

Conversion of Cobalt(II) and Nickel(II) Fixed on the Ion Exchange Resin into Their Trifluoroacetylacetonates and Gas Chromatography of the Chelates

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The conversion of cobalt(II) and nickel(II) ions collected on the ion exchange resin into the chelate compounds with trifluoroacetylacetone (Htfa) has been studied in various solvents. In the presence of pyridine, cobalt and nickel ions were quantitatively extracted from the resin into organic phase in the form of the base adducts $[\text{Co}(\text{tfa})_2(\text{py})_2]$ and $[\text{Ni}(\text{tfa})_2(\text{py})_2]$, respectively. The thermogravimetric and gas chromatographic behaviors of these compounds have been investigated. A gas chromatographic separation of $[\text{Ni}(\text{tfa})_2]$ from $[\text{Co}(\text{tfa})_2]$ was successfully performed.

The gas chromatography of metal chelates, particularly those with ligands of the β -diketone type, has been noted and reviewed.^{1,2)} The application of the gas chromatography to inorganic analysis has been limited by the problems involved in the quantitative conversion of metal ions in aqueous solution into the suitable metal chelates with adequate volatility and thermal stability for elution from gas chromatographic column.³⁾ The application of gas chromatography to divalent transition metal ions in the form of β -diketonates has proved particularly difficult, since the dihydrates of the bis chelates are hardly volatile.⁴⁾ Attempts have been made to separate cobalt(II) and nickel(II) ions as their 2-thenoyltrifluoroacetates by gas chromatography,^{5,6)} and it was reported that the peak shapes of the chelates could be improved when the chelates were injected as the corresponding adducts with diethylamine.⁶⁾

We have reported that iron(III),⁷⁾ copper(II),⁸⁾ nickel(II),⁹⁾ and cobalt(II)¹⁰⁾ ions fixed on the ion exchange resins were quantitatively extracted with acetylacetone or 2-thenoyltrifluoroacetone into organic medium by the aid of a small amount of pyridine or pyridine-water mixture.

It is worthwhile to examine the utility of the synergistic extraction of metal ions previously fixed on the ion exchange resin in the preparation of the chelate compounds suitable for gas chromatography. In this work, the synergistic extraction of cobalt(II) and nickel(II) with trifluoroacetylacetone in the presence of pyridine is studied and the gas chromatographic behavior of the resulting chelates is discussed.

Experimental

Apparatus. A Hitachi 508 atomic absorption spectrometer was used for the cobalt and nickel absorption measurements at 240.7 and 231.4 nm, respectively, in air-acetylene flame. The thermogravimetric data were obtained using a Shimadzu TG-20 thermogravimetric analyzer with ca. 5 mg of sample. The heating rate was programmed at 5°C min^{-1} and helium was passed through the sample chamber at a flow rate of $30\text{ cm}^3\text{ min}^{-1}$. A Hitachi 063 gas chromatograph equipped with a thermal conductivity detector was used.

Reagents. Trifluoroacetylacetone (1,1,1-trifluoropentane-2,4-dione, Wako Pure Chemicals Co.) was distilled and used. Pyridine and all other reagents used were of the

guaranteed reagent grade.

Extraction of Metal Ions from the Resin with Htfa. The resin used was a sulfonate cation exchanger, Amberlyst 15, with a macroreticular structure. The Co(II)- and Ni(II)-form resins were prepared according to the method reported previously.^{9,10)} It was found that 3.43 meq of cobalt and 3.31 meq of nickel ions were adsorbed on 1.00 g of the airdried Co(II)- and Ni(II)-form resins, respectively. A 5-cm^3 portion of 0.1 mol l^{-1} Htfa in organic medium was poured onto the 25 mg of airdried Co(II)- or Ni(II)-form resin in an eggplant type flask and a small amount of pyridine was added. The mixture was shaken at a room temperature for 20 min for cobalt and 10 min for nickel. The resin was separated by filtration and washed with ethanol and then water. The cobalt or nickel ion remaining on the resin was eluted by 2 mol l^{-1} hydrochloric acid and determined by atomic absorption spectrometry.

