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Note

Use of high-molecular-weight "neo" hydroxamic acids as the stationary phase in column extraction chromatography

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In recent years considerable interest has been shown in high-molecular-weight hydroxamic acids. The ability of these compounds to form very stable chelates with a number of metal ions (particularly those relevant to nuclear technologies) has enabled them to be used as selective extractants in liquid–liquid extraction[1]. Various aliphatic hydroxamic acids of the type $(R,R_1,R_2)C-CO-NH-OH$ ("neo" structure) were synthesized by the Reprocessing Research Laboratory of the Energy Research Centre of Cassaccia (Italian Commission for Nuclear and Alternative Energy); the first was neo-tridecanohydroxamic acid (HX-70)[2], which was largely utilized in solvent extraction[3], and also in column extraction chromatography[4]. Compounds with better properties than HX-70 were then synthesized[5–7]: among them, tri-*n*-butylacetohydroxamic acid (TBAH) and 2-*n*-butyl-2-ethyl-nonanohydroxamic acid (BENHA) were selected for liquid–liquid extraction and extraction chromatography[8] because of their solubility in organic diluents and their insolubility in water.

Carrying on the Italian analytical research started in 1960 on reversed-phase partition chromatography[9,10], this paper describes the utilization of TBAH and BENHA supported on microporous polyethylene for the preparation of columns suitable for chromatographic separations of metal ions.

EXPERIMENTAL

Apparatus

The following were employed: Beckman Model Zeromatic SS-3 pH-meter; Hitachi Model 100.40 spectrophotometer; ELBE Model Minicofra automatic sample collector; glass chromatographic columns, 300 × 7 mm I.D.

Reagents

TBAH (>99% pure) was supplied by the Reprocessing Research Laboratory of Casaccia Center. BENHA was also supplied by the same Laboratory, but only 70% pure. Therefore it was necessary to purify it by use of a silica gel column and elution with benzene, followed by a gradient elution with chloroform–ethyl acetate. The final product was 97% pure and had a melting point of 39–41°C.

Silica gel Kieselgel 60 (70–230 mesh) and DC Alufolien Kieselgel 60 for thin-layer chromatography (TLC) were supplied by E. Merck (F.R.G.). Microthene-651

(50 100 mesh), a microporous polyethylene, was supplied by Società Italiana Chimici (Rome, Italy).

The other chemical reagents were analytical grade (Carlo Erba, Milan, Italy).

Stationary phases and column preparation

On the basis of the solubility of TBAH and BENHA in three different diluents and in water, and taking into account the solubility of these diluents in water (Table I), two stationary phases were supported on Microthene-651, namely 0.08 M TBAH in benzene (column A) and 0.50 M BENHA in mesitylene (column B). In the preparation, 3 ml of the organic solution were added, with stirring, to 5 g of Microthene-651; the slurry so obtained was treated with hydrochloric acid having the same concentration as the first feed solution and then transferred into the chromatographic column. Air-bubbles were eliminated and the bed was gently compressed. Such columns had dimensions of about 140 × 7 mm.

TABLE I

SOLUBILITY OF TBAH AND BENHA IN WATER AND IN THREE ORGANIC DILUENTS; SOLUBILITY OF THESE DILUENTS IN WATER

Solute (MW)	Solubility, g/l (moles/l)			
	Water	Chloroform	Benzene	Mesitylene
TBAH (243.4)	0.02 ($7 \cdot 10^{-5}$)	107.1 ($4.4 \cdot 10^{-1}$)	18.45 ($7.6 \cdot 10^{-2}$)	7.8 ($3.2 \cdot 10^{-2}$)
BENHA (257.4)	0.01 ($4.7 \cdot 10^{-5}$)	525 (2.04)	660 (2.56)	425 (1.65)
Benzene (78.1)	0.82 ($1 \cdot 10^{-2}$)			
Mesitylene (120.2)	0.02 ($1.7 \cdot 10^{-4}$)			
Chloroform (119.4)	7.42 ($6.2 \cdot 10^{-2}$)			

