August, 1971] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2147—2149 (1971) 2147

The Separation and Concentration of Acetylacetonato Chelates Using a Benzene Column

Kazuo Maruyama and Micho Mashima
Faculty of Engineering, Niigata University, Nagaoka

(Received February 4, 1971)

This paper is concerned with the application of the zone-melting technique to metal-chelate compounds. An organic solvent which is liquid at room temperature such as benzene, and several acetylacetonato and thenoyltrifluoroacetonato chelates as solutes were prepared. The effective distribution-coefficient k dependence on the molecular weight was revealed by the normal freezing technique. In the deployment process, the acetylacetonato chelates of Fe and Th were chosen as solutes because their k values were different. The experiment was carried out at 2 cm/hr, the rate of zone travel. When a 30-cm column was used, the "removal percentages" of Fe from Th were 41 and 85% for 3 and 5 zone passes respectively. However there was a 22% loss of Th in the latter case. Furthermore, a remarkable concentration was found, and it was shown that the concentration effect may be useful for micro-analysis. At this stage, a relatively large bubble of benzene was observed at the liquid and solid interface; therefore we can call this "three-phase zone-melting."

The zone-melting technique[1] has recently been adopted for various fields,[2-4] but there have been few reports an its application to metal-chelate compounds.[5-7] In our previous experiment,[8] as a first step of this application, aluminum was succesfully separated from iron with an organic solid solvent after these metals had been converted to complex compounds.

In this paper, as an enlargement of the application, an organic solvent which is liquid at room temperature, such as benzene,[9] was used. Several metal acetylacetonato and thenoyltrifluoroacetonato chelates were prepared as solutes. The effective distribution-coefficient (k) of the chelates was determined and discussed in connection with the variation in the center metal. Then, a deployment chromatogram was obtained by the combination of acetylacetonato chelates of iron and thorium. A remarkable concentration was found when a molten zone traveled downward along the charge of the benzene solution of the chelate; thus, this method seems to be useful for micro-analysis.

Experimental

Materials. The acetylacetone, 2-thenoyltrifluoroacetone, metal salts, and organic solvents such as benzene were all reagent-grade. The metal acetylacetonato chelates, $Fe(AcAc)_3$,[10] $Cr(AcAc)_3$,[11] $Co(AcAc)_3$,[12] $Al(AcAc)_3$,[13] $Th(AcAc)_4$,[14] $Zr(AcAc)_4$,[15] and $Be(AcAc)_2$,[16] and the 2-thenoyltrifluoroacetonato chelates, $Fe(TTA)_3$,[17] $Al(TTA)_3$,[18] and $Co(TTA)_2$,[19] were prepared by the standard procedure and were purified by recrystallization with a suitable solvent.

Apparatus and Procedure. As is shown in Fig. 1A, the zone apparatus used in this experiment consisted of five ring heaters composed of electrified nicrom wire, and a refrigerator to keep the benzene solution in the glass tube solid during the zone-melting. The refrigerator was made of a six-part aluminium box with a circulation of −20°C ethyleneglycohol. The rate of the molten zone could be varied at will, but 2- and 6-cm/hr rates were mainly adopted. The zone width was 0.8—1 cm. All the glass tubes were 5 mm in inner diameter and about 20 cm in length.

A tube for the deployment process was first charged with pure benzene and then frozen to 3 cm by dipping it in −20°C

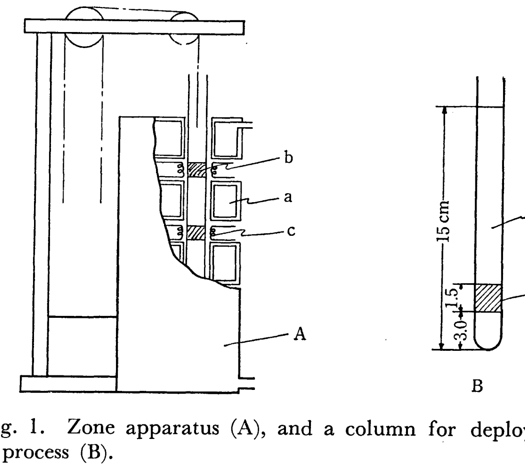

Fig. 1. Zone apparatus (A), and a column for deployment process (B).
a) cooler, b) molten zone, c) heater, d) solvent, e) chelates and solvent.

---

[1] W. G. Pfann, *Trans. AIME*, **194**, 747 (1952).

[2] W. R. Wilcox, *Chem. Rev.*, **64**, 187 (1964).

[3] G. L. Pearson and M. Tanenbaum, *Phys. Rev.*, **90**, 153 (1953).

[4] J. D. Loconti and J. W. Cahill, *J. Polym. Sci., Part A*, **1**, 3163 (1963).

