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111. Keiichi Tanikawa, Katsumi Hirano, and Kiichi Arakawa : Organometallic Compounds. V.[*1] Gas Chromatographic Analysis of Metal Trifluoroacetylacetonates.[*2]

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The separation of various metal trifluoroacetylacetonates is found to be easier than that of acetylacetonate. Although the separation of acetylacetonate of Cr^{3+}, Cu^{2+}, Fe^{3+} and other was found to be not possible due to overlapping, it became possible with trifluoroacetylacetonate. The columns using XE-60, that is nitrile sillicone polymer, as a solid phase liquid gave favorable results. As to those which shows short retention time, the use of Daifl oil, namely Trifluorotrichloroethylene, gave a good chromatogram. In the separation of stereoisomers also XE-60 as well as QF-1 facilitated separation.

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Previously, the authors reported on the studies of β-diketone metal chelate compounds by gas chromatography (abbreviated as GC hereinafter).[1] In this paper the separation of 13 kinds of metal trifluoroacetylacetonate (TFA-chelate) synthesized are described by GC using a thermal conductivity detector.

Metal trifluoroacetylacetonate, similar to the metal acetylacetonate, has a melting point like organic compounds, and its melting point is considerably low as compared with AA-chelate. For instance, $Fe(TFA)_3$ has a melting point of 116° which is 64° lower than that of $Fe(AA)_3$ (180°) and also the difference by 102° is observed in Cr compounds. Almost all of them are insoluble in water, but soluble freely in organic solvents.

Staniforth, *et al.*[2] described that metal chelates of trifluoroacetylacetone have low melting point, high solubility in organic solvent, and high thermal stability as compared with those of acetylacetone. Therefore, it is possible that metal ions can be separated gas chromatographically as trifluoroacetylacetonates. Although the mechanism of increase of volatility, which is observed when the hydrogen atoms of CH_3 of acetylacetone are substituted with fluorine atom, has never been adequately elucidated, the studies on the gas chromatographic separation of metal chelates of trifluoroacetylacetone have been really reported. Although the mechanism of the increase of volatility has never been fully elucidated, the volatility of TFA chelate actually is increased as compared with that of AA-chelate, and studies on GC of chelates have been developed recently.[3~9]

The authors have obtained the following new informations by separating various kinds of metal-TFA chelate using a column newly prepared. a) The chromatogram

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[*1] Part Ⅳ. K. Tanikawa, K. Arakawa : This Bulletin, **13**, 926 (1965).

[*2] Presented at the 14th Annual Meeting of the Japan Society for Analytical Chemistry. Nov. 21, 1965 (Kyoto).

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1) K. Yamakawa, K. Tanikawa, K. Arakawa : This Bulletin, **11**, 1405 (1963).

2) A.E. Martell, M. Calvin : "Chemistry of the metal chelate compounds," p. 180 (1956). Prentice-Hall, Inc., Englewood Cliffs, N.J.

3) R.E. Sievers, B.W. Ponder, M.L. Morris, R.W. Moshier : Inorg. Chem., **2**, 693 (1963).

4) J.E. Schwarberg, R.W. Moshier, J.H. Walsh : Talanta, **11**, 1212 (1964).

5) R.D. Hill, H. Gesser : J. Gas Chromatog., **1**, 11 (Oct. 1963).

6) W.D. Ross : Anal. Chem., **35**, 1596 (1963).

7) W.D. Ross, R.E. Sievers : *Ibid.*, **37**, 598 (1965).

8) W.G. Scribner, W.J. Treat, J.D. Wies, R.W. Moshier : *Ibid.*, **37**, 1136 (1965).

9) G.P. Morie, T.R. Sweet : *Ibid.*, **37**, 1553 (1965).

shows generally symmetric sharp peaks and is stable as compared with that of AA-chelate, b) it has a high sensitivity, and c) separation may be possible at comparatively low column-temperature.

Furthermore, the authors attempted separation of *cis-trans* isomers, occurring in Metal *tri*-TFA and succeeded in with such metal chelates as Cr, Ga and Rh respectively.

