Journal of Chromatography A, 1223 (2012) 79–83

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Matrix-elimination with steam distillation for determination of short-chain fatty acids in hypersaline waters from pre-salt layer by ion-exclusion chromatography

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ARTICLE INFO

Article history:
Received 7 July 2011
Received in revised form 5 December 2011
Accepted 9 December 2011
Available online 14 December 2011

Keywords:
Short-chain fatty acids
Steam distillation
Ion-exclusion chromatography
Hypersaline waters
Pre-salt

ABSTRACT

A method for determination of formic, acetic, propionic and butyric acids in hypersaline waters by ion-exclusion chromatography (IEC), using steam distillation to eliminate matrix-interference, was developed. The steam distillation variables such as type of solution to collect the distillate, distillation time and volume of the 50% v/v H_2SO_4 solution were optimized. The effect of the addition of NaCl different concentrations to the calibration standards on the carboxylic acid recovery was also investigated. Detection limits of 0.2, 0.5, 0.3 and 1.5 mg L^{-1} were obtained for formic, acetic, propionic and butyric acids, respectively. Produced waters from petroleum reservoirs in the Brazilian pre-salt layer containing about 19% m/v of NaCl were analyzed. Good recoveries (99–108%) were obtained for all acids in spiked produced water samples.

1. Introduction

The occurrence of carboxylic acids in connate and produced waters has a great importance in the petroleum geochemistry. Experimental investigations have shown that these acids are produced by maturation of the organic material deposited in a process roughly parallel to the petroleum generation. Because of that, in connate waters, organic acids may act as possible gas and petroleum precursors, indicators of microbial activity in petroleum and indicators of maturity and proximity of this fluid. Also, they are relevant for the discharge process of produced waters, since they cause corrosive effects, and for oil recovery studies with water injection to predict the scale formation in reservoir rocks [1].

Short-chain fatty acids (SCFA) such as acetic, propionic, butyric and valeric represent a considerable part (60–98% in the North Sea) of the total organic matter in the produced waters [2]. Acetic acid in connate and produced waters has been found in higher concentrations than the other organic acids [1,3,4]. Tibbetts et al. [3] observed that the dominant component in produced waters was acetic acid, which comprised 60% or more of the volatile fatty acids.

In 2006, the discovery of the first petroleum field in the pre-salt layer deeply changed the petroleum exploration in Brazil. The oil rests under an extensive layer of salt, which in certain areas of the coast can be as much as 2000 m thick. Thus, connate waters have a huge salinity, and NaCl contents can reach up to 25% m/v. Therefore, the analyses of these waters have demanded new analytical methods, free from saline interferences.

Besides the geological processes and (bio) geochemical reactions, the carboxylic acids are also originated from biological sources and anthropogenic emissions. As consequence of the great demand, different analytical methods have been employed for determination of these acids. Chromatographic techniques, especially ion-exclusion liquid chromatography (IEC), have been much used for determination of such acids because it presents many advantages. Excellent suitability for aqueous matrices and no loss of very hydrophilic or volatile compounds are some arguments for employing IEC [5].

In general, chromatographic procedures involve sample pretreatments to separate interfering substances that may affect the chromatographic performance by masking peaks of interest or being irreversibly retained causing a permanent damage to the column [6].

Many pretreatments for liquid samples have been reported for determination of organic acids by IEC. For solutions from forest floor, the pretreatment was restricted to centrifugation followed

