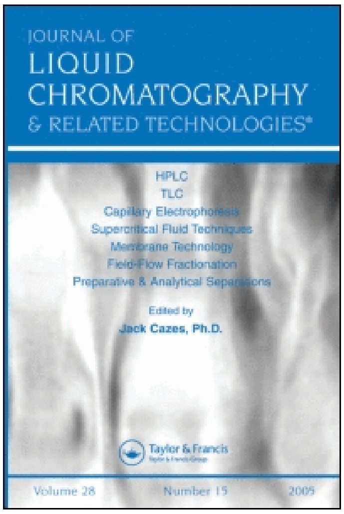

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Analyses of Mercury(II) Halides by Reverse-Phase Ion-Pair Chromatography

Kooji Tajima[a]; Masaaki Nakamura[b]; Shun-Ichi Takagi[b]; Fumiaki Kai[b]; Yutaka Osajima[c]
[a] Kumamoto Municipal, Institute of Public Heath 269, Tamukae, Kumamoto, Japan [b] Department of Chemistry Faculty of Science, Kumamoto University Kurokami, Kumamoto, Japan [c] Department of Food Science and Technology Faculty of Agriculture, Kyushu University Hakozaki, Fukuoka, Japan

To cite this Article Tajima, Kooji , Nakamura, Masaaki , Takagi, Shun-Ichi , Kai, Fumiaki and Osajima, Yutaka(1986) 'Analyses of Mercury(II) Halides by Reverse-Phase Ion-Pair Chromatography', Journal of Liquid Chromatography & Related Technologies, 9: 5, 1021 — 1032

To link to this Article: DOI: 10.1080/01483918608076687

URL: http://dx.doi.org/10.1080/01483918608076687

JOURNAL OF LIQUID CHROMATOGRAPHY, 9(5), 1021-1032 (1986)

ANALYSES OF MERCURY(II) HALIDES BY REVERSE-PHASE ION-PAIR CHROMATOGRAPHY

Kooji Tajima[1], Masaaki Nakamura[2],
Shun-ichi Takagi[2], Fumiaki Kai*[2],
and Yutaka Osajima[3]
[1]Kumamoto Municipal Institute of Public Heath
269, Tainoshima, Tamukae
Kumamoto 862, Japan
[2]Department of Chemistry
Faculty of Science
Kumamoto University
Kurokami, Kumamoto 860, Japan
[3]Department of Food Science and Technology
Faculty of Agriculture
Kyushu University
Hakozaki, Higashi-ku
Fukuoka 812, Japan

ABSTRACT

Utilizing properties of mercury(II) halides to form a complex (HgX_4^{2-}, X = Cl, Br and I) with an excess of halide ions and its charge transfer band appearing in UV range, a method has been established to analyze mercury(II) halides by reverse-phase ion-pair high performance liquid chromatography in the presence of counter ions (tetra-n-butylammonium halides, TBAX). According to this method, the determination limit of mercury content was 2 ng.

The capacity factor, k', of ion-pair, $(TBA^+)_2(HgX_4^{2-})$, is related to hydrophobicity of the halides. The relation

0148-3919/86/0905-1021$3.50/0

of k' to concentrations of three kinds of TBAX is shown as follows.

$$\log k'_{TBAI} = 0.7939 \log[TBA^+] + 2.7566$$

$$\log k'_{TBABr} = 0.5110 \log[TBA^+] + 1.4499$$

$$\log k'_{TBACl} = 0.3449 \log[TBA^+] + 0.8292$$

It was considered that slopes in the above equations were connected with stability constants of HgX_4^{2-}.

INTRODUCTION

The toxicity of mercury in environmental and food samples has been to date evaluated by their total and alkyl mercury contents. Since, on the other hand, the toxicity differs according to the valence and chemical form of mercury, attempts have been made to establish an analytical method capable of identifying its chemical forms.

