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## CONCENTRATION AND SEPARATION OF $\text{Ni}^{2+}$ , $\text{Cu}^{2+}$ AND $\text{Co}^{2+}$ BY BACK EXTRACTION CHROMATOGRAPHY USING LIX 64N AND CATIONIC RESINS

### I. CONCENTRATION OF $\text{Ni}^{2+}$

A. PISOSCHI\* and S. TÁ TARU

*Research and Design Centre for Radioactive Metals, 51 Atomiştilor Street, Măgurele, Bucureşti (Romania)*

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#### SUMMARY

The extraction of  $\text{Ni}^{2+}$  from aqueous solutions using Lix 64N solutions in various inert diluents has been studied and the optimum extraction conditions ascertained. The organic phase loaded with  $\text{Ni}^{2+}$  is passed through a column of a cationic resin ( $\text{H}^+$ ), which contains only the water taken up on swelling. The effect of the pH of the aqueous film surrounding the resin grains on the capacity of Vionit CS-3 ( $-\text{SO}_3\text{H}$ ), CM-14 ( $-\text{SH}$ ) and CC-1 ( $-\text{COOH}$ ) has been established. The loading curves of these resins have been drawn, at the optimum pH of the aqueous film, and the resin capacities shown to increase in the order  $-\text{COOH} < -\text{SH} < -\text{SO}_3\text{H}$ . The effects of the diluent and of the flow-rate on the loading of the mercaptan resins, and the optimum elution conditions with HCl solution, have also been determined. A mechanism for the ion-exchange process is proposed.

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#### INTRODUCTION

According to Poitrenaud<sup>1</sup>, who extended the work of Small<sup>2</sup>, chromatographic extraction by ion exchange may be defined as the chromatographic separation process which occurs on an organic mobile phase, immiscible with water and loaded with metal species, and where the stationary phase is the retained water on an ion-exchange resin. The combination of the selectivity of the extraction agents (having low capacities) with the relatively high capacity of the ion exchangers (the selectivity of which for certain metal species is sometimes hard to achieve) enables high degrees of concentration and purification to be attained. The advantages of this process have been demonstrated by the results obtained with carboxylic acid extraction agents on cationites and on anionites<sup>3,4</sup>.

In the present study the ion exchange on resins in non-aqueous media immiscible with water has been examined. The results obtained suggest the application of this method to recovery of metals from dilute aqueous solutions, a process of interest in industry.

## EXPERIMENTAL

The hydroxyoximes used as extraction agents were developed by General Mills (Tucson, AZ, U.S.A.) under the name Lix, and have been widely used for the recovery of metal species from aqueous solutions, especially for  $\text{Cu}^{2+}$  (refs. 5 and 6). Lix 64N, a mixture of 5,8-diethyl-7-hydroxy-6-dodecanoxime and (2-hydroxy-5-nonyl-phenyl)phenyl-metanon oxime, was successfully used for metal recovery<sup>7,8</sup>.

For the extraction of  $\text{Ni}^{2+}$  from standard aqueous solutions of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (Reactivul, Bucharest, Romania), 10% Lix 64N (General Mills) in  $\text{CCl}_4$  was used. The dependence of the recovery upon the pH of the aqueous phase and the influence of the contact time were studied. The influences of the Lix concentration and of the nature of the diluent were also determined, and loading curves were drawn. Extractions were made in 100-ml separation funnels.

The organic phase loaded with  $\text{Ni}^{2+}$  was passed through columns filled with cationic resins, which had been previously swelled with water and then treated with acid. The effect of the aqueous film surrounding the resin grains on the exchange capacity of the sulphonic resin Vionit CS-3 and mercaptan resin Vionit CM-14 (made by CC Victoria, Victoria, Romania) was determined. The loading curves for the cationic resins were drawn.

The effects of the diluent and the flow-rate on the loading were studied. Elution was made with HCl solutions, after washing the columns with diluent and then with distilled water. The optimum conditions for the elution of the mercaptan resins were established.

For pH measurements, a Type OP 205 pH-meter (Radelkis, Hungary) was used, and for polarographic analyses a Type OH 104 square-wave polarograph (Radelkis) was employed.

