

IN-LINE CONTROL OF A WASTE TREATMENT PROCESS BY SOLID SCINTILLATION COUNTING

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ABSTRACT. An in-line process control was developed for decontamination of aqueous solutions from Am and Pu by two-stage column chromatography operated in the breakthrough mode. The control is based on monitoring the column effluent by solid scintillation counting. The detector is placed between two columns, thus allowing the acquisition of a complete chromatogram without exhausting the extraction capacity of the whole set. The detector cell is adapted to a glove box over a commercially available connection for transport containers. The solid scintillator has a tendency to absorb tetravalent actinides, thus producing erroneous measurements during column loading and elution. The effect could be avoided by reducing Pu(IV) in the feed prior to loading the column and using a reducing agent for the column elution. Wall effects cause an early breakthrough of the α emitters, which occurs below the detection limits but affects adversely the decontamination factors. This breakthrough is assessed using an appropriate chromatogram evaluation, which can be built as a subroutine into the existing commercial measurement program.

INTRODUCTION

The Safeguards Analytical Laboratory (SAL) of the International Atomic Energy Agency (IAEA) uses destructive analytical procedures on industrial nuclear material, thus producing discards containing or contaminated with alpha-bearing components. Low-level α activity wastes are exported to the Austrian Research Centre Seibersdorf (ÖFZS) for further treatment. Discards containing nuclear material in a recoverable state are returned to the countries of origin. One category of discards derives from the analysis of Pu compounds and mixed (U, Pu) O_2 , and consists of aqueous solutions of high acidity with an average specific α activity of 500 Mbq liter⁻¹. Such discards can neither be accepted at the ÖFZS nor transported economically to the countries of origin.

At SAL, we developed a process for isolating and concentrating the α emitters of the discards. The process is based on column extraction chromatography using organic phosphine oxides as extractants and operated in the breakthrough mode. The columns are loaded with the feed solution until the α emitters are detected in the column effluent. Then the columns are washed, the α emitters are eluted with chelating agents and subsequently concentrated by evaporation. Finally, the columns are conditioned for re-use.

The activity of the column effluent must be monitored continuously during operation to assure adequate decontamination during column loading and complete recovery during column elution. The monitor should detect an early breakthrough and the very end of elution at extremely low concentrations of the α emitters, but will also be exposed to the highly concentrated eluate. These considerations (in-line detection of α emitters, sensitive response, wide concentration range) led almost automatically to solid scintillation counting, as the scintillator is reported to be sufficiently inert against the solution components and thus allows a direct exposure to the column effluent. External and internal interferences caused by beta and gamma radiation can be discriminated. I describe here the features of the device and report on the results.

DETECTION PARAMETERS

A detector for monitoring a chromatographic decontamination is placed at the column outlet where the changes in concentration or related variables of the column effluent are measured. The

decontamination factor achieved depends on the concentration in the effluent when the operation is discontinued. Ideally, the monitor should be capable of detecting the concentration, c_e , which corresponds to the decontamination factor prescribed by the separation problem. When high decontamination factors are to be achieved, c_e may be hidden in the detector background and must be calculated using separation parameters either taken or derived from the chromatogram.

In breakthrough chromatography with a feed concentration, c_0 , the effluent's concentration, c , follows the Laplace function (the error function with the argument, t)

$$c/c_0 = 0.5 - \frac{1}{\sqrt{2\pi}} \int_0^t e^{-t'^2/2} dt \quad (1)$$

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

The breakthrough volume, V_{BT} , depends on the stationary phase volume, V_0 , in the column and the distribution coefficient, K_D , of the chromatographic system

$$K_D = V_{BT}/V_0 \quad (3)$$

The number of theoretical plates, N , depends on the residence time of the mobile phase required to reach equilibrium. N can be calculated using Equation (2), as the t values are tabulated. Assuming a constant linear velocity of the flow, N should remain constant over the whole curve. Chromatograms taken with a varying flow velocity but the same chromatographic system should have varying N and, thus, different slopes but the same breakthrough volume.

