Article

Total Mercury Determination in Petroleum Green Coke and Oily Sludge Samples by Cold Vapor Atomic Fluorescence Spectrometry

Adriana S. Camera,[a] Tatiane A. Maranhão,[a] Fernando J. S. Oliveira,[b]
Jessee S. A. Silva*,[a] and Vera L. A. Frescura[a,#]

[a]*Departamento de Química, Universidade Federal de Santa Catarina (UFSC),*
88040-900 Florianópolis-SC, Brazil

[b]*Petróleo Brasileiro S.A, Gerência de Meio Ambiente,Coordenação de Resíduos e Áreas Impactadas,*
20031-004 Rio de Janeiro-RJ, Brazil

A fast, simple and reliable method for Hg determination in green coke and oily sludge samples by atomic fluorescence spectrometry is described. Microwave digestion and extraction procedures were evaluated for highly complex samples of coke and oily sludge. The concentrations of $SnCl_2$ and HCl to promote Hg vapor, were optimized, as well as the concentration of $KMnO_4$, to stabilize the Hg^{2+} before the atomic vapor formation. Accuracy of the method was evaluated through certified reference material, for green coke, and comparison with cold vapor atomic absorption spectrometry (CV AAS), for oily sludge. Recovery tests were also performed. Limits of detection and quantification were 0.8 and 2.6 μg kg^{-1}, respectively. Ten green coke and nine sludge samples were analysed and Hg concentrations in coke are very low, between 0.005 and 0.065 mg kg^{-1}, but oily sludge samples have high concentrations, ranging from 42.5 to 376.6 mg kg^{-1}, requiring careful management.

Keywords: complex sample, microwave digestion, waste

Introduction

Mercury is an element harmful to human health and environment and nowadays has received great attention and extensive studies concerning its toxic effects and potential accumulation.[1,2] According to a list of harmful substances organized biennially since 1991 and updated by the Agency for Toxic Substances and Disease Registry (ATSDR) mercury occupies the third position among 275 substances hazardous to human health. Mercury is found naturally in the environment and occurs in several forms, such as gaseous element in atmosphere and inorganic and organic compounds.[3] However, release from anthropogenic sources has drastically affected Hg natural cycle through the atmosphere, water bodies and sediments, becoming an important global pollutant.[4] Mercury is naturally present in crude oil and natural gas, whose concentrations are highly dependent on the geological location,[5] but causing a direct negative impact on petroleum industry.[6-9]

The consumption of petroleum products and the use of heavier fossil oil have increased greatly, especially due to the growing demand for fuels. Nevertheless, according to a recent report of the United Nations Environment Programme (UNEP), oil refining activities are between the minor agents of Hg emissions to the air, considering that crude oil is processed in great amounts and refinery plants are geographically distributed. However the processing of crude oil has as consequence the steadily expanding of wastes, such as coke and oily sludge. Studies have shown that the major part of Hg in crude oil remains in these two residues.[4,10,11]

Petroleum coke is a final by-product obtained in large amounts through thermal treatment of residues after refining process. Green coke, a solid with a high content of carbon, is generate in this process from heavy oil fractions and is used as fuel in industry.[6,12] From green coke, other types of coke are produced, such as calcined coke, fluid coke and flexicoke.[13,14] In a search of new alternatives for energy and raw materials petroleum green coke appears as an interesting option since it can be used as fuel in electricity production, metallurgy and brick industries and

*e-mail: jesseesevero@yahoo.com.br
#INCT de Energia e Ambiente from CNPq, UFSC, www.inct.cienam.ufba.br

also as graphite electrodes, which is essential to electric arc furnaces in steel industry. However, to be used as raw material, it is necessary to evaluate the quality of the coke to assure no harm, to both human and environment, and the determination of trace elements, such as mercury (Hg) is essential. However, the determination of trace elements in petroleum green coke is one of the most challenging tasks in analytical chemistry due to the high complexity of the sample, with high carbon content, causing the sample treatment to be laborious, prone to contamination and losses of the analyte.[6,15]

