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# Twin column chromatography for industrial-scale decontamination processes

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**Abstract**

A frontal chromatographic unit was devised consisting of a column–detector–column array. The unit is either equipped with identical columns (identical twins) or with columns of varying length (fraternal twins). Due to the finite nature of the columns, a prerun is formed at the column walls following the same regularities as the main stream. These regularities are used for the identification of the process termination below the detection limits of the monitor. For the implementation, a clear preference is given to the employment of fraternal twins, as the feed assay can be integrated into the separation process.


*Keywords:* Frontal chromatography; Twin column unit; Preparative chromatography; Instrumentation

## 1. Introduction

Frontal chromatography, as defined by Tiselius [1], is a mode of operating chromatographic columns that allows industrial-scale separations. The great potential of this technique lies in decontaminating solutions by retaining tracer quantities of a single or a group of hazardous solutes with similar properties on the column bed. However, despite the large number of chromatographic systems now being available, frontal chromatography has not really found a broad technical application with the exception of the desalination of water using ion chromatography [2]. This is mainly due to the special requirements imposed on monitoring such a process.

(1) Real time, i.e. on-line monitoring is required for a technical-scale chromatographic process.
(2) For a decontamination, the column effluent constitutes the product of the process and must not be destroyed or altered by the monitoring.
(3) In frontal chromatography, monitoring aims at the determination of the termination point for discontinuing the process. The corresponding solute concentration should meet the process goals which, however, are often below the detection limits of commercially available detectors.

Ideally, a frontal chromatographic decontamination unit should involve a multi-component, element-specific monitoring system with low detection limits, such as atomic spectroscopy techniques (inductively coupled plasma atomic emission or mass spectrometry (ICP-AES or ICP-MS)). These methods have long been used for monitoring analytical-scale elution chromatography separations [3,4]. Unfortunately, they are destructive methods and conflict with one of the above requirements. We overcame this limitation by devising a sample station [5] which allows a continuous or intermittent diversion of a small portion of the solution for being monitored during the separation process.

In our own field of research, the treatment of α-bearing nuclear wastes, we do not recommend the employment of destructive techniques for process monitoring, as they will create a new type of waste which is difficult to handle. We developed detectors which show a certain selectivity for α-emitters [6]. Their detection limits are about 5 Bq α/ml for pure α-solutions, but deteriorate significantly in the presence of high energy β-emitters. Thus, their use in process monitoring may be limited by the total activity of the process solution and may yield products that do not meet

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the specifications established for decontaminated α-bearing wastes.

To this end, we evaluated frontal chromatograms in order to find regularities at low effluent concentrations [7]. We discovered deviations from the pertinent theory of frontal chromatography [8] which we interpreted as a prerun occurring between column wall and adjacent vertical particle layer. This prerun is caused by the extractant deficiency at the column wall. We devised a model for adapting the deviations to a mathematical function having two inflection points, one for the prerun and one for the main stream. We verified he validity of our model experimentally and showed that the ratio of the two inflection points is neither affected by kinetic parameters nor by the chemical system chosen. By determining the second inflection point, we could infer the first one that normally escapes detection.

We already indicated in our previous paper [7] that this constant ratio of the two inflection points could be employed for terminating the chromatographic separation at a defined effluent concentration below the detection limits. We suggested the "column–detector–column" array. In this paper, we wish to report the results we obtained when we put this array into effect.

## 2. Model

Assuming a linear extraction isotherm, Glueckauf [8] described a frontal chromatogram by the cumulative standardized normal distribution function (error function = erf($t$)):

$$\frac{c_{\text{effluent}}}{c_{\text{feed}}} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{t} \mathrm{e}^{-t^2/2}\,\mathrm{d}t = \mathrm{erf}\,(t) \tag{1}$$

with the argument $t$:

$$t^2 = N \frac{(V_{\text{BT}} - V)^2}{V_{\text{BT}} V} \tag{2}$$

$c_{\text{effluent}}$ is the solute concentration in the effluent; $c_{\text{feed}}$ the solute concentration in the feed; $V$ the effluent volume; $V_{\text{BT}}$ the breakthrough volume at $c_{\text{effluent}} = 0.5 c_{\text{feed}}$ (inflection point); $N$ the number of theoretical plates.

