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Determination of As and Se in coal and coal combustion products using closed vessel microwave digestion and collision/reaction cell technology (CCT) of inductively coupled plasma mass spectrometry (ICP-MS)

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ABSTRACT

Toxic elements arsenic and selenium in coal are of great concern mainly because of their adverse effects on human health during coal combustion. This paper describes the concentration determination of As and Se in coal and coal combustion products (CCPs), performed by collision/reaction cell technology (CCT) of inductively coupled plasma mass spectrometry (ICP-MS; collectively ICP-CCT-MS) after closed vessel microwave digestion. The reagents for 50-mg coal sample digestion are 2-ml 40% (v/v) HF and 5-ml 65% (v/v) HNO_3 but for the CCP samples, the reagents include 5-ml 40% HF and 2-ml 65% HNO_3. To significantly diminish the argon-based interferences at mass to charge ratios (m/z) 75 ($^{40}Ar^{35}Cl$) and 78 ($^{40}Ar^{38}Ar$), a helium and hydrogen mixture was used in the optimized hexapole collision cell. The results showed that CCT technology can effectively diminish the spectral interferences of the Ar-based polyatomic ions $^{40}Ar^{35}Cl$ and $^{40}Ar^{38}Ar$ to ^{75}As and ^{78}Se, respectively. The method detection limit of As and Se is 0.024 and 0.095 μg/l, respectively, and their linearity of the calibration curves in the range 0–100 μg/l has a determination coefficient $r^2 > 0.9999$. The determination of As and Se in NIST standard reference materials of coal and fly ash samples showed that ICP-CCT-MS plus closed vessel microwave digestion is a reliable method for concentration determination of the two elements in coal and CCPs.

1. Introduction

The concentration, modes of occurrence, and origin of As and Se in coal and coal combustion products (CCPs) are of great concern not only because of human health problems (endemic arsenosis and selenosis) caused by both toxic elements released from coal combustion (Belkin et al., 1999; Dai et al., 2012; Finkelman et al., 2002; Liu et al., 2007; Wang, 2009, 2010; Yang et al., 1983; Zheng et al., 1999), but also because of being a rare metal, Se could be potentially utilized from CCPs (Seredin and Finkelman, 2008; Seredin et al., 2013).

A couple of analytical methods have been used in the concentration determination of As and Se in coal and CCPs, including hydride generation/atomic absorption spectrometry (ASTM D 4606-03, 2007; GB/T 3058-1996, 1996; GB/T, 16415-1996, 1996), atomic fluorescence spectrometry (AFS), inductively coupled plasma optical emission spectrometry (ICP-OES), and instrumental neutron activation analysis (INAA) (Dai et al., 2003; Finkelman et al., 2002; Kolker, 2012; Low and Zhang, 2012; Ren et al., 1999; Riley et al., 2012; Sia and Abdullah, 2012; Swanson et al., 2013). However, each of these analytical methods has its own limitation either of high detection limit, only one-element detection in a run, or of a long time consumption of analytical procedure. For example, AAS and AFS can only detect one element in a run; although ICP-OES and INAA can simultaneously detect a couple of elements in a run, the former has a high detection limit and the time of the analytical procedure for the latter is much longer and the operation is rather complicated.

Inductively coupled plasma mass spectrometry (ICP-MS) has become an established method since the 1980s for trace multi-element concentration determination (Ammann, 2007; Barnes, 1993; Dufailly et al., 2006, 2008; Houk et al., 1980; Papaefthymiou et al., 2010; Phan-Thien et al., 2012) in geological samples including those in coal and coal-related materials (Dai et al., 2013; Finkelman et al., 2002; Jarvis and Jarvis, 1992; Shao et al., 2003; Sia and Abdullah, 2012; Swanson et al., 2013; Wagner and Tlotleng, 2012). ICP-MS has several of advantages including low detection limit, high sensitivity, relatively simple spectra, wide linearity range, and simultaneous determination of trace multi-elements in a run. However, like any sensitive analytical techniques, ICP-MS also has some limitations such as polyatomic spectral interferences generated by the plasma gas (Ar), matrix components (O, C, N, Cl), or solvent acid (HNO_3, HCl) (Dai et al., 2013; Dufailly et al., 2006, 2008). For example, the Ar-based polyatomic ions $^{40}Ar^{35}Cl$ and $^{40}Ar^{38}Ar$ interfere the isotopes of ^{75}As and ^{78}Se, respectively, leading to the wrong results of As and Se concentrations in the samples if the interferes were not diminished. Although several methods, e.g., correction equations, cool plasma approach, shield torch technology, and ion

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Table 1
Microwave program for sample digestion.

Step	Time (min)	Temperature (°C)	Pressure (bar)	Microwave power (Watt)
1	12	60	100	1000
2	20	125	100	1000
3	8	160	130	1000
4	15	240	160	1200
5	60	240	160	1000
Cooling time	60			

Table 2
Optimized instrumental parameters for ICP-CCT-MS.

