# STUDIES ON ACTINIDE PARTITIONING OF HIGH LEVEL WASTE SOLUTIONS AT THE FORSCUNGSZENTRUM JÜLICH

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## ABSTRACT

Twin column chromatography is introduced as a new technique for decontaminating aqueous solutions. The separation unit is operated in the front chromatographic mode and consists of two identical columns arranged in series with a detector placed between them. According to theoretical considerations, the effluent concentrations of the two columns are unchangeably correlated to each other at well defined effluent volumes. These considerations have been experimentally verified, and twin column chromatography is used to decontaminate artificial solutions from all actinides present in HLW solutions in one single step.

### INTRODUCTION

Partitioning of high level radioactive waste (HLW) is now under discussion as an alternative to conventional nuclear waste management concepts (1). This strategy aims at reducing the long-term hazard potential of waste repositories and provides for a fractionation of the HLW into long-lived and short-lived radionuclides. The short-lived nuclides are to be subjected to the usual treatment, i.e. immobilization in a stable matrix and final disposal, while those compounds with long-lived isotopes shall be either stored in extremely safe geological formations or incinerated in nuclear reactors.

Before this concept can be accepted for implementation, it must be carefully examined with respect to the expected costs, the potential risks and the resulting benefits. Such an assessment has to be based not only on experimental data from pure research, but also on technical scale tests of the relevant partitioning processes.

Most likely, countercurrent solvent extraction will be the chosen technique for isolating the actinides from HLW streams. However, by employing this technique in our research work, we are confronted with a number of problems that exceed by far the financial capacity of a research institute:

Suitable solvents like substituted carbamoyl phosphonate (2), carbamoyl phosphine oxide (3) or bifunctional diamide extractants (4) are extremely expensive, derivatives of dithiophosphinic acid (5) are not even available in the required quality or have to be completely synthesized (6). This conflicts with the rather high solvent consumption of continuous extractors.

The continuous mode of operating the extractors requires shift or at least overtime work multiplying the operational costs by a factor of ~ 3 (including health physics and medical services)

The radioactivity in the large volumes of feed solution and process end streams can only be handled by applying non-routine safety measures, even if simulated fission products are used.

Therefore, we sought for an alternative technique which can be scaled down further than continuous liquid-liquid extraction, which can be operated batchwise on a technical scale and is still sufficiently related to the liquid-liquid extraction systems to be investigated. We found that solid phase extraction would best comply with the above conditions when it is operated in the front chromatographic mode. We can use the same solvents, but reduce the annual amount needed by more than an order of magnitude. The safety measures of an isotope laboratory suffice, as the process streams volumes are minimized, and the front chromatographic mode allows a bench scale plant to be operated by processing a batch within a working day.

We set up a partitioning unit for testing a variety of chemical systems with daily throughputs varying between 0.1 l/d and 5 l/d. In this paper, we report on the technical features of this unit and illustrate its operation choosing as an example the isolation of all actinides present in HLW solutions, namely Np, Am, Cm and the non-recovered portions of U and Pu from an artificial solution in a single step

## FRONT CHROMATOGRAPHIC PARTITIONING

Front chromatography is a mode of operating a chromatographic column which was first described by Tiselius (7) in 1943, but has not yet found broad technical application apart from water desalination by ion chromatography. Therefore, the principles of this mode will be briefly described, as the functioning of the partitioning unit is largely based on the theory of front chromatography respectively on the deviations we noted during our preliminary experiments.

### Principles of Front Chromatography

A chromatographic column is operated in the front mode by permanently conveying feed solution through the column, until a breakthrough of the solute of interest is observed in the column effluent. The resulting chromatogram shows an S-shaped concentration course in the effluent until the original concentration of the feed solution is obtained. The entire chromatogram is depicted in Figure 1 using data from a Cm-244 separation on Amberchrom 71 C™ carrying 60 wt% of a 0.32 M CMPO/l TBP solution (CMPO ≡ n-octyl phenyl carbamoyl N,N diisobutyl methyl phosphine oxide, TBP ≡ triisobutyl phosphate). The Cm-244 concentration in feed and effluent is expressed as the corresponding specific activities $\bullet_{Feed}$ and $\bullet$.

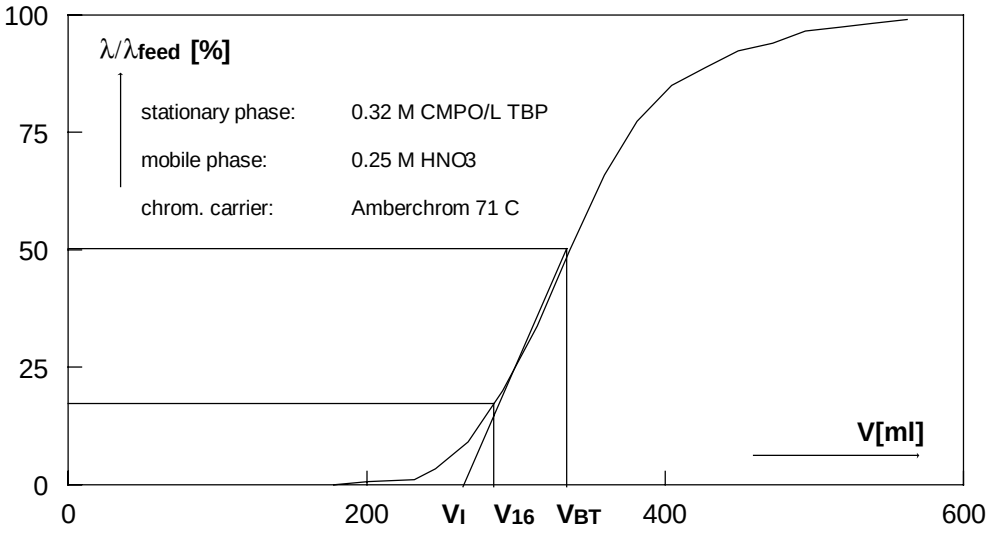


**Figure 1: Front Chromatogram of a Cm-244 Separation (λ ≡ spec. activity)**

Employing this operational mode to solutions with various solutes, we obtain a chromatogram composed of breakthrough curves that are piled up on each other. This is illustrated in Figure 2 showing a separation of Sr-90, Y-90 and Cm-244 in 0.2 M $HNO_3$ on the same chromatographic carrier as in Figure 1, but impregnated with 0.65 M CMPO/l TBP.

