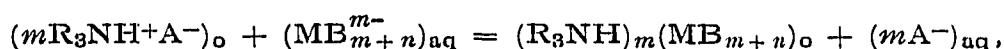


The radiochemical separation of some metals by partition chromatography with reversed phases on teflon in the system tri-*n*-octylamine–electrolyte

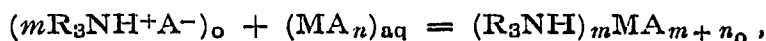
Partition chromatography in a liquid–liquid system, where one of the two phases is stationary and adsorbed on the inert, solid support as described by MARTIN AND SYNGE¹, finds more and more applications in the radiochemical analysis of inorganic compounds.

In studies on the conditions of separation of metal ions by partition chromatography with reversed phases the pulverised organic polymers are often used as the inert supports of the stationary phase. These include polytrifluorochloroethylene (KEL-F)^{2–4}, polytetrafluoroethylene (teflon)^{5,6} and polyvinyl chloride with vinyl acetate⁷. Recently CERRAI AND TESTA⁸ used tri-*n*-octylamine (TNOA) adsorbed on powdered cellulose for the separation of some metals, and TESTA⁹ separated lanthanides by this method.

The reaction between the tertiary amines and metal ions $(MB_{m+n}^{m-})_{aq}$ can be described in the form of the equation characterizing the ion exchange:



or as an addition reaction of the neutral molecule of the inorganic salt (MA_n) :



where o indicates the organic phase and aq the aqueous phase.

According to the experimental data reviewed by COLEMAN¹⁰, ISHIMORI AND NAKAMURA¹¹, the partition coefficients for the salts studied, when determined by the static extraction method using tri-iso-octylamine (TIOA) and hydrochloric acid differ according to the HCl concentration. Similarly in the case of TNOA, the choice of an appropriate concentration of HCl as eluant should afford the separation of some mixtures of metal halogenides, owing to the different values of their partition coefficients.

Experimental

A glass column (2.8 mm in diameter, 75–80 mm long) was used in the studies on the separation of mixtures of various metal chlorides. Powdered teflon $(-CF_2-CF_2-)_n$ (150–250 mesh) was introduced into the column as a suspension in benzene, washed with ethanol and then with water. About 375 mg TNOA (Fluka, Buchs S.G., Switzerland) was then adsorbed onto the teflon. After washing with water and 1 *N* HCl the column was ready for use. The radiotracer method was used in the investigations on metal separation. The experiments were carried out at room temperature ($20^\circ \pm 2^\circ$). The flow rate of the eluants was regulated by means of a pressure of 0.3–0.5 kg/cm²; one drop of eluate (0.03 ml) passed every 60 sec. The drops, collected on polystyrene foil, were dried with an infrared lamp. The measurements of the activity of the initial solutions and the eluates were performed with the aid of a Geiger-Müller end-window counter (AAH 55 type), while a flow counter 2π (AET-60 type) was used for measuring the activity of the ⁶³Ni isotope, and the activity of uranium was determined with a scintillation counter according to the method de-

TABLE I
CONCENTRATIONS OF METALS USED IN THE SEPARATIONS

Salt	Concentration of metal ion (M)	Radio-indicator	Half-life
CaCl ₂	4.5 · 10 ⁻⁴	⁴⁵ Ca	163.5 d
MnCl ₂	2.5 · 10 ⁻⁶	⁵⁴ Mn	291 d
FeCl ₃	1 · 10 ⁻³	^{55,59} Fe	2.6 y 45.1 d
CoCl ₂	1.2 · 10 ⁻⁶	⁶⁰ Co	5.24 y
NiCl ₂	2.1 · 10 ⁻³	⁶³ Ni	125 ± 6 y
CuCl ₂	5 · 10 ⁻⁴	⁶⁴ Cu	12.9 h
ZnCl ₂	7 · 10 ⁻³	⁶⁵ Zn	244.3 d
SrCl ₂	1.3 · 10 ⁻⁵	⁹⁰ Sr	27.7 y
YCl ₃	Carrier-free	⁹⁰ Y	64.6 h
CdCl ₂	1.1 · 10 ⁻⁴	¹¹⁵ Cd	42.6 d
ThCl ₄	Carrier-free	²³⁴ Th	24.1 d
PaCl ₅	Carrier-free*	²³³ Pa	27 d
UO ₂ Cl ₂	1.9 · 10 ⁻²	Natural	

* In the presence of ThCl₄, conc. 1 · 10⁻⁴ M.

scribed previously¹². The concentrations of the chlorides of the separated metals, labelled with the radioactive isotopes, are given in Table I.

It was found during the course of the experiments that chlorides of iron, zinc, and cadmium are strongly adsorbed from 1 N HCl-solution, in contrast to chlorides of manganese, cobalt, copper, calcium, strontium, and yttrium, which are not adsorbed and are eluted in the first free volume of the column. The ferric chloride adsorbed was eluted with 0.01 N HCl, but zinc and cadmium chlorides formed stable complexes with TNOA which are not eluted with diluted HCl or HNO₃.

