

Application of capillary electrophoresis in atmospheric aerosol analysis: determination of cations

Ewa Dabek-Zlotorzynska*, Joseph F. Dlouhy

Chemistry Division, Environmental Technology Centre, Environment Canada, 3439 River Road, Ottawa, Ontario K1A 0H3, Canada

Abstract

The feasibility of using capillary electrophoresis (CE) with a new electrolyte system for the analysis of alkali metal, alkaline-earth metal cations and ammonium in atmospheric aerosols has been demonstrated. 1,1'-Di-*n*-heptyl-4,4'-bipyridinium (DHPB) hydroxide was used as the UV-absorbing species, which allowed for the indirect UV detection of cations at 280 nm. while glycine, 18-crown-6 ether and methanol were employed to improve the separation of the studied cations. The precision of migration time and peak area was better than 0.2% and 5%, respectively. Separation efficiencies were between 90 000 and 600 000 theoretical plates per meter, and detection limits between 9 and 60 ng/ml. With the described electrolyte composition it is also possible to determine manganese and cadmium, and short-chain aliphatic amines. The comparison of CE results with ion chromatography obtained for cations in atmospheric aerosols is presented.

1. Introduction

Previous reported work [1] demonstrated the applicability of capillary electrophoresis (CE) with indirect UV detection to analyze inorganic and organic anions in atmospheric aerosols. The highly efficient separation of CE with high accuracy, precision, short analysis time and low reagent consumption makes it an excellent tool for such analysis. The introduction of CE in an environmental analytical laboratory allows also methods and results validation.

This work has been continued to investigate the usefulness of CE in the analysis of inorganic

cations in atmospheric aerosols. At present, ion chromatography (IC) is extensively used by this laboratory in the analysis of alkali metal, alkaline-earth metal cations and ammonium in such samples [26,27]. Several reports have appeared recently describing the application of CE for the analysis of inorganic and organic cations with indirect UV detection [2–23]. Various electrolyte compositions using different UV absorbing carrier electrolytes and complexing agents have been employed. Because most inorganic cations have similar ionic mobilities, additional components in the electrolyte are required for the efficient separation. These components, typically negatively charged weak anionic complexing agents [2–7,9,10,12–23] or electroneutral crown ethers [8,11,14,17–23], selectively reduce

* Corresponding author.

the mobility of inorganic cations and thus improve resolution of cationic analytes. In order to optimize cation CE separation and indirect UV detection efficiencies, it is important to choose a suitable combination of a UV-sensitive carrier electrolyte and complexing reagent [6,9,10, 12,14,16,23].

In this paper a new electrolyte composition will be described which permits separation of alkali metal, alkaline-earth metal cations and ammonium. 1,1'-Di-*n*-heptyl-4,4'-bipyridinium (DHPB) hydroxide was used as the UV-absorbing agent, which allowed the indirect UV detection of cations at 280 nm. Complexing agents such as glycolic acid, glycine and 18-crown-6 ether were tested in order to improve separation of the studied cations. The present work deals with the application of CE for the determination of cations of interest in atmospheric aerosols. This study was also performed to obtain independent complementary confirmation of the IC results.

2. Experimental

2.1. Capillary electrophoresis

A Beckman P/ACE 2100 instrument (Fullerton, CA, USA) with System Gold version 7.11 software was used for all CE measurements. The system features a UV detector, an autosampler and a liquid-cooled capillary cartridge. Capillaries from Polymicro Technologies (Phoenix, AZ, USA) with 57 cm (50 cm to detector) \times 75 μ m I.D. \times 375 μ m O.D. were used. Approximately 0.5 cm of the polyimide coating was burned off from the capillary to make a transparent window for the detector cell. Indirect UV detection was employed at 280 nm. All experiments were conducted at 25°C. A positive power supply of 25 kV was used and all injections were achieved by applying a 0.5-p.s.i. pressure for 10 s, unless otherwise noted.

A Beckman pH meter with a combination electrode was used to measure the pH of electrolytes.

2.2. Ion chromatography

A Dionex 4000i IC system (Dionex, Sunnyvale, CA, USA) equipped with a gradient pump (GPM), an advanced chromatography module (ACM) and a conductivity detector (CDM-2) was utilized for IC determination. A Dionex automated sampler (ASM) with 5-ml vials was used for sample loading. A 50- μ l sample loop was used for the injection of samples.

