https://dx.doi.org/10.21577/0103-5053.20220118

J. Braz. Chem. Soc., Vol. 34, No. 3, 414-425, 2023

Article

Assessment of Chlorine, Fluorine, and Sulfur Concentrations in Depth Profile of Drill Cuttings from Onshore and Offshore Oil and Gas Exploration Wells

Renan G. Marim,[a] Gilberto S. Coelho Junior,[a] Paola C. C. de Azevedo,[a] Daniel L. G. Borges,[a] Tatiane A. Maranhão,[a] Fernando J. S. de Oliveira,[b] Vera L. A. F. Bascunãn[a] and Eduardo S. Chaves*,[a]

[a] *Departamento de Química, Campus Trindade, Universidade Federal de Santa Catarina, 88040-900 Florianópolis-SC, Brazil*

[b] *Petróleo Brasileiro S. A., Gerência de Meio Ambiente, Av. Henrique Valadares, 28, 20231-030 Rio de Janeiro-RJ, Brazil*

The assessment of chlorine, fluorine, and sulfur concentrations in depth profile of drill cuttings was performed using ion chromatography after sample preparation by pyrohydrolysis. The parameters for pyrohydrolysis were optimized using a Box-Behnken design, and the established conditions were 300 mg of sample, 300 mg of V_2O_5, temperature of 1000 °C, reaction time of 25 min, and absorbing solution of 50 mmol L^{-1} NH_3 + 150 mmol L^{-1} H_2O_2. The accuracy was evaluated by the analysis of certified reference materials and recovery tests, and the results showed a good agreement between determined and certified values and recoveries (89-108%). The precision (relative standard deviation (RSD) < 10%), and the limits of detection (0.5-2.5 mg kg^{-1}) were suitable for drill cuttings analysis. The concentration of chlorine, fluorine, and sulfur in drill cuttings at different depths was at mg g^{-1} range, and its variation is related to the mineral composition of the samples.

Keywords: sulfur, halogens, drill cuttings, ion chromatography, pyrohydrolysis

Introduction

The oil and gas industry are amongst the most relevant sectors for the world economy. Brazil is in a privileged geological position with substantial oil reserves and ranks among the world's main oil producers.[1-4] However, environmental issues associated with oil and gas exploration deserve attention due to the high polluting potential associated with this activity.[5]

In the oil and gas industry, the exploration stage is responsible for the generation of substantial amounts of waste, including drill cuttings.[6,7] This waste is mainly composed of fragmented rocks, which are transported from exploration wells to the surface by the drilling fluid.[5,8-10] However, in addition to the characteristics inherent to the composition of the rock where the well is located, the drill cuttings may contain traces of drilling fluid, a fact that, depending on the characteristics of the fluid, can make it even more harmful to the environment.[11] Organic compounds and metals at potentially toxic levels are part of the composition of petroleum, derivatives and their wastes, and are some of the main contaminants of the environment. Additionally, arsenic (As), phosphorus (P), sulfur (S), and halogens (Br, Cl, F, and I) are also potential environmental contaminants.[3,12]

Information related to the drill cuttings generated by the oil activity is still limited, especially regarding exploration wells in ultra-deep waters.[1] Considering that thousands of tons of drill cuttings are produced, it is critical and necessary to monitor their chemical composition, not only to minimize environmental impacts but also for the geological characterization of the region. Taking into account that there is no data about the concentration of non-metals in drilling cuttings from deep water wells, knowledge about the Cl, F, and S concentrations in geological samples, as well as other elements, can offer important geological information. The concentration Cl, F, and S in rocks can provide valuable information regarding the origin of metamorphic fluids.[13-15] Furthermore, knowledge about the chemical composition

---

*e-mail: eduardo.chaves@ufsc.br

Editor handled this article: Rodrigo A. A. Muñoz (Associate)

of sedimentary rocks can contribute to information about marine geochemical cycling and paleoenvironmental conditions.[16] However, monitoring the concentration of these elements is not trivial, as these elements, especially the halogens, are volatile and can be lost during the process. Hence, for chemical analysis the sample preparation is a critical step.[17]

Sample preparation using microwave-induced combustion,[18-20] ultrasound and microwave-assisted extractions[21,22] and pyrohydrolysis[23-27] are widely applied for further non-metal determination. However, pyrohydrolysis stands out for being a relatively simple, efficient, and low-cost technique. It is based on the pyrolysis of samples in the presence of water vapor at high temperatures, where the non-metals are hydrolyzed forming their respective hydrogen halides, which are subsequently condensed and collected in an alkaline absorbent solution.[28] Pyrohydrolysis has been successfully applied for sample preparation, such as for the determination of Br, F and I in mineral,[27] Br, Cl and F in glass,[29] Br, Cl, F and I in soil,[30] B and Cl in plants,[31] S in uranium ore,[32] and Cl and F in iron ore.[23]

It is important to emphasize that, for the first time the determination of Cl, F and S in drill cuttings from oil exploration wells have been performed by ion chromatography (IC). In this sense, the determination of Cl, F, and S in drill cuttings using IC after sample preparation by pyrohydrolysis was proposed. A Box-Behnken design was applied to optimize the sample preparation conditions. The analytes concentration was determined in drill cuttings samples from oil drilling wells (onshore and offshore) collected in different depth profiles.

Experimental

Drill cuttings samples

Samples of drill cuttings from onshore and offshore oil exploration wells from different exploration fields were provided by a company in the oil and gas industry. Samples were collected from two offshore exploration wells, at depths between 2,857-3,809 meters from the well, coded as PS, and between 4,119-6,256 meters from the well, coded as PRS. Additionally, samples from an onshore exploration well were collected at depths between 77-715 meters. The samples were stored under refrigeration (7 ± 1 °C) in properly identified plastic containers until the analysis. For the analysis, the samples were dried at a temperature of 80 ± 5 °C until constant mass and then ground and sieved through a 250 µm mesh.

Instrumentation

The samples were previously dried in an oven model 238 (Biomatic, Porto Alegre, Brazil), ground in a ball mill model MM200 (Retsch, Haan, Germany). The samples were weighted using an analytical balance model Mark Serie M (BEL Engineering, Monza, Italy). All the standard solutions and sample dilution were performed with ultrapure water (resistivity of 18.2 MΩ cm) obtained in a water purifier model Purelab Ultra (Elga LabWater, Buckinghamshire, UK).

The concentrations of Cl, F and S were determined as Cl^-, F^- and SO_4^{2-}, respectively, in an ion chromatograph model 761 Compact IC (Metrohm, Herisau, Switzerland) with a pre-column model Metrosep A Supp 4/5 Guard (Metrohm) and a chromatographic column model Metrosep A Supp 5-150/4.0 mm (Metrohm) with a stationary phase composed of polyvinyl alcohol with quaternary ammonium groups (NR_4^+). The measurements were performed with an injection volume of 20 µL and a mobile phase flow rate of 0.7 mL min^{-1}. For the preparation of samples by pyrohydrolysis, a lab-made system was used (Figure 1) consisting of a muffle furnace model R1800 (EDG, São Carlos, Brazil) with temperature control operating at

