Technical Note

Determination of Thorium in Thorotrast Patient's Liver by Inductively Coupled Plasma - Mass Spectrometry[†]

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Thorium in a Thorotrast patient's liver was determined by a new analytical technique, ICP-MS. In the sample dissolution semi-fusion method with NH_4HSO_4 as a flux was used. The resultant cake was dissolved in aqua regia and diluted for the ICP-MS measurement. The obtained result showed good accordance with that by α -spectrometry, showing the present combination of the dissolution and ICP-MS is quite suitable for the determination of Th in the Thorotrast liver.

Key Words: thorium, Thorotrast liver, inductively coupled plasma-mass spectrometry, semi-fusion with ammonium hydrogensulfate

1. Introduction

Biological effects of a radiological contrast medium, Thorotrast, and its consequences are interesting from the view point of human health and radiation^{1),2)}. To quantify the effects and to clarify the relationship between the dose and the response, information on the amount of Thorotrast deposited in the patient's tissues must be correctly known. Several radiometric analytical methods have been utilized in the study of Thorotrast. In this short paper, the application of a new analytical technique, inductively coupled plasma - mass spectrometry (ICP-MS)^{3),4)}, is described.

2. Experimental

The subject was a male Thorotrast patient, who was a 76-year-old ex-serviceman injected with Thorotrast during World War II, and died from generally spread angiosarcoma in 1989. The weight of the liver from the patient was 985 g. A part of the liver specimen (about 50 g) obtained at the autopsy was used for this study. It was ashed overnight at 450 °C on a quartz dish using an electric muffle furnace. The ash was pulverized with an agate mortar to obtain homogeneity. About 100 mg of the ash was processed.

The sample was taken in a 100 ml beaker and was added with about 10 ml of conc. HNO_3 . It was heated on a hot plate with a watch glass cover. In order to decompose the organic matter completely, 2 ml of HNO_3 and 5 drops of HClO_4 were also added and the heating was continued. The solution was evaporated and then 10 g of NH_4HSO_4 (analytical grade, Kanto

[†] 誘導結合プラズマ質量分析法によるトロトラスト患者の肝臓中のトリウムの定量。五十嵐康人, 石川雄一*, 白石久二雄*, 高久雄一**, 増田公彦**: 放射線医学総合研究所環境生態学研究部, 311-12 那珂湊市磯崎 3609, *癌研究会癌研究所病理部, 170 東京都豊島区上池袋 1-37-1, **^(株)丸文第三事業本部, 103 東京都中央区日本橋大伝馬町 8-1。

Chemical Co.) was added to the beaker. The temperature of the hot plate was raised to fuse the flux (more than 250 °C). The heating was sustained for about 45 min. The melt was allowed to cool and the resultant cake was dissolved in 20 ml of aqua regia with moderate heating. After the cooling, it was transferred to a 250 ml measuring flask and filled with a HNO₃ solution. The solution thus obtained was colored yellow and the HNO₃ concentration was about 3 M. This solution contained about 0.4 mg ash per ml. Thorium concentration was suspected to be more than 10% of the ash concentration. This concentration level was too high for the measurement by ICP-MS because of the "memory effect". Therefore the sample solution was further diluted to have the Th concentration level of ng/ml.

The measurement was performed on a VG Elemental (PlasmaQuad PQ2 Plus) installed at Marubun Co., Minamisuna, Koto-ku, Tokyo. The operating conditions of the spectrometer were almost the same as those reported for the measurement of Th and U in biological samples⁵⁾ except the mass range scanned. The mass range was set at 207–236, and 210 to 230 was skipped. Thorium content in the sample solution was determined with the Bi internal standardization⁹⁾. The accuracy of the measurement was examined by measuring Th in NIST SRM 1571 Orchard Leaves and a standard solution.

3. Results and Discussion

Thorotrast granules deposited in the tissue are of ThO₂ and the decomposition of ThO₂ is of significance and seems critical in the analysis. Dissolution of ThO₂ by a mixture of HNO₃ and HF was first tried using a PTFE decomposition vessel (San-ai Kagaku, Nagoya). However, we

failed to achieve a complete dissolution of ThO₂. Then the semi-fusion using NH₄HSO₄ as a flux was attempted. This method has been applied to the determination of Pu involving refractory oxide in soil samples by Yamamoto⁶⁾, which was successful. The present amount of NH₄HSO₄ used (10 g) may be excessive; if the smaller appropriate vessel is used, it can be reduced. Though the detailed mechanism of the dissolution is unknown, this method seems very effective and simple for the dissolution of the refractory oxide of actinide elements.

Though we also attempted to dissolve the resultant cake by the semi-fusion in diluted acids, bulky precipitation persistently remained in the solution. This precipitation was thought to be calcium sulfate. Since calcium sulfate is soluble in aqua regia, this process was incorporated into the analytical procedure.

Table 1 shows Th content in the sample together with that in the Orchard Leaves. From the result of the Orchard Leaves obtained, the value of the Thorotrast liver also seems to involve about 10% negative systematic error. The result is also compared with ones obtained by other methods including isotope dilution-ICP-MS⁷⁾. These values show a good accordance with each other.

In conclusion, the present combination of the semi-fusion with NH₄HSO₄ and ICP-MS was quite successful in determining Th in the Thorotrast liver. If ammonium and sulfate ions and other acids do not cause any interferences, the present dissolution procedure can be combined with other spectroscopic techniques that can be used in determining Th, such as ICP-atomic emission spectroscopy and colorimetry, etc.

Table 1 Th concentration in Thorotrast liver

Method	Sample	Th concn.
Direct analysis (internal std.; Bi)	Thorotrast liver	1.95±0.03 mg/g wet
	Orchard Leaves (certified)	58.4±0.1 ng/g dry (64)
Isotope dilution ICP-MS ⁷⁾ α -Spectrometry	Thorotrast liver	2.05±0.33 mg/g wet
	Thorotrast liver	1.70±0.08 mg/g wet

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