The separations of alkali metal, alkaline-earth metal cations and ammonium were carried out on an IonPac CS12 column (250 mm \times 4 mm I.D.) with an IonPac CG12 guard column (50 mm \times 4 mm I.D.) at a flow-rate of 1.0 ml/min. A step gradient from 16 mM methanesulphonic acid (MSA) to 40 mM MSA at 8.0 min was used. Conductivity detection was carried out using a cation self-regenerating suppressor (CSRS-I) in the recycle mode.

The chromatograph was controlled and data were collected and processed on a personal computer using Dionex AI-450 software.

2.3. Reagents

MSA was obtained from Fluka (Ronkonkoma, NY, USA). All other chemicals were purchased from either Fisher Scientific (Ottawa, Canada) or Aldrich (Milwaukee, WI, USA) in the highest purity available, and were used without further purification. Deionized water obtained from a reversed-osmosis and an ion-exchange system (Millipore, Model RO 20 and Model SuperQ) was used for the preparation of all solutions, electrolytes and standards.

The ammonium standard solution was prepared from ammonium chloride. A stock solution of other used inorganic cations were prepared from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) standards. All standard solutions were stored in polyethylene containers. Diluted working standard solutions were prepared daily.

2.4. Electrolytes and procedures

A 25 mM DHBP bromide, 100 mM 18-crown-

6 ether and 100 mM glycolic acid or 100 mM glycine were used for the preparation of the working electrolytes. OnGuard A cartridges (Dionex) in the hydroxide form were used to convert DHBP bromide to DHBP hydroxide. The electrolytes were adjusted to the final pH using acetic acid.

All electrolyte solutions were filtered through a 0.22- μm syringe PTFE membrane filter (Nalgene Brand Products, Rochester, NY, USA) and degassed by creating vacuum inside the syringe.

Each day before starting analysis, the capillary was rinsed with 0.1 M NaOH and water for 10 min, followed by the used electrolyte for 5 min. Between each run the capillary was flushed with the running electrolyte for 1 min.

Quantitation was based on multi-component calibration runs. Five mixed standards were employed to fit a calibration graph using the linear regression analysis of the corrected peak area.

Detection limits were defined as three times the standard deviation of eighteen replicate analyses of a standard with a concentration equal to about ten times the estimated detection limit, the latter being the concentration giving a signal-to-noise ratio of 3.

2.5. Extraction of atmospheric aerosols

Atmospheric aerosols, collected on PTFE-coated borosilicate glass fiber filters (Pallflex, TX40HI20WW) using Hi-Vol samplers and on thin PTFE filters using virtual dichotomous samplers, were obtained from the Pollution Measurement Division, Environmental Technology Centre, Canada.

Two 37-mm-diameter discs, cut out from Hi-Vol filters, were placed in a 100-ml beaker. The filters were wetted with two drops of 30% Triton TX-100 and then 25 ml of deionized water were added. The beakers were then covered with Parafilm 1“M” and extracted for 30 min in an ultrasonic bath (Branson and Smithkline, Shelton, CT, USA).

The extraction of water-soluble atmospheric aerosols collected on PTFE filters was performed

with 15 ml of water by sonication in the ultrasonic bath. Before addition of water, the filters with collected aerosols were wetted with 100 μl of isopropanol.

Analysis was carried out as soon as possible after extraction (within less than 24 h). The unused extracts were preserved by storage at -20°C [32].

3. Results and discussion

3.1. Optimization of separation

The experimental parameters such as concentration of a carrier electrolyte, type and concentration of a complexing reagent, pH and effect of organic solvents were optimized to achieve suitable separation, the highest sensitivity and the shortest time of analysis. A mixture of cations of interest (NH_4^+ , K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , Ba^{2+} , 2 mg/l; Li^+ , 0.5 mg/l) was pressure-injected for 5 s during these experiments.

In this study, DHBP hydroxide was selected as the UV-absorbing carrier electrolyte. DHBP absorbs strongly in the vicinity of 262 nm with a large molar absorptivity ($2.4 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) [28]. Because of the availability of a 280-nm filter in a used CE instrument, 280 nm was chosen as a representative detection wavelength throughout this work. DHBP is a quaternary ammonium ion, available commercially as the bromide, and it is in the form of a divalent ion over a wide pH range [28].

