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ARTICLE

Surface Dose Evaluation of a Reactor Pressure Vessel Based on a Representative Nuclide Selection Methodology

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In our previous study, separation of americium (Am) from curium (Cm) was successfully achieved using N,N,N',N'-tetraoctyl diglycolamide (TODGA) in 1 mol/L hydrochloric acid (HCl) through chromatographic techniques. To gain a better understanding of Am and Cm behavior towards different concentration of HCl, in this study, we performed Am/Cm separation in varying concentrations of HCl, we conducted experiments at 0.1M, 0.5M, 0.8M, and 1.2M HCl as comparison. The effectiveness of separation of each HCl concentration is analyzed by calculating some key parameters such as separation resolution (R), separation factor (α), and the number of theoretical plates (N). The result shows that 1.0M of HCl shows significant separation compared to other mentioned concentration, as indicated by highest R and N value. Separation system in 1.2M of HCl shows higher separation factor than 1.0M, however, broader peaks and tailing between Am and Cm in this condition reduce efficiency of separation. This study provides valuable insights into optimizing HCl concentration for effective Am/Cm separation by considering R, N and α values with implications for applications in nuclear waste management and radiochemistry.

KEYWORDS: TODGA, Americium, Curium, Chromatograph, Separation, Resolution, Efficiency

I. Introduction

The separation of americium (Am) and curium (Cm) has been extensively studied to develop methods for nuclide separation as a pre-treatment for highly precise and accurate actinide analysis in spent fuel and nuclear fuel debris using mass spectrometry techniques, such as inductively coupled plasma tandem mass spectrometry (ICP-MS/MS). The application of inductively coupled plasma mass spectrometry (ICP-MS) in elemental and isotopic analysis of actinides has been widely explored across various disciplines, including nuclear applications.[1-5)]

In research on Am/Cm separation, oxidation of Am from its stable trivalent state (Am^{3+}) to higher oxidation states (Am^{5+} or Am^{6+}), followed by chemical separation in nitric acid, has been achieved by several researchers.[6-9)] However, altering the oxidation state of Am and Cm is challenging due to their natural stability as trivalent actinides. Complete separation of Am from Cm was demonstrated by Suzuki et al. using pyridine resin as an ion exchange medium in a nitric acid/methanol mixed solvent. While effective, this method poses safety and environmental concerns due to the involvement of methanol and concentrated nitric acid.[10)]

Another approach investigated Am/Cm separation using a cation exchange resin, Dowex 50, in hydrochloric acid (HCl) solution. Although this method yielded only slightly separated peaks for Am and Cm, it highlighted the need for improved resolution in separation techniques.

In nuclear reprocessing, the EXAm (Extraction of Am) hydrometallurgical process was developed to specifically isolate Am from Cm and other fission products using organic extractants. To enhance separation during the extraction and scrubbing phases, the complexing agent N,N,N',N'-tetraethyl-diglycolamide (TEDGA) is incorporated into the aqueous phase. Additionally, strong diamide-type extractants containing ether oxygen in their central structure, such as diglycolamides (DGA), have shown significant promise for separating trivalent actinides from lanthanides, particularly for the selective separation of Am from Cm.

In previous studies, the separation of Am from Cm was successfully achieved using N,N,N',N'- tetraoctyl diglycolamide (TODGA) in 1.0M HCl via chromatographic techniques. A new simplified method using impregnated resin under low concentrations of HCl has been developed for the separation of Am(III)/Cm(III), serving as a pretreatment for highly precise and accurate actinide analyses of spent fuels and nuclear fuel debris by using mass-spectrometry such as ICP-MS/MS. This method enables high-resolution separation of Am/Cm even at low HCl concentrations, making it particularly suitable for application in nuclear facilities with stringent safety requirements. Previous batch experiments indicated that lower concentrations of HCl offer higher potential for Am/Cm separation.[11)]