Another important waste produced in large amounts in petroleum industry is oily sludge, a highly hazardous residue with great potential to affect ground water and soil resources and, consequently, human health. Oily sludge is produced in different steps in petroleum industry, such as transportation, storage and refining. It contains high concentration of hydrocarbons and other unmanageable components, making it difficult the proper remediation. Many treatments and applications have being proposed to give an effective and environmental friendly destination to these residues, but to meet that, complete characterization of oily sludge, including the heavy metal content, is mandatory.[16-18]

One of the most important steps in elemental determination is the sample treatment and it is even more critical for complex samples, as petroleum coke, and volatile elements, which is the case of Hg. Many procedures for matrix decomposition or element extraction in different types of samples, including some new techniques, have been described for Hg determination.[19-21] Microwave assisted digestion using closed vessels has been reported to be a very advantageous procedure due to the high pressure and temperature, reduction in losses and contamination, increasing in the digestion efficiency and its safety for the analyst. The complete digestion of the complex samples assisted by microwave is reported not to be always accomplished, but when performed with oxidizing acids it is considered to be the most efficient procedure to release the analytes from the sample matrix to the digestion medium. Also, many studies describe extraction procedures for total determination of Hg in a variety of samples with good accuracy showing that the complete digestion is not always necessary.[22-25]

Many different methods for determination of Hg in various types of samples have been reported in the current literature.[23,25-32] Some of them are cold vapor atomic absorption spectrometry (CV AAS),[29,33-35] cold vapor inductively coupled plasma mass spectrometry (CV ICP-MS),[33] chemical vapor generation electrothermal vaporization inductively coupled plasma mass spectrometry (CVG ETV ICP-MS).[28] However a very attractive technique for Hg determination in trace concentrations is cold vapor atomic fluorescence spectrometry (CV AFS).[36] Among the advantages of CV AFS are the high sensitivity, the separation of the matrix and the analyte prior the measurement, which reduces greatly the interferences, the use of a trap for pre-concentration, the introduction of almost 100% of the analyte into the instrument and the simplicity and low cost of the equipment.[37]

The aim of this work is to propose a method for the determination of total mercury in petroleum green coke and oily sludge samples by cold vapor atomic fluorescence spectrometry, a simple, low cost and robust technique. Samples of petroleum coke have highly complex matrices and Hg is a volatile element, so the sample treatment is an important step in its determination. Therefore various sample treatment procedures were evaluated and also the conditions for the vapor generation to achieve a fast and reliable method. Both samples are related to very important environmental issues and Hg is a persistent and bioaccumulative element, consequently any information regarding their impact on the environment is of particular interest when it comes to find proper management for these by-products.

Experimental

Instrumentation

All studies for Hg determination in petroleum green coke and oily sludge samples were carried out with an atomic fluorescence spectrometer Mercur Duo Plus from Analytik Jena (Jena, Germany). The instrument uses an Hg low pressure lamp (UVU5) operated at the wavelength of 253.7 nm to promote the atomic vapor excitation. The sample, reducer and acid solutions were continually aspirated by a peristaltic pump reaching the PEEK reactor in an incidence angle of 90° between sample/acid and reducing agent to accomplish the mixture and achieve the Hg vapor formation. The mixture vapor-liquid was separated in a gas/liquid separator and desolvated in a membrane with argon in counter flow, before reaching the collector. Two enrichment stages through gold and platinum collectors (AuPt10) are possible to be used. The atomic vapor was released from the collector and the integrated fluorescence intensity (peak area) measured. The system is completely closed to avoid losses of the vapor. Argon with 99.997% purity (White Martins, SP, Brazil) was used as carrier gas at a flow rate of 166.7 mL min^{-1}.

A high resolution continuum source atomic absorption spectrometer (HR-CS AAS) model ContrAA 700

(Analytik Jena, Jena, Germany) coupled to a chemical vapor generator model HS 60 (Analytik Jena) was used to compare the results of the developed method for oily sludge samples. The instrument is equipped with a high-intensity xenon short-arc lamp operated in a hot-spot mode, a high-resolution double monochromator and a charge coupled device (CCD) array detector. The cold vapor was generated in a flow system mode carried to the atomization unit, a quartz cell closed at the ends with quartz windows, and electrically heated to 150 °C. The wavelength used was 253.652 nm. Argon 99.996% purity (White Martins, São Paulo, Brazil) was the carrier gas at a flow rate of 100.0 mL min^{-1}.

