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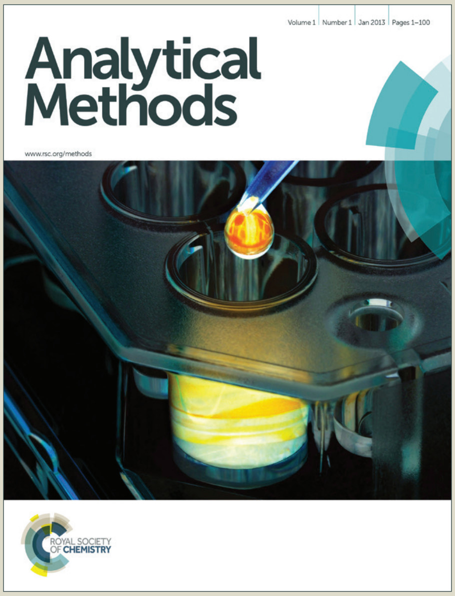

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Determination of chlorine and sulfur in high purity flexible graphite using ion chromatography (IC) and inductively coupled plasma optical emission spectrometry (ICP OES) after pyrohydrolysis sample preparation

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ABSTRACT

Pyrohydrolysis method was applied for digestion of high purity flexible graphite (FG) used in nuclear applications and subsequent determination of Cl and S by inductively coupled plasma optical emission spectrometry (ICP OES) and ion chromatography (IC). Instrumental parameters for pyrohydrolysis were studied as reaction time, air and water flow-rate pumped through the reactor, the type and concentration of absorbing solution (water, 10 to 200 mmol L^{-1} NH_4OH or 100 to 1000 mmol L^{-1} H_2O_2) and the use of V_2O_5 as accelerator. Sample masses up to 250 mg were decomposed using pyrohydrolysis at 1100^{o}C for 30 min. Quantitative recoveries for Cl and S were obtained using air and water flow-rate pumped through the reactor at 0.1 L min^{-1} and 0.5 mL min^{-1}, respectively without using of V_2O_5. Absorbing solution of 50 mmol L^{-1} NH_4OH and 250 mmol L^{-1} H_2O_2 were suitable for quantitative absorption of Cl and S. Limit of detection (LOD) was 1 µg g^{-1} for Cl determination by IC that was 20 fold better than those obtained by ICP OES. In this sense, IC determination is recommended for Cl determination in FG in order to meet with General Electric (GE) recommendation for nuclear materials. On the other hand, LODs obtained for S using IC and ICP OES were similar (1 µg g^{-1}). For S determination by IC absorbing solution should be H_2O_2 in order to convert all S species to SO_4^{2-}. For comparison, Cl and S were also determined in digests obtained using microwave-induced combustion (MIC). In spite of high chemical inertness that allowed combustion of only 25 mg of FG, statistical difference between pyrohydrolysis and MIC results was not observed. Evaluation of accuracy was carried out using certified reference materials (NIST 1632c - bituminous coal and SARM 19 coal) and significant differences were not observed between certified reference values and pyrohydrolysis results. After optimizing conditions, pyrohydrolysis was suitable for quality control of Cl and S impurities in FG used for nuclear applications.

Keywords: flexible graphite, pyrohydrolysis, chlorine, sulfur, IC and ICP OES

1. Introduction

Flexible graphite (FG) is a flexible sheet made by compressing a collection of exfoliated graphite flakes.[1] Exfoliation of graphite is performed at temperature around 1200 ^{o}C with a phase transition involving the vaporization of the intercalate compound in the graphite. Graphite should be intercalated before an exfoliation process and the most common intercalation compound is graphite bisulfate obtained by reaction of graphite with a mixture of concentrated sulfuric and nitric acid.[2-3] Expansion caused by vaporization result in decreasing of specific mass of graphite due to the pressure increase between graphene sheets and also by diffusion of intercalated compounds from FG structure. Exfoliation process promotes some attractive properties in FG as resilience, impermeability to fluids, chemical inertness and high-temperature stability. In this sense, FG sheets has been used in different applications as gasket, packing and sealing in different industries.[2-7] In addition, FG is used in nuclear applications due to elevated nuclear radiation resistance even when exposed to massive doses of radiation.[7] However, for nuclear applications the purity of FG should be at least 99.5%.[7] The main non-metallic contaminants present in FG occurs due the trace elements present in graphite raw materials and also by residual amount of decomposed intercalate (such as sulfur) that remains in the structure of FG material. According to General Electric (GE) specification for nuclear material, Cl, S and nitrate should be determined in FG materials.[8] Leachable Cl, S and nitrate from FG materials can accelerate pitting corrosion of metallic tubes by permeating stainless steel chromium oxide film.[8] Maximum concentration allowed for S, for a FG sample with negligible of Cl and nitrate (both concentration lower than 1 $\mu g\ g^{-1}$), is 630 $\mu g\ g^{-1}$. On the other hand, the maximum concentration of Cl in absence of S and nitrate (both concentration lower than 1 $\mu g\ g^{-1}$) is 450 $\mu g\ g^{-1}$. Finally, the maximum concentration of nitrate is 820 $\mu g\ g^{-1}$ for FG sample with both Cl and S concentration lower than 1 $\mu g\ g^{-1}$, according to GE specification for nuclear material.[8]

