GAS CHROMATOGRAPHY OF METAL CHELATES WITH CARRIER CONTAINING LIGAND VAPOUR

——Co(II)-trifluoroacetylacetonate——

BY

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ABSTRACT

With the conventional gas chromatographic method using helium as a carrier gas, Co (II)-trifluoroacetylacetonate (Co(II)-TFA) was not quantitatively eluted. But, by using trifluoroacetone (H-TFA) vapour as the carrier-gas additive, the gas chromatography of Co(II)-TFA was successful for the case when the column with not only the non-polar liquid and weaker polar liquid phase, but also with stronger polar liquid phase was used. The gas chromatography using carrier gas containing ligand vapour was fundamentally investigated, and it was found that the effectiveness of the additive appeared at above 1 $\mu l/ml$ of the ligand concentration in the gas phase and that the effectiveness of the H-TFA vapour was observed for the column having a stronger polar liquid phase at a high column temperature. It was also found that the separation of Co(II)-TFA and Co(III)-TFA was obtained by using the ligand carrier method.

1. Introduction

It has previously been reported[1),2),3)] that the gas chromatographic elution of thorium (IV)-trifluoroacetylacetonate chelates are remarkably improved by using a carrier gas containing ligand vapour. The present paper extends the same method to the gas chromatography of other metal chelates which are not quantitatively eluted or not consistently successful.

In recent years, the gas chromatography of cobalt β-diketonates has been studied by several groups[4–13)] of workers, but the majority of works on cobalt chelates except for a few studies[5),11),12)] of divalent cobalt chelates has dealt almost exclusively with trivalent cobalt β-diketonates.

In the studies on Co(II) chelates, it was reported that bis(2-thenoyltrifluoro-acetyl-acetonato) cobalt(II)[11)] and bis (pivaloyltrifluoroacetonato)cobalt(II)[12)] have been quantitatively eluted by the conventional gas chromatography, respectively, but bis(acetyl-acetonato)cobalt(II)[5)] has not been eluted and bis(dipivaloylmethanato)cobalt(II)[14)] easily decomposes in air.

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In the present paper, the gas chromatography of bis(trifluoroacetylacetonato)-cobalt (II) has been fundamentally investigated by using a carrier gas containing ligand vapour as a carrier gas additive. From the results of the gas chromatographic study of bis (trifluoroacetylacetonato) cobalt(II), some chracteristics of the stationary phase and the behavior of Co(II) chelate in column have been clearly obtained.

2. Experimental

2-1. Instrumentation

A Yanagimoto Model YANACO G-1800 gas chromatograph equipped with a vapour generator for supplying carrier-gas additive was used as shown in the previous reports[1)2)3]. In the present work, in order to regulate the amount of carrier-gas additive, the vapour generator was jointed to the main stream of the carrier gas with a three-way tap. The amounts of carrier-gas additive could be regulated with a needle valve and a pressure gauge.

A Hitachi-Perkin Elmer model 115 differential thermo-balance was used to obtain the thermalgravimetric curves of the metal chelates. A programmed heating rate(2.5°C/min.) was used with an argon gas atomosphere.

2-2. Reagents

All reagents were of special grade. Trifluoroacetylacetone (1,1,1-trifluoropentane-2,4-dion, H-TFA) was obtained from Nakarai Chemicals Ltd., and was stored in a refrigerator. Hexahydrated cobaltous chloride ($CoCl_2 \cdot 6H_2O$) and cobalt(II) hydroxyl-carbonate (approx. $2CoCO_3 \cdot Co(OH)_2 \cdot nH_2O$) were obtained from the same company.

2-3. Preparation of Chelates

(1) Co(II)-TFA: Bis(1,1,1-trifluoroacetylacetonato) cobalt(II) was prepared by the procedure used for dihydrated bis(acetylacetonato)cobalt(II), reported by J. B. Ellern et al[15].

H-TFA(6.2 g or 4.9 ml) was added slowly to the aqueous solution of sodium hydroxide (1.6 g of NaOH was dissolved in 30 ml of water). This solution was added drop by drop and stirred vigorously in the aqueous solution of cobalt(II) (4.8 g of $CoCl_2 \cdot 6H_2O$ was dissolved in 30 ml of water). The precipitate was filtered with a glass filter and washed with about 100 ml of water. The solid product was purified by recrystallization from hot mixed solvent of ethyl alcohol(40 ml) and chloroform (20 ml). The cobalt(II) chelate obtained was air-dried at room temperature.