Glycolic acid and glycine were tested as the complexing reagents in order to obtain separation of the studied cations. Both reagents form weak complexes with alkali metal and alkaline-earth metal cations [29]. Transition metal cations are more strongly complexed by glycine [29]. 18-Crown-6 ether was added to the electrolyte containing a glycine or glycolic acid in order to separate NH_4^+ and K^+ cations. The crown ether complexes with potassium which permits the separation from ammonium. The migration times of barium and strontium are also increased due to complexation with the crown ether.

Preliminary experiments showed that separa-

tion of cations of interest could be obtained either with glycolic acid at pH 4 or glycine at pH 6.5 with incorporation of 18-crown-6 ether. However, strong drifts of the baseline due to the variation of Joule heating [17] in the electropherograms observed at a pH lower than 6 restricted the choice to glycine as a complexing agent.

On the basis of the performed experiments, the electrolyte containing the 5 mM DHBP, 6 mM glycine, 2 mM 18-crown-6 ether and 2% methanol at pH 6.5 was found to give the best compromise between peak separation, sensitivity and acceptable baseline noise. Methanol was added to the electrolyte in order to improve the resolution between sodium and magnesium. Organic solvents have successfully been used in adjusting the selectivity in CE [10,23,24]. Fig. 1 shows an electropherogram of a mixed cation standard under optimum conditions. Under these conditions cesium, rubidium, manganese and cadmium in addition to other cations of interest could be separated. Because glycine forms strong complexes with most transition metal cations, these cations could not be separated.

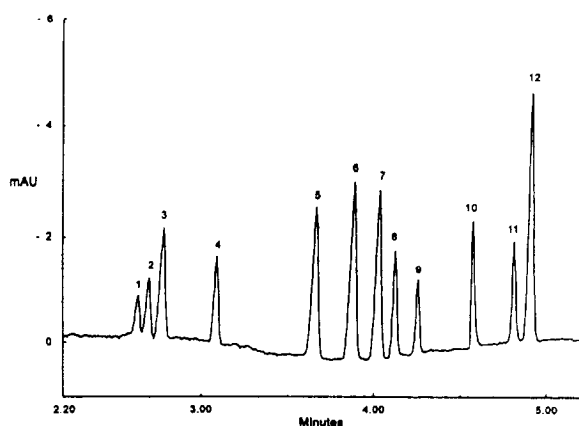


Fig. 1. Separation of inorganic cations under optimum conditions: electrolyte, 5 mM DHBP, 6 mM glycine, 2 mM 18-crown-6 ether, 2% methanol, pH 6.5; applied voltage, 25 kV; current, 12.5 μ A; injection time, 5 s; indirect detection, 280 nm. Peaks: 1 = Cs⁺ (4 mg/l); 2 = Rb⁺ (4 mg/l); 3 = NH₄⁺ (2 mg/l); 4 = K⁺ (2 mg/l); 5 = Ca²⁺ (2 mg/l); 6 = Na⁺ (2 mg/l); 7 = Mg²⁺ (1 mg/l); 8 = Mn²⁺ (1 mg/l); 9 = Sr²⁺ (1 mg/l); 10 = Cd²⁺ (3 mg/l); 11 = Ba²⁺ (2 mg/l); 12 = Li⁺ (0.5 mg/l).

rated. However, glycine may be used to selectively mask cations to prevent their precipitation at higher pH and comigration of ions of similar mobilities.

The peak shape for most of the tested cations is symmetric although there is some peak fronting on the fast-migrating cations. The ionic mobility of DHBP measured with the 5 mM phosphate buffer at pH 6.5 was slightly lower ($2.8 \cdot 10^{-4}$ cm² V⁻¹ s⁻¹) than the mobility of inorganic metal ions (around $4 \cdot 10^{-4}$ cm² V⁻¹ s⁻¹). Separation efficiencies were between 90 000 and 600 000 theoretical plates per meter at a concentration of 1 mg/l with a 10-s pressure injection.

Another example of the capability of the proposed method is the separation of alkyl amines. They are well separated from the inorganic cations, as can be seen in Fig. 2.