Chromatographic behaviour of single ions

The metal ions investigated were Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, Al^{3+}, La^{3+}, Th^{4+}, UO_2^{2+} and ZrO^{2+}. Solutions containing known quantities of these ions (0.025 mequiv./ml for column A and 0.125 mequiv./ml for column B) in hydrochloric acid at different pH values were then prepared. The retention and elution characteristics of these ions on the two columns are shown in Table II and are in good agreement with previous liquid–liquid extraction data[5]. The feed solutions consisted of 1 ml of hydrochloric acid at different pH values; generally, a quantitative elution of an ion from the column was obtained by using 20–40 ml of a suitable eluent, at a flow-rate of 0.5 ml/min.

Chromatographic separation of metal ions

Taking into account the previous results, some multiple separations were achieved by using columns A and B (Figs. 1–5). These chromatograms were always obtained by using a flow-rate of 0.5 ml/min and collecting 10-ml fractions. From

TABLE II

ELUTION ORDER OF SOME METAL IONS AS A FUNCTION OF HYDROCHLORIC ACID
CONCENTRATION

HCl (M)	0.08 M TBAH in benzene		0.5 M BENHA in mesitylene
10^{-5}		Alkali and alkaline earth metals, Co^{2+}, Ni^{2+}, Al^{3+}, La^{3+}	
10^{-2}	Cu^{2+}, UO_2^{2+}		
10^{-1}			Cu^{2+}, UO_2^{2+}
1		Th^{4+}	
6		Fe^{3+}	
0.1 M Oxalic acid		ZrO^{2+}	

these figures it appears that quantitative separations of three or four metal ions in
10–40 ml of solution can be obtained just by changing the elution pH.

Recovery of metal ions from dilute solutions

  TBAH and BENHA columns were tested for their ability to concentrate metal
ion traces from dilute solutions: Cu^{2+} and UO_2^{2+} were investigated starting from 1
l of solution (Figs. 6,7). The experimental conditions are shown in Table III. It ap-
pears that the mean final recovery is about 95% if 30 ml are used for the elution.

Exchange capacity and kinetics

  The exchange capacity of columns A and B was obtained by loading them with
solutions of 10^{-5} M hydrochloric acid containing respectively 0.1 mg/ml and 0.5 mg/ml
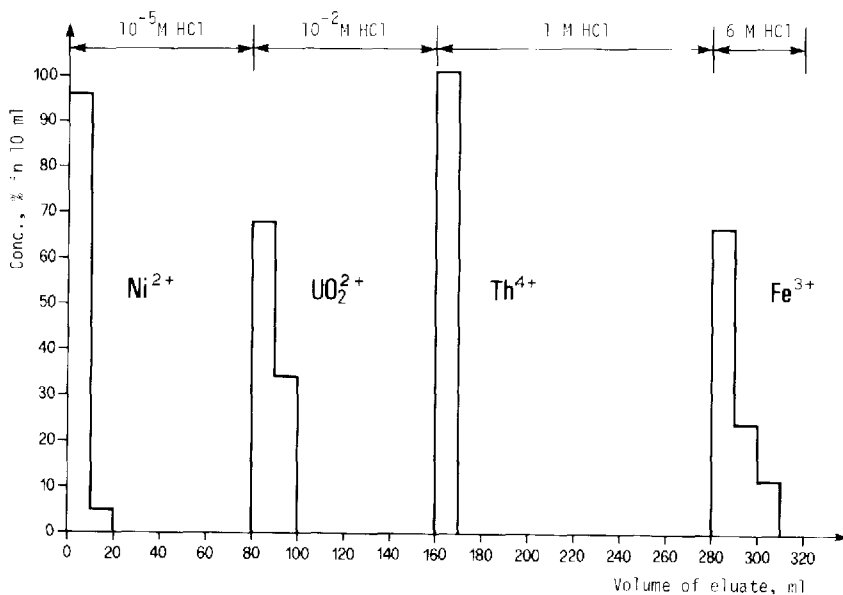