In our model we postulated two effluent fractions, the prerun (wall stream) and the main stream, each following the error function:

$$\frac{c_{\text{effluent}}}{c_{\text{feed}}} = a\,\mathrm{erf}\,(w) + b\,\mathrm{erf}\,(i) \tag{3}$$

$w$, $i$ the arguments of the error functions for prerun ($w$) and main stream ($i$).

The factors $a$ and $b$ shall reflect the dilution of the individual streams by the total column effluent and are established by the geometrical conditions of the column and the chromatographic pebble bed. We considered two cases for the pebble bed, a plain and a space centered cubic structure. Then we obtain an a value of $2(\phi_{\text{P}}/\phi_{\text{C}})$ for the plain cubic and $\sim 3(\phi_{\text{P}}/\phi_{\text{C}})$ for the space-centered cubic structure. Accordingly, the $b$ value amounts to $(1–2(\phi_{\text{P}}/\phi_{\text{C}}))$ and $(1–3(\phi_{\text{P}}/\phi_{\text{C}}))$, respectively.

We followed Eq. (2) for the two arguments in Eq. (3):

$$w^2 = N \frac{(V_{\text{BT w}} - V)^2}{V_{\text{BT w}} V} \tag{4}$$

$V_{\text{BTw}}$, $V_{\text{BTI}}$ are the breakthrough volumes of prerun ($w$) and main stream ($i$).

Under routine conditions prevailing in chromatography ($\phi_{\text{P}}/\phi_{\text{C}} \leq 0.01$; $N \geq 10$), we showed that $V_{\text{BTI}}$ differs by less than 1% from $V_{\text{BT}}$ in Eq. (2). We approached $V_{\text{BTw}}$ by comparing the active surface of a wall channel with its entire surface and obtained for a plain cubic structure (pc):

$$V_{\text{BT w}}(\text{pc}) = V_{\text{BT I}} \frac{\pi}{(\pi + 2)} = 0.611\, V_{\text{BT I}} \approx 0.611\, V_{\text{BT}} \tag{5a}$$

and for a space-centered cubic structure (sc):

$$V_{\text{BT w}}(\text{sc}) = V_{\text{BT I}} \frac{\pi}{(\pi + 4/3)} = 0.7\, V_{\text{BT I}} \approx 0.\, V_{\text{BT}} \tag{5b}$$

We assumed the same number of theoretical plates for prerun and main stream. This is merely a best estimate and somewhat outdated by recent findings [9] visualizing that the linear velocity of the mobile phase is greater at the column wall than in the column interior. However, the authors did not quantify the difference, and the position of the prerun's inflection point remains unaffected by velocity changes. Thus, we felt justified in disregarding the difference.

Following our proposition, the ratio $V_{\text{BTw}}/V_{\text{BT}}$ is neither influenced by kinetic parameters nor by changes in the chemical system. Thus, we can identify $V_{\text{BTw}}$ with a corresponding effluent concentration below the detection limits by determining $V_{\text{BT}}$ at a measurable concentration. The application of this principle to a chromatographic decontamination process would require a second column behind the process monitor. Then we can measure $c_{\text{BT}}$ $(=0.5 c_{\text{feed}})$ in the effluent of the first column, determine the corresponding breakthrough volume $V_{\text{BT1}}$ and terminate the decontamination at the calculated $V_{\text{BTwT}}$ (the breakthrough volume of the prerun for the entire set) according to Eq. (5a) or (5b).

We conceived two types of deviations from this model. For a small number of theoretical plates $N$, we must expect an overlapping of the wall fraction by the main stream. For a quantification of $N_{\text{min}}$ (the $N$ value at which overlapping ceases), we postulated:

$$b\,\mathrm{erf}\,(i_{\text{BT w}}) \leq 0.25 \frac{\phi_P}{\phi_C} \tag{6}$$

i.e. we assume an uncertainty of ~25% for the concentration measurement around $c \sim 0.01 c_{\text{feed}}$, so that we cannot distinguish between a measurement error and a concentration increase due to overlapping. We calculated erf($i_{\text{BTw}}$) from

Eq. (6) and obtained the corresponding, tabulated $i_{BTw}$ value [10]. We determined $N_{min}$ according to Eq. (4):

$$N_{min}(pc) \geq 2.47(i_{BTw})^2 = 21;$$
$$N_{min}(sc) \geq 5.44(i_{BTw})^2 = 46 \quad (7)$$

The values given in Eq. (7) apply to a ratio $\phi_P/\phi_C = 0.007$. $i_{BTw}$ shows no significant difference for plain and space-centered cubic structures.