Preparation of Chelates. A 100-cm^3 portion of 0.5 mol l^{-1} Htfa in benzene was poured onto 4 g of the air-dried Co(II)- or Ni(II)-form resin in an eggplant type flask and 8 cm^3 of pyridine was added. The mixture was shaken for 1 h at a room temperature. After filtration, the filtrate was gently warmed and the solvent was removed with a stream of nitrogen gas. The residue was dissolved in benzene or ethanol and the adduct $[\text{Co}(\text{tfa})_2(\text{py})_2]$ or $[\text{Ni}(\text{tfa})_2(\text{py})_2]$ was recrystallized from the solution. The results of elemental analysis were: Found: C, 45.50; H, 3.86; N, 5.21; Co, 11.23%. Calcd for $[\text{Co}(\text{tfa})_2(\text{py})_2]$: C, 45.91; H, 3.47; N, 5.35; Co, 11.26%. Found: C, 45.62; H, 3.58; N, 5.58; Ni, 11.15%. Calcd for $[\text{Ni}(\text{tfa})_2(\text{py})_2]$: C, 45.92; H, 3.47; N, 5.36; Ni, 11.22%.

Results and Discussion

Extraction of Nickel(II) and Cobalt(II) from the Resin with Htfa. The removal of nickel and cobalt ions from the resin with Htfa into the organic solvent was successfully carried out in the presence of a small amount of pyridine, as shown in Figs. 1 and 2. Upon the addition of pyridine blue or dark orange color was immediately developed in the organic phase, indicating the formation of the base adduct, $[\text{Ni}(\text{tfa})_2(\text{py})_2]$ or $[\text{Co}(\text{tfa})_2(\text{py})_2]$.

Nickel(II) ions on the resin were quantitatively extracted into Htfa-carbon tetrachloride and Htfa-benzene solution in the presence of pyridine in 1—6 and 1—4% (v/v), respectively. Cobalt(II) ions were also quantitatively extracted into Htfa-carbon tetrachloride, Htfa-benzene, and Htfa-cyclohexane solu-

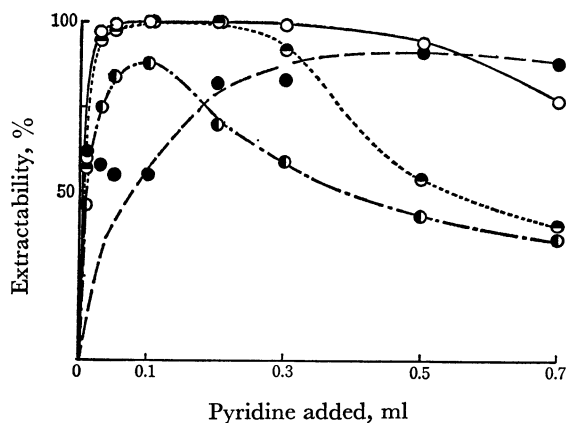


Fig. 1. Effect of pyridine on the extractability of Ni(II) ions from the resin with 0.1 mol l^{-1} Htfa in various solvents.
○: Carbon tetrachloride, ◐: benzene, ◑: chloroform, ●: cyclohexane.

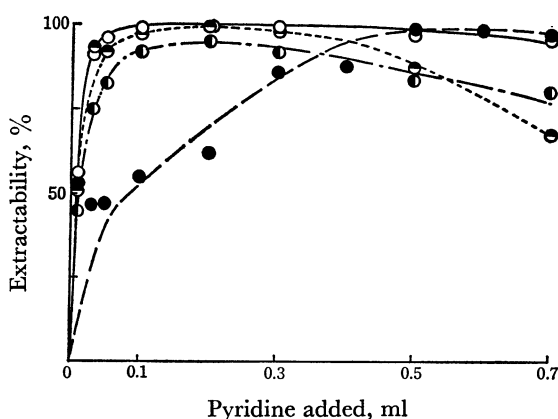


Fig. 2. Effect of pyridine on the extractability of Co(II) ions from the resin with 0.1 mol l^{-1} Htfa in various solvents. Keys to the symbols are similar to those in Fig. 1.

