

Short communication

Speciation of chromium in Australian fly ash

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Abstract

The concentrations of chromium (III) and (VI) in fly ash from nine Australian coal fired power stations were determined. Cr(VI) was completely leached by extraction with 0.01 M NaOH solution and the concentration was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). This was confirmed by determining Cr(III) and Cr(VI) in the extracts of fly ash that had been spiked with chromium salts. These analytical measurements were done using a combination of ion-exchange chromatography and ICP-AES. The elutant was 0.05 M HNO₃ containing 0.5% CH₃OH. When the column was operated at a flow rate of 1.2 ml min⁻¹ and samples were injected by use of a sample loop with a volume of 100 μl, Cr(III) and Cr(VI) in sample solution was exclusively separated within approximately 10 min. The detection limits (3σ) were 5 ng for Cr(III) (0.050 mg l⁻¹) and 9 ng for Cr(VI) (0.090 mg l⁻¹), respectively. A relative standard deviation of 1.9% (n = 6) was obtained for the determination by IC-ICP-AES of 0.25 mg l⁻¹ Cr(III) and Cr(VI).

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1. Introduction

Chromium compounds are widely distributed in nature and are commonly used in industry. Generally, the chemical species of naturally occurring chromium is Cr(III) although anthropogenic Cr(VI) can be found in recent sediments. While Cr(III) is essential for metabolic processes, Cr(VI) is toxic and carcinogenic. Accordingly, the environmental concentration of Cr(VI) or total Cr is strictly regulated. Therefore, it is important to not only accurately determine the amount of total Cr in environmental samples, but also the proportions of Cr(III) and Cr(VI). A number of procedures for the determination of total Cr as well as Cr(III) and Cr(VI) in environmental samples have been reported. These include solvent extraction [1], coprecipitation [2], activated alumina in combination with flame atomic absorption spectrometry [3], electrospray mass spectrometry [4], ion-exchange [5], pretreatment-flame atomic absorption

spectrometry or electrothermal atomic absorption spectrometry [6–10]. Recently, methods that couple liquid chromatography (LC) or ion chromatography (IC) to inductively coupled atomic emission spectrometry (ICP-AES) or inductively coupled mass spectrometry (ICP-MS) have been reported [11–19]. The methods adopted for the disposal of fly ash from power stations and industrial incinerators have environmental significance as fly ash is a significant anthropogenic source in the environmental circulation of trace elements in nature and there have been several studies of trace elements (including Cr) in fly ash, coal, soil and related materials [20–32]. However, in many cases, the total leached Cr is reported and not the actual concentrations of Cr(III) and Cr(VI). There are exceptions, fly ash has been leached with CaCl₂ solution and the Cr species determined. [25,26] Leaching with Na₂CO₃–NaOH for Cr(VI) in soil samples has been used [33]. An IC-ICP-MS technique to determine Cr(III) and Cr(VI) in fly ash has been reported [34].

In this work, Cr in fly ash was leached with 0.01 M NaOH. The concentrations of total Cr leached were measured using ICP-AES. As well, IC-ICP-AES was used to confirm the speciation of the Cr present in the extracting solution.

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2. Experimental

2.1. Reagents

High purity acids and water (Milli Q) as well as analytical grade (or better) reagents were used throughout this study.

2.1.1. Cr(III) and Cr(VI) standard solutions

There were prepared by diluting Cr(III) (1000 mg l⁻¹, Cr(NO₃)₃·9H₂O in 2–5% HNO₃, or Cr(VI) (1000 mg l⁻¹, (NH₄)₂Cr₂O₇ in H₂O.

2.1.2. 0.01 M-NaOH solution for extract

0.40 g of NaOH was dissolved in 1000 ml water, and the resulting solution was used for extraction.

2.1.3. 0.05 M-HNO₃/0.5%-CH₃OH elution solution

This was prepared as follows: 3.46 ml of HNO₃ was diluted with 995 ml water, and the resulting solution was degassed prior to the addition of 5 g CH₃OH to make up the solution, which was used in the elution experiments.

