CHROM. 3319

INORGANIC CHROMATOGRAPHY ON CELLULOSE ACETATE PRE-TREATED PAPER IMPREGNATED WITH 2-THENOYLTRIFLUOROACETONE

S. KAWAMURA, T. FUJIMOTO AND M. IZAWA
Chemistry Division, National Institute of Radiological Sciences, Anagawa-cho, Chiba (Japan)
(Received November 13th, 1967)

SUMMARY

The R_F values of inorganic ions on paper pre-treated with 0.25–2.0 % cellulose acetate and impregnated with various concentrations of 2-thenoyltrifluoroacetone (TTA) was studied by using acetate buffer as a developing agent. 1 % cellulose acetate pre-treated paper impregnated with 0.2 *M* TTA was found suitable for reversed phase paper chromatography.

The R_F values of inorganic ions were examined on the impregnated paper by using various pH's of the developing agent (0.1 *M* acetate buffer). Separations of Pb–Cu, Co–Cu, Zn–Cu and Fe–Co–Ni were performed in this system.

Reversed phase paper chromatography has been applied to the separation of various radionuclides[1,2]. Most of the results, however, were obtained with liquid ion exchangers as the stationary phase and mineral acids of various concentrations as the mobile phase. In this paper, an attempt was made to use 2-thenoyltrifluoroacetone (TTA) as a substitute for the liquid exchangers. TTA is a chelating agent effective for the solvent extraction of some fission products and the related nuclides[3–17]. Alkaline earth metals were successfully separated with this reagent by reversed phase partition chromatography on a column of Kel-F[18]. The authors have studied the behavior of some fission products and related nuclides on a paper pre-treated with cellulose acetate and impregnated with TTA in benzene. From the results so far obtained, some of these elements could be separated from each other by this technique.

MATERIALS AND METHODS

Toyo filter paper No. 50 (2 × 40 cm) was washed with 10 % hydrochloric acid and distilled water three times alternately, and dried. The paper was extracted with 40–60° petroleum ether, followed by drying at 60° for 1 h. After the pre-treatment of the paper as described later, the treated paper was immersed in a solution of TTA in benzene for 1 h, equilibrated with the developing solution (acetate buffer). Then, it was dried by warm air to remove the excess of benzene.

^{51}Cr, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{85}Sr, ^{90}Y, ^{95}Zr, ^{140}La, ^{144}Ce and ^{137}Cs were used as tracers, to which was added the nitrate of each element as a carrier to make an 0.05 *M*

solution. 0.05 *M* solutions of Al, Cu, Ba and Pb were prepared without adding radioisotopes. For mixtures, the concentration was 0.02 *M* for each element. 0.5 μl of the solution was applied to the paper. Then, paper chromatographic separation was carried out by the descending technique at about 25°, using acetate buffer of various pH's and concentrations as the developing agent. The location of radionuclides on the paper was determined by autoradiography. Ba was detected by spraying a solution of 0.1% (w/v) sodium rhodizonate, a red spot being obtained. Cu was detected by spraying 0.05% (w/v) dithizone in chloroform solution, a brownish red spot being obtained. The spot of Al was detected by spraying a solution of 0.1% (w/v) alizarin-S solution; the spot obtained became purplish red on exposure to the vapour of ammonia and acetic acid. Pb was detected by exposing to hydrogen sulphide, a black spot being obtained.

PRE-TREATMENT OF THE PAPER

Before impregnation of the filter paper with TTA in benzene, pre-treatment of the paper was necessary, in order to make the paper hydrophobic. The pre-treatment method with vaseline or silicone described by BROWN AND KRITCHEVSKY[19] was examined but the migration of the developing agent on the paper impregnated with TTA in benzene yielded irregular fronts. Silanized paper was prepared by placing the paper in a desiccator over dichlorodimethylsilane, allowing it to stand overnight, washing thoroughly and drying at 110°. The pre-treated paper was brittle, and the R_F values observed on this paper were generally low. Acetylation of the paper with acetic anhydride and sulfuric acid[19] caused damage to the paper.