3.2. Analytical performance

Table 1 summarizes the migration time and peak-area precision (R.S.D.) for the tested cat-

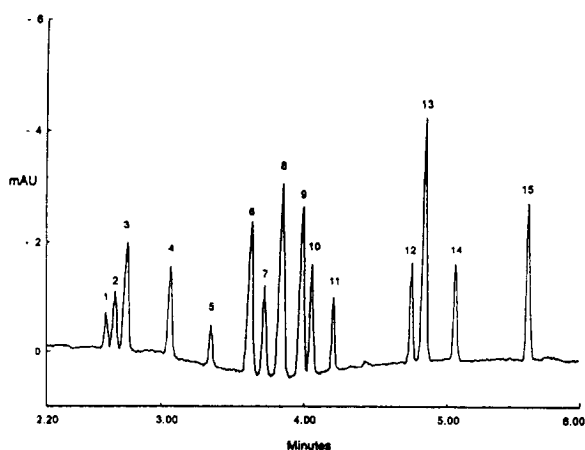


Fig. 2. Simultaneous separation of alkali metals, alkaline-earth metals, ammonium and amines. Conditions are the same as in Fig. 1. Peaks: 1 = Cs⁺ (4 mg/l); 2 = Rb⁺ (4 mg/l); 3 = NH₄⁺ (2 mg/l); 4 = K⁺ (2 mg/l); 5 = methylamine (2 mg/l); 6 = Ca²⁺ (2 mg/l); 7 = dimethylamine (2 mg/l); 8 = Na⁺ (2 mg/l); 9 = Mg²⁺ (1 mg/l); 10 = trimethylamine (2 mg/l); 11 = Sr²⁺ (1 mg/l); 12 = Ba²⁺ (2 mg/l); 13 = Li⁺ (0.5 mg/l); 14 = ethylamine (2 mg/l); 15 = triethylamine (4 mg/l).

Table 1
Precision and detection limits

Cation	R.S.D. ^a (%)		Detection limit (ng/ml)	
	Migration time	Peak area		
			CE ^b	IC ^c
Ammonium	0.13	1.92	42	12
Potassium	0.12	4.28	47	7
Calcium	0.12	2.81	42	9
Sodium	0.12	4.67	46	14
Magnesium	0.11	1.87	18	5
Manganese	0.18	3.17	39	10
Strontium	0.11	3.64	38	6
Barium	0.11	2.61	57	9
Lithium	0.11	2.65	9	2

^a Relative standard deviations from eighteen replicates of a mixed standard solution at a concentration of 2 mg/l (Li⁺ 0.5 mg/l) using the described method.

^b Capillary electrophoresis utilizing the proposed electrolyte composition with a 10-s pressure injection.

^c Ion chromatography with a 50- μ l sample loop.

ions in a mixed standard under the conditions listed in Fig. 1. The precision of migration times and peak areas was better than 0.2% and 5%, respectively.

Table 2
Determination of major cations in water samples using capillary electrophoresis with the proposed electrolyte composition

	Interlaboratory median (μ g/ml)	Found (μ g/ml)	R.S.D. ^c (%)
Ammonium	0.900 ^a — ^b	0.948 —	3.35 —
Potassium	0.101 ^a 0.500 ^b	0.089 0.348	10.21 6.75
Calcium	3.200 ^a 13.500 ^b	3.122 13.348	1.29 0.90
Sodium	0.334 ^a 1.340 ^b	0.324 1.314	5.98 1.57
Magnesium	0.980 ^a 2.820 ^b	1.025 2.684	0.97 0.44

^a LRTAP 34/8 [30].

^b LRTAP FP 64/3 [31].

^c Reported results are the means and relative standard deviations from nine replicates with a 10-s pressure injection.

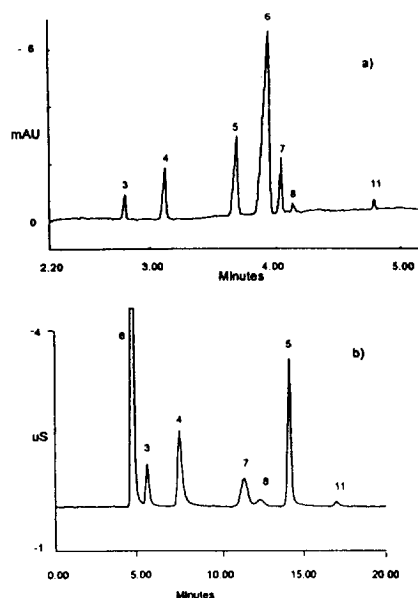


Fig. 3. Analysis of Hi-Vol-sampled atmospheric aerosol extract using (a) CE with a 10-s pressure injection and (b) IC methods. Peaks and other conditions are the same as in Fig. 1.

