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ULTRA-TRACE DETERMINATION OF IRIDIUM BY ETV/ ICP-MS USING CHEMICAL MODIFIERS

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ABSTRACT

An analytical method using ammonium nitrate as a chemical modifier was proposed for the determination of iridium at ultra-trace levels by inductively coupled plasma mass spectrometry (ICP-MS) with electrothermal vaporization (ETV). A detection limit of 2.2 fg of Ir was obtained after optimization of the chemical modifier and instrumental parameters. Electrolysis using glassy carbon electrodes was also employed as a pretreatment method to remove interfering substances and preconcentrate iridium from seawater selectively. The concentration of iridium at ppq levels in seawater was successfully determined by the isotope dilution method.

KEYWORDS

Iridium , Ultra-trace determination, ETV/ICP-MS, Chemical modifier, Electrolytic separation and concentration, Seawater

1. INTRODUCTION

Although ICP-MS is widely used as a high sensitive analytical method for many elements. There are still strong requirements for increasing the sensitivity of ICP-MS in the fields such as semiconductor industry, life science and astrophysics . The ETV technique has potential ability as a high-efficiency sample introduction technique in ICP-MS. But there are not so many reports concerning ICP-MS analysis using the ETV technique. This situation is in marked contrast to the successful situation in atomic absorption spectrometry (AAS) using a similar ETV. It seems to be several reasons for this big difference in ETV applications between ICP-MS and AAS . The most negative reason seems to be in terribly bad reproducibility and not so much increasing of signal intensity . We have here proposed two ideas to solve these problems lying on the use of the ETV technique in ICP-MS. The isotope dilution method was employed to improve the reproducibility of signal intensity and chemical modifiers was introduced to increase the efficiency of vaporization of the analyte.

2. EXPERIMENT

2.1 INSTRUMENTS AND APPARATUS

A YOKOGAWA HP-4500 attached with ETV apparatus was operated under the conditions : Rf power ;1100 W, Carrier gas; 0.95 l/min, Plasma gas; 15 l/min, Sampling depth; 6cm. A MATSUSADA PK-80L direct current supplier was used for the electrolytic reduction procedure. A Teflon electrolytic cell (50 ml) was handmade. All analytical procedure was performed in a class 100 clean bench placed in a class 10000 clean room.

2.2 MATERIALS AND REAGENTS

TAMAPURE-AA-10 grade aqueous ammonia and nitric acid were purchased from Tama Chemicals (JAPAN) and nitric ammonium was prepared by neutralization of them. ^{191}Ir enriched spike was obtained from Oak Ridge National Lab.(USA) and dissolved in aqua regia. Glassy carbon (5 ϕ x 100 mm) was purchased from Tokai Carbon (JAPAN) . Iridium standard solution (1000 ppm) was purchased from Kanto Chemicals (JAPAN). Standard seawater CASS-4 was obtained from National Research Council (CANADA). All Teflon vessels and glassy carbon electrodes were immersed into 50 % acid mixture solution (at 40℃) for 5 days before use to wash out any metallic contaminants.

3. RESULTS AND DISCUSSION

3.1 Modifiers

Because more than ten million times amount of a modifier is usually added over the analyte of interest, in searching modifiers of the ETV for ICP-MS, the most important factor is the purity of the modifiers. We have examined many reagents to select the most appropriate chemical modifier for iridium. The reagents tested were ammonium carbonate, ammonium chloride, ammonium formate, ammonium oxalate and ammonium nitrate as well as some organic reagents. Among the reagents tested, ammonium nitrate was the most effective as a modifier for iridium .

3.2 Addition Amount of a Modifier and Vaporization Temperature

The amount of ammonium nitrate was optimized by varying the concentration of them stepwise. The optimum amount of ammonium nitrate as the modifier was determined as the 0.5 % concentration. The optimum vaporization temperature was also estimated under the other optimized conditions. The maximum signal intensity was obtained in setting the vaporization temperature of ETV at 1100 ℃. With out ammonium nitrate the vaporization of iridium needs the temperature of 2700 ℃. The use of the modifier decreased the vaporization temperature about 1600 ℃ . This means that it is possible to vaporize iridium selectively from the complex matrix samples

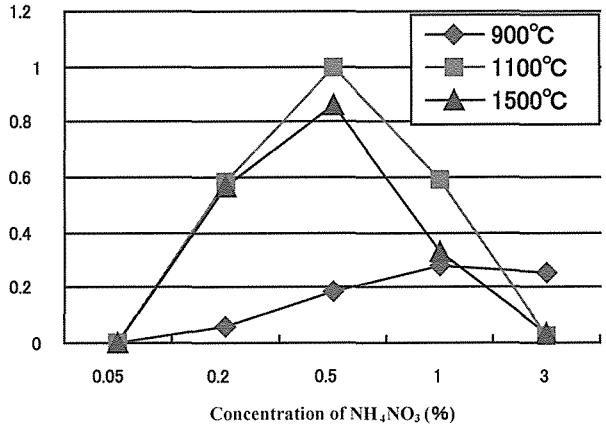

Fig. 1. Effects of the concentration of NH_4NO_3 and vaporization temperature.

3.3 Detection Limits

The detection limits of the ETV methods with and with out the

modifier as well as that of a common pneumatic nebulizer are summarized in Table.1. The detection limit of the ETV with the modifier was 2.2 fg and that of without one was 772 fg respectively. The use of ammonium nitrate as a modifier resulted in more 350 times sensitive than common ETV without a modifier.

3.4 Real Sample Analysis

To estimate this ETV method from the stand point of practical use, the concentrations of iridium in seawater samples were determined. In case of the analysis of complex matrix samples such as seawater. It is better to separate the analyte of interest in some degree from the matrix components. Electrolytic reduction using glassy carbon electrodes was attempted to remove interference substances and preconcentrate iridium from seawater. An applied voltage of 2.7 V and stirring of the solution was essential to obtain more than 10 % recovery within 2 hours. The iridium concentrations of three seawater samples , Tsuruga port, Nishinomiya port and CASS-4 were 24±5, 41±8 and 60±17 ppq respectively.

Table 1. Detection limits and vaporization temperatures

Sample introduction	Vaporization temperature (℃)	Detection limit* (fg)
Pneumatic nebulizer	—	790
ETV without modifier	2700	772
ETV with NH_4NO_3	1100	2.20

* calculated as 1ml for pneumatic nebu.and 20 μl for ETV respectively

4. CONCLUSIONS

We have developed the ETV method using ammonium nitrate as a chemical modifier for the determination of iridium of ultra-trace levels by ICP-MS. The modifier effects in more than three hundred times increased signal intensity and lowering the vaporization temperature of iridium from 2700 ℃ to 1100 ℃. Only using 50 ml samples, the concentration of iridium at ppq levels in seawater could be determined by the isotope dilution method .

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