



Application of WDXRF and EDXRF Spectrometry for Major and Minor Elemental Analysis in Oil Sludge by Fundamental Parameter Algorithm

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1. Introduction

Oily sludge is a waste product generated by the oil industry, comprised of organic compounds (predominantly heavy hydrocarbons), inorganic compounds (sediments and metallic/non-metallic oxides), water and oil processing residues [1]. In addition, radionuclides from the ²³⁸U and ²³²Th decay chains (²²⁶Ra, ²²⁸Ra, ²¹⁰Pb, and others) are found in oily sludge, warranting its classification as Naturally occurring Radioactive Material (NORM) [2].

The oil industry generates approximately 60 million tons of oily sludge annually [3]. In Brazil, adherence to CNEN Standard NN 8.01 governs the storage of this material. The escalating generation of oil sludge mandates additional disposal sites every year, incurring substantial costs. Furthermore, the storage and transportation of oily sludge pose significant environmental contamination risks. The development of a methodology for analysis and classification of oily sludge is pivotal for compliant management and facilitating alternative treatment and reuse options [4].

X-ray fluorescence spectrometry is an analytical technique with potential for classifying oily sludge. It enables direct, non-destructive analysis, reducing waste generation and analysis costs. Another advantage is the streamlined sample treatment process [5], contrasting with other techniques such as Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Atomic Absorption Spectrometry (AAS), and others.

In this study wavelength dispersive x-ray fluorescence (WDXRF) and energy dispersive x-ray fluorescence (EDXRF) techniques were compared to evaluate their performance in analysis of major (1-100%) and minor (0.01-0.99%) constituents in oily sludge samples. Quantification of elements is accomplished using the Fundamental Parameters Algorithm (FP) [6].

2. Methodology

Sampling: Four samples of oily sludge were collected from the Campos Basin (Macaé – Rio de Janeiro). Analyses of both dry and wet samples followed the outlined procedure; **Wet samples:** 3 g of each previously homogenized sample were added to an *XRF X-CellTM Sample Cups* – Spex-31 mm, using polypropylene film (SPEX *SamplePrep*, polypropylene 3520, 5 µm thick) on the surface. The samples were manually compressed with cellulose supports against the polypropylene film; **Dry samples:** 20 g were homogeneized and dried according to ASTM D482 (Standard Test Method for Ash and Petroleum Products) [7]. Subsequently, 5 g aliquots were added in an aluminum holder (± 95cm³) and compacted in a hydraulic press (H. G. Herzog, model HTP40) with 147 kN for 20 seconds. Under these conditions, pellets of approximately 35 mm in diameter and 3 mm thick were obtained.

Both wet and dry samples were analyzed by WDXRF and EDXRF under the following experimental conditions:

WDXRF: RIGAKU Co spectrometer, model RIX 3000, Rh tube (50 kV x 50 mA), scintillation detector (NaI/Tl) and proportional, air and vacuum atmospheres. Data acquisition was achieved using the 2-theta scan model ^[8].

EDXRF: Shimadzu Co spectrometer, model EDX-720, Rh tube (50kv x 1 mA) with Si(Li) detector cooled with liquid nitrogen, 5mm collimator, air and vacuum atmospheres.

Validation: Five replicate measurements were performed using pressed powdered certified reference materials (CRMs) 2711 (Montana soil) and 2709 (San Joaquin soil) from the National Institute of Standards and Technology (NIST). The following parameters were evaluated: precision in terms of relative standard deviation (%RSD) and acceptability criteria, Horwitz ratio (HO_R); accuracy in terms of relative error (%RE) and acceptability criteria, Z-score test (Z) ^[9]. The Limit of Quantification was determined using the equation 1 ^[10].

$$L_0Q = 2 * \sqrt{\sum_{m=1}^n \frac{(c_m - \bar{c})^2}{n - 1}} \quad (1)$$

3. Results and Discussion

WDXRF: Precision in terms of %RSD was satisfactory for the elements Si, Al, K, Fe, S and Ti (major constituents) and Zr, Rb, Sr, Mn, Zn and Pb (minor constituents), as HO_R values were ≤ 2 for both CRMs (NIST 2709 and 2711). Accuracy in terms of %RE was satisfactory for the elements Si, Al, K, Fe, S, Ti, P and Ca (major constituents) and Ni, Cu, As and V, as the Z-score was ≤ 2 for both CRMs (NIST 2709 and 2711). The limits of quantification are sufficient for the determination of major constituents (0.3 - 4.0%) and minor constituents (1 - 10 µg/g).

EDXRF: Precision in terms of %RSD was satisfactory for the elements Si, Al, K, Fe and Ca (major constituents) and Zr, Rb, Sr, Cr, Mn, Zn, Ni and Cu (minor constituents), as HO_R values were ≤ 2 for both CRMs (NIST 2709 and 2711). Accuracy in terms of %RE was satisfactory for the elements Si, Al, K, Fe, S, Ti, P and Ca (major constituents) and Zr, Rb, Sr, Cr, Mn, Zn, Ni, Cu, V and Ba as the Z-score was ≤ 2 for both CRMs (NIST 2709 and 2711). The limits of quantification are sufficient for the determination of major constituents (0.1 - 4.0%) and minor constituents (58 - 244 µg/g).

