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Transportable frontal chromatographic unit for decontamination purposes based on the twin column concept

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Abstract

The design and operation of a separation unit based on frontal chromatography is described. The important feature of the design is the array column → detector → column which allows process monitoring below the detection limits of the monitor. By using "fraternal twin columns" an in-process calibration of the detector is achieved reducing the waste production. The design contains provisions for on-line destructive and non-destructive monitoring. Tests of the unit prove its versatility with respect to decontamination processes. Due to its compactness, the unit is transportable, if not portable, and the module construction allows easy posting and set-up in areas with restricted access. The unit is capable of processing up to 5 m^3 solution per year depending on the chemical system used.
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Keywords: Frontal chromatography; Twin column concept; Instrumentation

1. Introduction

Recently [1,2], we discussed frontal chromatographic separations with respect to their industrial-scale applicability. We identified a great potential for this mode of operating chromatographic columns for the decontamination of aqueous streams from hazardous trace compounds due to the innumerable chemical systems available. However, we also noted the deficiency in implementing this technique due to the lack of appropriate monitoring systems. To date, frontal chromatography has only been employed in a technical scale for the desalination of water [3] in combination with a conductivity measurement. Other processes were developed in the nuclear fuel cycle [4–6] for the simultaneous purification of and decontamination from Pu, but they could not meet the required specifications during the test phase. In our opinion, these processes failed because the bulk compound Pu was loaded onto the columns and the trace contaminants were not retained. Thus, the columns were operated beyond the range of the linear extraction isotherm and the concentration course in the column effluent became less predictable. Consequently, these processes depended on an accurate on-line monitoring at low effluent concentrations which was not feasible with the available detectors.

In our investigations, we pursued a different approach. We chose systems that sorbed only the trace contaminants, while the bulk compound passed the column. Thus, the entire chromatographic process was governed by the linear extraction isotherm. When we analyzed the low concentration region of the column effluent, we discovered a prerun which we ascribed to the solvent deficiency at the column wall [1,7]. We developed a model to mathematically describe the prerun assuming the same regularities as for the column main stream. We verified the model experimentally and showed that the entire concentration curve in the column effluent has two inflection points the volume and the concentration ratio of which depend only on the column/particle geometry [2] and are independent of the chemical system employed. The inflection point of the prerun would be an ideal point for terminating a chromatographic decontamination process, as its position is independent of flow velocity changes and its concentration varies between 0.1 and 1% of the feed concentration. As we restricted the application of frontal chromatography to the linear extraction isotherm region, this concentration amounts to $\leq 10^{-5}$ mol/L and the detection of the termination point by an on-line concentration

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measurement would be disguised in most cases by the monitoring background noise.

We overcame that problem by introducing the twin column concept [2]. We divided the column into two parts and set-up a separation unit consisting of the array "column 1 → detector → column 2". Thus, we could determine the second inflection point in the first column effluent ($c_{effluent}/c_{feed} \approx 0.5$) and with that value calculate the first inflection point of the entire set. We started our experiments with identical columns (identical twins), but extended our studies to columns with different lengths and the same diameter (fraternal twins). We anticipate a rather large field for employing frontal chromatography, especially at those facilities where limited amounts (up to $5\,m^3$ solution) of hazardous wastes are temporarily stored. We wanted to provide a separation unit to meet the following requirements:

(i) Compact construction.
(ii) Transportability, if not portability.
(iii) Easy adaptation of columns with different sizes.
(iv) Compatibility with areas of restricted access (hoods, glove boxes).

In addition, we wanted to introduce detectors based on destructive analysis into this unit. We reported earlier [8] on a sample distribution device which allows a continuous or intermittent diversion of small amounts of liquid for on-line analysis. This device was originally thought to monitor the effluent of a single column; its compatibility with the twin column concept has not yet been proven.

In this paper, we wish to report on the design and operation of our frontal chromatographic separation unit aiming at facilitating the implementation of this technique.

2. The twin column concept

We designed the separation unit following the twin column concept. This concept is based on a special wall effect in a chromatographic column, which is produced by the extractant deficiency between column wall and adjacent vertical particle layer and which generates a prerun of the solute in the column effluent [1]. We approximated that prerun mathematically by designing a model, which provides for the same regularities for both column prerun and main-stream. Within the range of validity of the linear extraction isotherm, frontal chromatograms are described by the standardized cumulative normal distribution function (error function) $y = \mathrm{erf}[x]$. By applying this function to prerun and main-stream, we obtain:

$$\frac{c_{effluent}}{c_{feed}} = a\,\mathrm{erf}[w] + b\,\mathrm{erf}[i] \quad (1)$$

where a, b are the dilution factors; w, i the arguments of the error function and c the solute concentration.

Thus, we got a concentration curve with two inflection points, one for the prerun at a low effluent concentration c_{BO} (the subscript stands for breakoff), the other for the main-stream at an effluent concentration c_{BT} (the subscript stands for breakthrough) at about $0.5\,c_{feed}$.

We calculated the dilution factors in Eq. (1) considering the geometrical factors of the column (ϕ_c) and the pebble bed structure (ϕ_p), while we used the conventional approach [16] for the arguments of the error function, thus transforming the equation into:

$$\frac{c_{effluent}}{c_{feed}} = 3\frac{\phi_p}{\phi_c}\mathrm{erf}\left[\sqrt{N}\frac{(V_{BO} - V)}{(V\,V_{BO})^{0.5}}\right] + \left(1 - 3\frac{\phi_p}{\phi_c}\right)\mathrm{erf}\left[\sqrt{N}\frac{(V_{BT} - V)}{(V\,V_{BT})^{0.5}}\right] \quad (2)$$

where V_{BO}, V_{BT} are the volumes of the two inflection points corresponding to $c_{BO}/c_{feed} = 1.5\,\phi_p/\phi_c$ and $c_{BT}/c_{feed} \approx 0.5$ and N = number of theoretical plates.We assessed the ratio of the volumes of the two inflection points by comparing the active surface at the column wall with that of the column interior and for that, we assumed a space centered cubic structure:

$$\frac{V_{BO}}{V_{BT}} = \frac{\pi}{(\pi + 4/3)} \approx 0.7 \quad (3)$$

The location of the two inflection points of the concentration curve does not depend on the extraction kinetics. The volume ratio in Eq. (3) is even independent of the chemical system (mobile and stationary phase) used, but is only affected by the geometry of column and column bed. We published in [1] a detailed description of the model we designed to derive the above equations.

