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Application of WDXRF and EDXRF Spectrometry for Chemical Characterization in Oil Sludge using the Fundamental Parameter Algorithm

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Abstract: Oil sludge is a waste product generated by the oil industry, comprising organic substances (primarily long-chain polyaromatic, aromatic, and aliphatic hydrocarbons), inorganic compounds (such as sediments and metallic and non-metallic oxides), water, and oil processing residues. Radionuclides from the ^{238}U and ^{232}Th decay chains can be present in oil sludge, which justifies its classification as naturally occurring radioactive material (NORM). The oil industry produces approximately 60 million tons of oil sludge annually. Given the continuous generation of this waste, the development of additional storage sites will be necessary, incurring substantial costs. Furthermore, the storage and transportation of oil sludge pose significant environmental contamination risks. Due to its complex and heterogeneous composition, establishing a standardized methodology for classifying oil sludge presents considerable challenges. The development of an effective methodology for the analysis and classification of oil sludge is essential for proper waste management, as well as for facilitating the creation of treatment and reuse alternatives. X-ray fluorescence spectrometry (XRF) emerges as a promising analytical technique for classifying oil sludge, enabling direct, non-destructive analysis, thereby reducing both waste and analysis costs. In this study, wavelength dispersive X-ray fluorescence (WDXRF) and energy dispersive X-ray fluorescence (EDXRF) techniques were compared to assess their performance in analyzing the major (1–100%) and minor (0.01–0.99%) constituents in oil sludge samples. The elements were quantified using the Fundamental Parameters (FP) algorithm. The objective of this work is to develop a methodology for determining both major and minor elements in oil sludge, contributing to a more effective management of this waste.

Keywords: Oil Sludge, WDXRF, EDXRF, Fundamental Parameters Algorithm.

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Aplicação das Espectrometrias WDXRF e EDXRF para Caracterização de Borra de Petróleo Através do Algoritmo dos Parâmetros Fundamentais

Resumo: A borra oleosa é um resíduo gerado pela indústria petrolífera, composto por substâncias orgânicas (principalmente hidrocarbonetos poliaromáticos, aromáticos e alifáticos de cadeia longa), compostos inorgânicos (sedimentos e óxidos metálicos e não metálicos), água e resíduos do processamento do petróleo. Radionuclídeos das cadeias de decaimento do ^{238}U e ^{232}Th podem ser encontrados na borra oleosa, o que justifica a sua classificação como material radioativo de ocorrência natural (NORM). A indústria petrolífera gera, anualmente, aproximadamente 60 milhões de toneladas de borra oleosa. Com a produção contínua deste resíduo, será necessário o desenvolvimento de novos depósitos para seu armazenamento adequado, implicando custos substanciais. Além disso, o armazenamento e o transporte da borra oleosa representam riscos significativos de contaminação ambiental. Devido à sua composição complexa e diversificada, estabelecer uma metodologia única para a classificação das borras oleosas apresenta desafios consideráveis. O desenvolvimento de uma metodologia eficaz para a análise e classificação da borra oleosa é crucial para uma gestão adequada, além de facilitar o desenvolvimento de alternativas para tratamento e reutilização. A espectrometria de fluorescência de raios X (XRF) se destaca como uma técnica analítica promissora para a classificação das borras oleosas, permitindo uma análise direta e não destrutiva, o que resulta na redução de resíduos e custos de análise. Neste estudo, as técnicas de fluorescência de raios X por dispersão de comprimento de onda (WDXRF) e de fluorescência de raios X por dispersão de energia (EDXRF) foram comparadas para avaliar seu desempenho na análise dos constituintes majoritários (1–100%) e minoritários (0,01–0,99%) em amostras de borra oleosa. A quantificação dos elementos foi realizada por meio do algoritmo de Parâmetros Fundamentais (PF). O objetivo deste trabalho é desenvolver uma metodologia para determinar os elementos majoritários e minoritários presentes na borra oleosa, com o intuito de possibilitar uma gestão mais eficiente deste resíduo.

Palavras-chave: Borra Oleosa, WDXRF, EDXRF, Método dos Parâmetros Fundamentais.