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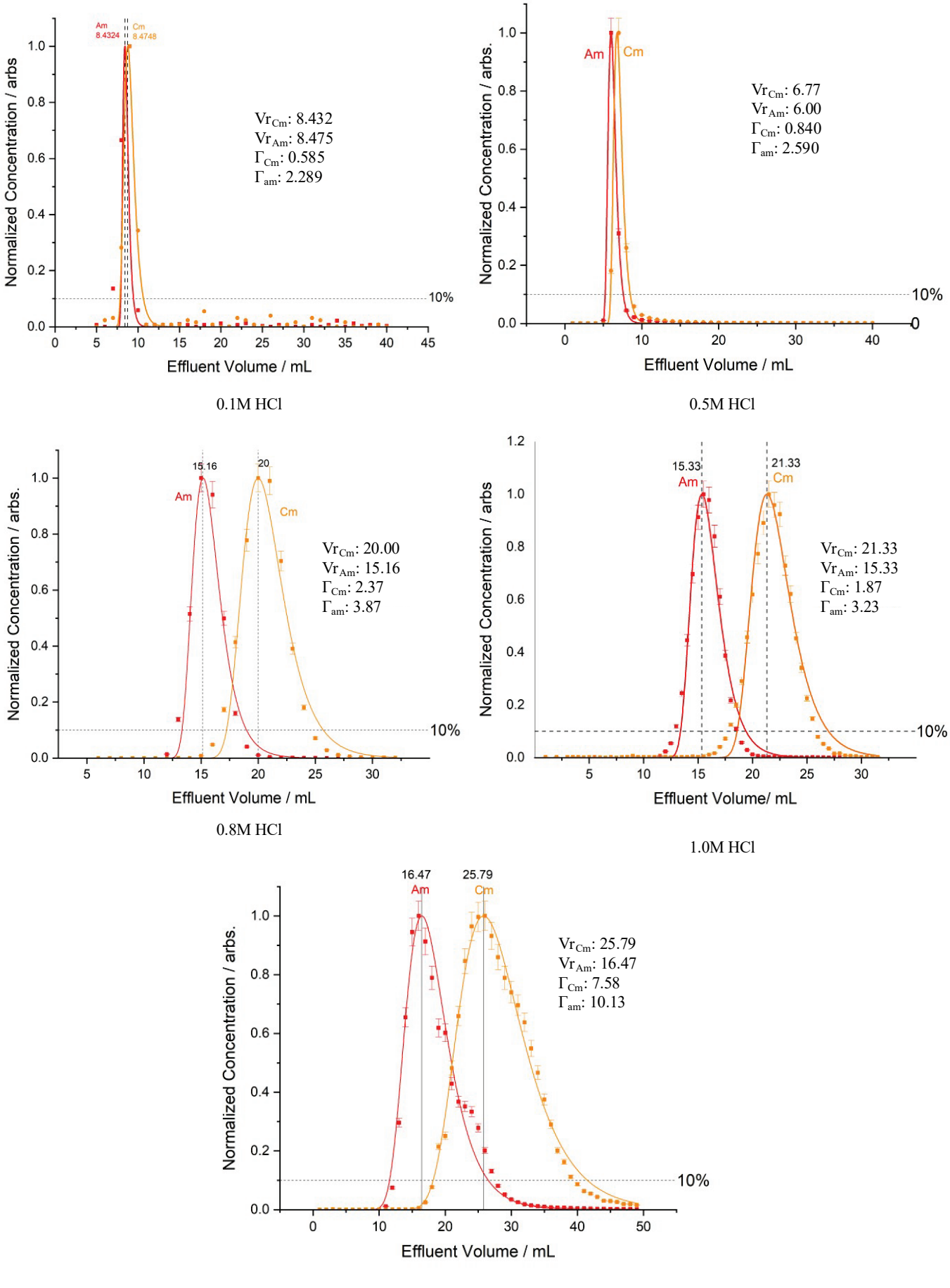