Due to its invariable location at a low concentration, the prerun's inflection point would constitute an ideal termination of a frontal chromatographic decontamination process. Unfortunately, the corresponding concentration c_{BO} is usually too low to be detected by commercially available on-line monitoring systems and thus, the termination volume V_{BO} cannot be determined. With the aid of Eq. (3), it is calculable, but this requires the determination of V_{BT} at the measurable concentration $c_{BT} \approx 0.5\,c_{feed}$, when a significant solute amount had already passed the column and contaminated the product.

To this end, we devised the twin column concept [2]. With the array column 1 → detector → column 2, we measure the concentration $c_{BT\,1}$ in the first column effluent and determine the corresponding volume $V_{BT\,1}$. With that value, we calculate $V_{BO\,1}$ according to Eq. (3) and terminate the separation, when the breakoff volume of the entire set $V_{BO\,T}$ is reached. The subscripts 1 and 2 refer to the first and the second column and subscript T to the entire set.

We provided for two options: In the first one, we equipped the separation unit with two identical columns, i.e. with the same diameter ϕ and the same length L (identical twin columns). The total breakoff volume amounted to:

$$V_{BO\,T} = 1.4 V_{BT\,1} \quad (4)$$

This first option requires an extra feed assay for the determination of c_{feed} prior to the process operation.

In the second option, we used columns with an identical diameter, but with different lengths $L_1 < L_2$ (fraternal twin columns). The corresponding breakoff volume was calculated to:

$$V_{BOT} = 0.7 V_{BT1} \left(L_1 + \frac{L_2}{L_1} \right) \quad (5)$$

Employing the second option, we can do without the feed assay, as the first column is saturated long before the volume V_{BOT} passes the entire set. The feed concentration in the first column effluent is measured by the detector and identified by its constant value and, in addition, serves to calibrate the detector during the process. Furthermore, we reduce the total process waste by the portion generated during the feed assay and the subsequent detector cleaning.

The twin column concept is only applicable, if the solute concentration of the prerun is not or only insignificantly overlapped by the main-stream concentration at the first inflection point. We arbitrarily set the condition that this overlapping should not exceed 25% of c_{BO} (0.375 ϕ_p/ϕ_c) With that value and Eq. (2), the minimum number of theoretical plates N_{min} is calculated, which is required to meet the above condition. For the chromatographic system described herein (space centered cubic structure, $\phi_p/\phi_c = 0.007$), N_{min} amounts to 60. Scaling up the columns to $\phi_c = 10$ cm, N_{min} would increase to 82. The corresponding linear flow velocity u_{max} has to be empirically determined using a simplified van Deemter equation [11] (eddy and longitudinal diffusion are neglected, the subscript m refers to measured values):

$$u_{max} = \frac{u_m N_m}{N_{min}} \quad (6)$$

We wish to stress that the twin column concept only applies within the region of validity of the linear extraction isotherm. In the non-linear region, the chromatographic breakthrough curve does not show inflection points. We further wish to clarify that the above equations are derived from a very simple model; they do not result from theoretical considerations. We experimentally verified the equations and confirmed their applicability within the effluent volume range $0 \leq V \leq V_{BT}$ [1], however, we do not claim that the derivation constitutes a theory.

3. Experimental

We carried out our study within the framework of our Research and Development program on partitioning high-level radioactive waste solutions. Consequently, we devised our experiments such that our solid-phase extraction systems were capable of retaining selected fission products and actinide nuclides, and we set-up our detection systems accordingly.

3.1. Chemicals and equipment

If not otherwise stated, chemicals and reagents were purchased from Merck, Darmstadt, Germany, or Riedel-de Haën, Hanover, Germany, in analytical-reagent grade quality. CMPO (*n*-octyl phenyl carbamoyl-*N*,*N*-diisobutylmethyl phosphine oxide) was obtained from ELF Atochem Deutschland, Düsseldorf. Amberchrom CG 71 (polymethacrylate) was procured from Sigma-Aldrich, Chemie, Dept. Suplelco, Deisenhofen, Germany. The actinide nuclides and radioactive fission product isotopes were supplied by Isotopen Dienst, Waldburg, Germany. α-Spectra, as provided by the supplier, showed no impurities in the nuclide solutions within the detection limits; the β-emitters decay to stable nuclides that do not interfere with the detection.

For our separation unit, we used columns made of Perspex and machined in the laboratory workshop. Fittings, valves and tubes were supplied by B.E.S.T., Bornheim, Germany, the local representative of Swagelok, USA. We used membrane pumps from Leva, Leonberg, Germany. All other pieces of equipment consisted of ordinary labware.

Process control was carried out with the radioactivity monitor LB 508 C, from EG&G Berthold, Bad Wildbach, Germany, which we equipped with the custom-made detector flow cell WUW-ML 9 [9]. We dismantled the monitor and installed the detection unit (detector cell and chamber, multipliers and preamplifiers) together with the separation unit inside a hood, while the electronic parts together with the processor from Sontag, Waldfeucht, Germany, were left outside the hood. For comparison purposes, we also performed off-line process control and calibration analyses of the radioisotopes with the liquid scintillation counter Tricarb 1900CA from Canberra Packard, Dreieich, Germany, using the scintillator Instant Scint Gel Plus from the same company.

On-line destructive analysis was carried out using an inductively coupled plasma-atomic emission spectrometry (ICP-AES) system from ARL, Lausanne. The sample distributor was made of Swagelok fittings and assembled in the institute's workshop.

3.2. Resin preparation and column packing

We dissolved 12 g CMPO in ∼75 mL TBP (tri-*n*-butyl phosphate) applying gentle heating. The solution was cooled down to room temperature and then made up with TBP to 90 mL. Approximately 200 mL C_6H_{12} (cyclohexane) was added and 60 g Amberchrom CG 71 (particle diameter 125–160 μm) suspended in the diluted solution. C_6H_{12} was then evaporated at room temperature, and the last traces of this solvent were removed at 60 °C. The yield of the dry, coated resin amounted to 143 g with an average particle diameter of 140 μm. The resin beads were suspended in water and the suspension was filled into a pressurized vessel. Using a circulatory system (vessel–column–pump–vessel), the suspension was conveyed into the column which was

closed at the lower end with a frit. During packing, the column was vibrated and the pressure drop in the system kept constant by varying the flow [10]. After packing, the flow was discontinued and the upper column end covered with another frit. The quality of the column packing was controlled by determining the porosity (interstitial column volume/column volume) as 0.41. This value indicates that a space-centered cubic structure prevails in the column bed.