1. INTRODUCTION

Oil sludge is a complex waste product comprised of hydrocarbons (40 to 60%), water (30 to 90%), sediments and heavy metals (5 to 40%) [1], including radionuclides from the uranium (^{238}U) and thorium (^{232}Th) decay chains, mainly radium (^{226}Ra and ^{228}Ra) and lead (^{210}Pb) isotopes, therefore being classified as Naturally Occurring Radioactive Material (NORM) [2]. The hydrocarbons present in oil sludge are mainly aromatic (benzenes, naphthalenes and xylenes) and long-chain aliphatic compounds.

Every year, approximately 60 million tons of oil sludge are generated by the oil industry globally [3]. According to Brazilian legislation, all NORM waste generated during oil extraction must be removed from platforms and disposed of onshore. Therefore, managing NORM waste is considered crucial, as improper handling, treatment, and/or disposal can lead to negative consequences for living beings and the environment. As the accumulation of this waste continues to increase yearly, more facilities with the necessary specifications will be required to ensure its safe storage.

Given the growing need to manage oily sludge effectively, it is essential to conduct a thorough chemical characterization of this waste. This requires developing analytical methodologies to accurately quantify the various components of oily sludge. Several methods for treating radioactive oil sludge are being considered globally, as the accumulation of large quantities of waste, even with low levels of radioactivity but significant hazardous potential, incurs high costs for the industry [4-10]. Published studies have focused on mitigating accidents and proposing treatments for the final disposal of this material [11]. However, these studies are still insufficient and lack systematic analytical methodologies for a full characterization of the components that form the oil sludge.

Therefore, this study aims to develop an analytical methodology using wavelength dispersive X-ray fluorescence spectrometry (WDXRF) and energy dispersive X-ray fluorescence spectrometry (EDXRF) to quantify major (concentrations in % m/m) and minor (concentrations from 0.01% to 0.99%) constituents in oil sludge samples.

In EDXRF, the sample is irradiated by a primary beam coming from the X-ray tube, a component of the equipment. The secondary beam, coming from the sample, is measured by a Si/Li semiconductor detector. The detector is capable of identifying and separating the characteristic energies of the elements present in the sample [12]. In EDXRF, the spectrum is acquired simultaneously, allowing immediate elemental analysis of a given sample.

In WDXRF, the sample is irradiated by a primary beam from the X-ray tube. An analyzer crystal, moved by a goniometer, diffracts the wavelengths of the secondary beam at a specific angle, according to Bragg's law [13]. This system reduces spectral interference, making it possible to select specific spectral regions [14].

The following detectors are used in WDXRF: scintillation counter (SC) and proportional counter (PC). These detectors reduce the effects of overlapping spectral lines, increasing the sensitivity of the technique and providing greater resolution in data acquisition. WDXRF spectra are acquired point-by-point, resulting in longer analysis time [15].

As an advantage, WDXRF analyses present reduced spectral interference, due to the high resolution provided by the crystal/goniometer system, enabling a precise selection of wavelengths of interest [12]. Additionally, the equipment can be configured with filters to suppress interference and intensify the signal of interest. The use of various analyzing crystals further allow the selection of specific spectrum regions, tailoring the analysis to specific applications. However, these advanced optical components contribute to the relatively higher cost of WDXRF compared to EDXRF.

The purpose is to compare both techniques in terms of their efficiency and effectiveness in the characterization of oily sludge. Additionally, this approach offers reduced costs, and is environmentally friendly, as it aims to minimize waste production in the analytical process.

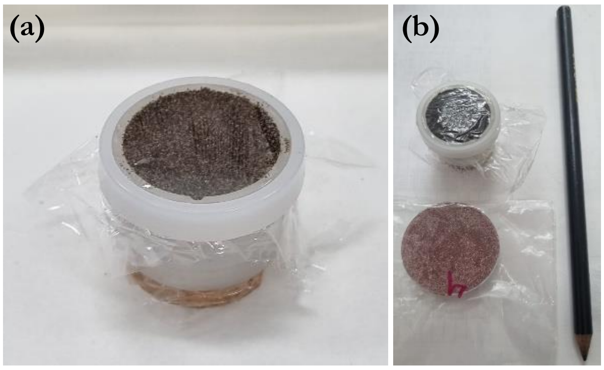
2. MATERIALS AND METHODS

2.1. Sample preparation

Four samples of oil sludge were collected from the Campos Basin (Macaé – Rio de Janeiro). To evaluate the influence of sample preparation on the method's performance, the four samples were analyzed in wet and dry conditions. Analyses of both dry and wet samples followed the outlined procedure:

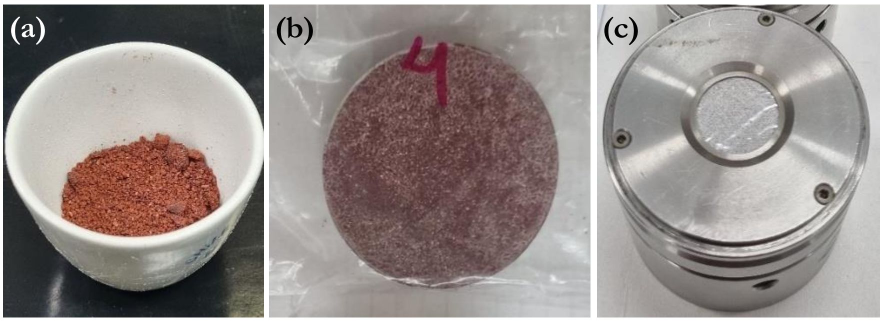
Wet samples (*as received*): 3.0000 ± 0.0001 g of each previously homogenized sample were added to an *XRF X-Cell*^{TM} *Sample Cups* – Spex-31 mm, using polypropylene film (SPEX *SamplePrep*, polypropylene 3520, 5 µm thick) on the surface. On the posterior side of the sample cup, cellulose supports were used to compress the samples against the polypropylene film. The samples obtained were analyzed by WDXRF and EDXRF.

Figure 1: Wet sample of oil sludge at the *XRF X-Cell*^{TM} *Sample Cups* – Spex-31 mm (a). Pellet made with dried sample and a wet sample of oil sludge at the *XRF X-Cell*^{TM} *Sample Cups* – Spex-31 mm (b). Source: Pinto, A. L. M. (2024).



Dry samples: 20.0000 ± 0.0001 g were homogenized and dried according to ASTM D482 (Standard Test Method for Ash and Petroleum Products) [16]. Subsequently, 5.0000 ± 0.0001 g aliquots were added in an aluminum holder (approximately 9.5 cm^3) 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. One of the dried samples to be analyzed by WDXRF and EDXRF is presented in Figure 2.

Figure 2: Dried sample of oil sludge (a). Pellet made with dried sample (b). Pellet at the sample holder for XRF (c). Source: Pinto, A. L. M. (2024).



2.2. Instrumental conditions

Both wet and dried samples were analyzed by WDXRF on a RIGAKU Co. spectrometer, model RIX 3000, with a Rh tube, scintillation (NaI/Tl) and proportional detectors, under the following experimental conditions: 50 kV maximum acceleration, 50 mA current and with rotation. The wet samples were analyzed under atmospheric conditions, while the dried samples were analyzed in vacuum.

The presence of atmospheric air affects the results by scattering and attenuating the primary and secondary beams. The interference is particularly pronounced for elements with lower atomic numbers. As the atomic number decreases, the fluorescence yield becomes lower, resulting in low-energy radiation, characteristic of light elements, such as silicon. In contrast, elements with higher atomic number, like iron, emit characteristic radiation with higher energy, making the impact of atmospheric air less critical for the precision and accuracy of element determination. However, applying vacuum to the wet samples could induce the polypropylene film to rupture, consequently leading to internal contamination of the spectrometer .

Table 1 presents the diffraction crystals and detectors for each measurement condition.

Table 1: Measurement conditions for WDXRF analyses.

Measurement conditions	**Spectrum**	**Crystal Diffraction**	**Detector**
HV00	Ti - U	LiF (200)	SC
Na00	Na-Kα	RX-35	PC
Mg00	Mg-Kα	RX-35	PC
Al00	Al-Kα	PET	PC
Si00	Si-Kα	PET	PC
P00	P-Kα	GE	PC
S00	S-Kα	GE	PC
K00	K-Kα	GE	PC
Ca00	Ca-Kα	GE	PC

In the EDXRF analysis, the wet and dried samples were analyzed on a Shimadzu Co. spectrometer, model EDX-720, with a Rh tube (50kv x 1 mA), Si(Li) detector cooled with liquid nitrogen, 5 mm collimator and rotation. Regarding the analytical atmosphere, a protocol similar to that used in WDXRF analysis was followed: wet samples were analyzed under atmospheric air and the dried samples were analyzed under vacuum. The application of vacuum to the wet samples could compromise the integrity of the polypropylene, potentially causing its rupture and culminating in internal contamination of the spectrometer. Table 2 presents the measurement conditions.