A linear relationship between corrected peak area and concentration was obtained in the 0.1–10 mg/l range for most tested cations. Correlation coefficients were ranged from 0.9990 to

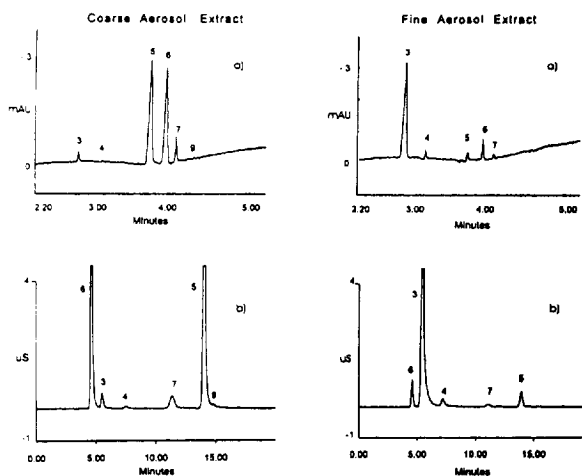


Fig. 4. Analysis of coarse and fine atmospheric aerosol extracts using (a) CE with a 10-s pressure injection and (b) IC methods. Peaks and other conditions are the same as in Fig. 1.

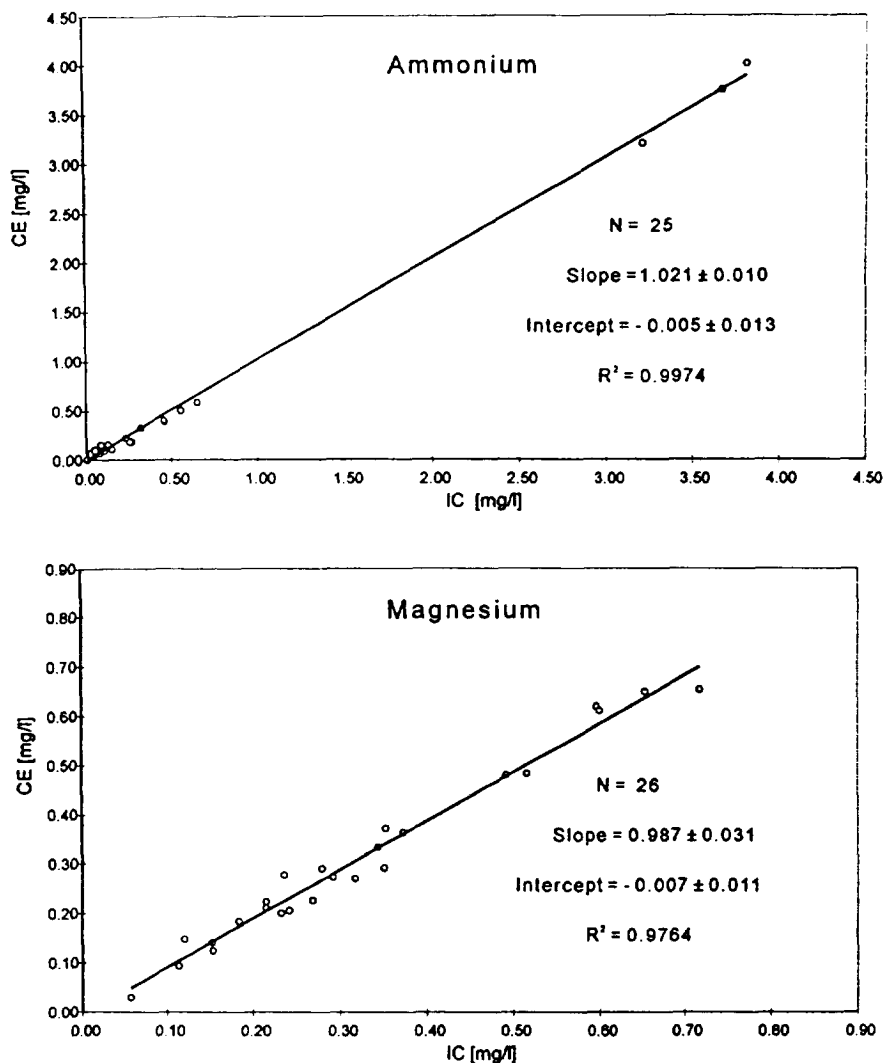


Fig. 5. Correlation plots for ammonium and magnesium determined by CE and IC methods in Hi-Vol-sampled atmospheric aerosols (\pm values are the confidence limits at 95% level).

0.9999 for all tested cations. Although the quantitation is possible at the $10 \mu\text{g}/\text{ml}$ level, the peaks become broader and the resolving power due to differences between the electrolytes and analyte mobilities [25] is diminished. The calibration linearity and sensitivity are much better in the lower concentration range when a 10-s pressure injection is used. When the analyte concentration is high, the injection time should be decreased or the DHBP concentration should be increased.

In order to evaluate the quantitative performance and accuracy of the method, two water samples used for round robin studies were analyzed. The results shown in Table 2 are in a good agreement with the interlaboratory median values [30,31]. The analytical results were also precise as shown by the standard deviation of nine replicates.

Detection limits of analytes (for a 10-s pressure injection) using the described method are listed in Table 1. It can be seen that most

Table 3
Statistical analysis results ($\pm 95\%$ confidence limit) [33]

Cation	Concentration range (mg/l)	N	Slope ^a (A)	Intercept ^a (B)	r ²
Ammonium	0.04-3.82	25	1.021 \pm 0.010	-0.005 \pm 0.013	0.9974
Potassium	0.18-2	26	1.086 \pm 0.043	0.007 \pm 0.039	0.9649
Calcium	0.4-8	26	0.891 \pm 0.021	0.055 \pm 0.065	0.9864
Sodium	1.2-8	26	1.041 \pm 0.025	-0.016 \pm 0.107	0.9840
Magnesium	0.06-0.7	26	0.987 \pm 0.031	-0.007 \pm 0.011	0.9764

(CE) = A \times concentration (IC) + B (mg/l).

cations have detection limits at the tens of ng/ml level. The results indicate that the proposed method gave better detection limits than obtained with other reported carrier electrolytes [4,7,11].