[5] H. Kobayashi and K. Ueno, *Bunseki Kagaku*, **15**, 1181 (1966).

[6] K. Ueno, H. Kaneko, and N. Fujimoto, *Talanta*, **11**, 1371 (1964).

[7] K. Ueno, H. Kaneko, and Y. Watanabe, *Microchem. J.*, **10**, 244 (1964).

[8] M. Mashima and K. Z. Maruyama, This Bulletin, **44**, (1971), in press.

[9] A. G. Anikin and G. M. Dugacheva, *Russ. J. Phys. Chem.*, **36**, 1115 (1962).

[10] J. P. Mckaveny and H. Freiser, *Anal. Chem.*, **29**, 290 (1957).

[11] J. P. Mckaveny and H. Freiser, *ibid.*, **30**, 1965 (1958).

[12] R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 440 (1958).

[13] E. W. Berg and J. T. Truemper, *Anal. Chim. Acta*, **32**, 245 (1965).

[14] R. W. Moshier and R. T. Sivers, "Gas Chromatography of Metal Chelates", Pergamon Press Ltd., Oxford, 1965.

[15] W. B. Brown and J. F. Steinbach, *Anal. Chem.*, **31**, 1805 (1959).

[16] J. A. Adams, E. Booth, and J. D. H. Strickland, *Anal. Chim. Acta*, **6**, 462 (1952).

[17] R. A. Bolomey and L. Wish, *J. Amer. Chem. Soc.*, **72**, 4483 (1950).

[18] H. C. Eshelman and J. A. Dean, *Anal. Chem.*, **31**, 183 (1959).

[19] J. C. Reid and M. Calvin, *J. Amer. Chem. Soc.*, **72**, 2948 (1950).

ethyleneglycohol. The supercooling at the bottom can be defended against by this charging. The tube was then charged with a solution of a metal chelate in benzene on the frozen benzene layer and frozen to 1.5 cm. The remaining 10.5 cm was filled with pure benzene, which was also frozen, as is shown in Fig. 1B. Zone melting was started at the bottom of the tube. The tube for the normal freezing and concentration process was charged with a benzene solution of the chelate; only the tube for the latter purpose was frozen to 15 cm. In the concentration process, the zone was started from the top of the charge and a bubble of benzene was formed by increasing the heater temperature. The effective distribution-coefficient was measured by the normal freezing technique.[27–29]

Analysis. After the zone-melting procedure, the solidified charge was removed from the glass tube and cut into sections, and the metal concentrations in the various fractions were determined photometrically after the separation of the solvent. The analytical methods are summarized in Table 1.

Table 1. Methods of analysis

Zone melted charge → Metal ion solution.
{separated from the solvent
{by treating with 6 N HCl

		Refferences
Th^{4+}	Thorin method	20
Zr^{4+}	Alizarin S method	21
Cr^{3+}	Diphenylcarbazide method	22
Co^{3+}	Nitroso-R salt method	23
Al^{3+}	Oxine method	24
Fe^{3+}	*o*-Phenanthroline method	25
Be^{2+}	Aluminon method	26

Results and Discussion

The effective distribution-coefficient (*k*) may be important in the actual zone-melting procedure,[27–29] and so it is necessary to study the factors governing the *k* value. Seven metal acetylacetonate chelates were, therefore, subjected to normal freezing at the rate of 6 cm/hr, and the concentration of chelate along the charge was determined as the metal concentration. The initial concentration was 1.5%. These *k* values of seven metal acetylacetonato chelates were examined in relation to various characteristics of these chelates.

As a result of this examination, these *k* values, when plotted against the molecular weight as in Fig. 2, were found to reveal a molecular weight dependence and to show the greatest fractionation in the case of $Be(AcAc)_2$. Ideally, the size of the solute molecule is one of the most important factors in determining the *k* value.

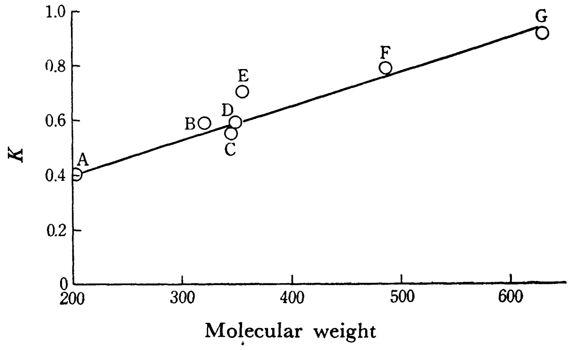

Fig. 2. Dependence of distribution-coefficient, *k* on molecular weight.
A) $Be(AcAc)_2$, B) $Al(AcAc)_3$, C) $Cr(AcAc)_3$,
D) $Fe(AcAc)_3$, E) $Co(AcAc)_3$, F) $Zr(AcAc)_4$,
G) $Th(AcAc)_4$.

