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# Innovative sample preparation method using a conductively heated digestion system for trace element analysis of radioactive oil sludge by ICP-OES†

Aline Leone Muguet Pinto, *[a] Alexandre Luiz de Souza,[a] Leandro Goulart de Araujo, [b] Julio Takehiro Marumo,[a] Marycel Elena Barboza Cotrim[a] and Sabine Neusatz Guilhen *[a]

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This study presents a novel and efficient sample preparation method based on conductively heated digestion in closed vessels (CHDS), employing collagen capsules as a transfer medium. The method was specifically developed for the treatment of oil sludge—a complex waste product generated by the oil industry, typically composed of hydrocarbons, water, sediments, processing residues, and radionuclides from the uranium-238 and thorium-232 decay chains. Compared to conventional open-vessel digestion techniques using heating blocks, this approach offers several advantages, including reduced sample and reagent volumes, significantly shorter preparation times, and minimized contamination risks. Trace element concentrations in the digested samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

## Introduction

Oil sludge is a complex waste product generated by the oil industry, composed of hydrocarbons (30–90%), water (30–70%), sediments (2–15%) and oil processing residues.[1] It may also contain radionuclides from the uranium ($^{238}U$) and thorium ($^{232}Th$) decay chains, predominantly radium ($^{226}Ra$ and $^{228}Ra$) and lead ($^{210}Pb$).[2] In general, oil sludge accumulates at all stages of the oil production chain, from pipelines to equipment.[3] Globally, the oil industry generates approximately 60 million tons of oil sludge annually.[4] This residue poses significant risks to workers in the oil industry, especially during waste transportation, maintenance, and decommissioning activities.[5,6]

Several analytical techniques have been applied to characterize oil sludge.[7–12] Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is a promising technique for quantifying trace elements in oil sludge samples. ICP-OES offers several advantages, including high sensitivity, excellent stability, and low background emission intensity.[13]

The sample preparation stage is fundamental for optimizing the performance of ICP-OES.[14] Proper preparation enhances the analytical signal, lowers the detection limit, and minimizes undesirable interferences. In addition, it ensures reliable results by reducing experimental errors.[15]

Working with small but representative sample portions is advantageous, as it reduces the volume of reagents required, thereby lowering analytical costs.[15] Small portions also improve the efficiency of acid digestion, mitigating matrix effects and facilitating the breakdown of complex matrices such as oil sludge. Consequently, sample preparation emerges as a critical step in attaining high-quality ICP-OES results, directly impacting key parameters such as accuracy and precision.[16]

Sample preparation using open-vessel digestion blocks is a widely employed technique, primarily due to its low acquisition and maintenance costs.[16] However, this approach presents significant limitations, including a high risk of sample contamination, increased reagent consumption, and extended digestion times when compared to more modern and efficient methods.[17]

Currently, microwave-assisted digestion is the most extensively used sample preparation technique.[18] Despite its popularity and efficiency, the equipment used for microwave digestion is expensive to acquire and maintain.[17]

As an alternative for preparing various types of samples for ICP-OES analysis, the Conductively Heated Digestion System (CHDS) using closed vessels is an efficient technique, offering lower equipment acquisition and maintenance costs.[16,17] In this system, hermetically sealed vessels are subjected to conductive

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[a] *Nuclear and Energy Research Institute, IPEN/SP, Av. Prof. Lineu Prestes, 2242, São Paulo, Brazil. E-mail: aline.leone@usp.br; alexquim@iq.usp.br; jtmarumo@ipen.br; mecotrim@ipen.br; snguilhen@ipen.br*

[b] *Université de Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON UMR 5256, 69626 Villeurbanne Cedex, France. E-mail: leandro.goulart@ircelyon.univ-lyon1.fr*

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heating *via* direct contact with temperature-controlled metal blocks.

In CHDS, as the closed vessels are heated, the internal pressure increases. As a result, the boiling point of the acid rises, enhancing digestion efficiency. This improvement allows for a reduction in the volume of reagents required, thereby decreasing reagent costs and waste generation—key considerations in green chemistry.[19] Additionally, CHDS minimizes the potential for sample contamination, commonly associated with open-system preparation techniques, while also reducing exposure to volatile substances that may pose health risks to laboratory personnel.