In the literature, articles devoted to the determination of non-metallic contaminants in FG material are scarce. Additionally, in GE specification for nuclear material there is no clear recommendation for the most appropriate method for the digestion FG samples.[8] It can be explained by chemical inertness of FG that does not allow the complete digestion of this material using conventional wet digestion methods. In this way, methods that employ more drastic conditions of temperature and pressure, such as combustion methods are recommended for the digestion of FG.[9] Combustion bomb and oxygen flask were used for digestion of many organic samples, but some drawbacks related to contamination by metallic parts and low sample mass can be observed.[9] Alternatively, microwave-induced combustion (MIC) has been used for digestion of organic matrices and sample masses up to 500 mg can be used.[10-15] Chlorine and S determinations were carried out in refractory organic samples (such as residues of crude oil distillation and carbon nanotubes) after MIC digestion that allowed low residual carbon in digest and suitable agreement for certified reference materials (CRMs).[14-15]

Taking into account the chemical inertness of FG samples, pyrohydrolysis can be considered one alternative method for digestion, because it allows the hydrolysis of halogens, sulfur, boron and other elements from refractory samples at temperatures around 1000 ^{o}C which can be absorbed in diluted solutions for posterior analysis.[16-26] The use of acid or alkaline diluted solutions is suitable for introduction on chromatographic systems and nebulization in plasma-based techniques. Additionally, Cl and S are separated from sample matrix minimizing interferences in ion chromatography (IC) and inductively coupled plasma optical emission spectrometry (ICP OES) analysis.[17,19] During pyrohydrolysis, volatilization of Cl and S occurs as HCl and SOx volatile species, respectively. Accelerator reagent as V_2O_5, can be used mixed with sample in order to improve recoveries for Cl and S.[19] According to the literature, water or alkaline diluted solutions are preferably used as absorbing solution for Cl and S determination. Moreover, since the volatilization of S during pyrohydrolysis reaction can occurs as SO_2 and SO_3 small amount of H_2O_2 should be added to promote the oxidation of all sulfur species to SO_4^{2-} allowing the determination of total S as SO_4^{2-} by IC.[19]

In this work, pyrohydrolysis was used as sample preparation of FG for further determination of Cl and S using IC and ICP OES. Parameters of pyrohydrolysis method as reaction time, air-flow rate and water flow-rate pumped through the reactor, effect of V_2O_5 and absorbing solution were optimized in order to assure the complete recovery of Cl and S from FG matrix. Additionally, nitrate was determined by IC in solutions obtained by extraction of FG sample using Soxhlet method according to recommendation of General Electric specification for nuclear materials.[8] In order to evaluate the accuracy of proposed method, FG samples were also digested using MIC and digests were analyzed by ICP OES and IC. Finally, accuracy was also evaluated using CRMs of coal (NIST 1632 c and SARM 19 from South Africa) once a CRM for FG is not commercially available.

2. Experimental

2.1 Reagents, solution and samples

All solutions used in this work were prepared using water previously purified by a Milli-Q system (Milipore, Bedford, USA) resulting in water with a conductivity of 18.2 MΩ cm. All chemicals used were analytical grade and purchased from Merck (Darmstadt, Germany). Nitric acid 65% (Merck, Darmstadt, Germany) has been purified by subboilling distillation still (Milestone, Sorisole, Italy). Oxygen with purity better than 99.6% (White Martins, São Paulo, Brazil) was used for MIC digestions. Argon used for plasma generation in ICP OES has purity higher than 99.998% (White Martins, São Paulo, Brazil). Determination of S, Cl and NO_3^- was carried out using external calibration by dilution of 1000 mg L^{-1} standard solutions (Spex CertiPrep, Metuchen, USA). In this work four samples of flexible graphite sheet donated by Graftech International (Ohio, USA) and Centerflon Indústria e Comércio (São Paulo, Brazil) were used. Accuracy of the proposed method was evaluated using CRMs with high carbon content matrices - NIST 1632c (National Institute of Standard and Technology, Trace elements in coal) and SARM 19 (Council for Mineral Technology, coal – South Africa).