Sr-90 is not retained by the chromatographic support and appears in the column effluent after the void volume $V_V$ (total volume composed of tubing and interstitial column volume) has passed the column. Y-90 has a short retention time and follows almost immediately. Cm-244 is strongly extracted into the organic phase and appears last in the chromatogram. Again, the specific activity was used for the isotope detection and was measured with an on-line solid scintillation counting device (8).

In contrast to elution chromatography, an isolation of individual solutes cannot be attained by applying front chromatography to a separation. This mode is suited to fractionate feed solution into groups of solutes with similar properties, e.g. poisonous - non-poisonous compounds, radioactive - non-radioactive nuclides, fission products - actinides, lanthanides - actinides etc., provided an adequate chemical separation system (feed solution + chromatographic support) is available.

In principle, we can define two fields of technical applications for front chromatography:

*Purification of Solutes*, the chromatographic column is loaded to saturation and the effluent concentration of the solute equals the feed concentration (9). The column is washed in a 2nd step and the purified solute eluted in a 3rd. The resulting solution is the product of the process.

*Decontamination of Solutions,* the chromatographic column is loaded up to the very first detectable breakthrough of the solute. The effluent solution up to this point constitutes the product of the process. The column is then scrubbed and stripped of the contaminating solutes which are then disposed off.

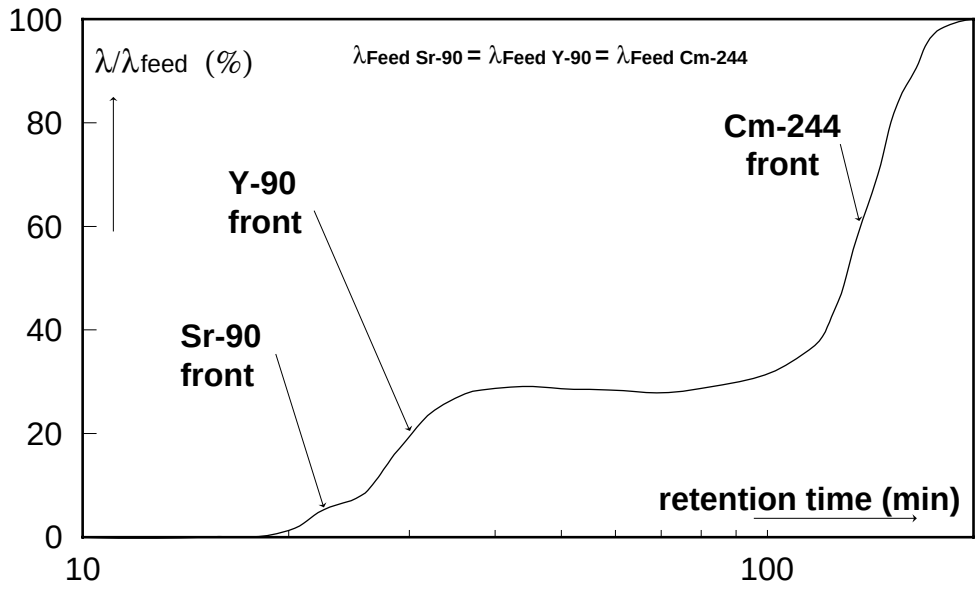


**Figure 2: Front Chromatogram of a Sr-90/Y-90/Cm-244 Separation**

We understand HLW partitioning as a decontamination process and will thus focus in the following on the latter application.

**FEATURES OF A FRONT CHROMATOGRAPHIC DECONTAMINATION**

Chromatographic techniques do not work in equilibrated states, regardless of the mode of operation employed. Their use is always connected with a detecting device. In front chromatography, the quality of the decontamination depends on the detection limits for the polluting solute. Conceiving the chromatogram in Figure 2 as a process for decontaminating a solution from α–emitters, the specific activities of the Sr/Y-90 couple in the feed form the background for the detection of Cm-244 and thus impair the corresponding detection limits. In real HLW solutions, the Sr/Y-90 activity exceeds that of Cm-244 by 2 orders of magnitude, and the Cm-244 breakthrough would be noted only at an activity detrimental to the desired decontamination.