The objective of this study is to develop and implement a novel and streamlined sample preparation methodology for oil sludge, aiming to obtain clear solutions suitable for ICP-OES analysis. This approach seeks to achieve satisfactory results in terms of precision and accuracy, validating the applicability and reliability, while simultaneously minimizing matrix effects arising from the complex composition of oil sludge.

## Materials and methods

### Instruments

A Conductively Heated Digestion System (CHDS), model Simplify Digestor (Vert Technologies, São Paulo, Brazil)[17] was used for sample decomposition. The equipment operates at 220 V with a power of 1600 W and a maximum operating temperature of 350 °C. It has a capacity for 24 tubes, each with the following dimensions: 220 millimeters (mm) in height, 16 mm in inner diameter and 20 mm in outer diameter. The tubes employed in this system are equipped with polytetrafluoroethylene (PTFE) caps, which are securely fastened to the flasks using polyvinyl chloride (PVC) locking mechanisms. Each cap contains a safety membrane that functions as a pressure relief system, designed to release excess pressure if it exceeds the maximum tolerance of the flasks (28 bar).[17]

The analysis was performed using PerkinElmer Optima 7000 DV spectrometer. This instrument operates with argon and nitrogen gases, and its optical system is purged with nitrogen to enhance performance in the low UV range (160–190 nm). The spectrometer has a spectral range of 160 to 900 nm and a resolution of <0.009 nm at 200 nm. Its resolution (half-width) is <7 pm. The system is connected to a computer equipped with WinLab32 software. It features a dual back-illuminated charge-coupled device (CCD) array detector, directly cooled using an integrated Peltier cooler operating at approximately −8 °C. The RF generator is a second-generation, 40 MHz free running solid-state, adjustable from 750 to 1500 W. The spectrometer uses an Echelle grating with 79 lines $\text{mm}^{-1}$, with a blaze angle of 63.4°. The nebulizer used in this study was a Burgener model T2100, equipped with Teflon PFA capillaries and a PTFE body. It is designed to operate with sample flow rates ranging from 0.5 to 3.0 mL $\text{min}^{-1}$, under a standard operating pressure of 45 PSI at a carrier gas flow rate of 1 L $\text{min}^{-1}$. The spray chamber employed was a Tracey cyclonic spray chamber (PerkinElmer), made of borosilicate glass, with a total internal volume of 50 mL.

### Sample preparation

ICP-OES was applied to determine trace elements (<0.1%), as previously reported,[20] in the inorganic portion of oil sludge samples collected in the Campos Basin (Macaé – Rio de Janeiro). The oil sludge samples collected were radioactive, but this characteristic does not interfere with the method, or the results obtained by ICP-OES. The oil sludge samples were prepared following the procedure described below.

Initially, the mass of each collagen capsule was recorded. Collagen capsules were employed as a carrier medium to prevent the sample from adhering to the inner walls of the quartz digestion tubes during weighing. This strategy minimized sample retention within the tubes, which could otherwise compromise digestion efficiency by limiting the availability of the material in the reaction medium, thereby resulting in a less homogeneous digestion solution. The use of collagen capsules facilitated the weighing process and prevented sample loss during transfer. Furthermore, their application as a transfer medium proved essential for optimizing sample preparation and demonstrated broad applicability for both viscous and powdered samples.

Notably, this is the first reported application of collagen capsules as a carrier medium for oil sludge samples. The capsules used in this study measured 23.5 mm in length and 8.1 mm in height, with a capacity of 0.95 mL and an average mass of approximately 120 mg. It is important to highlight that the presence of collagen did not interfere with the quantification of the elements of interest. This was confirmed through the analysis of analytical blanks, which were included throughout all stages of the procedure to monitor potential contamination. Approximately 100 mg of oil sludge were added into each capsule, which was then placed into a quartz vessel for digestion.