Finally, cellulose acetate pre-treated paper was prepared by the following procedure. The paper was dipped in 0.25–2.0% (w/v) cellulose acetate in dry acetone for 15 min, and dried at 60° for 1 h[20]. Migration of the developing agent on the pre-treated paper impregnated with 0.2 *M* TTA in benzene was uniform and the developed zone was well defined. Therefore, paper pre-treated with cellulose acetate was used throughout the subsequent experiments.

RESULTS AND DISCUSSION

R_F values of the ions at different pH values of developing agent (0.1 M acetate buffer)

Fig. 1 shows the R_F values of ions on paper pre-treated with 1% cellulose acetate in acetone and impregnated with 0.2 *M* TTA in benzene, as a function of the pH of the developing agent (0.1 *M* acetate buffer). Fe(III), Cu(II), and Zr(IV) remain at the origin. The R_F value of Cs is ~0.85 independent of the pH of the buffer, which may be due to non-interaction of Cs with TTA. R_F values of Al, Cr(III), Co(II), Zn, Sr, Y, Ba, Ca, Ce(III) and Pb decrease with increasing pH of the buffer. The relation between R_F and distribution ratio[21] (the ratio of the concentration of the inorganic ion, in the organic and the aqueous phases), obtained from the liquid–liquid extraction between 0.2 *M* TTA in benzene and ~10^{-4} *M* Sr, Ce(III), Zn and Co aqueous phase, seemed to show the establishment of reversed phase partition on the paper.

Relation between R_F values and the percentage (w/v) of cellulose acetate in acetone

Fig. 2 shows that the R_F values of Co and Ba on the paper impregnated with 0.2 *M* TTA in benzene are nearly constant over the range from 0.25 to 2.0% (w/v)

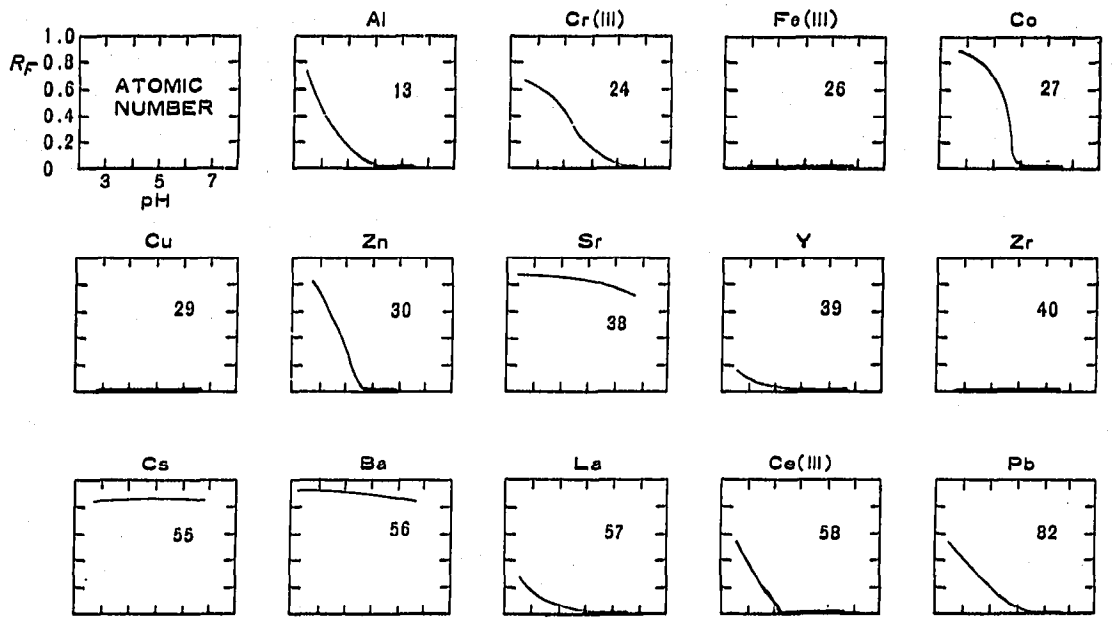

Fig. 1. R_F values of inorganic ions plotted against the pH of the developing agent (0.1 *M* acetate buffer). Paper was pre-treated with 1% cellulose acetate in acetone and impregnated with 0.2 *M* TTA in benzene.