The previous paper(1) reported that six mercury unbranched alkane thiolates, the stable products from mercury(II) and thiols, were separated by high performance liquid chromatography (HPLC) using reverse-phase column(ODS packing). In this study, a method for analyzing mercury(II) halides in the presence of counter ion by reverse-phase ion-pair high performance liquid chromatography has been developed, utilizing properties of mercury(II) halides to form a type of complex(2-6), HgX_4^{2-}, with a charge transfer band in UV range. The elution behavior of ion-pairs formed has also been investigated by changing the column temperature, the content of organic solvent in the mobile phase and the counter-ion concentration.

EXPERIMENTAL

Apparatus

The liquid chromatograph was a Model TRI ROTAR-V equipped with a Model UVIDEC-100-IV UV monitor(Japan Spectroscopic Co., Tokyo, Japan). The column was 250 x 4.6 mm Finpak SIL C_{18} of 10 μm particle size(Japan Spectroscopic Co.).

The column temperature was controlled by using a column jacket in which water at a given temperature was circulated by a pump through the water bath(a Model TS-13, Tabai MFG. Co., Osaka, Japan) adjusted to the constant temperature.

Reagents

Tetra-n-butylammonium iodide(TBAI), tetra-n-butylammonium bromide(TBABr) and tetra-n-butylammonium chloride(TBACl) were obtained from Eastman Kodak Co.(N.Y., USA); mercury(II) chloride, mercury(II) bromide and acetonitrile from Wako Co. (Osaka, Japan); mercury(II) iodide from Katayama Co.(Osaka, Japan).

Standard solutions of mercury(II) halides were prepared by dissolving mercury(II) salts in the aqueous solution of acetonitrile which was the same as in analysis by HPLC.

RESULTS AND DISCUSSION

With TBACl, TBABr and TBAI as counter-ions, mercury(II) halides, of which the halide ion was the same as the pair-ion to be paired with the counter-ion, were isolated by reverse-phase ion-pair chromatography(IPC). Fig. 1 shows chromatograms of mercury(II) halides. The results indicated the

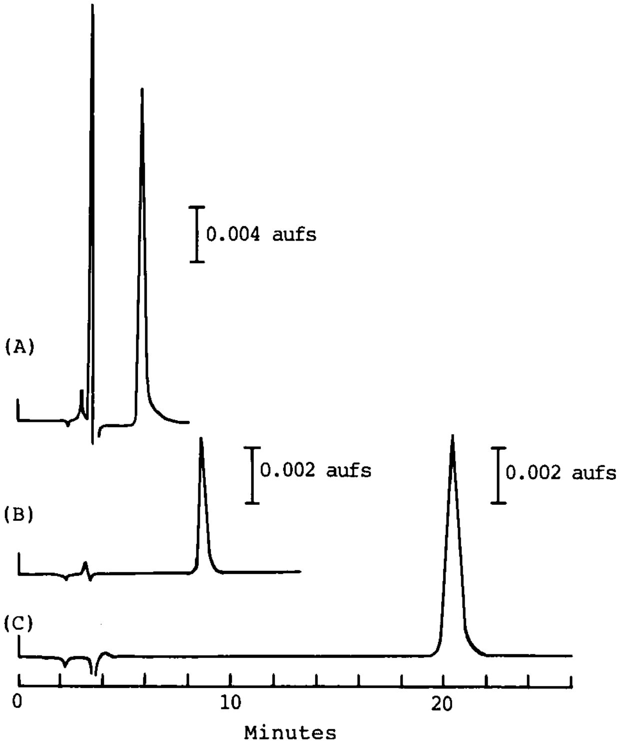

FIGURE 1. Reverse-phase ion-pair chromatograms of mercury(II) halides. Operating conditions were: column, Finpak SIL C_{18}; eluent, 0.01 M TBAX in 60% CH_3CN, (A) X = Cl, (B) X = Br, (C) X = I; flow rate, 1 ml/min; detection wavelength, (A) 232 nm, (B) 250 nm, (C) 270 nm; detector sensitivity, (A) 0.08 aufs, (B) and (C) 0.04 aufs; column temperature, 25°C.
(A) $HgCl_2$, (B) $HgBr_2$, (C) HgI_2.