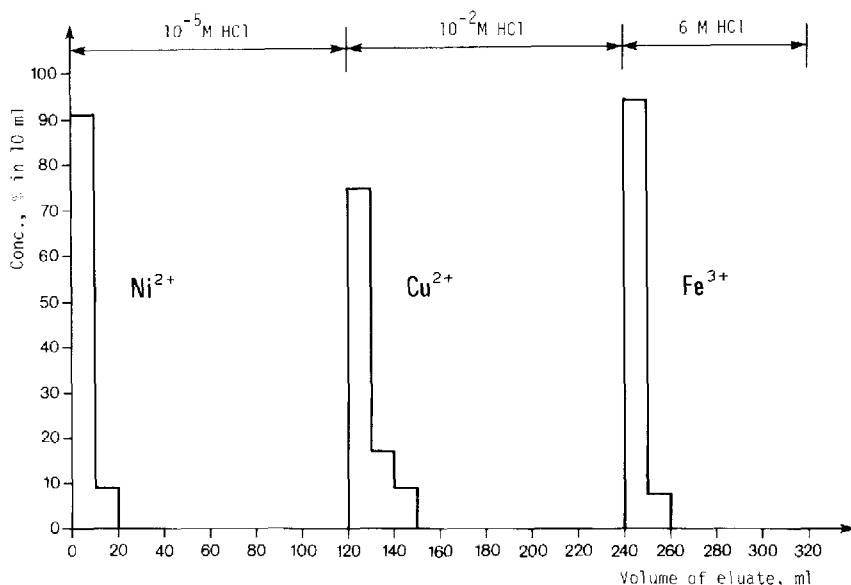Fig. 1. Separation of Ni^{2+}, UO_2^{2+}, Th^{4+} and Fe^{3+} on column A.

Fig. 2. Separation of Ni^{2+}, Cu^{2-} and Fe^{3+} on column A.

of Cu^{2+}. Taking into consideration the retained Cu^{2+}, the experimental total exchange capacity was found to be 0.20 mequiv. for column A and 1.05 mequiv. for column B (0.037 and 0.196 mequiv. per ml of wet slurry respectively). These values correspond to 87.3% and 70.4% respectively of the theoretical exchange capacities.

As far as UO_2^{2+} and Cu^{2+} were concerned, the kinetics were such that flow-rates of up to 5 ml/min · cm² were tolerated by column A.