2.2. Apparatus

A Spectro CIROS CCD ICP-AES instrument equipped with a concentric nebulizer and a Scott chamber was used for the determination of major, minor elements and total Cr in the fly ash samples. A SPS 4000 ICP-AES instrument equipped with a concentric nebulizer and a cyclone chamber was used for monitoring chromium signals on speciation of Cr(III) and Cr(VI). A TSK gel – IC–Anion – PW_{XL} PEEK column (diameter 4.6 mm × length 75 mm), packed with anion exchange resin (–Et₂Me⁺ groups) with a particle size of 6 μm (30 ± 3 meq l⁻¹) was used for separating Cr(III) and Cr(VI). The metal free six port injection valves combined 100 μl sample loop (PEEK tubing) and MODEL325DI&CH-2-D HPLC pump were used in the experiments. The chromatographic system was connected to the nebulizer with PEEK tubing. A metal free syringe with PEEK needle was used for sample injection.

A domestic microwave oven (maximum power 1200 W) was used in the sample dissolution procedure.

2.3. Samples

Fly ash samples (A–I) were obtained from nine coal-fired power stations in Australia. The stations were in Queensland, New South Wales and Western Australia and all burn local bituminous coal. The ash yields of the coals vary from less than 10% to greater than 30%. Generally a small proportion of the ash (0–20%) is identified as being effectively utilised; most is deposited in landfill or in wet ash dams [35]. The major and minor elements concentrations in the fly ash samples are shown in Table 1. These were prepared using the procedure described below, and the analyses completed using a Spectro CIROS CCD ICP-AES. The optimized analytical conditions are shown in Table 2. NIST–SRM 1633b (Coal Fly Ash) was

Table 1
Concentration of major and minor elements in fly ash samples

Sample	Mean (%)							
	Al	Ba	Ca	Fe	Mg	P	Si	Ti
A	12.7	0.352	0.90	6.07	0.425	0.736	24.2	0.924
B	10.8	0.065	2.14	4.83	0.605	0.065	26.2	0.493
C	12.1	0.039	0.63	1.99	0.361	0.096	28.9	0.543
D	14.0	0.077	0.81	1.14	0.595	0.042	26.5	0.984
E	13.4	0.039	0.26	0.71	0.171	0.072	28.3	0.709
F	14.7	0.119	2.74	9.09	0.887	0.376	18.8	1.030
G	10.8	0.016	0.04	0.28	0.068	0.024	31.1	0.750
H	16.4	0.023	0.98	8.40	0.600	0.023	23.2	1.140
I	14.6	0.091	0.26	1.82	0.061	0.173	27.2	0.738
NIST 1633b	15.05	0.0707	1.53	7.76	0.481	0.239	22.99	0.793
Certificate ^a	15.05	0.0709	1.51	7.78	0.482	0.230 ^b	23.02	0.791

Results of acid decomposition in microwave oven.

^a Certified value.

^b Non-certified.

used as the certified reference material to validate the analytical procedures.

2.4. Procedure

2.4.1. Sample preparation for measurement of major, minor elements and total Cr

A precisely weighed 30 mg sub-sample of fly ash was transferred into a polycarbonate container to which 0.50 ml of HCl, 0.50 ml of HF and 0.25 ml of HNO₃ were added. The container was placed in a screw top jar in a microwave oven; the sample and acids were heated at 20% power for 5 min and 10% power for 15 min to complete the decomposition. After cooling, the digest was made up to 30 ml with water. The resulting solution was used for major, minor elements and total Cr measurements by ICP-AES.

Table 2
Instrumental operating parameters

Spectro CTROS CCD ICP-AES	
Wavelength	Al 167.08 nm Ba 455.40 nm Ca 317.93 nm Fe 259.94 nm Mg 279.08 nm P 178.29 nm Si 251.61 nm Ti 334.94 nm Cr 267.72 nm
RF power	1.4 kW
Carrier gas flow rate	0.85 l min ⁻¹
Plasma gas flow rate	14 l min ⁻¹
Coolant gas flow rate	1.0 l min ⁻¹
Seiko SPS4000 ICP-AES	
Wavelength	283.56 nm (Cr, Ionic line)
RF power	1.3 kW
Observation height	9.0 mm
Carrier gas flow rate	0.80 l min ⁻¹
Plasma gas flow rate	16 l min ⁻¹
Coolant gas flow rate	0.50 l min ⁻¹

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