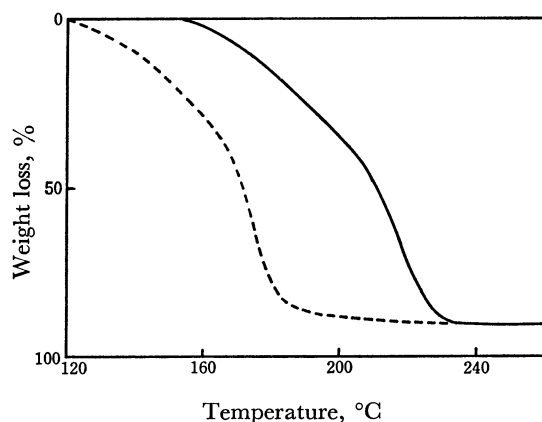


Fig. 3. Thermogravimetric analysis of $[\text{Co}(\text{tfa})_2(\text{py})_2]$ (----) and $[\text{Ni}(\text{tfa})_2(\text{py})_2]$ (—).

tion in the presence of pyridine in 2—6, 2—4 and 10—14% (v/v), respectively.

Thermogravimetric Analysis. Thermogravimetric behavior of the chelates is shown in Fig. 3. A considerable volatility difference between the chelates was

observed, while both chelates were not completely volatile. Some black residue was left in the sample pan after each run. The loose weight loss observed at the beginning of thermograms is attributed to the thermal dissociation of pyridine from the adduct. For comparison with the gas chromatographic behavior, the thermograms were obtained under the conditions in which the chelates were sublimated through a small amount of the column packing, *i.e.* 10% SE-30 or 5% Apiezon L on Chromosorb WAW was placed on the chelate in the sample pan. No remarkable differences were found with and without the column packing.

Thermal Dissociation of Pyridine from the Adducts.

The thermal dissociation of pyridine from the adducts was investigated by gas chromatography as follows. A 25-cm glass column packed with 30% PEG 4000 on Celite 545 was used. The column temperature was held at 75°C and injection port temperature was varied from 100 to 300°C . An appropriate dead space was placed between the packing and injection port to avoid the thermal decomposition of the packing. The sample solution containing 33.8 mg of $[\text{Co}(\text{tfa})_2(\text{py})_2]$ or 42.1 mg of $[\text{Ni}(\text{tfa})_2(\text{py})_2]$ in 1.5 cm^3 of benzene was prepared and a $10\text{-}\mu\text{l}$ portion of ethylbenzene was added. Sample size injected was $2 \mu\text{l}$ for cobalt and $4 \mu\text{l}$ for nickel, respectively. The relationship between the injection port temperature and the amount of dissociated pyridine was examined with ethylbenzene as the internal standard. As shown in Fig. 4, the peak height ratio of

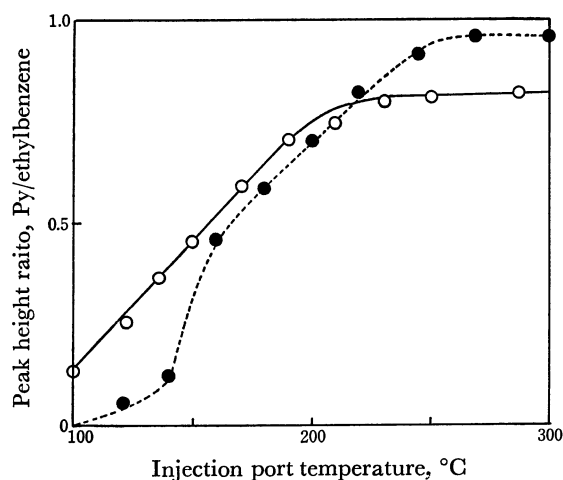


Fig. 4. Thermal dissociation of pyridine from the adduct.
○: $[\text{Co}(\text{tfa})_2(\text{py})_2]$, ●: $[\text{Ni}(\text{tfa})_2(\text{py})_2]$.

pyridine to ethylbenzene became constant above the injection port temperature around 230 and 270°C for cobalt and nickel chelates, respectively. It is safely assumed that under the appropriate gas chromatographic conditions the liberation of pyridine takes place immediately after the sample injection, and hence, cobalt and nickel are eluted from the column in the form of $[\text{Co}(\text{tfa})_2]$ and $[\text{Ni}(\text{tfa})_2]$, respectively.