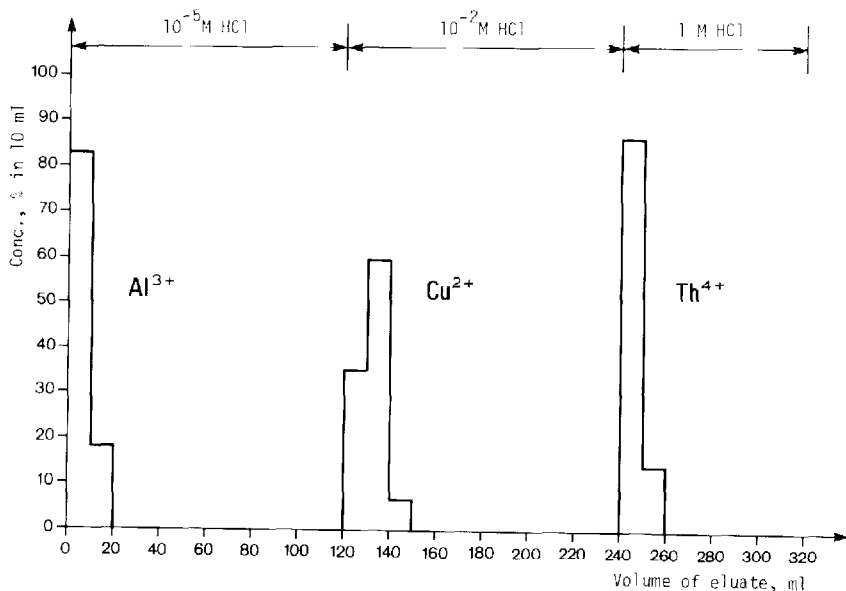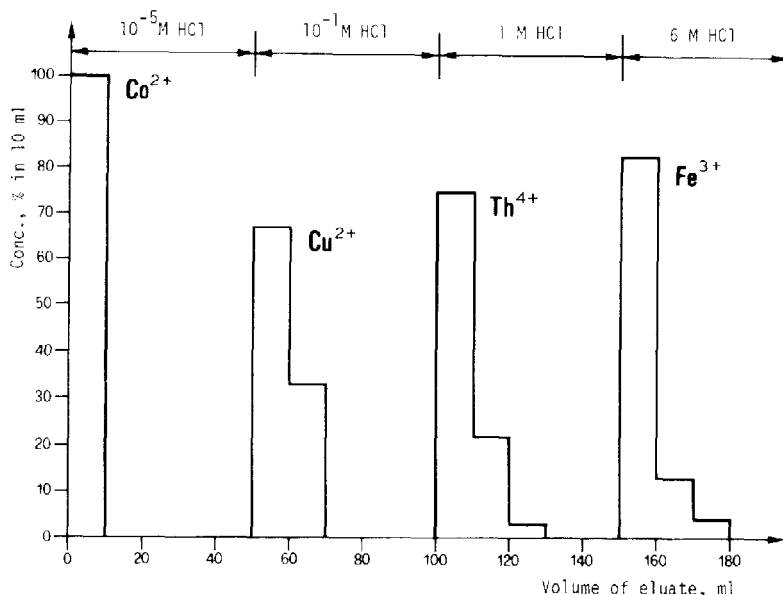Fig. 3. Separation of Al^{3+}, Cu^{2+} and Th^{4+} on column A.

Fig. 4. Separation of Co^{2+}, Cu^{2-}, Th^{4+} and Fe^{3-} on column B.

Unfortunately a significant loss of the stationary phase was observed, particularly from column A, when large volumes of solution were passed through the columns: after 1.5 l the exchange capacity was reduced to 22% (column A) and to 59% (column B) of the initial experimental exchange capacities (which were 87.3% and 70.4% respectively of the theoretical values).
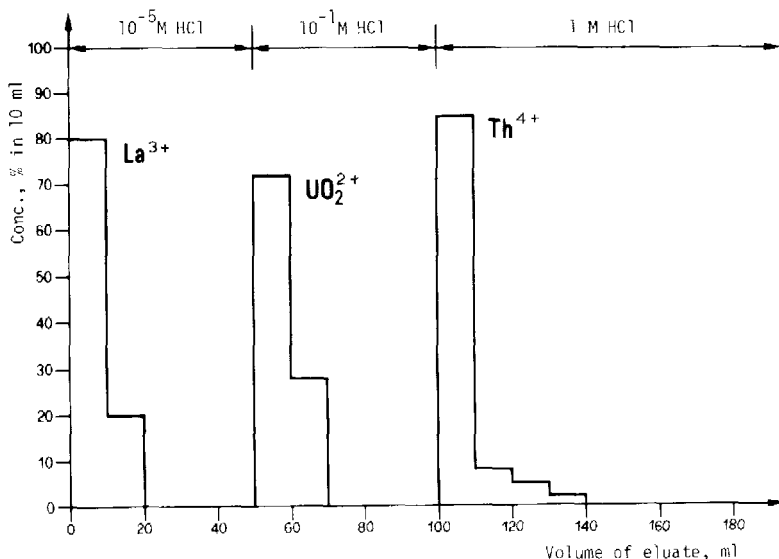