We determined the number of theoretical plates either graphically or by linear regression using the equation [7]:

$$N = \frac{\pi}{2}\frac{V_{BT^2}}{(V_{BT} - V_I)^2} \quad (8)$$

$V_I$ is the intercept of the tangent at $V_{BT}$ with the $V$ axis.

We assume another deviation for a very large number of theoretical plates already in the first column. Wall fraction and main stream are mixed in the first column effluent and in the detector. An extended wall fraction due to large $N$ values could act in the second column as another feed and produce its own inflection point. However, we have not yet been able to set up appropriate experimental conditions for verifying this assumption.

## 3. Experimental

We carried out our study within the framework of our R&D 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*-octylphenylcarbamoyl-*N*,*N*-diisobutylmethyl phosphine oxide) was obtained from Elf Atochem Deutschland, Düsseldorf, Germany Amberchrom CG 71 (polymethacrylate) was procured from Sigma–Aldrich Chemie, Department SUPELCO, Deisenhofen, Germany. The actinide nuclides and radioactive fission product isotopes were supplied by Isotopen Dienst, Waldburg. 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 out 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 [11]. 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, 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.

### 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 is 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 [12]. 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) to 0.41. This value indicates that a space-centered cubic structure prevails in the column bed. We verified the active amount of chromatographic support with an Y-90 feed. Table 1 summarizes the characteristics of the columns used. The term "double column" refers to a set consisting of a small and a long column, and the parameters of the total set are determined.

### 3.3. Operation of the separation unit

The separation unit serves to carry out the two process stages of loading and elution. It consists of the supply (feed and strip) and removal (eluate and product) tanks, the pump, two columns and the process monitoring devices, i.e. the on-line detector and the sampling stations for off-line analyses (Fig. 1). We used simple overflow vessels for the sampling stations and placed one station in each loop in order to avoid cross-contamination. We determined the void volume of the stages between upper three port valve and detector (on-line mode) or sampling station (off-line mode). For that,

Table 1
Characteristics of the columns

| Parameters | First small column | Second small column | Long column | Double column |
|---|---|---|---|---|
| $M_{\text{chrom.support}}$ (g) | 18.2 | 18.2 | 72.8 | 91 |
| Particle size (cm) | 0.014 | 0.014 | 0.014 | 0.014 |
| Column length (cm) | 9.6 | 9.5 | 39.4 | 49.1 |
| Column diameter (cm) | 2 | 2 | 2 | 2 |
| Porosity | 0.41 | 0.4 | 0.42 | 0.41 |
| $V_{\text{BT}}$ (ml) | 82 | 84 | 326 | 427 |
| $N$ | 7 | 9 | 31 | 45 |

we used either Sr-90 present in the feed solution or a Cs-137 feed in an additional test and measured the flow by time control and conveyed volume in the removal tanks. Usually, we determined the solute concentration in the feed by acquiring complete chromatograms during loading. It was thus possible to avoid separate detector calibration. However, we could also bypass the column to measure the feed solution and clean the detector prior to the operating the column.

The retained solutes were removed from the columns with a 0.1 M citric acid solution adjusted to pH 3. Then, we reconditioned the columns with 1 M $HNO_3$ before we resumed operation, but we also tested unconditioned columns.