Fig 1. Chromatogram of Am and Cm Separation by using TODGA-resin in different HCl concentration (0.1M, 0.5M, 0.8M, 1.0M, and 1.2M)

In column chromatography, resolution (R) reflects how completely target components in a sample are separated as they pass through the column, considering factors such as efficiency, selectivity, and retention. The separation factor (α) measures the chromatographic system's ability to chemically distinguish between sample components. Theoretical plates (N), introduced by Martin and Synge, represent discrete sections within the chromatographic column, with each plate signifying the distance necessary for one adsorption-desorption cycle between the stationary and mobile phases. Calculating resolution, selectivity, and theoretical plates is essential for analyzing the performance of separations. Understanding these fundamental parameters can guide the development and optimization of separation methods.

In chromatogram graph interpretation, the term "Resolution" refers to the ability of the chromatographic system to distinguish between two closely eluting compounds or analytes. It quantifies how well two peaks in a chromatogram can be separated from each other. Higher resolution means better separation, where the peaks are more distinct and well-separated. In general, R can be calculated in different ways, such as using full width at half maximum or baseline widths. However, R_{v10} provides a more detailed look at the separation at 10% height, which is helpful for understanding peak overlap or asymmetry in this system. This approach is considered to evaluate the separation of Am and Cm when the peaks are asymmetrical.

In this study, the separation experiment of Am from Cm using TODGA resin in varying concentrations of HCl (0.1M, 0.5M, 0.8M, and 1.2M) was conducted and compared the result with the previous separation Am/Cm result in 1.0M HCl to investigate the separation behavior of Am and Cm at lower HCl concentrations. The efficiency of the separation was analyzed by calculating the resolution, separation factor, and number of theoretical plates for each HCl concentration.

II. Experimental

The feed preparation and chromatographic separation using TODGA were carried out as follows:

a) Preparation of the Chromatography Column: Approximately 8.5 mL of TODGA resin was packed into a Muromac mini column L, with a column height of 10 – 10.5 cm. The column was pre-washed with the same concentration of HCl as the elution solution to ensure consistency.

b) Preparation of Feed Solution: First, the feed was dried to remove any unnecessary acids, such as HNO_3, and any organic compounds that might be present. After drying, a specific concentration of HCl was added to the feed solution containing Am and Cm. the concentration of HCl in the feed solution was adjusted with HCl concentration in the elution solution that used in the chromatograph separation. For separation of Am/Cm experiment in 1.0M HCl, the same concentration of HCl was adjusted in the feed solution. We used approximately 1 kBq of Am and 37 kBq of Cm in every separation experiment.

c) Chromatographic Separation: To begin the separation process, 1 mL of the feed solution containing Am and Cm was injected into the column. This was followed by the continuous injection of 45 mL of HCl aqueous solution at a flow rate of ~0.8 mL/min to elute the Am and Cm from the resin. Effluents were collected in 1 mL fractions. The concentrations of Am and Cm were measured using ICP-MS/MS (Agilent 8900) at mass numbers 241 and 244 in no-gas mode. All eluted fractions were measured without applying reaction or collision cell modes. The concentration profiles presented in the chromatograms were normalized to the peak maximum of each element in each run. That is, each data point was divided by the maximum count for the corresponding nuclide in that particular experiment, allowing relative concentration comparisons across experiments. Experimental variations: five separate chromatographic experiments were conducted using different concentrations of HCl (0.1M, 0.5M, 0.8M, and 1.2M) to investigate the effect of HCl concentration on the separation efficiency.

III. Result and Discussion

Figure 1 showed the results of a series of separation experiment in five different HCl concentration by using TODGA resin. Besides the distance of peaks, it is important to observe the overlap area from chromatogram graphs of Am and Cm. The overlap area in the graph shows how Am and Cm were mixed in the fraction. Every graph from chromatography was fitted by extreme gaussian.