The ion-exchange columns were of glass ( $46 \times 7.4$  mm).

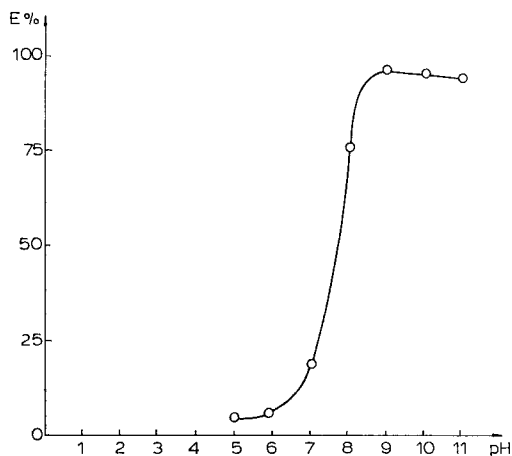


Fig. 1. Extraction of  $\text{Ni}^{2+}$  as a function of the pH of the aqueous phase. Conditions:  $\text{Ni}^{2+}$  concn., 1 g/l; 10% Lix 64N in  $\text{CCl}_4$ ; phase ratio, 1:1; contact time, 5 min.

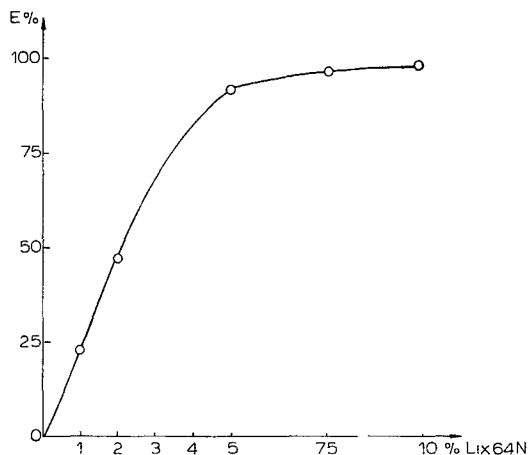


Fig. 2. Extraction of  $\text{Ni}^{2+}$  as a function of the Lix 64N concentration at pH 9. Conditions as in Fig. 1.

## RESULTS

### Liquid-liquid extraction

The optimum pH for extraction of  $\text{Ni}^{2+}$  from aqueous solutions is  $>8$  (Fig. 1). The pH was adjusted by adding ammonia solution, and to prevent precipitation the solution was buffered with small amounts of  $\text{NH}_4\text{Cl}$ .

The contact time is not a determining factor for extraction of  $\text{Ni}^{2+}$  with Lix 64N at pH 9, the same extraction efficiencies being obtained for 1 min, 2 min and 5 min. However, decrease of Lix concentration in  $\text{CCl}_4$  leads to lower efficiencies (Fig. 2), as does an increase of the phase ratio, A:O, from 1:1 to 10:1 (Fig. 3).

Various behaviours of the diluents were found: the most polar diluents lead

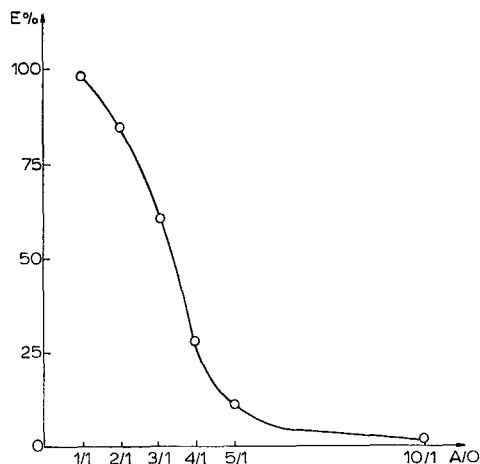


Fig. 3. Extraction of  $\text{Ni}^{2+}$  as a function of the phase ratio at pH 9. Other conditions as in Fig. 1.

TABLE  
EXTRACTION EFFICIENCY AS A FUNCTION OF DILUENT

Diluent	Extraction efficiency (%)
Chloroform	35.48
Benzene	98.27
Toluene	96.35
Carbon tetrachloride	97.87
Kerosene	93.47

to in a decrease of the extraction efficiency. The results are shown in Table I, at a phase ratio of 1:1, pH 9 and contact time of 5 min.