formation of single compounds from mercury salts and counter-ions. The concentrations of mercury(II) halides applied to HPLC were 2.49 x 10^{-4} mol/dm^3 for $HgCl_2$ and 2.49 x 10^{-5} mol/dm^3 for $HgBr_2$ and HgI_2. Meanwhile, the counter-ion concentration of the eluent was 10^{-4} – 10^{-1} mol/dm^3, and thus an excess amount of halide ion as the pair-ion at a given counter-ion concentration was supplied to the column, considering the dilution of mercury halides in HPLC system —— the volume of mobile-phase in the column was about 2 ml.

Table 1 summarizes stability constants and molar absorptivities of HgX_4^{2-} (X = Cl, Br and I). Since stability constants of all the complexes are fairly large, formation of ion-pairs presumably undergoes the following reaction with an excess of counter-ions:

$$HgX_2 + 2TBAX \rightleftharpoons (TBA)_2HgX_4$$

Fig. 2 shows the relationship between logarithm of capacity factor(k') of the ion-pair and atomic weight of the halogen. Considering that linearity was also found between log k' and electronegativity or ionic radius of the halogen, it appeared that k' of the ion-pair was closely related to characteristics of the halogen in the ion-pair.

TABLE 1 Stability Constants(7) and Molar Absorptivities(8) of HgX_4^{2-}

	HgI_4^{2-}	$HgBr_4^{2-}$	$HgCl_4^{2-}$
log β_4	29.8	22.23	15.3
log ε (λ_{max})	4.51 (269)	4.59 (250)	4.52 (232)

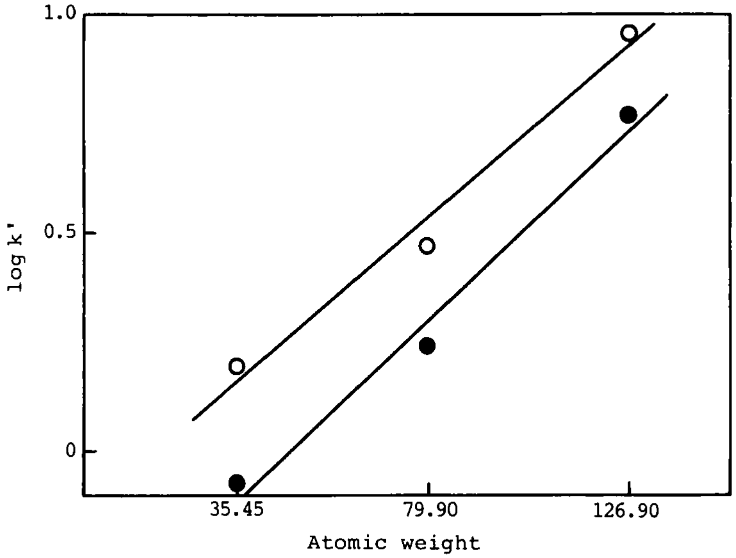

FIGURE 2. Relationship between capacity factor and atomic weight of halides. Operating conditions were: column, Finpak SIL C_{18}; eluent, (o) 0.01 M TBAX(X = Cl, Br, I), (●) 0.0033 M TBAX(X = Cl, Br, I); flow rate, 1 ml/min; column temperature, 25°C.

In this experiment, some of the factors affecting the extraction constant of the ion-pair, such as the organic solvent, its content in the eluent and the column temperature, were all the same, with a nearly constant pH range, 7.6-7.7, of the eluent containing the counter ion. It was estimated, on the other hand, that ionic strengths of the eluents were also the same by nearly complete dissociation of TBAX therein.

