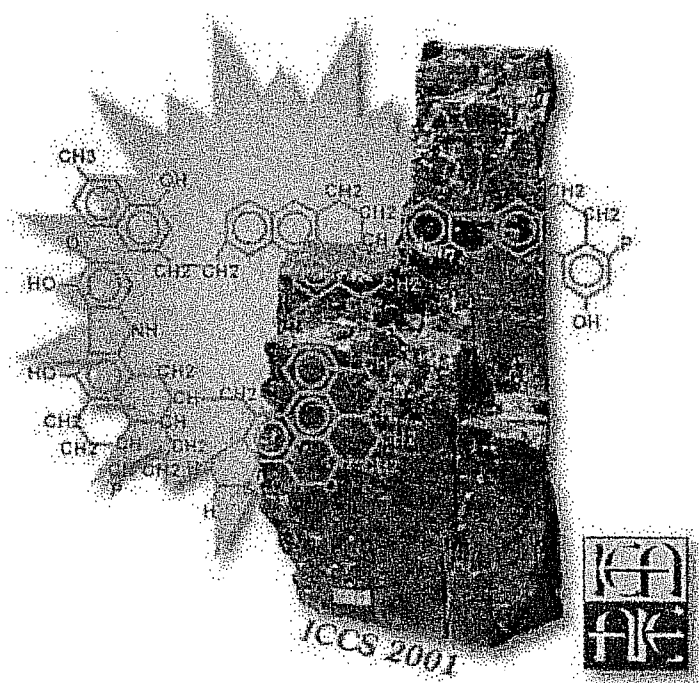

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Application of Microwave Induced Plasma-Mass Spectrometer (MIP-MS) for Routine Analysis of Trace Elements in Coals

Atul Sharma¹, Akira Tomita¹, Shinji Kambara² and Tsuyoshi Teramae²

¹Institute of Multidisciplinary Research for Advanced Materials,

Tohoku University, Sendai, JAPAN

²Coal Research Laboratory, Idemitsu Kosan Co. Ltd. Chiba, JAPAN

Email:sharma@icrs.tohoku.ac.jp; Phone: +81-22-217-5627; Fax: +81-22-217-5626

Introduction

Trace elements emissions from coal fired power plants have attracted a lot attention due their detrimental effects on human health. A key factor in developing control strategies is not only accurate measurement of their concentrations but also an ability to do it rapidly. It is also desired that the technique should not be expensive in order to perform the day to day analysis. In general, the trace elements are first brought into solution by acid digestion, which is then measured by a suitable analytical technique like ICP-MS. The acid digestion method is a lengthy time consuming method and running cost of ICP-MS is high due to the use of costly argon gas (99.999%) for plasma making this process unsuitable for routine analysis. Another technique, which so far has not been used for coal sample analysis but is relatively less expensive than ICP-MS is MIP-MS. Operating cost of MIP-MS is significantly lower than ICP-MS because of use of N₂ (99.9%) gas as plasma gas. If coal can be injected directly as powder into MIP-MS plasma, the technique will be a rapid inexpensive analysis technique. However, before developing the direct injection method, it is necessary to understand and elucidate the problems associated with coal analysis by MIP-MS. This study is the first part of the project aimed to develop a rapid inexpensive MIP-MS technique for routine analysis of trace elements in coals.

