

NEW GAS CHROMATOGRAPH WITH CARRIER CONTAINING LIGAND VAPOUR

—The Instrumentation and the Fundamental Characteristics—

BY

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ABSTRACT

By using the carrier gas containing ligand vapour, it was found that the metal chelates are quantitatively eluted. Accordingly, the ligand vapour generator was devised for the gas chromatography of metal chelate compounds and its instrumentation and the fundamental characteristics were clarified.

1. Introduction

In the previous papers¹⁾²⁾³⁾, it was reported that the metal chelates can be eluted quantitatively by using a carrier gas containing ligand vapour in gas chromatography. Since there have been some discussions about this problem, we will clarify the details of the apparatus used for the experiments and its fundamental characteristics in this paper.

The ligand vapour generator which is used to add a definite amount of ligand vapour to the helium carrier by passing through the vessel containing ligand solution was manufactured. The carrier gas containing ligand vapour which is prepared by this generator was used for the gas chromatography of metal chelates instead of the original carrier gas. The ligand vapour in carrier gas was continuously supplied into the column and distributed to the gas and liquid phase at a uniform ratio.

2. Experimental

2-1. Gas Chromatograph

A Yanaco Model G-1800 equipped with a GCG-252 recorder (Yanagimoto Co., Ltd.) was used.

2-2. Gas Chromatographic Column

Columns were prepared from 3 mm i.d. \times 100 cm long stainless steel tubing and the column support was 60–80 mesh Gas Chrom-CLH-AW-DCMS. For the stationary liquid

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phase, 5% Silicone DC-550 oil was used, and 5% Apiezon L and 0.5% Polyethylene glycol (PEG) #20000 were used for comparative investigations.

2-3. Gas Chromatographic Conditions

For the most experiments, the column oven was maintained at a temperature of 160°C. The injection port and the detector block was maintained at a temperature of 220°C. The filament current of the thermal conductivity cell was 80 mA and the scale of the recorder was set at 2 mV/20 cm. The water bath temperature was maintained at $20 \pm 0.05^\circ\text{C}$.

Under these conditions, it was found that the areas of H-TFA(trifluoro acetylacetone) sample were proportional to the amounts of H-TFA as shown in Fig. 2-b, and this calibration curve was used for the following experiments.

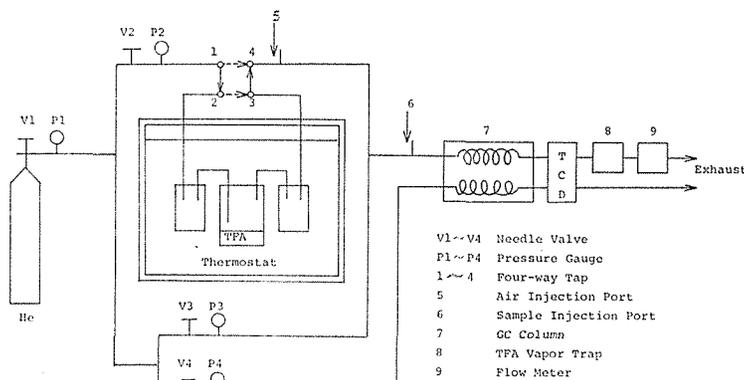


Fig. 1. Outline of apparatus.

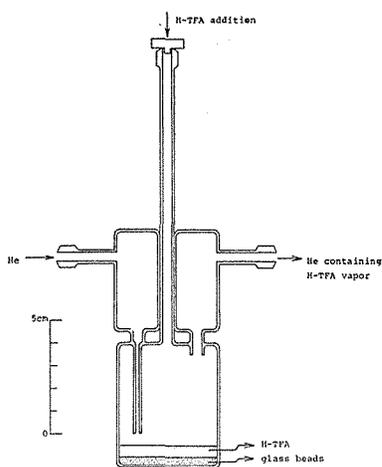


Fig. 2. Ligand vapour generation cell.

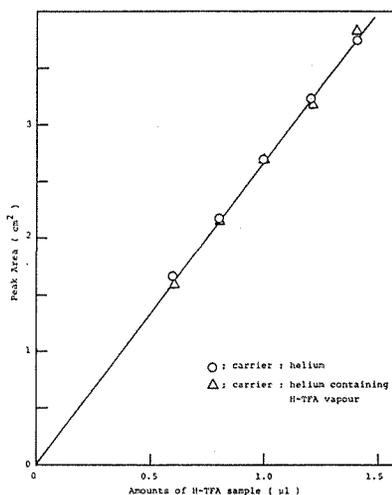


Fig. 2-b Relation between peak area and amounts of H-TFA sample. Column; 5% Silicone DC-550, Flow rate; 33 ml/min.

