Determination of Halogens and Sulfur in Pitch from Crude Oil by Plasma-based Techniques after Microwave-induced Combustion

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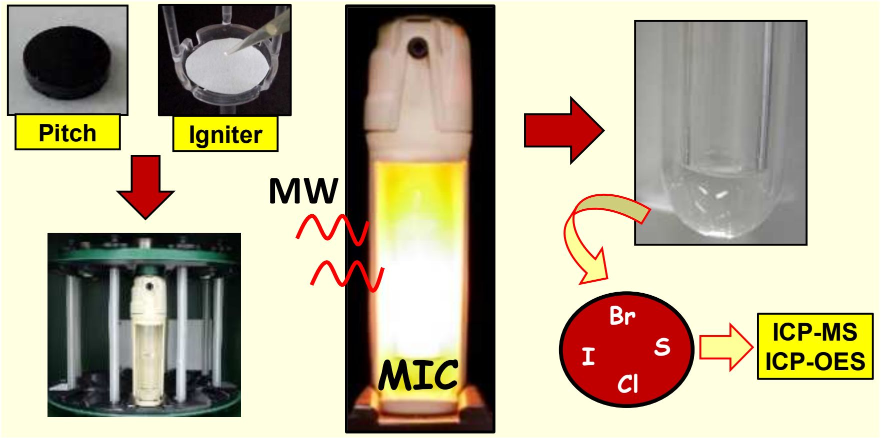

Sample preparation method for pitch digestion using microwave-induced combustion for further determination of halogens by ICP-MS and sulfur by ICP-OES.

Determination of Halogens and Sulfur in Pitch from Crude Oil by Plasma-based Techniques after Microwave-induced Combustion

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Abstract

In this work is demonstrated the feasibility of halogens and sulfur determination in pitch produced from crude oil residues by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES), respectively, after digestion by microwave-induced combustion (MIC). Using the proposed system, it was possible to achieve a very effective digestion of pitch (up to 400 mg) using 20 bar of oxygen and 50 µL of 6 mol L^{-1} of ammonium nitrate as ignition aid. Water and NH_4OH solutions (10 to 100 mmol L^{-1}) were evaluated for analytes absorption and a reflux step was applied after combustion in order to ensure quantitative analytes absorption. The volume of absorbing solution (6, 8, 10 and 12 mL) was also evaluated and best results were obtained using 6 mL confirming results of previous works. Accuracy was evaluated by comparison of results with those obtained using total Cl and S analyzer, X-ray fluorescence (XRF, for Cl and I determination) and pyrohydrolysis followed by ICP-MS determination (Br and I). By using 50 mmol L^{-1} NH_4OH as absorbing solution the agreement with reference values ranged from 95 to 103% for all analytes. Results obtained using MIC presented an agreement of 101 and 100% to those obtained using total Cl and S analyzer, respectively. Results were also compared with XRF analysis (for Cl and S) and agreement was 102 and 92%, respectively. In the same way, results obtained by MIC were in agreement with those obtained by pyrohydrolysis method (agreement of 97 and 105% for Br and I, respectively). The residual carbon content for MIC digests was always below 1% showing the high efficiency of pitch digestion. Using 400 mg of samples mass and 6 mL of NH4OH as absorbing solution, limits of detection were 3.1 µg g^{-1} for S by ICP-OES and 3.2, 0.02 and 0.002 µg g^{-1} for Cl, Br and I by ICP-MS, respectively.

Keywords: Microwave-induced combustion; Halogens determination; Sulfur determination; Sample preparation; Inductively coupled plasma optical emission spectrometry; Inductively coupled plasma mass spectrometry; Pitch analysis.

1. Introduction

Pitch is a byproduct of petroleum coke production and can be considered as a complex matrix containing mainly a variable composition of heterocyclic and aromatic compounds with softening temperature about 200 °C.[1] The use of pitch in several applications has increased due to its excellent binding properties and determination of its chemical composition become mandatory.[2-6] The content of metals and non-metals in electrodes depends upon the level of these impurities contained in the respective raw materials (petroleum coke and/or recycled anode components).