2.2. Instrumentation

FG sheet samples were ground in cryogenic mill (Spex Certiprep, model 6750, Metuchen, USA). A pre-cooling time of 60 s was used followed by 2 min of milling. This procedure was repeated three times and sample with particle size lower than 80 µm was obtained. All weighing procedures were carried out using an analytical balance (model AY 220, Shimadzu do Brasil, São Paulo, Brazil).

Chlorine, sulfur (as SO_4^{2-}) and nitrate were determined using an ion chromatograph (Metrohm, Herisau, Switzerland) consisting of a pump, a conductivity detector, a Metrosep A Supp 5 analytical column (150×4 mm i.d., particle size of 5 µm and polyvinyl alcohol with quaternary ammonium groups) and a guard column Metrosep packed with the same material and particle size of the analytical column. Additionally, a self-regeneration suppressor was used to reduce the conductivity of the mobile phase. Mobile phase was a solution of 3.2 mmol L^{-1} Na_2CO_3 and 1 mmol L^{-1} $NaHCO_3$. The flow-rate was set at 0.8 mL min^{-1} and a sample loop of 100 µL was used.

For comparison, Cl and S were also determined using an inductively coupled plasma optical emission spectrometer (Ciros CCD model, Spectro, Kleve, Germany) equipped with a Scott-type double pass spray chamber (glass material), a cross-flow nebulizer (glass material), a torch and a injector of quartz. The operating conditions were: radio frequency power of 1.6 kW, principal plasma gas flow-rate of 14.0 L min^{-1}, auxiliary gas flow-rate of 1.0 L min^{-1} and nebulizer gas flow-rate of 0.80 L min^{-1}. Chlorine and sulfur were determined at 134.724 and 180.731 nm, respectively.

Microwave-induced combustion of FG samples was performed using a Multiwave 3000 microwave system (Anton Parr, Graz, Austria) equipped with up to eight pressurized quartz vessels. Maximum pressure, internal volume and temperature allowed by quartz vessels were 80 bar, 80 mL and 280°C, respectively.

2.3. Nitrate determination

Sample masses up to 5 g were directly weighed in to a Soxhlet cellulose cartridge and positioned inside the Soxhlet extraction system. Nitrate was extracted from the sample using water during 48 h according to the recommendation of General Electric specification for nuclear material.[9] Leached solution obtained by Soxhlet extraction was made up to 250 mL and determination of nitrate was carried out using IC.

2.4. Microwave-induced combustion method

The main procedures used for MIC are summarized in Figure 1. Pellets of FG samples with masses of 25, 50, 100 or 200 mg were prepared and placed together with paper disk on a quartz holder. Subsequently, 50 µL of 6 mol L^{-1} NH_4NO_3 was added on paper filter as ignition aid. Quartz holder with sample and paper filter wetted with NH_4NO_3 solution was introduced into the quartz vessel containing 6 mL of absorbing solution. Alkaline and H_2O_2 solutions were suitable for absorbing Cl and S species produced during MIC.[13,15] In this sense, H_2O_2 (100, 250, 500 and 1000 mmol L^{-1}) and NH_4OH (10, 50, 100 and 200 mmol L^{-1}) were evaluated as absorbing solutions for Cl and S. Quartz vessels were sealed and pressurized with 20 bar of oxygen. The heating program used for MIC contained two stages: *i*) 1400 W for 10 minutes (combustion and refluxing steps); *ii*) 0 W for 20 minutes (cooling step). Solution resulting of combustion was diluted to 10 ml with water and Cl and S determinations were performed using

IC and ICP-OES. Decontamination of quartz vessels and holders were performed using concentrated HNO_3 with the same microwave heating program used for combustion of samples. After decontamination, vessels and holders were washed with water.