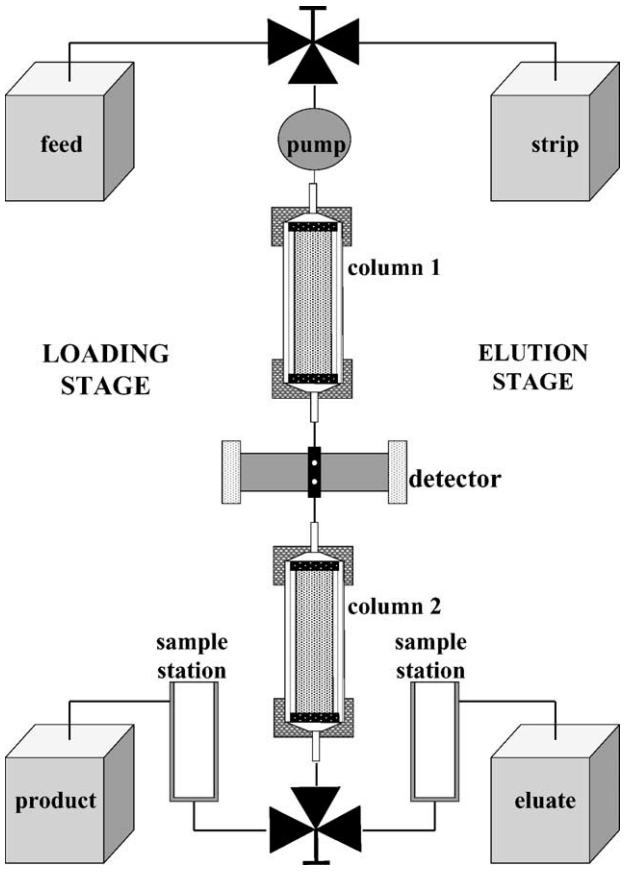


Fig. 1. Drawing scheme of the twin column unit.

## 4. Results and discussion

The model does not involve the column length as a parameter affecting volume and concentration ratios of the two inflection points. Identical columns appear to suggest themselves for the model verification, though their use is by far not imperative. We first set up a separation unit with two identical columns (identical twins), but extended our experiments to columns having the same diameter, but different, though well defined, lengths (fraternal twins). We used a feed solution composed of a carrier-free, equilibrated mother/daughter couple (Sr/Y)-90 as solutes in 1 M $HNO_3$. Sr-90 is not retained on our stationary phase, thus, we avoided additional tests for the determination of the void volume. Y-90 is weakly retained on CMPO, thus saving valuable experimental time. We carried out some tests with Eu-152, either carrier-free or in a 0.001 M Eu solution, in order to identify the deviations from our model as discussed above.

We operated the separation set by monitoring the first column effluent with our on-line detector and the second column effluent by sampling and off-line scintillation measurements. We aimed at the identification of the inflection point of the wall fraction in the effluent of the second column. Hereinafter, we shall refer to this point using the subscript BO (breakoff point).

The reported values for volumes are already corrected for the void volume $V_{\text{v}}$, concentration values are background corrected. Measured, not corrected values are identified by the subscript m (e.g. $V_{\text{BTm}}$).

### 4.1. Identical twins

We tested our identical twin column unit with 10 cm columns (see Table 1). We separated a carrier-free Sr/Y-90 solution in 1 M $HNO_3$. The corresponding frontal chromatogram of the Y compound is depicted in Fig. 2. We obtained the expected values for the breakthrough volumes and the numbers of theoretical plates, i.e. $V_{\text{BTT}} \approx 2\ V_{\text{BT1}}$ and $N_{\text{T}} = 2\ N_1 = 16$. The subscript 1 refers to the first column, T to the entire column set. However, we could not identify the breakoff point. At the calculated breakoff volume $V_{\text{BOTc}}$, we already found a significant amount of Y-90 in second column effluent. This is due to the low $N$ value of

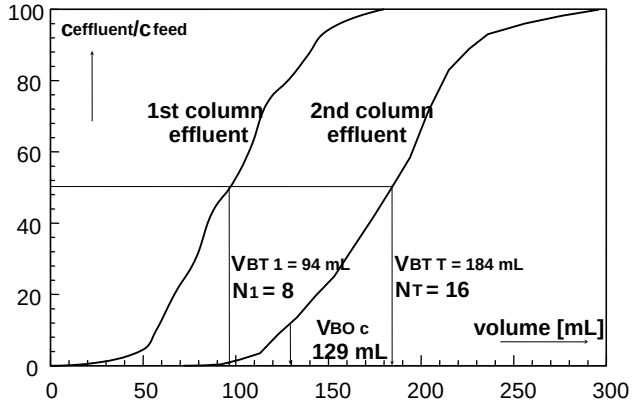


Fig. 2. Frontal chromatograms of $Y^{3+}$ using identical twins.

16. According to Eq. (7), at least 46 theoretical plates are required for a distinguishable breakoff point.

Therefore we repeated our test with a 0.001 M $Eu^{3+}$ solution in 1 M $HNO_3$ spiked with Eu-152. We knew from previous experiments [7] that our separation system shows not only a higher separation capacity, but also faster kinetics for lanthanide ions. The corresponding frontal chromatogram is depicted in Fig. 3, while we summarized the essential separation parameters in Table 2.