Items	Values/status	Items	Values/status
Plasma RF power	1400 W	Collision gas	Mixture of He and H_2
Nebulizer gas flow	1.00 l/min	Collision gas flow	4 ml/min
Auxiliary gas flow	0.8 l/min	Pole bias	−16 V
Cool gas flow	13.0 l/min	Hexapole bias	−19 V
Sampling depth	130 steps	Number of main runs	3 times
ICP-MS interface	Nickel Xt	Dwell time	10 ms
Peristaltic pump speed	30 RPM	Acquisition mode	Peak jumping mode
Nebulizer	Teflon Nebulizer	Resolution	Standard

chromatography coupled to ICP-MS, have been exploited to decrease the polyatomic spectral interferences (Evans and Giglio, 1993; Iglesias et al., 2002; Tanner, 1995; Wahlen et al., 2005), they have limitations for a multi-elementary analysis (Dufailly et al., 2008). Collision/reaction cell technology (CCT) was proved to be an effective method for diminishing the spectral interferences (Rowan and Houk, 1989) and thus allow the accurate determination of the isotopes ^{75}As and ^{78}Se (Dufailly et al., 2008). The details of CCT method have been described by Dufailly et al. (2006, 2008), Kadar et al. (2011), Tanner (1995), and Tanner et al. (2002).

The spectral interference problem was also applicable to ICP-MS analysis in coal and CCPs (Shao et al., 2003) but it has not been well solved. This paper described the method of As and Se concentration determination in coal and CCPs, using closed vessel microwave digestion and collision/reaction cell technology of inductively coupled plasma mass spectrometry (collectively, ICP-CCT-MS), which has rarely been reported in detail in the analysis of coal and its CCP materials (Dai et al., 2013).

2. Experimental

2.1. Instrumentation

A ThermoFisher ICP-MS (X Series II), equipped with an Automated 3rd Generation Collision Cell Technology (CCT_{ED}), was used for As and Se determination in coal and CCPs. Prior to ICP-CCT-MS analysis, the samples were digested using an UltraClave Microwave High Pressure Reactor (Milestone). A Milli-Q™ A10 system (Millipore) was used for ultra pure water (18.2 MΩ cm) preparation. A DuoPUR acid purification system (Milestone) was used for guaranteed reagent (HNO_3) further purification. The TraceCLEAN Automatic Acid Reflux System (Milestone) was used for vessel cleaning at 300–350°C for 2 h.

2.2. Reagents, gasses, and investigated samples

Standard solution 100 μg/ml, (Inorganic Ventures, CCS4) was used for preparation of five concentration levels (0, 1, 10, 50, and 100 μg/l), which were used for establishing calibration curves of As and Se. The standard stock solution of ^{103}Rh (10 μg/ml; IV-ICPMS-71C, Inorganic Ventures) was used for preperation of 10 μg/l internal standard solution because Rh is extraordinarily low in coal and CCPs. The standard solution (100 μg/ml, THM-TS-1, Inorganic Ventures) containing multi-elements Li, Co, In, and U, was used to prepare the tuning solution (1 μg/l). All standards were used without further purification and prepared in 2% (v/v) HNO_3 (65%).

The metal-oxide-semiconductor (MOS) reagent HF and the further-purified guaranteed reagent HNO_3 were used for sample digestion. Ultra-pure (99.999% pure) mixed gasses composed of 93.33% He and 6.67% H_2 were used without further purification as carrier grade collision gasses.

NIST (National Institute of Standards and Technology) standard reference materials including three coals (NIST 1632c, 1635, and 2685b) and one fly ash (NIST 1633b) were used for As and Se determination using ICP-CCT-MS. In addition, two coal (C-1 and C-2) and three fly ash samples (R-3, R-4, and R-5) from China were also determined by ICP-CCT-MS and AFS for comparison. The two coal samples C-1 and C-2 were respectively collected from the No. 8 Coal of Lubanshan Mine (Huayingshan Coalfield, Sichuan province) and the No. B1 Coal of Laibin Mine (Yunnan province). The fly ashes R-3, R-4, and R-5 were respectively collected from the Damo (Inner Mongolia), Luohuang and Anwen power plants (both Chongqing).

2.3. Sample digestion

Taking into consideration the volatile behavior of As and Se in coal (Clarke and Sloss, 1992; Dai et al., 2010; Swanson et al., 2013), the samples were digested using the closed TFM vessel UltraClave Microwave High Pressure Reactor. All the samples were crushed to 200 mesh (75 μm) prior to digestion. The reagents for 50-mg coal sample digestion were 2-ml 40% (v/v) HF and 5-ml 65% (v/v) HNO_3 but for the CCP samples, the reagents included 5-ml 40% HF and 2-ml 65% HNO_3.

The basic load for the digestion tank of UltraClave Reactor was composed of 330-ml distilled H_2O, 30-ml 30% H_2O_2, and 2-ml 98% H_2SO_4. Initial nitrogen pressure was set at 50 bars and the highest temperature was set at 240 °C that lasted for 75 min. The microwave digestion program is presented in Table 1.

Table 3
Calibration curves and method detection limit (MDL) of As and Se.

Elements	Isotopes	Linearity (μg/l)	Determination coefficient	MDL (μg/l)	RSD (%)
As	75	1–100	0.999982	0.024	1.654
Se	78	1–100	0.999936	0.095	1.996