4. Results

As stated in Section 2, we gave preference to the fraternal twin columns variant. In the following, we shall exclusively refer to that alternative.

4.1. Design of the separation unit

Following our goals, we chose a module construction for our twin column set. We devised a foldable PVC [poly(vinylchloride)] rack (50 cm × 30 cm) as a basis for easy posting in glove boxes. We mounted the operational modules onto the rack using rawlplug connections. We divided the set into three vertical levels, the switchboard housing the valves and fittings as the front level, the columns as the medium level and the pump and pump circuit as the rear level. The levels were interconnected with quick lock connects allowing a fast assembly and disassembly of the unit.

The switchboard is depicted in Fig. 1 and was a PVC panel (50 cm × 10 cm) which carried 12 three-port valves including two spare ones (the latter not shown in the figure). These valves directed the feed and the regeneration solutions from the supply tanks through the columns and the monitoring system into the removal tanks. In total, we provided four stages for the frontal chromatographic separation:

(i) feed stage (marked with a ✠); the feed stage served to load the columns with the feed solution and comprised the following components (VX three-port valve, TX T-union):

pump–T1–V1–V2–column A–V7–T2–V3–detector–V5–V8–V4–column S–V9–V10–product tank.

Tubes and fittings behind the bottom of column S are considered to remain free of contamination.

(ii) Scrub stage (marked with a ♠). During the scrub stage, feed solution was to be displaced from the components. We applied counter-current flow to keep the components behind column S free of contamination. The stage comprised the components:

pump–V10–V9–column S–V4–V8–T2–V7–column A–V2–V1–T1–V3–detector–V5–V6–T3–feed tank.

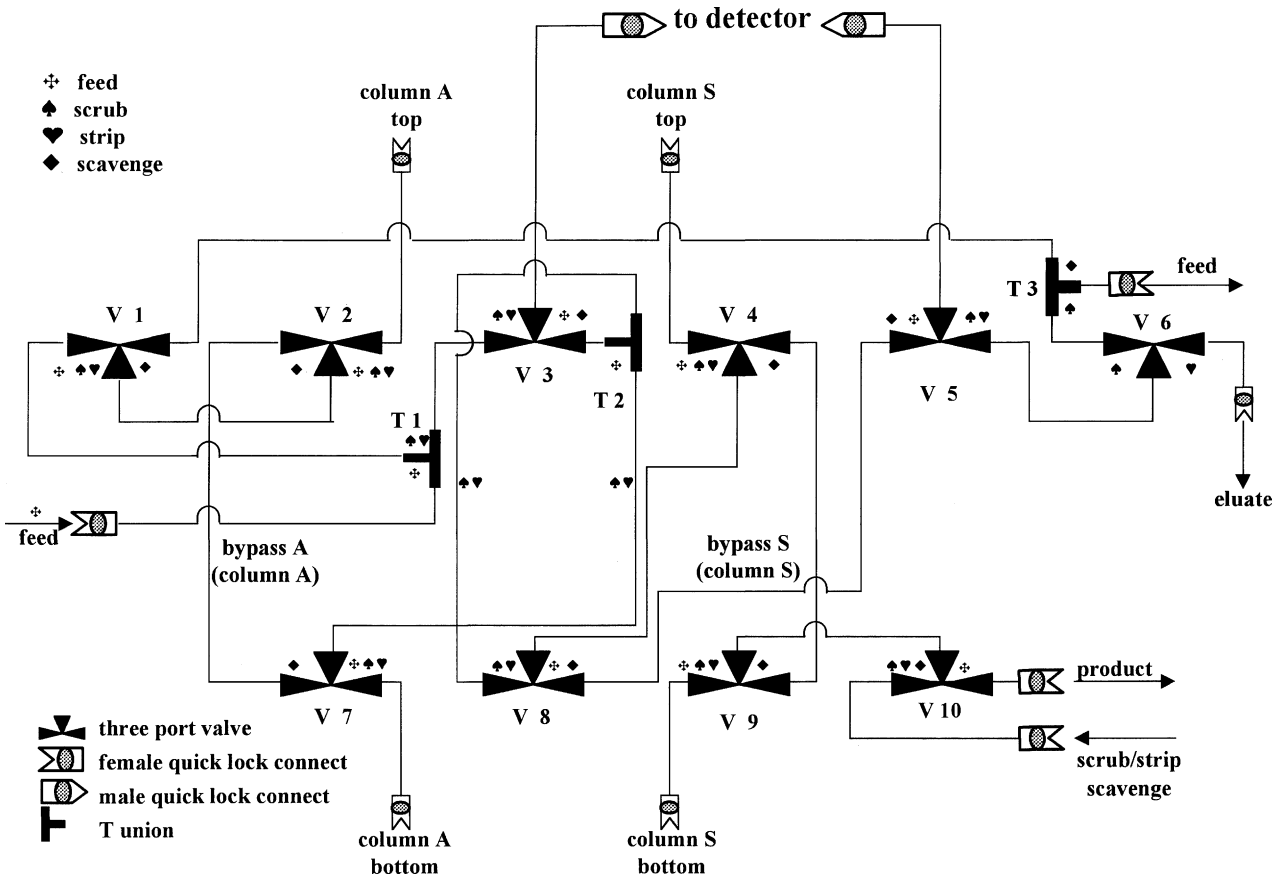

Fig. 1. Front level of the separation unit, switchboard.

