Separation and Determination of Citric Acid by Ion Chromatography in Radioactive Concrete Waste

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During the dismantling of nuclear facilities, a large quantity of radioactive concrete is generated and chelating agents are required for the decontamination process. However, disposing of environmentally persistent chelated wastes without eliminating the chelating agents might increase the rate of radionuclide migration. This paper reports a rapid and straightforward ion chromatography method for the quantification of citric acid (CA), a commonly used chelating agent. The findings demonstrate acceptable recovery yields, linearities, and reproducibilities of the simulated samples, confirming the validity of the proposed method. The selectivity of the proposed method was confirmed by effectively separating CA from gluconic acid, a common constituent in concretes. The limits of detection and quantification of the method were 0.679 and 2.059 mg·L^{-1}, respectively, while the recovery yield, indicative of the consistency between theoretical and experimental concentrations, was 85%. The method was also employed for the quantification of CA in a real concrete sample. These results highlight the potential of this approach for CA detection in radioactive concrete waste, as well as in other types of nuclear wastes.

Keywords: Chelating agent, Ion chromatography, Citric acid, Gluconic acid, Radioactive concrete waste, Quantitative analysis

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1. Introduction

Chemical decontamination activities are the principal source of chelating agents in low- and intermediate-level radioactive waste (LILW). Polycarboxylic acids such as citric acid (CA) and aminopolycarboxylic acids such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) are commonly employed chelating agents [1]. The metal complexing capability of these compounds is crucial for their application as decontamination agents for both nuclear facility operations and decommissioning. The structures of some chelating agents are shown in Fig. 1.

Polyhydroxycarboxylic compounds can be also present in nuclear wastes as degradation products of other organic materials, particularly cellulose, or as additives in the concrete used in containers [2]. Diverse cement additives are present in concrete packaging and waste cementation. These additives can be also found in the grout used as a backfill around the containers in the repository. Simultaneously, the multidentate ligand behavior of these compounds may result in the solubilization of radionuclides, such as ^{60}Co, ^{238}Pu, ^{241}Am, and ^{90}Sr, thus rendering their disposal challenging [3-5]. Consequently, in accordance with the Nuclear Safety and Security Commission Notice No. 2021-16, the determination of the chelating agent content in radioactive wastes is mandatory for their secure disposal. Although EDTA, NTA, and CA are commonly employed decontaminants in nuclear facilities in South Korea, only a few methods have been proposed for their quantification in radioactive wastes.

Owens et al. reported the application of capillary electrophoresis for chelate analysis, where electropherograms for NTA and EDTA and their metal complexes were obtained in a phosphate buffer by direct UV detection [6]. Furthermore, Padarauskas and Schwedt employed capillary zone electrophoresis to separate Co(III), Bi(III), Fe(III), Cr(III), V(IV), Pb(II), Hg(II), Co(II), Cu(II) and Ni(II) metal ions complexed with common aminopolycarboxylic acids [7]. Conductimetric [8], chromatographic [9],
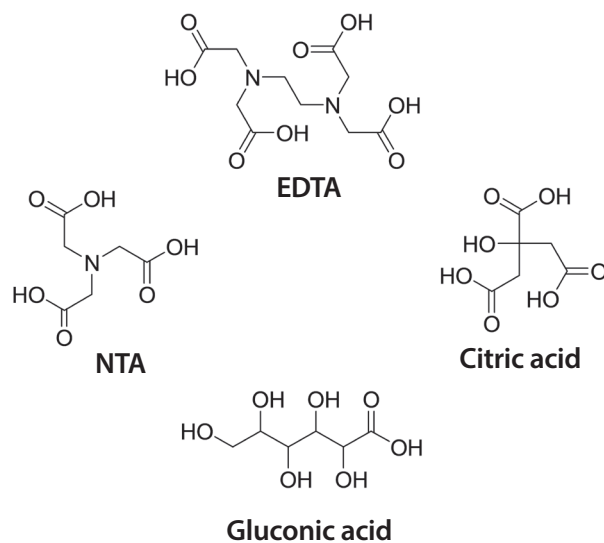

Fig. 1. Structural formulas of the chelating agents.

and enzymatic [10] methods have been employed for the detection of CA. For instance, the classical method for the determination of CA relies on enzymatic reactions of citrate lyase, lactate dehydrogenase, and malate dehydrogenase while spectrophotometrically monitoring the consumption of the reduced nicotinamide adenine dinucleotide at 340 nm. Although the gas chromatographic detection of CA is highly sensitive and with a high separation efficiency, it requires several preparation steps [11]. Consequently, these two methods are time-consuming [12].