In order to elute zinc and cadmium, the column was washed with water till a neutral reaction was obtained and then eluted with the buffer 0.2 M ammonium acetate-ammonium hydroxide (pH = 10). The results obtained allowed the separation

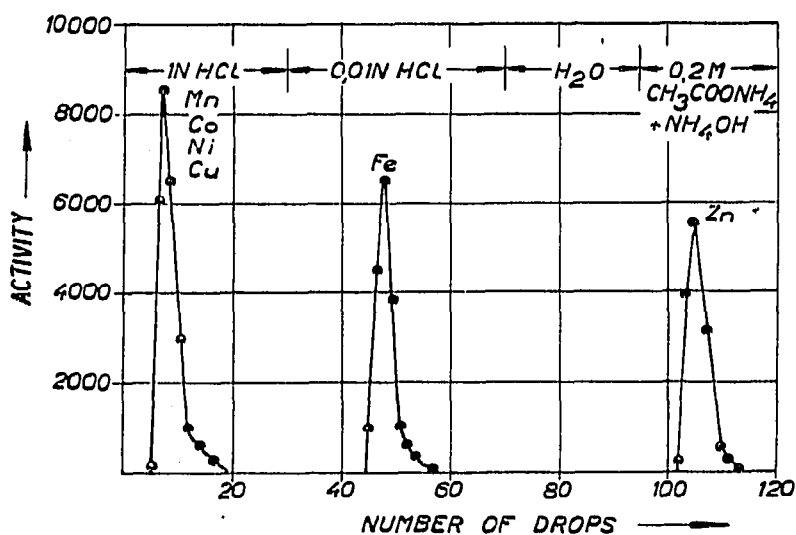


Fig. 1. Separation of (Mn,Co,Ni,Cu)-Fe-Zn.

of mixtures containing cobalt chloride and chlorides of other divalent metals from iron and zinc or cadmium. 0.03 ml samples of the solutions of chlorides in 1 N or 6 N HCl were used for the separation. Fig. 1 shows a chromatogram of the separation of certain chlorides from iron and zinc; manganese, cobalt, nickel and copper are eluted with 1 N HCl, iron with 0.01 N HCl, and zinc with 0.2 M ammonium acetate buffer (pH = 10), after washing the column with 0.75 ml of water.

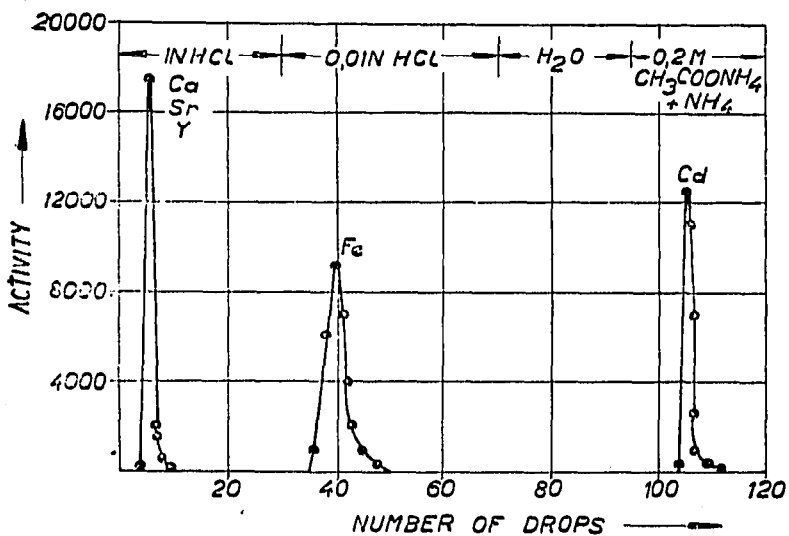


Fig. 2. Separation of (Ca, Sr, Y)-Fe-Cd.

Fig. 2. gives the chromatogram of separation of calcium and strontium chlorides and yttrium chloride from iron and cadmium; calcium, strontium and yttrium were washed with 1 N HCl, iron with 0.01 N HCl, and cadmium with 0.2 M ammonium acetate buffer (pH = 10), after washing the column with 0.75 ml of water.

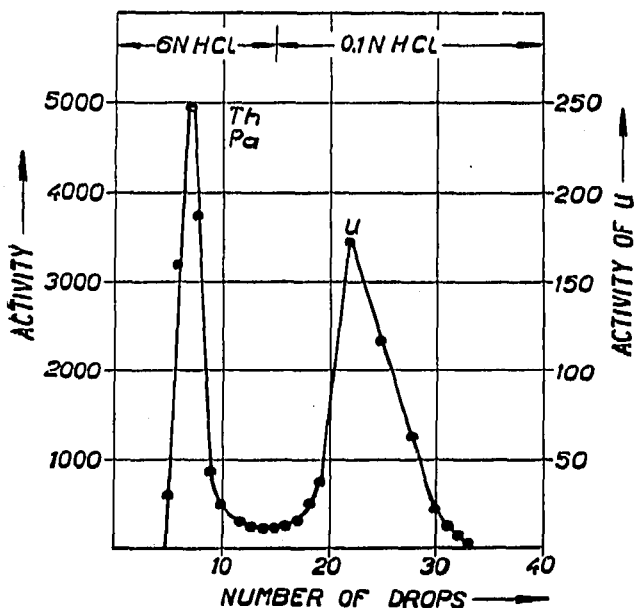


Fig. 3. Separation of (Th, Pa)-U.

In the case of thorium, protactinium, and uranyl chlorides it was shown that only uranyl chloride was adsorbed from 6 *N* hydrochloric acid, while thorium and protactinium do not adsorb and are not retarded by the column at all. Uranyl chloride could be eluted with 0.1 *N* HCl.

It was thus possible to obtain the carrier-free ^{234}Th (UX_1) isotope, formed as a result of an α -emission from the nucleus of ^{238}U . The UO_2Cl_2 preparation containing UX_1 was introduced into the column as a solution in 6 *N* HCl. Under these conditions the isotope of thorium was washed out in the first free volume of the column, but the uranium was adsorbed and could be eluted with 0.1 *N* HCl. Fig. 3 shows the chromatogram for the separation of thorium or protactinium from uranium.

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*Institute of Nuclear Physics,
Laboratory of Chemistry and Radiochemistry,
Cracow (Poland)*

J. MIKULSKI
I. STROŃSKI

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