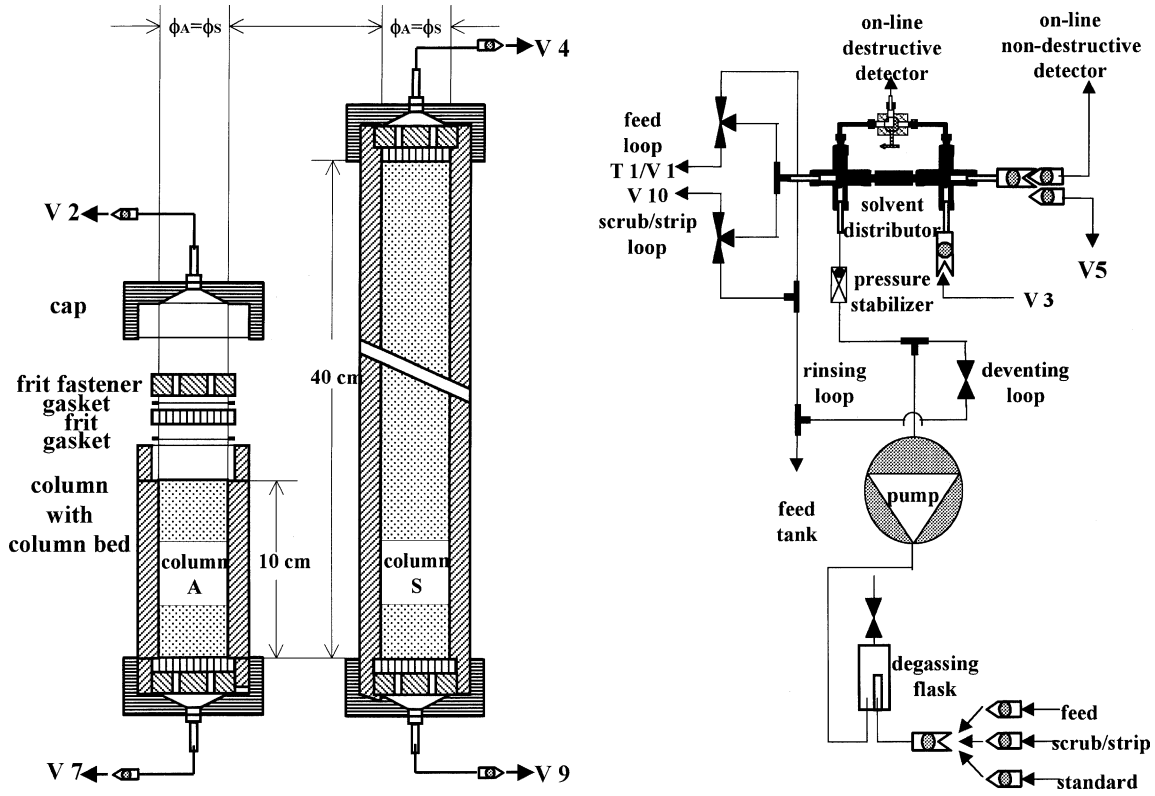

Fig. 2. Medium (left) and rear (right) level of the separation unit, columns and pump with pump circuit.

We did not apply the principle of the twin column concept, when we scrubbed the unit, as we wanted to measure the end of this stage. The final solution was composed of a mixture of scrub and feed solution. We collected that solution in the feed tank in order to process it during the next separation thus avoiding additional waste.

(iii) Strip stage (marked with a ❤). During the strip stage, we removed the contaminants from the columns. Again, we applied a counter-current flow and placed the detector behind the columns. The strip was collected in the eluate tank for a further waste management. The stage comprised:

pump–V10–V9–column S–V4–V8–T2–V7–column A–V2–V1–T1–V3–detector–V5–V6–eluate tank.

(iv) Scavenge stage (marked with a ◆). The counter-current flow during the above regeneration stages requires an additional scavenge stage, as some tubes and valves are not cleaned during scrub and strip. This applies to the connection “V4–V8–V5”. The stage comprises:

pump–V10–V9–bypass S–V4–V8–V5–detector–V3–T2–V7–bypass A–V2–V1–T3–feed tank.

Again, we collected the scavenge solution in the feed tank for further processing.

The medium vertical level (Fig. 2, left part) of our separation unit carries the columns and the column support. We chose a column length ratio $(L_A + L_S)/L_A = 5$ to assure that a complete chromatogram is acquired in the effluent of column (analytical), before the first breakthrough is observed in the effluent of column (separation). Following the twin column concept, the columns have the same diameter ϕ_c $(= \phi_A = \phi_S)$. The unit can be equipped with columns up to a diameter of 10 cm, corresponding to a height of 14 cm for the analytical and 56 cm for the separation column.

The third vertical level carries the pump with the pump circuit and the solvent distributor which is connected to the monitoring system (Fig. 2, right part). We decided in favor of a single pump for the individual supply solutions and connected the supply tanks to the pump suction pipe via quick lock connects for easily switching from one solution to another. The pump circuit consists of a deventing loop for removing gas bubbles from the pump. This loop terminates in the feed tank regardless of the original nature of the solution to be displaced. The pump conveys the solution against a pressure stabilizer, a check valve with an opening pressure of 1.7 bar, which guarantees a constant flow. The solution is then transported to the “verification line” (left part) of the solvent distributor [8] (Fig. 3) which is fully operative only for on-line destructive monitoring. The “monitoring line” (right part of the solvent distributor) is not part of the pump circuit, it receives flow from valve V3 and connects either to a non-destructive detector or to V5 bypassing the detector. Prior to starting a new process stage, the pump circuit must be cleaned. This is done with the rinsing loop which terminates in the feed tank and connects with the feed

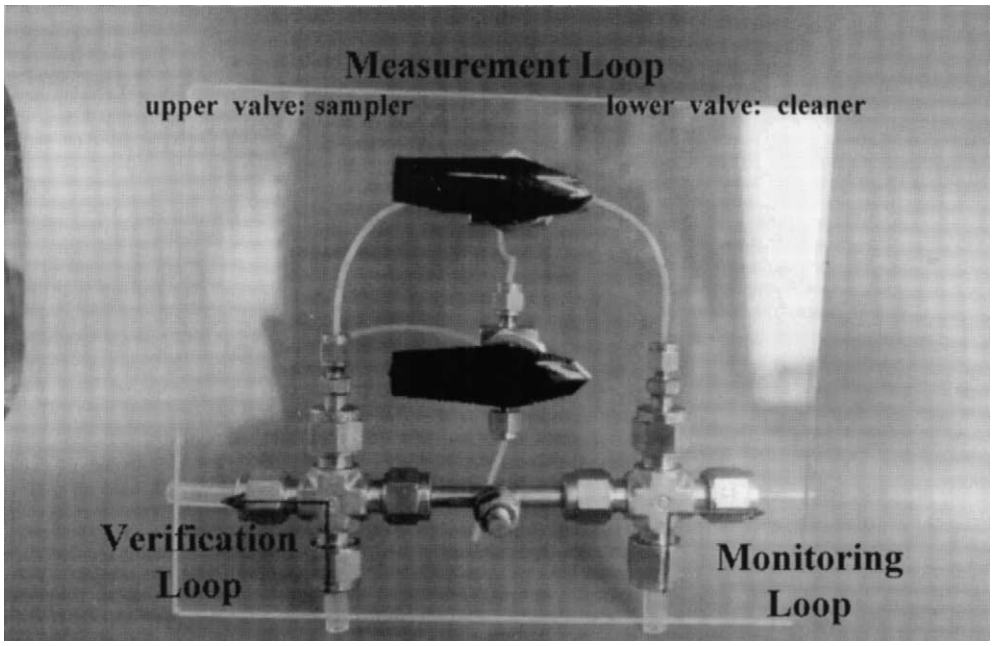

Fig. 3. Solvent distributor.

stage or the regeneration stages via two additional three-port valves.