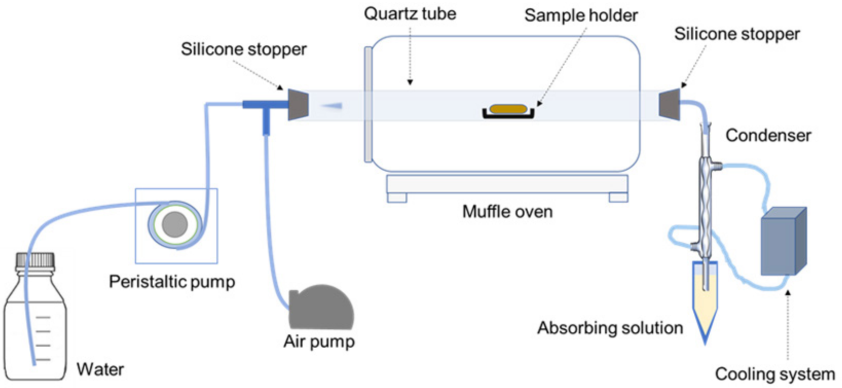

Figure 1. Schematic representation of the lab-made pyrohydrolysis system. Quartz tube (17 mm i.d., 400 mm length); alumina sample holder (55 mm length, 10 mm width and 6 mm depth).

a maximum temperature of 1000 ºC, an air pump model U-2800 (Boyu, Chaozhou, China) operating at 0.2 L min^{-1} and a peristaltic pump model IPC 4 (Ismatec, Wertheim, Germany) operating at 0.1 mL min^{-1}.

The mineralogical characterization of the samples was performed by X-ray diffraction (XRD), using a MiniFlex600 X-ray diffractometer (Rigaku, Tokyo, Japan), equipped with a copper radiation source (λ = 1.54 Å). The analyses were performed at a temperature of 25 °C, using a scanning range from 5 to 90 °C, with a 0.02° step and scan speed of 2° min^{-1}. Data processing was performed using the HighScore Plus software.[33]

Reagents and solutions

For the calibration curves, stock standard solutions of F^- (IsoSol, Jacareí, Brazil), SO_4^{2-} and Cl^- (SpecSol, Jacareí, Brazil) at concentrations of 1000 mg L^{-1}, were used. From these solutions, a multi-ion standard solution (100 mg L^{-1}) containing all analytes (F^-, SO_4^{2-} and Cl^-) was prepared. The calibration standard solutions were prepared in a concentration range of 0.025 to 10.0 mg L^{-1}. The mobile phase was composed by a solution of 3.2 mmol L^{-1} Na_2CO_3 (Sigma-Aldrich, Steinheim, Germany) and 1.0 mmol L^{-1} $NaHCO_3$ (Merck, Darmstadt, Germany). A solution of 100 mmol L^{-1} H_2SO_4, prepared from H_2SO_4 95-99% m/m (Vetec, Rio de Janeiro, Brazil), and ultrapure water were used for cleaning the sodium suppressor in the regeneration system of the ion chromatograph. For the pyrohydrolysis, vanadium pentoxide (V_2O_5) (Merck, Darmstadt, Germany) was used as accelerator, and hydrogen peroxide (H_2O_2) (Neon, Suzano, Brazil) and ammonia (NH_3) (Merck) as absorbing solution.

Pyrohydrolysis

Sample preparation by pyrohydrolysis was optimized by Box-Behnken design, using the software Statistica version 6.0 (StatSoft, Tulsa, USA),[34] in which the following parameters were evaluated: sample mass (200-400 mg), temperature (800-1000 °C), and reaction time (15-25 min). Subsequently, the type of absorbing solution (50 mmol L^{-1} NH_3, 100 mmol L^{-1} NH_3, H_2O, 3.2 mmol L^{-1} Na_2CO_3 + 1.0 mmol L^{-1} $NaHCO_3$, and 32 mmol L^{-1} Na_2CO_3 + 10 mmol L^{-1} $NaHCO_3$), concentration of the oxidizing agent (0, 50, 150, 250 and 350 mmol L^{-1} H_2O_2) and accelerator mass (V_2O_5-150, 200 and 300 mg) were optimized.

For pyrohydrolysis, the drill cuttings masses, as well as the accelerator masses, were directly weighted in an alumina support, which was introduced into a quartz reactor tube (400 mm × 20 mm external diameter) positioned inside of the muffle oven. During the sample decomposition stage, compressed air with a flow rate of 0.2 L min^{-1} and water with a flow rate of 0.1 mL min^{-1} were injected. Then, the steam containing the analytes was condensed and collected in a polypropylene bottle containing 10.0 mL of absorbing solution. Subsequently, the volume of the solution was made up to 50.0 mL with ultrapure water. The samples were properly diluted, filtered and the analytes concentrations measured by ion chromatography (IC). The analyses were performed in triplicate and, after pyrohydrolysis process, the alumina support was washed with ethyl alcohol and water, dried, and cleaned for 5 min at 1000 °C in the pyrohydrolysis equipment. The blanks were obtained following the same pyrohydrolysis procedure, and the concentration of the analytes was calculated considering the blank signal correction for each experiment/analysis performed.

The reaction time, reaction temperature, and the sample mass used for sample preparation by pyrohydrolysis were optimized by means of a Box-Behnken experimental design. The optimized parameters, as well as the air flow rate (0.2 L min^{-1}) and the water flow rate (0.1 mL min^{-1}), which were kept constant, were defined based on the literature.[35,36] The variables and the respective levels evaluated are shown in Table 1.

Table 1. Variables and levels evaluated in the Box-Behnken design for sample preparation by pyrohydrolysis

Variable	Levels		
	−1	0	+1
Reaction time / min	15	20	25
Reaction temperature / °C	800	900	1000
Mass / mg	200	300	400

The effects and interactions of the variables were evaluated considering the multiple responses (MR). The MR function was calculated based on the combination of concentrations obtained in each experiment, for the individual analytes, divided by the maximum concentration of the analyte obtained for the set of experiments, as shown in equation 1.[37]

$$MR = ([S]_i/[S]_{max}) + ([F]_i/[F]_{max}) + ([Cl]_i/[Cl]_{max}) \qquad (1)$$

where $[S]_i$, $[F]_i$, and $[Cl]_i$ represent the concentrations of S, F, and Cl, respectively, in each of the experiments and $[S]_{max}$, $[F]_{max}$, and $[Cl]_{max}$ represent the maximum concentration of the analytes obtained in the experiments. The matrix used in the Box-Behnken design, with the real and coded variables and the MR is shown in Table 2.

Table 2. Box-Behnken design matrix with real and coded variables and the obtained MR, for sample preparation by pyrohydrolysis

Experiment	Mass / mg	Reaction temperature / °C	Reaction time / min	MR
1	200 (−1)	800 (−1)	20 (0)	0.51
2	400 (+1)	800 (−1)	20 (0)	0.49
3	200 (−1)	1000 (+1)	20 (0)	1.75
4	400 (+1)	1000 (+1)	20 (0)	1.81
5	200 (−1)	900 (0)	15 (−1)	0.77
6	400 (+1)	900 (0)	15 (−1)	1.05
7	200 (−1)	900 (0)	25 (+1)	1.00
8	400 (+1)	900 (0)	25 (+1)	1.50
9	300 (0)	800 (−1)	15 (−1)	0.43
10	300 (0)	800 (−1)	15 (−1)	2.03
11	300 (0)	1000 (+1)	25 (+1)	0.70
12	300 (0)	1000 (+1)	25 (+1)	2.26
13	300 (0)	900 (0)	20 (0)	1.13
14	300 (0)	900 (0)	20 (0)	1.24
15	300 (0)	900 (0)	20 (0)	1.24

MR: multiple response.