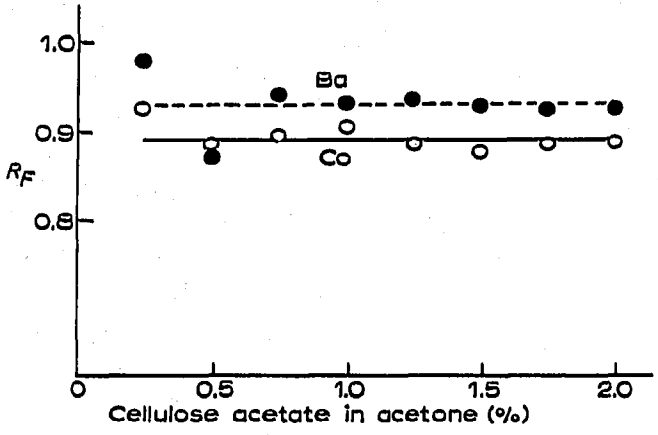

Fig. 2. Relation between R_F values and the percentage (w/v) of cellulose acetate in acetone. Cellulose acetate pre-treated paper was impregnated with 0.2 *M* TTA in benzene. 0.1 *M* acetate buffer (pH 2.5) was used as the developing agent.

cellulose acetate in acetone. The paper pre-treated with >1.5 % solution showed a marked decrease of the rate of migration of developing agent.

Relation between R_F values and the concentration of TTA in benzene

Fig. 3 shows the R_F values of Sr, Pb, Zn, Fe(III), Zr(IV) and Ce(III) as a function of the concentration of TTA in benzene used for the impregnation of the paper, after pre-treatment with 1 % (w/v) cellulose acetate in acetone.

The R_F values of Sr and Ba are both 0.85, independent of the concentration of the TTA in benzene, whereas, those of Pb, Zn, and Al gradually decrease with increasing concentration of TTA and remain constant over the concentration range from 0.15 to 0.4 *M*. Fe(III), Ce(III) and Zr(IV) remain at the origin over the whole pH range.

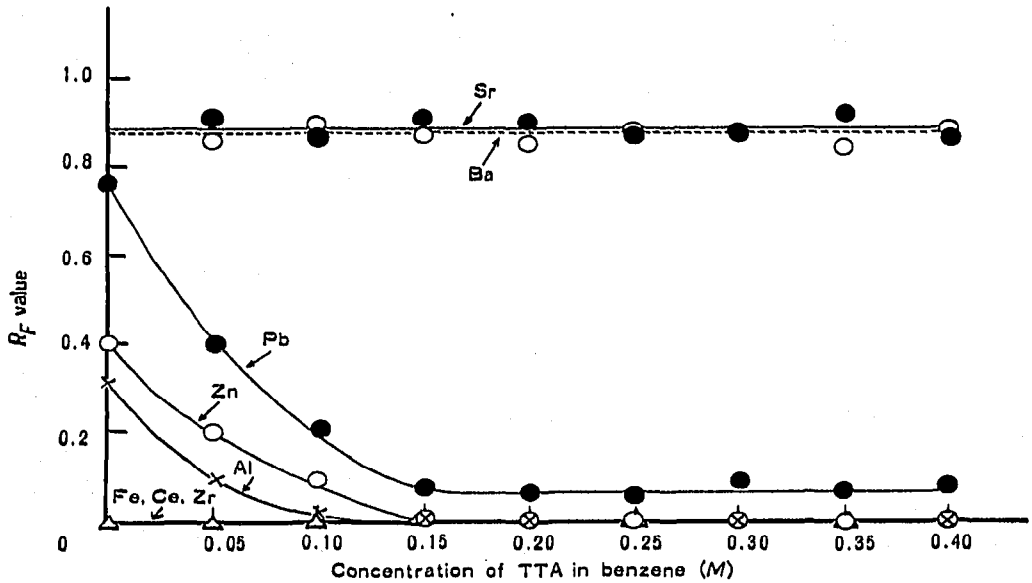

Fig. 3. R_F values for various ions as a function of the concentration of TTA in benzene. Paper was pre-treated with 1 % cellulose acetate in acetone and impregnated with various concentrations of TTA in benzene. 0.1 *M* acetate buffer (pH 4.5) was used as the developing agent.