This paper investigates a rapid and automated method for CA analysis using ion chromatography (IC) without the need for pretreatment steps. The mechanisms governing the separation using an IC unit equipped with an ion-exclusion column encompass electrostatic interactions (Donnan exclusion), hydrophobic (reversed-phase) interactions, and size exclusion [13]. The ability of the designed method to separated CA from gluconic acid (GluA), a major interfering substance was investigated. The linearity, limit of detection (LOD), limit of quantification (LOQ), and recovery yield of the method were also calculated. Finally, the developed method was employed to determine the CA of an actual radioactive concrete sample.

2. Experimental

2.1 Chemicals

All organic acids were of ACS grade reagent quality (≥ 99.5%) and purchased form Merck. Perfluorobutyric acid (PFBA, > 99% GC purity, eluent) and tetrabutylammonium hydroxide (0.1 M TBAOH, HPLC grade, suppressor regenerant) were obtained from FLUKA Chemie AG and Thermo Fisher Scientific, respectively. All aqueous solutions and dilutions were prepared using ultrapure Milli-Q water.

2.2 Instruments

The analysis was conducted using a Dionex Aquion system, comprising a dual-piston serial pressure pump, a degasser unit for eluent and suppressor regenerant, an injection valve with a 25-μL sample loop, a DS6 conductivity cell, and a Dionex autosampler. The IonPac ICE-AS6 column, housed in a column heater, enabled the adjustment of separation temperatures in the range of 30 to 60°C. Elution was performed using different concentrations of PFBA at a flow rate of 1.0 mL·min^{-1}. A Dionex chemically regenerated suppressor (CRS 500) was positioned between the column and detector cell to suppress the background conductivity of the eluent. The suppressor regenerant, an aqueous TBAOH solution (5 mM), was delivered at a flow rate of 1.2 mL·min^{-1}. System control, data acquisition, and processing were managed using the Chromelon 7 software. To enhance the chromatographic versatility and ensure substance identification, samples were analyzed under different chromatographic conditions, such as flow rates and eluent concentrations.

2.3 Sample Preparation

Standard preparation: CA and GluA stock solutions (0.1 M) were prepared by dissolving the corresponding commercially available product in deionized (DI) water. The diluted solutions were freshly prepared on a daily basis.

Sample preparation: The studied radioactive concrete, produced from the dismantling process of nuclear facilities in Korea Atomic Energy Research Institute (KAERI), was crushed into particles with sizes ranging between 0.5 and 1 cm. The crushed samples were sieved with a 300 μm-mesh and used without any further treatment. To validate the method, blank and uncontaminated concrete samples were also prepared in the same manner. The sample was prepared as follows. Initially, the crushed concrete particles (5 g) were sonicated in deionized water (150 mL) for 1 h to extract all organic acids. The particles were then removed by vacuum filtration. If necessary, the suspended particles were further removed by centrifugation at 4,000 rpm for 0.5 h using a cellulose membrane filter (10 kD). To prepare the simulated samples for validation, the CA standard solution was spiked into the blank samples. The spiked samples were then dried at 80°C for 1 h before the leaching step. The prepared leachates, characterized by high salt concentrations (Ca-concentration = 0.001–0.1 M) and basic pH (pH 10–12), similar to cement pore waters [14], were stored in a refrigerator until the time of analysis.