Accuracy

Due to the lack of a specific certified reference sample for drill cuttings, the accuracy evaluation was carried out through the analysis of two certified reference materials (CRMs): NSC DC 73303 (rocks) with certified concentrations for F (700 ± 44 mg kg^{-1}) and informed concentration for Cl (114 mg kg^{-1}) and S (100 mg kg^{-1}), as well as JB-1A (basalt) with certified concentration for F (357 ± 19 mg kg^{-1}) and informed concentration for Cl (171 mg kg^{-1}) and S (102 mg kg^{-1}). The *t*-student test, at a confidence level of 95%, was applied to verify the significance of the results. Additionally, the accuracy was evaluated by recovery tests in three levels of concentration 50, 100 and 200 mg kg^{-1} for Cl and F, and 500, 1000 and 2000 mg kg^{-1} for S. The drill cuttings were spiked with an appropriate aliquot of a multi-ion solution, dried at 60 ± 5 °C (2 h) and then submitted to the pyrohydrolysis procedure.

Results and Discussion

Pyrohydrolysis parameters

The parameters for sample preparation by pyrohydrolysis were optimized by means of a Box-Behnken experimental design and, based on these results, it was possible to obtain the Pareto chart (Figure 2), which allows assessing the significance of the evaluated variables, as well as the interactions between them.

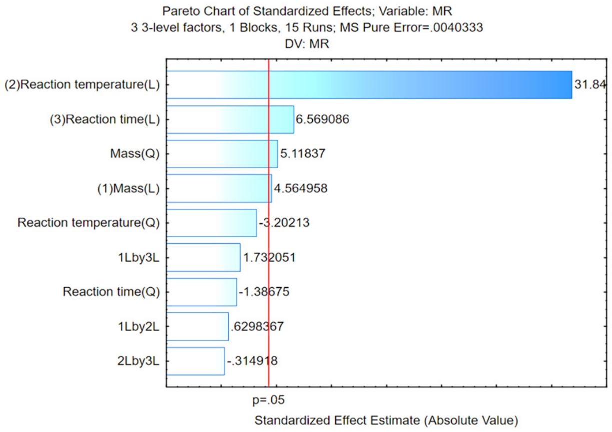

Figure 2. Pareto chart of the variables evaluated in the Box-Behnken design for sample preparation by pyrohydrolysis (L: linear; Q: quadratic and MR: multiple response).

As shown in the Pareto chart, the linear effect of the three variables evaluated and only the quadratic mass interaction was significant ($p < 0.05$) considering a confidence level of 95%. It was also possible to observe that the reaction temperature has greater significance among the variables evaluated, followed by the reaction time and the sample mass. The reaction temperature as a main influence was predicted and is in agreement with previous study in the literature, because in this sample preparation technique the release of the analytes occurs in a temperature range of 700-1400 °C, depending on the matrix constitution.[28]

All significant variables presented positive effects values, which means that the use of larger sample masses, higher temperature, and prolonged reaction times tend to favor the process. The influences and interactions between the variables evaluated can also be observed through the response surfaces (Figure 3).

The response surfaces shown in the Figure 3 indicate that the conditions present in the red regions are adequate, maximizing the multiple responses (MR) values, while in the regions in green indicate conditions that are not adequate to the experiment. In the graphs involving the reaction temperature (Figures 4a and 4b), it is possible to observe a greater slope in the response surface, showing the temperature significance for pyrohydrolysis. On the other hand, time and mass, especially in Figure 3c, promoted less pronounced MR variation, the parameters are of little significance. This fact can be proven through analysis of variance (ANOVA), as shown in Table 3.

As shown in ANOVA, temperature had the highest significant value for $p < 0.05$ considering a confidence level of 95%, while mass and time presented minor significance value. Furthermore, the interactions between the variables were not significant. These values are in

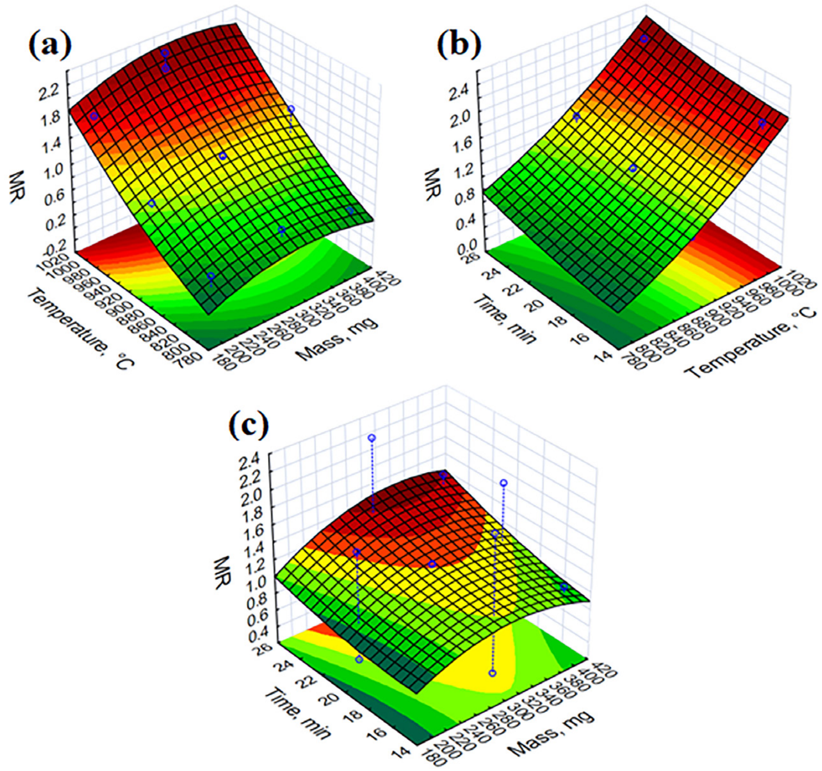

Figure 3. Box-Behnken design response surfaces for mass, temperature, and reaction time optimization for the preparation of drill cuttings samples by pyrohydrolysis, in which (a) temperature *versus* mass, (b) time *versus* temperature and (c) time *versus* mass. MR: multiple response.

Table 3. ANOVA results from the Box-Behnken design ($R^2 = 0.9730$)

Factor	SS	df	MS	*F*-value	*P*-value
(1) Mass L + Q	0.189714	2	0.094857	23.5183	0.040786
(2) Temperature L + Q	4.131156	2	2.065578	512.1268	0.001949
(3) time L + Q	0.181806	2	0.090903	22.5380	0.042485
1*2	0.001600	1	0.001600	0.3967	0.593162
1*3	0.012100	1	0.012100	3.0000	0.225403
2*3	0.000400	1	0.000400	0.0992	0.782643
Lack of fit	0.11750	3	0.039167	9.7107	0.094799
Pure error	0.008067	2	0.004033		
Total SS	4.655160	14			

L: linear; Q: quadratic; SS: sum squared; df: degrees of freedom; MS: media squared.

agreement with expectations, taking into account that the model does not show lack of fit, indicating that the data obtained experimentally are well adjusted to the proposed mathematical model. Then, the compromise conditions selected for the preparation of the drill cuttings samples by pyrohydrolysis were: reaction temperature of 1000 °C, mass of 300 mg, reaction time of 25 min, air flow rate of 0.2 L min^{-1}, and water flow rate of 0.1 mL min^{-1}.

