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Determination of trace multi-elements in coal fly ash by inductively coupled plasma mass spectrometry

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Abstract: The contents of Cr, Cu, Ni, As, Cd and Pb in coal fly ash were determined by a high resolution inductively coupled plasma mass spectrometry method. The sample digestions were performed in closed microwave vessels with HNO_3, $HClO_4$ and HF. The optimum conditions for the determination were obtained. The applicability of the proposed method was validated by the analysis of coal fly ash reference material (NIST SRM 1633a). The results show that most of the spectral interferences can be avoided by measuring in the high resolution mode (maximum mass resolution R=9 000). The detection limit is from 0.05 to 0.21 μg/g, and the precision is fine with relative standard deviation less than 4.3%.

Key words: coal fly ash; microwave digestion; inductively coupled plasma mass spectrometry; determination

1 Introduction

Coal contains large amounts of metallic elements. The determination of trace elements in coal fly ash samples is important with respect to health and environment. Thus, a sensitive, rapid and reliable analytical method for analysis of trace elements in coal fly ash is required. Several analytical techniques, including atomic absorption spectrometry (AAS) methods[1−3], inductively coupled plasma atomic emission spectrometry (ICP-AES)[4−7], neutron activation analysis (NAA)[8], X-ray fluorescence spectrometry (XRF)[9−10], and inductively coupled plasma mass spectrometry (ICP-MS)[11−14] have been applied for trace elemental determination in coal fly ash samples. ICP-MS has emerged as one of the favored methods due to its unique combination of low detection limits, wide dynamic range, capabilities for rapid multi-elemental and isotopic determination. However, in spite of many advantages of quadrupole based ICP-MS, it still suffers from spectral interferences due to overlaps of atomic and molecular ions. As complete digestion of coal fly ash sample requires perchloric acid, the determination of As and Cr by quadrupole ICP-MS (ICP-QMS) is susceptible to being interfered by $^{40}Ar^{35}Cl$, $^{35}Cl^{16}O^{1}H$, and $^{37}Cl^{16}O$ at ^{75}As, ^{52}Cr, and ^{53}Cr, respectively. An alternative of ICP-QMS cannot resolve isobaric interferences at the masses of As and Cr. ICP-QMS is difficult to differentiate analyte ions and interring polyatomic ions.

High resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) is capable of resolving many plasma-, water-, and matrix-based polyatomic interferences, and the technique has been used for the successful determination of elements which subject to spectral interference in complex matrices[14]. HR-ICP-MS is characterized by its high sensitivity, low detection limits, and the possibility of separating analytic signals from spectral interferences using higher mass resolution techniques[15].

In this study, a microwave-assisted digestion procedure for dissolution of coal fly ash samples was investigated and the contents of Cr, Cu, Ni, As, Cd and Pb were determined by HR-ICP-MS.

2 Experimental

2.1 Instruments

A Micromass Plasma Trace 2 HR-ICP-MS (Micromass Ltd, Manchester, England) was used for the determination of trace elements. The instrumental parameters were as follows: power 1.45 kW, coolant gas flow 14.5 L/min, auxiliary gas flow 0.9 L/min, nebulizer gas flow 1.2 L/min, sampling cone nickel (1.1 mm orifice diameter), skimmer cone nickel (0.8 mm orifice diameter), ion sampling depth 11 mm, sample uptake rate 0.25 mL/min, dwell time 20 ms, accelerating voltage 6 kV, resolution 400−10 000, ion lens adjusted to obtain the maximum signal intensity.

A microwave oven (MDS-81D, CEM Corporation,

USA) was used for sample digestion. A peristaltic pump (MP-32, Tokyo Rikakikai, Tokyo, Japan) was used to regulate the flow rates of the carrier solutions.

2.2 Standard solution and reagents

Ultrapure water from a Milli-Q deionization unit (Millipore, Milli-Q SP) was used throughout the experiment. Single element calibration solutions were prepared from 1 g/L stock solutions of Cr, Cu, Ni, As, Cd and Pb in 10% HNO_3 by dilution with ultrapure water. The same procedure was followed for the preparation of the working solution to be used as the internal standard for mass spectrometric determinations. Multi-element standard solutions were prepared from single element stock solutions. These solutions were freshly prepared. Reference material SRM 1633a was used to study the accuracy.