A microwave oven model Ethos Plus (Milestone, Sorisole, Italy) was used to accomplish the sample treatment. For the extraction procedures, a thermal bath (Centauro Inovações Tecnológicas Ltda, Paraná, Brazil), an ultrasonic bath (Thornton model T50, Brazil) and a centrifuge (2.000 RPM) (Q222T, Quimis, São Paulo, Brazil) were used.

Reagents, standards and samples

All chemicals used in the studies and determinations were at least of analytical grade. High purity water in a resistivity of 18.2 MΩ cm was purified in a Milli-Q (Millipore, Beadford, USA) system and used to prepare all samples and solutions. Both, nitric acid (HNO$_3$) 65% (Carlo Erba Reagenti, Milan, Italy) and hydrochloric acid (HCl), 37% (Vetec, Rio de Janeiro, Brazil), were purified by double sub-boiling distillation in a quartz system (Kürner Analysentechnik, Rosenheim, Germany), and hydrofluoric acid (HF) 50% (Química Moderna Indústria e Comércio Ltda, SP, Brazil) was submitted to a triple sub-boiling distillation in a poly(tetrafluoroethylene) system (Kürner Analysentechnik) prior the use in the sample digestion and calibration solutions preparation. Hydrogen peroxide (H$_2$O$_2$) 30% supra pure (Vetec) was also used in the microwave digestion evaluation. For the extractions only concentrated nitric acid 65% (Carlo Erba) was used.

Mercury monoelemental standard solution 1.000 mg L^{-1} (SpecSol, São Paulo, Brazil) was properly diluted to prepare the calibration curve solutions, in a range from 0 up to 400 ng L^{-1}. For Hg vapor generation tin(II) chloride (SnCl$_2$) 98% (Sigma Aldrich, USA) was used as reductant. To guarantee the stability of Hg^{2+} potassium permanganate (KMnO$_4$) 99% (Merck, Rio de Janeiro, Brazil) was added prior the Hg vapor generation to the digested and extracted solutions and to eliminate the excess of the permanganate hydroxylamine hydrochloride (HONH$_3$Cl) 99% (Merck, Darmstadt, Germany), was added. The reducing agent

SnCl$_2$ was prepared by dissolving the solid reagent in HCl medium. To assure the high purity of SnCl$_2$ and HCl solutions a simple procedure was carried out to eliminate possible contamination with Hg, the solutions were bubbled with argon during 30 min.

Ten petroleum green coke and nine oily sludge samples from oil refining industry were used in the development of this work to determine the Hg concentration. In the absence of certified material of petroleum coke containing concentration values for Hg, a similar matrix certified material, coking coal, BCR 181 (Community Bureau of Reference, Brussels, Belgium) was used. Since there is no certified reference material for sludge sample comparison with another technique (CV AAS) as well as addition and recovery tests were performed.

Sample preparation and analytical procedures

Petroleum green coke samples were grinded in an agate mortar, then powdered in a ball mill and sieved to achieve fine particle size smaller than 85 µm. Approximately 100 mg of the samples were used for all experiments and Hg determinations.

For the extraction procedures approximately 100 mg of the certified material, BCR 181, or petroleum green coke were weighed directly into polyethylene tubes. Afterwards, 8.0 mL of nitric acid 65% were added and the mixture was submitted to ultrasound radiation for 15 min, one procedure at room temperature and other at the temperature of 85 °C. After the extractions, the mixtures were centrifuged, the supernatant separated from the solids, transferred to polyethylene tubes and filled up with purified water to a final volume of 14.0 mL. An aliquot of the supernatant, containing 0.05% of KMnO$_4$ and 0.025% of HONH$_3$Cl to stabilize the analyte, was diluted 20 times immediately before the measurements by CV AFS, using HCl and SnCl$_2$, both solutions at the concentration of 3%.

Five digestion procedures assisted by microwave were carried out using approximately 100 mg of the certified material, directly weighed into the microwave vessels. The reactants were added and the mixture was submitted to the microwave program presented in Table 1.