2.5. Pyrohydrolysis apparatus and procedure

The pyrohydrolysis system used in this work is described in a previously published study.[16] Pyrohydrolysis reaction was performed using a high purity fused silica reactor tube (35 cm of length, 1.6 cm of i.d. and 1.9 cm of e.d.) and heating was carried out by resistive tubular furnace (Sanchis Fornos Elétricos, model Especial, Porto Alegre Brazil) with a maximum temperature of 1100 °C. Water was pumped through the heated alumina capillary by peristaltic pump (IPC8 ISM931 model, Ismatec, Zurich, Swiss) and thus was converted to a vapor after introduced inside the heated reactor tube. Air flow-rate was controlled by a fluxometer and introduced inside reactor tube. All parameters evaluated for pyrohydrolysis are shown in Figure 1. Preliminary tests for pyrohydrolysis optimization were carried out in order to evaluate recoveries for Cl and S. In this sense, FG sample masses of 250 mg, temperature of 1100 ^{o}C, reaction time varying from 10 to 50 min and use of auxiliary reagent (V_2O_5) were evaluated. Additionally, absorbing solutions - H_2O_2 (100, 250, 500 and 1000 mmol L^{-1}), NH_4OH (10, 50, 100 and 200 mmol L^{-1}) and only water - were checked in order to assure the quantitative absorbtion of all analytes. Finally, water flow-rate ranging from 0.2 mL min^{-1} to 0.5 mL min^{-1} pumped through the heated capillar and air flow-rate varying from 0.2 to 1.0 L min^{-1} were also evaluated (Figure 1). Pyrohydrolysis reaction products were condensed on a serpentine and absorbed in 10 mL of suitable solution. After pyrohydrolysis reaction, absorbing solution was diluted up to 25 mL and determination of Cl and S was performed using ICP-OES and IC. Alumina boat was soaked with a nitric acid solution (1+1) for 15 min, rinsed with water and dried prior to analysis. After the pyrohydrolysis reaction, system was heated for another 30 min to minimize contamination.

3. Results and Discussion

3.1. Sohxlet extraction and microwave-induced combustion

According to GE specification, nitrate determination by IC is carried out in solution obtained by Soxhlet extraction. For nitrate all FG samples showed results lower than the LOD (1 µg g^{-1}) that are in agreement with GE specification (Table 1). Additionally, Cl and S (determined as sulfate) were also determined in Soxhlet extract and concentration was lower than the LODs (1 µg g^{-1} for both analytes). In this sense, Soxhlet extraction was not suitable for Cl and S determination in FG samples because did not allow the quantitative recovery of these analytes. On the other hand, FG samples were digested using MIC and analyzed for Cl and S using IC and ICP-OES. Samples masses of only 25 mg of FG were efficiently digested (digests solution without insoluble materials) using MIC that also promoted deleterious effect on LOD for non metallic determination. According to previous works, NH_4OH and H_2O_2 solutions were suitable for Cl and S absorption during MIC digestion.[14,17] For this reason, NH_4OH (10 to 200 mmol L^{-1}) and H_2O_2 (100 to 1000 mmol L^{-1}) were evaluated as absorbing solution for Cl and S analysis by MIC. Recoveries results for Cl and S showed that 50 mmol L^{-1} NH_4OH and 250 mmol L^{-1} H_2O_2 were suitable as absorbing solution for MIC analysis. MIC digests were analyzed by IC and ICP OES and only 250 mmol L^{-1} H_2O_2 solution was suitable for both techniques because this solution promoted oxidation of all S species allowing determination of S as sulfate. Additionally, 250 mmol L^{-1} H_2O_2 solutions did not present interferences on peaks for Cl and SO_4^{2-} (peaks for Cl and SO_4^{2-} at about 5 and 18 min, respectively) in IC chromatogram. Spectral interferences on ICP OES determination at 134.724 nm (Cl emission line) and 180.669 nm (S emission line) were not observed for H_2O_2 solutions used in MIC digestion. Additionally, LOD for Cl obtained using ICP OES was worst in comparison with that obtained by IC, even using spectrometer with purged optics. LOD for S using IC and ICP OES were considered similar.

Regarding to S results obtained by MIC and IC, all FG samples presented this non metallic impurity as contaminant. On the other hand, Cl was only quantified in FG I sample and, thus, S and Cl results obtained by MIC for FG I sample were adopted as reference values to evaluate the recoveries of pyrohydrolysis method.

In order to obtain the maximum combined concentration (MCM) of halogens, sulfur and nitrates allowed for FG, the concentration of halogens (in µg g^{-1}) should be divided by 35.453, concentration of sulfur (in µg g^{-1}) divided by 48.096 and nitrate concentration (in µg g^{-1}) divided by 62.004. Finally, the sum the above three divisions should be lower than 13.2.[8] The maximum combined concentration of Cl, S and nitrate could not be calculated for the results of MIC and IC, because the LOD for Cl was 5 µg g^{-1} which is higher than allowed by the GE specification (1 µg g^{-1}). Thus, it is important to point out that MIC was not suitable for Cl determination, even using IC analysis, because LOD did not meet the requirements of GE specification for nuclear materials. In this sense, pyrohydrolysis method was optimized to allow the analysis of FG samples.