3. Results and Discussion

Initially, the chromatogram of the concrete leachate from the blank sample was recorded. Three peaks (represented by 3 arrows in Fig. 2(a)) were detected within 10 min under an PFBA concentration of 0.4 mM. These peaks can be thus attributed to three different aliphatic carboxylic acids. Owing to the characteristics of ion-exclusion columns, electrostatic interactions play a crucial role in the retention and separation of analytes. When the pH of the eluent was approximately 3.4 (a PFBA concentration of 0.4 mM), organic acids with low pKa values, such as oxalic acid, are expected to be rapidly eluted. The first peak appearing at 5.257 minutes was thus attributed to oxalic acid [15].
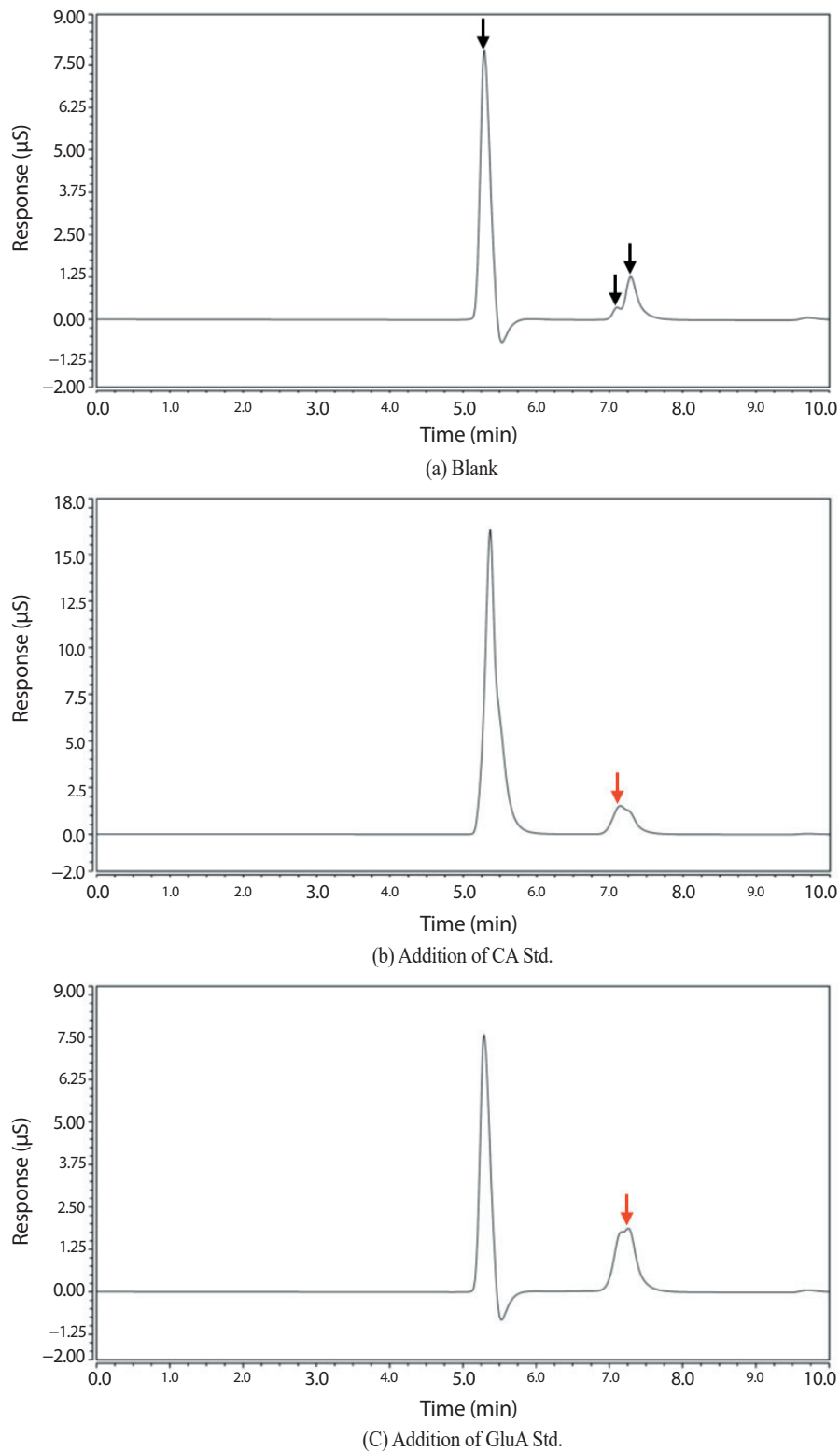
Fig. 2. Chromatograms of concrete leachates from the (a) blank, (b) sample spiked with a standard addition of CA solution (10 mg·L^{-1}), and (c) standard addition of GluA (100 mg·L^{-1}).
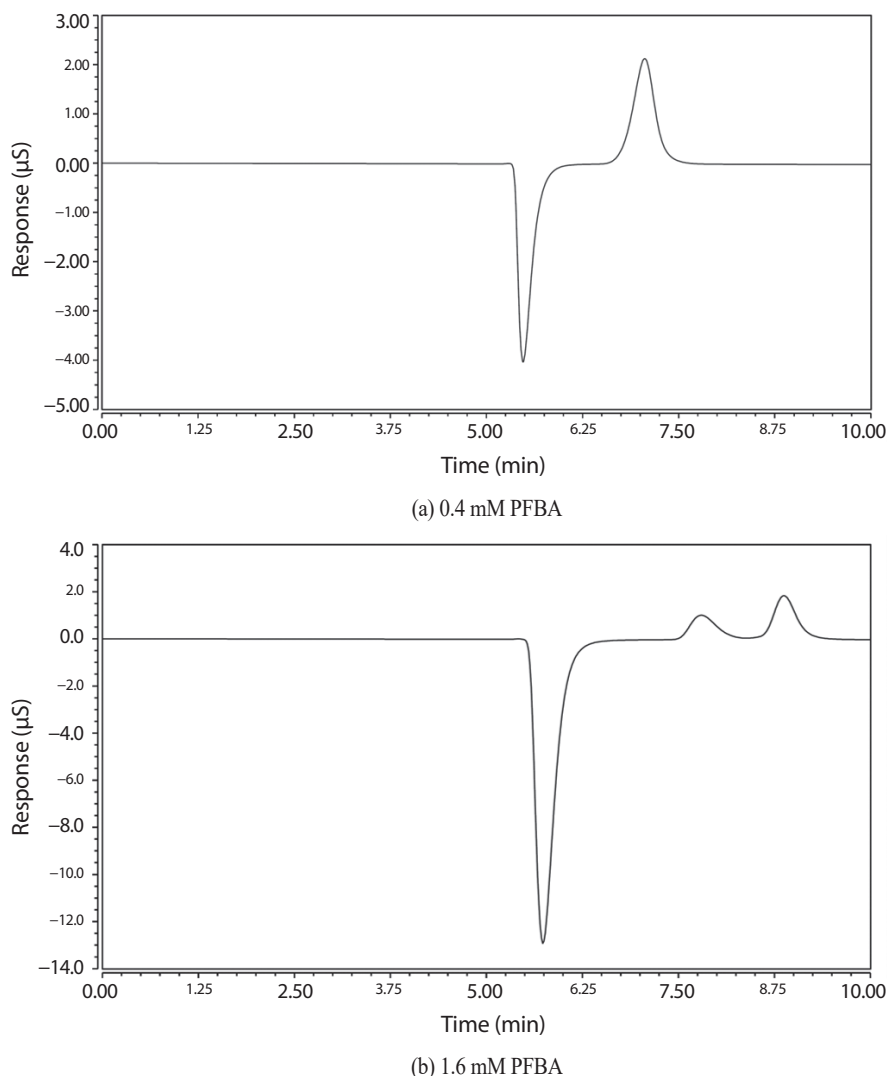
(a) 0.4 mM PFBA