At low effluent concentrations, one observes strong deviations from the model due to effects at the column walls. Nevertheless, I apply the model by replacing N in Equation (1) by a variable "number of effective plates N_{eff} " and determining empirically the function, $N_{eff} = f(V)$, using the measured effluent concentration and the corresponding tabulated t values. We have done this for a number of chromatographic systems and found that the resulting curves can be extrapolated beyond the concentration detection limits to $N_{eff} = 0$. The corresponding effluent volume depends again only on the stationary phase volume, V_0 , and the ratio, $V(N_{eff} = 0)/V_{BT}$, remains constant, even if solvent losses are observed for a repeated use of the column. I conclude that the wall effects determine the concentration at that effluent volume, and I suggest selecting that volume for discontinuing column loading for a chromatographic decontamination process. In the following, I refer to that volume as the breakoff volume, V_{BO} . We determined V_{BO} by measuring the feed concentration, c_0 , the breakthrough volume, V_{BT} , at $c_0/2$ and the effluent concentrations for a number of effluent volumes, $V_n < V_{BT}$. We could now use the above data and parameters to derive V_{BO} by calculating $N_{eff} = f(V_n)$, plotting the function $N_{eff} = f(V)$ and determining the breakoff volume, V_{BO} , by extrapolating graphically $N_{eff}(V)$ to $N_{eff} = 0$.

METHODS

Experimental work focused on the adaptation of the scintillation counting device, the determination of the characteristics of the adapted detector and the operation of the detector under routine conditions. The complete decontamination unit, including the detection device, was installed in a custom-made glove box supplied by Jacomex, Paris, France, because of the high α activity of the

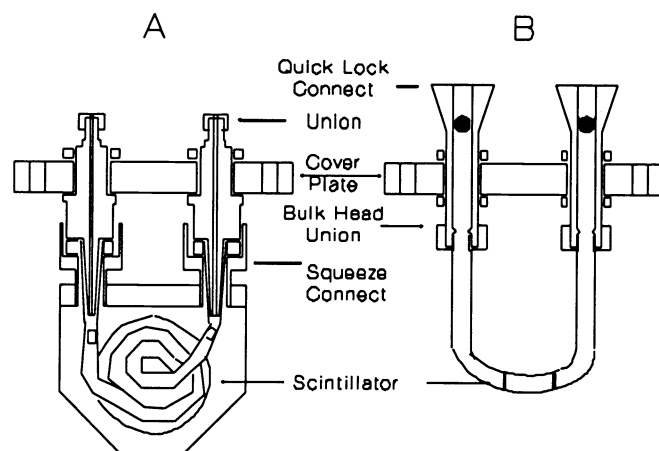


Fig. 1. A. Commercial detector; B. Custom-made detector

investigated solutions. The box was equipped with a transfer container from SNE La Calhène, Vélizy, France, which allows the fast and contamination-free transport of small items between two unconnected glove boxes. The solid scintillation counter, LB 506 A, was supplied by Berthold Instruments, Wildbach, Germany, including the measurement cell and the yttrium silicate scintillator particles. We used the two-channel Wallac 1214/1219 Rackbeta scintillation counter for reference and calibration measurements. The same company supplied the liquid scintillator, Opti-phase HiSafe™ 2. We prepared the chromatographic support by coating silica gel 100 produced by Merck, Darmstadt, Germany, with CMPO (an organic phosphine oxide) acquired from ATOCHEM, Philadelphia, Pennsylvania, USA. All other chemicals were procured in p. a. grade from Merck.

The LB 506 monitor is equipped with a detector (Fig. 1A) consisting of a Teflon spiral (internal diameter 2.3 mm) of an active length of 16 cm filled with ≈ 10 g yttrium silicate. The tube is accommodated in an Al frame, and attached with squeeze connects to the cell inlet and outlet, which are fastened with bulk head connects to the cell cover plate. Two photomultipliers are placed perpendicularly at either side of the frame. They are protected against light by the holder tubes screwed into the cell frame.