3.3. Analysis of cations in atmospheric aerosols

The proposed CE method was applied to the determination of inorganic cations in atmospheric aerosols. Fig. 3 shows the typical electropherogram and chromatogram of aqueous extract of atmospheric aerosols collected with Hi-Vol sampler. Ammonium, potassium, sodium, calcium and magnesium were the major cations in these samples. Barium was present at the mid- $\mu\text{g}/\text{ml}$ level. Manganese and strontium were found only in a few samples. Some unidentified peaks were sometimes present in the electropherogram at a migration time close to 6 min.

Typical electropherograms of coarse and fine atmospheric aerosol extracts are presented in Fig. 4. Coarse atmospheric aerosol particles contain sodium, magnesium and calcium as the major cations. Ammonium is the major cation of fine atmospheric aerosols. Manganese was present at mid- $\mu\text{g}/\text{ml}$ level in a few samples. The concentration of other cations was frequently under the detection limit.

The CE results were compared with those obtained by IC. A comparison of ammonium and magnesium results by CE with those obtained by IC for a series of Hi-Vol-sampled atmospheric aerosols is shown in Fig 5. Linear least-squares adjustment of each set of results

yielded the equations ($\pm 95\%$ confidence limits [33]) presented in Table 3. As can be seen the values determined from both techniques agree quite well. Some problems were encountered in the determination of calcium by IC. The calcium IC concentrations were significantly larger than the CE concentrations, also for quality control samples. These problems are not resolved yet. Attempts to do this are now in progress.

4. Conclusions

In conclusion, the results of this work show that CE utilizing the proposed electrolyte composition can be used for the detection and separation of alkali metal, alkaline-earth metal cations and ammonium in atmospheric aerosols. This method provides high separation efficiencies and a very good detectability at 280 nm. Results obtained are in a good agreement with those obtained by IC. CE offers a complementary method and allows easy peak confirmation.

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