The maximum loading of the organic phase was 2.7 g/l  $\text{Ni}^{2+}$  (Fig. 4).

#### The ion exchange

The columns were filled with cationic exchangers ( $\text{H}^+$ ), pre-treated with hydrochloric acid solutions having different pH values. In this way, most of the water is removed from the columns. The organic phase loaded with  $\text{Ni}^{2+}$  was then passed through the resin bed. The pH of the aqueous film surrounding the resin grains was found to have a strong influence on the ion exchange (Fig. 5).

The organic phase was passed through the column until the concentrations of the influent and effluent were equal. The capacity of the resin was then determined by eluate analysis. The capacity of carboxylic resin Vionit CC-1 is independent of pH, and is very low (0.14 mequiv./ml) in the studied pH range.

The loading curves for the three resins studied are shown in Fig. 6, as a function of the solution volume ratio,  $V_s$ , at a resin volume,  $V_r$  (bed equivalent volume, BEV).

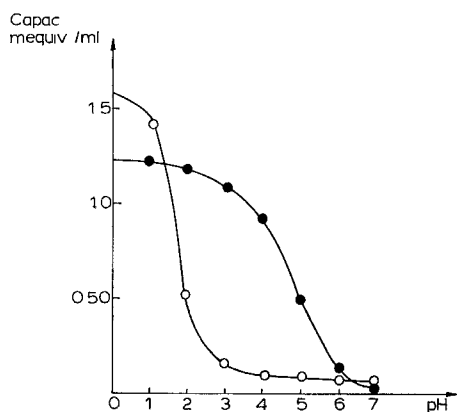
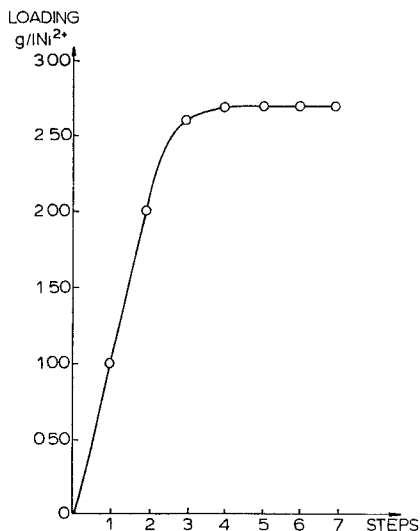


Fig. 4. Loading curve of 10% Lix 64N in  $\text{CCl}_4$  with  $\text{Ni}^{2+}$  at pH 9. Conditions as in Fig. 1.

Fig. 5. Capacity as a function of the pH of the aqueous film. ○, Vionit CS-3 ( $-\text{SO}_3\text{H}$ ); ●, Vionit CM-14 ( $-\text{SH}$ ). Column,  $46 \times 7.4$  mm; flow-rate, 4 BEV/h;  $\text{Ni}^{2+}$  concn., 2.5 g/l in 10% Lix 64N in  $\text{CCl}_4$ .

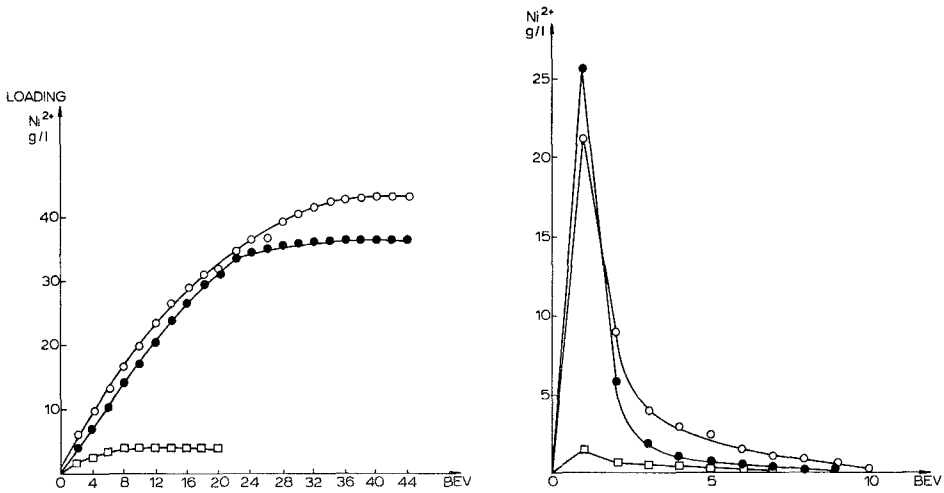


Fig. 6. Loading and elution curves for Vionit CS-3 (○); CM-14 (●) and CC-1 (□). pH of aqueous film, 0. Elution with 2 *N* HCl solution; flow-rate 1 BEV/h. Other conditions as in Fig. 5.