We did not include the monitoring system in our design. Primarily, we devised the separation unit for the removal of radioisotopes from waste solutions. Such operations are done in highly contaminated restricted areas (hot cells, glove boxes), and the monitoring system must be adapted to remote operations. We solved that problem by welding our measurement cell onto the bottom of a double-lock container, as provided by the company La Calhène, France, and mounting that assembly on the glove box wall. Details of this design are given in [12]. The system is applicable to an on-line, non-destructive α-, β- and γ-counting, but it forms a component part of the restricted area, not of the separation unit.

As for destructive monitoring systems, they are often sophisticated and complex, bulky and susceptible to failures due to strong vibrations and other mechanical impacts. This led us to the concept of a transportable separation unit, as it appeared easier to install the separation unit around the monitoring system than vice versa. We illustrated that in Fig. 4 showing the separation unit in front of an atomic absorption spectrometry (AAS) system together with a 200 L supply tank. We placed the unit on a rolling table (60 cm × 40 cm). The unit was connected with the AAS system via the solvent distributor with flexible tubes. The folded separation unit including the columns but without pump is depicted in Fig. 5.

4.2. Operations with the separation unit

In addition to the four process stages, i.e. loading, scavenge, scrub and strip, we investigated the operational parameters of the unit, we optimized its commissioning and we studied the different effects of non-destructive and destructive monitoring.

4.2.1. Commissioning

During commissioning of the unit, air bubbles must be removed as far as possible. We achieved that by filling tubes and fittings through the scrub line and the column bypasses. Then we installed column S and removed the air bubbles collected at the top of the column during filling and closing. Bypass A was still operative. We then repeated the entire procedure for column A.

4.2.2. Pressure build-up

We measured the pressure build-up at a flow velocity of 25 mL/min. We installed a pressure gauge behind the pressure stabilizer (Fig. 1) and divided the separation unit into four components: (1) tube and fittings, (2) columns, (3) non-destructive monitor, (4) destructive monitor. The results are summarized in Table 1.

These values apply to 1/8 in. tubes and fittings (1 in. = 2.54 cm) and a ϕ_c of 2 cm. The high value for the monitoring systems is caused by the protective filters at detector inlet and outlet showing a total pressure build-up of 0.7 bar. We installed the filters at the beginning of our investigations because we observed a periodic breaking of the column frits followed by detector plugging. However, this mishap no longer arose with the final column design (Fig. 3, left part). The bundle itself did not show a measurable pressure drop ($\Delta p \leq 0.1$ bar) [9]. A scaling-up of the unit only affects tubes and columns, the detection systems remain unchanged. In our racks, we can easily accommodate 1/4 in. tubes and fittings and columns with a ϕ_c of 10 cm. According

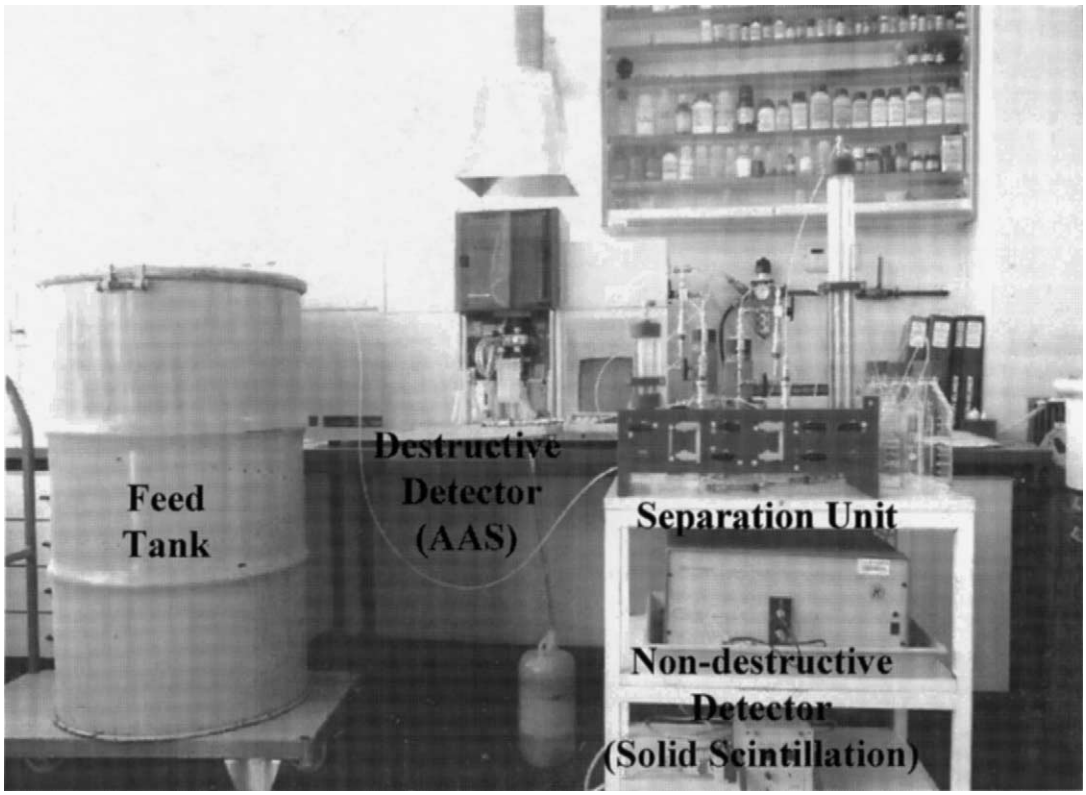

Fig. 4. Separation unit with monitor (atomic absorption spectrometer) and 200 L supply tank.