Choice of Column Packing. The following experiment was carried out to select the column packing suitable to elute the chelates. A J-shaped glass tube, the round part of which was packed with column packing, was affixed to injection port in the column oven.

The linear part of the tube stuck through a hole out of the wall of the oven, so that it was cooled to a room temperature resulting in the deposition of the metal complex at the inner wall of glass tube. The injection port temperature and column temperature were held at 210 and 230 °C, respectively. A benzene solution containing a known amount of the chelate was injected successively. Then the chelate condensed at the inner wall of the protruding section of tube was washed with methyl isobutyl ketone into a volumetric flask and the metal ion content was determined by atomic absorption spectrometry and compared with the injected amount. Among the several stationary liquids examined, the best result was obtained with silicone SE-30. With the use of 5% SE-30 on silanised Chromosorb W (80–100 mesh), 80, 84, and 86% of the injected amount of the cobalt chelate were found to be eluted from the glass tube, the packed length of which was 26, 10.5, and 4.5 cm, respectively. For nickel chelate 77% of the injected amount were found to be in the effluent from a 28 cm packed tube. On the other hand, no detectable amount of the chelate was found in the effluent from the tube packed with Apiezon L. This fact clearly indicates that the recovery does not depend on the packing length, but seriously depends on the packing material. No evidence of the thermal decomposition of the chelate at the injection port was found. It is supposed that the loss of the chelate is mainly due to the adsorption of chelate on the column packing adjacent to the injection port.¹¹⁾

Gas Chromatography. A glass column (25 cm long and 4 mm i.d.) packed with 10% SE-30 on Chromosorb WAW (60–80 mesh) was used. Gas chromatographic conditions were as follows. For $[\text{Co}(\text{tfa})_2(\text{py})_2]$, column temperature, 170 °C; injection port temperature, 210

°C; detector temperature, 200 °C. For $[\text{Ni}(\text{tfa})_2(\text{py})_2]$, column temperature, 230 °C; injection port temperature 260 °C; detector temperature, 240 °C. Detector current, 115 mA; helium flow rate, 25 cm³ min⁻¹. The typical chromatograms are shown in Fig. 5. Sample quantities are 32 µg $[\text{Co}(\text{tfa})_2(\text{py})_2]$ and 113.4 µg $[\text{Ni}(\text{tfa})_2(\text{py})_2]$ in benzene. In the case of cobalt, a good separation of

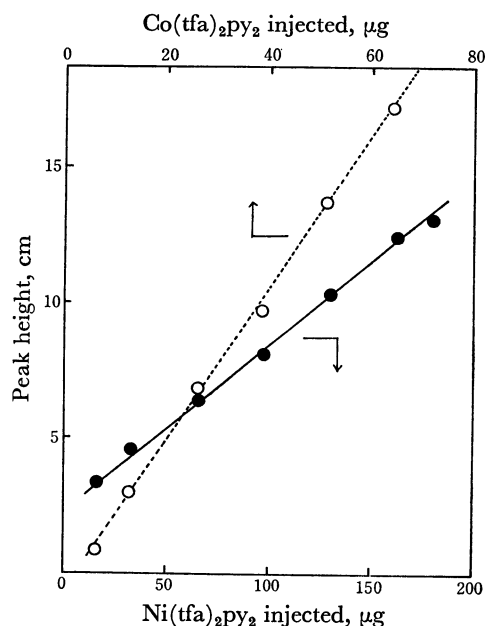


Fig. 6. Plot of the chelate peak height against the sample amount injected. ○: $[\text{Co}(\text{tfa})_2(\text{py})_2]$, ●: $[\text{Ni}(\text{tfa})_2(\text{py})_2]$.

