

# GAS CHROMATOGRAPHY OF METAL CHELATES WITH CARRIER CONTAINING LIGAND VAPOUR

—Th(TFA)<sub>4</sub> · TBP—

BY

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## ABSTRACT

The gas chromatography of the thorium mixed-ligand complex of trifluoroacetylacetone (TFA) and tri-*n*-butylphosphate(TBP) was investigated by using a carrier gas containing ligand vapour. Th(IV)-TFA-TBP was eluted at a column temperature above 170°C, by the conventional method using helium as the carrier, but the elution was not quantitative and anomalous elution was observed at the front of the peak. By using trifluoroacetylacetone as the carrier-gas additive, the mixed ligand complex was quantitatively eluted. It was found that the molar ratio of TBP to Th(TFA)<sub>4</sub> was 1 : 1. Furthermore, the study of the extraction-gas chromatography was undertaken for the mixed-ligand complex and it was found that Th(IV)-TFA-TBP could be analyzed by the ligand-carrier method.

## 1. Introduction

In recent years, new  $\beta$ -diketone derivative reagents for metals are developed and a lot of attention is being given to their application in gas chromatographic analysis. However, there are many problems on the approaches for analytical technique and one of them is the preparation of a sample which is injected into a gas chromatograph. In general, solid chelates are prepared and dissolved in organic solvents prior to injection into gas chromatograph, but practically many metal  $\beta$ -diketonates are not easily dissolved in non polar solvents and this preparation method is less desirable than preparation by solvent extraction.

For reason mentioned above, C. V. Banks, et al.<sup>1)</sup> have reported that tri-butylphosphate(TBP) provides a synergic enhancement of the extraction of rare earths with hexafluoroacetylacetone(HFA) and the mixed ligand complex Th-HFA-TBP can be gas-chromatographed. Similarly, the mixed ligand complex of uranyl and thorium in the TBP-HFA system have been investigated by combining solvent extraction with gas-chromatography.<sup>2)3)</sup> But, the quantitative elution of the mixed ligand complexes have not been obtained up to the present.

The authors<sup>4,5,6)</sup> have reported that thorium(IV)-trifluoroacetylacetonate is quantitatively eluted by using trifluoroacetylacetone as a carrier-gas additive. Similarly, the method of using ligand vapour as a carrier-gas additive is thought to be desirable for the quantitative elution of the mixed-ligand complexes.

In the present paper, the mixed-ligand complex of thorium(IV) with trifluoroacetyl-

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acetone and tri-*n*-butylphosphate was investigated by the gas chromatography using trifluoroacetylacetone as a carrier-gas additive. It was found that the quantitative elution of the mixed-ligand complex could be obtained by this method.

## 2. Experimental

### 2-1. Instrumentation

A Shimadzu Model GC-1B gas chromatograph equipped with a vapour generator was used to supply the ligand vapour to the carrier gas.

### 2-2. Reagents

All reagents were of reagent grade unless otherwise specified.

Trifluoroacetylacetone(H-TFA) was obtained from the Dojindo Co., Ltd., Research Laboratories. This compound was distilled at a temperature of 106–107°C and was immediately used for experiments.

Thorium(IV)-trifluoroacetylacetonate(Th(IV)-TFA) was synthesized by the method suggested by E. W. Berg et. al. and the chelate was purified by sublimation *in vacuo*. The elemental analysis of the purified Th(IV)-TFA gave 28.39% of carbon and 2.07% of hydrogen, the melting point of the compound is 128°C.

### 2-3. Preparation of the sample solution for Gas Chromatography

The mixed-ligand complex of Th(IV)-TFA with tri-*n*-butylphosphate(TBP), Th(IV)-TFA-TBP, was obtained as follows. Th(IV)-TFA was dissolved in a mixture of benzene and TBP(7 : 3). 10  $\mu$ l of the solution was injected into the gas chromatograph after the addition of small amounts of dehydrated sodium sulfate.

### 2-4. Gas Chromatography

The chromatographic conditions for the conventional method using helium as a carrier gas were as follows.

column temperature: 180°C,  
injection temperature: 310°C,  
detector temperature: 250°C,  
cell current of thermal conductivity detector: 150 mA,  
flow rate: 28 ml/min. at the outlet,  
column: 0.5% Silicone XE-60/Gas Chrom-CLH(80–100 mesh),  
column tubing: 4 mm i.d. and 150 cm length of stainless steel.