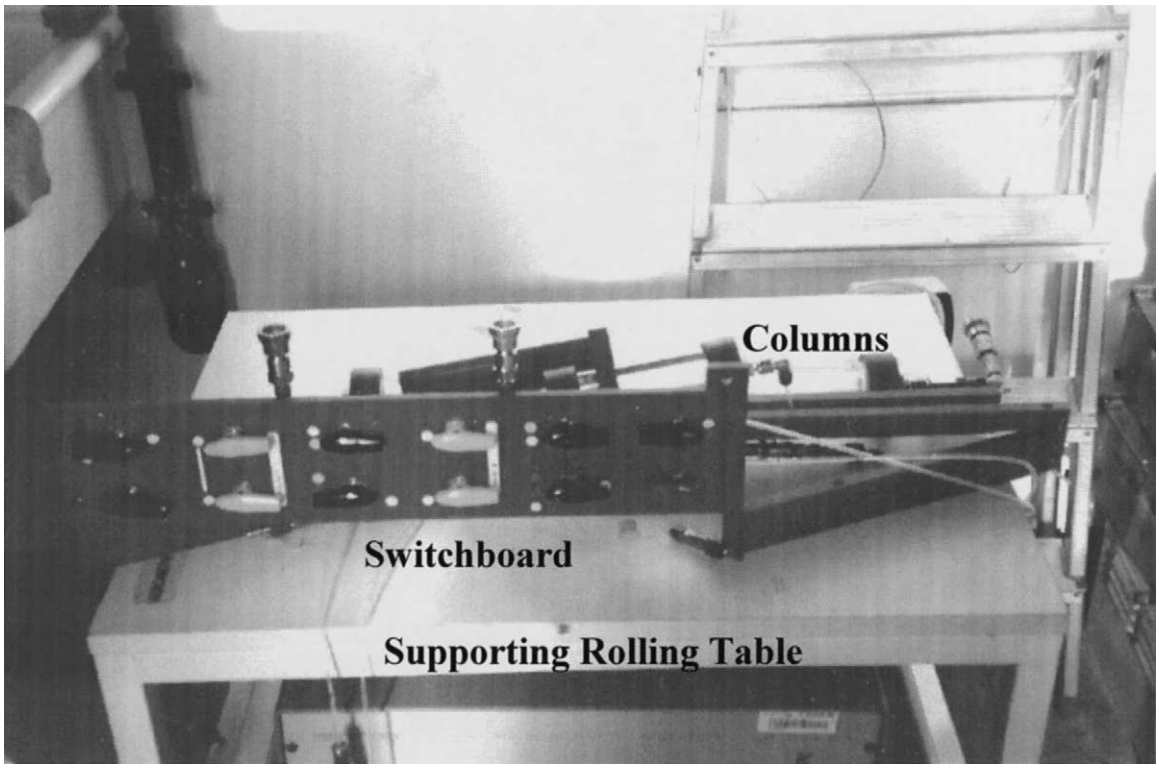

Fig. 5. Folded separation unit.

Table 1
Pressure build-up and void volume of the unit components

Component	Tubes and fittings	Columns	Non-destructive monitor (WUW-ML bundle detector)	Destructive monitor
Pressure build-up (bar)	0.5	0.6	0.9	0.9
Void volume (mL)	42	63	11	4

to Hagen–Poiseuille, this would reduce the pressure build-up of columns and fittings to $\Delta p < 0.1$ bar and the entire pressure build-up in the set would be determined by the monitoring system.

4.2.3. Void volume

We determined the void volume with Cs-137, as described in [1,2]. The values for the individual components are depicted in Table 1. We could achieve a significant reduction of the void volume by dispensing with the protective filters at the detector inlet and outlet (additional 4 mL) and by using simple unions instead of quick lock connects (∼4 mL per couple) at the expense of easy mounting of the separation set. The void volume amounted to 120 mL for the entire set and can be reduced to 84 mL by applying the measures described above.

4.2.4. Loading of the columns

In our present study, we paid little attention to the loading stage as this was thoroughly discussed in [1,2]. For a quick illustration of the loading procedure, we show a fully fledged chromatogram of a Y separation in Fig. 6 acquired with a fraternal twin column unit. We used on-line scintillation between the columns and sampling and off-line scintillation behind the separation column.

By comparing the two chromatograms we obtained the typical features of a fraternal twin column ($L_T = 5L_A$) separation, i.e. $V_{BTT} = 5V_{BTA}$; $N_T = 5N_A$ (subscript A refers to the analytical column, subscript T to the entire column set). The V_{BOT} value was clearly identified by the expected effluent concentration ($1.5\,\phi_p/\phi_c = 1.1\%\ c_{feed}$) and total effluent volume 0.7 V_{BTT}. In addition, we demonstrated the most important criterion for selecting fraternal twins, namely $V_{A\,100\%\,feed} < V_{BOT}$.

4.2.5. Monitoring systems

We developed the twin column concept by employing non-destructive analytical techniques for monitoring the frontal chromatographic separation. In our own field of work, the decontamination of radioactive wastes from long-lived, hazardous nuclides, we designed a number of processes for the removal of actinides using α-selective, but not element-specific detectors [13,14]. Our measurement chambers can be easily adapted to energy-specific γ-radiation and gross β-determination [15]. For non-nuclear applications, destructive analytical techniques appear to be indispensable for monitoring the separation process. We designed a solvent distributor [8] for single column operations which diverted a small portion of the column effluent to the measurement chamber of a destructive analytical instrument (such as the ICP-AES) system. The adaptation of the distributor to twin column operations suggests itself, but requires an investigation of the effect of the first column effluent loss on the separation in the entire set.

To this end, we connected the sample distributor to the measurement pump of an ICP-AES instrument. We determined a flow of 2.5 mL for the diverted solution and chose a flow of 25 mL for the chromatographic separation ignoring the needs for an appropriate N_{min}. We determined the effluent concentration behind the analytical column with the aid of the solvent distributor and mounted a second distributor behind the separation column. As usual, we acquired the effluent volume by a time measurement assuming a constant throughput. Fig. 7 illustrates the results. The

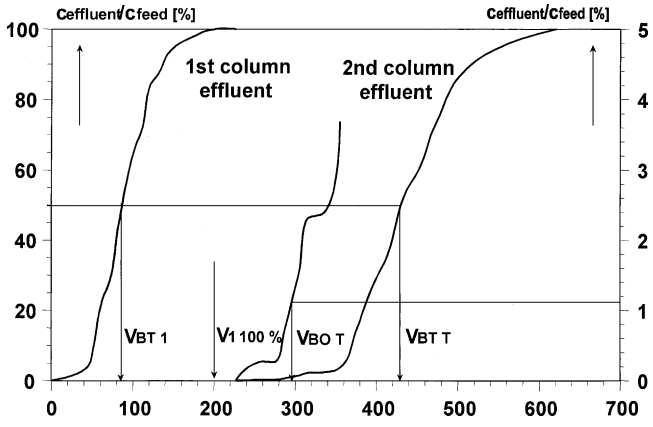

Fig. 6. Y^{3+} separation with a fraternal twin column unit.