The chemical reactions described above are assumed as follows:

$$H\text{-}TFA + NaOH = Na(TFA) + H_2O$$

$$2Na(TFA) + CoCl_2 \cdot 6H_2O = Co(TFA)_2 \cdot 2H_2O + 2NaCl + 4H_2O$$
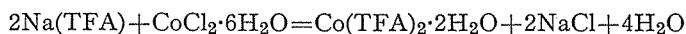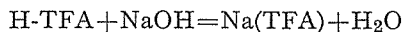
The elemental analysis*) for the purified Co(II)-TFA gave 28.81% of carbon, 3.28% of hydrogen, 27.86% of fluorine and 14.06% of cobalt. Calculated for $Co(C_5H_4F_3O_2)_2 \cdot 2H_2O$; 29.94% of carbon, 3.02% of hydrogen, 28.42% of fluorine and 14.69% of cobalt.

(2) Co(III)-TFA: Bis(1,1,1-trifluoroacetylacetonato)-cobalt(III) was prepared by the procedure used for bis-(acetylacetonato)cobalt(III), reported by B. E. Bryant et al.[16].

The estimated chemical reaction is presented in the following equation

$$2CoCO_3 + 6H\text{-}TFA + H_2O_2 = 2Co(TFA)_3 + 4H_2O + 2CO_2$$
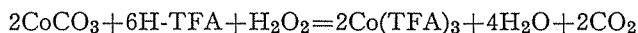
The elemental analysis[*] for the purified Co(III)-TFA gave 34.99% of carbon, 2.16% of hydrogen, 33.24% of fluorine and 11.43% of cobalt.   Calculated, for $Co(C_5H_4F_3O_2)_3$; 34.77% of carbon, 2.33% of hydrogen, 33.00% of fluorine and 11.37% of cobalt.

2-4. Chromatographic Columns

Columns were 100 cm stainless steel tubings with a 3 mm i.d..   The fillers used in this experiments were as follows;
    Column-A: 5% Silicine DC-550 oil/Celite-545-AW-DMCS (60/80 mesh)
    Column-B: 5% Apiezon-L/Celite-545-AW-DMCS (60/80 mesh)
    Column-C: 0.5% Polyethyleneglycol #20000/Celite-545-AW-DMCS (60/80 mesh).

2-5. Conditions for Gas Chromatographic Analysis

Column temperature: 160°C for Column-A and Column-B, and 220°C for Column-C unless specified,
    injection temperature and detector temp.: 220°C,
    flow rate at outlet: 23 ml/min., except for Column-C (37.5 ml/min.),
    cell current of detector: 80 mA,
    recorder sensitivity: 2 mV/20 cm,
    chart speed: 10 mm/min.,
    temperature of vapour generator: 20°C,
    concentration of H-TFA in carrier gas: about 90 μg/ml,
    carrier gas: helium,
    carrier-gas additive: H-TFA vapour.
    These conditions were used for all gas chromatographic analysis, except where noted.

2-6. Procedure of Gas Chromatographic Analysis

Sample solution (2.25 μg/μl as cobalt) was obtained by dissolving 20.1 mg of Co(II)-TFA in the mixed solvent of acetone (250 μl) and carbon tetrachloride (1 ml).   The sample solution was prepared fresh every day and 20 μl of the solution was injected into the gas chromatograph with a microsyringe.

By using the ligand-carrier method in the experiments, the concentrations of H-TFA vapour in the carrier gas were regulated with the needle valve and the heater of the vapour generator.   The amounts of H-TFA additive which was being continuously supplied, were measured by the isothermal desorption method reported by S. J. Gregg and R. Stock[17,18].

The peak area of the chromatograms obtained were measured with a planimeter and were corrected for the gas chromatographic conditions.