Experimental

Sample——Samples subjected to the separation were chelates of Be^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Al^{3+}, Co^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+}, In^{3+}, Rh^{3+}, and Th^{4+}, and all of them were synthesized in the authors' laboratory by the method similar to the synthesis of AA-chelate[1] reported previously. They are shown in Table II.

Apparatus and Method——The apparatus used was Shimadzu GC-1B (dual column) of thermal conductivity type with a stainless column 150 cm. (75 cm. U-shap × 2) × 4 mm. i. d. The column temperature resided in the range of 120∼140°, helium gas was passed through as a carrier gas at a rate of 40∼60 ml./min. the room temperature for vaporizing the sample was 30∼50° higher than that of the column, and the temperature of the detector was adjusted at 200°. The sample was dissolved in chloroform at a concentration of 5∼10%, 0.5∼3 μl. of the chloroform solution was injected by the use of microsyringe.

Preparation of the Column——The fillers used in this paper were shown in Table I. Some of them were used for the separation of acetylacetone chelates, as well as ferrocene derivatives.[*1]

Table I. Gas Chromatographic Column[a]

Columns	He (ml./min.)	Col. temp. (°C)
a) 1% Apiezon-L on Chromosorb-W	60	130
b) 1% SE-30 on Chromosorb-W	40	120
c) 1% QF-1 on Chromosorb-W	40	130
d) 0.5% Daifl oil 200 on Chromosorb-W	60	140
e) 1% XE-60 on Chromosorb-W	40	140
f) 0.5% XE-60 on Chromosorb-W	60	120
g) 0.5% QF-1 on Glass beads	50	130
h) 0.5% XE-60 on Glass beads	40	140

Column length 1.5 m. × 4 mm., Range 2mV, 200 mA.
a) Trifluorotrichloroethylen Daikinkogyo K.K., Nitrile silicone polymer G.E.

As a carrier, Chromosorb-W (60∼80 mesh) and Glass beads (60∼80 mesh) which had been pretreated conventionally with dimethyldichlorosilane after the previous washing with acid and water, were used.

As a solid phase liquid, Apiezon-L, SE-30, QF-1, XE-60 and Daifl oil 200 were used, respectively.

Results and Discussion

Since metal chelates of trifluoroacetylacetone are thermally stable as mentioned above, the gas chromatographic separation of them are fairly easy. The temperature of the column and the flow rate of helium gas for the separation of the mixture of the metal chelates were shown in Table I, and satisfactory results were obtained in each case within the temperature of 120 to 140° except Zn(TFA)$_2$. The retention time of individual metal chelate was shown in Table II. In this case, the following modified conditions were used; *i.e.*, for the metal chelate which has a short retention time such as Be(TFA)$_2$, the column temperature was lowered, and for the chelate having a long retention time, the flow rate of carrier gas was increased. In general the retention time of Be(TFA)$_2$ is short with column a∼h, but among them column d keeps a suitable retention time effecting clear separation. XE-60 used for column f similarly to column d, gives a better result which never be found in the report so far, and generally good results were obtained.

Table II. Retention Time of Metal Trifluoroacetylacetonates (Column h)

Chelates	m.p. (°C)	Ret. time (min.)	Isomer (Col.)
$\mathrm{Be(TFA)_2}$	98～100	1.6	
$\mathrm{Cu(TFA)_2}$	120	12.16	
$\mathrm{Mg(TFA)_2}$	280	9.75	
$\mathrm{Mn(TFA)_2}$	280	12.35	
$\mathrm{Zn(TFA)_2}$	168～169	—	
$\mathrm{Al(TFA)_3}$	280	4.4	
$\mathrm{Cr(TFA)_3}$	122	13.0	a, c, e, f, g
$\mathrm{Fe(TFA)_3}$	115～117	12.50	
$\mathrm{Rh(TFA)_3}$	170～172	25.25	c, e, f, g
$\mathrm{In(TFA)_3}$	130～132	13.70	
$\mathrm{Ga(TFA)_3}$	125～127	8.45	e
$\mathrm{Co(TFA)_3}$	120	12.52a)	
$\mathrm{Th(TFA)_4}$	135～137	18.93a)	