Table 2: Measurement conditions for EDXRF analyses.

Measurement conditions	**Voltage (kV)**	**Filter**
Ti – U	50	-
Na – Sc	15	-
Rh – Cd	50	-
Zn – As, Pb	50	Ag

The certified reference material (CRM) 2711 (Montana soil) from the National Institute of Standards and Technology (NIST) was used to validate the methodology for the determination of the major (1–100%) and minor constituents (0.01–0.99%).

2.3. Fundamental Parameters Method

The Fundamental Parameters (FP) Method is a mathematical method that correlates the fluorescent intensity of chemical elements, obtained experimentally, with the theoretical intensity of chemical elements of known standards and defined concentrations. The theoretical intensity is obtained by applying a mathematical equation using software, which considers parameters such as the distribution of the primary beam (coming from the X-ray tube), the mass absorption coefficient, the photoelectric absorption coefficient, fluorescence yield, instrumental conditions, and equipment configuration [17].

The FP method involves two stages: calibration and composition determination [18]. In the calibration phase, the FP method equation is applied to predict the characteristic intensities using Certified Reference Materials (CRMs) in the calibration, considering the instrumental conditions and characteristics of the equipment used. In the composition determination stage, the element content is obtained with a 95% confidence level.

Correlating the theoretical intensity and that obtained experimentally, a sensitivity curve is constructed for the equipment, which allows the chemical composition of the sample of interest to be determined. This method allows the composition of samples without commercially available reference standards to be determined.

2.4. Methodology evaluation

The methodology developed was validated according to the parameters recommended in document DOQ-CGCRE-008 [19] from the National Institute of Metrology, Quality and Technology, INMETRO (*Instituto Nacional de Metrologia, Qualidade e Tecnologia*). The Horwitz equation is applied to assess the acceptability and precision of the proposed method, using HORRAT (HO_R) values. The HO_R values are obtained using the following equation (1):

$$HO_R = \frac{DPR_E}{DPR_H} \qquad (1)$$

DPR_E represents the relative standard deviation obtained experimentally and DPR_H the relative standard deviation obtained from the Horwitz equation, at the concentration of interest.

The relative error (RE) allows the accuracy of the method to be assessed. It is obtained using the following equation:

$$RE = \frac{X_{det} - X_{cert}}{X_{cert}} . 100 \qquad (2)$$

X_{det} is the arithmetic mean of the values obtained experimentally and X_{cert} is the value of the certified material.

The relative standard deviation (*RSD*) allows the precision of the proposed method to be assessed. It is calculated using the following equation:

$$RSD = \frac{\sigma}{x_D} . 100 \qquad (3)$$

x_D is the average of the values obtained experimentally and σ the standard deviation.

To evaluate the accuracy of the method, the normalized error (E_N) was applied, using the following equation (4):

$$E_N = \frac{x_D - x_C}{\sqrt{\sigma_D^2 + \sigma_C^2}} \qquad (4)$$

x_D is the average of the values obtained experimentally, σ_D^2 is the experimental variation, x_C is the value provided by the certified material and σ_C^2 is the variation value obtained for the reference material.

The limit of quantification (*LoQ*) indicates the smallest amount of the analyte identified in the sample [20]. It is obtained using the following equation (5):

$$L_0Q = 2 * \sqrt{\sum_{m=1}^{n} \frac{(c_m - \bar{c})^2}{n-1}} \qquad (5)$$

c_m is the measured value, $\bar{c}$ is the average of the number of measurements and n is the number of measurements.

2.5. Data analysis

The results acquired by WDXRF and EDXRF were compared using the Principal Component Analysis (PCA), performed with STATISTICA 7.0 software. Sixteen cases were considered in the matrix construction: four wet samples analyzed by WDXRF, four dry samples analyzed by WDXRF, four wet samples analyzed by EDXRF and four dry samples analyzed by EDXRF. Seventeen elements were also considered: Si, Al, K, Fe, S, Ti, P, Ca, Rb, Sr, Mn, Ni, Pb, Cr, Zr, Zn, and Ba.

3. RESULTS AND DISCUSSIONS

NIST 2711's certified reference material (CRM) was employed to validate the methodology applied in WDXRF and EDXRF analyses, ensuring alignment with the experimental conditions used for the samples. X-ray fluorescence spectrometry is a widely employed analytical technique for the analysis of geological samples [28-29]. Given its geological origin, as it is derived from oil residues, oil sludge can, therefore, be characterized using X-ray fluorescence spectrometry.