The results in terms of precision, accuracy and limit of quantification for the MRCs revealed that the fundamental parameters algorithm is suitable for the analysis of major and minor constituents for WDXRF and EDXRF techniques.

Samples: The concentration of the elements analyzed by WDXRF and EDXRF were compared using Principal Component Analysis (PCA). A matrix was constructed considering sixteen cases (eight wet samples and eight dry samples) and seventeen variables (Si, Al, K, Fe, S, Ti, P and Ca - major constituents; Rb, Sr, Mn, Ni, Pb, Cr, Zr, Zn and Ba - minor constituents). The results were clustered according to their variance. The PCA revealed the following correlation factors: factor 1 = 34% and factor 2 = 14% (Figure 1).

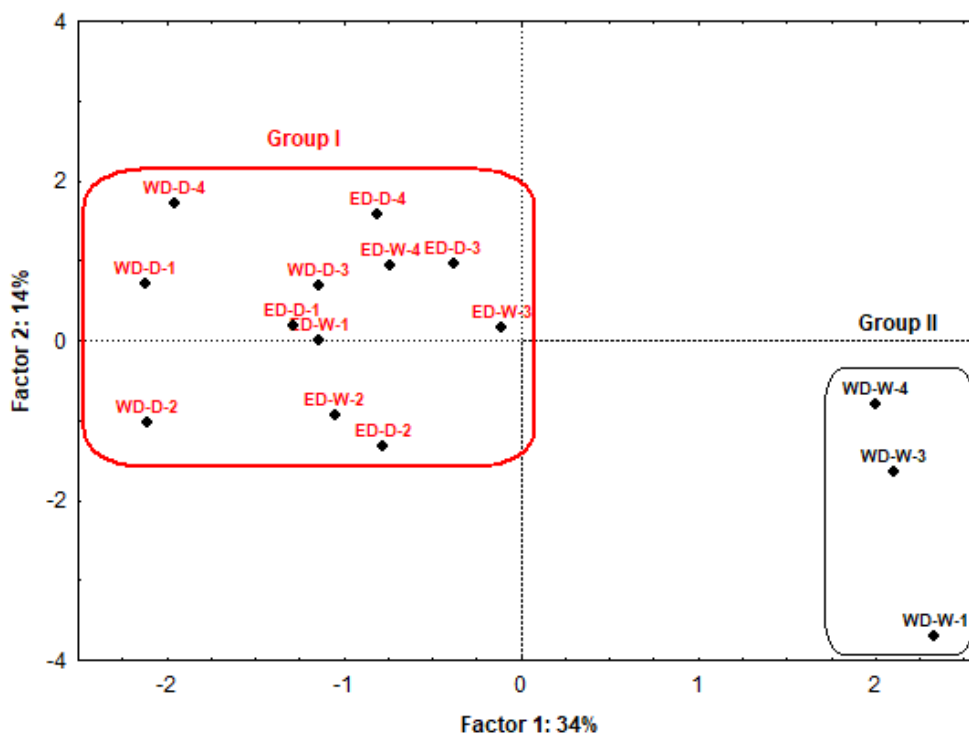


Figure 1: Principal component analysis (PCA), correlating the results obtained by WDXRF and EDXRF for the dry and wet samples. WD-W = wet samples analyzed by WDXRF; WD-D = dry samples analyzed by WDXRF; ED-W = wet samples analyzed by EDXRF; ED-D = dry samples analyzed by EDXRF.

The PCA produced two distinct groups. Group I: dry and wet samples analyzed by EDXRF and dry samples analyzed by WDXRF. Group II: wet samples analyzed by WDXRF. The results obtained for the dry samples analyzed by WDXRF were statistically similar to the results for the analyses of the dry and wet samples analyzed by EDXRF. This indicates that sample preparation influenced the results of the WDXRF analyses but had no significant influence on the results obtained by EDXRF. Furthermore, the samples in Group I were similar in composition, so it is reasonable that the samples were grouped together. The wet samples analyzed by WDXRF (Group II) were not statistically similar to the dry samples analyzed by WDXRF. This suggests that sample preparation is required for WDXRF analysis.

Therefore, it is preferable to analyze oily sludge samples by EDXRF, as it is a cheaper technique than WDXRF, and the results are statistically the same for wet and dry samples. This behavior indicates that sample preparation had no significant influence on EDXRF analysis, enabling the development of a methodology for direct determination.

4. Conclusions

The results revealed that the fundamental parameters algorithm is satisfactory for analyzing major and minor elements in oil sludge. The drying process statistically influenced the results obtained through WDXRF. In contrast, the results obtained via EDXRF showed minimal impact from the drying process, thus facilitating the development of a methodology for the direct determination of composition without the need for preliminary treatment. Future endeavors will involve comparing this direct determination methodology for elements with other analytical techniques.

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