From the chromatogram graphs in Fig. 1, Am and Cm could not be separated in 0.1M. Separated peak of Am and Cm can be distinguished starts from 0.5M HCl. In 0.5M HCl, the peaks are slightly separated where the peak of Am was detected in 5.9 mL and Cm in 6.8 mL of effluent volume. The distance between two peaks is increasing in higher concentration, in 0.8M, 1.0M and 1.2M, the distance between peak of Am and Cm is ~5 mL, ~6 mL, and ~9 mL, respectively.

To quantitatively assess the separation performance, the recovery rates of Am and Cm in each experiment were calculated and are presented in **Table 1.** The recovery rate is an important parameter that indicates the efficiency of elution and the degree to which each element was retained and then recovered from the resin. It is calculated by comparing the total amount of Am or Cm detected in the collected fractions to the amount originally loaded onto the column.

The chromatogram graphs of Am/Cm separation in 0.8M, 1.0M and 1.2M of HCl can be easily compared by looking at the height and wideness of the area. From the Fig. 1.0M has smallest overlapped area among the result. Although 1.2 shows a larger overlapped area compared to 0.8M. Although a quick visual inspection of a chromatogram—such as observing the depth of valleys between peaks—can give an initial sense of separation, a proper evaluation should be based

Table 1. Recovery rate of Am/Cm separation in HCl

HCl (mol/L)	^{241}Am (%)	^{244}Cm (%)
0.1	96.40	91.62
0.5	100	98.56
0.8	94.003	92.42
1	100	96.55
1.2	100	99.8

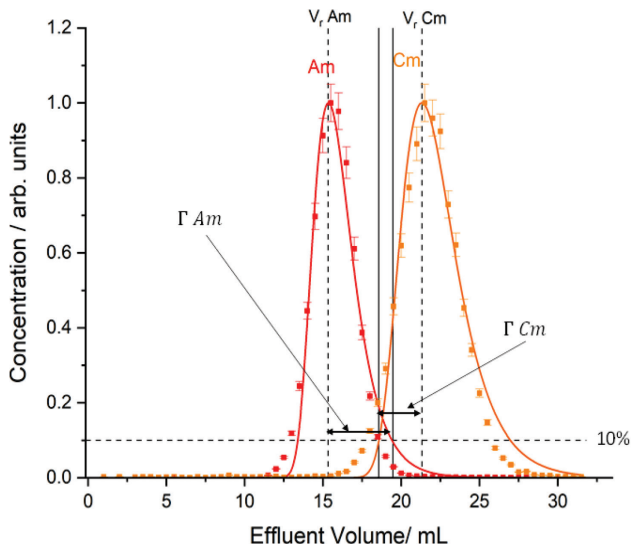

Fig 2. Chromatograms of Am and Cm by using TODGA-resin in 1.0M HCl aqueous solution

on quantitative parameters like resolution, separation factor, and the number of theoretical plates.

The R_{v10} was calculated by using following formula.[9)]

$$R_{v10} = \frac{Vr_{Cm} - Vr_{Am}}{\Gamma_{Cm} + \Gamma_{Am}} \quad (1)$$

where the Vr is the effluent volume at the elution peak, Γ_{Am} and Γ_{Cm} are the left-side width and the right-side width at 10% height of each peak maxima, respectively. **Figure 2.** shows the chromatograms of Am and Cm in 1.0M HCl, where the peak of Am is 15.33, and 21.33 for Cm. while, Γ_{Am} and Γ_{Cm} are 3.23 and 1.86, respectively.