The very first experiments with real discard solutions revealed that this system was not applicable because the high activity of the solution caused an overflow in the multipliers, and the pressure buildup in the tube did not allow safe handling of the separation unit. Thus, we adapted the detector by replacing the spiral tube with a bent Teflon tube measuring 4 mm ID and 13 cm long. The scintillator was placed in the tube bend and fastened by frits with a pore diameter of $\approx 70 \mu\text{m}$ at either side. The tube frame was dropped. We used 0.5 g of scintillator, which resulted in an active length of 1.1 cm. The tube was connected with two bulkhead quick-lock connects fastened at the cell cover plate. Figure 1B shows a cross-section of the adapted detector tube. In test experiments, the detector yielded a satisfactory count rate and had a sufficiently low pressure drop.

The LB 506 is a compact apparatus that enables separating the measurement components (cell, multipliers and preamplifiers) from the electronics. The La Calhène connection permitted installation of the sensitive photomultipliers and preamplifiers outside the box. The La Calhène connection consists of a transfer flange fastened around a box port and tightly closed with a lid that has a bayonet lock. The closed container is locked from outside into the flange by intertwining

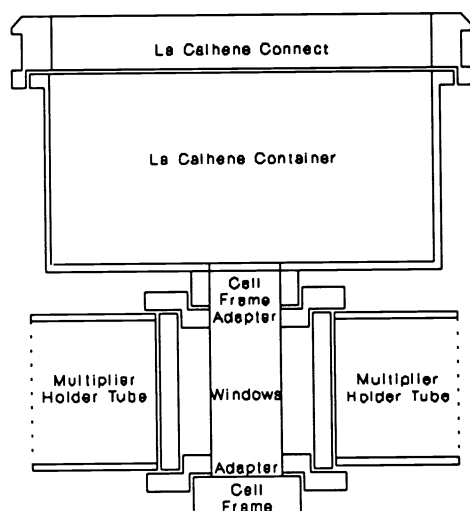


Fig. 2. Glove box adaptation of the detector

container lid and box port lid. The two lids can now be removed from inside the box, thus opening the container. The surfaces of container lid and port lid remain free of contamination, as they are pressed tightly together when the container is attached to the box.

Figure 2 shows the adapted detector. The detector cell frame was welded at the bottom of a La Calhène container. Two adapters were placed between the cell frame and the multiplier holder tubes to accommodate two plexiglass windows, which are tightly pressed against O-ring gaskets by the holder tubes. The cover plate with the scintillator tube (Fig. 1B) is fastened on top of the cell and inside the La Calhène container with two bolts. When the container is attached to the box, it forms together with the cell frame, the adapters and the plexiglass windows component part of the biological shieldings. Multipliers and preamplifiers are now outside the box and can be removed easily.

Figure 3 represents the chosen chromatographic array. The detector monitoring the column effluent is placed between two columns. Thus, a complete chromatogram is acquired from the first column, while the second column is still not exhausted. As a first approximation, I assume that the chemical behavior of the individual columns does not differ significantly. Separation parameters subject to deterioration during an extended column lifetime should, in most cases, change identically in both columns (extractant losses, chemical degradation). The deterioration of separation parameters that prevails in the first column (radiolytic decomposition of the extractant by the extractable compounds) would not affect adversely the quality of the separation, but feign a larger reduction of the overall capacity as actually occurs and would, hence, not lead to an early breakthrough at the outlet of the second column. Only a partial degradation of the second column support (air bubbles carried with the elutriant) would not be detected by the monitor, and would result in a contamination of the purified product.