Depending on sulfur and halogen content in pitch, deleterious effects can be observed during pitch industrial processing or modification of physical and chemical properties of final products, such as release of sulfur during carbon anode production and obtaining of more porous materials.[7-12]

In this sense, knowledge of sulfur and halogens composition is important and feasible analytical methods are increasingly required for industrial applications. However, digestion of pitch, as well as for crude oil and its high molecular weight derivatives, is well-known as a very difficult task. Moreover, halogens determination in this matrix is still more difficult when considering the risks of losses and contamination during sample preparation step.[2-4,10,14]

Despite the determination of major elements, such as sulfur, in pitch can be carried out using elemental analyzers,[5,13,15,16] these equipment are not suitable for other non-metals determination (e.g., Br and I). Moreover, there are no methods in literature for pitch digestion for further simultaneous determination of halogens and sulfur.

Sample digestion is a critical step especially for further halogens determination. The use of microwave radiation for sample preparation has been applied for many matrices due to its high digestion efficiency, relatively low consumption of solvents, low blanks and others.[17] However, conventional acid digestion methods are unsuitable for halogens and significant losses can be observed even using closed vessels.[18] Similarly, also methods involving halogens extraction could be not suitable to quantitative recoveries of these elements.[19-21] Additionally, it is important to point out that pitch matrix contains a high content of aromatic compounds which are very refractory to digestion by conventional wet digestion.

In recent years, microwave-induced combustion (MIC) has been employed for the digestion of many kinds of samples, especially those considered as "hard to digest".[22-24] An important aspect of MIC method is the possibility of using diluted solutions (acid or alkaline) for analytes absorption, minimizing interferences during determination step and reducing blank values.[25] The feasibility of MIC has been described for digestion of samples such as coal, petroleum coke, crude oil (light, heavy and extra heavy) and crude oil distillation residues.[25-27] Practically in all cases, alkaline or even water provided suitable recoveries for further halogens and sulfur determination.[25-27]

In this work, taking into account the difficulties involved in pitch digestion even using high temperature and pressure conditions, the feasibility of MIC was evaluated for further determination of halogens (Cl, Br and I) and sulfur by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES), respectively. The operational parameters of MIC, such as the type, volume and concentration of absorbing solution and sample mass were investigated. Residual carbon content (RCC) in digests was determined in order to assess the efficiency of MIC digestion. Accuracy was evaluated by comparison of results obtained by MIC with those obtained by total Cl and S analyzer and X-ray fluorescence (XRF) (both for Cl and S) and by pyrohydrolysis followed by ICP-MS analysis (for Br and I).

2. Materials and methods

2.1 . Instrumentation

A microwave digestion system (Multiwave 3000®, Anton Paar, Austria) equipped with up to eight high-pressure quartz vessels (maximum operating pressure and temperature of 80 bar and 280 ºC, respectively) was used for MIC method. Commercial quartz holders (Anton Paar) were used to insert the sample and filter paper inside the quartz vessel.

For the determination of Cl, Br and I, an inductively coupled plasma mass spectrometer (Model ELAN DRC II, PerkinElmer, Canada) equipped with a concentric nebulizer (Meinhard® Associates, USA), a cyclonic spray chamber (Glass Expansion, Inc., Australia) and a quartz torch with a quartz injector tube (2 mm i.d.) was used. Chlorine was determined using dynamic reaction cell (DRC) system using ammonia (minimum purity of 99.999%) as reaction gas.[21] The DRC parameters were adjusted in order to minimize the interferences on $^{35}Cl^+$ and $^{37}Cl^+$ isotopes. Adjustment of the reaction gas flow rate and the rejection parameter q (RPq) were optimized in order to obtain the lowest limit of detection (LOD). RPq and NH_3 values were 0.45 and 0.35 mL min^{-1}, respectively. Operational conditions of ICP-MS instrument are shown in Table 1.

An inductively coupled plasma optical emission spectrometer (Optima 4300 DV, PerkinElmer, USA) equipped with a GemCone® nebulizer and a cyclonic spray chamber was used for sulfur determination. This instrument was also used for RCC determination in MIC digests. Argon 99.996% (White Martins) was used for plasma generation, nebulization and auxiliary gas. The instrumental parameters selected for sulfur and RCC determination by ICP-OES are also shown in Table 1.

A total Cl and S analyzer (model Multi EA® 5000, Analytik Jena AG, Germany) was used for Cl and S determination in pitch samples in order to compare the results with those obtained after MIC followed by the determination using ICP-MS and ICP-OES, respectively. Chloride determination was based on coulometric titration and sulfur was determined by ultraviolet fluorescence detection, according to ASTM D 5453-06.[28] The determination of Cl and S was carried out using argon and oxygen gas was selected for as carrier gas and combustion aid, respectively (flow rate of each gas was 100 mL min^{-1}). The temperature used in the combustion tube was 1050 ºC and sample mass used for determination of Cl and S was 100 and 1 mg, respectively. A microbalance (Sartorius, model M2P, Germany) was used for weighting the samples.