3. Apparatus

The ligand vapour generator was constructed with two parts; a ligand vapour generation cell and a thermostat(water bath). An outline of the flow circuit from the vapour generator to the gas chromatograph is shown in Fig. 1. The generator was connected to the original flow circuit before the sample injection port and the portion of the gas line from the generator to the injection port was wrapped with asbestos. As shown in Fig. 2, the carrier gas was passed through the ligand vapour generation cell containing ligand reagent in the water bath maintained at a constant temperature. The ligand vapour generation cell which is made with glass was constructed with three units; a chelate reagent reservoir, the mixing unit and the prevention of backward current. The reservoir was filled with approximately 5 ml ligand reagent and about 2 g of 50-80 mesh glass beads. The flow rate of the carrier was regulated with needle valves $V_1 \sim V_4$ and pressure gauges $P_1 \sim P_4$ which were installed in the line just before the generator. In addition, the stainless steel four way stopcock 1~4 was used for changing the flow path of the carrier gas.

4. Results and Discussion

4-1. Relation between the Water Bath Temperature and the Amounts of Generated H-TFA Vapour

The amount of generated H-TFA(trifluoroacetylacetone) vapour was regulated by changing the temperature of the water bath. Then, the amount of generated H-TFA was calculated from the area which is surrounded by the difference of the heights of the base lines of helium carrier and H-TFA additive carrier per unit time.

As shown in Fig. 3, the amounts of generated H-TFA was in proportion to the temperature of the water bath over the range of $10^\circ \sim 25^\circ \text{C}$ and the amount of H-TFA fluctuation in carrier gas was 5% for a 1°C change of water bath temperature.

4-2. Relation between the Amounts of H-TFA Vapour Generated and the Flow Rate of the Carrier Gas

The amounts of H-TFA vapour generated depends on the flow rate of the carrier gas,

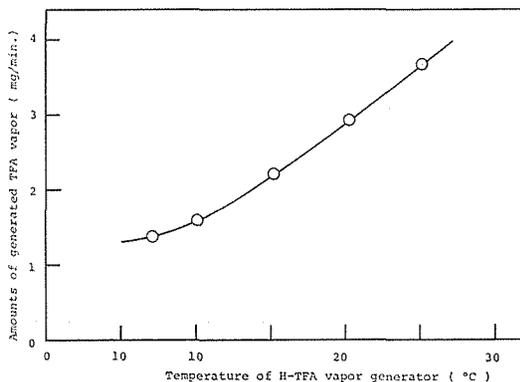


Fig. 3. Relation between thermostat temperature and amounts of generated H-TFA vapour.

Column; 5% Silicone DC-550, Flow rate; 33 ml/min.

because the generator was constructed by utilizing the stream of the helium carrier. As a result, the amount of H-TFA in the carrier gas increases proportionally when the flow rate is above 20 ml/min., but not when it is below 20 ml/min.. The results are shown in Fig. 4. From these results, it was estimated that the decrease in the amounts of H-TFA were caused by the dilution effect which is due to the flow circuit. It was found that the amount of H-TFA in the carrier gas was regulated to $\pm 0.2 \mu\text{g/ml}$ by the flow rate of the carrier.

4-3. Amounts of H-TFA in the liquid phase

The amount of H-TFA in the liquid phase was obtained by using the method of measurements for the surface area⁴⁾⁵⁾. After the base line on the helium carrier settled,

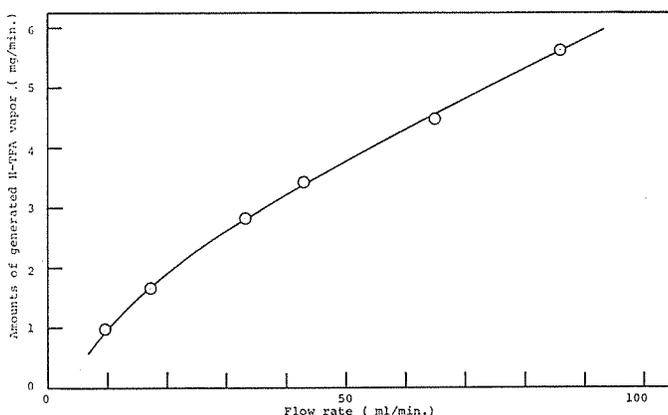


Fig. 4. Relation between flow rate and amounts of generated H-TFA vapour. Column; 5% Silicone DC-550, H-TFA bath; $20 \pm 0.05^\circ\text{C}$.

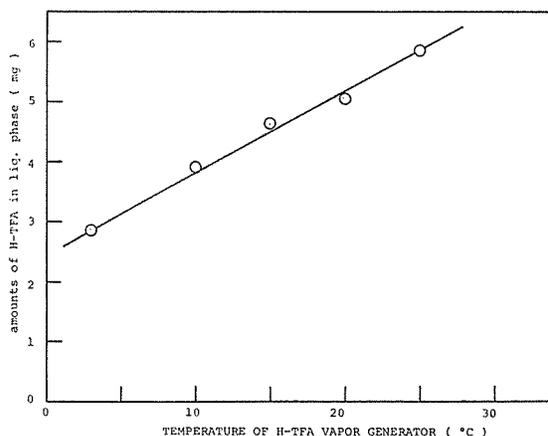


Fig. 5. Relation between temperature of H-TFA vapour generator and saturated amounts of H-TFA in liq. phase at the equilibrium. Column; 5% Silicone DC-550, Column Temp.; 160°C , Flow rate; 43 ml/min.