It is important to emphasize that the development of direct testing methodologies for the analysis of oil sludge is highly valuable, as it reduces sample preparation time, enhances analyst safety, and generates less waste, aligning with the principles of green chemistry. In the absence of specific Certified Reference Materials (CRMs) for oil sludge, the

NIST 2711 CRM can be utilized to validate the presence of the elements of interest in oil sludge through matrix similarity.

The results of the WDXRF analysis for the referred CRM are summarized in Table 3. The results indicate that precision in terms of RSD was satisfactory for the elements Si, Al, K, Fe, S, P, and Ca (significant constituents) and Zr and Ba (minor constituents), as HO_R values were ≤ 2. Accuracy in terms of RE% was satisfactory for the elements Si, K, Fe, and S (significant constituents). The limits of quantification are sufficient for the determination of major constituents (0.01–0.38%) and minor constituents (24.21–179.61 μg/g).

Table 3: Results achieved in the WDXRF validation for the NIST 2711 CRM. X Det. corresponds to the experimentally determined result and X Cert. the value of the certified reference material.

Element	X Det. ± σ	X Cert. ± σ	RSD%	E_N	Horwitz	RE%	LoQ
Si (%)	30.5 ± 1.5	30.4 ± 0.2	0.30	0.34	0.15	0.30	0.38
Al (%)	6.27 ± 0.31	6.53 ± 0.09	0.39	2.54	0.20	4.16	0.10
K (%)	2.46 ± 0.12	2.4 ± 0.1	0.28	0.09	0.14	0.28	0.02
Fe (%)	2.81 ± 0.14	2.9 ± 0.1	1.95	0.87	0.97	2.97	0.15
S (%)	0.050 ± 0.010	0.04 ± 0.01	4.05	0.80	1.01	8.54	0.01
P (%)	0.070 ± 0.010	0.09 ± 0.01	1.83	1.27	0.46	17.79	0.01
Ca (%)	3.00 ± 0.15	2.88 ± 0.08	0.31	1.40	0.15	4.12	0.07
Zr (μg g^{-1})	263 ± 13	230*	2.19	-	0.55	12.41	24.21
Rb (μg g^{-1})	123 ± 6	110*	8.58	-	2.15	10.28	38.54
Ba (μg g^{-1})	801 ± 40	726 ± 38	0.00	1.97	0.00	9.34	179.61

*Uncertainty values for zirconium (Zr) and rubidium (Rb) were not reported in the certificate of the reference material.

The results obtained by EDXRF, for the analysis of CRM NIST 2711, are presented in Table 4. The results indicate that precision in terms of RSD was satisfactory for the elements Si (significant constituent) and Zr, Rb, Sr, Mn, Zn, Cu, and Ba (minor constituents), as HO_R values were ≤ 2. Accuracy in terms of RE% was satisfactory for the elements Al, K, Fe, Ti, P, and Ca (significant constituents) and Sr, Mn, and Cu, as the E_N was ≤ 1. The limits of quantification are sufficient for the determination of significant constituents (0.06–1.37%) and minor constituents (44.72–384.19 μg/g).

Table 4: Results achieved in the EDXRF validation for the NIST 2711 CRM. X Det. corresponds to the experimentally determined result and X Cert. the value of the certified reference material.

Element	X Det. ± σ	X Cert. ± σ	RSD%	E_N	Horwitz	RE%	LoQ
Si (%)	29.7 ± 1.5	30.4 ± 0.2	1.89	1.31	0.94	2.62	1.37
Al (%)	6.6 ± 0.4	6.5 ± 0.1	8.02	0.07	4.01	0.56	1.11
K (%)	2.6 ± 0.2	2.5 ± 0.1	7.43	0.49	3.71	3.95	0.45
Fe (%)	3.0 ± 0.4	2.9 ± 0.1	6.10	0.37	3.05	2.35	0.38
S (%)	0.08 ± 0.01	0.04 ± 0.01	30.00	1.56	7.50	46.82	0.06
Ti (%)	0.31 ± 0.02	0.31 ± 0.02	10.04	0.12	2.51	1.48	0.08
P (%)	0.11 ± 0.03	0.09 ± 0.01	50.40	0.49	12.60	24.83	0.12
Ca (%)	3.0 ± 0.2	2.9 ± 0.1	4.35	0.27	2.17	1.40	0.31
Zr (μg g^{-1})	336 ± 20	230 *	0.003	-	0.00	31.56	170.29
Rb (μg g^{-1})	99 ± 5	110 *	0.002	-	0.00	11.24	56.57
Sr (μg g^{-1})	245 ± 10	245 ± 1	0.002	0.11	0.00	0.03	127.28
Mn (μg g^{-1})	638 ± 30	638 ± 28	0.0003	0.00	0.00	0.00	44.72
Zn (μg g^{-1})	381 ± 20	350 ± 5	0.003	6.42	0.00	8.09	203.96
Cu (μg g^{-1})	114 ± 6	114 ± 2	0.003	0.00	0.00	0.00	70.71
Ba (μg g^{-1})	570 ± 30	730 ± 40	0.003	4.08	0.00	27.15	384.19