Experimental

A standard reference coal SARM 19, a South African Standard Reference Material was selected for investigation. A sample of 200 mg was digested using microwave after adding with 5ml ultra pure HNO₃ and HCl acids. The water used for sample preparation was ultra pure water of 18.2 MΩ from Millipore system Co. The microwave was from OI Analytical Inc. The sample was digested using a four-step-temperature programmed

microwave decomposition condition; 1stg: 120°C, 6 min; 2stg: 140°C, 6 min; 3stg: 160°C, 6 min; 4stg: 170°C, 6 min. The MIP-MS used was P5000-3DQMS, from Hitachi Instruments, Ltd. The digested samples were first filtered to remove the residue and the solutions were then made to final 40 ml volume using ultra pure water. The solutions were then further diluted corresponding to a dilution factor (DF) of 1000. The solutions were analyzed by ICP-MS (Idemitsu Kosan Co. Ltd.) and MIP-MS (IMRAM, Tohoku University) for 10 elements viz; *Be, Cr, Mn, Ni, Co, As, Se, Cd, Sb* and *Pb*. Mercury, *Hg* was excluded from analysis as it shows memory effect in ICP-MS system.

Results and Discussion

Table 1 shows a comparison of results of ICP-MS and MIP-MS. *Be* could not be measured by MIP-MS because ion trapping efficiency of MIP-MS for lower mass number ions is poor and hence removed from the MIP-MS analysis.

Table 1: Comparison of ICP-MS and MIP-MS analysis results.

Element	ICP-MS (ppm)	MIP-MS (ppm) (short channel)	MIP-MS (ppm) (long channel)	RSD (%) (long channel)
Be	2.0	-	-	-
Cr	42.7	41.5	39.7	4.0
Mn	116.1	103.4	108.3	0.4
Co	4.4	28.7	17.6	6.8
Ni	11.9	84.0	81.8	2.0
As	5.2	5.8	6.0	7.3
Se	1.2	-6.93	9.55	3.4
Cd	0.2	0.2	0.9	-
Sb	0.2	1.2	1.1	6.7
Pb	25	21.7	22.5	2.8

In case of MIP-MS, two sampling cones with different channel design and hole length were used. The results from short channel cone show a good agreement with ICP-MS results for all elements except *Co, Ni* and *Se*. However, the lifetime of this cone is short because of the enlargement of sampling cone hole after 7 to 8 measurements. Because of this reason a cone with long channel was used. The results using this long channel cone are also shown in Table 1 and show a good agreement with the results from short channel cone. The Relative Standard Deviation (RSD) values for all elements are also

less than 8%. However, it can be seen that *Co*, *Ni* and *Se* do not show agreement with ICP-MS results.

Nickel and Cobalt

For *Ni* and *Co*, the values from MIP-MS were much higher than ICP-MS. These high values from MIP-MS suggest formation and interference of polyatomic/molecular ions due to plasma gas and/or sample matrix. For ^{58}Ni it was found that ^{58}Fe isotope is the interfering ion.

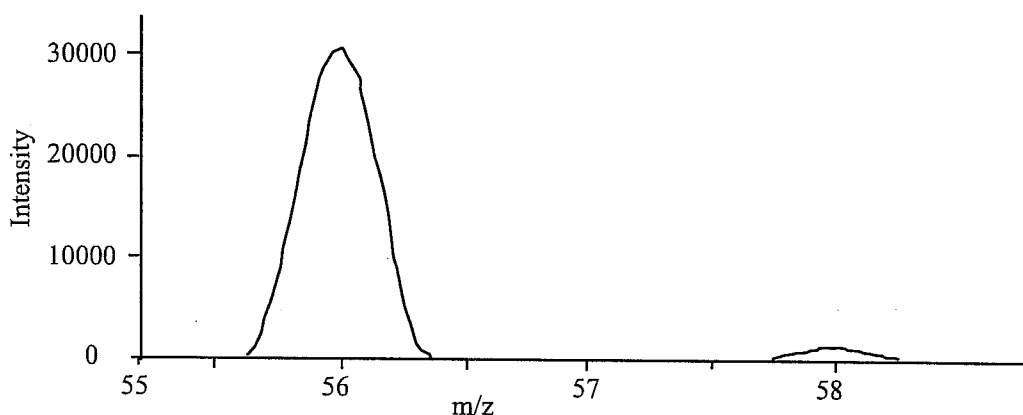


Figure 1. Intensity curve for ^{56}Fe and ^{58}Fe by MIP-MS for a 15 ppm Fe solution