An XRF instrument (model S8 Tiger wavelength dispersive, Bruker, Germany) was used for comparison of results for Cl and S. Pitch samples (about 200 mg) were weighed and pelletized (5 ton, 13 mm diameter stainless steel die press). Pellets were kept by individual stainless steel spring loaded cup holders with 8 mm diameter windows and placed in the XRF instrument, which was equipped with a 4 kW Rh X-ray tube, scintillation counter, flow proportional counter with P10 gas flow, automatic mask, collimator, filter and crystal changers, and robotic sample loader. An 8 mm X-ray mask was manually placed in the mask holder. The automatic QuantExpress routine was used with the "best detection" option under vacuum with a 50 µm beryllium plate in place to protect the tube window. The QuantExpress routine performed three scans covering 56 to 0.5 keV with automatic filter, collimator, crystal (LiF (200) or PET crystals) and counter selection over 17 min. The spectral data were evaluated manually with the Spectra*Plus* program[29] with the "Organic" calibration method with the pellet weight and dimensions (height and diameter) considered for each pellet. The Spectra^{Plus} routines adjusted the total mass to 100% with the addition of a CH_2 matrix and performed the matrix and inter-elemental interference correction with automatic line selection.

A pyrohydrolysis system, used for pitch digestion for further Br and I determination by ICP-MS was used according to previous publications[21,30,31] for further comparison of results.

2.2 Sample, reagents and standards

Three pitch samples (A, B and C) were supplied by a Brazilian industry (in powder form) and sample pellets for MIC were prepared using a hydraulic press (Specac, UK, 3 ton, 1 min). Sample A was characterized using analyte spike and used for method optimization. The results for Cl, Br, I and S obtained after this characterization was used as reference for evaluation of recovery of MIC method.

Ultrapure water was purified in a Milli-Q system (Millipore Corp., USA, 18.2 MΩ cm) and used to prepare the standards and solutions, as well as for sample dilution when necessary.

The standard solutions for the determination of Cl, Br and I by ICP-MS were obtained by dilution of chloride, iodide and bromide stock solutions. These solutions of Cl, I and Br were prepared by dissolution of respective salts (Merck) in 10 mmol L^{-1} NH_4OH.

For sulfur determination by ICP-OES, a stock solution containing 1000 mg L^{-1} of S (Spex Certiprep Inc., Canada) was used to prepare standard solutions by sequential dilution in 5% HNO_3 (Merck). Standard solutions used for RCC determination by ICP-OES were prepared by sequential dilution of a stock solution prepared using citric acid

(Merck) dissolution in water. Yttrium (Fluka, Sigma Aldrich) was used as internal standard (1 mg L^{-1}).

Standard organic solutions were used for calibration of total Cl and S analyzer. The calibration for sulfur was carried out using standard lubricant oil (5000 mg kg^{-1} of sulfur, Accustandard, SWMO-SOX-4, USA) diluted with toluene (Tedia, Brazil). The standard solutions for Cl were also prepared in toluene by sequential dilution of a stock solution of 1000 µg g^{-1}, which was previously prepared from chlorobenzene (Merck). Electrolyte solution for Cl determination was prepared by mixing 0.03 mol L^{-1} sodium acetate (Vetec, Brazil) and 13.9 mol L^{-1} glacial acetic acid (Vetec) solutions.

Ammonium nitrate (6 mol L^{-1}, Merck) used as ignition aid was dissolved in water. Small discs of cellulose filter paper (15 mm of diameter, 12 mg) with low ash content (Black Ribbon Ashless, Schleicher and Schuell, Germany) were used to aid the combustion process. Paper disks were previously cleaned with 5% HNO_3 (immersion for 24 h), followed by cleaning with ethanol (purity of 95%, Merck) for 20 min in an ultrasonic bath, rinsed with water and dried in a class 100 laminar bench (CSLH-12, Veco, Brazil). Ammonium hydroxide solution (10 to 100 mmol L^{-1}, Merck) was used as absorbing solution and it was prepared after dilution of commercial reagent (25% ammonia, m/m) in water. Oxygen (99.6%, White Martins) was used for pressurization of digestion vessels used in MIC method. For recovery evaluation, samples were spiked by addition of standard solution (same used for calibration) containing all halogens and sulfur, which was placed on the sample pellet before the combustion step.