From the point of view of mutual separation, a large difference in molecular weight may be desired. Therefore, $Fe(AcAc)_3$ (0.58) and $Th(AcAc)_4$ (0.90) were chosen as the solutes in the deployment process. In order to eliminate Fe from Th, the Fe must be greatly moved; therefore the effects of speed and zone passes on the movement of the Fe chelate were examined. The concentration effects of Fe were increased with a decrease in the zone speed and with an increase in the number of passes. For comparison, the *k* value of $Fe(AcAc)_3$ was 0.91 in benzoic acid, 0.95 in naphthalene, 0.96 in stearic acid, and 1.10 in ectyl alcohol.

Chromatograms after 3 and 5 zone passes using a 15-cm column at 2 cm/hr are shown in Fig. 3, using a mixture of Fe and Th chelates. Both Fe and Th weighed about 13 μg. The sample column was divided into five equal sections. The metal concentration was plotted *versus* a fractions of the charge. Judging from the *k* value, only $Fe(AcAc)_3$ was concentrated at the top of the charge; thus, a great difference in their distribution was observed. If the top section is removed, 39 and 55% of the total Fe may be eliminated from Th by 3 and 5 zone passes respectively.

Figure 4 shows the results in a 30-cm column. The zone speed, metal weight, and number of zone passes

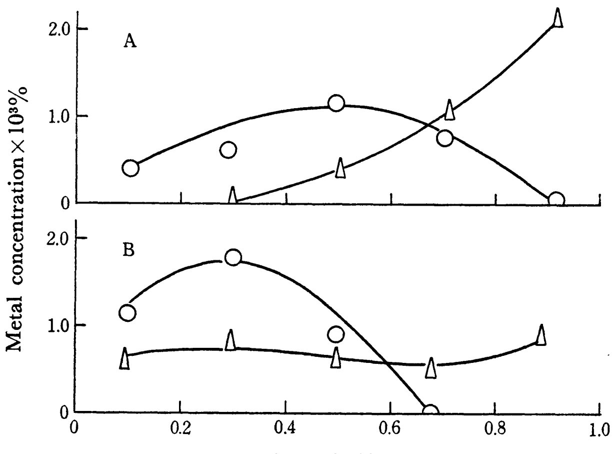

Fig. 3. Distribution of $Fe(AcAc)_3$ and $Th(AcAc)_4$ after 3 (B) and 5 (A) zone passes, using 15 cm-column, Fe; △ Th; ○.

---

20) V. I. Kuznetsov, *Rept. Acad. USSR*, **31**, 895 (1941).
21) D. E. Green, *Anal. Chem.*, **20**, 370 (1948).
22) R. T. Ptlaum and L. C. Howick, *J. Amer. Chem. Soc.*, **78**, 4862 (1956).
23) O. Hoffman, *Ber.* **18**, 46 (1885).
24) T. Dupuis and C. Duval, *Anal. Chim. Acta*, **6**, 394 (1949).
25) J. Hoste, *Anal. Chim. Acta*, **9**, 263 (1953).
26) C. L. Luke and M. E. Campbell, *Anal. Chem.*, **24**, 1056 (1952).
27) R. H. Mcfee, *J. Chem. Phys.*, **15**, 856 (1947).
28) J. A. Burton and W. P. Slichter, *ibid.*, **21**, 1987 (1953).
29) W. G. Pfann, *J. Appl. Phys.*, **35**, 258 (1964).

are the same as in the above experiment. The distribution of the solute in the 30-cm column was similar to that in the 15-cm column. In this case, if the top section is removed, 41% of the Fe may be eliminated by 3 zone passes, while and if the top two sections are removed, 85% of the total Fe may be eliminated by 5 zone passes, with a 22% loss of Th.

When the zone moved toward the bottom along with the uniform charge, a remarkable concentration was observed, as is shown in Fig. 5. With only 3 passes, the solute was fairly well concentrated at the bottom of the column. In this case, 56% of the Fe, 72% of the Co, and 41% of the Th of each metal were concentrated in the 3-cm region at the bottom. At this stage, there was a relatively large bubble of benzene between the liquid and solid phases; therefore, we can call this "three-phase zone-melting." This phenomenon may be attributed to the great difference in the vapor pressure of the chelate and solvent at this temperature.