3. Results and Discussions

3-1. Thermogravimetric Analysis

Fig. 1 shows the thermalgravimetric curve of Co(II)-TFA obtained with the thermal-balance.   From the figure, it can be seen that the chelate has the thermal properties complicated with dehydration, sublimation and decomposition.   The decrease of the weight at 60°C is thought to be caused by dehydration or by releasing something of organic solvent which is adducted to the chelate.   The dehydration of the chelate is observed at about

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[*] The carbon, hydrogen and fluorine data were obtained from the Elemental Analysis Center of Kyoto University and the cobalt data were obtained from the authors' chelatometric titration.
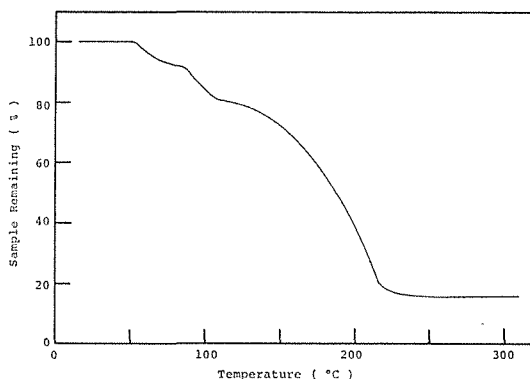
Fig. 1.   Thermalgravimetric curve of Co(II)-TFA

Sample; Co(TFA)$_2\cdot$2H$_2$O, recrystalized from ethyl alcohol, Sample size; 10.0 mg

100°C.   And then, the chelate sublimes at about 140°C, and finally, 15% of the chelate remains at 220°C.

3-2. Gas Chromatography of Co(II)-TFA

From the results of the thermogravimetric analysis, it is assumed that Co(II)-TFA is not quantitatively eluted from chromatographic columns by using helium alone as a carrier gas.   Fig. 2 shows the gas chromatograms of Co(II)-TFA obtained by the conventional method.   The chelate was able to be insufficiently separated from the organic solvents when Column-A and Column-B were used.   When using Column-C, the elution of the chelate was almost not seen, even at the high column temperature between 200°C and 240°C.

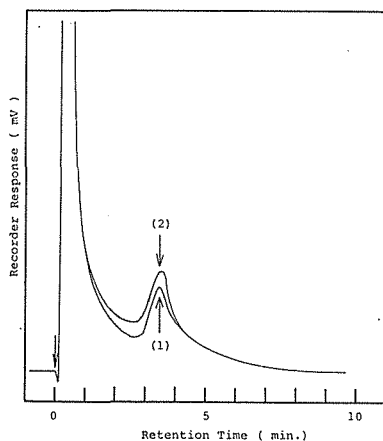The ligand-carrier method was already demonstrated to be extremely effective for

Fig. 2.   Chromatograms of Co(II)-TFA by the conventional method

Sample size; 45 μg Co(II)
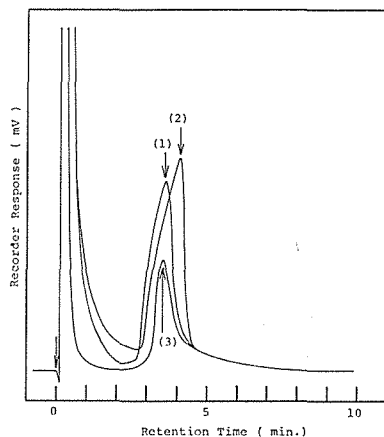
(1) Column-B

(2) Column-A

Fig. 3.   Chromatograms of Co(II)-TFA obtained by using H-TFA vapour
as carrier gas

(1); Column-B,   (2); Column-A,   (3); Column-C
Sample size; 45 μg Co(II)

the quantitative elution of unstable metal complexes[3].   Fig. 3 shows the gas chromato-
grams of Co(II)-TFA obtained by using H-TFA vapour as a carrier-gas additive.   The
chelate was sufficiently separated from the organic solvent and quantitatively eluted, if
Column-C was used.   In the present work, the gas chromatographic conditions of the
ligand-carrier method were fundamentally investigated for Co(II)-TFA.

3-3. Column Temperature

The relationship between the peak area and the column temperature was obtained for
Column-A, -B and -C by using the conventional and the ligand-carrier method.   From the
results shown in Fig. 4, it is clear that Co(II)-TFA chelate is quantitatively eluted by
using the ligand vapour as a carrier-gas additive and the elution of chelate is influenced

