

THE USE OF TRI-*n*-OCTYLAMINE-CELLULOSE  
IN CHEMICAL SEPARATIONSE. CERRAI AND C. TESTA  
*Laboratori C.I.S.E., Milan (Italy)*

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In two recent papers<sup>1,2</sup> the potentialities of chromatographic procedures using cellulose paper treated with a liquid anion exchanger, such as tri-*n*-octylamine, were discussed. Paper treated in such a way behaves like a film of anionic resin, which has a different affinity for the different anionic complexes of the elements. Since cellulose is the basic constituent of the paper, our purpose was to investigate the properties of treated cellulose powder beds in order to separate appreciable quantities of substances. Like in the case of paper strips, the cellulose powder was treated with tri-*n*-octylamine.

## EXPERIMENTAL

*Preparation of the cellulose powder*

Twenty grams of Whatman No. 1 cellulose powder were dried for 2 hours at 80° and then allowed to cool at room temperature in a desiccator. At the same time 100 ml of 0.1 *M* tri-*n*-octylamine (TNOA) in benzene were shaken for 10 min with twice the volume of the solution selected for conditioning the column. The organic phase was then separated and passed through cotton lint to remove any residual water droplets. The dried and cooled cellulose powder was put into a 500 ml bottle and after the addition of the amine solution, the mixture was stirred overnight by means of a magnetic stirrer. After the treatment, the cellulose powder was allowed to settle and then filtered through a fast paper filter. The liquid was allowed to drip off and the wet powder was gently pressed with a paper disk to improve the removal of liquid; finally, the powder was placed between two filter paper sheets to eliminate completely the organic solution that still adhered to the external surface of the powder grains. Afterwards, the powder was dried for 2 h at 85° to volatilize the benzene solvent, and then it was allowed to cool in a desiccator. Before use, the treated cellulose was crushed in a mortar and then put into a column up to the required height; the voids were eliminated by carefully pressing the bed with a glass rod.

The columns, which were fitted at the bottom with a fritted glass disk to retain the powder, had a cross-section area of 1 cm<sup>2</sup>.

*Chemical separations*

A number of chemical systems were selected to test the behaviour of the tri-*n*-octylamine-cellulose (TOAC) powder that had been prepared as described in the preceding section. The experimental conditions and results are reported below.

*Separation of Fe<sup>3+</sup>-Co<sup>2+</sup>-Ni<sup>2+</sup>*

The adsorption curves of anionic resins reported by KRAUS AND NELSON<sup>3</sup> show that nickel does not form anionic complexes in 8 *M* HCl ( $D_v = 0$ ), whereas iron and cobalt are highly complexed ( $D_v$  about 10,000 and about 100, respectively). Iron is still complexed in 3 *M* HCl ( $D_v$  about 100) while cobalt is not ( $D_v < 1$ ). Descending chromatography with tri-*n*-octylamine-treated paper and 4 *M* HCl as the eluent, had shown how these elements would behave<sup>1</sup>; in fact, the  $R_F$  values obtained were 0, 0.5 and 0.97 for iron, cobalt and nickel respectively. The same principle can be applied for the separation of appreciable amounts of the elements, as shown by the column experiments with cellulose powder.

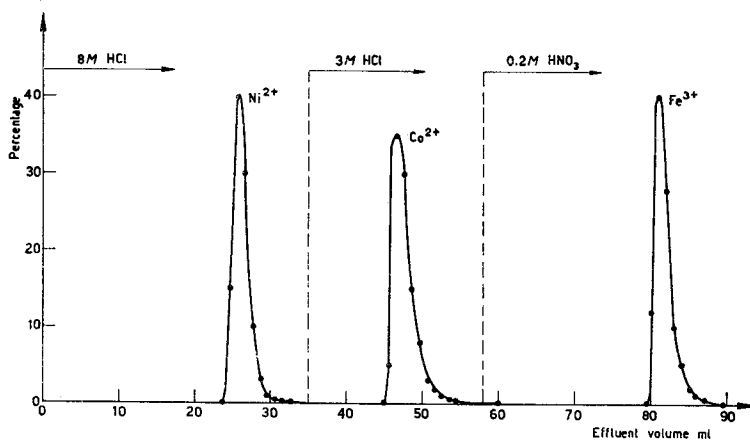


Fig. 1. Separation of Ni-Co-Fe (5 mg of each element). Percentage of initial amount detected in the effluent vs. effluent volume. Bed: 25 cm × 1 cm<sup>2</sup>; elution rate 0.2 ml/min.cm<sup>2</sup>.