3.2. Optimization of pyrohydrolysis conditions

In order to improve the LODs for Cl and S in comparison with those obtained by MIC, important parameters of pyrohydrolysis were optimized. In this sense, influences of air and water flow-rate through the reactor, reaction time, absorbing solution and use of V_2O_5 were firstly studied in order to improve the recovery for Cl and S. Sample mass of 250 mg of FG I sample, 10 min of reaction time and 10 mL of 100 mmol L^{-1} NH_4OH (absorbing solution) were used for initial studies. Pyrohydrolysis reaction was carried out using 1100 ^{o}C that is the maximum temperature allowed by the furnace. This temperature is in agreement with previous work published in literature for the determination of Cl and S in geological materials.[26] After pyrohydrolysis reaction, sample residue was not observed, probably due to complete gasification of graphite.

3.2.1. Evaluation of air-flow rate and water flow-rate pumped through the reactor

Air and water flow-rate are important parameters for pyrohydrolysis because they are involved in hydrolysis reaction and can affect the temperature inside the reactor. Initially, was observed that an air flow-rate higher than 0.1 L min^{-1} should not be used because a part of the sample was carried together with the air stream, probably due to the low density of FG sample. Similar behavior was observed for water flow-rate pumped through the reactor for values higher than 0.5 L min^{-1}. In this sense, for subsequent determination by pyrohydrolysis, air flow-rate and water flow-rate pumped through the reactor was fixed at 0.1 L min^{-1} and 0.5 mL min^{-1}, respectively.

3.2.2. Optimization of reaction time

Pyrohydrolysis reaction time is an important parameter that should be optimized to assure quantitative recovery of analyte and the cleaning of the reactor before analysis of other sample. Moreover, the time required for complete volatilization of analyte depends on the characteristics of element. In this sense, pyrohydrolysis reaction time was evaluated with time ranging from 10 to 50 min for 250 mg of FG with temperature set to 1100 ^{o}C. It was possible to observe that the vaporization of S required more time for quantitative recovery in comparison with Cl. Reaction time equal or higher than 30 min was considered suitable allowing quantitative recoveries for Cl and S. For subsequent experiments for evaluation of recovery for Cl and S, reaction time was fixed in 30 min. Finally, using the optimized conditions (water flow-rate pumped through the reactor at 0.5 mL min^{-1} and reaction time of 30 min) the total volume of water produced during pyrohydrolysis reaction it was about 15 mL.

3.2.3. Effect of V_2O_5

Pyrohydrolysis analysis of some samples requires use of auxiliary reagent in order to aid the volatilization of analytes during hydrolysis reaction at high temperature. The most common auxiliary reagent is V_2O_5 that is reported in literature for pyrohydrolysis analysis of different matrices and subsequent determination of halogen and S.[19] In this way, recoveries studies for Cl and S were carried out using masses of 250, 500 and 1000 mg of V_2O_5 and compared with recovery results in absence of V_2O_5. Significant differences were not observed when recoveries values obtained using V_2O_5 were compared with results without V_2O_5 (ANOVA, 95% confidence level). Thus, based on these results, FG analysis using pyrohydrolysis was carried out without V_2O_5.

3.2.4. Evaluation of absorbing solution

The choice of absorbing solution for pyrohydrolysis analysis depends on the characteristics of analyte. Diluted alkaline solutions were preferred to assure the quantitative recovery of sulfur and halogens species produced during pyrohydrolysis reaction.[17,19,26] Additionally, H_2O_2 can be used in order to convert all S species to SO_4^{2-} allowing the determination by IC. The conversion of all S species to sulfate is preferred because sulfite is very unstable and poor chromatographic separation for these two S species can be observed using IC determination.[27] In this sense, water, NH_4OH solutions (10, 50, 100 e 200 mmol L^{-1}) and H_2O_2 solutions (100, 250, 500 e 1000 mmol L^{-1}) were evaluated as absorbing solution to collect the analytes during pyrohydrolysis reaction. Water was not suitable as absorbing solution because recoveries of 75 and 80% were observed for S and Cl, respectively. On the other hand, when at least 100 mmol L^{-1} NH_4OH solution was used, recoveries higher than 98% were obtained. However, it is important to point out that 100 mmol L^{-1} NH_4OH solution did not convert all S species to SO_4^{2-} because two peaks were observed in IC chromatogram (peak for SO_3^{2-} at 14 min, and peak for SO_4^{2-} at 18 min). In this sense, IC analysis was not possible for S determination using 100 mmol L^{-1} NH_4OH solution. Additionally, when H_2O_2 was used to absorb pyrohydrolysis products, recoveries higher than 99% for Cl and S were observed for solution with concentration higher than 250 mmol L^{-1}. In this case, all S volatile compounds were converted to SO_4^{2-} (only one peak was observed in IC chromatogram) and determination was carried out using IC system. Interferences on the determination of Cl by IC were not observed. Additionally, diluted solution of H_2O_2 (250 mmol L^{-1}) was selected for FG pyrohydrolysis and was considered also suitable for Cl and S determination by ICP OES. Diluted solutions of H_2O_2 are suitable for analysis by IC and plasma based techniques because minimize interferences and improves LOD in comparison with digests containing concentrated reagents.