We tried to overcome this problem by comparing real chromatograms as in Figure 1 with the corresponding theoretical values. Glückauf (10) described such curves using the cumulative standardized normal distribution function (error function) (Equation 1):

$$\frac{c}{c_{Feed}} = (2\pi)^{-0.5} \int_{-\infty}^{t} e^{-t^2/2}\, dt \equiv \mathrm{erf}[t] \qquad \text{(Eq.1)}$$

with the argument according to Equation 2:

$$t^2 = N \frac{(V - V_{BT})^2}{V\, V_{BT}} \qquad \text{(Eq.2)}$$

| | |
|---|---|
| c | concentration |
| V | effluent volume |
| $V_{BT}$ | breakthrough volume (at $c = c_{Feed}/2$), inflection point of the curve |
| N | number of theoretical plates |

Equation 2 is used for calculating the number of theoretical plates N at an effluent concentration rate of 16 % ($V_{16}$) corresponding to a $t^2$ value equal to 1. We obtained, however, more reproducible results using the 1st derivative of Equation 1 (11):

$$N = \frac{V_{BT}V_{16}}{(V_{BT} - V_{16})^2} = \frac{\pi}{2}\frac{V_{BT}^2}{(V_{BT} - V_I)^2} \qquad \text{(Eq.3)}$$

$V_I$ intercept of the tangent at $V_{BT}$ with the V axis (see Figure 1)

The slope of the curve depends on the linear flow velocity, the inflection point at the breakthrough volume $V_{BT}$ remains unchanged, i.e. a series of curves recorded at varying flow velocities has the same inflection point, if acquired with the same chemical system. The breakthrough volume is a measure of the distribution coefficient $K_D$ and fits the equation:

$$V_{BT} = K_D V_o \qquad \text{(Eq.4)}$$

$V_o$ stationary phase volume

We calculated N from the chromatogram in Figure 1 and established the theoretical curve with that value. We found the expected deviations from the real curve at high solute concentrations ($V > V_{BT}$) which are due to packing inhomogeneities already outlined and experimentally verified (12,13). These deviations would not adversely affect a front chromatographic decontamination process, as it would have been terminated long before they occur. However, we also noted deviations at low effluent concentrations ($V << V_{BT}$) the causes of which have so far not been described. By evaluating a number of chromatograms (11) we concluded that a prerun most likely takes place during column operation which we ascribed to the lower amount of stationary phase in the column channels between column wall and adjacent particle bed. We assumed that the size of the relevant channels depends on the column (D) and the particle (d) diameter and the stationary phase volume is half as great as in the channels of the bed interior, but that the mass transfer between the phases still follows Equation 1. With these presuppositions, we established the equation:

$$\frac{c_{Effluent}}{c_{Feed}} = \underbrace{\frac{2d}{D}[\text{erf}(w)]}_{\textit{wall fraction}} + \underbrace{\left(1 - \frac{2d}{D}\right)[\text{erf}(i)]}_{\textit{interior fraction}} \qquad \text{(Eq.5)}$$

Either fraction is presumed to have an inflection point, the corresponding breakthrough volume of which is derived from arguments w and i:

$$w^2 = N_w\frac{(V_{BT\,w} - V)^2}{V_{BT\,w}\,V} \qquad \text{(Eq.6a)}$$

$$i^2 = N_i\frac{(V_{BT\,i} - V)^2}{V_{BT\,i}\,V} \qquad \text{(Eq.6b)}$$

We have so far not found a relation between $N_w$ and $N_i$, but we derive that $V_{BT\,w} = 0.5\ V_{BT\,i}$ considering the reduced stationary phase volume in the wall channels, and for a sufficiently great ratio of D/d we can assume that $N_i \approx N$ and $V_{BTi} \approx V_{BT}$, the values of the real chromatogram. According to Equation 5, the effluent concentration at the $V_{BT\,w}$ should be:

$$c_{Effluent}\ (V = V_{BT\,w}) \quad = \quad (d/D)\ c_{Feed} \qquad \text{(Eq.7)}$$

i.e. in routine column operations with ratios D/d > 200 below 0.5 % of the feed concentration and, hence, in many cases below the detection limits of commercially available on-line detectors.

The Twin Column Concept

The breakthrough volume $V_{BT\,w}$ of the prerun has properties similar to $V_{BT}$, i.e. it is independent of the flow velocity. Due to the corresponding low effluent concentration, it would be an ideal point for terminating the decontamination run. Unfortunately, it can be only determined indirectly by measuring $V_{BT}$, when the effluent is already significantly contaminated by the solute.

We overcame that difficulty by establishing the twin column concept (Figure 3) with the following main features:

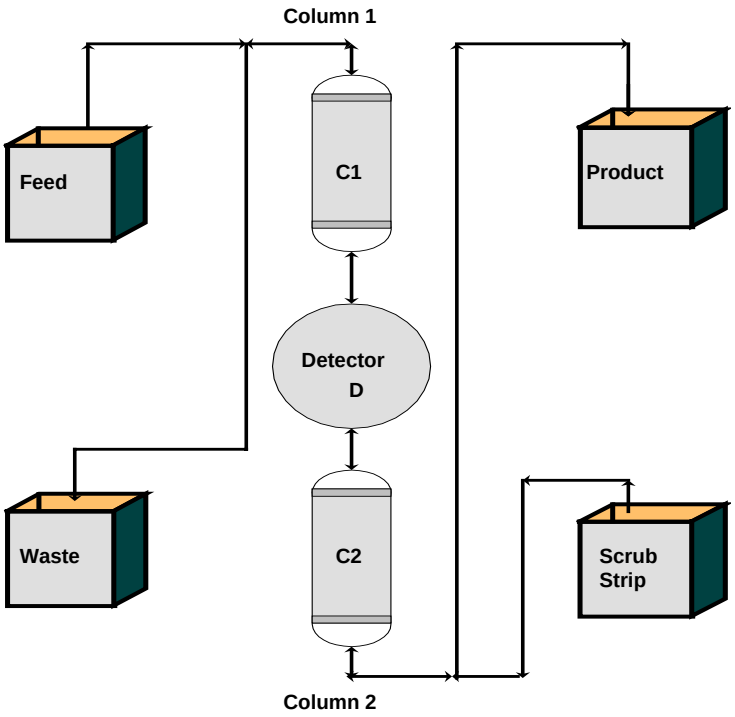


**Figure 3: Scheme of the Twin Column Concept (Loading Step)**

- The column is divided into two identical parts, i.e. the entire chromatographic support is accommodated in two identical columns.
- During column loading, an on-line detector is placed between the two columns monitoring the 1st column effluent.
- Column scrubbing and stripping is carried out by applying a countercurrent flow.
- The detector remains between the columns during scrubbing (optional), but is switched behind column 1 during stripping (mandatory).