Relation between R_F values and the concentration of the developing agent (acetate buffer)

Fig. 4 shows that R_F values of Ce(III) and Pb on 1 % cellulose acetate pre-treated paper impregnated with 0.2 *M* TTA increase with the increase of the concentration of the acetate buffer. The result indicates that interaction exists between these ions and acetate buffer, as described by CERRAI AND GHERSINI[21].

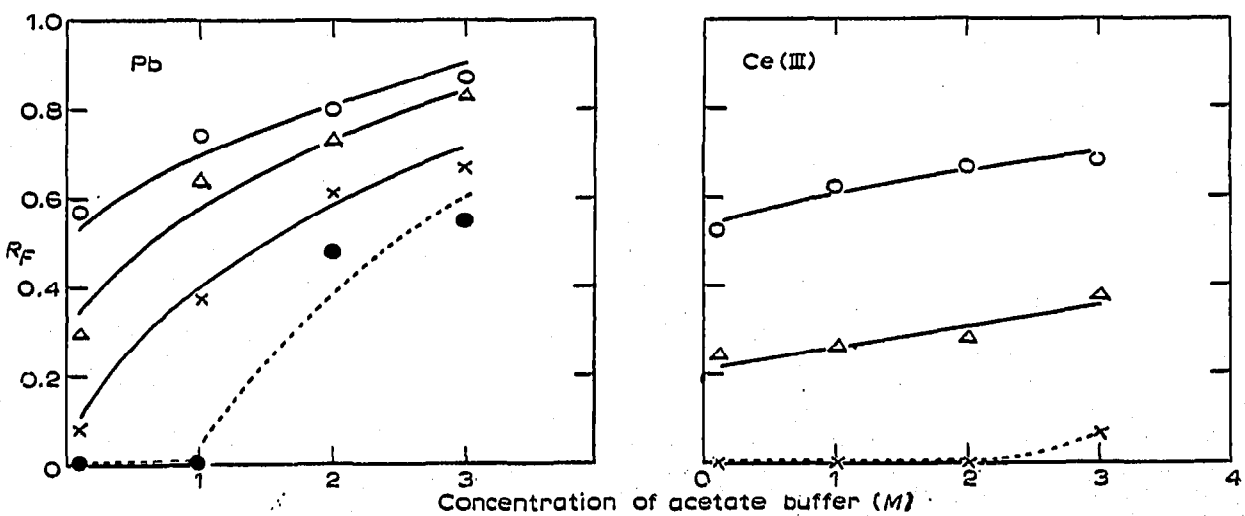

Fig. 4. Relation between R_F values and the concentration of the developing agent (acetate buffer). (—○—) pH of acetate buffer 2.5; (—△—) pH of acetate buffer 3.5; (—×—,---×---) pH of acetate buffer 4.5; (---●---) pH of acetate buffer 5.3. Paper was pre-treated with 1 % cellulose acetate in acetone and impregnated with 0.2 *M* TTA in benzene.