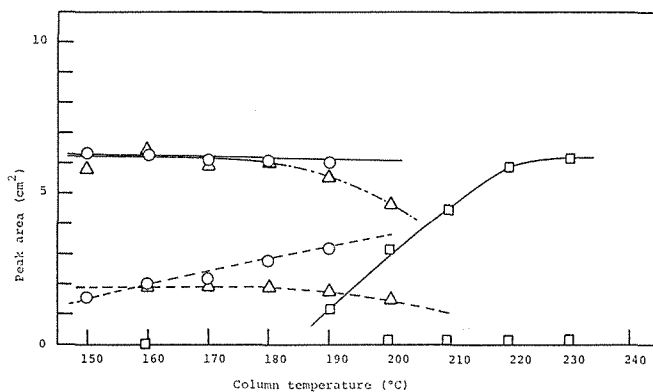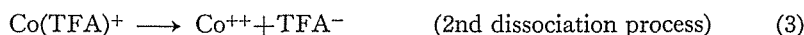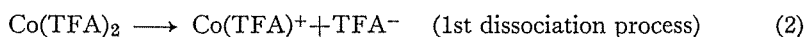Fig. 4.   Relation between column temperature and peak area of Co(II)-TFA
○; Column-A,   △; Column-B,   □; Column-C
Solid line; the present method,
Dashed line; the conventional method

by the column temperature or column properties. The elution is greatly affected by the differences of the polarity of the stationary liquid.
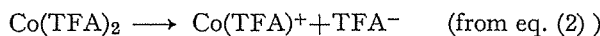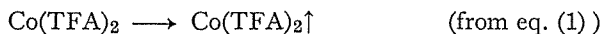
3-4. The Model of the Elution Mechanism

From the facts described above, it seems reasonable to conclude that the model of the elution mechanism of metal chelates in column are as follows. A part of Co(II)-TFA chelate is thermally dissociated in the column. The behaviors of metal chelates in the liquid phase of the column are classified into 3 processes, *i.e.*
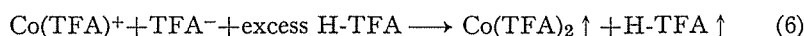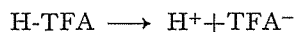
$$Co(TFA)_2 \longrightarrow Co(TFA)_2 \uparrow \qquad \text{(vaporization process)} \qquad (1)$$

$$Co(TFA)_2 \longrightarrow Co(TFA)^+ + TFA^- \quad \text{(1st dissociation process)} \qquad (2)$$

$$Co(TFA)^+ \longrightarrow Co^{++} + TFA^- \qquad \text{(2nd dissociation process)} \qquad (3)$$

The 2nd dissociation process is omitted to shorten the discussion. The stationary liquids (H-R) in the column are thermally dissociated as follows.

$$H\text{-}R \longrightarrow H^{\delta +} - R^{\delta -} \qquad \text{(weaker polar liquid)} \qquad (4)$$

$$H\text{-}R \longrightarrow H^+ + R^- \qquad \text{(stronger polar liquid)} \qquad (5)$$

a) In the non polar liquid phase (Column-B); the following chemical equations are anticipated for the conventional gas chromatography.

$$Co(TFA)_2 \longrightarrow Co(TFA)_2 \uparrow \qquad \text{(from eq. (1))}$$

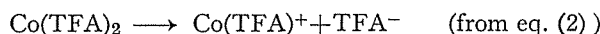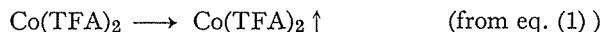$$Co(TFA)_2 \longrightarrow Co(TFA)^+ + TFA^- \qquad \text{(from eq. (2))}$$

From equation (2), it seems that the leading and tailing of the gas chromatographic peaks are made comparatively stronger, because of the time lag of the equilibrium and the incomplete elution of the chelate. In the ligand carrier method, it is supposed that the carrier-gas additive, H-TFA, acts as follows.
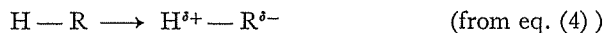
$$H\text{-}TFA \longrightarrow H^+ + TFA^-$$

$$Co(TFA)^+ + TFA^- + \text{excess } H\text{-}TFA \longrightarrow Co(TFA)_2 \uparrow + H\text{-}TFA \uparrow \qquad (6)$$