*Uncertainty values for zirconium (Zr) and rubidium (Rb) were not reported in the certificate of the reference material.

The major constituents are defined as the ones that are in a concentration range of 1 to 100%, while the minor constituents are in a concentration range of 0.1 to 0.99% [21]. The results revealed that the fundamental parameters algorithm is suitable for the analysis of the major and minor constituents for the WDXRF and EDXRF techniques, in terms of precision, accuracy and limit of quantification for the CRM NIST 2711.

The oil sludge samples were analyzed by WDXRF, in both wet and dry form, to assess the effect of heat treatment on the performance of the method. The sample preparation procedure for WDXRF and EDXRF directly impacts on the quality of the results, especially in quantitative analysis. Characteristics such as thickness, density, state of aggregation, particle size and the presence of water can affect the accuracy of determinations by intensifying the matrix effect [22]. Drying samples to produce pressed pellets is a well-established and robust approach, capable of producing the best results in terms of reproducibility and reducing the matrix effect for a wide variety of samples (geological, mineralogical, etc.) [22].

In X-ray fluorescence analysis, the presence of water may significantly impact the results, leading to the underreporting of elements present in the samples. Water molecules cause diffraction of the primary beam coming from the X-ray tube, directly interfering in the acquisition of spectra [23-25].

The results indicate that the heat treatment influenced the sensitivity of the method, essentially for light elements (Al, Si and K) and for minor elements (Zr, Rb, Sr, V, and Ba). The moisture and the fact that wet samples were analyzed in atmospheric air, to avoid contamination of the equipment with the volatile elements present in oily sludge, influenced the results. Therefore, the heat treatment of the samples is essential to apply the method by WDXRF.

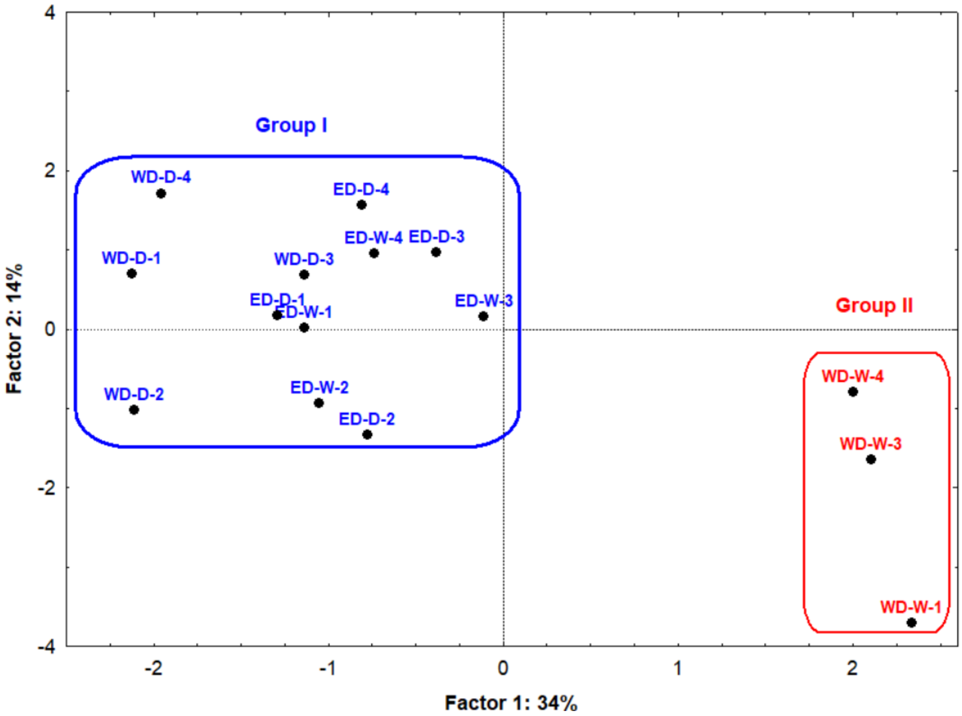
The oil sludge samples were also analyzed by EDXRF, in both wet and dry form, to assess the influence of heat treatment on the performance of the method. According to the results, the heat treatment had no significant influence on the sensitivity of the method for EDXRF analyses. The major elements (Si, Al, K, Fe, S, and Ca) and the minor elements (Zr, Rb, Sr, and Ba) presented values of the same order of magnitude, despite the moisture and the atmospheric air present in the analyses of wet samples.