The TNOA solution used for the treatment of the cellulose powder was pre-equilibrated with 8 *M* HCl and the same acid was used for conditioning the TOAC in the column itself. The cellulose bed was 25 cm high and the feed solution (2 ml of 8 *M* HCl) contained 5 mg of each element. As soon as the feed solution was completely adsorbed by the bed, elution with 8 *M* HCl, 0.2 ml/min, was started. Iron exhibited a yellow immobile band at the top of the bed, cobalt a pale green band which moved downwards very slowly, and nickel a green band which travelled with the eluent. After nickel had been completely collected, cobalt was eluted with 3 *M* HCl, and finally iron was removed from the bed with 0.2 *M* HNO<sub>3</sub>. The three elements were determined by spectrophotometry. The elution curve is reported in Fig. 1.

*Separation of Th-Zr-U<sup>6+</sup> in a hydrochloric acid medium*

The separation of Th, Zr and U<sup>6+</sup> in a hydrochloric acid medium is possible on the basis of the following considerations<sup>3</sup>: thorium is not complexed by HCl of whatever molarity, zirconium is not complexed by 6 M HCl ( $D_v < 1$ ), but is complexed by 10 M HCl ( $D_v$  about 1000) and uranium(VI) is complexed by 6 M as well 10 M HCl ( $D_v$  about 1000). For these reasons, 10 M HCl was used to pre-equilibrate the TNOA and the TOAC in the column. The bed height was 15 cm, and the feed solution (5 ml of 10 M HCl) contained Zr (13 mg) + U (5 mg) + Th (1 mg). Thorium was marked with <sup>234</sup>Th. During the elution with 10 M HCl to remove thorium, uranium gave a yellow band situated at the top portion of the bed. Zirconium was eluted with 6 M HCl and finally uranium with 0.05 M HNO<sub>3</sub>. The elution rate was 0.25 ml/min. In the eluted fractions thorium was determined by beta counting, zirconium by complexometry and uranium by spectrophotometry. The elution curve is shown in Fig. 2.

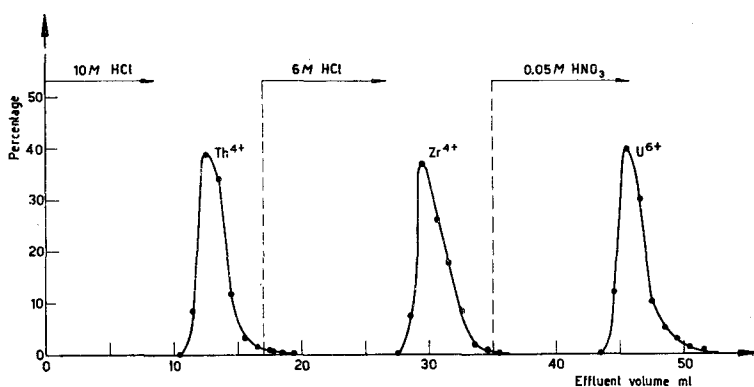


Fig. 2. Separation of Th (1 mg + <sup>234</sup>Th) - Zr (10 mg) - U (5 mg). Percentage of initial amount detected in the effluent vs. effluent volume. Bed: 15 cm × 1 cm<sup>2</sup>; elution rate 0.25 ml/min.cm<sup>2</sup>.