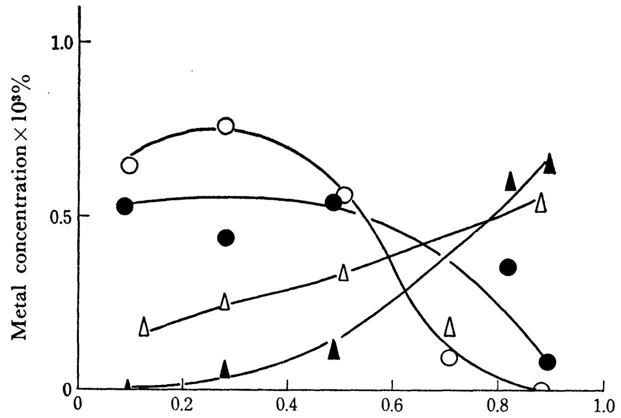

Fig. 4. Distribution of Fe(AcAc)$_3$ and Th(AcAc)$_4$ after 3 and 5 zone passes, using 30 cm-column, and about 13 μg, both of Fe and Th.

Fe; 3 passes △, 5 passes ▲, Th; 3 passes ○, 5 passes ●.

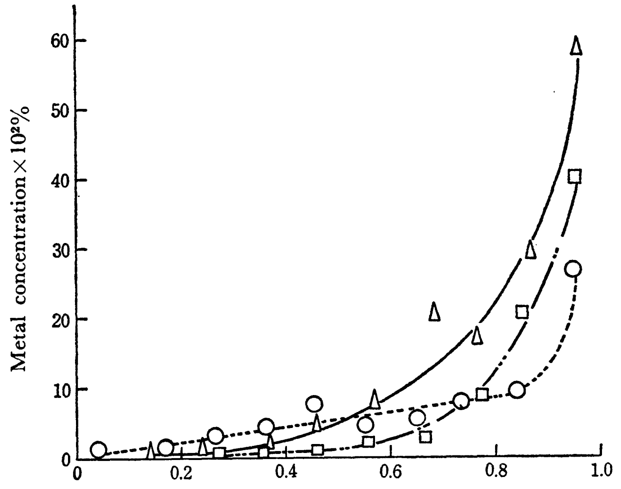

Fig. 5. Distribution of chelates in concentration process, Fe(AcAc)$_3$; △, Co(AcAc)$_3$; □, Th(AcAc)$_4$; ○.

The same experiments were also done quantitatively with thenoyltrifluoroacetonato chelates of Co, Al, and Fe. The distribution after 3 passes at 2 cm/hr is shown in Fig. 6. The relative concentration is there plotted *versus* the fraction solidified. The results reveal that the concentration effect was great in this order: Fe>Al>Co; this corresponds to the decrease in the vaper pressure at this temperature.[13]

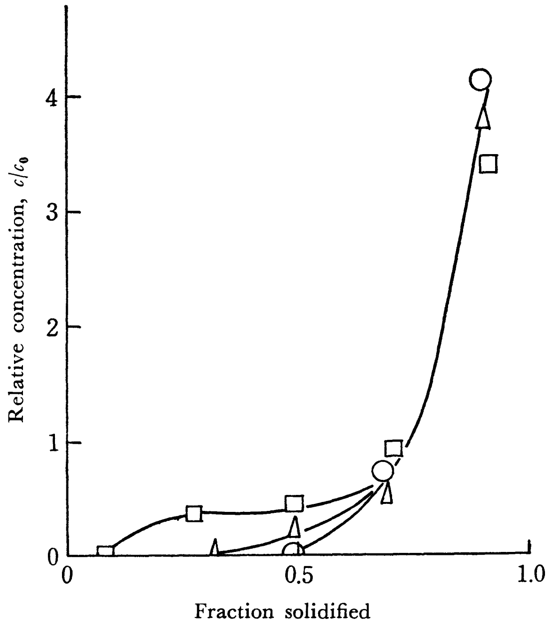

Fig. 6. Quantitative concentration of TTA chelates after 3 zone passes, using 5—6 μg as metal.
Fe(TTA)$_3$; ○, Al(TTA)$_3$; △, Co(TTA)$_2$; □.

Conclusion

As an application of the zone-melting technique for chelate-solvent systems, several metal acetylacetonato chelates in benzene were zone-melted. The molecular-weight dependence of the *k* value was revealed by the normal freezing technique. In the deployment process, the application was proved to be a promising method for the elimination of Fe from Th after they had been converted into metal chelates; the percentages of the removal of Fe were 39 and 55% for 3 and 5 zone passes respectively. When a 30-cm column was used, the percentages were 41 and 85% for 3 and 5 zone passes respectively. In the latter case, there was a 22% loss of Th.

A remarkable concentration was also found, and it was shown that this effect may be useful for microanalysis; 56% of the Fe, 72% of the Co, and 41% of the Th were concentrated in the 3-cm region of the bottom, with only 3 zone passes.

Furthermore, the possibility of the separation of one metal from another will increase when the concentration process is combined with the deployment process.