With that array, we can load the column unit, until we measure 50 % of the feed concentration in the effluent of column 1. At that point, the volume $V_{BT\,1}$ has passed the column, and according to the concept, this volume equals $V_{BT\,w}$ of the entire column set. To this volume, we assign the term breakoff volume $V_{BO}$.

Scrubbing the columns serves to displace the non-retained components of the feed solution in the mobile phase. The extracted solutes are normally not affected by that process stage, and the columns, though loaded differently, can still be considered identical. Therefore, the detector may remain between the two columns. The different column loading appears to be significant, when the retained solutes are stripped. A proper monitoring of that stage can only be accomplished, if the detector is placed behind column 1, since it is the 2$^{nd}$ column during stripping due to the countercurrent flow.

We apply a reversed flow to the scrubbing and stripping stages to avoid contamination of the tubings behind column 2 and to counteract a potentially incomplete solute elution, as those solute portions would gather at the top of column 1 during stripping and be immediately reextracted during the next run

The Partitioning Unit

Based on the principles of the twin column concept, we built up a partitioning unit the schematic drawing of which is depicted in Figure 4. In detail, the unit consists of a number of components listed below which are connected via a complex valve system:

- two supply tanks for feed and scrub/strip (we decided to use the same solution for these process stages in our test partitioning), and two removal tanks for the product (decontaminated waste solution) and the eluted solutes
- two pump loops each consisting of a membrane pump, a no return valve and a flow rate meter,
- two partitioning columns of identical size,
- the detector loop comprising the analytical column and the detector. The analytical column has a much smaller capacity than the other two and serves to characterize the feed solution.

With this unit, we can carry out the following process stages:

Feed Assay

**feed tank - P1 - V8 - V13 - V10 - Ca - V11 - D - V12 - V5 - feed tank**

The feed assay serves to determine the detector's background and maximum response to a solute. The detector may react to several feed components. In such cases, the feed solution has to be fractionated on the analytical column Ca. The feed assay could ,of course, be carried out off-line, however, we prefer to use the same detector for feed assay and process control, as this allows us to calibrate the detector prior to each run. After measurement the feed solution is directed back to the feed tank to avoid additional waste.

Detector Scrub

**scrub tank - P2 - V8 - V13 - V10 - V11 - D - V12 - V5 - feed tank**

The detector loop must be cleaned before it can be used for further process control. The scrub solution displaces the feed in the loops which is conveyed to the feed tank. The stage is terminated when the detector signal reaches background. During that stage, the analytical column is bypassed to avoid an undue dilution of the feed.

Loading

**feed tank - P1 - V1 - V2 - C1 - V7 - V13 - V10 - V11 - D - V112 - V3 - V4 - C2 - V9 - V6 - decont. waste**

The columns are loaded in accordance with the principles of the twin column concept. Thus, the solution leaving C2 is practically free of contamination and will not pollute the tubing system behind the column

Scrubbing

**scrub tank - P2 - V9 - C2 - V4 - V3 - V7 - C1 - V2 - V1 - V8 . V13 - V10 - Ca - V11 - D - V12 - V5 - feed tank**

Countercurrent flow is applied for scrubbing the unit to keep the system behind C2 free of contamination. The scrub solution ends up in the feed tank as it is basically a depleted feed solution. We chose to place the detector behind C1 in order to get a direct signal for terminating this process stage. The analytical column Ca is included in the scrub loop.

Stripping

**strip tank . P2 - V9 - C2 - V4 - V3 - V7 - C1 - V2 - V1 - V8 - V13 - V10 - Ca - V11 - D - V12 - V5 - eluate tank**

Stripping the system serves to remove the solutes from the columns. It follows the scrub loop up to valve V5, where the solution is directed to the eluate tank. Normally, we use the same solution for scrubbing and stripping the columns. The beginning of stripping is indicated by a drastic increase of the detection signal.