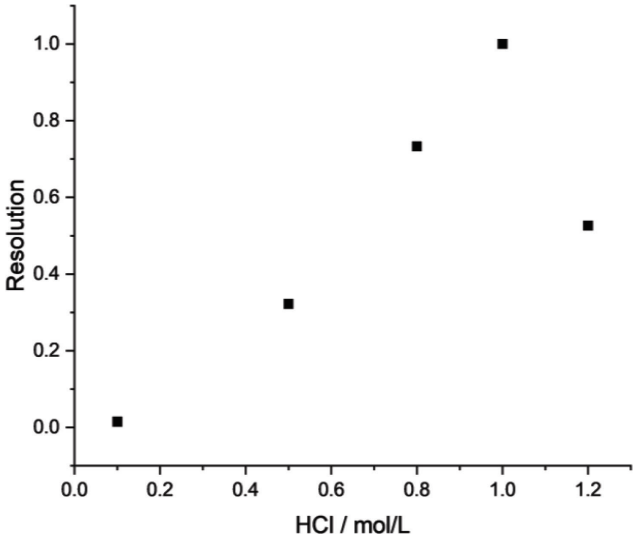

Fig. 3 Resolution of Am/Cm separation by using DGA in different concentration of HCl aqueous solution

The resolution of the Am and Cm separations at 0.1 M, 0.5 M, 0.8 M, 1.0 M, and 1.2 M HCl concentrations was calculated and is shown in **Fig. 3**. Among these, the resolution was highest at 1.0 M HCl, indicating the most effective separation with minimal peak overlap. The overlap-related width term includes Γ_{Am} and Γ_{Cm} are the left and right widths at 10% of the peak height, respectively. These values reflect peak broadening and tailing, both of which directly contribute to the extent of peak overlap. Therefore, although we did not explicitly calculate the overlapping area, the resolution calculated using this method provides a reliable and quantitative indicator of separation quality, incorporating the influence of both peak spacing and overlap.

A common limitation of resolution-based evaluation is that it typically applies to only two adjacent peaks at a time. Additionally, traditional resolution formulas often assume symmetrical, Gaussian-distributed peaks, which do not always reflect real chromatographic behavior.[12)] In practical applications, peak asymmetry due to tailing or fronting is frequently observed. To account for this, resolution in the present study was calculated using peak widths at 10% of the peak height.[13)] This method enables resolution to be quantitatively evaluated even for asymmetric peaks and does not rely on the assumption of a perfect Gaussian distribution. Despite the limitations of classical resolution theory, this approach remains effective for assessing separation performance under non-ideal conditions.

The separation factor (α) in chromatography (also called the selectivity factor), often denoted as α (alpha), is a critical parameter that quantifies how well two components are separated during a chromatographic process. α measures the relative separation between two analytes based on their retention factor (k) or distribution coefficients (K_d). α indicates how much longer one component is retained over another. The retention factor is defined as:

$$k = \frac{(V_r - V_0)}{V_0} \quad (2)$$

Where V_r is the effluent volume at the peak solution and V_0 is the dead volume. The K_d is defined as:

$$K_d = \frac{(V_r - V_0)}{V_s} \quad (3)$$

Where V_s is the stationary phase volume or volume of resin. α is calculated by comparing the distribution coefficients of the two analytes:

$$\alpha = \frac{K_{d_{Am}}}{K_{d_{Cm}}} = \frac{Vr_{Am} - V_0}{Vr_{Cm} - V_0} \quad (4)$$

Based on the result, 1.2M has highest α and followed by 1.0M and 0.8M. This order is like the number of distances between peak of Am and Cm. From **Fig. 4**. In this system, relationship between separation factor and concentration of HCl are linier. The distance between peak of Am and Cm is increasing in higher concentration of HCl.

Greater than 1.0 indicates that the two components are separated, with higher values representing better separation. Typically, a separation factor between 1.1 and 2.0 is considered good, depending on the complexity and requirements of the analysis.