Scheme 1 presents the flowchart of reactants and volumes used in the extraction and digestion procedures. When H$_2$O$_2$ was used, the mixture was kept standing for one hour before submitting to the microwave radiation in order to avoid strong reactions inside the instrument. After the digestion program, the mixtures were quantitatively transferred to polyethylene tubes and filled up to a final volume of to 50.0 mL with purified water. Since, at the end of the digestion, solid particles remained in all solutions,

Table 1. Temperature program for microwave digestion procedure of petroleum green coke and oily sludge samples for Hg determination by CV AFS

time / min		Step	
Coke	Oily sludge	Coke	Oily sludge
4	2.5	Heating from 20 to 90 °C	Heating from 20 to 90 °C
8	8	Heating from 90 to 155 °C	Heating from 90 to 155 °C
5	3.5	Heating from 155 to 180 °C	Heating from 155 to 200 °C
25	20	Plateau, 180 °C	Plateau, 200 °C
30	30	Cooling down to 20 °C	Cooling down to 20 °C

the same dilution procedure applied to the supernatant of the extracts was used for the digested samples. After that measurements were carried out by CV AFS.
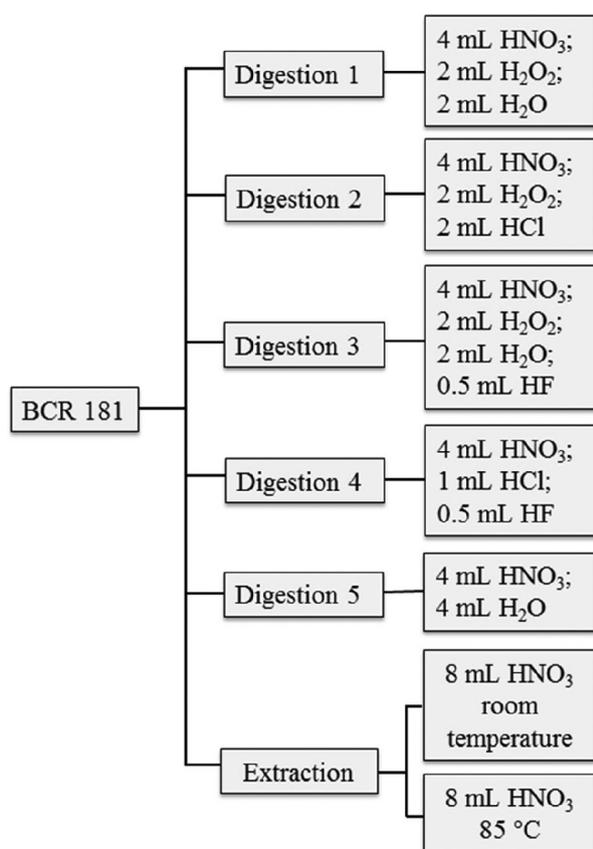
Scheme 1. Procedures and media used for sample preparation evaluation using certified reference material BCR 181.

The procedure applied to determination of Hg in green coke samples was digestion 4, in which 4.0 mL of HNO_3, 1.0 mL of HCl and 0.5 mL of HF was used.

The oily sludge sample treatment was performed using 100.0 mg of the sample, 4.0 mL of nitric acid, 3.0 mL of hydrogen peroxide and 1.0 mL of water, following procedure recommended by the Environmental Protection Agency (EPA) method 3052 for organically based matrices.[38] The samples were weighed directly into the microwave

vessels, the reactants were added and the mixture was kept standing for one hour to avoid strong reactions inside the microwave instrument. The microwave program used to promote the digestion is the same presented in Table 1. After the cooling, the mixtures were transferred to polyethylene tubes and filled up with purified water to a final volume of 50.0 mL. The solutions were clear without any solid particles, indicating the good performance of the sample treatment. Because of the work range of the instrument, up to 1.0 µg L^{-1}, the samples were diluted by factors of 1.000 to 3.000 times following the same procedure used for coke and certified material, immediately before the measurements carried out by CV AFS.