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doi:10.1016/j.chroma.2011.12.032

by membrane filtration [7]. Centrifugation followed by membrane filtration, ultrafiltration (twice) and finally cation exchange was also used for soil solutions [8–10]. Pretreatment of samples such as grape juices have included filtration or dilution and filtration or filtration and precipitation [11]. Beal et al. [12] pretreated samples of fermented liquid pig diets with a 7% (v/v) sulfuric acid solution to denature the protein in the sample and to fully protonate the organic acids under investigation. After that, the samples were diluted in water, stirred in a vortex, centrifuged, and the supernatant was carefully removed and analyzed by IEC. This procedure, except the dilution in water, was also used by Niven et al. [13] for similar matrices. Fischer et al. [14] used centrifugation followed by membrane filtration and filtration through a polyvinylpyrrolidone filter cartridge to remove strongly adsorbing and humin-like substances from effluents of landfills. Also, acidification of samples by adding an acidic ion-exclusion chromatography eluent for carbonate elimination and subsequent ultrasonic agitation was used for waste related samples and biomass hydrolysates [5]. Parkes and Taylor [15] tested vacuum distillation for determination of carboxylic acids (formic, acetic, propionic, butyric, isobutyric, valeric, isovaleric and capric) in marine pore waters by IEC. However, only acetate and propionate were well separated and quantitatively determined at sub-ppm levels (<5 ppm) in seawater samples.

The determination of carboxylic acids by IEC is based on their separation on a column packed with polystyrene-divinylbenzene (PS-DVB) copolymer functionalized with sulfonic groups forming a negatively charged shield on the polymeric surface, often referred as "Donnan membrane". Once the analytes enter the column, they interact with the sulfonated PS-DVB copolymer in such a way that the dissociated fraction of the analyte is repelled from the vicinity of the Donnan membrane into the bulk of the interstitial eluent, while the protonated fraction penetrates the membrane and enters the occluded fraction of the eluent, where it may experience additional retention by surface adsorption onto the unfunctionalized parts of the resin. The higher is the pK_a of an individual acid, the higher is the protonated fraction and consequently the longer is its retention time [16,17].

Besides IEC, other liquid chromatographic methods and gas chromatography have been used for determination of carboxylic acids in saline waters. Reversed-phase ion-pair liquid chromatography after derivatization has been used for determination of SFCA in seawater [18] and pore-water [18,19] samples. Reversed-phase liquid chromatography of the reaction product obtained by an alternative enzymatic method has been applied for determination of acetate concentrations in marine pore waters [20]. Some organic acids, SFCA for example, have been determined by gas chromatography (GC) after their pre-concentration and separation from inorganic salts by using a diffusion technique [21]. A method based on USEPA 625 gas–liquid chromatography/mass spectrometry has been applied for determination of the acid fraction silylated product in seawater and produced water samples using N-methyl-N-trimethylsilyltrifluoroacetamide [3].

Steam distillation has also been used to separate SFCA from nonvolatile inorganic salts in analyses of food, *e.g.*, cheese, by gas chromatography [22] and biological samples, *e.g.*, fecal samples, by gas–liquid chromatography [23] or from leaves and seeds of plants. The introduction of an inert vapor, which contributes with the vapor pressure of the system, allows the separation of substances at lower temperatures, which is useful, since many organic compounds tend to decompose at high sustained temperatures which regular distillation would require [24].

The main goal of this work was to use a steam distillation apparatus to extract the formic, acetic, propionic and butyric acids from previously acidified hypersaline waters. The distillate was then collected into water and the anions from the acids were determined by IEC. Produced waters collected from the petroleum reservoirs of the Brazilian pre-salt layer were analyzed.

2. Experimental

2.1. Apparatus and operating conditions

A Metrohm chromatography system (Herisau, Switzerland) consisting of an IC filtration sample processor model 788, a vacuum degasser model 837, a CO_2 suppressor unit model 853, a conductivity detector model 819 and an ion-exclusion column Metrosep Organic Acids 6.1005.200, packed with PS-DVB copolymer functionalized with sulfonic groups, with a particle diameter of 9.0 μm, was used for determination of formate, acetate, propionate and butyrate. The conductivity detector was operated in the positive mode at a full scale of 10.0 μS cm^{-1}. Peak heights were used to quantify the ion concentrations because the standard deviations of the height measurements were lower than those obtained for area measurements for butyric acid. Isocratic elution with a solution recommended by the column manufacturer (0.5 mmol L^{-1} $HClO_4$ solution) [25] was kept at 0.6 mL min^{-1}, the column temperature was 35 °C, the work pressure was 4.1 MPa and the running time was 25 min. The sample loop volume was 10 μL. A solution of 10 mmol L^{-1} LiCl, recommended by the column manufacturer [25], was pumped simultaneously with ultra pure water through the conductivity suppressor unit. The eluent and suppressor solutions were filtered under vacuum through a 0.22 μm filter from Millipore (Bedford, MA, USA) and degassed in an ultrasonic bath prior to use.