As a results, $Co(TFA)_2$ chelate peak is considerably improved. The activity of the stationary solid was neglected because of the DCMS (Dimethylchlorosilane) treatment in this model.
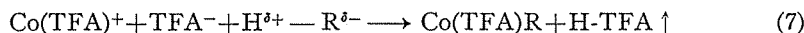
b) In the weaker polar liquid phase (Column-A); the following equation are considered,

$$Co(TFA)_2 \longrightarrow Co(TFA)_2 \uparrow \qquad \text{(from eq. (1))}$$

$$Co(TFA)_2 \longrightarrow Co(TFA)^+ + TFA^- \qquad \text{(from eq. (2))}$$

moreover,

$$H - R \longrightarrow H^{\delta +} - R^{\delta -} \qquad \text{(from eq. (4))}$$

Accordingly,

$$Co(TFA)^+ + TFA^- + H^{\delta +} - R^{\delta -} \longrightarrow Co(TFA)R + H\text{-}TFA \uparrow \qquad (7)$$
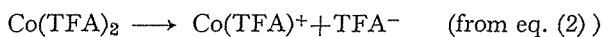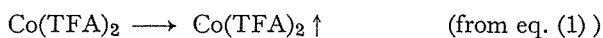
Here, the expression of Co(TFA)R is shown as $Co(TFA)^+$ combined with R^- of the end group of the liquid phase. Therefore, on the conventional method, the tailing or leading

of the chelate appeared and the elution of the chelate is not quantitative. In the ligand-carrier method, the equilibrium of eq. (7) proceeds to right, that is,

$$\text{Co(TFA)R} + \text{excess H-TFA} \longrightarrow \text{Co(TFA)}_2 \uparrow + \text{H} - \text{R} \qquad (8)$$
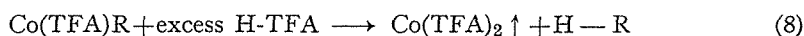
As a result, it is considered that Co(TFA)$_2$ chelate is eluted quantitatively.

c) In the stronger polar liquid (Column-C);

$$\text{Co(TFA)}_2 \longrightarrow \text{Co(TFA)}_2 \uparrow \qquad \text{(from eq. (1))}$$
$$\text{Co(TFA)}_2 \longrightarrow \text{Co(TFA)}^+ + \text{TFA}^- \qquad \text{(from eq. (2))}$$
$$\text{H-R} \longrightarrow \text{H}^+ + \text{R}^- \qquad \text{(from eq. (5))}$$

From the above equations, the following reactions are obtained.

$$\text{TFA}^- + \text{H}^+ \longrightarrow \text{H-TFA} \uparrow \qquad (9)$$
$$\text{Co(TFA)}^+ + \text{R}^- \longrightarrow \text{Co(TFA)R} \qquad (10)$$

It is estimated that Co(II)-TFA chelate is not eluted at the same temperature as Column-A. Similarly, even in the H-TFA ligand-carrier method, it is found that the Co(II)-TFA chelate is not eluted at the conventional temperature, but is eluted when the column temperature increase gradually to over 200°C. It is therefore assumed that H-TFA additive acts as follows,

$$\text{Co(TFA)R} + \text{excess H-TFA} \longrightarrow \text{Co(TFA)}_2 \uparrow + \text{H-R} \qquad (11)$$
$$\text{(at high column temp.)}$$
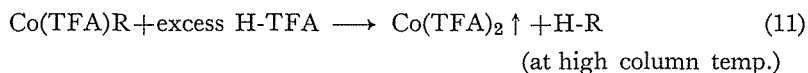
Here, the excess H-TFA can be obtained at the higher column temperature compared to the case of Column-B. Therefore, it is necessary to use the high column temperature when the stronger polar liquid is used as the stationary phase.

From the above, the differences of the column characteristics are expressed as a degree of the polarity of the liquid phase. The mechanisms of the elution of Co(II)-TFA chelate are estimated by the thermal dissociation process model in the column.

3-5. Concentration of H-TFA Vapour in Carrier Gas

The relationships between the peak area and the H-TFA concentration was obtained as shown in Fig. 5. Co(II)-TFA was quantitatively eluted when the H-TFA vapour was carried more than 1 μg/ml into the column. When using Column-B, similar results were obtained as well as Column-A.

In this experiment, the splitting phenomena of the chelate's peak was occasionally observed at a H-TFA concentration lower than 0.7 μg/ml. The Co(II)-TFA peak was split into two; the front peak had a large peak area and a constant retention time, and the rear peak had a small peak area. The retention time of the rear peak increased according to the decrease of H-TFA concentration (see Fig. 6).