a) Column f

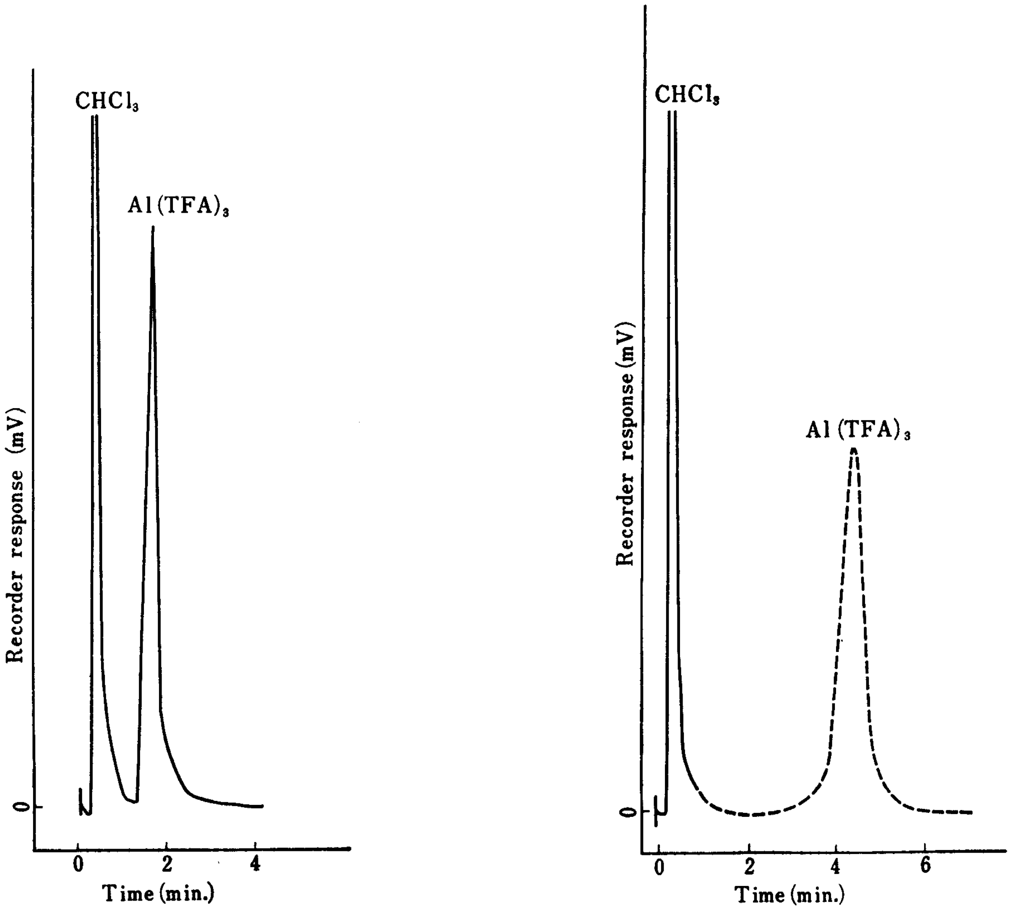

Fig. 1. Separation of $\mathrm{Al(TFA)_3}$

0.5% XE-60 on Chromosorb-W
Column Temp. 120°C
He 60 ml/min.

0.5% XE-60 on Glass beads
Column Temp. 140°C
Detector Temp. 200°C
He 40 ml/min.
Range 2 mV 200 mA in $\mathrm{CHCl_3}$

Separation of the Mixture of Metal Trifluoroacetylacetonates——The results of separation of a single and a mixture of metal trifluoroacetylacetonate by GC is shown in Fig. 1~6. The chromatogram shown in Fig. 1. is an example of separation of Al^{3+} using XE-60 as a solid phase liquid, where the solid line indicates the state when Chromosorb-W was used as a carrier and the dotted line shows the state when glass beads were used as a carrier. In this case good results can be obtained with respect to the symmetry of peak, the width of peak, and the retention time, whenever the glass beads are used as a carrier, being suitable for quantitative analysis.