*Separation of Zr-U<sup>6+</sup>-Th with NH<sub>4</sub>NO<sub>3</sub>*

The separation of these three elements can also be obtained in a medium other than HCl. Sometimes it is necessary to separate small quantities of uranium and thorium from a large amount of zirconium. This is the case, for instance, when trace amounts of the former two elements have to be determined in zirconium ore, such as zircon, for geochemical or geochronological purposes. It is convenient therefore to use a procedure by which zirconium is not retained on the bed, whilst the two trace elements are retained. It has been reported<sup>2,4</sup> that 10 M NH<sub>4</sub>NO<sub>3</sub> forms complexes with uranium ( $D_v > 100$ ) and with thorium ( $D_v > 1000$ ), but not with zirconium. Furthermore, with 5 M HNO<sub>3</sub> thorium ( $D_v > 100$ ) is more complexed than uranium ( $D_v > 10$ ), so that a separation of these elements can be achieved. A 10 M solution of NH<sub>4</sub>NO<sub>3</sub> was used to equilibrate TNOA and TOAC.

After the feed solution has been deposited on the top of the bed washing with a 10 M NH<sub>4</sub>NO<sub>3</sub> solution must be carried out to remove zirconium. The overall proce-

ture is slightly different according to whether small or large amounts of zirconium are present.

The two cases are described below.

(a) *Small amount of zirconium.* At the top of a 12.5 cm high column, 5 ml of a 10 M  $\text{NH}_4\text{NO}_3$  solution containing U (5 mg), Zr (10 mg) and Th (1 mg marked with  $^{234}\text{Th}$ ) were deposited. Elution at 0.25 ml/min with 10 M  $\text{NH}_4\text{NO}_3$  was continued until the removal of zirconium was complete. Uranium was eluted with 6 M  $\text{HNO}_3$  and thorium with 8 M  $\text{HCl}$ . The elution plot is given in Fig. 3.

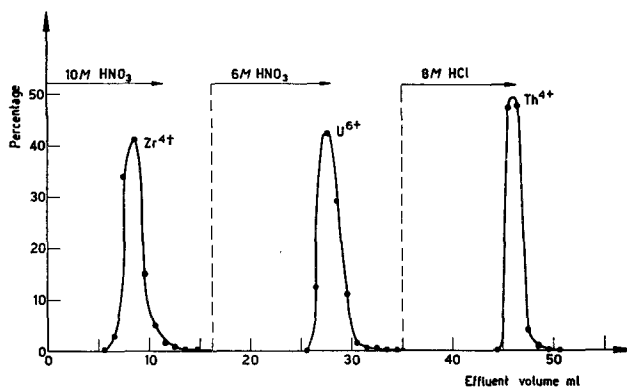


Fig. 3. Separation of Zr (10 mg) - U (5 mg) - Th (1 mg +  $^{234}\text{Th}$ ). Percentage of initial amount detected in the effluent vs. effluent volume. Bed: 12.5 cm  $\times$  1 cm<sup>2</sup>; elution rate 0.25 ml/min.cm<sup>2</sup>.

(b) *Large amount of zirconium.* To simulate the case in which traces of uranium and thorium must be determined in a zirconium ore, such as zircon, the following solution was prepared: Zr (500 mg which corresponds to about 1 g zircon), U (2 mg) and Th +  $^{234}\text{Th}$  (2 mg). Because of the relatively high content of zirconium, the feed solution could not be prepared in pure 10 M  $\text{NH}_4\text{NO}_3$ . It was possible, however, to obtain a solution by using 2 M  $\text{HNO}_3$  saturated with  $\text{NH}_4\text{NO}_3$ . This solution (10 ml) was fed to a 6 cm high bed and prolonged washing was carried out with 100 ml of 10 M  $\text{NH}_4\text{NO}_3$ . The washing with this solution is necessary to remove almost all the zirconium without contamination with uranium. After that, uranium was eluted with 50 ml of 6 M  $\text{HNO}_3$  and then thorium with 8 M  $\text{HCl}$ . The recovery of zirconium was about 96%, that of uranium 1.5% higher and that of thorium was 100%.

#### *Separation of $\text{U}^{6+}$ and Th from $\text{Ti}^{4+}$ and $\text{Fe}^{3+}$*

Another interesting case in the chemistry of some titanium ores is the determination of traces of uranium and thorium in ilmenite. Separation of  $\text{U}^{6+}$  and Th from the main constituents of the ore (Ti and Fe) can be achieved by following the procedure described for the separation of large amounts of zirconium from uranium and thorium. In fact neither titanium nor iron give nitrate complexes and therefore they are not retained by TOAC.