The chromatographic conditions for the present method using H-TFA as the carrier-gas additive were as follows.

temperature of the water bath for the vapour generation: 25°C,  
other conditions: same as the conventional method.

## 3. Results and Discussions

### 3-1. Gas Chromatography of Th(IV)-TFA-TBP

The solubility of Th(IV)-TFA was low in non-polar organic solvents such as benzene, chloroform and cyclohexane, but it increased as the amounts of TBP increased<sup>8,9</sup>. 30 mg of Th(IV)-TFA were completely dissolved in the mixed solvent containing at least 20%v/v

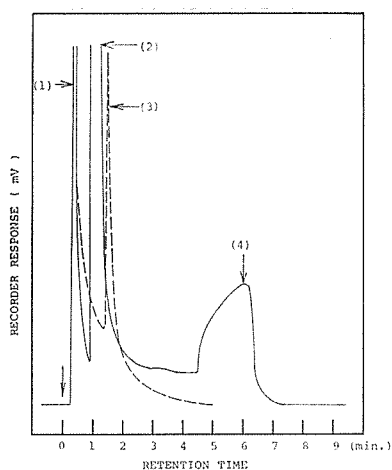


Fig. 1. Chromatograms of  $\text{Th}(\text{TFA})_4$  and  $\text{Th}(\text{TFA})_4 \cdot \text{TBP}$  by the conventional method  
He-carrier; 28 ml/min.

----; 20 w/v %  $\text{Th}(\text{TFA})_4$ , 33 % TBP/Benzene; 5  $\mu\text{l}$

—; 20 w/v %  $\text{Th}(\text{TFA})_4$ /Acetone; 5  $\mu\text{l}$

(1) organic solvent (Acetone, Benzene)

(2) TBP

(3)  $\text{Th}(\text{TFA})_4$

(4)  $\text{Th}(\text{TFA})_4 \cdot \text{TBP}$

of TBP and benzene. In this solution, it was assumed that  $\text{Th}(\text{IV})\text{-TFA-TBP}$  formed a mixed-ligand complex. The solution was injected into the gas chromatograph. The result is shown in Fig. 1, together with the chromatogram of  $\text{Th}(\text{IV})\text{-TFA}$ . As shown in Fig. 1, it was found that an elution peak appeared at the retention time of 6 min.. The molecular weight of the solute corresponding to the new peak may be higher than that of both  $\text{Th}(\text{IV})\text{-TFA}$  and TBP, because the retention time of the new peak is longer than that of  $\text{Th}(\text{IV})\text{-TFA}$ . After considering these facts, it seems most reasonable to conclude that the new peak is interpreted as a mixed-ligand complex,  $\text{Th}(\text{IV})\text{-TFA-TBP}$ .

The chromatographic conditions were investigated for the elution of  $\text{Th}(\text{IV})\text{-TFA-TBP}$ . As a result, the column temperature has to be  $170^\circ\text{C}$  above and the injection temperature has to be  $250^\circ\text{C}$  above. Moreover, it was found that non-polar liquids or slightly polar liquids are suitable for the stationary phase.

### 3-2. Gas Chromatography of the $\text{Th}(\text{IV})\text{-TFA-TBP}$ using H-TFA Vapour as the Carrier-gas Additive

In the case of the helium carrier,  $\text{Th}(\text{IV})\text{-TFA}$  and  $\text{Th}(\text{IV})\text{-TFA-TBP}$  were not quantitatively eluted and not completely separated from the solvent or TBP. Therefore, the method using H-TFA vapour as the carrier-gas additive was applied to the gas chromatography of  $\text{Th}(\text{IV})\text{-TFA-TBP}$ . The chromatogram obtained by the present method was found to be quantitatively separated (Fig. 2). The relation between the peak area of the mixed-ligand complex and the amount of sample was proportional and passed through the original point as shown in Fig. 3.

As mentioned in the previous paper, the decomposition of the metal chelates are suppressed by using H-TFA additive. Similarly, it was found that the H-TFA vapour

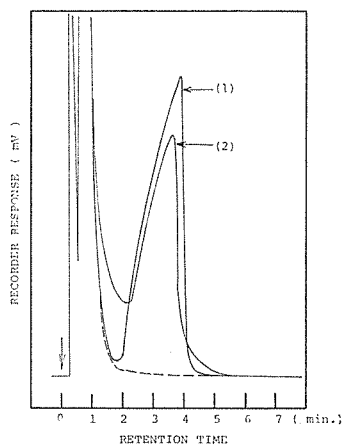


Fig. 2. Chromatograms of  $\text{Th}(\text{TFA})_4 \cdot \text{TBP}$

Column Temp.:  $190^\circ\text{C}$ , Flow rate: 58 ml/min.