2.3 Microwave-induced combustion

Microwave-induced combustion was evaluated using sample mass ranging from 100 to 500 mg. This study was performed in order to monitor and optimize the combustion process and to achieve safety conditions during digestion. Pellets of samples were placed on a small disk of filter paper on the quartz holder, followed by addition of 50 µL of 6 mol L^{-1} NH_4NO_3 solution. The holder containing sample and filter paper was placed inside the quartz vessel charged previously with absorbing solution. Absorbing solutions (H_2O or 10, 25, 50 and 100 mol L^{-1} NH_4OH solution) were evaluated, as well as the volume of absorbing solution (6, 8, 10 and 12 mL). After closing the vessels and capping of rotor, vessels were pressurized with oxygen at 20 bar. The microwave heating program was immediately started: 1400 W for 5 min (optional reflux step) and 0 W for 20 min for cooling. After cooling, digests were diluted up to 25 mL with water for further determination step. After each run, vessels were cleaned using 6 mL of concentrated HNO_3 and microwave irradiation at 1400 W for 10 min and 0 W for 20 min (cooling) and rinsing with water.

An important aspect that must be considered, especially for further determination of trace halogens, is related to contamination. All the quartz materials must be carefully cleaned and filter paper should be decontaminated as previously reported.[25,33]

3. Results and discussion

Initial experiments were performed with sample mass ranging from 100 to 500 mg and oxygen pressure of 20 bar, in order to achieve safe conditions and a reproducible combustion of pitch. The oxygen pressure was selected based on previous work[25] where digestion of extra-heavy crude oil was successfully performed. Using 100 to 400 mg of pitch the combustion was always complete and no apparent residues were observed. The maximum pressure reached during the combustion process was 32 bar that corresponds to about 40% of the limit pressure recommended by the manufacturer

(80 bar). However, when 500 mg of sample were used it was observed an incomplete combustion (visible residues remaining in quartz holder). In order to avoid this problem, higher oxygen pressure could be applied and probably the sample mass increased, but due to safety reasons 20 bar was selected as the maximum pressure for this matrix. Subsequent experiments were carried out using 400 mg of pitch and 20 bar of oxygen.

It is well-known that the choice of absorbing solution is a key parameter of combustion methods, since it can influence the analytes recovery.[32] The chosen absorbing solution needs to be compatible with the detection technique. In this sense, acid or alkaline solution has been successfully used for metals or non-metals determination, respectively.[17] In this sense, a study for selecting the more suitable absorbing solution for halogens and sulfur was performed. Thus, sample masses of 400 mg and 6 mL of water or NH_4OH (10, 25, 50 and 100 mmol L^{-1}) as absorbing solutions were evaluated. Pitch sample "A" was arbitrarily selected for these experiments and results obtained by analyte spike were used as reference values. After MIC, analysis of digests was carried out using ICP-MS (for Cl, Br and I determination) and ICP-OES (for S determination).

As can be seen in Figure 1, the recoveries for all analytes ranged from 87 to 115% using water as absorbing solution. Moreover, it is important to notice that using water as absorbing solution, relative standard deviation (RSD) was significantly high (up to 19%), making difficult its use. In the same way, using 10 mmol L^{-1} NH_4OH the recovery for Br, I and S was higher than 95%. However, this solution was not feasible for Cl and a recovery of about 84% was obtained. On the other hand, using 25 mmol L^{-1} NH_4OH as absorbing solution recoveries ranging from 96 to 101% were obtained for all the analytes (RSDs below 11%). Finally, using 50 mmol L^{-1} NH_4OH solution (or higher, 100 mmol L^{-1}), recoveries ranging from 95 to 103% were obtained for all analytes as well as the RSDs were lower in comparison with other absorbing solutions. Thus, it was possible to use 50 mmol L^{-1} NH_4OH as absorbing solution for MIC method and subsequent determination of all analytes (Cl, Br and I by ICP-MS and S by ICP-OES). Taking into account that other studies[24-26] using MIC did not evaluate higher volumes of absorbing solution than 6 mL, this aspect was investigated in order to evaluate a possible reduction on concentration of absorbing solution (10 or 25 mmol L^{-1} NH_4OH) especially for Cl considering that even 10 mmol L^{-1} NH_4OH concentration was considered as suitable for Br, I and S. Thus, experiments were carried out using 400 mg of sample, varying the volume of absorbing solution of 6, 8, 10 and 12 mL of 10 mmol L^{-1} NH_4OH. However, no statistical difference (analysis of variance, confidence level of 95%) was observed when the volume of absorbing solution was increased (6 to 12 mL). Even using 12 mL of 10 mmol L^{-1} NH_4OH, recovery was not better than 89% for Cl. Thus, the volume originally selected (6 mL of 50 mmol L^{-1} NH_4OH as absorbing solution) was used for further experiments. This solution provided suitable recoveries for all analytes (99, 103, 95 and 100% for Cl, Br, I and S, respectively).