It is known, in general, that with carboxylic acids and n-alkanes(9), alkylanthraquinones(10) and mercury alkane thiolates(1), all the homologs for each of them have a linear relationship between the length of alkyl chain and log k' of the homologs, and also that the linearity accounts for

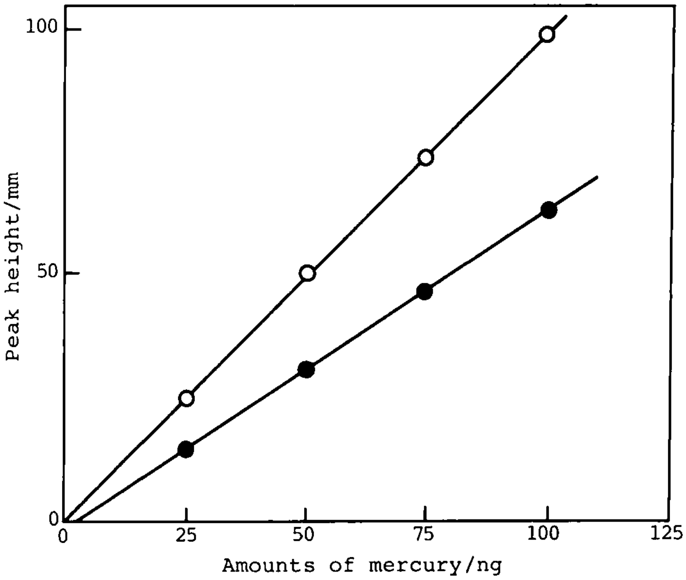

FIGURE 3. Calibration curves of mercury(II) halides by IPC. Operating conditions were: column, Finpak SIL C_{18}; eluent, 0.01 M TBAX in 60% CH_3CN, (o) X = I, (●) X = Br; flow rate, 1 ml/min; detection wavelength, TBABr = 250 nm, TBAI = 270 nm; detector sensitivity, 0.04 aufs; column temperature, 25°C.

an increase in hydrophobicity due to an increase in the number of methylene group. Accordingly it is considered that, with the three ion-pairs of mercury(II) halides in this study, hydrophobicity of the halides most remarkably influences the value of k'.

Fig. 3 shows the calibration curve for mercury determination utilizing the ion-pair formation. With either of TBAI and TBABr as the counter-ion, a linearity was obtained with mercury content up to 100 ng. Furthermore, as shown in Table 1, HgI_4^{2-} had a higher sensitivity than $HgBr_4^{2-}$ with the

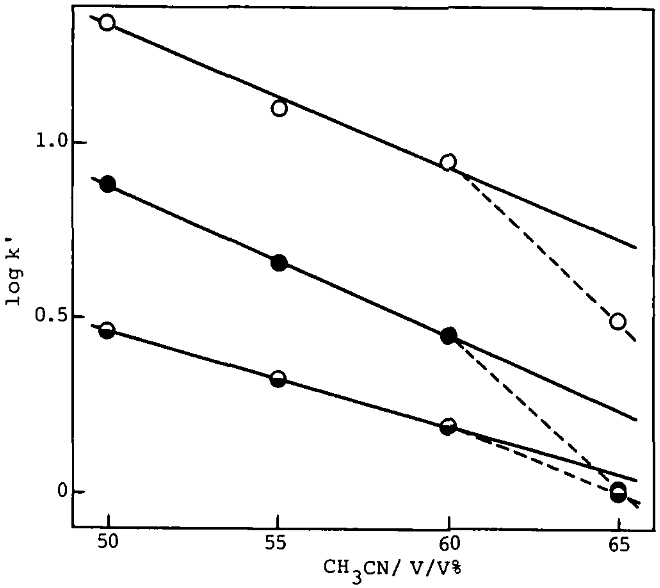

FIGURE 4. Relation between capacity factor and acetonitrile concentration in eluents. Operating conditions were: column, Finpak SIL C_{18}; eluent, 0.01 M TBAX; flow rate, 1 ml/min; column temperature, 25°C.
(o) $(TBA^+)_2HgI_4{}^{2-}$, (●) $(TBA^+)_2HgBr_4{}^{2-}$,
(◒) $(TBA^+)_2HgCl_4{}^{2-}$.