The principal component analysis (PCA) was applied to compare the normalized concentration of elements in the wet and dry samples obtained by WDXRF and EDXRF.

The results were clustered according to their variance. The PCA revealed the following correlation factors: factor 1 = 34% and factor 2 = 14% (Figure 3).

The PCA resulted in two different groups. Group I: dry and wet samples analyzed by EDXRF, and dry samples analyzed by WDXRF. Group II: wet samples analyzed by WDXRF.

Figure 3 : The PCA correlatind the results obtained by WDXRF and EDXRF for 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 samples clustered in group 1 indicate that the dry samples analyzed by WDXRF had statistically similar results to the wet and dry samples analyzed by EDXRF. This suggests that the heat treatment of the samples influenced the results obtained by WDXRF but had no significant influence on the results obtained by EDXRF. The Group 2 is composed of the wet samples analyzed by WDXRF. The dry and wet samples analyzed by WDXRF belong to different groups, indicating that they are not statistically similar.

As the results of the dry and wet samples were statistically similar to the samples analyzed by EDXRF, it is preferable to analyze oil sludge samples by EDXRF, since it is a cheaper technique and provides faster analysis compared to WDXRF. Based on the results obtained, it is possible to develop a methodology for directly determining the major and minor constituents of the sedimentary portion of oil sludge samples by EDXRF.

The concentrations of uranium compounds, thorium, and elements associated with the ^{238}U and ^{232}Th radioactive decay chains were below the detection limits of the methods employed. During the extraction of oil from natural reservoirs, it is accompanied by water and sediments that transport the radionuclides present in the rocks to the surface [26]. The isotopes ^{238}U and ^{232}Th are found in underground formations in varying concentrations, along with the radionuclides that are part of their respective radioactive decay chains. The compounds of uranium and thorium exhibit lower solubility, which results in these elements being less effectively transported by the oil extraction fluid [27]. Consequently, the concentrations of uranium and thorium were anticipated to be low.

The composition of oil sludge is contingent upon the source from which it is extracted. Consequently, it is plausible that other oil reserves may yield oil sludge with higher concentrations of uranium and thorium compounds, thereby allowing this technique to be utilized for quantifying these compounds in oil sludge. However, it is of paramount importance to determine both the primary and secondary components in oil sludge, as this facilitates the optimization of radioactive waste management processes and supports the development of recycling techniques for sludge that does not qualify as radioactive waste. Through recycling, the accumulation of oily sludge is minimized, thereby reducing the need for extensive disposal sites. Building on this proposal, EDXRF represents a highly significant analytical technique, as it enables the direct characterization of samples, thereby minimizing waste generated during sample preparation.

4. CONCLUSIONS

The results presented demonstrate that the fundamental parameters algorithm is effective for determining and classifying both major (1–100%) and minor (0.1–0.99%) constituents in oil sludge, using WDXRF and EDXRF. Sample preparation and the analysis environment influenced the results obtained by WDXRF. However, in EDXRF analyses, sample preparation had no significant impact, allowing for the direct determination of oil sludge components. The advantages of EDXRF include its ability to perform rapid analyses with minimal waste generation, satisfactory accuracy and precision, and lower costs compared to WDXRF, which requires more expensive optical components. The direct determination of elements is particularly beneficial, as it reduces both sample preparation waste and the analyst's exposure time to potentially hazardous materials. This is especially crucial, given that oil sludge may be classified as radioactive waste. Future studies will incorporate additional analytical techniques to further compare results and assess the developed methodology.

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CONFLICT OF INTEREST

The authors have no conflicts of interest to declare.

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