Although the nature of the diluents (except chloroform) had little influence on the distribution ratio during liquid-liquid extraction, this was not the case during the ion exchange (Fig. 7).

The kinetics of the ion exchange in non-aqueous media immiscible with water are slow; low flow-rates are advantageous, the loading curves these cases having higher slopes (Fig. 8).

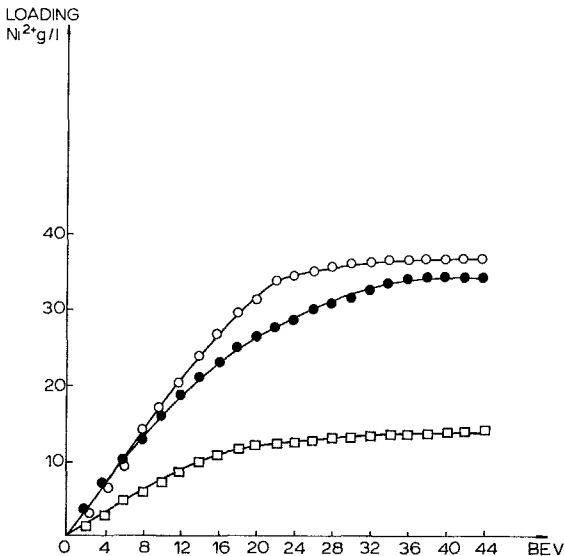


Fig. 7. Loading curves for Vionit CM-14 as a function of the diluent: ○, carbon tetrachloride; ●, kerosene; □, benzene. pH of aqueous film, 0. Other conditions as in Fig. 5.

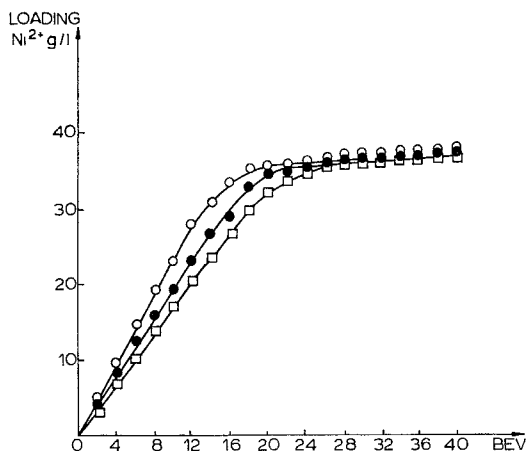


Fig. 8. Loading curves for Vionit CM-14 resin curves as a function of the flow-rate:  $\circ$ , 0.25 BEV/h.  $\bullet$ , 1 BEV/h;  $\square$ , 4 BEV/h. Conditions as in Fig. 5.

The elution was studied as a function of the HCl concentration, the best results being obtained with more concentrated solutions (Fig. 9). In order to elute 90% of the retained  $\text{Ni}^{2+}$ , 3 BEV of 2 N HCl, 6 BEV of 1 N and 8 BEV of 0.5 N are needed. For total elution, 10, 15 and 19 BEV respectively are required.