Similar conditions for sample preparation by pyrohydrolysis are reported in the literature. Peng *et al.*[38] proposed a methodology using pyrohydrolysis to determine F, Cl, I, and S in charcoal. In this method, the temperature and reaction time defined by the authors were 1050 °C and 25 min, respectively. Muhammad *et al.*[25] developed a methodology based on the pyrohydrolysis process for the extraction of F and Cl in complex samples of Pb and Zn concentrate, which the optimal parameters were: mass of 200 mg, temperature of 1150 °C, and time of 15 min; while Hoehne *et al.*[35] proposed a methodology using pyrohydrolysis as sample preparation for the determination of F in high purity alumina, which the optimal parameters were: mass of 500 mg, temperature of 950 °C, and time of 20 min.

Effect of the absorbing solution

The absorbing solution has an extremely important role in pyrohydrolysis sample treatment, since the hydrogen halides formed in the pyrohydrolysis reaction can be easily lost in an acid solution. Therefore, the absorbing solution must be alkaline and maintain this characteristic until the end of the reaction. Absorbing solutions composed of substances such as NH_3, NaOH, or buffer solution ($Na_2CO_3/NaHCO_3$) are commonly used.[25,28,30,31] Thus, the influence of different absorbing solutions (50 mmol L^{-1} NH_3, 100 mmol L^{-1} NH_3, H_2O, 3.2 mmol L^{-1} Na_2CO_3 + 1.0 mmol L^{-1} $NaHCO_3$ and 32 mmol L^{-1} Na_2CO_3 + 10 mmol L^{-1} $NaHCO_3$) containing 150 mmol L^{-1} of H_2O_2 on the concentration of Cl, F and S in drill cuttings were evaluated and the results are shown in Figure 4.

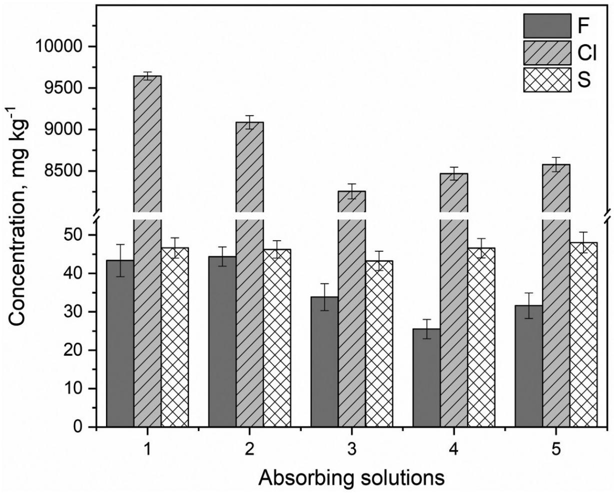

Figure 4. Influence of the absorbing solution on the concentration of Cl, F, and S in drill cuttings samples obtained by IC after pyrohydrolysis. Where: (1) 50 mmol L^{-1} NH_3, (2) 100 mmol L^{-1} NH_3, (3) H_2O, (4) 3.2 mmol L^{-1} Na_2CO_3 + 1.0 mmol L^{-1} $NaHCO_3$ and (5) 32 mmol L^{-1} Na_2CO_3 + 10 mmol L^{-1} $NaHCO_3$. The concentration of 150 mmol L^{-1} of H_2O_2 was added in all absorbing solution.

It is possible to observe in Figure 4 a negative influence of the buffer solutions and water on the concentration of Cl and F. However, for S, significant difference was not observed on the measured concentration for all the evaluated absorbing solutions (ANOVA, confidence level of 95%). Therefore, for Cl and F, the concentrations using H_2O and the buffer solutions showed a significant difference compared to the results using NH_3. Additionally, the NH_3 solutions provided an increase in the concentrations of the three analytes (Cl, F, and S), which for Cl the concentration of 50 mmol L^{-1} of NH_3 was even significantly higher than 100 mmol L^{-1} NH_3 solution (ANOVA, confidence level of 95%). The Cl concentration decreasing with an increase in NH_3 concentration in absorbing solution has also been reported by other authors.[39,40] In this context, the absorbing solution containing 50 mmol L^{-1} NH_3 was selected for the determination of Cl, F, and S in drill cuttings.

Effect of hydrogen peroxide in the absorbing solution

In pyrohydrolysis, S can be released in different forms, including sulfur dioxide (SO_2) and sulfuric anhydride (SO_3).[28] In this study, the determination of S was performed by monitoring the sulfate ion (SO_4^{2-}) in solution. Then, it was necessary to ensure that all species of S were in the form of SO_4^{2-}. In this sense, the addition of an oxidizing agent, such as H_2O_2, to the absorbing solution in an alkaline medium (pH between 9 and 10) promoted the oxidation of the different species of S to SO_4^{2-}.[28] The effect of the H_2O_2 concentration added in the absorbing solution, as well as on the Cl, F, and S concentrations is shown in the Figure 5.

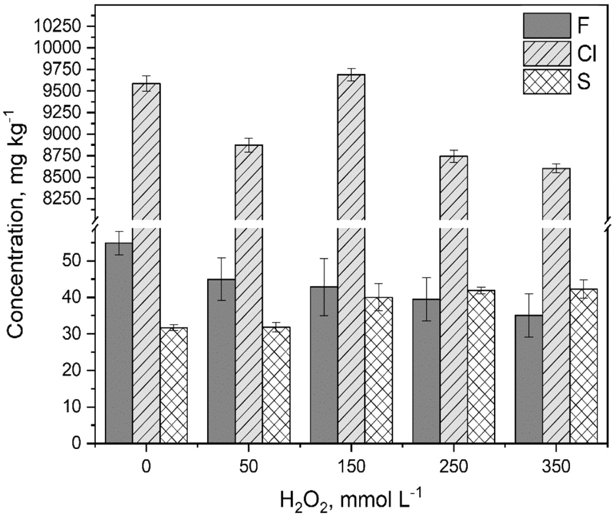

Figure 5. Effect of the H_2O_2 concentration in the absorbing solution (NH_3 50 mmol L^{-1}) on the concentration of Cl, F, and S in drill cuttings samples obtained by IC after pyrohydrolysis.

In the evaluated range of H_2O_2 concentrations, significant difference (ANOVA, confidence level of 95%) was not observed for S concentrations using 150, 250 and 350 mmol L^{-1} H_2O_2. As observed, concentrations equal to or higher than 150 mmol L^{-1} H_2O_2, provided a significant increase (ANOVA, confidence level of 95%) in S concentration compared to the absence of H_2O_2 and to the lowest H_2O_2 concentration (50 mmol L^{-1}). The concentration of 150 mmol L^{-1} of H_2O_2 in the absorbing solution for S determination is in accordance with the concentration reported in the literature.[36,41] Additionally, this concentration is considered suitable for analysis by IC without interference in the peaks of the analytes.[36,41] The slight variation observed in the concentration for Cl and F may not be related to a specific interference from H_2O_2, but it may possibly be due to the high dilution factor applied for samples containing high concentration of Cl. The concentration of Cl obtained by using an absorbing solution containing 150 mmol L^{-1} of H_2O_2 was not significantly affected, but the F concentration was slightly affected (ANOVA, confidence level of 95%). However, comparing the mean value and uncertainties obtained for F concentration in the absence (ultrapure water) and presence of H_2O_2 150 mmol L^{-1}, a good agreement was observed. Thus, the concentration of 150 mmol L^{-1} of H_2O_2 in the absorbing solution was selected as a compromise condition for the determination of Cl, F and S in drill cuttings by ion chromatography (IC) after pyrohydrolysis.