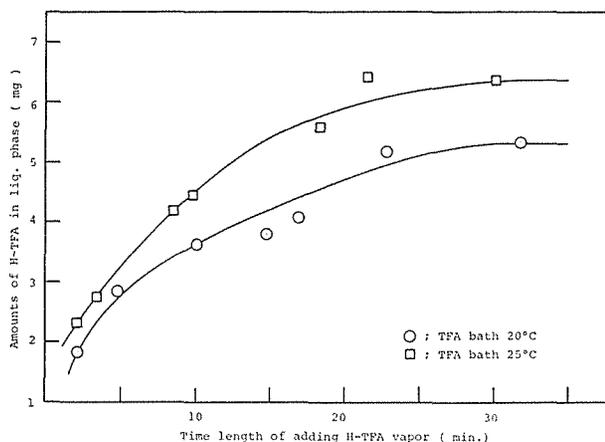


Fig. 6. Relation between time of H-TFA vapour addition and amounts of H-TFA in liq. phase.

Column; 5% Silicone DC-550; Column Temp.; 160°C, Flow rate; 43 ml/min.

H-TFA vapour was added to the carrier gas. When the amount of H-TFA was equilibrated in the column, the addition of H-TFA to the carrier gas was stopped. The amount of H-TFA in the liquid phase can be obtained graphically as the area which is recorded from the time of the end of the H-TFA addition to the time required for the return to the base line. But, the correction of the amount of H-TFA has to be done for the gas phase, because the area is obtained as the total of the amounts of H-TFA in the liquid and gas phases. The results are shown in Fig. 5.

Moreover, the time required for the amounts of H-TFA to be equilibrated in the liquid phase was demonstrated by setting the water bath at the temperature of 20°C and 25°C, respectively. As a result, it was found that the amount of H-TFA in the liquid phase was equilibrated after 30 minutes as shown in Fig. 6. Therefore, a definite amount of H-TFA had to be added for above 30 minutes into the carrier gas in order to keep the amount of H-TFA in the liquid phase.

4-4. Relation between the Amounts of H-TFA in the Liquid Phase and the Amounts of H-TFA in the Gas Phase

From the results mentioned above, it was clear that the relation between the amount of H-TFA in the liquid and gas phases gives straight line when the flow rate of the carrier gas is fixed. Accordingly, it was found that any amount of H-TFA in the liquid phase can be controlled by changing the temperature of the water bath and the flow rate of the carrier gas.

4-5. Gas-Liquid Partition of H-TFA Vapour on the Various Stationary Phases

It has been shown empirically that stationary liquids such as non-polarized Apiezon L and weaker polarized Silicone DC-550 are suitable for the elution of metal chelates. But the elution characteristics of metal chelates very remarkably according to the kind of stationary liquid. In view of the above facts, it appeared of interest to investigate the effects of stationary phases on H-TFA vapour. Accordingly, the gas-liquid partition coefficient

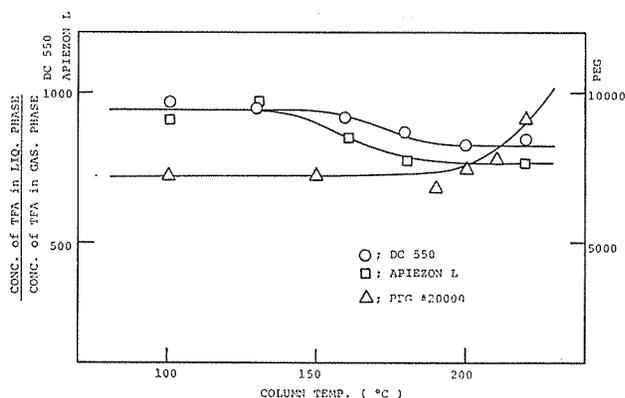


Fig. 7. Relation between column temperature and the partition coefficient of H-TFA.

of H-TFA was obtained at various temperature by using three stationary liquids, that is Apiezon L, Silicone DC-500 and PEG #20000. From Fig. 7, it can be seen that the values of the partition coefficients, k , of H-TFA on Apiezon L and Silicone DC-500 did not vary significantly under the column temperature of 130°C but decreased gradually at temperatures above 130°C. In the case of PEG #20000, the values of k , were constant under 200°C but increased rapidly at temperatures above 200°C. In other words, it seemed reasonable to assume that the gas-liquid partition properties of the H-TFA in stationary liquids expresses the degree of solubility of H-TFA vapour in the stationary liquid at higher temperature.

5. Conclusion

The ligand vapour generator was devised for the gas chromatography of metal chelate compounds. In this apparatus, the amounts of H-TFA in the carrier gas were precisely regulated to within $\pm 0.2 \mu\text{g}$ per 1 ml of carrier gas by the flow rate of the carrier gas and the temperature of the water bath.

The behavior of H-TFA vapour in stationary liquids was fundamentally investigated and clarified. In addition, it was found that the concentration of H-TFA in PEG #20000 having stronger polarity are very high compared with those in stationary liquids such as Silicone DC-500 and Apiezon L having weaker polarity.

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