Peak splitting was not always observed at a low H-TFA vapour concentration. However, the splitting was more reproducible in the experiments as follows. The high concentration H-TFA vapour (about 90 μg/ml) was carried through the column, and then addition of the H-TFA additive was stopped by using the three-way tap. After about 10 min. or 1 hr. past, the sample solution of Co(II)-TFA was injected.

A remarkably splitted chromatogram of the chelate was obtained as shown. in Fig. 7 by the above procedure. The reason for this phenomena is more complex, because the
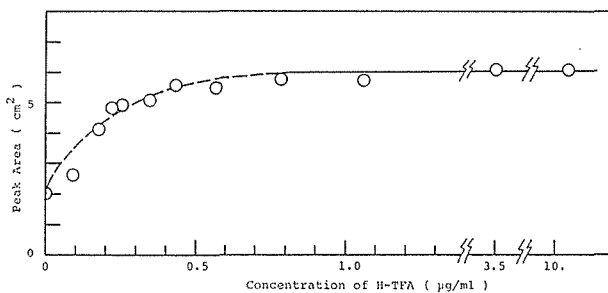
Fig. 5. Relation between concentration of H-TFA additive and peak area
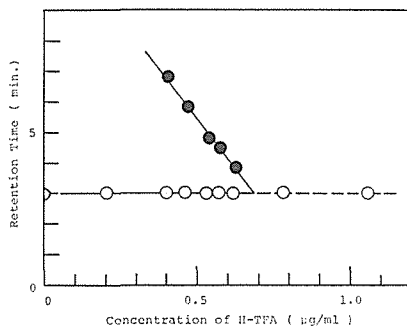of Co(II)-TFA

Column; A

Fig. 6. Retention times of splitted peaks at low concentration of H-TFA additive

○ ; the front peak,   ● ; the rear peak
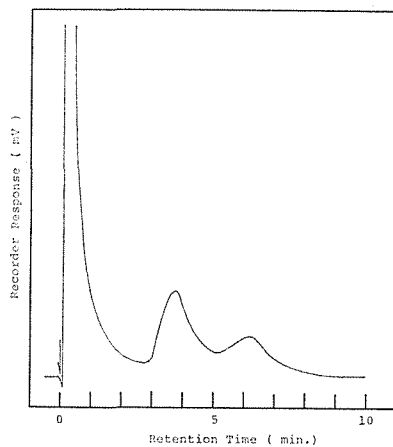Solid lines; splitting region, Column; A

Fig. 7. Chromatograms of Co(II)-TFA at low concentration
of H-TFA additive

Column; A, Injection time; 20 min. after stopping
H-TFA additive, Sample size; 45 μg Co(II)

splitting is not readily reproducible and Co(II)-TFA has the complicated thermal properties described in the previous sections.　It can be said that the solute of the front peak is just the chelate, Co(II)-TFA, because the retention time is the same as the peak obtained at the high concentration of H-TFA vapour.

3-6. Amounts of Co(II)-TFA

Fig. 8 shows the relation between the peak area and the amounts of Co(II)-TFA. From the figure, it can be seen that the quantitative elution of the chelate is obtained by using the ligand-carrier method for Column-A, -B and -C.　In the case of using the conventional method, the chelate is not quantitatively eluted below 10 μg as cobalt metal.　In Fig. 8, the dashed line shows the total area of the two peaks splitted by using helium a as carrier gas after stopping the H-TFA vapour.

3-7. Separation of Co(II)-TFA and Co(III)-TFA

Co(III)-TFA was already reported to be gas chromatographable by the conventional method[6),7),8)].　In the present work, it can be also assumed that Co(III)-TFA is quantitatively eluted by using helium alone as a carrier gas.　However, by using the ligand-carrier method, Co(III)-TFA is quantitatively eluted as shown in Fig. 9.