Fig. 2 shows the separation of Ga^{3+}, Fe^{3+}, and Cu^{2+}. As described by Hill, *et al.*,[5] the peaks of Fe^{3+} and Cu^{2+} in the mixture of Ga^{3+}, Fe^{3+}, and Cu^{2+}, overlap often, but by using column d clear separation into each component was done. By using column e the retention time becomes longer in the separation of Fe^{3+} and Cu^{2+}. Moreover the peaks of Fe^{3+} and Cu^{2+} obtained by Hill, *et al.* appears to be reversed as compared with the peak obtained by the authors using column d and e. Namely Fe^{3+} is detected first in the authors' experiments, while they detected Cu^{2+} first. However, if column g is used, even in the authors' case, the peaks partially overlap and Cu^{2+} precedes Fe^{3+} similarly as the result above.

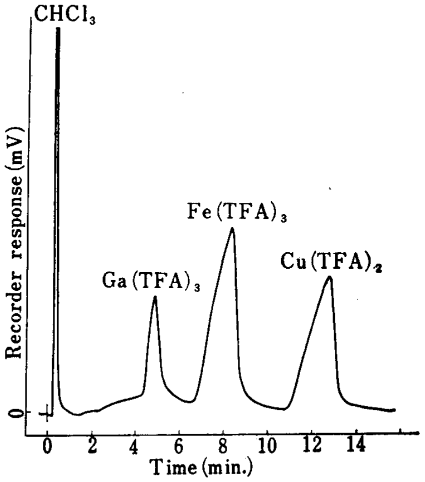

Fig. 2. Separation of $Ga(TFA)_3$, $Fe(TFA)_3$ and $Cu(TFA)_2$

0.5% Daifl oil on Chromosorb-W
Column Temp. 140°C
Detector Temp. 200°C
He 60 ml/min.
Range 2 mV 200 mA in $CHCl_3$

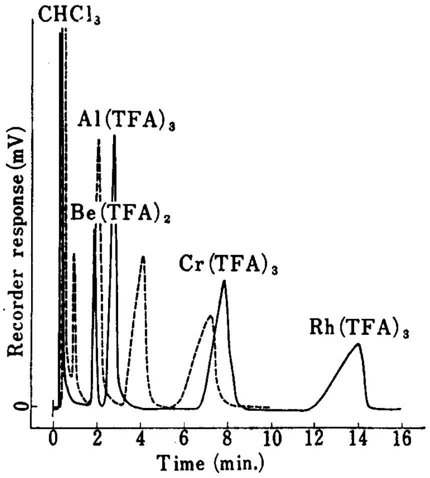

Fig. 3. Separation of $Be(TFA)_2$, $Al(TFA)_3$, $Cr(TFA)_3$, and $Rh(TFA)_3$

‐‐‐‐ 1% SE-30 on Chromosorb-W
—— 0.5% Daifl oil on Chromosorb-W
Column Temp. 140°C (—) 125°C (···)
Detector Temp. 200°C
He 60 ml/min. (—) 40 ml/min.(···)
Range 2 mV 200 mA in $CHCl_3$

Fig. 3 presents the separation of Be^{2+}, Al^{3+}, Cr^{3+} and Rh^{3+} using SE-30 and Daifl oil 200. In all columns except column d, the retention time of Be^{2+} and Al^{3+} is short, and especially Be^{2+} is sometimes detected as the shoulder of the solvent. When column d is used, the elution time is longer and appropriate retention time may be maintained, so that this is also suitable for the identification of the metal chelate having a disposition to be eluted quickly. Even when metal chelate, retention time of which is long, are contained, the method of programming temperature gives stable chromatograms.