We prepared reference Pu feed, Am feed and elution solutions from actual process solutions to reproduce exactly the properties of the media. For the Pu feed, we passed 100 ml of discard solution through a column filled with 12 g silica gel coated with 10 weight % CMPO and 1 weight % TBP. The resulting effluent was completely decontaminated from α emitters and was then spiked with varying amounts of MP2 reference material from CETAMA, Paris, France. The above column was then washed with 20 ml 2 M HNO_3 and eluted with 100 ml 0.01 M $(\text{NH}_4)_2\text{EDTA}$,

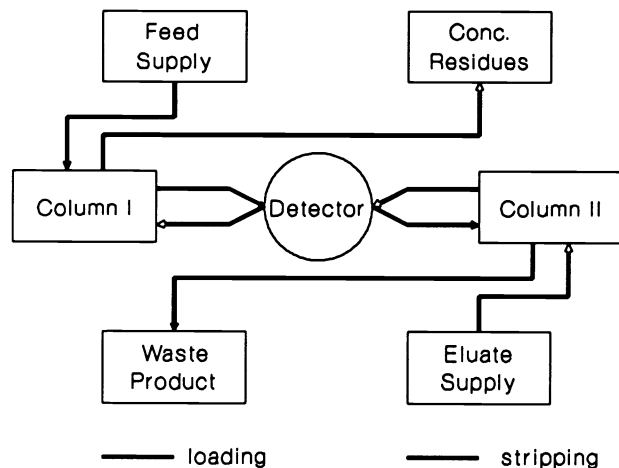


Fig. 3. Chromatographic monitoring array

pH \approx 4. Pu and Am were stripped from the column and the total contents of α emitters were determined with liquid scintillation counting (LSC). Varying concentrations were produced by diluting the solution with the elutriant. We prepared the Am feed solution by absorbing U and Pu from the discard solution in a column filled with 3 g silica gel with 10 weight % TOPO. Am was not extracted and remained in the effluent. The Am concentration was determined by LSC and γ spectroscopy. Varying concentrations were produced by mixing effluent aliquots with decontaminated feed.

We conducted three types of experiments to establish the parameters of an effective process control:

1. The behavior of the scintillator was tested with a simple device. A funnel was connected to the inlet of the scintillator tube and gravitational flow directed upward in the cell was applied. Through these experiments, we studied loading, scrubbing and calibration of the scintillator.
2. We acquired chromatograms by connecting the outlet of a chromatographic column with the scintillator tube inlet. The column eluate was fractionated after having passed the detector and off-line comparison measurements were made with LSC.
3. We performed decontamination studies using the full process design as shown in Figure 2, except that the same flow direction was used for column loading and elution. Decontamination factors were determined by taking samples from the second column effluent and measuring the α activity with LSC.

RESULTS AND DISCUSSION

Figure 4 describes the scintillator loading and scrubbing. The scintillator (1.8 ml dead volume of the measurement system; 0.04 ml interstitial volume of the scintillator bed) interacts without delay to the activity increase in the solution and reaches after 3.5 ml (net 1.7 ml) a constant maximum value. I did not observe an accumulation of activity due to a possible absorption of the α emitters in the glass.

I tested a variety of scrubbing solutions individually and in sequence. When scrubbing is performed quickly after loading, the scintillator shows a fast reduction of the measurement signal down to a certain level with all elutriants. With HNO_3 in various concentrations, \approx 75 % of the activity could