(b) 1.6 mM PFBA

Fig. 3. Chromatograms of standard mixtures of GluA and CA under PFBA (eluent) concentrations of (a) 0.4 and (b) 1.6 mM.

In the retention time range of 7.09–7.29 min two peaks were observed. A similar peak was observed in the spiked sample with the standard addition of a CA solution (10 mg·L^{-1}) under the same elution conditions. Consequently, the peak at 7.09 min was attributed to the CA present in the blank leachate upon CA addition (Fig. 2(b)). To identify the unknown peak at 7.2 min, we spiked the leachate with various organic acids, including GluA in addition to galacturonic and tartaric acids. The addition of GluA increased the area of the unknown peak at a retention time ~ 7.2 min

(Fig. 2(c)). This result is consistent with the fact that GluA is a common admixture in concrete production [16]. It was thus concluded that CA and GluA should be separated for the determination of CA in concrete waste.

In general, an increase in the PFBA concentration decreases the pH of the eluent while suppressing the dissociation of organic acids. This can increase the residence time of the analyte in the column by: 1) reducing the ion exclusion efficiency, 2) increasing the penetration of the acids into the micropores, and 3) increasing hydrophobic interactions
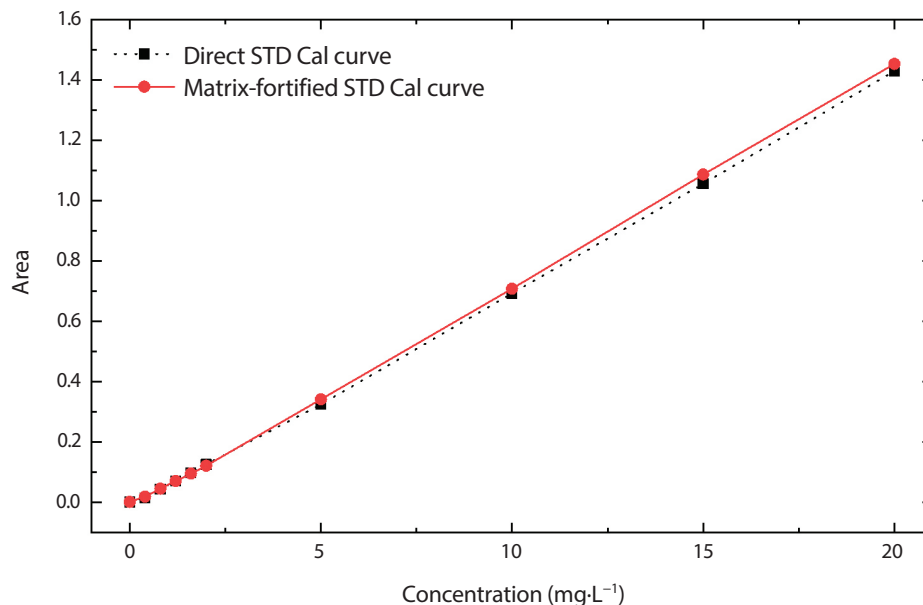
Fig. 4. Matrix-fortified and direct standard calibration curves for the evaluation of the matrix effect.

Table 1. R^2, LOD, and LOQ values of a standard dissolved in DI and concrete leachates

	Least-squares equations	Correlation coefficients (R^2)	LOD ($mg \cdot L^{-1}$)	LOQ ($mg \cdot L^{-1}$)
Direct standard	y = 0.0717x − 0.0166	0.9996	0.679	2.059
Matrix-fortified standard	y = 0.0732x − 0.0163	0.9997	0.666	2.018

[15]. Consequently, we investigated the effect of the PFBA concentration on the separation of CA and GluA. The results revealed that CA and GluA were successfully separated upon increasing the PFBA concentration from 0.4 to 1.6 mM (Fig. 3). Notably, CA was retained in the column longer than GluA at higher PFBA concentrations. This presumably resulted from the presence of more carboxylic acid groups in CA which might have protonated it.

The validity of the IC method for CA quantification in a concrete matrix was then investigated. The evaluation of the matrix effect (selectivity) involved comparing the calibration curve from the CA standards with that of the concrete leachates spiked with these standards (Fig. 4). Both curves were obtained from ten different standard concentrations each repeated thrice. They also both exhibited a similar slope, thus indicating the absence of a significant matrix interference.

Table 1 presents the regression equations and coefficients of determination (R^2) for the analyses of the CA added to water and concrete leachate. These values were obtained during linearity assessment within a concentration range of 0.05 to 20 $mg \cdot L^{-1}$. The results indicated that the linear regression model was suitable because the R^2 of the curves exceeded 0.999, providing strong evidence that the regression equation aligned well with the experimental data which is in accordance with the European [17] and ICH [18] recommendations requiring R^2 values higher than 0.990 and 0.995, respectively.

We gauged the precision of our methodology by evaluating its repeatability, expressed as relative standard deviation (RSD) [19]. Repeatability, which is an indicative of precision under consistent operating conditions within

Table 2. Data obtained from the average of 3 different analyte concentrations

Concentration (mg·L^{-1})		
0.8	1.6	15.0
Mean ± SD (RSD)	Mean ± SD (RSD)	Mean ± SD (RSD)
0.828 ± 0.008 (0.010)	1.582 ± 0.022 (0.014)	14.947 ± 0.114 (0.008)

a short period, aligns with the within-run precision. The repeatability was assessed by spiking the concrete blank leachate with varying concentrations of the CA standard at three different levels. The proposed method demonstrated RSD values below 1.5% (Table 2), thus aligning with the criteria specified by the ICH [18] requirement that the RSD value should not exceed 20%. The precision of the proposed method in the detection of CA was thus confirmed.

The LOD and LOQ values of the method were calculated using equations 1 and 2, respectively [18]:

$$LOD = \frac{3.3 \times SD}{S} \quad (1)$$

$$LOQ = \frac{10 \times SD}{S} \quad (2)$$

Where, SD is the standard deviation of the y-intercept and S is the slope of the calibration curve. The LOD and LOQ values turned out to be 0.679 and 2.059, respectively, and were thus adequately low for the determination of the concentration of CA within the concrete matrix.