A Tecnal model TE 036/1 semiautomatic steam distillation apparatus (Piracicaba, SP, Brazil) coupled to a Nova Ética thermostatic bath (Ribeirão Preto, SP, Brazil) fed with ultrapure water was used for carboxylic acid extraction. The heating rate of the boiler was adjusted to level 5.

2.2. Reagents, standards and samples

All chemicals were analytical grade. The water was purified with a reverse osmosis system model Elix 5 coupled to a Milli-Q Gradient model, from Millipore (Bedford, MA, USA). In the steam distillation, a 50% v/v H_2SO_4 solution was used to promote the carboxylic acids volatilization. Water was used to collect the distillate. An alkaline solution was not used because this solution could absorb CO_2 from the environment. The calibration standards of formate, acetate, propionate and butyrate in the concentration range of 1–100 mg L^{-1} were obtained by dilution of 1000 mg L^{-1} stock solutions in water. Moreover, calibration standards of these anions were prepared by dilution with a saline solution containing 500 mg L^{-1} Br^- + 500 mg L^{-1} SO_4^{2-} + 200 mg L^{-1} NO_3^- and different concentrations (1, 15 or 30% m/v) of NaCl. The blank solutions also contained these anions and NaCl. For the variable study of the proposed method, an aqueous standard solution containing a 50 mg L^{-1} mixture of formate, acetate, propionate and butyrate (solution A) and a saline standard solution containing 50 mg L^{-1} mixture of formate, acetate, propionate and butyrate in 30% m/v NaCl + 500 mg L^{-1} Br^- + 500 mg L^{-1} SO_4^{2-} + 200 mg L^{-1} NO_3^- (solution AS) were used. Three hypersaline produced water samples from petroleum reservoirs in the Brazilian pre-salt layer were analyzed.

2.3. Procedure

The determination of formic, acetic, propionic and butyric acids, listed in Table S1 [26], in hypersaline waters by the proposed method consisted on the previous separation of the carboxylic acids from the saline matrix by steam distillation. The distillation procedure consisted of initially turning on the boiler heating of the

Table 1
Average correlation coefficients, sensitivities ($n = 3$) and linear range of the calibration curves prepared in water and in different NaCl concentrations (% m/v) for determination of formic, acetic, propionic and butyric acids (standard deviations between brackets).

Matrix	Water[a]	Water[b]	NaCl 1%[b]	NaCl 15%[b]	NaCl 30%[b]
Acid			Formic		
Correlation coefficient (R^2)	0.9991	0.9897	0.9992	0.9987	0.9998
Sensitivity (mV mg^{-1} L)	9.78(0.02)	5.96(0.06)	6.26(0.13)	7.44(0.17)	8.08(0.18)
Linear range (mg L^{-1})[c]	1–10	10–100	10–100	10–100	10–100
Acid			Acetic		
Correlation coefficient (R^2)	0.9994	0.9958	0.9983	0.9991	0.9960
Sensitivity (mV mg^{-1} L)	5.98(0.02)	4.12(0.16)	3.88(0.12)	4.56(0.03)	4.82(0.12)
Linear range (mg L^{-1})[c]	1–10	10–100	10–100	10–100	10–100
Acid			Propionic		
Correlation coefficient (R^2)	0.9995	0.9963	0.9979	0.9990	0.9967
Sensitivity (mV mg^{-1} L)	3.70(0.04)	3.42(0.13)	3.09(0.15)	3.46(0.06)	3.50(0.06)
Linear range (mg L^{-1})[c]	2.5–10	25–100	25–100	25–100	25–100
Acid			Butyric		
Correlation coefficient (R^2)	0.9961	0.9972	0.9988	0.9995	0.9979
Sensitivity (mV mg^{-1} L)	2.44(0.05)	2.54(0.05)	2.39(0.05)	2.44(0.05)	2.54(0.05)
Linear range (mg L^{-1})[c]	1.0–10	10–100	10–100	10–100	10–100