Separation of Geometrical Isomer——Regarding to the separation and identification of two geometrical isomers of octahedral complexes of unsymmetrical bidentate ligands, Fay, *et al.*[10~12] described that they separated *cis* and *trans* isomers depending

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[10] R.C. Fay, T.S. Piper: J. Am. Chem. Soc., **84**, 2303 (1962).
[11] *Idem*: *Ibid.*, **85**, 500 (1963).
[12] R.A. Palmer, R.C. Fay, T.S. Piper: Inorg. Chem., **3**, 375 (1964).

upon the differences of the solubility of chelates benzoylacetylacetone or trifluoroacetylacetone coordinated with trivalent metal, in ethanol, and that the ratio of isomers were determined by NMR measurements. They stated also that the *trans* isomer is generally more stable and easy in formation.

The separation of stereoisomers of Cr^{3+} by GC has been performed by Sievers, *et al.*[3] separated the isomers of Cr^{3+} trifluoroacetylacetone by using a column 5% D.C. silicone grease (high-vacuum)/chromosorb-W (30~60 mesh) and also the separation of Rh^{3+}[7] was made similarly. In both cases, the larger peak of the *trans* isomer was detected prior to the small peak of the *cis* isomer.

As to the separation of geometrical isomers, the authors attempted to separate the chelates of trifluoroacetylacetone with Al^{3+}, Co^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+}, In^{3+}, and Rh^{3+}, and succeeded in separating the stereoisomers of Cr^{3+}, Ga^{3+}, and Rh^{3+} respectively. Initially an attempt to separate the isomers in the mixture of Al^{3+}, Cr^{3+}, and Rh^{3+} was made and succeeded in the separaton of Cr^{3+} and Rh^{3+} isomers, but the separation of Al^{3+} was not succeeded. In Fig. 4 it gives the chromatogram as well as the condition during the column chromatography.

The chromatogram in the separation of stereoisomers of Cr^{3+}-trifluoroacetylacetonate using QF-1 as the solid phase liquid was shown in Fig. 5.

The separation of the stereoisomers of Ga^{3+}-trifluoroacetylacetonate is shown in Fig. 6. From the paper of Fay, *et al.* dealing with NMR spectra and the isomorphism of crystals, it is considered that the smaller peak with shorter retention time corresponds to *cis* form and the larger peak to *trans* form in the separation of the stereoisomer of Ga^{3+}.

In the case of Ga^{3+}, as compared with Cr^{3+} and Rh^{3+}, the separation of *cis* and *trans* isomers is not effected completely, and owing to partial overlapping it is detected as a shoulder.

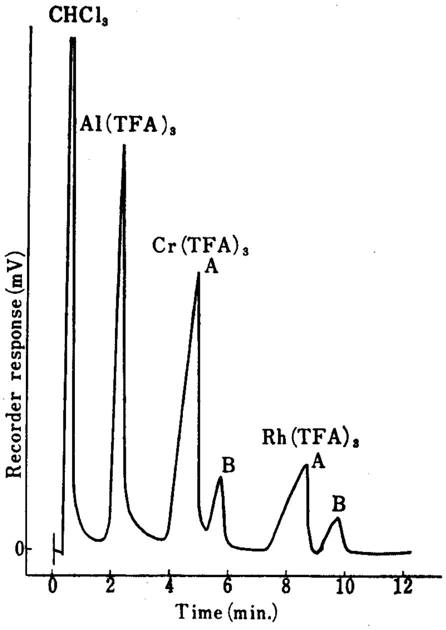

Fig. 4. Separation of *cis* and *trans* isomer of Al(TFA)$_3$, Cr(TFA)$_3$ and Rh(TFA)$_3$ A. *trans* B. *cis*

1% XE-60 on Chromosorb-W
Column Temp. 130°C
Detector Temp. 200°C
He 40 ml/min.
Range 2 mV 200 mA in CHCl$_3$

In the next place, columns used by the authors in separating isomers will be explained hereinafter, referring to Table II. With column c only the isomer of Cr^{3+} could be separated, but with other metals separation was unsuccessful. With column e it was successful with isomers of Cr^{3+}, Ga^{3+} and Rh^{3+}.