Fig. 5. Separation of La^{3-}, UO_2^{2+} and Th^{4+} on column B.
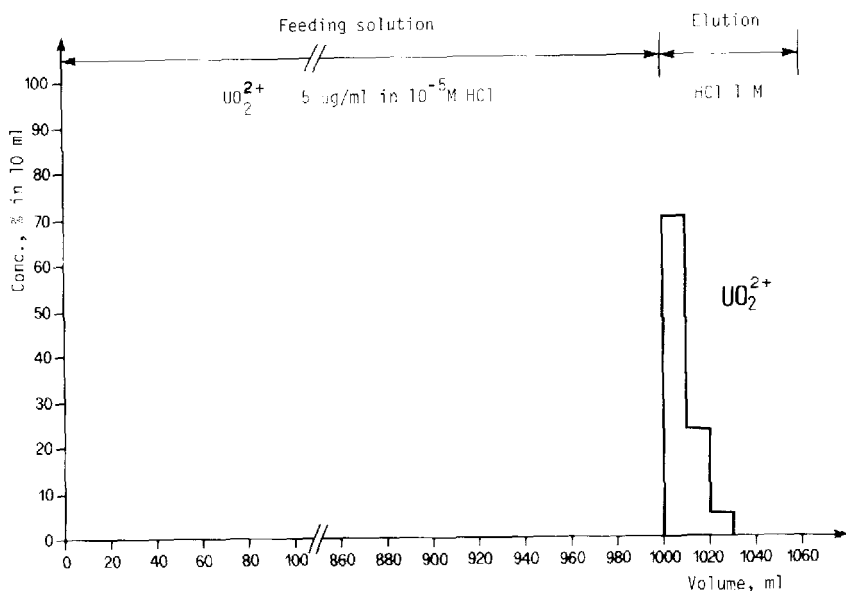
Fig. 6. Recovery of UO_2^{2+} from a dilute solution (column A).

HETP calculation

Fig. 8 shows a chromatogram of Cu^{2+} in 10^{-3} M hydrochloric acid on column A. Taking into consideration the shape of the peak and the relation $N = 8(V_{max}/W)^2$, where W is volume corresponding to $\dfrac{1}{e}$ of the peak height, V_{max} is volume corresponding to peak maximum and N is the theoretical plate number; $N = 595$ and the column height is 140 mm, the height equivalent to a theoretical plate showed a value of 0.23 mm. A similar value was obtained for column B.
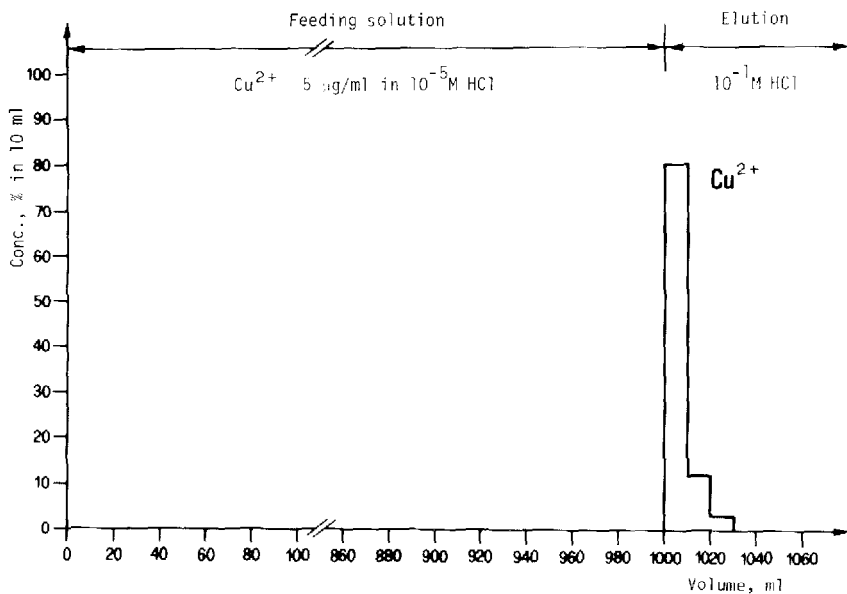

Fig. 7. Recovery of Cu^{2+} from a dilute solution (column B).