Effect of V_2O_5

For some samples, mainly geological ones, it is necessary to use auxiliary reagents to increase the efficiency of analyte vaporization during sample preparation by pyrohydrolysis.[28,42] To promote the fast and complete analyte release from inorganic matter, several reagents have been applied as accelerators during pyrohydrolysis, for example, WO_3,[43,44] and V_2O_5.[29,45,46] However, V_2O_5 is a widely used accelerator for the determination of halogens and S.[28,42] Thus, the influence of V_2O_5 on the concentration of analytes in the drill cuttings was evaluated and the results are shown in Figure 6.

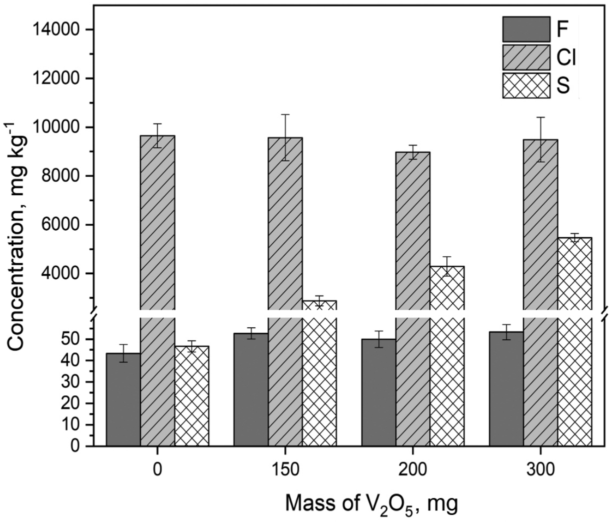

Figure 6. Effect of V_2O_5 on the concentration of Cl, F, and S in drill cuttings samples obtained by IC after pyrohydrolysis.

Analyzing Figure 6, it is possible to observe that the addition of V_2O_5 in the samples resulted in a considerable increase in the concentration of S, especially when 300 mg of V_2O_5 was used, increasing the S signal by more than 100 times, when compared to the absence of V_2O_5. On the other hand, V_2O_5 had no relevant influence on the concentration of F and Cl. This indicates that the use of V_2O_5 improves the release of S from the samples of drill cuttings. In this sense, a mass of 300 mg of V_2O_5 was selected to guarantee the efficient release of S during drill cuttings samples preparation by pyrohydrolysis. The optimized V_2O_5 mass is in accordance with previous studies, which used V_2O_5 to improve the release of S from different samples.[29,45,46]

Figures of merit and accuracy

At the optimized conditions the analytes were properly separated and quantified as their respective ions Cl^-, F^- and SO_4^{2-} in drill cuttings by IC after pyrohydrolysis sample preparation. Figure 7 shows a typical chromatogram obtained for a drill cuttings sample after pyrohydrolysis compared to a multi-ion standard solution.

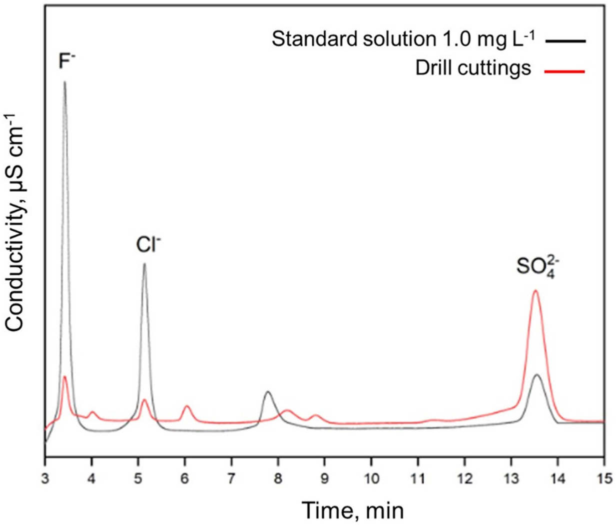

Figure 7. Chromatogram obtained for drill cuttings sample after pyrohydrolysis sample preparation compared to a multi-ion standard solution (1.0 mg L^{-1}). Drill cuttings sample using NH_3 50 mmol L^{-1} + 150 mmol H_2O_2 as absorbing solution. Mobile phase 3.2 mmol L^{-1} Na_2CO_3 and 1.0 mmol L^{-1} $NaHCO_3$, flow rate of 0.7 mL min^{-1}, injection volume of 20 µL and conductivity detection.

As observed in the chromatogram, the peaks of the analytes in the drill cuttings were separated without any interference. However, it should be mentioned that non-identified peaks were observed in retention time of 4 and 6 min for drill cuttings in the presence of H_2O_2. These non-identified peaks may be from the reagent impurities, and although in the proposed analysis no interference was observed, the presence of impurities may affect the limit of detection (LOD). The impurities of reagents could interfere in the baseline detector noise and, consequently, reduce the signal-to-noise ratio, resulting in increased LODs values.[47]

The figures of merit obtained for the determination of Cl, F, and S in drill cutting samples by IC, after sample preparation by pyrohydrolysis, are shown in Table 4. The limit of detection (LOD) and quantification (LOQ) of the proposed method were calculated as 3 and 10 times, respectively, the standard deviation of the signal corresponding to 10 consecutive measurements of blank solutions divided by the slope of the calibration curves.[48] The LODs and LOQs, as well as the coefficient of determination (R^2) and the relative standard deviation (RSD) obtained for Cl, F, and S, by IC after pyrohydrolysis, are shown in Table 4.

Table 4. Figures of merit for determination of Cl, F, and S in drill cuttings after sample preparation by pyrohydrolysis and determination by IC using external calibration with aqueous standard solutions

Analyte	R^2	LOD / (mg kg^{-1})	LOQ / (mg kg^{-1})	RSD (n = 3) / %
Cl	0.9995	1.2	4.0	2-12
F	0.9998	0.5	1.6	0.7-11
S	0.9998	2.5	8.0	1-18

R^2: coefficient of determination; LOD: limit of detection, LOQ: limit of quantification; RSD: relative standard deviation.

The values of LODs and LOQs for determination of analytes by IC were in the order of mg kg^{-1} and are in agreement with those reported in the literature for determination of Cl, F, and S by IC using pyrohydrolysis as sample preparation in similar matrices. Nunes *et al.*[36] used pyrohydrolysis to prepare high-purity flexible graphite samples for subsequent determination of Cl and S, and according to the authors, LOD of 1.0 mg kg^{-1} was obtained for both analytes. Muhammad *et al.*[25] extracted Pb and Zn halides using pyrohydrolysis for sample preparation and IC to determine these halides, in which were reported LODs of 0.5 and 1.1 mg kg^{-1} for F and Cl, respectively. Hoehne *et al.*[35] determined F in high-purity alumina, using pyrohydrolysis for sample preparation by IC, a LOD of 2.0 mg kg^{-1} was reported by the authors. Pereira *et al.*[30] proposed the determination of F and Cl in soil samples by using pyrohydrolysis as sample preparation and IC, the reported LODs were 1 and 2 mg kg^{-1} for F and Cl, respectively.

As shown in the Table 4, the proposed method allowed to reach a good linear correlation coefficient for all analytes ($R^2 > 0.999$). The precision of the proposed method was evaluated through the RSD, and the obtained values were generally lower than 10%; however, values up to 11% for F, 12% for Cl, and 18% for S were obtained for some samples. Nevertheless, considering that the analyzed samples are of high complexity and heterogeneity, the obtained figures of merit can be considered adequate for the determination of Cl, F, and S in drill cuttings samples.

Verification of trueness was performed by analyzing CRMs of geological matrices. Table 5 shows the certified concentrations in the analyzed CRMs, as well as the concentrations determined by IC after the sample preparation by pyrohydrolysis.