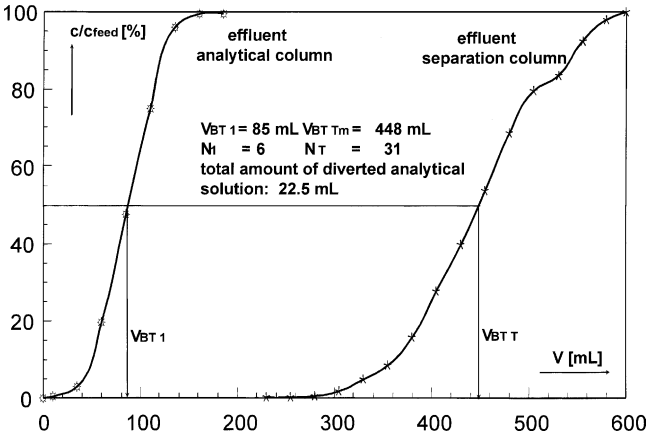

Fig. 7. Y^{3+} separation with a fraternal twin column unit using ICP-AES monitoring.

chromatogram of the analytical column was not affected by the effluent diversion, its breakthrough volume V_{BTA} amounted to 85 mL (reached at 3.4 min) like that of Fig. 3. After 9 min (=225 mL), the 100% feed value was attained, and we switched to the second column effluent. At that time, only 202.5 mL (225 − (9 × 2.5) mL) flowed through the second column. We determined the total breakthrough point at 18 min corresponding to a V_{BTT} value of 450 − 22.5 mL, i.e. we observed an ostensible delay of 9 min which precisely corresponded to the diverted analytical solution. As for the number of theoretical plates, we obtained the expected ratio $N_T/N_A = 5$.

We conclude that a diversion of effluent solution does not significantly affect the separation parameters, even if the flow ratio is as unfavorable as in our experiment. We suggest that the ostensible delay should be regarded as a safety measure and ignored for the calculation of V_{BOT}.

By introducing the solvent distributor, the field of applying frontal chromatography is greatly enhanced. All on-line monitoring systems available in analytical scale chromatographic separations can now be adapted to industrial scale frontal chromatography.

4.2.6. Regeneration stages

The regeneration stages comprise the scavenge for cleaning the tubes, the scrub for removing the feed containing mobile phase and the strip for eluting the chromatographic support. We chose the same elutriant solution for all the stages. We investigated the effect of the flow direction, either concurrently with the feed or counter-currently to the feed, and the effect of the flow velocity on the regeneration volumes. We divided the entire regeneration into two steps. We started the first step directly after the loading stage and terminated the step when a constant effluent concentration was attained. We resumed operation after a delay of 24 h. The different elution chromatograms are shown in Fig. 8.

Applying a concurrent flow, the elutriant was conveyed through the loading line, and all tubes and fittings were involved in the regeneration. An extra scavenge stage was not necessary. After one void volume had passed through the unit, the remaining feed solution was removed and the columns were stripped. We obtained a constant effluent concentration after an additional 1.5 void volumes (Y_1 axis). After a 24 h delay, we needed an additional void volume until the background signal in the effluent (Y_2 axis) was reached.

The counter-current flow required the additional scavenge stage for cleaning some of the tubes. We observed the background signal after 0.5 void volumes, as the columns were bypassed during that stage. The subsequent scrub and strip stages did not deviate significantly from those carried out with a concurrent flow regarding the effluent concentration.

Despite the higher elutriant consumption, we recommend counter-current regeneration. The scavenge portion corresponds precisely to the void volume of tubes and fittings (see Table 1), and we have already indicated how that volume can be reduced. Using larger columns, this portion becomes more and more negligible. The counter-current flow keeps the product line free of contamination after the separation column, while the highest contaminant concentration would pass that line using a concurrent flow. Assuming an incomplete removal with counter-current flow, the contaminant would be collected at the top of the analytical column and not really interfere with the following separation. However, with a concurrent flow, the contaminant would be retained at the bottom of the separation column and directly conveyed into the product tank during the next process.

We did not note any significant effect of the flow velocity on the column regeneration. We investigated three different flow velocities (Fig. 9) in the counter-current mode and obtained practically the same results for scavenge and scrub. The strip appears to be more affected by the time required for the loading stage and elapsing between loading and regeneration than by the flow velocity. This is most likely due to a diffusion of the contaminants within the stationary phase. In each case, we could not completely strip the columns in a single step. However, we always reached the background by passing one additional void volume through the columns after a delay of 24 h. Regarding Fig. 8, a throughput of 25 mL/min corresponding to a linear velocity of 0.33 cm/s ($u = V/tF_cE$) appears to be the

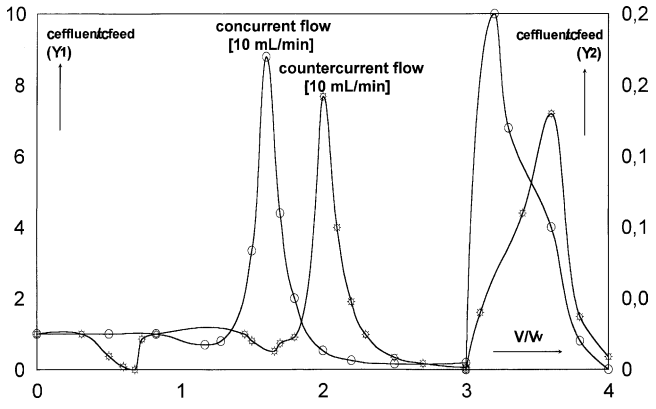

Fig. 8. Effect of the flow direction on the regeneration stages.