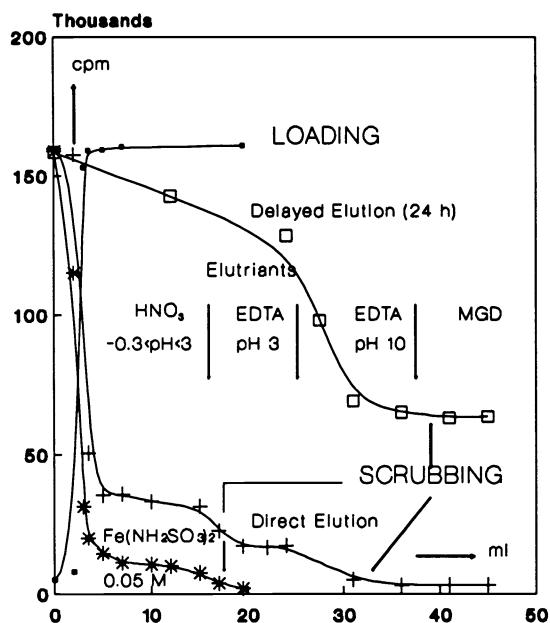


Fig. 4. Scintillator loading and scrubbing

be removed quickly; the signal remained almost constant thereafter. A further reduction could be achieved with EDTA solution of pH ≈ 3 ; however, a significant, residual activity was measured. The pH of the eluate was determined to be ≈ 2 ; consequently, the glass had absorbed H^+ ions, which probably prevented the complete formation and subsequent removal of the Pu-EDTA complex. The scintillator was cleaned completely using EDTA, pH ≈ 10 , as elutriant. I obtained different results after exposing the glass to the feed solution for a longer period. Neither HNO_3 nor EDTA, pH 3, reduced significantly the activity in the scintillator bed. Elution with EDTA, pH 10, was only modestly successful. Sufficient cleaning to background level was attained with an $Fe(NH_2SO_3)_2$ solution, which reduced Pu(IV) to Pu(III) on the scintillator.

I conclude that the scintillator absorbs easily tetravalent actinides, whereas it is almost inert toward trivalent actinides. This is confirmed by quenching effects observed during the comparison of reference feed and eluate solutions that showed different calibration curves. I assume that the scintillator forms a stationary phase with aqueous solutions, and most light pulses are produced in that phase.

We carried out single-stage column experiments and acquired complete chromatograms for loading and elution. A breakthrough chromatogram of an actual feed solution is depicted in Figure 5. The activity curve is composed of two branches. The Am(III) front appears first in the effluent and shows the expected shape. The Pu(IV) front behaves quite differently; it does not monotonously approach a constant end value, but has a maximum quite above the activity in the feed, and then slowly decreases to the feed value. This is due to the presence of U(VI) in the feed, which is even better extracted than Pu(IV), saturates the upper regions of the chromatographic support and displaces Pu(IV).

This combined Pu loading/displacement would render the chromatogram evaluation extremely difficult. However, for the present problem, it is insignificant, as the process would be discontinued when the Am breakthrough is observed, and the Am(III) and Pu(IV) fronts are well resolved. We

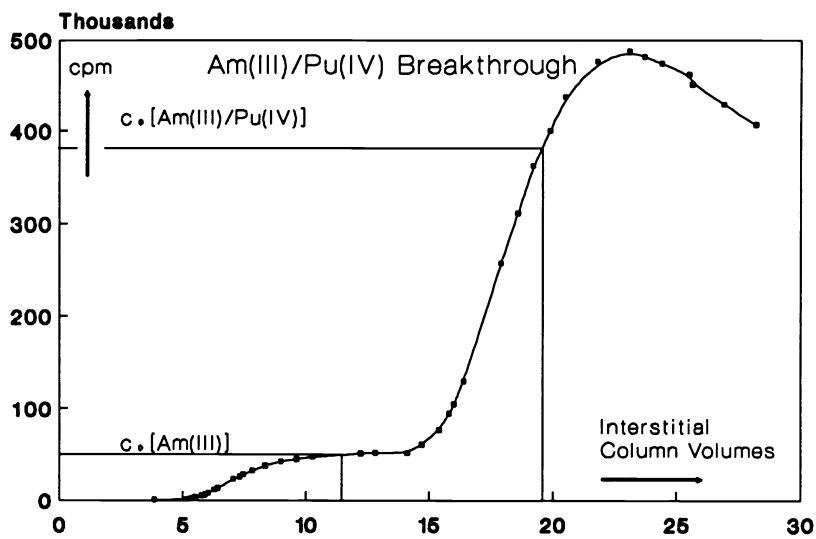


Fig. 5. Breakthrough chromatogram of Pu(IV)/Am(III)-bearing feed solutions

found by examining the chromatogram that the Am effluent concentration reached its feed value at $2.5 V_{BO}$. This would allow the in-line determination of c_0 by using columns of similar size.

After loading, the column was eluted with a 0.01 M EDTA solution, pH ≈ 3 . Simultaneously, we fractionated the column effluent and measured the activities of the fractions off-line by LSC. Figure 6 presents the Am(III)/Pu(IV) elution curves. The α activity determined in-line shows a large increase in the initial effluent fractions and then decreases very slowly. In contrast, the off-line determination proves that the effluent activity decreases significantly. As expected, Pu is absorbed by the scintillator, thus preventing monitoring of the elution.