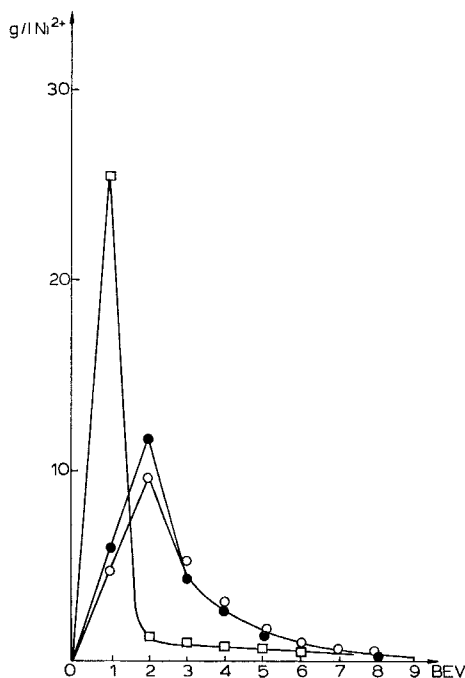


Fig. 9. Elution curves on Vionit CM-14 as a function of the HCl concentration:  $\circ$ , 0.5 N;  $\bullet$ , 1 N;  $\square$ , 2 N. Column,  $46 \times 7.4$  mm; flow-rate, 2 BEV/h.

## DISCUSSION

The optimum parameters for the extraction of Ni<sup>2+</sup> with Lix 64N were: pH > 8; 10% Lix in CCl<sub>4</sub>. Non-polar diluents give similar results, unlike chloroform which leads to a marked decrease in efficiency.

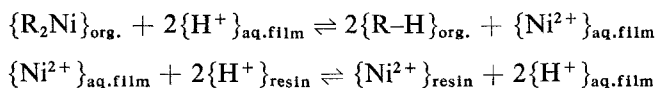
The ion exchange is especially favourable in case of the sulphonic and mercaptan resins, which have maximum capacities of 1.58 and 1.24 mequiv./ml respectively when the pH of the aqueous film tends to zero.

The process of ion exchange between the organic phase, immiscible with water, and the swollen resin occurs in two steps. In the first step the metal ion diffuses from the organic phase into the acidic aqueous film by a simple back extraction in which the metal organic complex is destroyed. As a consequence the extraction agent is re-formed and can be recirculated. This back extraction depends upon the pH of the aqueous film: when the pH increases, the exchanger capacity is diminished, as in Fig. 5. There is a correlation between the extraction (Fig. 1) and the sorption process (Fig. 5), which are both functions of pH.

The carboxylic resin doesn't lead to satisfactory results because it cannot operate in media of pH less than 4, where the back extraction is optimal. Similar results (0.16 mequiv./ml) were obtained using another carboxylic resin (Duolite CC-3; Diaprosim, Vitry, France). The wider pH range over which the mercaptan resin exhibits maximum capacity can be explained by a high affinity of Ni<sup>2+</sup> for S<sup>2-</sup>, but the increase of the pH of the aqueous film leads to a slower process.

In the second step, ion exchange takes place between protons of the resin and the metal ions of the film. This exchange takes place stoichiometrically, so that it can be assumed that the film acidity is practically constant.

The overall mechanism can be illustrated as follows:



The determining step of the process is suggested to be that of metal organic complex destruction and the back extraction of metal ions into the film.

The poor results in the case of benzene as diluent can be explained by partial destruction of the aqueous film by solubilization between benzene and water with water in the eluent.

The kinetics of ion exchange are generally slow so that slow flow-rates are favoured. At low pH values, when the back extraction is rapid, the slowest step is the ion exchange on the resin, and at higher pH values the slowest step is the back extraction into the film.

Accordingly, we consider that the chromatographic processes involving an organic mobile phase immiscible with water and at a stationary phase comprising the water fixed on an ion-exchange resin be best described by the expression "back extraction by ion-exchange chromatography" or "stripping by ion-exchange chromatography". These expressions correspond to the results previously obtained both by Poitrenaud<sup>1</sup> and Small<sup>2</sup>, and do not lead to confusion with "real" chromatographic extraction<sup>9,10</sup>.

The same mechanism, involving the aqueous film surrounding the resin grains, was confirmed in the case of  $\text{Cu}^{2+}$  (loading, 1.52 mequiv./ml) and  $\text{Co}^{2+}$  (loading, 0.2 mequiv./ml). This study will be presented elsewhere.

The described process appears to be highly efficient even for the recovery of trace amounts of  $\text{Ni}^{2+}$  from ammonia solutions, the maximum loading of the organic phase being achieved in more steps, followed by the ion exchange, leading to high concentration. We anticipate important technological applications.

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