Column g is permitted to the separation of Cr^{3+} and Rh^{3+}. In the case of column f favorable results were obtained with Cr^{3+} and Rh^{3+}. From above results it was found that columns using XE-60 or QF-1 as a solid phase liquid are suitable for the separation of *cis-trans* isomers, and the other columns are inadequate except that only a is to a certain extent possible to separate Cr^{3+}. Since various investigations on the separation of geometrical isomers are being made the results with regard to the fractionation of eluate alumina column chromatography, and thin-layer chromatography will be published later elsewhere.

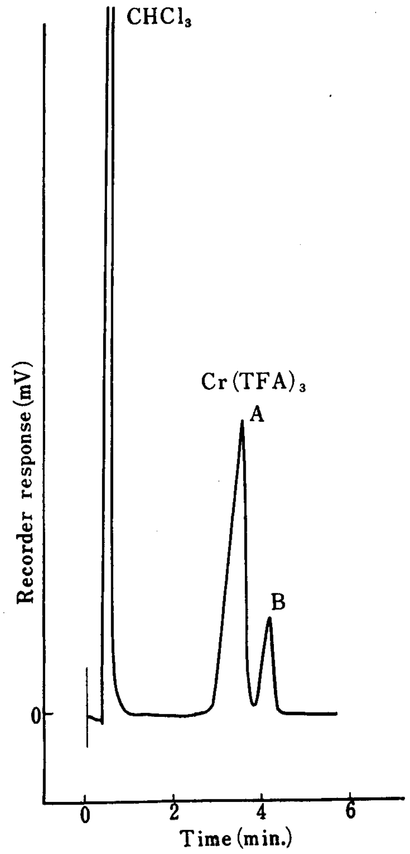

Fig. 5. Separation of *cis* and *trans* isomer of Cr(TFA)$_3$ A. *trans* B. *cis*

1% QF-1 on Chromosorb-W
Column Temp. 130°C
Detector Temp. 200°C
He 60 ml/min.
Range 2 mV 200 mA in CHCl$_3$

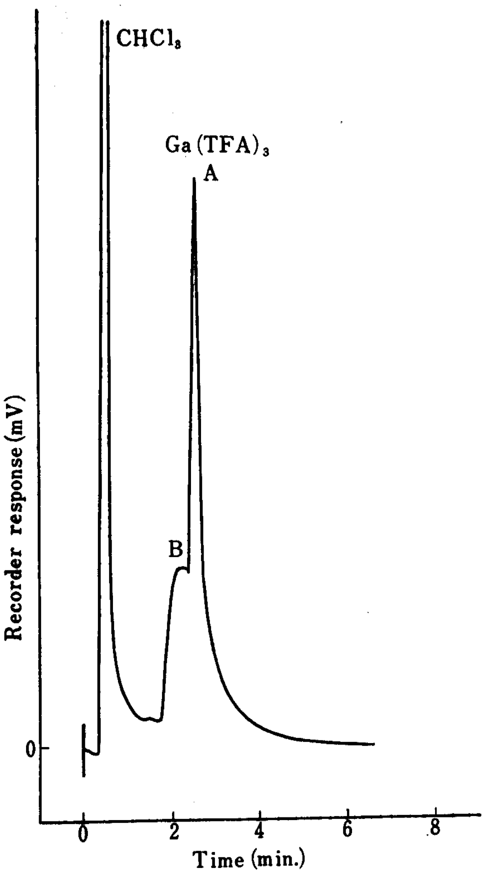

Fig. 6. Separation of *cis* and *trans* isomer of Ga(TFA)$_3$ A. *trans* B. *cis*

1% XE-60 on Chromosorb-W
Comumn Temp. 140°C
Detector Temp. 200°C
He 40 ml/min.
Range 2 mV 200 mA in CHCl$_3$

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