[a] Undistilled.
[b] Distilled.
[c] Original concentration values (before distilling).

steam distillation apparatus until boiling. Then, it was turned off. After that, 5 mL of the sample were transferred into the distilling tube, and 5 mL of the 50% v/v H_2SO_4 solution were carefully added to promote the carboxylic acid volatilization. The distillation apparatus was immediately closed, and the boiler heating was again turned on. The distillate was collected into a 50 mL polypropylene flask containing 5 mL of water. The distillation time was 5 min. Then, water was added up to 50 mL (sample dilution factor = 10). After that, the anions in the distillate solution were quantified by IEC. Calibration curves (10–100 mg L^{-1} of formate, acetate, propionate and butyrate) were prepared in 30% m/v NaCl + 500 mg L^{-1} Br^- + 500 mg L^{-1} SO_4^{2-} + 200 mg L^{-1} NO_3^- and distilled before the determination by IEC.

3. Results and discussion

3.1. Optimization of the steam distillation for the separation of the formic, acetic, propionic and butyric acids from the saline matrix

In the first optimization experiment, the effect of the distillation time on the carboxylic acid recovery was studied. Times of 1, 2, 3, 3.5, 4, 5, 6 and 7 min were tested. Aliquots containing 5 mL of solution A and solution AS (described in Section 2.2) were tested. An aliquot of 10 mL of the 50% v/v H_2SO_4 solution was used to promote the acid volatilization. Three replicates were carried out. The distillate was collected into 5 mL of water. Then, the volume of the distillate was completed to 50 mL with water. The acid recoveries in both distilled solutions A and AS increased with the increase of the distillation time up to 4 min. In the times from 1 to 4 min, the formic, acetic, propionic and butyric acid recoveries in the distilled solution A varied from 14 to 66, 25 to 81, 59 to 110 and 74 to 107%, while in the distilled solution AS, the recoveries varied from 25 to 76, 39 to 90, 72 to 110 and 94 to 108%, respectively. In the time range of 4–7 min, the recoveries of these acids varied from 66 to 75, 81 to 90, 110 to 94 and 107 to 102% in the distilled solution A, whereas in the distilled solution AS, the recoveries varied from 76 to 89, 90 to 93, 110 to 91 and 108 to 111%, respectively. We also observed that the recoveries obtained for the formic and acetic acids in all distilled solutions AS were from 9 to 15% and from 3 to 10% higher than those obtained in the distilled solutions A, respectively. In the distilled solutions A and AS, the recoveries for the propionic and butyric acids were similar (test-*t*, 95% confidence level). This fact indicated that the "salting out" effect (reduction in the solubility of the organic compounds in water caused by salt addition, with consequent increase of hydrophobicity of these compounds) [27] was more evident for the formic and acetic acids. The distillation time of 7 min did not improve the analyte recoveries (test-*t*, 95% confidence level) and therefore, the distillation times of 4, 5 and 6 min were selected for the next experiment. A typical chromatogram (not shown) obtained by elution of the distilled solution AS (distillation time of 4 min), started with a tailing broad peak, probably due to Cl^- and/or SO_4^{2-} which were swept out by mechanical forces in the distillation procedure and were not retained on the column. Consequently, this peak could affect the peak widths and peak shapes of the anions from the carboxylic acids. In an effort to reduce this interference, the volume of the 50% v/v H_2SO_4 solution was decreased by half in the next experiment.