The acids used to digest samples were high-purity concentrated HNO_3, $HClO_4$ as well as HF, respectively. High-purity H_3BO_3 was employed to neutralize HF in the solutions produced after the digestion of samples and decomposition of fluorides. All glass and plastic wares were cleaned by immersion in concentrated HNO_3 and concentrated HCl overnight, then steamed successively with HNO_3 and water vapor for 8 h.

2.3 Analytical procedures

Microwave digestion was adopted for sample preparation. About 0.1 g sample of coal fly ash was accurately weighed and transferred into Teflon vessel, followed by adding 3 mL HNO_3, 3 mL $HClO_4$ and 2 mL HF. 3 mL H_3BO_3 was added for buffering. The digestion program was as follows:

First, the samples were digested with HNO_3+ $HClO_4$+HF at microwave power of 300 W for 8 min followed by 600 W for 10 min and 450 W for 4 min, secondly H_3BO_3 was added into the solution at microwave of 300 W for 2 min and then at 600 W for 2 min.

On cooling at room temperature the vessels were opened, the mixtures were filtered and then diluted to 50 mL with ultrapure water. The solution was further diluted twice with ultrapure water so that the content of the total dissolved salt (TDS) was about 0.1%, and the solution was injected into the HR-ICP-MS. A blank reagent was also prepared in the same way.

3 Results and discussion

3.1 Spectral interferences

The increase of the mass resolution leads to a reduction of the number of transmitted ions, as a consequence, the sensitivity is reduced to a certain extent. Therefore, to measure the trace elements, suitable mass resolution should be chosen to separate analyte ion peaks from interfering polyatomic ion peaks. The measured peaks to determine contents in the samples are isotopes whose abundances are maximum, or isotopes which are not overlapped by the polyatomic or doubly charged ion peaks of matrix elements and Ar. The isotopes determined are listed in Table 1.

Table 1 Isotopes, resolution, detection limits and blank test

Isotope	Resolution	Detection limit/ ($\mu g \cdot g^{-1}$)	Blank value/ ($\mu g \cdot g^{-1}$)
^{52}Cr	5 000	0.12	0.15
^{63}Cu	3 000	0.07	<0.07
^{60}Ni	5 000	0.21	<0.21
^{75}As	9 000	0.07	<0.07
^{111}Cd	400	0.05	<0.05
^{208}Pb	400	0.03	<0.03

In ICP-MS, isotopes of all but two (Cd and Pb) of the elements determined may suffer from interferences caused by polyatomic ions resulted from the plasma gas, entrained atmospheric gases, water and acid. The Cd and Pb ion peaks without being overlapped by the interfering ion peaks were measured at $m/\Delta m$=400. The analyte ion peaks of Cr, Cu, Ni and As overlapped by polyatomic ion peaks at $m/\Delta m$=400. No visible interferences were found in the vicinity of Cu peak at $m/\Delta m$=3 000. The other analyte ion peaks can be separated from polyatomic ion peaks at $m/\Delta m$=5 000 to $m/\Delta m$=9 000 on calculation. The mass resolutions used are listed in Table 1.

The overlapping of ^{52}Cr with $^{40}Ar^{12}C$ and $^{35}Cl^{16}O^1H$ indicated in coal fly ash is shown in Fig.1, which might be caused by the decomposition of the sample by addition of $HClO_4$. It is very difficult to remove the chlorine ions in the digested samples. If low resolution ICP-MS is used, the interference of $^{40}Ar^{12}C$ on the ^{52}Cr will be significant[14]. The interference from $^{44}Ca^{16}O$ on ^{60}Ni is an example of spectral interferences in low resolution ICP-MS for the remainder of the coal fly ash with a high concentration of Ca. ^{52}Cr and ^{60}Ni were measured at $m/\Delta m$=5 000. Fig.2 shows the peaks of ^{75}As (100 μg/L) and interfering $^{40}Ar^{35}Cl$ obtained at $m/\Delta m$= 9 000. The isotope with relative atomic mass of 75 is the only available one for the determination of As. The overlapping does not affect the determination of As in coal fly ash because the concentration of As is high.