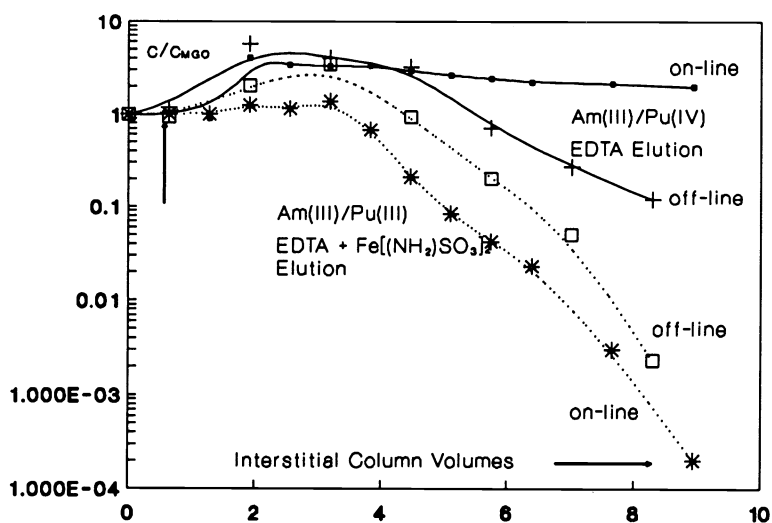


Fig. 6. Pu/Am elution curves; — = Am(III)/Pu(IV) elution curves; ... = Pu(III) elution curves

In summary, Pu(IV) appears to interfere with the monitoring of the process, but also with the elution of the chromatographic support, as large volumes of elutriant would be needed to strip Pu completely. Therefore, another process variant was tested by loading Pu(III) on the column. The feed solution was treated with $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ reducing Pu(IV) to Pu(III); then the trivalent actinides were extracted, and finally, the column was eluted with a 0.01 M EDTA + 0.01 M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ solution, pH ≈ 3 . The breakthrough chromatogram is presented in Figure 7, the elution curves (on- and off-line) in Figure 6. The breakthrough chromatogram (Fig. 7) shows no resolution of the Am(III) and Pu(III) front. Simultaneous off-line measurements revealed that the beginning of the breakthrough is still caused by Am(III). This disadvantage is clearly compensated by the favorable behavior of scintillator and chromatographic support during elution (Fig. 6). The trivalent actinides are not or little absorbed on the scintillator, and the activity decrease can be monitored directly. Further, the total elution volume is significantly reduced.

We evaluated the chromatogram in Figure 7 for the endpoint of the decontamination process using the total α activity in the feed, the sum of Am(III)/Pu(III) counts, and also the Am(III) α activity as feed concentration, c_0 . The resulting functions, $N = f(V)$, are noted in Figure 7. The bell-shaped curve for the total activity breakthrough appears distorted, as should be expected, because Pu(III) and Am(III) do not have identical K_D values. The straight line branch is not well developed.