The values of Table 2 are in good agreement with our model. We observed a factor two between the first and total column effluent regarding breakthrough volume and number of theoretical plates. We could distinguish between wall and main stream in the effluent of either column, because the $N$ values were high enough, and the measured breakoff volumes were very close to the calculated ones. Only the concentration of the breakoff points was lower than expected. However, we had to accept a very large measurement uncertainty at the pertinent concentration range for both on-line and off-line detection.

### 4.2. Fraternal twins

For our fraternal twin column unit, we installed a small column of 10 cm length and a long column of 40 cm length. We used a carrier-free Sr/Y solution in 1 M $HNO_3$, in order to compare the results with those obtained with the identical twin column unit. The parameters of the first column effluent concurred with those obtained with the identical twin column unit. The ratios of the breakthrough volumes and the numbers of the theoretical plates yielded a factor $\sim 5 = (L_1 + L_2)/L_1$.

According to the separation parameters, as compiled in Table 3, we could not expect a distinct wall stream in the first column effluent due to the low number of theoretical plates. Instead, we clearly identified the concentration curve of the wall stream in the second column effluent (see Fig. 4) with a position of the inflection point close to that predicted by the model.

### 4.3. Feed assay

The solute concentration in the feed solution is the reference value for monitoring the chromatographic separation process. In this paper, we did not pay much attention to measuring that concentration, as we acquired fully fledged chromatograms for both column effluents during our experiments and, thus, automatically obtained a 100% breakthrough

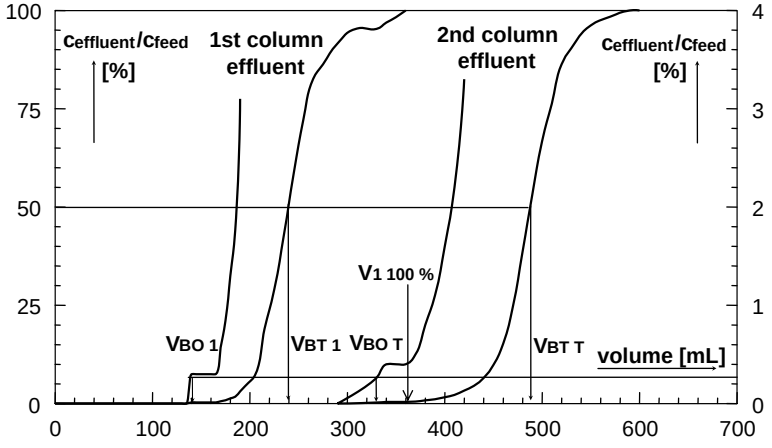


Fig. 3. Frontal chromatograms of $Eu^{3+}$ using identical twins.

Table 2
Parameters of a frontal chromatographic $Eu^{3+}$ separation using identical twin columns

| $V_{BT1}$ (ml) | $N_1$ | $V_{BO1}$ (ml) | | $V_{BTT}$ (ml) | $N_T$ | $V_{BOT}$ (ml) | |
|---|---|---|---|---|---|---|---|
| | | Calculated | Measured | | | Calculated | Measured |
| 240 | 87 | 168 | 173 | 486 | 161 | 340 | 334 |

Table 3
Parameters of a Frontal chromatographic $Y^{3+}$ separation using fraternal twin columns

| $V_{BT1}$ (ml) | $N_1$ | $V_{BTT}$ (ml) | $N_T$ | $V_{BOT}$ | | $c_{BOT}/c_{feed}$ (%) | |
|---|---|---|---|---|---|---|---|
| | | | | Calculated | Measured | Calculated | Measured |
| 88 | 9 | 431 | 48 | 302 | 312 | 1.0 | 0.8 |
| 89 | 9 | 413 | 50 | 289 | 297 | 1.0 | 1.2 |

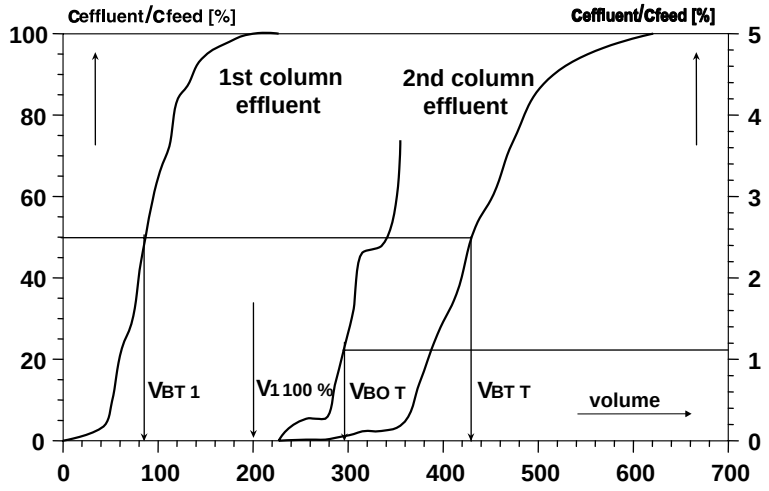


Fig. 4. Frontal chromatograms of $Y^{3+}$ using fraternal twins.