The theoretical plate number is a fundamental parameter used to evaluate the efficiency of a chromatographic column. It represents the number of hypothetical equilibrium stages between the mobile and stationary phases. N value defines

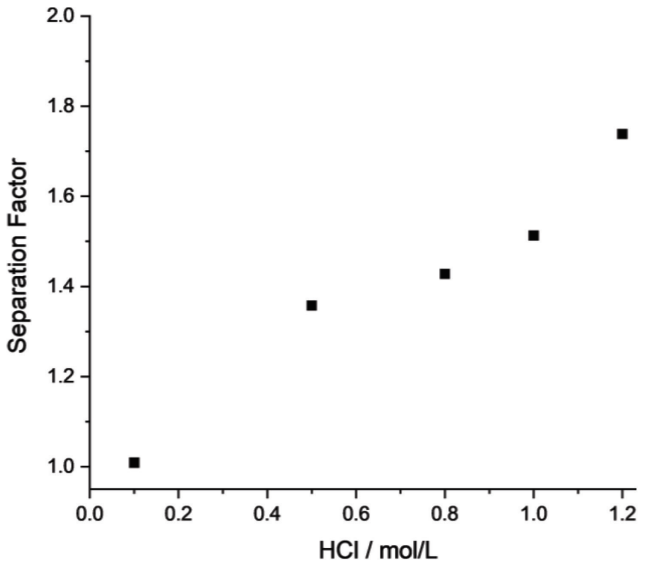

Fig. 4. Separation factor of Am and Cm in different concentration of HCl

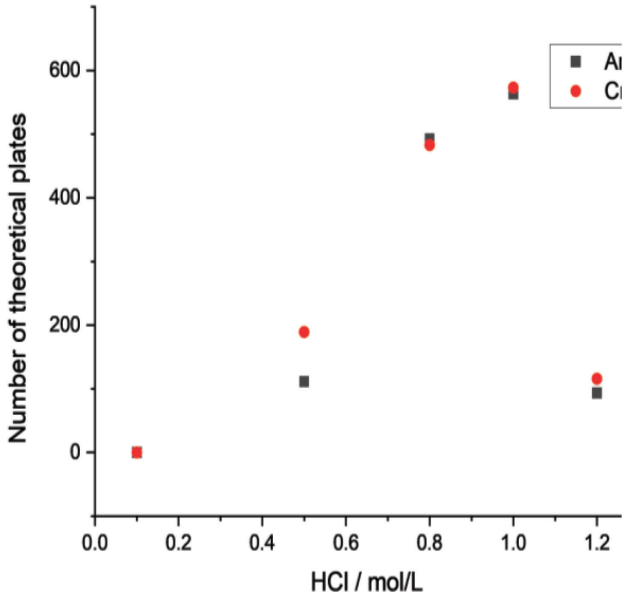

Fig. 5. Number of Theoretical Plates of Am/Cm separation by using DGA in HCl aqueous solution

peak sharpness or column efficiency. Reflects how well a column limits band broadening. While N does not inherently account for overlapping peaks, it is sensitive to peak broadness caused by tailing or fronting. In this work, N was calculated by using the following formula (**6**). This formula is adapted from the standard expression **(5)**. FWHM (Full Width at Half Maximum) obtained from a peak fitted with the extreme Gaussian function, by using OriginPro:

$$N = 5.54\,(\frac{T_R}{FWHM})^2 \quad (5)$$

$$N = 5.54(\frac{V_{R-V_0}}{FWHM})^2 \quad (6)$$

Where T_R is retention time, it can be calculated by diving the volume retention with flow rate. chromatograms use effluent volume (mL) on the x-axis rather than time, we replaced the retention time with retention volume and ensured that the FWHM was also measured in volume units for consistency.

The relationship between peak broadening and the number of theoretical plates is nonlinear and inversely proportional. As peak width increases due to broadening, the calculated N value decreases, indicating a decline in column efficiency. Thus, sharper (narrower) peaks correspond to a higher number of theoretical plates and improved chromatographic performance.

Figure 5. illustrates the number of theoretical plates for the separation of Am and Cm in various HCl concentrations. These results show a clear trend. At 0.5 M HCl, both Am and Cm peaks elute early and have relatively narrow FWHMs, but because of the short retention volume, the calculated N values are low. As the HCl concentration increases to 0.8 M and 1.0 M, retention volumes increase significantly, and although FWHM also increases slightly, the net effect is a higher N, indicating improved separation performance. However, at 1.2 M HCl, while retention volume remains high, the broadening of peaks (especially for Cm) leads to a significant drop in N reflecting reduced column efficiency despite longer retention.