To promote the vapor generation optimizations of the reducer, $SnCl_2$, and hydrochloric acid concentrations are necessary. Solutions containing from 0 up to 6.0% v/v of HCl and 0 up to 6.0% m/v of $SnCl_2$, were used and the fluorescence intensity measured for petroleum coke sample, certified reference material, BCR 181, and Hg aqueous solutions. In the same way, the concentration of potassium permanganate that better stabilizes Hg^{2+} must be optimized. This optimization was carried out by adding volumes of a 5% $KMnO_4$ solution, corresponding to concentrations from 0 up to 0.06%, when diluting the samples or preparing Hg aqueous solutions. To eliminate the excess of permanganate hydroxylamine hydrochloride in stoichiometric concentrations was added. The fluorescence intensity was measured as described for the HCl and $SnCl_2$ optimizations.

Results and Discussion

Sample treatment

To evaluate whether the analyte could be completely extracted from the sample in a mild and simpler leaching process, certified material BCR 181 sample was submitted to two extraction procedures in nitric acid under ultrasonic radiation, as described in the previous section. Since Hg is volatile and the extraction process was not possible in

sealed vessels, the maximum temperature and sonication time used were 85 °C and 15 min, respectively, to prevent losses of the analyte. Determinations were carried out using the supernatant of the extract solutions, after centrifugation, diluted 20 times, as described in the previous section, sample preparation and analytical procedures. The obtained concentrations were much higher than the certified value of the reference material, about 30 and 14 times. Since petroleum coke is very complex with high content of organic matter, it would be possible that other compounds present in this sample were extracted to the solutions generating vapors, interfering with the analyte signal and leading to concentrations higher than expected. This study showed that the extraction procedures are not adequate for Hg extraction from petroleum green coke samples. Therefore, five microwave assisted digestion procedures were performed using different media, as described in the previous section, to evaluate whether any of them would promote the complete dissolution of the sample or, at least, the total extraction of the analyte to the media. None of the five procedures achieved the total digestion of the sample and after the procedures, solid particles still remained in the solutions, which were dark colored. The determination carried out using the supernatant, diluted as described in the sample preparation and analytical procedures section, showed that for procedures 2 and 3 the concentration values were still higher than the certified value, 1.7 and 2.5 times. These two procedures were much more effective than the extractions, possibly achieving the decomposition of the organic matter and greatly reducing components that interfere with the Hg signal. The other procedures, 1, 4 and 5, were effective in leaching the analyte out to the solution and eliminating any concomitants since the obtained concentration values were in agreement with the certified. But the medium containing 4.0 mL of HNO_3, 1.0 mL HCl and 0.5 of HF was the most effective presenting not only concentration values in agreement with the certified reference material, but also lower relative standard deviation (RSD), as can be seen in the results presented in Table 3. So, this procedure was applied to green coke samples.

The digestion procedure adopted for the oily sludge samples was based on the EPA method 3052 for organically based matrices.[38] This procedure accomplished the complete dissolution of the samples leading to a clean solution, without any particles. The measurements were carried out immediately after dilution according to the same procedure adopted for the petroleum coke and certified material samples. Nevertheless, the concentration of the analyte in those samples is very high and it was necessary dilutions of 1.000 to 3.000 times before the measurements.

Mercury vapor generation

The reducing agent used to generate the Hg cold vapor before the measurements by CV AFS was tin chloride, $SnCl_2$. Also, HCl is used to acidify the sample solution prior the reaction with the reducer. The concentration of HCl, as well, $SnCl_2$ needs to be optimized to achieve the best condition in generating the atomic Hg. In this evaluation three solutions were used: 0.1 µg L^{-1} Hg in aqueous medium, certified reference material sample and green coke sample spiked with 0.1 µg L^{-1} Hg. The latter two solutions were prepared according to digestion procedure 4, presented in Scheme 1. The concentration range of HCl evaluated was from 0 up to 6.0%. No significant changes were observed in the signal intensity for the two samples, but for aqueous solution HCl concentrations of 4.0% achieved the best intensity. So, as a compromise condition between samples and calibration curve, the concentration of 4.0% was adopted for the determinations.

For the optimization of the reducing agent solutions containing from 0 up to 6.0% of $SnCl_2$ were used. Figure 1a presents the results for this study. The effect of $SnCl_2$ on the integrated fluorescence intensity was more significant than the effect observed for HCl. The first point of the curves shows that even in the absence of $SnCl_2$ the atomic vapor is generated. An increase is observed for the two samples, but more significant for the coke sample. For the certified material, BCR 181, no significant increase is observed over the entire range evaluated, probably because some concomitant present in the sample matrix contributes in the atomic vapor generation. Nevertheless, the behavior of the green coke sample and aqueous solution were very similar, presenting a significant increase in the intensity when 1.0% of the reducing agent is used. The concentration of the reducer adopted for the determinations, as compromise condition, was 3.0%.