Therefore, HR-ICP-MS provides a more effective and straightforward means to overcome the majority of

spectral interferences using the high resolution mode that is sufficient to resolve the analyte signal from interfering peaks[16].
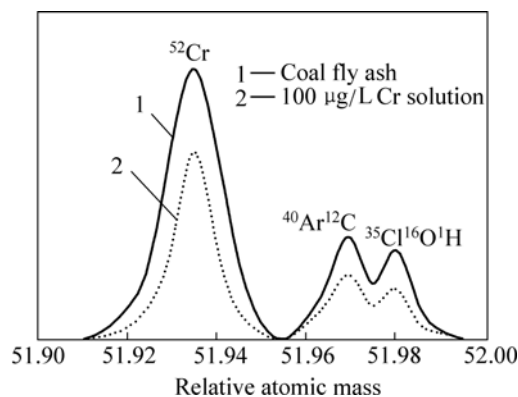

Fig.1 Mass spectra of ^{52}Cr obtained by HR-ICP-MS
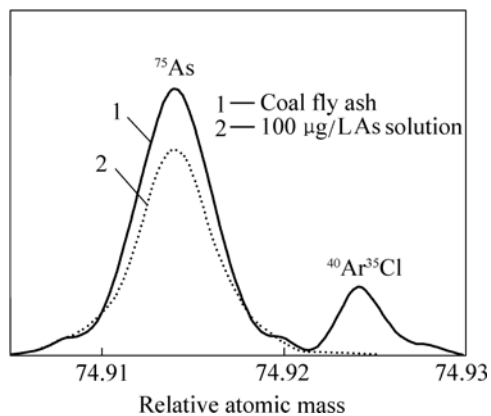

Fig.2 Mass spectra of ^{75}As obtained by HR-ICP-MS

3.2 Non-spectral interferences

Non-spectral interference is another problem in ICP-MS. Matrix effect resulted from the co-existing matrix element leads to signal suppression or enhancement for the elements. In order to evaluate the influence of non-spectral interferences on the determination of trace elements by HR-ICP-MS, the matrix effects should be corrected using internal standard elements. If the matrix effects for internal standard elements agree with those for analyte elements, these matrix effects can be corrected. It was reported that accurate correction for the matrix effect was possible using internal standard elements with relative atomic mass close to those of the analyte elements[17], ^{89}Y, ^{103}Rh and ^{115}In were selected to test respectively. These elements are frequently used as internal standards for drift correction in mass spectrometric measurements[18–21]. Five kinds solutions were prepared with SRM 1633a controlling the content of TDS in mass fraction range from 0.02% to 0.10% (0.02%, 0.04%, 0.06%, 0.08% and 0.10%). The ion peak relative

intensities of the three elements (1 μg/L) influenced by the TDS are shown in Fig.3.
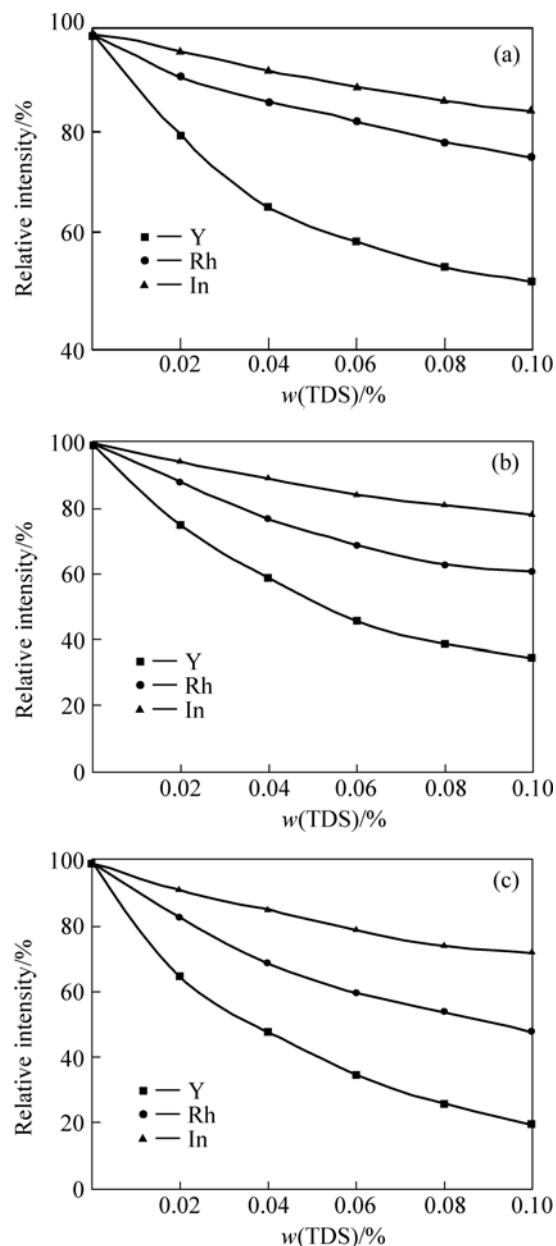