highest molar absorptivity, which was considered as to be due to the difference in their stability constants. With the former mercury complex, its recovery was found to be 81.4%. According to this ion-pair method, the limit for determination of mercury content was 2 ng, with 10 μl of injection volume for HPLC and 10^{-2} mol/dm^3 of TBAI. With TBABr, on the other hand, attempts were made to separate mercury(II) halides by the difference in halogens, but their k' values were the same, owing to an excess supply of Br^- from the counter-ion.

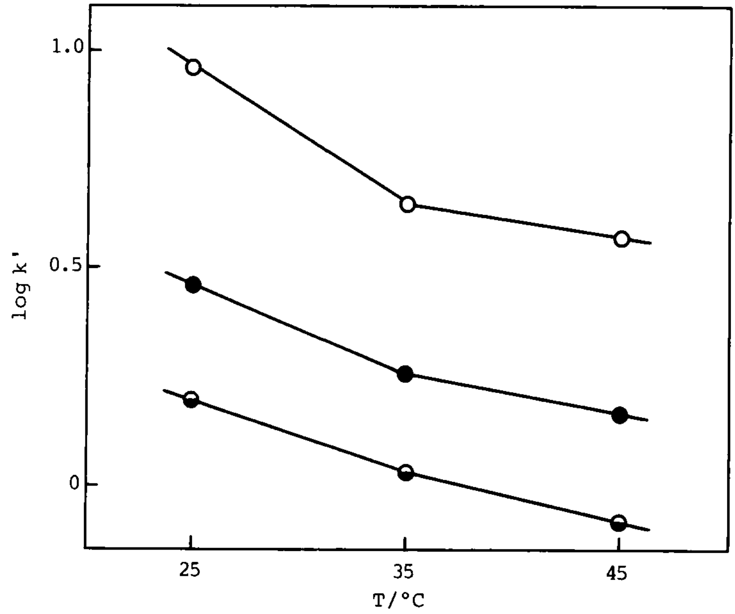

FIGURE 5. Temperature dependence of capacity factor. Operating conditions were: column, Finpak SIL C_{18}; eluent, 0.01 M TBAX in 60% CH_3CN; flow rate, 1 ml/min. (o) $(TBA^+)_2HgI_4^{2-}$, (●) $(TBA^+)_2HgBr_4^{2-}$, (◒) $(TBA^+)_2HgCl_4^{2-}$.

Fig. 4 shows the change in k' values of ion-pairs, where acetonitrile content in the eluent was varied by 5% successively in the range of 50 to 65%. In this range, the decrease in k' nearly paralleled the increase in acetonitrile content. With over 60% content of acetonitrile the decrease of k' was much larger.

The elution behavior of ion-pair, when varied the content of the organic solvent in the mobile phase and the column temperature(Fig. 5), indicated a structural similarity between the ion-pairs despite their difference in k' due to hydro-