While both retention volume and FWHM influence the number of theoretical plates, FWHM has a stronger impact due to its position in the denominator of the squared term. A small increase in peak width leads to a significant decrease in N, making peak sharpness (or minimizing band broadening) more critical for improving column efficiency than retention volume alone.

$$R_{v10} \propto R = \frac{\sqrt{N}}{4} \times \left(\frac{\alpha-1}{\alpha}\right) \times \left(\frac{k}{k+1}\right) \quad (7)$$

According to Eq. (7), R is propositional to R_{v10}. This demonstrates that while the separation factor is an important determinant of resolution, high column efficiency and optimal retention factor are equally essential. The balance of these three parameters is critical to achieving maximum resolution in chromatographic separations.

On **Fig. 6**, R was calculated using Eq. (7) and R_{v10} obtained from Eq. (1). R and R_{v10} show a consistent trend with the experimental resolution, supporting their proportional relationship. Both of result confirmed that 1M HCl shows the highest resolution. In most cases R was

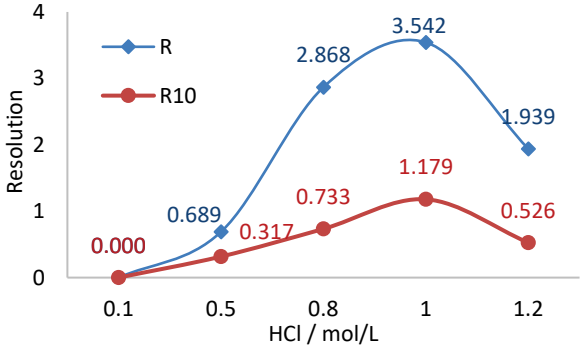

Fig. 6 Comparison R and R_{10}

calculated with FWHM (Full Width at Half Maximum), which corresponds to the width at 50% of peak height, assuming Gaussian symmetric peaks. While R_{10} Uses Γ, which is the sum of asymmetric left and right side widths at 10% peak height, near the baseline, to better account for overlapping and asymmetric peaks.The separation factor (α) primarily affects the distance between peak maxima, while column efficiency (N) determines peak sharpness, and the retention factor (k) reflects the interaction strength between the analyte and stationary phase. Notably, R increases approximately with the square root of N. R has a stronger dependence on α when α is close to 1. Adjusting any of these parameters can enhance resolution and overall chromatographic performance.

IV. Conclusion

The separation of Am and Cm was investigated across various HCl concentrations, revealing distinct differences in separation efficiency. At 0.1M HCl, effective separation was not achieved. However, at 0.5M HCl, separation began with relatively low resolution (0.0015) and separation factor (1.008 ± 0.05). As HCl concentration increased, the separation factor improved, with peak distances between Am and Cm reaching approximately 5mL, 6mL, and 9mL at 0.8M, 1.0M, and 1.2M HCl, respectively.

The most effective separation was observed at 1.0M HCl, where the highest resolution and number of theoretical plates were achieved, indicating superior column efficiency and sharper peaks. However, in 1.2M HCl, despite the larger peak distances, broader peaks and a larger overlap area reduced the overall resolution and column efficiency. This trade-off between peak broadening and separation effectiveness underscores the importance of optimizing both resolution and theoretical plates for achieving precise Am/Cm separation. While 1.2M HCl exhibited the highest separation factor, the broader peaks and lower efficiency compared to 1.0M HCl suggest that higher HCl concentrations may not always yield the best overall separation performance.

These results highlight that while the separation factor contributes to peak separation, achieving high resolution also depends critically on column efficiency and the retention factor. A balanced optimization of all three parameters is essential for effective chromatographic performance.

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