Decomposition of high ash content coals by microwave-induced combustion for As, Cd, Hg and Pb determination by ICP-OES

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Abstract

High ash content coals were digested by MIC for simultaneous determination of As, Cd, Hg and Pb by ICP-OES.

Introduction

Coal is one of the main energy sources used worldwide. Toxic elements, such as As, Cd, Hg and Pb are commonly found in coal and can be liberated to atmosphere, causing environmental impacts[1]. Thus, the determination of these elements in low concentrations is required. However, the difficulty to release the analytes from sample matrix makes the decomposition of high ash content coals a challenge. Microwave-assisted wet digestion (MAWD) is a method frequently used for coal. However, the high residual acidity of digests can interfere during the element determination as well as interferences promoted by high C content in digests can also occur, if digestion is not complete. The American Society for Testing and Materials (ASTM) proposes the decomposition of coal by dry ashing[1]. Nevertheless, losses and contamination may occur due to the high temperature and the use of an open system. Alternatively, the MIC method has been proposed to overcome these limitations combining the efficiency of combustion with the advantages related to sample preparation in closed systems. In this way, MIC was proposed for the decomposition of high ash content coals for further determination of As, Cd, Hg and Pb by inductively coupled plasma optical emission spectrometry (ICP-OES).

Results and Discussion

Coal samples with high ash content (14-54%) were digested by MIC using a microwave oven (Multiwave 3000, Anton Paar, Austria), equipped with 8 quartz vessels (280 °C of maximum temperature and 80 bar of maximum pressure). Homemade quartz holders were used and vessels were pressurized with O_2 at 20 bar. Samples (300 mg) were also digested by MAWD using HNO_3 and HF in PTFE vessels. Due to the high ash content of coals it was necessary to use 2 mL of HF for complete analyte recovery (ASTM D6357-11 was used to obtain reference values). The determination of As, Cd, Hg and Pb was performed using an inductively coupled plasma optical emission spectrometer (Spectro Ciros CCD, Spectral Analytical Instruments, Germany). Parameters related to the sample mass, the use of additives (NH_4Cl), the composition and concentration of the absorbing solution (HNO_3, HCl, mixtures of HNO_3 and HCl 2:1 or 1:1) and reflux step of absorbing solution (5 or 15 min) were evaluated. Sample masses of 300, 500 and 1000 mg were considered suitable for digestion of coal A, B and C, respectively, which were dependent on the content of ash. It was observed that quantitative recoveries were obtained for all elements only when NH_4Cl (300 mg) was added to the samples and a solution of HNO_3:HCl (2:1) was used. The heating program was performed using 5 min of reflux followed by 20 min of cooling step, performing 25 min for a complete digestion program. The residual carbon content (RCC) for MAWD method was about 30%, whereas RCC values were below 0.5% in digests obtained by MIC. In order to evaluate the accuracy of MIC, results were compared with MAWD and certified reference materials (NIST 1632c, SARM 19 and SARM 20) were digested under optimized conditions. No statistical difference (Student t-test, confidence interval of 95%) was observed between the results obtained by MIC and MAWD for As, Cd, Hg and Pb. In addition, agreement with certified values was also obtained, showing the accuracy of the proposed method. Limits of detection were from 0.04 μg g^{-1} (Cd) to 0.23 μg g^{-1} (Pb), which were at least 22 times better than those obtained using MAWD (300 mg, 6 mL HNO_3 and 2 mL HF).

Conclusions

The proposed MIC method for decomposition of high ash content coals was suitable for the determination of As, Cd, Hg and Pb by ICP-OES. The MIC method showed advantages, as the separation of analyte from matrix, the use of low amounts of reagents, low risk of contamination, low digestion time and lower limits of detection in comparison to MAWD.

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[1] Speight, J. G.; *Handbook of Coal Analysis*, Wiley, 2005.