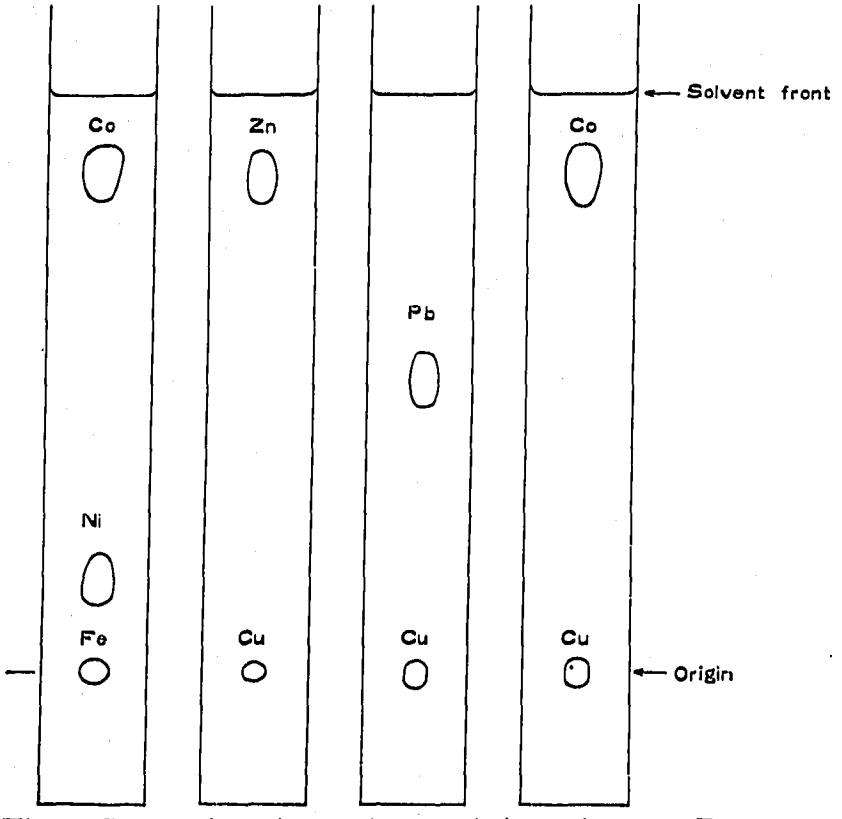

Fig. 5. Separation of some inorganic ion mixtures. Paper was pre-treated with 1 % cellulose acetate in acetone and impregnated with 0.2 *M* TTA in benzene. 0.1 *M* acetate buffer (pH 2.5) was used as the developing agent.

Separation of some inorganic ion mixtures

From Fig. 1, it would be anticipated that mixtures of some inorganic ions can be separated by the 1 % cellulose acetate pre-treated paper impregnated with 0.2 *M* TTA. Fig. 5 shows some typical results of such separations, *viz.* Pb–Cu, Co–Cu, Zn–Cu and Fe–Co–Ni.

REFERENCES

1 T. KIBA AND I. AKAZA, *Kagaku, Chemistry*, 19 (1964) 984.
2 T. KIBA, *Japan Analyst*, 15 (1966) 991.
3 R. A. BOLOMEY AND L. WISH, *J. Am. Chem. Soc.*, 72 (1950) 4483.
4 G. W. SMITH AND F. L. MOORE, *Anal. Chem.*, 29 (1957) 448.
5 T. KIBA AND S. MIZUKAMI, *Bull. Chem. Soc. Japan*, 31 (1958) 1007.
6 E. SHEPERD AND W. W. MEINKE, *U.S. At. Energy Comm. Rept.*, AECU-3879, (1958) 1.
7 H. L. SCHERFF AND G. HERRMANN, *J. Inorg. Nucl. Chem.*, 11 (1959) 247.
8 O. MENIS, T. C. RAINS AND J. A. DEAN, *Anal. Chem.*, 31 (1959) 187.
9 A. K. DE AND S. M. KHOPKAR, *Chem. Ind. (London)*, (1959) 854.
10 H. C. ESHELMAN, J. A. DEAN, O. MENIS AND T. C. RAINS, *Anal. Chem.*, 31 (1959) 183.
11 Y. YAMANE, *Japan Analyst*, 8 (1959) 264.
12 S. M. KHOPKAR AND A. K. DE, *Z. Anal. Chem.*, 171 (1959) 241.
13 S. K. MAJUMDAR AND A. K. DE, *Z. Anal. Chem.*, 177 (1960) 97.
14 S. K. MAJUMDAR AND A. K. DE, *Anal. Chem.*, 32 (1960) 1337.
15 S. F. MARSH, W. J. MAECK, G. L. BOOMAN AND J. E. REIN, *Anal. Chem.*, 33 (1961) 870.
16 A. M. POSKANZER AND B. M. FOREMAN, JR., *J. Inorg. Nucl. Chem.*, 16 (1961) 323.
17 I. AKAZA, *Bull. Chem. Soc. Japan*, 39 (1966) 971.
18 I. AKAZA, *Bull. Chem. Soc. Japan*, 39 (1966) 980.
19 H. G. CASSIDY, *Fundamentals of Chromatography*, Interscience, New York, 1957, p. 150–152.
20 P. HARRIS AND F. W. LINDLEY, *Chem. Ind. (London)*, (1956) 922.
21 E. CERRAI AND G. GHERSINI, *J. Chromatog.*, 13 (1964) 211.