3.3. Decomposition of FG samples using pyrohydrolysis method

Four FG samples were prepared using pyrohydrolysis method and the determination of Cl and S was carried out using ICP OES and IC and results are shown in Table 1. The MCM of halogens, sulfur and nitrates calculated from pyrohydrolysis and IC results was lower than 13.2 for all FG samples, with exception of FG I sample. For FG I sample the MCM of halogens, sulfur and nitrates value was 19.3 and then this material should not be used for nuclear applications. RSDs of results obtained by pyrohydrolysis and IC were lower than 10% and considered suitable for FG quality control. LODs achieved for Cl and S using pyrohydrolysis and MIC are shown in Table 2. It is possible to observe that LODs obtained using pyrohydrolysis are better than those obtained by MIC due to high sample mass that could be analyzed by pyrohydrolysis. Moreover, LODs obtained for Cl and S using pyrohydrolysis and IC were suitable according to GE specification for nuclear material. Finally, LODs obtained by pyrohydrolysis method are better than those reported in the literature (Table 2), probably due to larger sample mass used in the proposed method. Regarding to accuracy evaluation, significant differences (t test, 95% confidence level) were not observed for Cl and S results obtained by pyrohydrolysis and MIC (determination carried out by IC). Accuracy was also evaluated using certified reference materials (CRM 1632 c and SARM 19) and significant difference among certified reference material and results obtained by pyrohydrolysis was not observed (t test, 95% confidence level).

4. Conclusion

Pyrohydrolysis method showed to be suitable for Cl and S determination in high purity FG samples and it meets the requirements of GE specification for nuclear materials. MIC method can also be used for FG, but only 25 mg of sample was efficiently digested thus resulting in higher LOD values. Analysis of pyrohydrolysis digests using IC was preferred because it allows determination of all analytes and better LODs for Cl in comparison with ICP OES. In this case, absorbing solution of 250 mmol L^{-1} H_2O_2 must be used to promote oxidation of S species to SO_4^{2-}. Diluted solution of H_2O_2 was suitable for analysis by IC and ICP OES techniques. Additionally, interferences on Cl and S determination by IC and ICP OES were not observed. Significant differences between certified reference values and results obtained pyrohydrolysis were not observed. Finally, due to simplicity of the pyrohydrolysis method, it can be used for the quality control of Cl and S impurities in FG samples used for nuclear applications.

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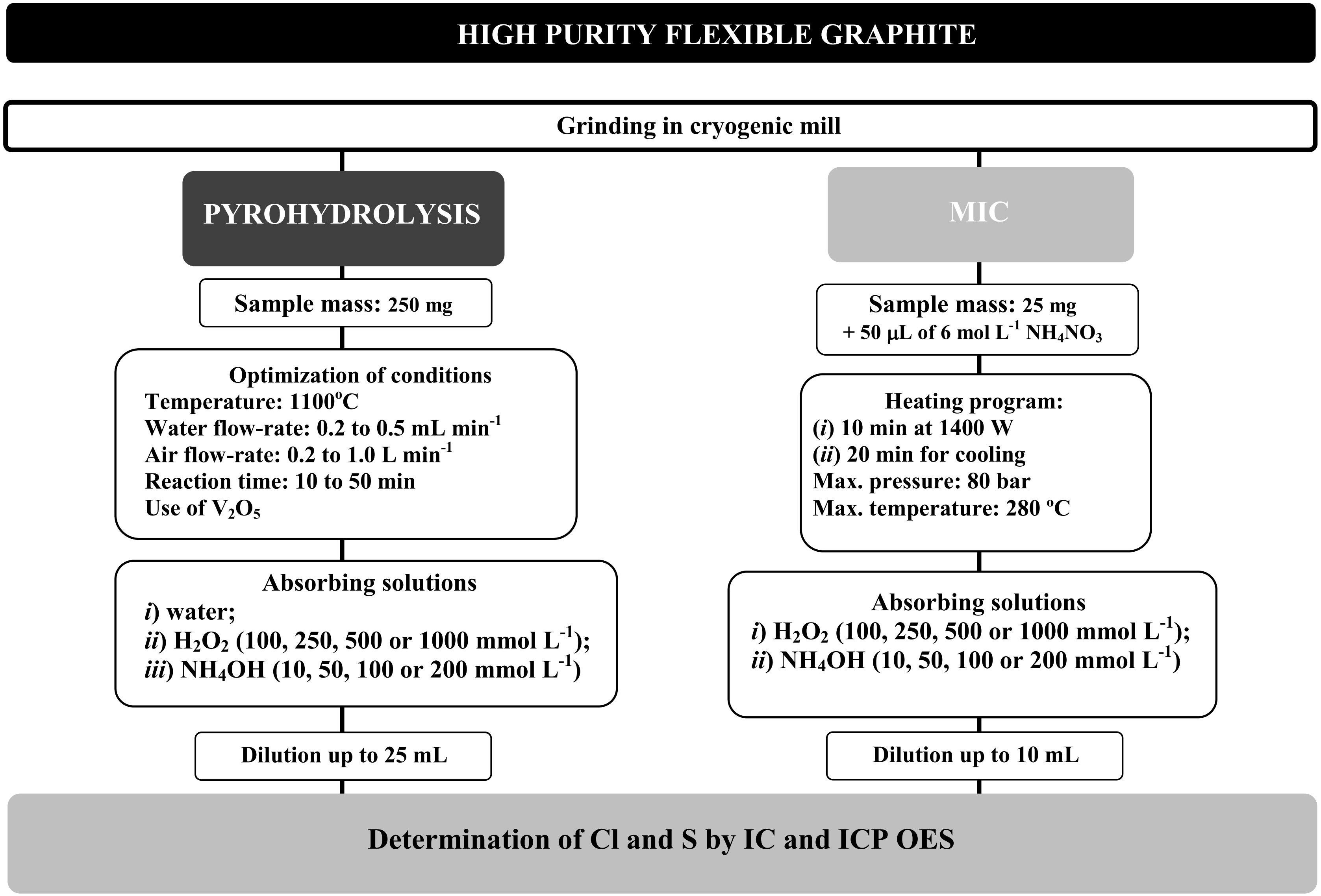