Approximately 2 mL of concentrated $HNO_3$ were added to the system, followed by 2 mL of $H_2O_2$. Both $HNO_3$ and $H_2O_2$ are oxidizing agents. When combined in the reaction medium, they enhance the oxidation and decomposition of the organic fraction present in the oil sludge. Hydrogen peroxide ($H_2O_2$) generates free radicals capable of oxidizing a wide range of organic compounds. The oxidative degradation of organic matter in the medium can lead to the formation of carbon dioxide ($CO_2$), carboxylic acids (R–COOH), alcohols (R–OH),

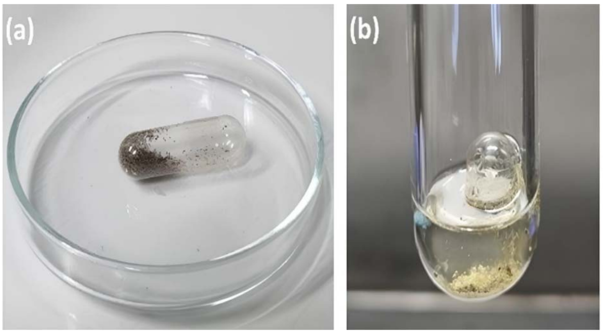

Fig. 1 Collagen capsule with oil sludge sample (a). Oil sludge sample after the addition of $HNO_3$ and $H_2O_2$ (b).

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among other compounds, depending on the specific composition of the organic matrix.[21,22] A collagen capsule used to encapsulate an oil sludge sample is shown in Fig. 1.

Before proceeding with the digestion step, the quartz vessels containing the mixture were left to react overnight at room temperature. This pre-reaction period allows the oxidizing agents to interact with the sample, facilitating the initial breakdown of the organic matrix and ensuring a more efficient digestion process when heated.

The quartz tubes containing the samples were positioned on the rack of the digestion system. After being hermetically sealed, the rack was inserted into the Vert Simplify digester to perform sample digestion in an acidic medium under controlled temperature conditions. The tubes were heated at a rate of 10 °C min$^{-1}$ until reaching a final temperature of 250 °C, which was maintained for 30 minutes. This controlled heating rate ensured a gradual increase in the reactivity of the medium, thereby enhancing the safety and efficiency of the process. At this final temperature plateau, the degradation of organic matter is achieved more efficiently.[15–17] In the closed system, the resulting pressure increase raises the boiling point of the acid, boosting its oxidative capacity and overall reactivity within the digestion medium. This procedure was adapted from EPA Method 3051 (ref. 23) (Microwave-Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils), which is intended for the partial digestion of the samples, *i.e.*, to extract leachable fractions of elements for subsequent determination by techniques such as ICP-OES.

Upon completion of the digestion process, the tubes were allowed to cool to room temperature before being safely opened under a fume hood—a precaution taken to prevent the release of hazardous vapors and to mitigate any risk of pressure-related incidents. As the digestion process was partial, residual silicates remained in the samples. These were removed by filtration after cooling. The filtered solutions were then transferred to polypropylene tubes and diluted to 15 mL with ultrapure water for subsequent analysis.

### ICP-OES analysis

Following digestion, the oil sludge samples were analyzed by ICP-OES. Two analytical methods were employed for elemental characterization: one targeting trace metals, and the other specifically developed for the determination of rare earth elements and uranium. The method developed for the determination of metals includes the following elements of interest: zinc (Zn), copper (Cu), chromium (Cr), nickel (Ni), manganese (Mn) and lead (Pb). The concentrations of the solutions used in the method's calibration curve for metals were: 0.05 mg L$^{-1}$, 0.1 mg L$^{-1}$; 0.5 mg L$^{-1}$; 1 mg L$^{-1}$; 5 mg L$^{-1}$; 10 mg L$^{-1}$.

To determine rare earth elements and uranium, the method developed includes the following elements of interest: uranium (U), erbium (Er), europium (Eu), lanthanum (La), lutetium (Lu), neodymium (Nd), samarium (Sm), scandium (Sc), ytterbium (Yb) and yttrium (Y). The concentrations of the solutions used in the method's calibration curve were: 0.05 mg L$^{-1}$, 0.1 mg L$^{-1}$; 0.5 mg L$^{-1}$; 1 mg L$^{-1}$; 2 mg L$^{-1}$; 5 mg L$^{-1}$ (Table 1).