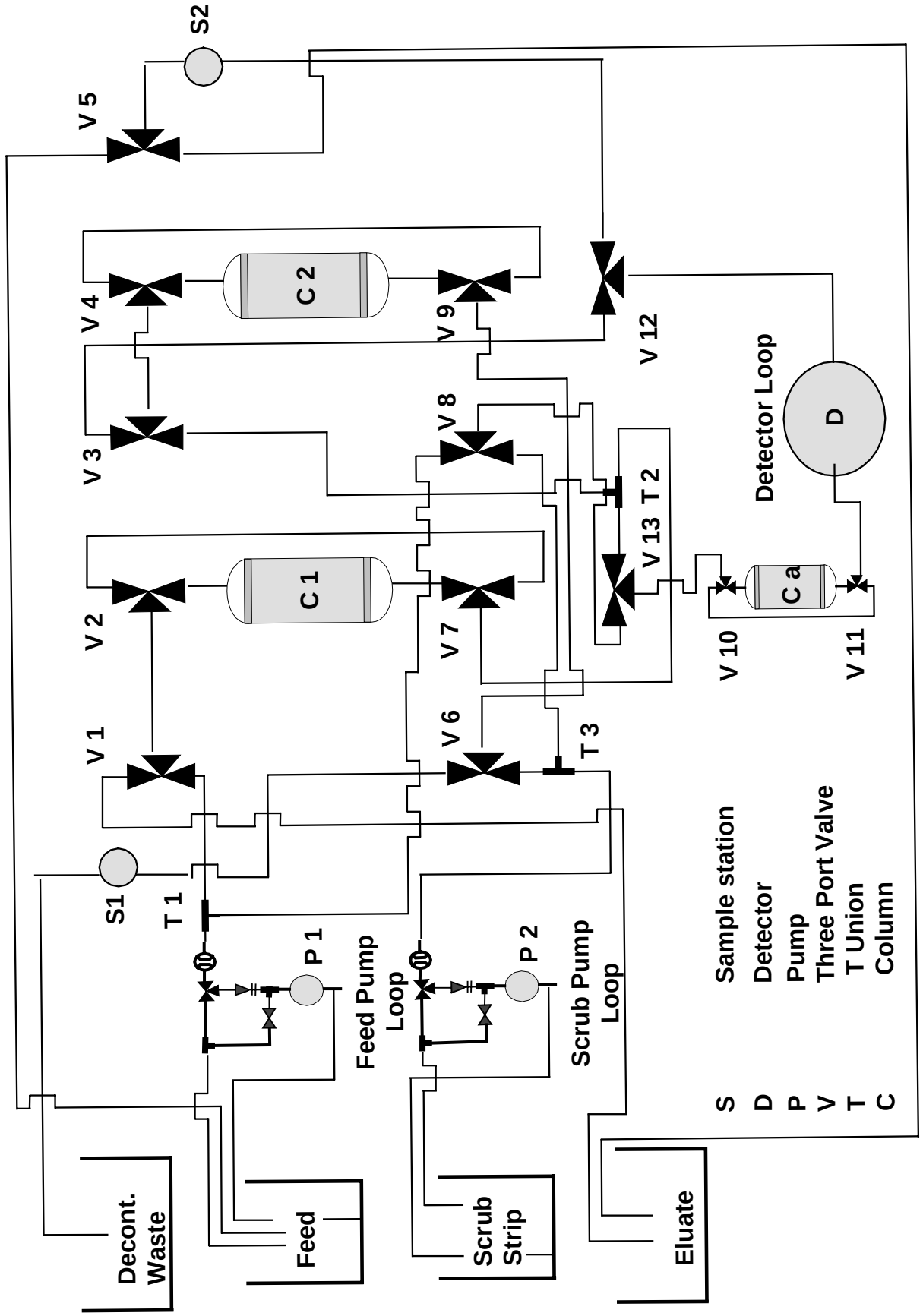


**Figure 4: Schematic Drawing of the Twin Column Unit**

## OPERATION OF THE PARTITIONING UNIT

We envisaged two goals in our experimental work as described below:

1) Verification of the twin column concept
2) Test of the partitioning unit

We pursued either objective within the framework of our HLW partitioning studies. We used the extraction system CMPO/$HNO_3$ well known (14,15) in this area and with actinide distribution coefficients that have already been published (see Figure 5).

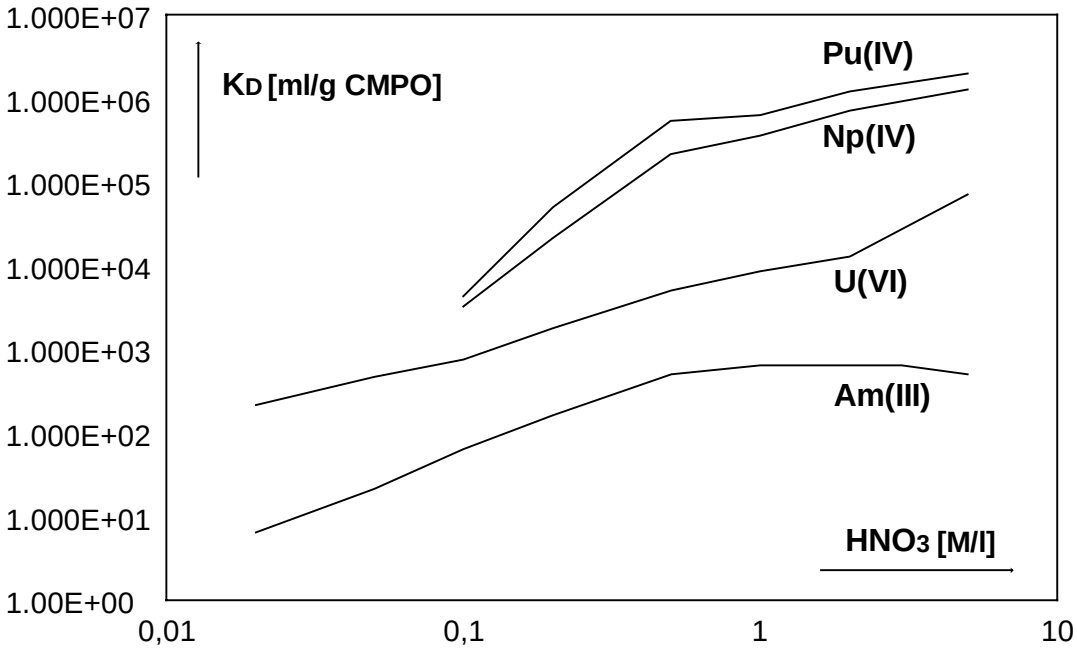


**Figure 5: Actinide Distribution Coefficients for the System CMPO/$HNO_3$**

Experimental

As commercial components for our unit, we used membrane pumps from LEWA, Leonberg, Germany, fittings from SAGELOK and PFA tubings from DUPONT (distributed by B.E.S.T., Bornheim, Germany), and the radioactivity monitor LB 508 C, BERTHOLD, Bad Wildbach, Germany, equipped with a handmade, $\alpha$–selective solid scintillation detector (8). The columns were machined in the institute's workshop, the supply and collecting vessels were conventional labware that happened to be available.