Recovery yield measures the ability of a method to extract a target analyte from a concrete matrix. The recovery yield was calculated using equations 3:

$$Recovery\ (\%) = \frac{C_L}{C_0} \times 100 \quad (3)$$

Where, C_L is the concentration of CA in the leachate and C_0 is the concentration of the CA added to the concrete blank sample. The recovery values were in the range of from 84% to 87% (Table 3) and thus were within the acceptable performance criteria of 70–110%, recommended by the European Commission [17].

Table 3. Analysis of CA in concrete samples

Added (g)	% Recovery (mean ± SD, n = 3)
0.005	85.20 ± 1.33

Fig. 5. A picture of the radioactive concrete sample.

The validated method was finally applied to waste samples (Fig. 5) obtained from the nuclear facilities of KAERI. The chromatogram of a real sample (Fig. 6) revealed the absence of the CA peak at a retention time of approximately 9 min. Simultaneously, the GluA peak, appearing at approximately 8 min, thus indicating its effective separation from CA. The results of the three analyses indicated that the concentration of CA in the samples was below the LOQ. The IC system employed, comprising ion exclusion chromatography coupled with conductivity detection, demonstrated adequate sensitivity and selectivity for the quantitative analysis of CA in authentic radioactive concrete samples.
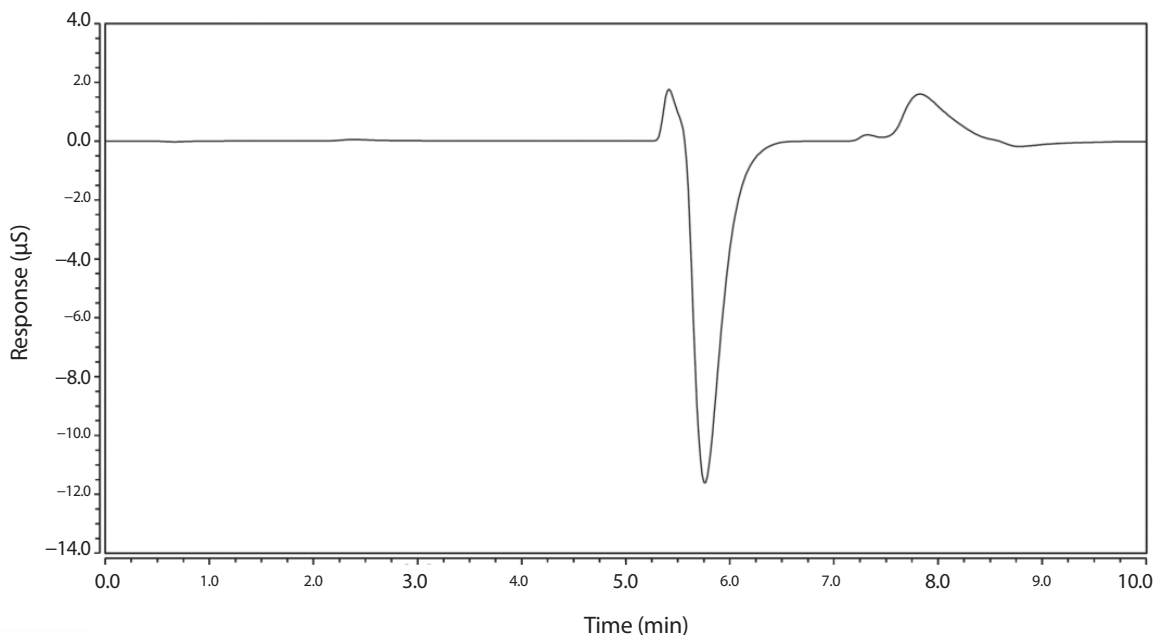
Fig. 6. Chromatogram of the actual sample.

4. Conclusion

This study reported a fast and simple method for the determination of CA in radioactive concrete waste by IC without the need for a pretreatment step. This method exhibited a notable sensitivity as it enabled the effective separation of CA from GluA, commonly found in concrete. The developed method was validated and successfully applied to authentic samples. The LOQ and recovery yield values satisfied international standard criteria for analytical analyses. Overall, the developed method does not only enable CA quantification in radioactive concrete waste, but might also have potential applications in routine analyses of diverse nuclear waste types owing to its sensitivity, selectivity, and simplicity.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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