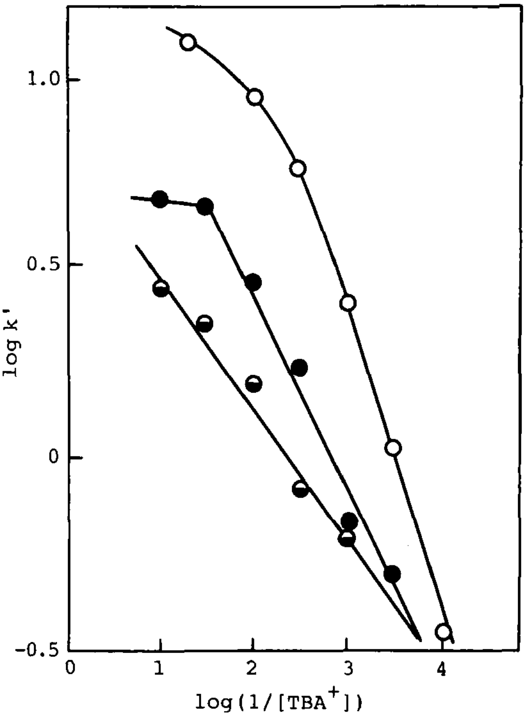

FIGURE 6. Relationship between capacity factor and concentration of counter-ion in eluents. Operating conditions were: column, Finpak SIL C_{18}; eluent, TBAX in 60% CH_3CN; flow rate, 1 ml/min; column temperature, 25°C. (o) $(TBA^+)_2HgI_4^{2-}$, (●) $(TBA^+)_2HgBr_4^{2-}$, (◒) $(TBA^+)_2HgCl_4^{2-}$.

phobicity. In this connection, a definite relation was demonstrated between hydrophobicity and k' of the halides, which supports the above finding and also suggests the ion-pairs to be separated mainly by the distinction between their partition factors.

Separation by IPC is partly characterized by proportionality between k' and the concentration in the mobile phase.

Fig. 6 shows the relation of log k' to the concentration of three kinds of TBAX. As seen in the Figure, the linearity was obtained in the following range of TBAX; 10^{-4} — 3.3×10^{-3} mol/dm^3 for TBAI; 3.3×10^{-4} — 3.3×10^{-2} mol/dm^3 for TBABr; 10^{-3} — 10^{-1} mol/dm^3 for TBACl. The linearity is, moreover, expressed by the following equations:

$$\log k'_{TBAI} = 0.7939 \log[TBA^+] + 2.7566$$

$$\log k'_{TBABr} = 0.5110 \log[TBA^+] + 1.4499$$

$$\log k'_{TBACl} = 0.3449 \log[TBA^+] + 0.8292$$

The less the stability constant of HgX_4^{2-}, the higher range in the concentration of TBAX became available for the linearity. This indicates that a large amount of halide ions from the counter-ion is required for ion-pair formation. IPC-separation was usually conducted by the ion-pair formation between the sample ion and the counter-ion, where it was assumed that the slope of the straight line representing the relation of log k' to the counter-ion concentration was related to the dissociation constant of the sample(11). The present experiment comprised a complex formation in the process of ion-pair formation which was not involved in IPC previously performed. It was, therefore, revealed that the slope of the line was related to the stability constant of the complex formation as of HgX_4^{2-}.

ACKNOWLEDGEMENTS

The authors are deeply grateful to Dr. M. Uchida, Emeritus Professor of Kumamoto University, for stimulating discussions and valuable advice concerning this work.

REFERENCES

1. Tajima, K., Fujita, M., Kai, F. and Takamatsu, M., J. Chromatogr. Sci., 22, 244(1984).
2. Hooper, M. A. and James, D. W., Aust. J. Chem., 24, 1331(1971).
3. Hooper, M. A. and James, D. W., Aust. J. Chem., 24, 1345(1971).
4. Goggin, P. L., King, P., McEwan, D. M., Taylor, G. E. and Woodward, P., J. Chem. Soc. Dalton Trans., 1982, 875.
5. Barr, R. M. and Goldstein, M., J. Chem. Soc. Dalton Trans., 1976, 1593.
6. Colton, R. and Dakternieks, D., Aust. J. Chem., 33, 2405(1980).
7. Smith, R. M. and Martell, A. E., "Critical Stability Constants", vol. 4, Plenum Press, New York, 1976.
8. Gunter, J. D., Schreiner, A. F. and Evans, R. S., Inorg. Chem, 14, 1589(1975).
9. Tanaka, N. and Thornton, E. R., J. Am. Chem. Soc., 99, 7300(1977).
10. Snyder, L. R., J. Chromatogr. Sci., 8, 692(1970).
11. Su, S. C., Hartkopf, A. V. and Karger, B. L., J. Chromatogr., 199, 523(1976).