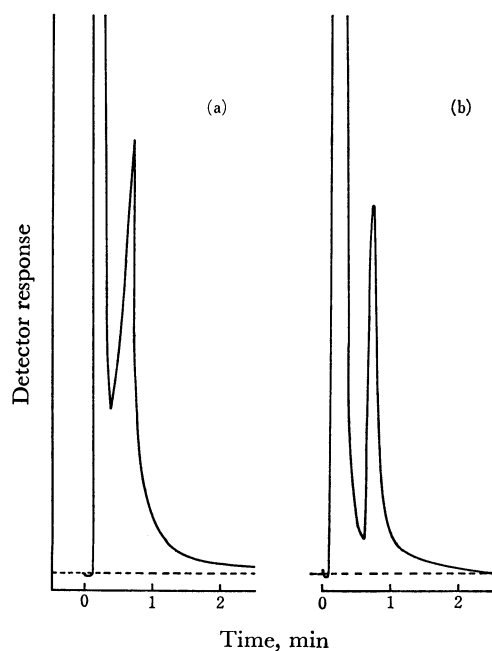


Fig. 5. Chromatograms of (a) $[\text{Ni}(\text{tfa})_2]$ and (b) $[\text{Co}(\text{tfa})_2]$. Column: 25 cm long \times 4 mm i.d., borosilicate glass, filled with 10% SE-30 on 60–80 mesh Chromosorb WAW.

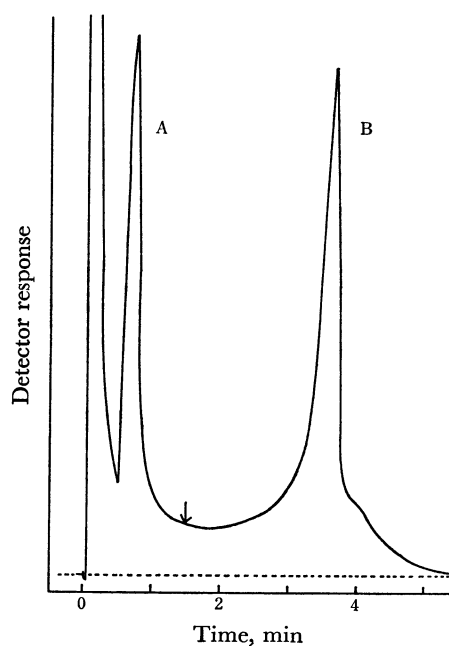


Fig. 7. Separation of $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ trifluoroacetylacetonates by the programmed temperature method. Column: 25 cm long \times 4 mm i.d., borosilicate glass, filled with 2% SE-30 on 80–100 mesh Chromosorb WHP. Temperature was programmed at the point indicated by an arrow from 165 to 230 °C at 20 °C min⁻¹. (A) $[\text{Co}(\text{tfa})_2]$, (B) $[\text{Ni}(\text{tfa})_2]$.

the chelate from the solvent was obtained. On the other hand, an isothermal separation of nickel chelate from the solvent was unsuccessful under the condition employed. The column temperature was too low for the chelate and too high for the solvent to give symmetrical peak shapes. The increase in the peak height with sample size was found to be linear as shown in Fig. 6.

Separation of Nickel(II) and Cobalt(II) Trifluoroacetylacetonates. The programmed temperature method was examined to separate these compounds. A 25-cm glass column packed with 2% SE-30 on Chromosorb WHP (80—100 mesh) was used. The temperatures of injection port and detector were held at 250 °C and 210 °C, respectively. The detector current was 125 mA and helium flow rate was 45 cm³ min⁻¹ at 165 °C. A mixture of 98.4 µg of [Co(tfa)₂(py)₂] and 205.0 µg of [Ni(tfa)₂(py)₂] in benzene was injected. The column temperature was held at 165 °C until the cobalt chelate was eluted, then programmed to 230 °C at 20 °C min⁻¹. A fair separation of cobalt and nickel trifluoroacetylacetonates was observed as shown in Fig. 7. A small shoulder was found for nickel chelate. An attempt was also made to separate these compounds in the extract from the resin. The column temperature was held at 110 °C until the solvent and the excess reagents were eluted, then programmed to 230 °C at 10 °C min⁻¹. A fairly good separation was attained, which indicates

that the synergistic extraction of nickel(II) and cobalt(II) ions from the ion exchange resin onto which the metal ions are previously collected from the aqueous solution is effective in the preparation of metal chelates to be separated by gas chromatography.

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