Figure 1 – Flowchart with conditions used for pyrohydrolysis and MIC methods.

Table 1 – Concentration of S and Cl in FG samples and CRMs determined by ICP OES and IC after decomposition using pyrohydrolysis and MIC and NO_3^- determinate by IC after Soxhlet extraction (n = 5, mean ± standard deviation)

	Pyrohydrolysis ($\mu g\ g^{-1}$)				MIC ($\mu g\ g^{-1}$)				NO_3^- ($\mu g\ g^{-1}$)
	Cl		S		Cl		S		
	ICP OES	IC	ICP OES	IC	ICP OES	IC	ICP OES	IC	IC
FG I	37± 4	35 ± 3	870 ± 36	880 ± 40	< 80	38 ± 6	877 ± 34	890 ± 45	< 1.0
FG II	< 20	< 1.0	395 ± 29	375 ± 25	< 80	< 5.0	383 ± 25	400 ± 31	< 1.0
FG III	< 20	< 1.0	379 ± 22	398 ± 20	< 80	< 5.0	368 ± 19	350 ± 30	< 1.0
FG IV	< 20	< 1.0	349 ± 25	320 ± 24	< 80	< 5.0	335 ± 23	310 ± 28	< 1.0
NIST 1632c	1140 ± 75	1155 ± 68	14700 ± 855	14730 ± 912	1160 ± 105	1115 ± 98	14750 ± 950	14800 ± 985	N.D.
SARM 19	34 ± 8	35 ± 3	5100 ± 870	5045 ± 825	< 80	34 ± 7	5020 ± 925	5045 ± 987	N.D.

NIST 1632c : 14620 ± 510 $\mu g\ g^{-1}$ for S and 1139 ± 41 $\mu g\ g^{-1}$ for Cl
SARM 19 : 4900 ± 700 $\mu g\ g^{-1}$ for S and 32 $\mu g\ g^{-1}$ (informed value) for Cl
N.D.: Not determined

Table 2 – Limits of detection obtained for Cl and S using pyrohydrolysis and MIC

	Pyrohydrolysis ($\mu g\ g^{-1}$)			MIC ($\mu g\ g^{-1}$)	
	ICP OES	IC	Literature values	ICP OES	IC
Cl	20	1.0	4.5[20]	80	5.0
S	1.0	1.0	20[26]	5.0	5.0