Table 1 Experimental conditions used in the developed methods

| Experimental conditions | |
|---|---|
| Power | 1450 W |
| Plasma view | Axial |
| Plasma flow | 15 L min$^{-1}$ |
| Auxiliary gas flow | 0.50 L min$^{-1}$ |
| Nebulization gas flow | 0.70 L min$^{-1}$ |
| Sample flow | 0.80 mL min$^{-1}$ |

Five aliquots were taken from each oil sludge sample and individually digested to evaluate analyte variability and to assess the impact of sample heterogeneity on the representativeness of the results. Following individual analysis, the five digested aliquots were combined into a single vessel to prepare a composite sample, which was subsequently analyzed to compare with the results obtained from the individual aliquots. Both the individual and composite samples were analyzed by ICP-OES using both analytical methods. The methodology was validated in accordance with the guidelines for analytical method validation established by the National Institute of Metrology, Quality and Technology (INMETRO). Details regarding the validation of the analytical procedure are available in the ESI.†

## Results and discussion

### Recovery test using certified reference material (CRM)

The certified reference material (CRM) NIST 2709 was used to assess the performance of the proposed method in extracting the elements of interest from the samples. CRM NIST 2709 was selected due to its predominantly inorganic matrix, which closely resembles the significant inorganic fraction present in oil sludge. Since the analytical technique employed targets inorganic elements leached from the sedimentary matrix during the digestion process, the use of a CRM with similar characteristics provides a rational basis for evaluating the method's accuracy. In the absence of a CRM specifically developed for oil sludge, this strategy is consistent with established validation practices, wherein a reference material with analogous properties is utilized when a perfect matrix match is unavailable. It is also noteworthy that NIST 2709 represents a geological matrix, further supporting its appropriateness for this application.

The average concentrations of the elements determined by the ICP-OES method are shown in Table 2, in addition to the certified concentrations of the reference material (as stated on the certificate), and the concentration range recovered by leaching the CRM (considering the lowest and highest limits of the range).[23] This allows a comparison between the results obtained from the partial digestion (or leaching) of the CRM and the concentration values provided on the CRM certificate.[24]

The analysis of the certified reference material (CRM) was performed in triplicate ($n = 3$). The RSD% represents the relative standard deviation obtained for the measurements. According to the results, the sample preparation method

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Table 2 Comparison of the concentration of leached elements using the developed method (experimental) with the reference values (CRM)

| Element | Concentration of leached elements (experimental) (mg kg$^{-1}$) | RSD% | Concentration of elements (CRM) (mg kg$^{-1}$) | Concentration of leached elements (CRM) (mg kg$^{-1}$) |
|---|---|---|---|---|
| Ni | 80.250 ± 0.0035 | 0.93 | 88 ± 5 | 65–90 |
| Zn | 107.250 ± 0.0044 | 0.88 | 106 ± 3 | 87–120 |
| Cu | 35.350 ± 0.0028 | 1.46 | 34.6 ± 0.7 | 26–40 |
| Pb | 15.290 ± 0.0013 | 2.32 | 18.9 ± 0.5 | 12–18 |
| Cr | 102.710 ± 0.0016 | 0.33 | 130 ± 4 | 60–115 |
| Mn | 503.50 ± 0.012 | 0.48 | 538 ± 14 | 360–600 |

developed for ICP-OES proved effective in extracting the elements of interest from the NIST 2709 CRM, as the concentrations determined were within the certified value ranges provided in the reference material's certificate. This agreement with the certified values further supports the applicability and reliability of the methodology, confirming its suitability for accurately determining the elemental composition of similarly complex matrices.

### ICP-OES analysis

The digested samples were analyzed by ICP-OES for the following target elements: Ni, Zn, Cu, Pb, Cr, and Mn. These elements were selected based on a preliminary screening, which indicated that other elements were below the limit of quantification. As a result, the method was optimized to focus on analytes that produced quantifiable signals. Calibration curves for the selected elements were prepared using a multielement standard solution, and the corresponding linear regression parameters and limits of quantification are summarized in Table 3.