*Separation of La-U-Th*

It has been reported<sup>2,4</sup> that lanthanum is complexed to a certain extent by  $\text{NH}_4\text{NO}_3$ . Nevertheless, since uranium and thorium are more strongly complexed in 10 *M*  $\text{NH}_4\text{NO}_3$  and firmly retained by TOAC, lanthanum can be eluted first by prolonged washing with 10 *M*  $\text{NH}_4\text{NO}_3$ . The procedure is the same as for the separation of Zr-U-Th.

*Separation of Zr-La*

As mentioned above, lanthanum is slightly complexed by 10 *M*  $\text{NH}_4\text{NO}_3$ , and this can be exploited to separate this element from zirconium which is not complexed at all. To test the operating conditions, a feed solution was prepared containing La (5 mg) and Zr +  $^{95}\text{Zr}$  (2 mg) in 5 ml of 10 *M*  $\text{NH}_4\text{NO}_3$ . The feed solution was applied to the top of a 13 cm high bed and elution was started with 10 *M*  $\text{NH}_4\text{NO}_3$  at 0.2 ml/min. After about one column volume, zirconium began to be collected in the eluted liquid and, immediately after zirconium had been completely eliminated, lanthanum appeared and was present for about three column volumes. While zirconium was determined by beta counting of  $^{95}\text{Zr}$ , lanthanum was evaluated by complexometry. As shown in Fig. 4, zirconium presents a narrow peak, and lanthanum a flat elution

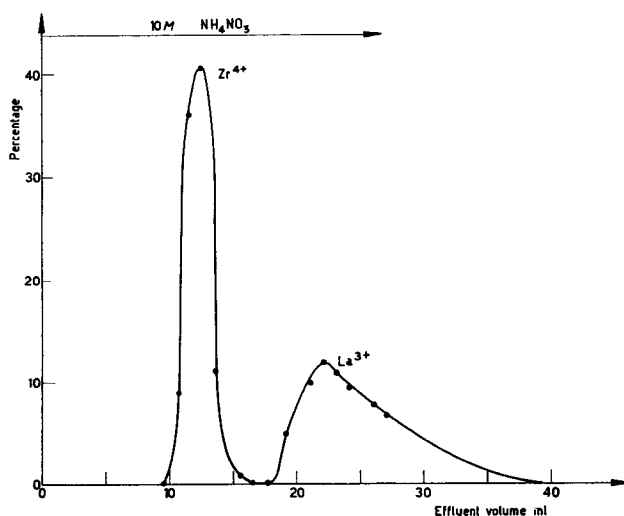


Fig. 4. Separation of Zr (2 mg +  $^{95}\text{Zr}$ )-La (5 mg). Percentage of initial amount detected in the effluent vs. effluent volume. Bed: 13 cm  $\times$  1 cm<sup>2</sup>; elution rate 0.2 ml/min.cm<sup>2</sup>.

curve. To speed up the removal of lanthanum, as soon as the collection of zirconium is completed the elution can be carried out with  $\text{HNO}_3$  or  $\text{HCl}$ .

The conditions reported in the last two examples can be successfully applied to the separation of the four elements Zr, La, U and Th, namely by using sequential elution with 10 *M*  $\text{NH}_4\text{NO}_3$ , 6 *M*  $\text{HNO}_3$ , and 8 *M*  $\text{HCl}$ .

### Separation of Zr-Hf

In spite of their chemical similarity, zirconium and hafnium have been easily separated from their mixtures by means of solvent extraction with TNOA in a hydrochloric-nitrate medium<sup>5</sup>. The extraction coefficient  $E_a^\circ$  is larger than 2 for zirconium and smaller than 0.01 for hafnium. The same hydrochloric-nitrate medium was also used in the paper chromatography with a TNOA-treated paper<sup>1</sup>, the  $R_F$  values being 0.25 for zirconium and 0.80 for hafnium. From the present experiment it appears that a good separation can be obtained also by using a TOAC column. In this case the TNOA solution used for the treatment of the cellulose powder, as well as the TOAC powder placed in the column, were pre-equilibrated with 8 M HCl mixed with 5% (vol.) of conc.  $\text{HNO}_3$ . The feed solution contained Zr (10 mg) and 3% (mol.) of Hf marked with  $^{181}\text{Hf}$ . After the feed solution had been adsorbed by the column (bed height 30 cm), elution with 8 M HCl + 5% conc.  $\text{HNO}_3$  was started at 0.2 ml/min. As the elution curve (Fig. 5) shows, hafnium, which was determined by beta