We procured CMPO from ELF/ATOCHEM, the resin AMBERCHROM 70 C was supplied by SUPELCO; Deisenhofen, Germany. All other chemicals were purchased in p.a. quality from MERCK; Darmstadt, Germany.

Radioisotopes were acquired from ISOTOPENDIENST, Waldburg, Germany. Np-239 was separated from an Am-243-solution by extracting Am into a CMPO/Amberchrom resin.

We prepared the chromatographic support by dissolving varying amounts ($6\ g \leq m\ CMPO \leq 36.6\ g$) of CMPO in ~ 100 ml TBP under heating and made up the cooled down solution to 150 ml with TBP. The resulting solution forms the stationary phase of the chromatographic support, it was diluted with 250 ml dodecane. 100 g Amberchrom 71 C were

suspended in the liquid under stirring until a homogeneous slurry developed. We evaporated $C_6H_{12}$ at room temperature and dried the coated resin at 60 $^oC$. The dried resin was sieved and the fractions with average particle diameters d of 110 μm and 140 μm were collected for further use.

We ensured a bubble-free column bed by slowly sucking water through the column outlet into the column. We evaporated the columns, until all air bubbles (mainly from the frits serving as column bed barriers) were removed. Then we opened the column head and displaced the water in the column with a slurry of coated resin in water. 1 g of coated resin yields 2 ml of column support.

Verification of the Twin Column Concept

We carried out a number of experiments to verify the theory of the twin column concept. We selected a Cm-244 separation as an example in this paper. We passed a solution of 0.1 M $HNO_3$/l containing 2000 Bq Cm-244/ml through the unit. We monitored the 1st column effluent with the detector and simultaneously took samples from the 2nd column effluent at the sample station S 1. We terminated the run shortly after the 1st column effluent activity reached 50 % of the feed solution activity.

For the graphical evaluation (Figure 6) of the breakthrough curves, we chose a Y2 axis (right ordinate) with a scaling for the concentration ratio corresponding to multiples of the particle/column diameter ratio d/D,

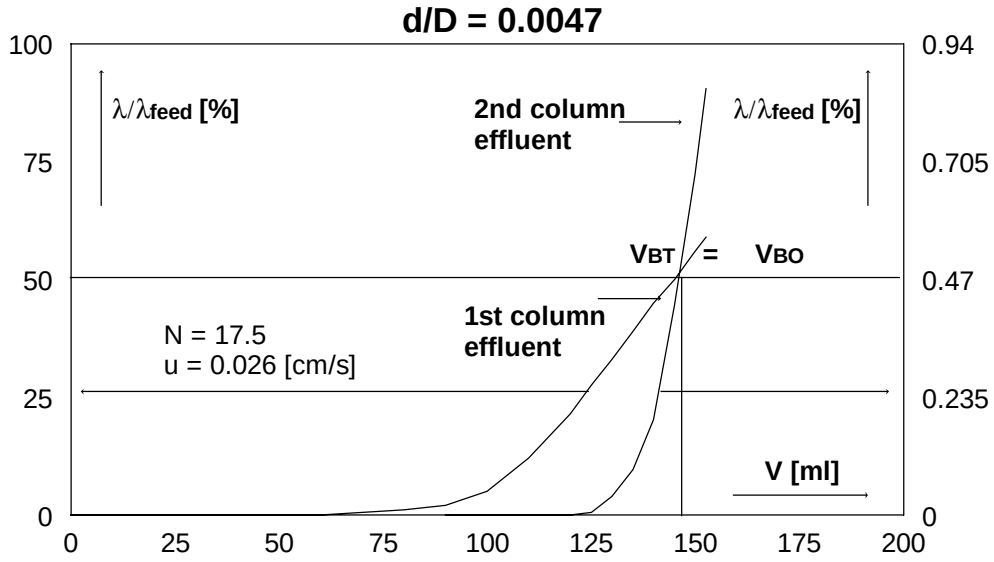


**Figure 6: Concentration Curves of the 1st and 2nd Column Effluent**

while the left ordinate shows the concentration ratio percentage. Under the chosen conditions, we obtain the intersection of the two curves at the breakthrough volume $V_{BT}$ determined for the 1st column effluent. In the 2nd column effluent, we found a concentration ratio of 0.47 % equal to the ratio of particle and column diameter, as predicted by our calculations. Thus, we can conclude that the entire concentration course of a front chromatogram can be described mathematically below the inflection point with the developed Equations 5 and 6.

Actinide Partitioning

According to Figure 5, the CMPO/$HNO_3$ system retains tri-, tetra-, and hexavalent actinides (An) in the range An(III) << An(VI) << An(IV), while An(V) are practically not extracted. In HLW solutions, Am and Cm are present in the trivalent, Pu in the tetravalent and U in the hexavalent state and thus extractable. For Np, however, the non-extractable pentavalent state prevails. Aiming at an actinide fraction, an HLW partitioning process is governed by two independent aspects:

1) the extraction behaviour of the trivalent actinides,
2) the stabilization of Np in an extractable state.