(1) carrier gas: helium containing H-TFA, vapour generator Temp.:  $30^\circ\text{C}$

(2) carrier gas: helium only

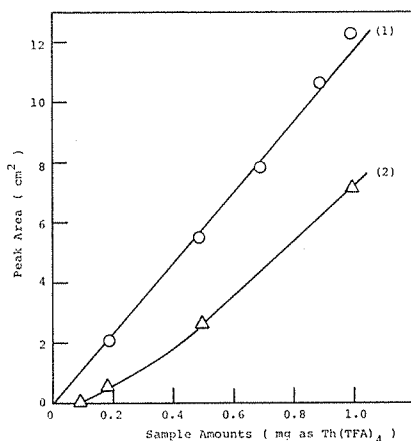


Fig. 3. Relation between the peak area and the sample amounts of  $\text{Th}(\text{IV})\text{-TFA-TBP}$

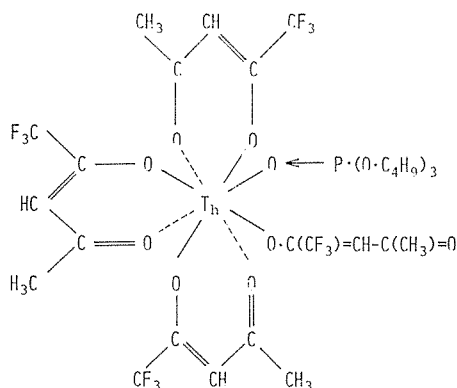
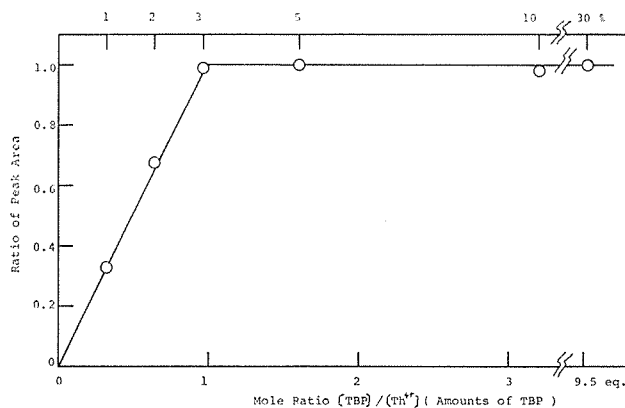
(1) the present method

(2) the conventional method

is effective to suppress the decomposition of the mixed-ligand complex. The structure of  $\text{Th}(\text{IV})\text{-TFA-TBP}$  can be estimated from that of the mixed-ligand complex of thorium(IV) with acetylacetonone and TBP which was reported by T. V. Hearly et. al.<sup>10</sup>, as shown in Fig. 4. After considering the structure, it was thought that the coordination bond of  $\text{Th-TFA}$  is weakened by the adduct formation of TBP, but is stabilized by the formation of H-TFA atmosphere due to the addition of H-TFA. Accordingly, it is considered that the mixed-ligand complex is quantitatively eluted by using the ligand-carrier method.

### 3-3. The Molar Ratio of TBP to $\text{Th}(\text{IV})\text{-TFA}$ in the Mixed-Ligand Complex

The molar ratio of TBP to  $\text{Th}(\text{IV})\text{-TFA}$  in the mixed ligand complex was determined

Fig. 4. Structure of  $\text{Th}(\text{TFA})_4 \cdot \text{TBP}$ Fig. 5. Dependence of relative peak area of mixed ligand complex on molar ratio of TBP to  $\text{Th}^{4+}$ 

by the gas chromatography. Definite amounts of  $\text{Th}(\text{IV})\text{-TFA}$  were added to the benzene solutions containing the various known concentration of TBP. The mixed-ligand complex in benzene solutions were provided to the gas chromatograph. Fig. 5 shows the peak areas of the mixed-ligand complex as a function of the ratio of TBP to  $\text{Th}(\text{IV})\text{-TFA}$  in benzene. From this relationship, it has been found that the mixed-ligand complex is formed at the molar ratio of 1 : 1. Namely, one molecule of TBP is adducted to  $\text{Th}(\text{IV})\text{-TFA}$ .