After optimization of the main parameters that affect MIC performance, the accuracy was evaluated by analysis of pitch sample by total Cl and S analyzer and XRF for Cl and S and using pyrohydrolysis combined with ICP-MS for Br and I determination. Results of this comparison as well as halogens and sulfur concentration for samples B and C are shown in Table 2. Using MIC for further Cl and S determination the respective results were in agreement with those obtained by total Cl and S analyzer (agreement of 101 and 100%, respectively) and XRF (102 and 92%, respectively). Moreover, differences between results for Cl and S using MIC and XRF methods were not observed (paired *t* test, 95% of confidence level). In the same way, when pyrohydrolysis system was used, an agreement of 97 and 105% was achieved for Br and I, respectively.

Regarding the precision of MIC method, it is possible to observe that the relative standard deviation (RSD) for all analytes was lower than 13% that is considered suitable for the determination of halogens and sulfur in a complex and refractory matrix such as pitch.

Using MIC method, the LODs obtained for Cl, Br and I by ICP-MS were 3.2, 0.02 and 0.002 µg g^{-1}, respectively. The LOD for S by ICP-OES was 3.1 µg g^{-1}. In comparison with other techniques, the LOD obtained for Cl and S by MIC were lower than those obtained by XRF (9.3 and 6.0 µg g^{-1}, respectively) and very similar to those obtained by using the total Cl and S analyzer (4.9 and 1.5 µg g^{-1}, respectively). The LODs for Br and I using pyrohydrolysis and ICP-MS (0.03 and 0.007 µg g^{-1}, respectively) were slightly higher than the proposed method. The LODs for MIC, total analyzer and pyrohydrolysis methods, were calculated as 3 times the standard deviation for 10 consecutive measurements of blank, divided by the slope of the calibration curve. For XRF, the LOD was calculated directly by the software of XRF instrument.

The RCC is also an important parameter to evaluate the efficiency of sample digestion methods. The RCC in MIC digests was always below 1% regardless the type and concentration of absorbing solution employed. This result was due to the high temperature achieved during combustion (generally higher than 1200),[33] resulting in almost complete oxidation of organic matrix. Under this condition practically all the organic matrix is oxidized, preventing eventual interferences in determination by ICP-MS caused by residual organic compounds in digests.[34,35] An important aspect is that blanks were always negligible and this fact was, very probably, due to the use of closed vessels and diluted reagents.

4. Conclusions

The proposed MIC method was suitable for pitch digestion and subsequent determination of halogens by ICP-MS and sulfur by ICP-OES. It was possible to use a single absorbing solution (6 mL of a 50 mmol L^{-1} NH_4OH solution) for all analytes absorption and fully compatible to both plasma-based techniques. By avoiding the use of concentrated reagents is important for decreasing the blank values and also the amount of laboratory residues, which is in agreement to green chemistry statements. Results obtained by MIC for all analytes were in agreement with those obtained by total Cl and S analyzer, XRF and pyrohydrolysis and LODs were considered as suitable for quality control of pitch used for industrial applications. Furthermore, MIC method allowed the combustion of relatively high sample mass (400 mg), providing good performance for pitch digestion and relatively high sample throughput (once eight samples can be simultaneously digested in 25 min).

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Figure captions

Figure 1. Evaluation of absorbing solution (H_2O or 10, 25, 50 and 100 mmol L^{-1} NH_4OH) for the determination of Cl (□), Br (░) and I (▒) by ICP-MS and sulfur (▓) by ICP-OES in pitch after MIC (error bars represents the standard deviation, n = 3).