To generate the cold vapor of Hg, it is necessary to convert all mercury present in the sample in Hg^{2+}, because other Hg species may not be reduced during the reaction with the reducing agent. To stabilize the Hg^{2+} and assure the complete conversion of the element in Hg^0 vapor, $KMnO_4$ is required and the effect of its concentration was evaluated for the same solutions used for the HCl and $SnCl_2$ optimization. To eliminate the excess of $KMnO_4$ and the characteristic pink color, hydroxylamine hydrochloride ($HONH_3Cl$) was added in stoichiometric concentration before the signal intensity measurements. Figure 1b presents the results of this study and the curves show no significant effect of $KMnO_4$ on the signal intensities for sample solutions, probably because some component present in the sample
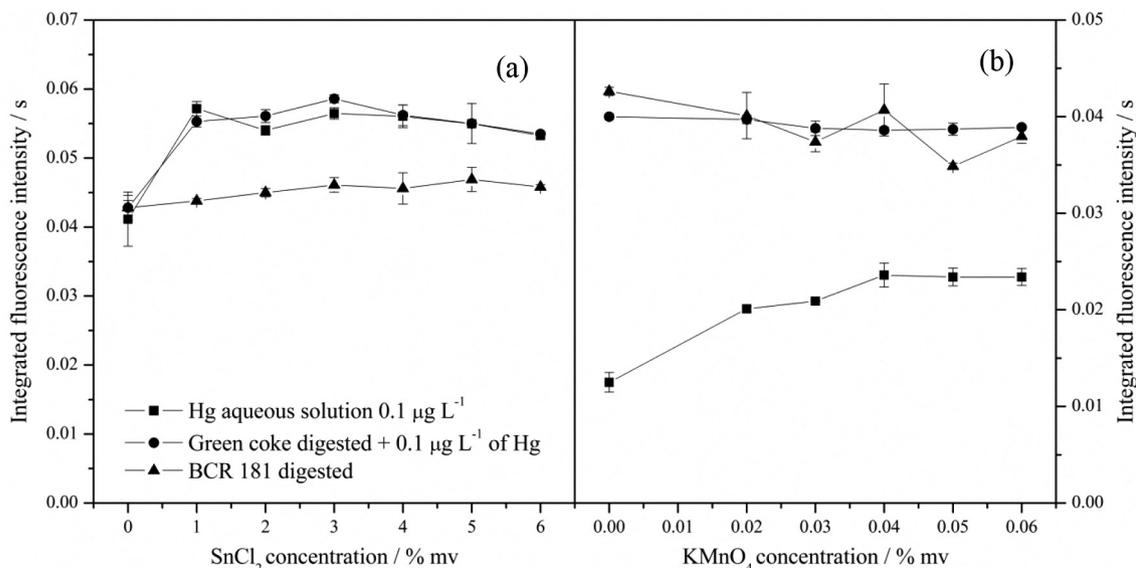
Figure 1. Effect of the SnCl$_2$ (a) and KMnO$_4$ (b) concentrations on the integrated fluorescence intensity for 0.1 µg L^{-1} Hg aqueous solution, green coke spiked with 0.1 µg L^{-1} of Hg and certified reference material, BCR 181.

matrices stabilizes the analyte. However, for aqueous solutions an increase on the integrated fluorescence intensity, with the increasing of the concentration of potassium permanganate up to 0.04%, is observed. So, a concentration of 0.04% was adopted as a compromise condition for the determinations.

Figures of merit

After the studies for sample preparation and the optimization of the hydrochloric acid, tin chloride and potassium permanganate the figures of merit, presented in Table 2, for Hg determination were obtained. Since the matrices of the certified reference material and coke sample are similar but not the same, calibration curves with the addition of the analyte for coking coal, BCR 181, and one green coke sample were carried out and compared with aqueous calibration curve. The obtained slopes for the three curves were similar, as shown in Table 2, and show that the method was equally efficient for both, certified reference material and green coke sample, and that aqueous calibration is possible.