In Figure 1, intensity curve for ^{56}Fe and ^{58}Fe from 15 ppm Fe solution is shown. Although ^{58}Fe is only 0.33 % of the Fe, due to percentage level concentration of Fe in the sample the concentration of ^{58}Fe becomes appreciable and hence increases the apparent concentration of ^{58}Ni . Attempts were made to measure nickel using its other isotopes like ^{60}Ni , ^{61}Ni , ^{62}Ni and ^{64}Ni . Isotopes ^{60}Ni , ^{62}Ni suffer from interference from N_2O_2 and NO_3 ions due to plasma gas. Isotope ^{64}Ni suffers interference from ^{64}Zn . Attempts to measure nickel using ^{61}Ni isotope were also not successful due very low concentration of nickel in coal sample and presence of high concentration of plasma ions on both sides. A high resolution is required for ^{61}Ni , which is difficult to achieve with the present machine. Therefore, interference factor for ^{58}Ni from ^{58}Fe must be obtained which is currently under progress. In case of ^{59}Co no ions which can interfere with ^{59}Co were found. However there is possibility of interference from doubly ionized $^{118}\text{S}^{++}$ ion. Another reason could be the low resolution and imprecise m/z position of ^{59}Co because of the interference by the neighboring plasma ions N_2O_2 .

Selenium

No interfering ions were found to present at and in close vicinity of 80Se position. One of the possible reasons for inability to measure Se accurately could be memory effect of selenium. Although there are no reports of memory effect of selenium, results from a preliminary investigation shown in Figure 2 support the presence of memory effect of selenium. In Figure 2, two elements Cr and Se were analyzed.

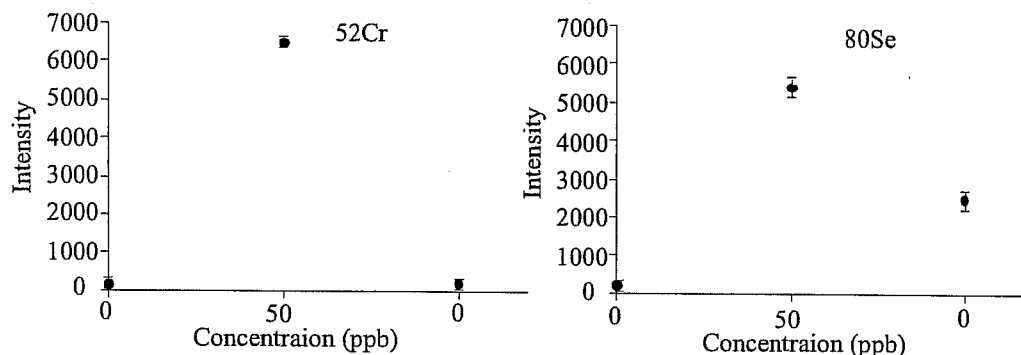


Figure 2. Observed memory effect for Se in MIP-MS using Cu cones

The two elements were measured in a blank solution followed by 50 ppb solution and again the blank solution. The intensity of Cr in blank solution before and after 50 ppb solution is almost same. However, in case of Se , the intensity from blank solution after 50 ppb solution measurement is much higher than the intensity from blank solution before 50 ppb solution measurement. This suggests that Se from 50 ppb solution is remained in the system causing memory effect problem. The most probable parts responsible for memory effect could be sampling and skimmer cones as these are made of copper. Copper has strong affinity to sulfur and possibly to selenium as it is below sulfur in the same group of the periodic table.

Conclusions:

Application of MIP-MS for trace elements analysis in coals was investigated. The results suggest that MIP-MS can be developed as a highly sensitive and accurate technique for routine trace element analysis. However, there have been some issues regarding type of sampling cone, inability to measure Be , interference factor for Ni and Co , which need to be addressed.