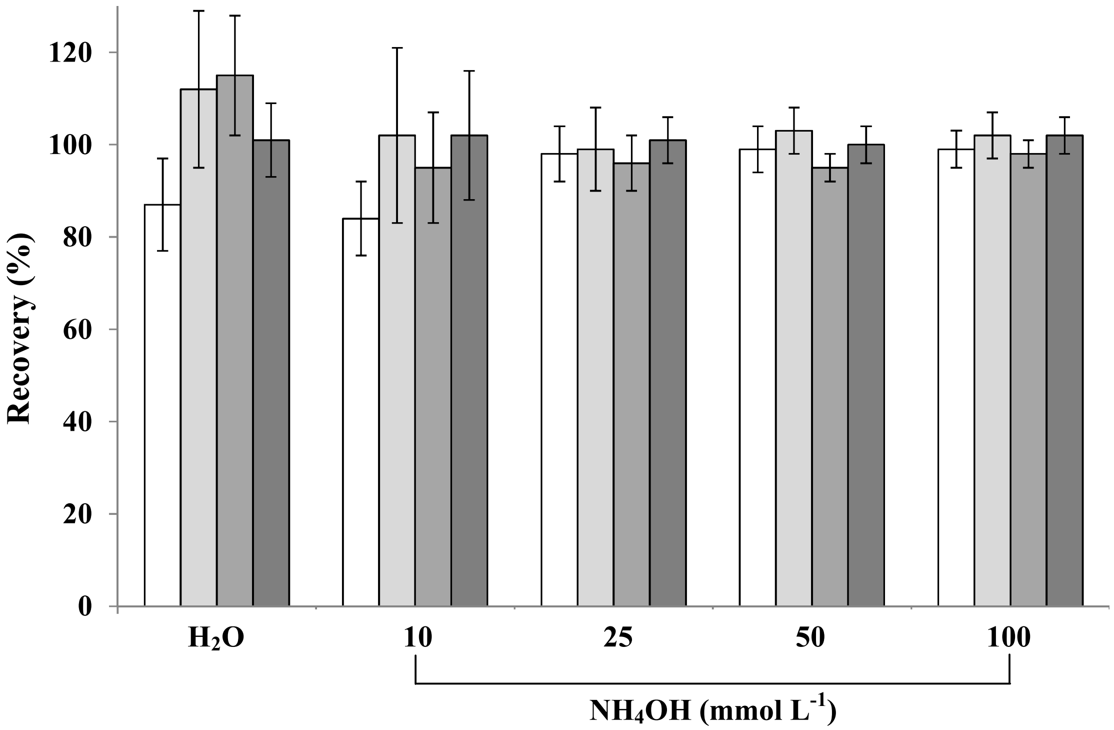

Figure 1

Table 1. Operational conditions for determination of Cl, Br and I by ICP-MS and sulfur by ICP-OES.

Parameter	ICP-MS	ICP-OES
RF power, W	1400	1400
Plasma gas flow rate, L min^{-1}	15.0	15.0
Auxiliary gas flow rate, L min^{-1}	1.2	0.2
Nebulizer gas flow rate, L min^{-1}	1.08	0.70
Sample flow rate, mL min^{-1}	1.4	2.1
Spray chamber	Cyclonic	Cyclonic
Nebulizer type	Concentric	GemCone®
Observation view	-	Axial
Isotope, *m/z*	^{35}Cl and ^{37}Cl[a]	-
	^{79}Br	-
	^{127}I	-
Wavelength, nm	-	S (180.669)
	-	C (193.091)[b]

[a] Determination using DRC-ICP-MS.

[b] Used for RCC determination.

Table 2. Results obtained for the determination of Cl, Br and I by ICP-MS and sulfur by ICP-OES in pitch sample using MIC, total Cl and S analyzer, XRF and pyrohydrolysis (n = 3).

Element	Concentration, µg g^{-1}					
	Sample A				Sample B	Sample C
	Total Cl and S analyzer	XRF	Pyrohydrolysis[a]	MIC	MIC	MIC
Cl[a]	69.3 ± 5.2	70.0 ± 11.8	nd	68.7 ± 1.3[a]	103 ± 4[a]	96.0 ± 2.1[a]
Br[a]	nd	< 1.9	1.05 ± 0.10	1.08 ± 0.09[a]	0.99 ± 0.13[a]	1.16 ± 0.07[a]
I[a]	nd	< 12.2	0.85 ± 0.06	0.81 ± 0.07[a]	0.93 ± 0.05[a]	1.03 ± 0.04[a]
S[b]	5562 ± 312	5100 ± 65	nd	5564 ± 200[b]	5931 ± 367[b]	4703 ± 240[b]

[a] determination by ICP-MS.
[b] determination by ICP-OES.
nd: not determined.