The limit of detection (LOD), calculated as 3 times the standard deviation of the 10 measurements of analyte fluorescence intensity in the blank solution divided by the

slope of the calibration curve, and the limit of quantification (LOQ) as 3.3 time the LOD, were 1.67 and 5.51 ng L^{-1}, respectively. These values show the high sensitivity of the CV AFS technique. The linear correlation coefficient R was higher than 0.999 for the three calibration curves.

Determinations were carried out for the certified reference material sample, BCR 181, after submission to treatment procedures 1, 4 and 5, and under the optimized conditions of HCl, SnCl$_2$ and KMnO$_4$ optimizations. The obtained concentrations are presented in Table 3. Although the three procedures led to concentration values in agreement with the certified value and could be applied to the real samples, the sample digestion procedure in which 4.0 mL of HNO$_3$, 1.0 mL of HCl and 0.5 mL of HF, presented lower confidence interval and was chosen as the developed method for the determination of Hg in coke samples. The precision of the method expressed as the RSD was evaluated by the repeatability of a set of measurements of the analyte fluorescence intensity in the samples, and the found values were lower than 10%. Additionally, recovery tests were performed by addition of the analyte in both samples, equivalent to a final concentration of 0.10 µg L^{-1}. The addition was made before the digestion procedure, in order to evaluate all steps of the method. Recoveries of 95% and 105% were achieved. Therefore, for the determination

Table 2. Figures of merit for Hg determination in petroleum green coke and oily sludge samples by CV AFS

Calibration curve	Calibration range / (ng L^{-1})	Slope / (s L ng^{-1})	R
Aqueous solutions	0-400	0.0009	0.9999
Green coke + analyte addition	0-400	0.0010	0.9989
BCR 181 + analyte addition	0-400	0.0010	0.9996

R: linear correlation coefficient

of Hg in green coke samples, the medium adopted was the one proposed according to digestion 4 presented in Scheme 1.

Table 3. Results obtained for Hg total for different preparations of samples with a confidence interval (n = 3) of 95%. Informed value for BCR 181 (0.138 mg kg^{-1} ± 0.011)

Preparation	Concentration / (mg kg^{-1})
Digestion 1	0.130 ± 0.030
Digestion 4	0.134 ± 0.008
Digestion 5	0.151 ± 0.013

The digestion carried out for oily sludge accomplished the complete decomposition of the sample remaining at the end of the procedure a clear solution. So the calibration for the determination of Hg was carried out using aqueous solutions. Since no certified reference material of sludge sample is available, the accuracy of the method was evaluated through the comparison with another technique, CV AAS. Six oily sludge samples were analyzed by CV AAS and since this technique is less sensitive than CV AFS, the samples were diluted 100 times. The obtained results were compared with the values found by CV AFS. Figure 2 presents the graphic of the correlation between the values for both techniques, which presented a very good correlation coefficient R and slope, 0.997 and 1.016 respectively, indicating agreement between the results. Also, recovery tests were performed by adding volumes of the analyte standard solution equivalent to a final concentration of 50 ng L^{-1}, before the sample digestion procedure to evaluate all steps of the method. Recoveries from 94% of 102% were achieved. Both, the comparison with CV AAS and the recovery tests, confirm the accuracy and the precision of the method developed for determination of Hg in oily sludge samples.
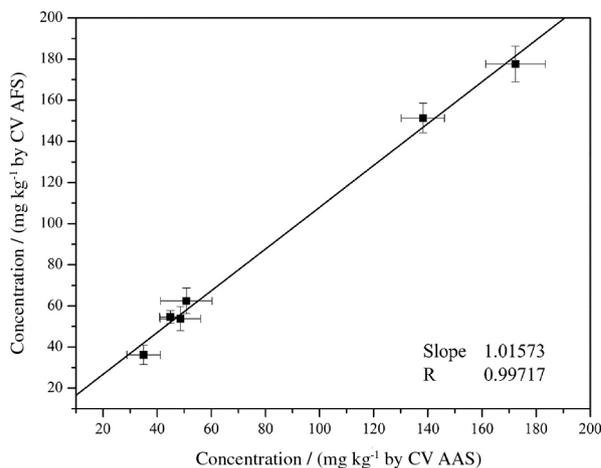

Figure 2. Graphic of the correlation between the concentration values by CV AFS *versus* the concentration values by CV AAS for six oily sludge samples.