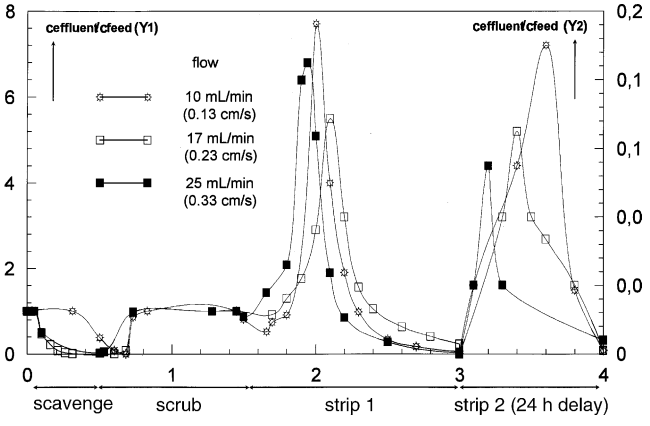

Fig. 9. Effect of the flow velocity on the regeneration volumes.

limiting value for a successful elution. Scrub and scavenge are not subject to such a limitation, but we suggest to keep the throughput constant, thus avoiding a multiple adjustment of the pump.

5. Conclusions

We set up and tested a unit for large-scale separations based on frontal chromatography. We employed the twin column concept using fraternal twins. We equipped the unit with devices for on-line monitoring with destructive and non-destructive analytical procedures. With this array, we anticipate an enhancement of the field of application for the technique:

(i) The use of twin column chromatography allows process monitoring below the detection limits of the analytical technique employed.
(ii) By equipping the unit with fraternal twins, we achieved an in-process calibration of the monitoring system and avoided an additional waste production as we dispensed with detector calibration and cleaning.
(iii) We provided the unit with links for non-destructive detectors conveying the individual process streams directly through the monitoring system and for destructive detectors diverting a small portion of the process streams for monitoring. Introducing the latter technique to twin column chromatography allows compound-specific monitoring for a variety of separation problems.
(iv) The compact module construction of the unit resulted in a portable unit with a small void volume. Thus, the unit is adaptable to either bulky supply and removal tanks or to space-consuming sophisticated measurement equipment. We indicated how void volume and pressure build-up can be further reduced.

On the other hand, the employment of twin column frontal chromatography is subject to some constraints that we wish to discuss briefly. In the first place, proper operation is only possible within the range of the linear extraction isotherm, otherwise the approach for monitoring the process is not applicable. Secondly, frontal chromatography is strictly a batch process. We regard as meaningless any attempt to change this technique into a quasi-continuous operation, as it must then compete with the much more powerful counter-current solvent extraction. Finally, one should avoid abundant waste production during the process.

We already stated that twin column chromatography was designed for the decontamination of solvents from trace contaminants, so that the linear extraction isotherm applies to the chemical system. Regarding the other two conditions, they should form the basis for a fully fledged cost–benefit analysis which must be tailored to the individual separation problem. Here, we only can provide some outlines.

We set the arbitrary requirement that the contaminant should be enriched during the process expressed by the volume balance (the scavenge stage is ignored):

$$V_{\text{loading}} \geq V_{\text{scrub}} + V_{\text{strip}} = V_{\text{v}} + 3V_{\text{v}} = 4V_{\text{c}}E \tag{7}$$

During loading, a feed volume is passed through the column equaling $0.7\,V_{\text{BT}}$ (see Eq. (3)). The breakthrough point of the chromatogram indicates the equilibrium between stationary (subscript stat) and mobile (subscript mob) phase and Eq. (10) applies:

$$V_{\text{mob}} = K_{\text{resin}}V_{\text{stat}} = K_{\text{resin}}V_{\text{c}}(1-E) = V_{\text{BT}} \tag{8}$$

By combining Eqs. (9) and (10), the distribution coefficient K_{resin} is obtained:

$$K_{\text{resin}} \geq \frac{4V_{\text{c}}E}{0.7V_{\text{c}}(1-E)} \approx 4 \tag{9}$$

We use the experimentally acquired values for the porosity E and the ratio $V_{\text{BO}}/V_{\text{BT}}$. The distribution coefficient refers to the volume of the chromatographic support and is affected by its coating. We found a K_{resin} of 4.5 for the system Y^{3+}/Amberchrom/CMPO which already meets the requirement of inequality (9), but this value can be increased by augmenting the CMPO coating.

We utilize the batch character of frontal chromatography to determine the daily throughput. We set the condition that a run comprising loading, scavenge, scrub and first strip should be completed within a working day, i.e. 8 h and be operated with the same flow velocity for all the stages, though this condition is by no means mandatory. With that approach we prevent the columns from an excessive exposure to aggressive solution components, we ensure an undisturbed operation by avoiding a multiple pump adjustment, and we save costs for shiftwork and overtime. The second strip is part of column reconditioning and not considered in the approach. We scale up the columns to a total length L_{T} of 70 (14+56) cm and a diameter ϕ_{c} of 10 cm, which are the maximum dimensions we can accommodate in our portable unit. The maximum ratio $\phi_{\text{c}}/L_{\text{A}} = 0.7$ for the analytical column was empirically proven to be effective when we developed the Salphar process [13]. Tubes and fittings of 1/4 in. are adequate for this layout, they contribute ≈5% to the void volume and are therefore not included in our considerations ($V_{\text{v}} \approx V_{\text{c}}\,E$). The total volume V_{T} conveyed through the unit per day is expressed by:

$$\begin{aligned} V_{\text{T}} &= V_{\text{loading}} + V_{\text{scrub}} + V_{\text{strip 1}} = 0.7V_{\text{BT}} + 3V_{\text{c}}E \\ &= V_{\text{c}}[0.7K_{\text{resin}}(1-E) + 3E] \end{aligned} \tag{10}$$

Using this equation, we calculated some operational parameters for various chemical systems identified by their distribution coefficients (Table 2). We compared these calculated values with corresponding values obtained experimentally for Y^{3+} and Eu^{3+} [2]. According to Eq. (7), the maximum flow velocity applicable to the Y^{3+} system amounts to 0.17 cm/s, and 0.62 cm/s for the Eu^{3+} system. The required velocities, as displayed in Table 2, are much

Table 2
Operational parameters of the twin column set

K_{resin}	V_{total} (L)	$V_{loading}$ (L)	V/t (mL/min)	u (cm/s)
4	15	9	32	0.018
10	30	23	61	0.033
20	53	46	110	0.058
50	122	115	254	0.135
100	238	230	494	0.260
Y^{3+}				
13.5	38	31	79	0.042
Eu^{3+}				
38	94	87	196	0.104

lower allowing a flexible design of the separation process, e.g. a shorter daily operation period or a smaller amount of extractant.

For the unit described, we need about 1 kg (or 1 L) of extractant. In operating such a unit, we did not discover any deterioration of the stationary phase during the entire period (approximately 0.5 a) [13]. Assuming a column life-time of 1 a and an average distribution coefficient of 20, about 5 m^3 solution can be decontaminated per year.

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