An Improved Anion-Exchange Separation for the Determination of Platinum in Environmental Samples by Inductively Coupled Plasma Mass Spectrometry

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A new and practical column separation/preconcentration method for the determination of Pt in environmental samples is proposed. The method has been successfully applied to the determination of Pt in a tunnel dust sample with isotope dilution ICP-MS. A key to its success is an anion-exchange separation of Pt from Hf.

The determination of platinum at natural levels is important for environmental monitoring and basic geological studies. Although neutron activation,[1] and GF-AAS[2,3] methods combined with preconcentration techniques have been used for this purpose, other sensitive techniques are required to increase the speed of analysis and to lower the detection limits.

Recently, inductively coupled plasma mass spectrometry(ICP-MS)[4-7] has been used for the determination of trace and ultra-trace amounts of many metallic elements, including platinum, in geological and related materials. However, because the platinum concentration in airborne particulate matter samples is very low, separation and preconcentration was necessary prior to isotope dilution(ID) ICP-MS. A necessary conditions for accurate ID ICP-MS determination is the availability of two isotopes free of interferences by overlapping polyatomic species. A difficulty of Pt determinations with ID ICP-MS in this regard is that the major platinum isotopes, ^{194}Pt, ^{195}Pt and ^{196}Pt, are subject to overlap interference by hafnium oxide species. A cation-exchange column separation of Pt from hafnium have been reported to be an effective solution to this problem.[5] However, as discussed in a previous report,[7] it was found that considerable amounts of Hf were present in the samples after an acid dissolution of airborne particulate matter followed by clean up with a cation-exchange column. In two recent papers, Pt determinations by ID ICP-MS were accomplished using an acid dissolution followed by an anion-exchange column separation.[6,7] Commercially available types of anion-exchange resins were found to adequately reduce the levels of interfering molecular ions. However, the elution of the element was carried out with more than 30 ml of 12 M (1 M =1 mol dm^{-3}) HNO_3 at 90-100 °C,[2] because of the high affinity of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ for the resin. In the present study, hence, a new and practical column separation/preconcentration method for the determination of Pt in airborne particulate samples is proposed.

A Perkin-Elmer/SCIEX Elan 500 ICP-MS instrument was used. A Gilson Minipuls 2 peristaltic pump was used to maintain the sample delivery to the nebulizer at 0.8 ml/min. Dissolution of materials was achieved using a commercial microwave oven, Model MDS-81 (CEM, USA). A 175×9 mm glass column fitted with a course sintered glass frit and Teflon stopcock was used for metal ion separation/preconcentrations. All laboratory manipulations were performed in a class 100 clean room.

Table 1. Effect of HCl concentration on the Pt, Hf and Ti adsorption onto the resin

	Adsorption(%)[a]		
[HCl/M]	Pt	Hf	Ti
0.1	100	99	60
0.5	100	70	18
1.0	99	40	5
5.0	99	8	0

[a]The procedure was carried out using 25 ml of aqueous solution containing 25 ng of Pt, and 5 μg of Hf and Ti, respectively.

The automobile tunnel dust material used and its dissolution procedure were the same as that reported previously,[7] except that perchloric acid was not used in the microwave digestion stage. A sample of enriched ^{194}Pt was obtained from U.S. Services (USA). Aliquat 336 (methyl tricaprylyl ammonium chloride) was obtained from the Aldrich Chemicals Co. Acid-resistant octadecylsilica (ODS) C_{18} resins (Wakogel LP-60C18, Wako Chemical Co.) were pre-cleaned by sequential additions of 20 ml of methanol, 50 ml of 1 M HCl and 10 ml of methanol gravity fed through the column. The material was then dried at room temperature under a clean laminar-flow bench.

The dynamically coated resin was prepared by adding 10 ml of hexane containing 3 wt% of Aliquat 336 to 600 mg of ODS resin. The resin slurry was quantitatively transferred to a glass column and washed with 20 ml of 3% Aliquat 336 in hexane. The resin was removed from the column, dried at room temperature and stored in a screw cap bottle. The batch capacity of the resin for Pt was 20.1 μmol/g for a solution in 0.6 M HCl.

The results for adsorption of Pt, Hf and Ti using the present column are shown in Table 1. Complete adsorption of both Pt(II) and Pt(IV), (the species adsorbed are probably $PtCl_4^{2-}$ and $PtCl_6^{2-}$), was confirmed for HCl concentrations between 0.1 and 5 M; acid concentration greater than 5 M were not studied. There was no uptake of Pt on untreated C_{18} under these conditions. Alkali, alkaline earth elements, and Al were not adsorbed from solutions between 0.1 and 5 M in HCl. The effect of elution volume on Pt recovery was examined. Complete recovery is obtained using 10 ml of a 1 M HCl/0.1 M $HClO_4$ mixture as eluting acid. Hafnium, which was appreciably adsorbed onto the column from the solutions between 0.1 and 5 M in HCl, was not removed during passage of up to 10 ml of the eluting acid mixture. Thus the major matrix elements of airborne particulate and geological samples (e.g., Fe, Ti) can be separated from Pt by this method, as can Hf, the most important interfering element. Iron in the dissolved samples is separated by preliminary washing the column with 10 ml of 0.5 M HCl prior to elution of Pt.

Absolute analytical blanks of this method were examined by

Table 2. Absolute blanks and detection limits

	This work	Other method [7]
Column blank/ng	0.043 ± 0.012	2.85 ± 0.23
Total blank/ng	0.39 ± 0.06	3.19 ± 0.45
Absolute detection limit/ng	0.17	1.4

spiked 0.58 ng of ^{194}Pt into the digestion vessels, then following the same procedure as for the samples. The column procedural blanks were also examined by using separate spiked solutions, and following the column procedure as same for the samples. The blanks and detection limit of the method are shown in Table 2, in which the values obtained by an anion-exchange column[7] are also listed.

About 300-400 mg of the tunnel dust sample were weighed into a quartz crucible, and then ashed for 2h at 550 ℃ prior to microwave digestion. The samples were digested with aqua regia and hydrogen peroxide, after addition of appropriate enriched isotope spikes of ^{194}Pt. The final sample solution was passed through the column; the HCl concentration in this sample solution was ca. 0.6 M. The sample was eluted from the present column, and then determined by ID ICP-MS. Platinum concentrations of 13.1±1.5 ng/g (n=6) were found by this method; the values obtained were similar to those reported in the earlier work,[7] i.e. 12.6±1.6 ng/g. The recovery efficiency of the column developed here did not change after 1 year of repeated use. The present column method can be used for the preconcentration and the determination of other platinum group elements, and this work is in progress.

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