Application to green petroleum coke and oily sludge samples

Ten green coke samples were submitted to the microwave assisted digestion procedure, using 4.0 mL of HNO$_3$, 1.0 mL of HCl and 0.5 mL of HF, and diluted according to the description in sample preparation and analytical procedures section, and the concentration of Hg was measured by CV AFS. The results presented in Table 4 show that, the concentration of Hg in these green coke samples is very low and the use of a technique with high sensitivity as CV AFS is suitable in this case. The RSD for a set of measurements of the analyte fluorescence intensity in the green coke samples presented values up to 9.3%, which is acceptable considering the low concentration of the analyte in the coke samples. The results also show that petroleum green coke can be used as an alternative source of energy, without any harm to the environment in which concerns the presence of Hg.

Table 4. Concentration values obtained for Hg in petroleum green coke and oily sludge samples, with a confidence interval (n = 3) of 95%, by CV AFS

Green coke	Concentration / (mg kg^{-1})	Oily sludge	Concentration / (mg kg^{-1})
Green coke 1	0.047 ± 0.003	Sludge 1	60 ± 25
Green coke 2	0.065 ± 0.004	Sludge 2	42 ± 9
Green coke 3	0.028 ± 0.002	Sludge 3	213 ± 38
Green coke 4	0.046 ± 0.007	Sludge 4	228 ± 77
Green coke 5	0.005 ± 0.001	Sludge 5	377 ± 105
Green coke 6	< LOD	Sludge 6	297 ± 63
Green coke 7	< LOD	Sludge 7	288 ± 67
Green coke 8	< LOD	Sludge 8	234 ± 74
Green coke 9	< LOD	Sludge 9	180 ± 50
Green coke 10	< LOD		

The determination of Hg concentration was carried out in nine oily sludge samples after microwave assisted digestion in a medium based on EPA method 3052.[38] The concentration values found for the analyte in oily sludge samples by CV AFS were very high, as can be seen in Table 4. The comparison with another technique, CV AAS, and the results of the recovery test show the robustness of the CV AFS technique even for samples with higher concentrations of Hg. The RSD for oily sludge were higher than for green coke, up to 16.6%, due to the high degree of heterogeneity of the samples. The study carried out to evaluate the concentration of Hg in oily sludge samples leads to the conclusion that these wastes are very dangerous to the environment and consequently to human health. The proper management of oily sludge, produced in great amounts by petroleum industry, is considered to be a worldwide problem due to the hazardous nature of this of waste. Nevertheless many treatments proposed take most in to account the reduction of the oil content. Some treatments proposed, such as landfarming and incineration, could affect even more the natural cycle of Hg through the environment.

Conclusions

A method for determination of total Hg concentration in petroleum green coke and oily sludge samples is proposed. Seven procedures for sample treatment were evaluated for green coke as well as the concentration of the vapor generation reactants and the Hg^{2+} stabilizing agent $KMnO_4$. Mild procedures of extraction were carried but they were not effective. None of the five digestions procedures accomplished the complete dissolution of the samples, but three of them were effective in extracting the analyte to the media, leading to accurate concentration values. The medium containing 4.0 mL of HNO_3, 1.0 mL of HCl and 0.5 mL of HF was applied to the real samples. The accuracy of the method was evaluated through certified reference material and recovery tests. The procedure adopted for the oily sludge samples treatment was based on the method EPA 3052.[38] In the absence of reference material recovery tests and comparison with CV AAS were applied. The good correlation between the values obtained between two techniques assured the good accuracy of the method. LOD and LOQ values were 1.67 and 5.51 ng L^{-1}, respectively, RSD values were lower than 9.3% for coke and 16.6% for oily sludge, and recoveries were between 95% and 105%. Petroleum green coke samples presented very low concentrations of Hg and can be used as fuel in producing energy, but oily sludge contains high concentrations of the Hg, which could be harmful to environment.

Acknowledgements

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