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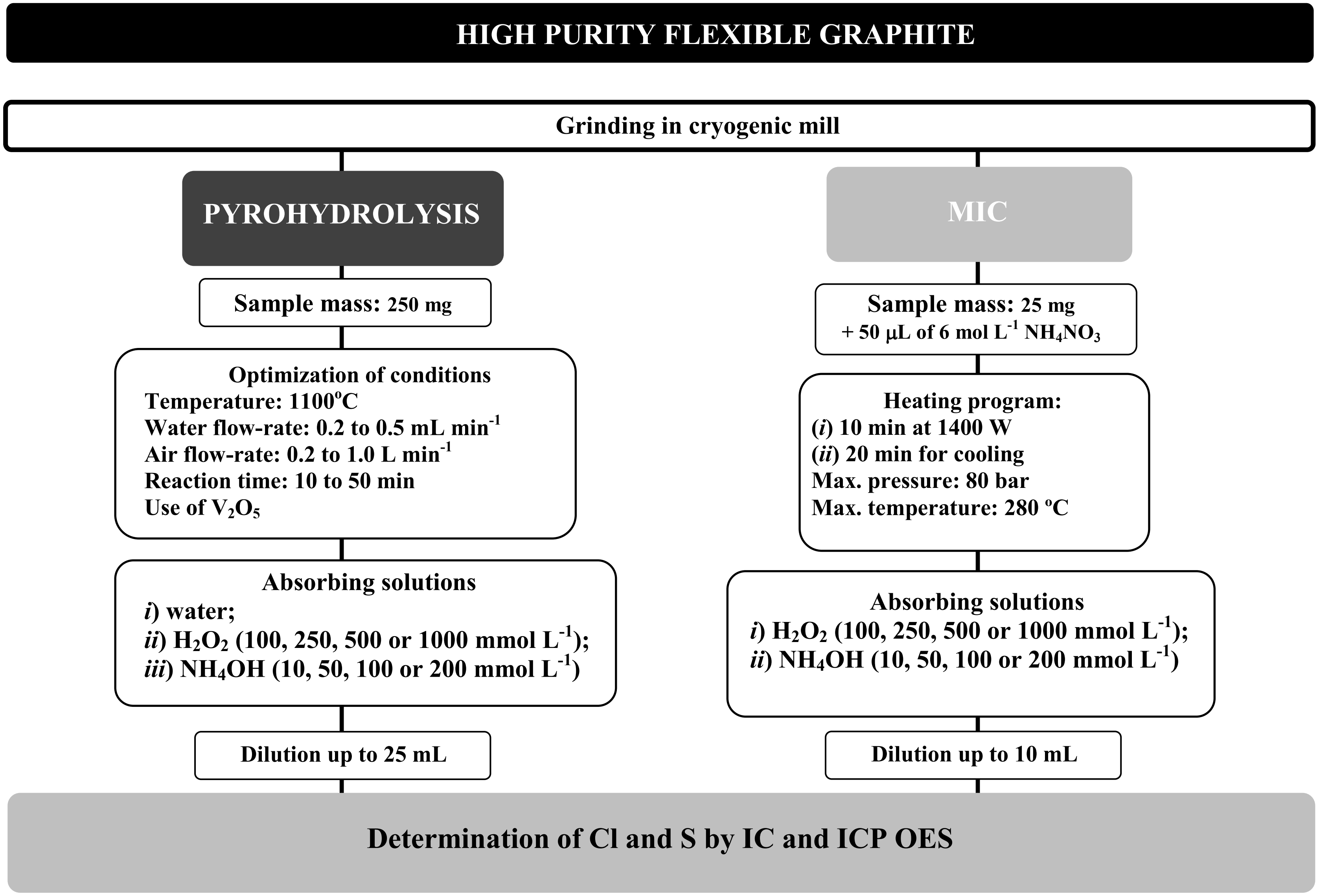
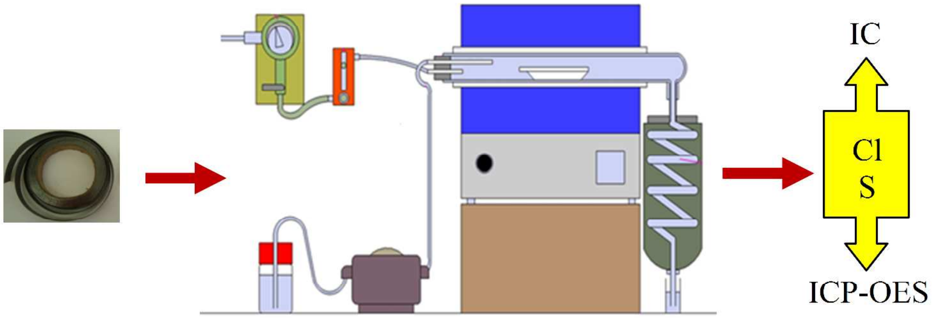


Figure 1 – Flowchart with conditions used for pyrohydrolysis and MIC methods.

Graphical abstract



Pyrohydrolysis method was used for high purity flexible graphite sample preparation and subsequent determination of Cl and S by IC and ICP OES.