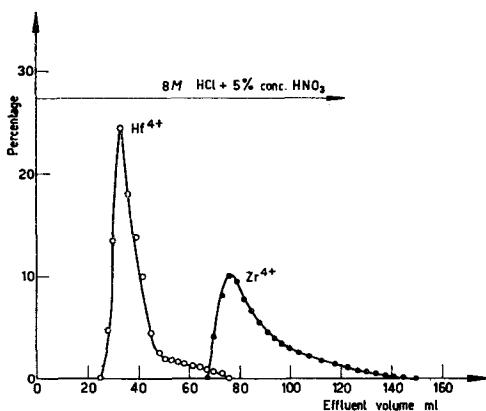


Fig. 5. Separation of Hf (0.3 mg)-Zr (9.7 mg). Percentage of initial amount detected in the effluent vs. effluent volume. Bed: 30 cm  $\times$  1 cm<sup>2</sup>; elution rate 0.2 ml/min.cm<sup>2</sup>.

counting, appeared in the effluent after about one column volume and was removed very rapidly, while zirconium, which was determined by complexometry, presented a less pronounced peak. The shape of the elution curve is very similar to that obtained with Dowex 2 and 9 M HCl by HUFFMAN *et al.*<sup>6</sup>. The elution of zirconium can be accelerated by using  $\text{HNO}_3$  as the eluent, after hafnium has been completely removed.

### Evaluation of the exchange capacity of TOAC

By treating the cellulose powder with TNOA solutions of different concentrations, some samples of TOAC with different exchange capacities were obtained. The exchange capacity was determined by allowing a 0.1 M HCl solution to flow through a 12.5 cm high bed (1 cm<sup>2</sup> cross-section), at 0.3 to 0.4 ml/min. The number of equivalents of HCl retained by the bed was estimated by determining the acidity of the effluent by titration with 0.1 M NaOH.

The results are collected in Table I, where the exchange capacity, in mequiv. per ml wet TOAC, are reported in comparison with the molarity of TNOA (0.05 to 1 *M*) used in the treatment of the cellulose powder. The TOAC prepared with TNOA up to 0.5 *M* revealed a very good stability with 0.1 *M* HCl, and no amine was removed from the column by the acid. The TOAC prepared with 1 *M* TNOA showed an excess of amine and a certain amount of this was removed by the acid.

TABLE I

EXCHANGE CAPACITY OF TOAC AS A FUNCTION OF THE MOLARITY OF TNOA IN THE SOLUTION USED FOR TREATMENT OF THE POWDER

Bed cross-section 1 cm<sup>2</sup>, height 12.5 cm, flow rate 0.4 ml/min.

Exchange capacity mequiv./ml (wet material)	TNOA molarity (treatment solution)
0.030	0.05
0.045	0.10
0.130	0.25
0.210	0.50
0.280*	1.00

\* Determined by saturation with  $(\text{UO}_2\text{Cl}_4)^{2-}$ .

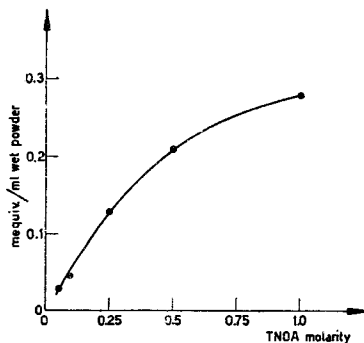


Fig. 6. Capacity of the cellulose bed (mequiv./ml wet powder) as a function of the molarity of the TNOA solution used in the treatment of the cellulose powder.