Stabilization of Np

In HLW (acidity ~ 2 M $HNO_3$), Np is stabilized in the pentavalent state by nitrous gases (16) which are produced by radiolysis. Oxidizing agents like $Ce^{4+}$ convert Np(V) to Np(VI), but also Pu(IV) to Pu(VI). Reducing agents like $Fe^{2+}$ or ascorbic acid ($C_6H_8O_6$) convert Np(V) to Np(IV) and Pu(IV) to Pu(III). Either method of stabilizing Np(IV) would impair the extractability of Pu, but not below that of Cm(III) and Am(III), so that the performance of the entire partitioning process would not be affected.

We chose ascorbic acid as a stabilizing agent, since it is decomposable and would not add to the final amount of solid waste. According to the equation:

$$2\ NpO_2^+ + C_6H_8O_6 + 6\ H^+ \Leftrightarrow 2\ Np^{4+} + C_6H_6O_6 + 4\ H_2O \qquad \text{(Eq.8)}$$

(*ascorbic acid*) (*dehydro ascorbic acid*)

this reaction takes place in strongly acidic media which may support the production of $NO_x$ thus impeding the reduction. Therefore, we added urea {0.1 M $CO(NH_2)_2$/M $HNO_3$} to the reaction vessel. We investigated the reduction at various $HNO_3$ concentrations using the feed assay loop including the analytical column of our unit. We conveyed the feed containing Np, ascorbic acid, urea and $HNO_3$ through the column, until the detector signal reached a constant value corresponding to the 100 % breakthrough of Np(V). Then we bypassed the column until we obtained the signal for the feed solution {Np(t)}. The difference of the two signals corresponds to Np(IV). The results are shown in Figure 7.

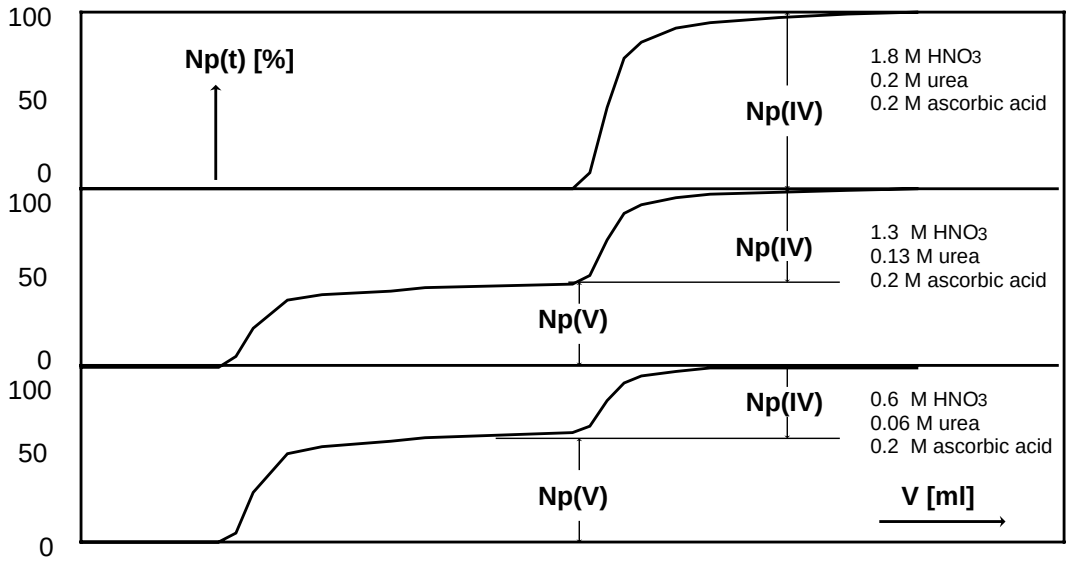


**Figure 7: Reduction of Np(V) with Ascorbic Acid in Various $HNO_3$ Concentrations**

Summarizing the results, we obtained a complete reduction at $HNO_3$ concentrations above 1.8 M/l, i.e. we do not need to adjust real HLW solutions.

Extraction Behaviour of Trivalent Actinides

The distribution coefficient of Am(III) in the CMPO/2 M $HNO_3$ system is reported to be 650 ml $g^{-1}$ CMPO (15). We collected the corresponding values for Cm(III) and Pu(III) from Figure 8 to be 500 ml $g^{-1}$ CMPO and 860 ml $g^{-1}$ . This front chromatogram was produced by conveying a feed solution through the feed assay loop with the analytical column carrying 7.8 g chromatographic support with 0.6 g CMPO. The feed consisted of a 2 M $HNO_3$ solution containing 0.2 M ascorbic acid and 500 Bq/ml Cm-244 and 1000 Bq/ml Pu-238.

Though the distribution coefficients of the two actinides are significantly distinct, we hardly identified any separated breakthrough curves. With Am added to the feed, any distinction would become negligible and one single breakthrough curve would appear. We thus cannot determine the feed concentration of the least extractable solute Cm(III), actually a prerequisite for employing the twin column concept. However, by conceiving the trivalent actinides as one single compound, twin column chromatography is still applicable; though the decontamination factor for Cm would decrease and we would measure a higher Cm-244 activity in our product solution. Nevertheless, this can be counteracted by increasing the column diameter.

Operation of the Unit

We operated the unit with pure actinide solutions containing Cm-244, Am-241, Np-239, Pu-238 and U-233 with a specific activity between 500 and 1000 Bq/ml for each isotope. We used twin columns having a diameter of 2.4 cm and a length of 10 cm, which each carried 23 g chromatographic support with 3.4 g CMPO. In one batch, we were able to decontaminate 2 l feed solution with a decontamination factor of ~ 3000, i.e. 2 Bq/ml.