corresponding to the feed concentration of the solute. Under real conditions, however, and following our suggestions, the separation is to be terminated at the breakoff volume $V_{BOT}$, and that volume can only be identified if the feed concentration of the solute is known in advance.

To this end, it is worthwhile to compare the two versions of the twin column concept regarding the 100% breakthrough. Using identical twins, the feed concentration of the solute is reached at a volume in the first column effluent $V_{1\,100\%} > V_{BOT}$ in the second column effluent. This applies even for the $Eu^{3+}$ separation with its fast exchange kinetics (Fig. 3). On the other hand, we observed a $V_{1\,100\%} < V_{BOT}$ for the carrier-free $Y^{3+}$separation with its slow exchange kinetics (Fig. 4) when we employed the fraternal twin column set.

Consequently, we need a feed assay as an additional stage for a chromatographic decontamination with identical twin columns, while we could waive this stage by integrating it into the separation stage choosing the fraternal twin column unit.

### 4.4. Scrub and strip

For the removal of the solute from the columns, we applied the same flow direction (concurrent flow) as for the loading (see Fig. 1), but we placed the on-line monitor behind the second column. We used a 0.1 M citric acid solution with a pH of 3. Fig. 5 shows a typical elution chromatogram for the fraternal twin column set. The feed solution was completely displaced in the mobile phase after ~1 void volume. Then the bulk amount of the solute is stripped from the stationary phase within 1.5 void volumes. At that point, we observed an almost constant concentration in the column effluent and we suspended the elution for 24 h leaving the column beds in the elutriant. When we resumed elution the next day, we needed additional 1.5 void volumes to reach the background of the detector. Also, the simultaneous off-line measurement proved that the effluent was practically free of solute activity.

Again, it should be noted that both columns were loaded with the solute up to saturation. Under real conditions, loading is terminated much earlier probably resulting in more favorable elution volumes.

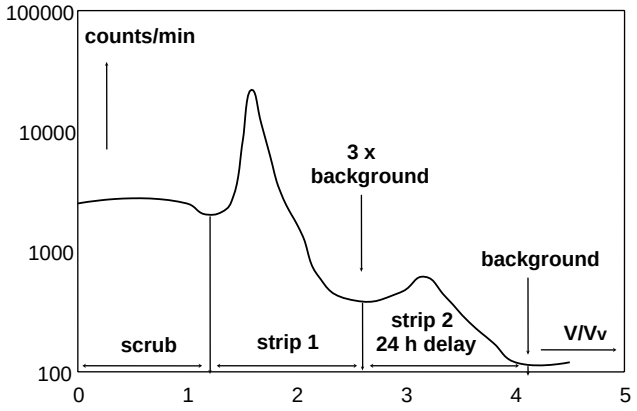


Fig. 5. Elution of $Y^{3+}$ using fraternal twins.

## 5. Conclusions

We devised a separation unit for the decontamination of process solutions based on frontal chromatography. We utilized previous findings that the concentration curve of a frontal chromatogram is composed of two branches for wall and main stream, and that regularities exist between the inflection points of the two branches which are independent of exchange kinetics and chemical system.

We set up a unit consisting of a "column–detector–column" array. Thus, we could identify the main stream inflection point in the first column effluent with our monitor and infer the wall stream inflection point in the second column effluent which is normally below the detection limits of commercial on-line monitoring systems.

We investigated this proposition with identical columns (identical twins) and with columns of varying length, but with the same packing structure (fraternal twins). We demonstrated that our concept is applicable to either alternative. However, we see a clear advantage in using fraternal twins, as the feed assay can be integrated in the separation stage of the process thus saving time and waste due to the regeneration of the detector.

We believe that we can enhance the field of application of frontal chromatography with our concept of the twin column chromatography, as it allows monitoring of the process below the detection limits of the monitor and, thus, eliminates the greatest impediment in implementing this technique.

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