#### 3-4. Application to the Gas Chromatographic Determination of Thorium Ion in Aqueous Solution by combining with the Solvent Extraction

(1) The solvent extraction- gas chromatographic method was examined in order to analyze thorium ion in aqueous solution as  $\text{Th}(\text{IV})\text{-TFA}\text{-TBP}$ .  $\text{Th}(\text{IV})\text{-TFA}$  chelate can be extracted to the mixture of non-polar organic solvent and TBP. The following experiments were done to investigate the dependence of the percentage extraction on pH. 65.7 mg portions of tetrahydrated thorium nitrate (27.6 mg as  $\text{Th}^{4+}$ ) were dissolved with 0.5ml portions of a 0.002-N hydrogen nitrate aqueous solution in 5 ml vial tube. 1 ml of benzene, 0.05 ml of TBP and 0.2 ml of T-HFA were added to the solution of thorium. After the pH was adjusted to the desired pH with 0.5 ml of buffer solution, the tubes were

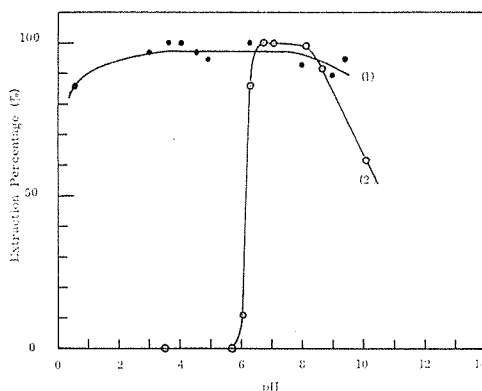


Fig. 6. Solvent extraction of  $\text{Th}^{+4}$  as  $\text{Th(IV)-TFA-TBP}$

- (1)  $\text{Th(IV)-TFA-TBP}$  in organic phase; determined by the gas chromatography (H-TFA carrier),
- (2)  $\text{Th(IV)-TFA}$  in organic phase; obtained from the amounts of  $\text{Th}^{+4}$  in aqueous solution which was determined by the colorimetric method.

sealed with a stopper and vigorously shaken. The aqueous solutions were removed with a syringe and the remaining organic solutions were injected into the gas chromatograph with a micro syringe, after the addition of small amounts of dehydrated sodium sulfate into the solution.

The relation between the percentage extraction of thorium and pH was obtained as shown in Fig. 6.

(2) The trace amounts of thorium were extracted into non-polar organic solvent without TBP from the aqueous solution. The relation between the percentage extraction of the  $\text{Th(IV)-TFA}$  and the various pH was investigated by the colorimetric method using Arsenazo-III. The results are shown in Fig. 6.

From these results, it was found that thorium ion is extracted in the pH range from 3 to 10 as the mixed-ligand complex. Accordingly, the gas chromatography combined with the solvent extraction of  $\text{Th(IV)-TFA-TBP}$  is more suitable for the analysis of thorium in aqueous than the method combined with that of  $\text{Th(IV)-TFA}$ .

#### 4. Conclusion

The mixed-ligand complex of thorium with H-TFA and TBP was eluted in the gas chromatography at a column temperature above  $170^\circ\text{C}$ , but the quantitative elution was not obtained with the conventional gas chromatography. It was found that the quantitative elution was obtained with the ligand-carrier method using H-TFA vapour as the carrier-gas additive. In addition, it has been established that (1) the molar ratio of TBP to  $\text{Th(IV)-TFA}$  is 1 : 1, and (2) thorium ion in aqueous solution is extracted as  $\text{Th(IV)-TFA-TBP}$ , and (3) the bond between thorium and TBP is more stable than that between thorium and H-TFA ligand.

In conclusion, the method using H-TFA vapour as carrier-gas additive is extremely effective for the gas chromatography of the mixed ligand complex,  $\text{Th(IV)-TFA-TBP}$ , as well as for that of  $\text{Th(IV)-TFA}$ . It may be concluded that the gas chromatographic determination of metal ions in aqueous solution can be greatly expanded by combining with the solvent extraction and using the ligand-carrier method.

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