TABLE III

RECOVERY OF Cu^{2+} AND UO_2^{2-} IN DILUTED SOLUTIONS ON MICROTHENE–TBAH A⋈ MICROTHENE BENHA COLUMNS

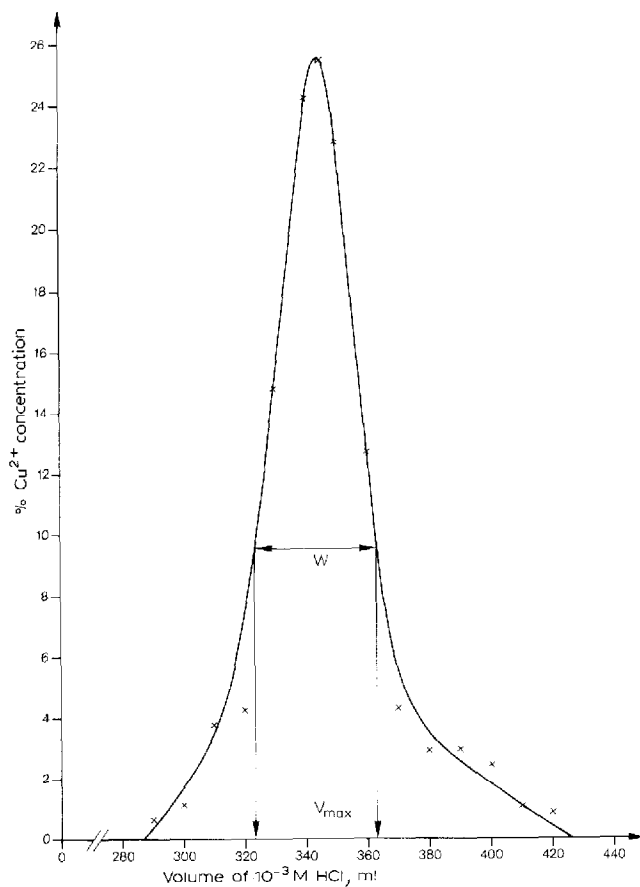| Experimental conditions	0.08 M TBAH in benzene, 3 ml + 5 g Microthene		0.5 M BENHA in mesitylene, 3 ml + 5 g Microthene	
Feed solution	1 1 10^{-5} M HCl containing 1 mg Cu^{2+}	1 1 10^{-5} M HCl containing 5 mg UO_2^{2+}	1 1 10^{-5} M HCl containing 5 mg Cu^{2+}	1 1 10^{-5} M HCl containing 21 mg UO_2^{2}
Flow-rate	1 ml/min	1 ml/min	3 ml/min	3 ml/min
Eluent	20 ml 1 M HCl	30 ml 1 M HCl	30 ml 0.1 M HCl	30 ml 0.1 M HCl
Recovery (%)	92.4	98.3	94.6	95.4

Fig. 8. Elution curve of Cu^{2+} used for the determination of the HETP for column A.

CONCLUSIONS

On the basis of the experimental results it appears that Microthene–TBAH and Microthene BENHA columns can be successfully used to separate and to concentrate metal ions. Although TBAH columns show an experimental exchange capacity nearer to the theoretical value and better kinetics, BENHA columns have a greater exchange capacity and are less subject to loss of stationary phase. Other studies are now in progress on the separation of other metal ions and the isolation of traces of single ions from large quantities of other elements.

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