introduction

Borated polyethylene is used as a neutron shielding material that is commercially available [1]. This material is made by boron compounds incorporation, such as boric acid, boron carbide, among others, into a high-density polyethylene mixture. The boron content 1 – 30% (wt. %) [2]. Material characterization can be by morphological analyses, using scanning electron microscopy and mechanical, thermal and neutron attenuation tests [2].

Energy dispersive X-ray fluorescence spectrometry (EDXRF) is an instrumental analytical technique that permits the identification and quantification of major and minor constituent elements simultaneously in different types of samples (metallic, geological, environmental, nuclear, forensic and others) [3-6]. However, it does not apply to hydrogen, helium and lithium elements because fluorescence does not occur. It also does not apply to beryllium, boron, carbon, nitrogen, oxygen, fluorine and neon elements due to the low-sensitivity of the detector. But using indirect methods such as coherent scattering (characteristic energy of the X-ray tube) or incoherent scattering (characteristic energy of the Compton Effect), it is possible to quantify the mentioned elements [7].

This study aimed to evaluate EDXRF performance to quantify boron content in polyethylene samples using the Rh-Kα-Compton line (ROI ≡ 18.0-20.0 keV). Therefore, provide a fast, non-destructive and low-cost methodology to collaborate with borated polyethylene characterization tests.

2. Methodology

The tests were conducted using a Banbury-type rotor (circa 80 rpm). The sodium tetraborate PA ($Na_2B_4O_7$) was incorporated within polyethylene in proportions of 10.0, 7.8, 5.9, 1.9, and 0.4 (wt.%). Subsequently, prepared samples with the dimensions: width ≈ 25 x 25 mm; height ≈ 3 mm. The boron (B) contents for each sample and their respective denominations showed in Table I.

Table I: Boron content incorporated in polyethylene.

Sample/Element	Bco	A1	A2	A3	A4	A5	R
B (%)	---	4.7±0.1	3.7±0.1	2.8±0.1	0.9±0.1	0.20±0.02	4.7±0.1

The A1, A2, A3, A4 and A5 samples were used for the calibration curve. The blank sample (Bco) was used to calculate limit detection (LD) and limit quantification (LoQ). The reference sample (R) was used to evaluate precision in terms of relative standard deviation (RSD %) and accuracy in terms of relative error (RE %). The acceptability criterion for RSD% was calculated by Horwitz equation (HOr) and ER% by Z-Score test [8].

Data acquisition was performed using a Shimadzu Co. model ED 720 Energy Dispersive X-ray Fluorescence Spectrometer (EDXRF); X-ray tube with an Rh anode (250 W), Si (Li) semiconductor detector, cooled with Liquid N_2, and a 10-mm collimator. The instrumental set up were: voltage 15 kV, auto adjustable current of max. 1 mA and vacuum atmosphere between (30-10 Pa). For each sample, 2048 points were measured, from 0.00 to 40.96 keV, with a 0.01 keV interval, exposure time for 20 s and detector "dead time" (DT) 39%. The measurements were carried out with replicates three.

Under established conditions, count rate acquisition (cps mA^{-1}) for boron (B) element was carried out using the Rh-Kα-Compton line (ROI ≡ 18.0-20.0 keV). Range of interest (ROI) adjustment was performed by coupled software EDXRF using Gauss fit single peak. Thus, the concentration (Table I) was related to count rates and was obtaining a calibration curve. Curve fitting was performed using the least squares method.

3. Results and Discussion

Fig. 1 shows the calibration curve (cps μA^{-1} versus content) using A1, A2, A3, A4 and A5 samples adjusted by the least squares method. The correlation coefficient (R^2) is adequate (≈ 0.95). The recovery varied between 0.1 and 0.6%, proving to be adequate.

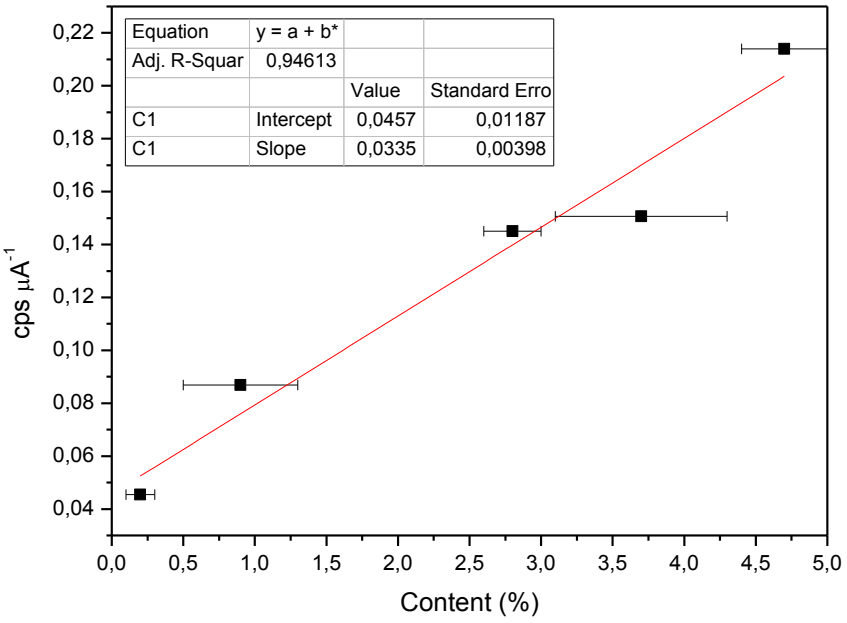

Figure 1: Calibration curve for boron in polyethylene determination.

The following parameters are presented in Table II: concentration and standard deviation ($\bar{x} \pm \sigma$) for the

nominal boron content (B) and determined in the reference sample (R); relative standard deviation (DPR%) and the calculated value for acceptability (HOr); relative error (ER%) and Z-Score value, calculated for acceptability; limit of detection (LD) and quantification (LoQ).

Table II – Parameters determined for the boron element (B).

	R (nominal)	R (determined)						
Element	($\bar{x}\pm\sigma$)	($\bar{x}\pm\sigma$)	DPR%	HOr	ER%	Z-Score	LD	LoQ
B (%)	4.7±0.1	4.8±0.1	1.9	1.0	2.6	0.9	0.2	0.7

$\bar{x}$ = average of measurements in triplicate; σ = standard deviation.

The results show that the precision in terms of DPR% is satisfactory (1.9%), since the HOr value (1.0) is < 2 [8]. The accuracy evaluated in terms of ER% (2.6%) is also satisfactory, as the Z-Score (0.9) is < 1 [8].

The detection (LD=0.2%) and quantification (LoQ=0.7%) limits are sufficient for the boron determination in the established working range.

4. Conclusions

The study allowed us to verify that the EDXRF technique applying the indirect method, that is, the Rh-Ka-Compton line, is precise and accurate for quantifying boron in polyethylene samples. Furthermore, not requiring prior chemical treatment when preparing samples (direct and non-destructive tests) allows samples to be preserved. The methodology is considerably promising for collaborating with the characterization of borated polyethylene. Future studies will allow the quantification of other elements of interest in this material.

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