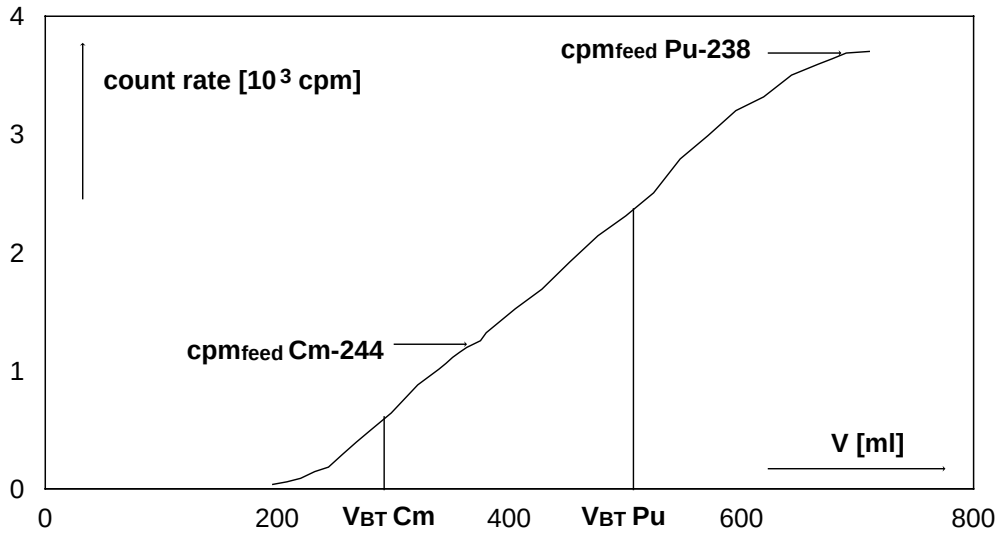


**Figure 8: Front Chromatogram of a Cm/Pu Separation**

We scrubbed and stripped the system with 0.1 M citric acid at a pH of 3. We needed one void volume for the scrub (~ 250 ml). During stripping, we observed a rather long tailing resulting in large eluate volumes. We reduced the volumes applying a batchwise stripping with an interval of 24 h.

After one year of operation, we have not noted a deterioration of the chromatographic support, though we had to empty and refill the columns several times at the beginning of our studies due to a malfunctioning of the partitioning unit.

## CONCLUSIONS

Within the framework of our studies on HLW partitioning, we looked for an alternative to liquid-liquid extraction in order to economize on the costs of our research and development program. We found that solid-liquid extraction operated in the front chromatographic mode can be built up to a bench scale unit which allows to investigate chemical systems on a technical scale.

We extended the theory on front chromatography by establishing and experimentally verifying mathematical approximations for those deviations which adversely affect the employment of this method for a decontamination of process solutions. Based on these approximations, we developed the twin column concept which allows process control below the detection limits of available monitoring systems.

We put the concept into operation by installing a partitioning unit which we tested by fractionating artificial actinide solutions. We decontaminated the solution from all actinides present in HLW in a single step by stabilizing Np in the tetravalent and Pu in the trivalent state with ascorbic acid.

We see a number of advantages in employing twin column chromatography in our research and development program:

1) The process is carried out batchwise, and we can choose the operational parameters such that one run is accomplished in one working day. Thus, costs for overtime and shiftwork do not arise.

2) Up to now, we have operated the unit for more than one year without changing the extractant. In that time, we processed approximately 100 l feed, we had to reload the columns several times with the same chromatographic support, but we did not notice any deterioration of the extraction capacity. In total, we consumed about 10 g of CMPO including the filling of the analytical column. This again increases savings in the costs of our investigations.
3) Switching to other chemical systems does not require significant modifications to the partitioning unit, but can be done simply by changing the columns.

We do, however, not claim that twin column chromatography will find a large field of industrial application in the main path of the nuclear fuel cycle. Principally, this technique will be restricted to research and development, but we anticipate a number of marginal problems in that area where this technique could be successfully employed, e.g. the decontamination of unusual process solutions of limited quantity or throughput, such as the treatment of wastes resulting from nuclear fuel analysis (17).

## REFERENCES

1) Z. Kolarik, report KfK 4945, (1991)
2) S.F.Marsh, S.L. Yarbro, report LA-11191 (1988)
3 E.P. Horwitz et al., Solvent Extr. Ion Exch. 3 (1985) 75
4) G. Thiollet, C. Musikas, Solvent Extr. Ion Exch. 7 (1989) 813
.5) Y.J Zhu, J. Chen, R. Jiao, Solvent Extr. Ion Exch. 14 (1996) 61
6) G. Modolo, R. Odoj, J. Alloys Compounds 271/73 (1998) 248
7) A. Tiselius, Ark. Kemi Mineral. Geol. 16a (1943) 1
8) U. Wenzel, W. Ullrich, M. Lochny, Nucl. Instr. Methods in Physics Research A, accepted for publication
9) D.A. Hill, P. Mace, D. Moore, J. Chromatogr. 523 (1990) 11
10) E. Glückauf, Trans. Faraday Soc. 51.1, (1955) 34
11) U. Wenzel, S. Deron, Solvent Extr. Ion Exchange 12 (1994) 789
12) J.H. Knox, R. Laird, P.A. Raven, J. Chromatogr. 122 (1976)129
13) T. Farkas, J.O. Chambers, G. Guiochon, J. Chromatogr. A 679 (1994) 231
14) E.P. Horwitz, R. Chiarizia, M.L. Dietz, H. Diamond, D. Nelson, Analyt. Chim. Acta 281 (1993) 361
15) Eichrom, Eichrom Ideas 4 (1997) 1
16) P. Feldhaus, Jül-3309 (1996)
17) U. Wenzel, Proc. 5th Int. Conf. Radioactive Waste Management and Environm. Remediation 2(1995)993