Table 5. Concentrations of Cl, F and S in CRMs, determined by IC after sample preparation by pyrohydrolysis

Analyte	Reference / (mg kg^{-1})	Determined / (mg kg^{-1})	Agreement / %
NSC DC 73303			
Cl	114[a]	107 ± 7	94
F	700 ± 44[b]	595 ± 32	85
S	100[a]	95 ± 4	95
JB-1A			
Cl	171[a]	161 ± 14	94
F	357 ± 19[b]	327 ± 10	92
S	102[a]	105 ± 13	103

[a]Informed and [b]certified concentration values. NSC DC 73303 (rocks) and JB-1A (basalt): certified reference materials.

The determined concentrations of the analytes in the CRMs were in good agreement with the reference values (85-103%). Significant difference was not observed between the values obtained by IC and reference values reported in the CRMs, for Cl and S, in both samples, considering the *t*-test with confidence level of 95%. For F, the values of $t_{\text{calculated}}$ for samples NSC DC 73303 (5.60) and JB-1A (4.98) were slightly higher than the t_{critic} to the established confidence level ($t_{\text{critic}} = 4.30$; confidence level of 95%). In this sense, considering the complexity of the drill cuttings and the analytes characteristics, it is possible to state that a good agreement was generally obtained between the experimental results and the certified CRMs concentrations. Consequently, the relative errors of 14.9 and 8.3% obtained for the CRMs NSC DC 73303 and JB-1, respectively, were acceptable. However, due to the lack of a specific certified reference material, the accuracy was also evaluated by recovery tests in three levels of concentration (Table 6).

As observed, suitable recoveries (higher than 89%) were obtained in the three evaluated concentration levels. Thus, the proposed method can be considered suitable for the determination of Cl, F and S in drill cuttings.

Concentrations of Cl, F and S in drill cuttings

The assessment of Cl, F and S concentration in drill cuttings samples from onshore and offshore oil and

Table 6. Recoveries of Cl, F and S in drill cuttings determined by IC after sample preparation by pyrohydrolysis

Addition / (mg kg^{-1})	F / (mg kg^{-1})	Cl / (mg kg^{-1})	S / (mg kg^{-1})
No addition	139 ± 2	84 ± 10	889 ± 10
50 (F and Cl)/500 (S)	183 ± 16	126 ± 8	1499 ± 30
100 (F and Cl)/1000 (S)	214 ± 22	200 ± 9	1879 ± 80
200 (F and Cl)/2000 (S)	313 ± 15	221 ± 20	2938 ± 114
Recovery / %	89-97	93-108	99-107

gas exploration wells was performed by the proposed method using pyrohydrolysis as sample preparation and quantification of the analytes by IC. Figure 8 shows the concentration (mg g^{-1}) of F, Cl and S at different depths for the onshore (77-715 m), offshore PS (2,857-3,809 m), and offshore PRS (4,119-6,256 m) wells.

As shown in Figure 8, in the onshore well (77-715 m) the concentrations of Cl (0.08-12.24 mg g^{-1}), F (0.139-0.297 mg g^{-1}) and S (0.89-48.61 mg g^{-1}) showed an increasing tendency with depth. This fact is possibly due to the mineralogical characteristics intrinsic to the rock of the respective oil wells and/or with the composition of the drilling fluid. The X-ray diffraction (XRD) analysis (Figure S1, Supplementary Information (SI) section) indicates that samples collected at depths of 77 and 399 m are composed of quartz (SiO_2), dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$). In the sample collected at the depth of 715 m, in addition to these minerals, the presence of calcium sulfate ($CaSO_4$) was also identified. The factors that can influence the mobility of F in the soil are the pH and the formation of aluminum and calcium complexes.[49] In more acidic soils, inorganic F concentrations are considerably higher at greater depths, due to the low affinity between F and organic matter, resulting in F leaching until it is retained by clayey minerals or more alkaline sediments, at greater depths.[50] This distribution profile is not observed in saline soils.[51]

The results obtained for samples from PS offshore well (2,857-3,809 m), shown in Figure 8, demonstrated that the Cl concentration (6.25-45.49 mg g^{-1}) increased with depth. Chlorine is an element that maintains its concentration in marine waters, it has low compatibility with marine carbonate and other sedimentary materials.[52,53] In contrast, the concentrations of F (0.073-0.421 mg g^{-1}) and S (6.43-18.43 mg g^{-1}) decreased at greater depths. Fluorine in marine waters is removed through the formation of F complexes with calcium compounds, noncomplexed F is usually removed by sedimentation.[50,54] The mineral characterization of the PS offshore well (Figure S2, SI section) indicates that the samples are mainly composed of quartz, dolomite, and calcite.

The analysis of samples from PRS offshore well (4,119-6,256 m), showed that the concentration of Cl (23.72-486.96 mg g^{-1}) and of F (0.073-0.421 mg g^{-1}) decreases as the drilling depth increases, due to less contact between the rock and the salt reservoir (NaCl). It is possible to observe that in the XRD analysis (Figure S3, SI section), the composition of the samples at the depths of 4,119 m and

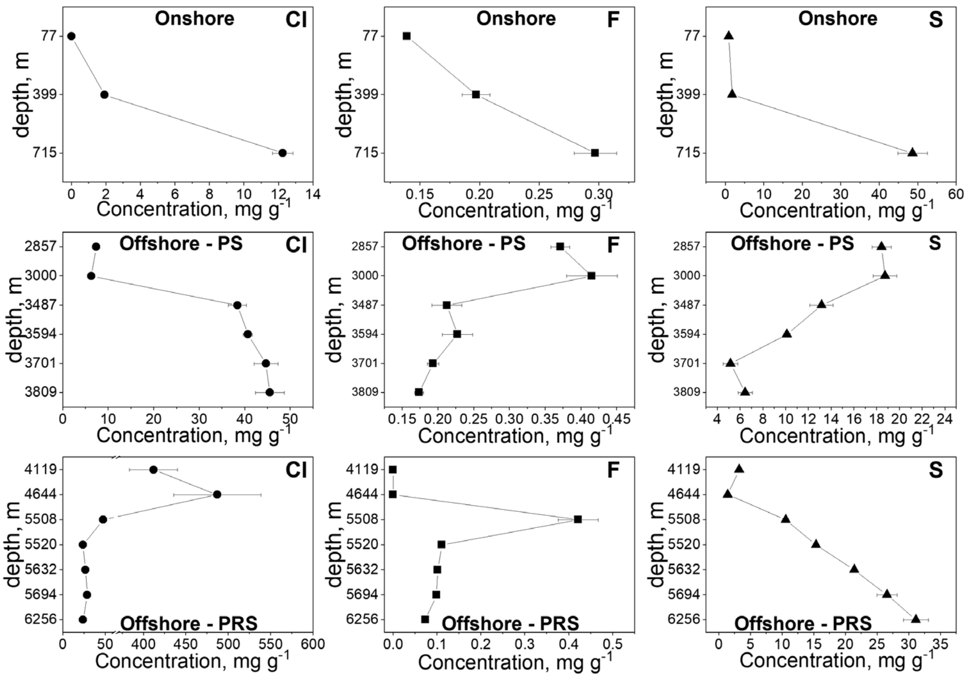

Figure 8. Assessment of Cl, F and S concentrations in drill cuttings at different depths from onshore (77-715 m), offshore PS (2,857-3,809 m) and offshore PRS (4,119-6,256 m) wells using pyrohydrolysis sample preparation and determination by IC. The error bars represent the standard deviation (n = 3).