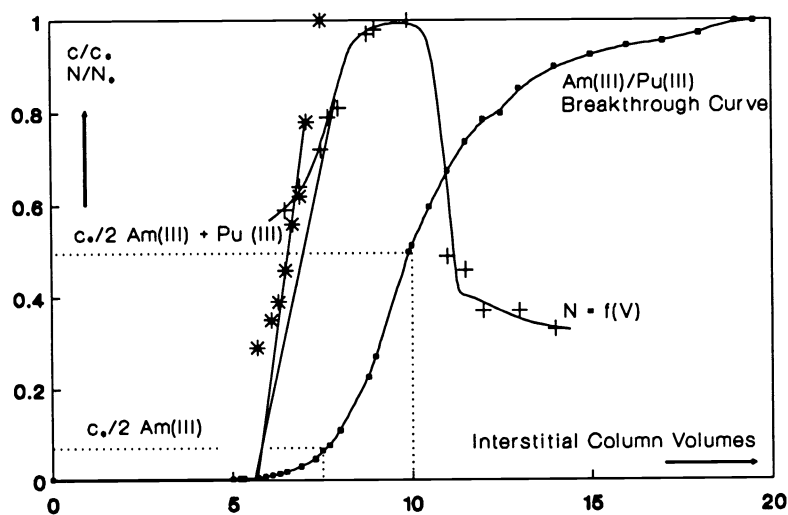


Fig. 7. Joint Am(III)/Pu(III) breakthrough curve; curved line = total activity; bell-shaped curve = V_{90} determination

A complete curve cannot be obtained for Am(III), as the descending branch is masked by the Pu breakthrough. However, the ascending branch of the curve shows an extended straight line and is easily extrapolated to $N = 0$. The important parameters of this graphic evaluation are compiled in Table 1. Corresponding to the delayed Pu activity increase, N_{\max} is much lower for Pu than for Am. This may be due to a partial oxidation during the phase transfer, but requires further study. The breakoff volumes are identical within the statistical uncertainty.

A number of two-stage operations were carried out by monitoring the column effluent at the outlet of the first column. The effluent of the second column was collected, homogenized and samples

TABLE 1. Chromatogram Evaluation Parameters

Parameters	Am-branch	Total curve
Concentration ratio c_0/c_T	0.13	1
Breakthrough volume V_{BT}	7.52 ICV*	9.93 ICV
Maximum number of theor. plates N_{max}	123	43
Breakoff volume V_{BO}	5.7 ICV	5.6 ICV

*ICV = Interstitial column volume

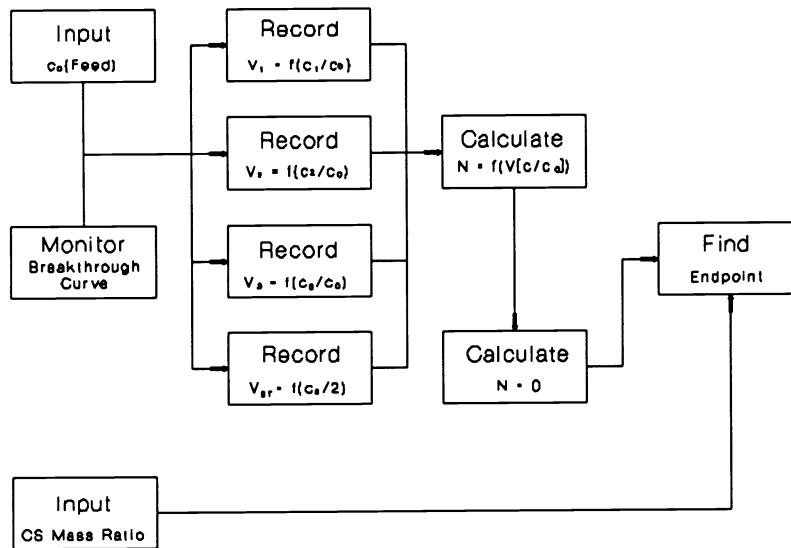


Fig. 8. Block scheme of the process control subroutine

were taken for determining the decontamination factor. The breakoff volume was determined employing the evaluation described above. Decontamination factors ~5000 could be achieved as confirmed by off-line measurements.

The evaluation procedure described here should be incorporated as a subroutine into the existing measurement program, which should comprise the following steps (Fig. 8):

1. The feed concentrations and corresponding α -activities are determined prior to the decontamination, converted into a measurement signal and input into the routine. The mass of the chromatographic support (CS) is known, when the columns are loaded.
2. When the column effluent is monitored, selected volumes, among them the breakthrough volume, V_{BT} , corresponding to prescribed concentration ratios are recorded.
3. The recorded values are used to calculate the number of theoretical plates as a function of the concentration ratio, c/c_0 , and extrapolated to $V_{BO}(N = 0)$.
4. The endpoint of the decontamination is found by multiplying V_{BO} with the mass ratio of the chromatographic supports.