For all the elements of interest, the coefficients of determination ($R^2$) obtained were very close 1. These results indicate the proportionality of the analytical signal generated for each concentration and the fit of the data to the mathematical model of linearity. The recommendation to work with models in which the $R^2$ value is closest to 1 is related to the degree of linearity between the measured data and the predicted values based on the calibration curve.[25]

The precision of the method was evaluated by comparing the mean concentrations of elements obtained from five individual aliquots of each sample with those from the corresponding composite sample. Precision, assessed in terms of relative standard deviation (RSD%) and HORRAT values (≤2), was considered satisfactory for all elements across all samples.[25] The detailed results for each element are provided in Table S1 of the ESI.†

Table 3 Calibration data for the elements of interest: coefficient of determination ($R^2$), limit of quantification (LQ) and wavelengths selected for determining the elements

| Element | $R^2$ | Limit of quantification (μg kg$^{-1}$) | Wavelength (nm) | Emission line |
|---|---|---|---|---|
| Ni | 0.9999 | 4.00 | 231.604 | Ionic |
| Zn | 0.9993 | 2.00 | 213.857 | Atomic |
| Cu | 0.9998 | 2.00 | 324.752 | Atomic |
| Pb | 0.9998 | 8.00 | 220.353 | Ionic |
| Cr | 0.9995 | 1.00 | 267.716 | Ionic |
| Mn | 0.9999 | 1.00 | 257.610 | Ionic |

Accuracy was assessed using both relative error (RE%) and $Z$-score values (acceptable when $Z \leq 2$). Satisfactory accuracy was observed for the following elements: Ni, Cr, and Mn in sample 1; Ni and Mn in sample 2; Ni, Cr, and Mn in sample 3; Ni, Zn, Cr, and Mn in sample 4; Mn in sample 5; Ni, Cr, and Mn in sample 6; Ni and Mn in sample 7; Ni, Cr, and Mn in sample 8; Ni, Cr, and Mn in sample 9; Ni, Cu, and Mn in sample 10; and Ni, Zn, and Mn in sample 11.

Conversely, unsatisfactory accuracy was observed for Zn and Cu in sample 1; Zn, Cu, and Cr in sample 2; Zn in sample 3; Cr in sample 5; Zn in sample 6; Zn, Cu, and Cr in sample 7; Zn, Cu, and Pb in sample 8; Zn and Cu in sample 9; Cr in sample 10; and Cu, Pb, and Cr in sample 11 ($z > 2$). Full accuracy data for each element are presented in Tables S1–S12 of the ESI.†

The elements that presented unsatisfactory accuracy results highlight the variability observed in aliquots taken from the same sample.[26] This variability is expected due to the highly heterogeneous composition and diverse physicochemical characteristics of the samples. For certain elements, the matrix effect – where the sample's composition interferes with the analytical measurement – can be more pronounced, directly influencing the accuracy of the results.

However, the results also indicate that the sample preparation method, developed using the Simplify Digester, was effective. Specifically, the aliquots containing 100 mg of sample and 4 mL of reagent yielded statistically similar results to those of the other composite samples formed by combining the five aliquots. This indicates that increasing the sample mass and reagent volume did not introduce significant changes in the results. Consequently, this finding reinforces the trueness of the digestion method for this sample type.

The standard measurement uncertainty is a metric associated with the standard deviation and reflects the variation of the measurements in relation to the true value of the measured quantity. The uncertainty calculated for each element in each sample indicates that the deviations are minimal across all situations. Therefore, the method responds adequately to all samples, with no significant interference. The diversity present in oil sludge matrices is evident in Fig. 2, which represents the trace elements present in oil sludge samples.

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Since the matrices are highly diverse, small variations in the extraction efficiency of the elements are to be expected. However, in most cases, the method developed was suitable for extracting and quantifying the elements of interest with acceptable precision and accuracy. This means that, despite the distinct characteristics of the oil sludge matrices, the developed method enables efficient sample digestion, reducing the matrix effect in ICP-OES determinations.

The maximum volume of reagents for each replicate was set at 4 mL and the mass at approximately 100 mg of sample, due to the capacity of the reaction flask used in the digester. Considering the characteristics of the applied method and the results statistically obtained for the elements of interest, it was demonstrated that the method is suitable for determining trace elements in oil sludge. Increasing the reagent volume and the sample mass (composite sample) did not significantly interfere with the quantification of trace elements.

This is supported by the fact that the results of the composite samples (composed of five aliquots) did not differ statistically from the results obtained for the average of the five aliquots of the same sample. Thus, it is possible to quantify the elements of interest with satisfactory precision and accuracy, using small volumes of reagent (4 mL) and small quantities of sample (100 mg).