4,644 m, which present the highest concentrations of Cl, is halite (NaCl). Wei *et al.*[55] reported that Cl concentrations in marine sediment samples also had different patterns of variation in different depth profiles.

For samples collected at depths of 4,119 m and 4,644 m, the F concentration was lower than the LOD (0.04 mg kg^{-1}). In this case, the high concentration of Cl in this region, 486.96 mg g^{-1} for 4,644 m and 411.82 mg g^{-1} for 4,119 m, required a large dilution of the samples, limiting the detection of F in these samples by the proposed method. The concentration of S varied from 3.23 mg g^{-1} to 31.09 mg g^{-1}, and increased concentrations were observed at greater depths, as well as in the onshore well. This is likely due to the characteristics of the sample, which at greater depths presents barite in its composition ($BaSO_4$) (Figure S3).

The increasing trend in the concentration of S in marine sediments as a function of depth was reported by Jørgensen *et al.*,[56] who claimed that this effect is related to the S cycle in marine sediments. In this case, the sulfate is reduced to sulfide, and a major portion of the sulfide can be re-oxidized back to sulfate, while a small fraction of the sulfides precipitate with iron and other metals or with organic matter. As observed, the concentration of F in all samples collected from the drill cuttings was much lower than the concentration of Cl. Mahn and Gieskes,[57] Rude and Aller,[58] and Wei *et al.*[55] when analyzing marine sediment samples, also observed that the concentrations of F were much lower than those of Cl.

Conclusions

The assessment of Cl, F and S concentrations in drill cutting samples collected at different depths of onshore and offshore oil exploration wells was successfully performed by the proposed method using pyrohydrolysis for sample preparation and determination by ion chromatography (IC). The proposed method proved to be simple and efficient for the analysis of drill cuttings samples. It also proved to be of low instrumental and operating cost, in addition to making minimal use of reagents, when compared to conventional digestion methods. The Box-Behnken design allowed the optimization of the mass, temperature, and reaction time used for the preparation of the samples by pyrohydrolysis to minimize the number of experiments necessary in this evaluation. The concentration of analytes was efficiently determined in drill cuttings samples collected in depth profiles of onshore and offshore oil drilling wells. The variation in the concentration of F, Cl and S as a function of depth is likely related to the mineral composition of the samples.

Supplementary Information

Supplementary data (drill cuttings X-ray diffractograms) are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

The authors acknowledge the financial support provided by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES). R.G.M. and G.S.C.J. were supported by scholarships from CNPq. P.C.C.A. was supported by scholarship from CAPES. E.S.C. and D.L.G.B. were supported by research scholarships from CNPq.

Author Contributions

Renan G. Marim was responsible for conceptualization, data curation, formal analysis investigation, writing original draft, validation, writing-review and editing; Gilberto S. Coelho Junior for data curation, formal analysis, investigation, and validation; Paola C. C. de Azevedo for data curation, formal analysis, investigation, and validation; Daniel L. G. Borges for resources, writing original draft and writing-review and editing; Tatiane A. Maranhão for resources, writing original draft and writing-review and editing; Fernando J. S. de Oliveira for writing original draft and writing-review and editing; Vera L. A. F. Bascunãn for resources, writing original draft and writing-review and editing; Eduardo S. Chaves for conceptualization, formal analysis, funding acquisition, resources, writing original draft and writing-review and editing.

References

1. Cordes, E. E.; Jones, D. O. B. B.; Schlacher, T. A.; Amon, D. J.; Bernardino, A. F.; Brooke, S.; Carney, R.; DeLeo, D. M.; Dunlop, K. M.; Escobar-Briones, E. G.; Gates, A. R.; Génio, L.; Gobin, J.; Henry, L.-A. A.; Herrera, S.; Hoyt, S.; Joye, M.; Kark, S.; Mestre, N. C.; Metaxas, A.; Pfeifer, S.; Sink, K.; Sweetman, A. K.; Witte, U.; *Front. Environ. Sci.* **2016**, *4*, 58. [Crossref]
2. de Souza, L. S.; Chaves Sgarbi, G. N. C.; *Bol. Geol.* **2019**, *41*, 175. [Crossref]
3. Jafarinejad, S.; *Petroleum Waste Treatment and Pollution Control*; Elsevier: Oxford, 2016.
4. Araujo, F. C.; Leoneti, A. B.; *The Extr. Ind. Society* **2019**, *6*, 906. [Crossref]
5. Martins, S. S. S.; de Azevedo, M. O.; da Silva, M. P.; da Silva, V. P.; *HOLOS* **2015**, *6*, 54. [Crossref]
6. Alves, G. M.; Petri Jr., I.; *J. Pet. Sci. Eng.* **2021**, *207*, 109137. [Crossref]