To check the values of the exchange capacity, the TOAC treated with 0.5 *M* TNOA was also investigated by saturating the bed with an 8 *M* HCl solution containing uranium. In view of the fact that the complex  $(\text{TNOA})_2\text{UO}_2\text{Cl}_4$  is formed, the result is identical to that obtained with 0.1 *M* HCl. The exchange capacity of the TOAC treated with 1 *M* TNOA was only determined with the uranium solution. In both these latter cases the bed was pre-equilibrated with 20 ml of 8 *M* HCl and then treated with a solution containing 12 mg/ml of uranium in 8 *M* HCl. The flow rate of the solutions was kept at 0.4 ml/min. The uranium capacity of the wet TOAC is 24 mg U/ml and 33.6 mg U/ml respectively for the 0.5 *M* TNOA type and for the 1 *M* type.

Because the common anionic resins exhibit an exchange capacity of about 1 mequiv./ml (wet resin), the results obtained with saturated TOAC are approximately 3 or 4 times lower.

For purposes of comparison with the aminated cellulose powders, Whatman diethylaminoethyl-cellulose (DEAE) was selected. DEAE is a commercial type of aminated cellulose, widely used for the chromatographic separation of amino acids, proteins, enzymes nucleic acids and hormones<sup>7,8</sup>. The exchange capacity, according to the suppliers, is 0.3 mequiv./ml, but this material did not prove very suitable for the retentions of uranium. In fact, when DEAE was pre-equilibrated with 20 ml of 8 M HCl, a brown zone formed in the bed which travelled rapidly with the front. The effluent was contaminated by organic substances and the uranium capacity of the wet DEAE proved to be 20.8 mg U/ml (about 0.17 mequiv./ml). Furthermore, uranium is much less strongly retained by DEAE than by TOAC. In fact, 8 M HCl completely removed uranium from DEAE by elution with less than two column volumes, while with TOAC the release was slight and very slow. The results are summarized in Table II.

TABLE II  
COMPARISON OF TOAC WITH DEAE AS REGARDS RETENTION OF URANIUM  
FROM HYDROCHLORIC SOLUTIONS.

	<i>Theoretical mequiv./ml</i>	<i>U fixed mg/ml</i>	<i>Exchange capacity (exp.) mequiv./ml</i>	<i>U release with 8 M HCl</i>
TOAC	—	33.6	0.28	very slow
DEAE	0.30	20.8	0.17	fast

#### CONCLUSIONS

From the experiments reported above it follows that good separations of many elements can be achieved by using TOAC columns instead of the common anionic resins.

Though TOAC has an exchange capacity that is three or four times lower than that of the common anionic resins, some advantages of TOAC can be pointed out. The main advantages are:

(1) Owing to the white colour of the TOAC powder, the position and the movement of coloured zones can be followed in the case of elements that form coloured bands in the bed.

(2) Since the active functional groups are concentrated at the surface of the powder grains, and the grain size is very small, TOAC has a high ability to fix also large molecules, which often cannot penetrate the complex structure of anionic resins.

(3) TOAC generally gives very narrow elution peaks and exhibits an exchange rate higher than that achieved with resins. Furthermore, TOAC can be successfully used in inorganic systems where elements that form anionic complexes must be sepa-



rated in inorganic acids of high concentration. In fact, unlike DEAE, TOAC is very stable also in HCl 8 to 10 *M* and in HNO<sub>3</sub> 5 to 7 *M*.

When required, TOAC can be easily regenerated and transformed into different forms with various acids.

(4) When working with radioactive tracers, a further advantage of TOAC powder is that it can easily be burned and the residue can be conveniently mounted in a source for radioactive counting. Obviously, this advantage is common to all the cellulose products, whereas the resins are less easily burned.

#### SUMMARY

A method is described for the preparation of tri-*n*-octylamine-cellulose (TOAC). A column of this substance behaves like an anionic resin column and permits the separation of many chemical elements. The following separations are given as examples: Fe-Co-Ni, U-Th-La, U-Th-Zr, La-Zr and Zr-Hf. The exchange capacity was evaluated and found to be three to four times lower than that of the common anionic resins. Some advantages are also indicated. TOAC was compared with Whatman's diethylaminoethyl-cellulose DEAE, as regards the retention of uranium from a very acid solution.

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