For the analysis of rare earth elements and uranium by ICP-OES, the following elements of interest were selected after a pre-scan: Er, Eu, Lu, Nd, Sm, Sc, Y, Yb, U, and La. Calibration curves were constructed using a multielement standard solution of uranium and rare earths. The linear regression and LQs are presented in Table 4.

Table 4 Calibration data for the elements of interest: coefficient of determination ($R^2$), limit of quantification (LQ) and wavelengths selected for determining the elements. Emission line: ionic

| Element | $R^2$ | Limit of quantification ($\mu$g kg$^{-1}$) | Wavelength (nm) |
|---|---|---|---|
| Er | 0.9990 | 4.64 | 369.265 |
| Eu | 0.9992 | 1.09 | 381.967 |
| Lu | 0.9999 | 0.60 | 291.139 |
| Nd | 0.9999 | 1.47 | 406.109 |
| Sm | 0.9999 | 5.42 | 359.260 |
| Sc | 0.9993 | 0.96 | 361.383 |
| Y | 1.0000 | 0.73 | 371.029 |
| Yb | 1.0000 | 0.84 | 328.937 |
| U | 0.9998 | 1.10 | 385.958 |
| La | 1.0000 | 1.50 | 398.852 |

The correlation coefficient of the calibration curves for each element, obtained for the concentrations of interest, was excellent, indicating proportionality between the obtained analytical signal (intensity) and the concentrations.

For each sample, accuracy was evaluated by comparing the mean concentrations of the elements obtained from five

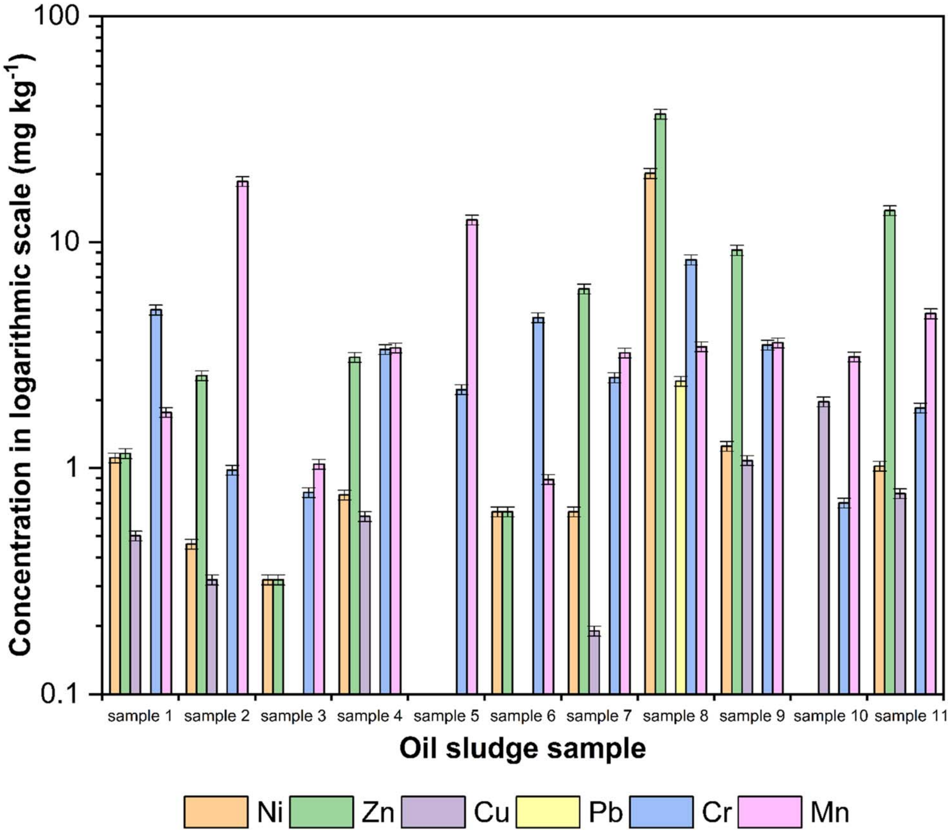

Fig. 2 Concentration of metallic elements (<0.1%) in oil sludge samples. The missing columns mean that the values are <LQ. The margin of error for all measurements is less than 5%.