7. Petri Jr., I.; dos Santos, J. M.; Ataíde, C. H.; Duarte, C. R.; *J. Pet. Sci. Eng.* **2020**, *195*, 107760. [Crossref]
8. Caenn, R.; Darley, H.; Gray, G. R.; *Composition and Properties of Drilling and Completion Fluids*; Elsevier: Oxford, 2011.
9. Ismail, A. R.; Alias, A. H.; Sulaiman, W. R. W.; Jaafar, M. Z.; Ismail, I.; *Chem. Eng. Trans.* **2017**, *56*, 1351. [Crossref]
10. Santos, J. M.; Pereira, M. S.; Júnior, I. P.; Pena, M. M. R.; Ataíde, C. H.; *Energy Technol.* **2014**, *2*, 832. [Crossref]
11. Vryzas, Z.; Kelessidis, V. C.; *Energies* **2017**, *10*, 540. [Crossref]
12. Kogbara, R. B.; Ayotamuno, J. M.; Onuomah, I.; Ehio, V.; Damka, T. D.; *Appl. Geochem.* **2016**, *71*, 1. [Crossref]
13. Hammerli, J.; Rusk, B.; Spandler, C.; Emsbo, P.; Oliver, N. H. S.; *Chem. Geol.* **2013**, *337-338*, 75. [Crossref]
14. Kusebauch, C.; John, T.; Barnes, J. D.; Klügel, A.; Austrheim, H. O.; *J. Petrol.* **2015**, *56*, 299. [Crossref]
15. Eggenkamp, H. G. M.; Marks, M. A. W.; Atanasova, P.; Wenzel, T.; Markl, G.; *Minerals* **2020**, *10*, 995. [Crossref]
16. Li, Y.; Liu, W.; Liu, P.; Luo, H.; Wang, X.; Zhang, D.; Yuan, Y.; *ACS Earth Space Chem.* **2022**, *6*, 44. [Crossref]
17. Tjabadi, E.; Mketo, N.; *TrAC, Trends Anal. Chem.* **2019**, *118*, 207. [Crossref]
18. Krzyzaniak, S. R.; Santos, R. F.; Dalla Nora, F. M.; Cruz, S. M.; Flores, E. M. M.; Mello, P. A.; *Talanta* **2016**, *158*, 193. [Crossref]
19. Novo, D. L. R.; Mello, J. E.; Rondan, F. S.; Henn, A. S.; Mello, P. A.; Mesko, M. F.; *Talanta* **2019**, *191*, 415. [Crossref]
20. Pereira, R. M.; Costa, V. C.; Hartwig, C. A.; Picoloto, R. S.; Flores, E. M. M.; Duarte, F. A.; Mesko, M. F.; *Talanta* **2016**, *147*, 76. [Crossref]
21. Mesko, M. F.; Costa, V. C.; Pereira, R. M.; Hartwig, C. A.; *J. Braz. Chem. Soc.* **2019**, *30*, 2191. [Crossref]
22. Stanišić, S. M.; Ignjatović, L. M.; Stević, M. C.; Dordević, A. R.; *J. Serb. Chem. Soc.* **2011**, *76*, 769. [Crossref]
23. Li, T.; Min, H.; Li, C.; Yan, C.; Zhang, L.; Liu, S.; *Anal. Lett.* **2021**, *54*, 2498. [Crossref]
24. Shimizu, K.; Suzuki, K.; Saitoh, M.; Konno, U.; Kawagucci, S.; Ueno, Y.; *Geochem. J.* **2015**, *49*, 113. [Crossref]
25. Muhammad, N.; Zhang, Y.; Asif, M.; Khan, M. F. S.; Intisar, A.; Mingli, Y.; Subhani, Q.; Cui, H.; Zhu, Y.; *Microchem. J.* **2020**, *159*, 105593. [Crossref]
26. Xie, P.; Guo, W.; Yan, X.; Zheng, X.; *Fuel* **2017**, *208*, 483. [Crossref]
27. Taflik, T.; Duarte, F. A.; Flores, É. L. M.; Antes, F. G.; Paniz, J. N. G.; Flores, É. M. M.; Dressler, V. L.; *J. Braz. Chem. Soc.* **2012**, *23*, 488. [Crossref]
28. Flores, E. L. M.; Flores, E. M. M.; Antes, F. G.; Duarte, F. A.; Barin, J. S.; Dressler, V. L. In *Métodos de Preparo de Amostra para Análise Elementar*; Krug, F. J.; Rocha, F. R. P., eds.; Sociedade Brasileira de Química: São Paulo, 2019.
29. Marks, M. A. W.; Kendrick, M. A.; Eby, G. N.; Zack, T.; Wenzel, T.; *Geostand. Geoanal. Res.* **2017**, *41*, 107. [Crossref]
30. Pereira, L. S. F.; Pedrotti, M. F.; Dalla Vecchia, P.; Pereira, J. S. F.; Flores, E. M. M.; *Anal. Chim. Acta* **2018**, *1010*, 29. [Crossref]
31. Mishra, V. G.; Das, M. K.; Shah, D. J.; Jeyakumar, S.; Tomar, B. S.; Ramakumar, K. L.; *J. Chromatogr. A* **2018**, *1532*, 144. [Crossref]
32. Fletcher, N. D.; Manard, B. T.; Bostick, D. A.; Bostick, W. D.; Metzger, S. C.; Ticknor, B. W.; Rogers, K. T.; Hexel, C. R.; *Talanta* **2021**, *221*, 121573. [Crossref]
33. Degen, T.; Sadki, M.; Bron, E.; König, U.; Nénert, G.; *The HighScore suite*, version 29; Malvern Panalytical, UK, 2014.
34. *Statistica*, version 6.0; StatSoft, USA, 2001.
35. Hoehne, L.; Picoloto, R. S.; Enders, M. S. P.; Druzian, G. T.; Muller, E. I.; Flores, E. M. M.; *Microchem. J.* **2019**, *146*, 645. [Crossref]
36. Nunes, T. S.; Muller, C. C.; Balestrin, P.; Muller, A. L. H.; Mesko, M. F.; Mello, P. A.; Muller, E. I.; *Anal. Methods* **2015**, *7*, 2129. [Crossref]
37. Trutna, L.; Spagon, P.; del Castillo, E.; Moore, T.; Hartley, S.; Hurwitz, A.; Multiple responses, https://www.itl.nist.gov/div898/handbook/pri/section5/pri5321.htm, accessed in September 2022.
38. Peng, B.; Wu, D.; Lai, J.; Xiao, H.; Li, P.; *Fuel* **2012**, *94*, 629. [Crossref]
39. Antes, F. G.; Pereira, J. S. F.; Enders, M. S. P.; Moreira, C. M. M.; Müller, E. I.; Flores, E. M. M.; Dressler, V. L.; *Microchem. J.* **2012**, *101*, 54. [Crossref]
40. Coelho Jr., G. S.; Rondan, F. S.; Hartwig, C. A.; Santos, R. F.; Mello, P. A.; Mesko, M. F.; *J. Anal. Methods Chem.* **2021**, *2021*, 6005481. [Crossref]
41. Evans, K. L.; Tarter, J. G.; Moore, C. B.; *Anal. Chem.* **1981**, *53*, 925. [Crossref]
42. Mishra, V. G.; Jeyakumar, S.; *MedCrave* **2018**, *2*, 389. [Crossref]
43. Rae, J. E.; Malik, S. A.; *Chemosphere* **1996**, *33*, 2121. [Crossref]
44. Rice, T. D.; *Talanta* **1988**, *35*, 173. [Crossref]
45. Duarte, F. A.; Pereira, E. R.; Flores, E. L. M.; Muller, E. I.; Flores, E. M. M.; Dressler, V. L.; *Quim. Nova* **2013**, *36*, 716. [Crossref]
46. Kusuno, H.; Matsuzaki, H.; Nagata, T.; Miyairi, Y.; Yokoyama, Y.; Ohkouchi, N.; *Nucl. Instrum. Methods Phys. Res., Sect. B* **2015**, *361*, 414. [Crossref]
47. Wenzl, T.; Haedrich, J.; Schaechtele, A.; Robouch, P.; Stroka, J.; *Guidance Document on the Estimation of LOD and LOQ for Measurements in the Field of Contaminants in Feed and Food*; Publications Office of the European Union: Luxembourg, 2016. [Link] accessed in September 2022
48. Lister, A. S. In *Handbook of Pharmaceutical Analysis by HPLC*; Ahuja, S.; Dong, M. W., eds.; Elsevier, 2005, p. 191. [Crossref]
49. Cuprys, A.; Pulicharla, R.; Brar, S. K.; Drogui, P.; Verma, M.; Surampalli, R. Y.; *Coord. Chem. Rev.* **2018**, *376*, 46. [Crossref]
50. Tanaka, K.; Ono, T.; Fujioka, Y.; Ohde, S.; *Mar. Chem.* **2013**, *149*, 45. [Crossref]

51. Gilpin, L.; Johnson, A. H.; *Soil Sci. Soc. Am. J.* **1980**, *44*, 255. [Crossref]
52. Kendrick, M. A. In The *Role of Halogens in Terrestrial and Extraterrestrial Geochemical Processes*; Harlov, D.; Aranovich, L., eds.; Springer: Cham, Switzerland, 2018. [Crossref]
53. Okumura, M.; Kitano, Y.; Idogaki, M.; *Mar. Chem.* **1986**, *19*, 109. [Crossref]
54. Clarkson, M. O.; Müsing, K.; Andersen, M. B.; Vance, D.; *Chem. Geol.* **2020**, *539*, 119412. [Crossref]
55. Wei, W.; Kastner, M.; Deyhle, A.; Spivack, A. J.; *Proc. ODP, Sci. Results* **2005**, *195*, 1. [Crossref]
56. Jørgensen, B. B.; Findlay, A. J.; Pellerin, A.; *Front. Microbiol.* **2019**, *10*, 849. [Crossref]
57. Mahn, C. L.; Gieskes, J. M.; *Mar. Geology* **2001**, *174*, 323. [Crossref]
58. Rude, P. D.; Aller, R. C.; *Cont. Shelf Res.* **1994**, *14*, 883. [Crossref]

Submitted: May 15, 2022