The mixed solution of Co(III)-TFA and Co(II)-TFA in the mixed solvent of acetone and carbon tetrachloride, was injected to the gas chromatograph equipped with Column-A. Fig. 10 shows the gas chromatograms obtained by using the conventional method and the present method.　From the figure, it is clear that the ligand-carrier method is more effective for the separation of Co(II)-TFA and Co(III)-TFA than the conventional method.
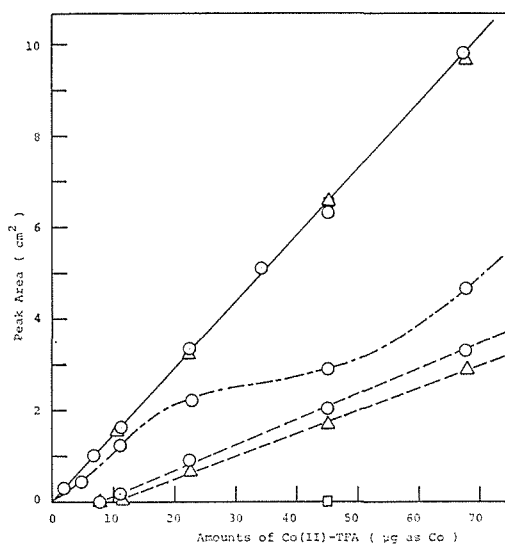
Fig. 8.　Relation between peak area and amounts of Co(II)-TFA

〇; Column-A,　△; Column-B,　□; Column-C,
Solid line; the present method, Dashed line; the conventional method, Pointed line; at low concentration of H-TTFA addition
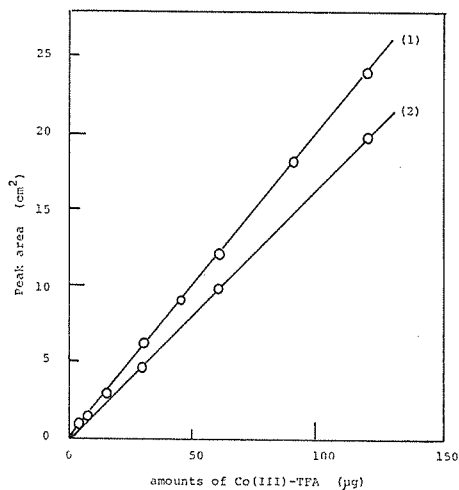
Fig. 9.   Relation between the peak area and the amounts of Co(III)-TFA

Column; A,

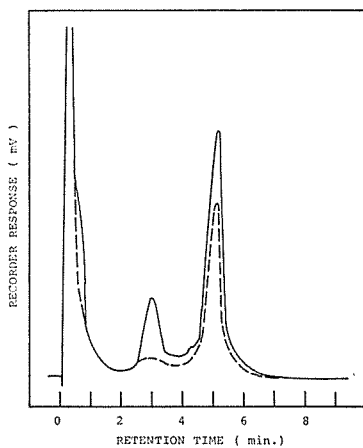(1) the present method,   (2) the conventional method.

Fig. 10.   Separation of Co(II)-TFA and Co(III)-TFA

Column; A, Solid line; the present method, Dashed line; the conventional method, Sample; Co(II)-TFA and Co(III)-TFA (1 : 1 as Co) in acetone-carbon tetrachloride (1 : 4 as volume), Sample size; 20 μl

4.   Conclusion

It was found by the thermogravimetric analysis that $Co(TFA)_2 \cdot 2H_2O$ is thermaly unstable, but 85% of the chelate is sublimed at 220°C.   In the conventional method, Co-(II)-TFA is eluted from Column-A (5% DC-550) and Column-B (5% Apiezon-L) at about 160°C, but the elution is not quantitative.

In the present paper, the gas chromotography using H-TFA vapour as carrier-gas additive was fundamentally investigated.   It was found that (a) Co(II)-TFA is quanti-

tatively eluted if the stronger polar liquid such as polyethylene glycol #20000 was used for the stationary phase in the column (Column-C), (b) The elution of Co(II)-TFA chelate is remarkably affected by the polarity of the stationary phase, (c) A high column temperature is necessary for the stronger polar liquid phase, (d) The concentration of H-TFA additive in the gas phase has to be above $1~\mu g/ml$ for the quantitative elution of Co(II)-TFA ($45~\mu g$ as cobalt), and (e) The splitting phenomena of the chelate's peak is observed when the concentration of H-TFA is below $0.7~\mu g/ml$. From the above results, it can be concluded that the H-TFA acts as suppressor against the decomposition of Co(II)-TFA.

In this study, the trifluoroacetylacetonate of divalent cobalt has come to be gas chromatographable by the present method. Furthermore, it was found that the gas chromatographic separation of Co(II)-TFA and Co(III)-TFA was obtained by using the present method.

ACKNOWLEDGEMENT

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