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individual aliquots with those from the corresponding composite sample. Precision, assessed through the relative standard deviation (RSD%) and HORRAT values (≤2), was satisfactory in all cases. Accuracy, evaluated in terms of RE% and *Z*-score, was also satisfactory in most cases, except for erbium (Er) in sample 2. For samples 1, 5, 7, 8, and 10, the concentrations of rare earth elements and uranium were below the detection limits. Detailed results for each element of interest are presented in Table S13 of the ESI.†

Precision was assessed by comparing the mean concentrations of elements obtained from five individual aliquots with those from the corresponding composite sample. For samples 2, 3, 4, 6, 9, and 11, the results demonstrated satisfactory precision, as indicated by relative standard deviation (RSD%) and HORRAT values ≤2. Accuracy was also acceptable for lanthanum (La) in sample 2, based on RE% and *Z*-score values, in accordance with the criteria established in the DOQ-CGCRE-008 guideline.[25]

In terms of RE% and *Z*-score accuracy was unsatisfactory for the elements Er, Nd, Sm, Sc and Y (sample 2); Nd (samples 3, 4, 6, 9 and 11). This result is consistent, since the concentration of rare earth elements in the samples is low and the matrix effect can have a more significant influence, depending on the sample. As with the determination of metals, for rare earths and uranium, increasing the volume of reagent and the mass of the samples did not significantly influence the results obtained. The results for each element of interest are presented in Tables S14–19, of the ESI.†

Considering the characteristics of the methodology applied and the results statistically obtained for the elements of interest, it can be said that the method proved to be suitable for the determination of trace elements in oil sludge. The uranium concentration was below the detection limit for the method developed by ICP-OES.

The absence of uranium compounds in certain analyses should not be attributed to inefficiencies in digestion but rather to their inherently low concentrations in the sludge from the outset.[27,28] To quantify uranium, inductively coupled plasma mass spectrometry (ICP-MS) would be more suitable. This technique can offer superior sensitivity and sub-ppt level of detection limits.[29] While it may be possible to quantify uranium using more sensitive techniques such as ICP-MS, radium compounds will invariably dominate. Their higher concentrations and significant contribution to the radiological dose associated with the sludge underscore the importance of focusing on radium isotopes when evaluating compliance with regulatory limits for the disposal or exemption of radioactive waste. The results are summarized in Fig. S3, on the ESI.†

According to the results for the analysis of trace elements present in oil sludge, it can be said that the samples differ in composition.[30] This was to be expected, since the composition of oil sludge depends on its origin.

## Conclusions

The sample preparation method based on conductively heated digestion using closed vessels proved to be effective, yielding satisfactory results in terms of both precision and accuracy. Among its advantages, the method offers rapid and cost-effective sample preparation, requiring only small sample quantities and minimal reagent volumes. Statistical comparison between the results obtained from replicate and composite sample analyses indicated that increasing the sample mass or reagent volume does not significantly influence the analytical outcomes. Thus, efficient digestion can be achieved using 100 mg of sample and 4 mL of reagents.

ICP-OES analysis produced reliable results, meeting the performance criteria established in DOQ-CGCRE-008, thereby confirming the technique's suitability for trace element determination in oil sludge. The only notable limitation of the method lies in the necessity for reaction control to ensure that the internal pressure within the vessels does not exceed 28 bar. To mitigate this, careful control of sample and reagent quantities, along with the implementation of a gradual heating rate, is essential to allow the reaction medium to become progressively more reactive.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

All authors have given approval to the final version of the manuscript. Aline Leone Muguet Pinto: conceptualization, data curation, formal analysis, investigation, methodology and writing – reviewing. Alexandre Luiz de Souza: conceptualization, data curation, formal analysis, investigation, methodology and writing – reviewing. Leandro Goulart de Araujo: formal analysis, investigation and writing – reviewing. Julio Takehiro Marumo: funding acquisition, project administration and supervision. Marycel Elena Barboza Cotrim: funding acquisition, project administration and supervision. Sabine Neusatz Guilhen: conceptualization, data curation, formal analysis, investigation, methodology, project administration, writing – reviewing and supervision.

## Conflicts of interest

There are no conflicts to declare.

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