Fig. 3 Sensitivity of three internal standard elements in SRM 1633a as function of TDS content
(a) Low-resolution mode; (b) Medium-resolution mode;
(c) High-resolution mode

From Fig.3, it can be seen that the relative intensities of the three elements gradually decrease with increasing the content of TDS. The respective sensitivity of 0.1% TDS solution for Y, Rh and In is decreased by about 60%, 30% and 15% in the medium-resolution mode ($m/\Delta m$=3 000). During a similar period, the sensitivity of the three elements gradually decreases with increasing TDS content in the low-resolution mode ($m/\Delta m$=400) and high-resolution mode ($m/\Delta m$=9 000). The optimum internal standard elements cannot be found.

Therefore, it is difficult to correct the matrix effects using internal standard elements. So the standard addition method was used for each sample throughout this study.

3.3 Detection limits and blanks

The detection limit was estimated as the analyte concentration corresponding to three times the standard deviation (3σ) of the blank signals obtained in the replicate measurements (n=10). The detection limits for analyte elements and blank tests are shown in Table 1. The detection limits obtained by HR-ICP-MS are below 0.1 μg/g for most elements. The results of blank tests for all the elements are below the detection limits but Cr, indicating that the samples are treated without any significant contamination.

3.4 Analysis of SRM 1633a

In order to validate the HR-ICP-MS method, the contents of Cr, Cu, Ni, As, Cd and Pb were determined in the SRM 1633a sample. The analytical results for the SRM 1633a standard sample together with certified values are listed in Table 2, showing that for Cu, Ni, As, Cd and Pb, the measured contents are in good agreement with the certified values. The relative standard deviations (RSDs) for all elements of the observed values are within 5%. These results indicate that the present method is precise enough to apply to the multielement analysis of the coal fly ash samples.

Table 2 Analytical results for coal fly ash reference material (SRM 1633a) determined by HR-ICP-MS

Element	M_{obs}[1]/ $(\mu g \cdot g^{-1})$	RSD/ %	M_{cer}/ $(\mu g \cdot g^{-1})$	Relative variance[2]/ %
Cr	193.00±3.00	1.6	196.00±0.40	−1.5
Cu	115.00±4.00	3.5	118.00±3.00	−2.5
Ni	130.00±1.00	0.8	127.00±4.00	+2.4
As	139.00±6.00	4.3	145.00±15.00	−4.1
Cd	1.03±0.04	3.9	1.00±0.15	+3.0
Pb	73.60±0.90	1.2	72.40±0.40	+1.7

1) Mean value±SD (standard deviation), n=5; 2) $[(M_{obs}−M_{cer})/M_{cer}]\times100\%$, where M_{obs} and M_{cer} are observed and certified values, respectively.

3.5 Analysis of natural samples

Table 3 shows the analytical results obtained for three natural coal fly ash samples from different power stations in China by using HR-ICP-MS. Each result is the average of five sample determinations. As a consequence the concentration in each sample is different. The three samples contain comparatively high contents of all elements.

Table 3 Contents of elements in three natural coal fly ash samples (n=5)

Ele-ment	Mean content/($\mu g \cdot g^{-1}$)			RSD/%		
	Sample A	Sample B	Sample C	Sample A	Sample B	Sample C
Cr	651±17	857±19	336±10	2.6	2.2	3.0
Cu	1 623±29	1 256±15	2 447±59	1.7	1.2	2.4
Ni	86±3	163±3	213±7	3.5	1.8	3.3
As	155±2	272±3	193±3	1.2	1.1	1.6
Cd	124±3	206±8	158±4	2.4	3.9	2.5
Pb	5 572±75	1 370±42	681±16	1.3	3.1	2.3

4 Conclusions

1) A novel and reliable method for simultaneous determination of trace elements in coal fly ash using HR-ICP-MS after microwave dissolution is established.

2) HR-ICP-MS is not only a powerful diagnostic tool for determining and resolving spectroscopic interferences, but also a versatile technique for quantitative determination of analytes in low-, medium-, and high-resolution modes. The measured values are in good agreement with the certified values, indicating that the accuracy is adequate for the determination of these elements.

3) HR-ICP-MS may provide a better alternative for measuring trace elements in coal fly ash because of shorter analytical time and less contamination.

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(Edited by CHEN Wei-ping)