In the second experiment, the effect of the distillation time (4, 5 and 6 min) on the carboxylic acid recovery, using a reduced volume (5 mL) of the 50% v/v H_2SO_4 solution, was studied. Water (5 mL) was used to collect the distillate. The procedure was similar to that described in the first experiment. The recoveries for the formic, acetic, propionic and butyric acids in the distilled solution A varied from 55 to 74, 70 to 85, 93 to 110 and 98 to 106%, whereas in the distilled solution AS, the recoveries for these acids varied from 71 to 90, 84 to 101, 89 to 110 and 95 to 103%, respectively. The carboxylic acid recoveries were similar for the distillation times of 5 and 6 min (test-*t*, 95% confidence level) and better than those obtained for the distillation time of 4 min. Hence, the distillation time selected was 5 min. We observed that the tailing broad peak, obtained in the first experiment, was attenuated due to the reduced volume of 5 mL employed for the 50% v/v H_2SO_4 solution. Consequently, the separation of the first peak from the formate peak was improved.

Table 2
Figures of merit of the proposed method for the determination of formic, acetic, propionic and butyric acids.

Acid	Formic	Acetic	Propionic	Butyric
LOD ($3s/S$) (mg L^{-1})	0.2	0.5	0.3	1.5
LOQ ($10s/S$) (mg L^{-1})	0.7	1.7	1.0	5.0
Linear range (mg L^{-1})	10–100	10–100	10–100	10–100
Correlation coefficient (R^2)	0.9998	0.9996	0.9967	0.9979
Sensitivity (mV mg^{-1} L)	8.08	4.81	3.50	2.54
RSD (%)	≤2.9	≤2.0	≤2.8	≤3.0

n.d., not determinate; RSD, relative standard deviation.

Table 3
Recovery of carboxylic acids from produced water samples from pre-salt layer ($n = 3$).

Sample	Acid original concentration (mg L^{-1})				Acid recovery (%)			
	Formic	Acetic	Propionic	Butyric	Formic	Acetic	Propionic	Butyric
S1	<0.2	419(8)	<0.3	<1.5	100(0.8)	107(1)	107(3)	103(2)
S2	<0.2	391(8)	<0.3	<1.5	103(3)	105(2)	102(1)	101(3)
S3	<0.2	420(8)	<0.3	<1.5	99(1)	108(1)	108(1)	105(2)

Anion concentration added before distilling: 40 mg L^{-1}; standard deviations between brackets.

This fact indicated that part of the contribution of the interfering signal was due to SO_4^{2-}.

Although the peak obtained at the beginning of the chromatogram (Fig. 1) did not cause any interference in the carboxylic acid determination, we tried to eliminate or reduce it (third experiment). Lower volumes (1.0 and 2.5 mL) of the 50% v/v H_2SO_4 solution were tested. The procedure was similar to that described in the second experiment, and the recoveries obtained by using 5 mL of the 50% v/v H_2SO_4 solution were used for comparison. The recoveries for the formic, acetic, propionic and butyric acids from the distilled solution A, using 1.0 and 2.5 mL of the 50% v/v H_2SO_4 solution, varied from 61 to 66, 72 to 74, 86 to 87 and 92 to 97%, whereas in the distilled solution AS, the recoveries for these acids varied from 76 to 77, 83 to 84, 86 to 102 and 97 to 98%, respectively. Again, the best carboxylic acid recoveries (from 80 to 101 and 80 to 107% for A and AS solutions, respectively) were obtained with 5 mL of the 50% v/v H_2SO_4 solution. Therefore, the first peak was neither eliminated nor decreased. However, this first peak was sharper than that interfering peak obtained in a typical chromatogram of an undistilled 10-fold diluted solution AS (Fig. 1), and did not cause any interference in the separation of the analyte peaks.

In the last experiment, the effect of the NaCl concentration on the calibration curves plotted for the determination of carboxylic acids by IEC was studied. Calibration standards containing formate, acetate, propionate and butyrate were prepared in NaCl solutions with different concentrations (1, 15 and 30% m/v) + 500 mg L^{-1} Br^- + 500 mg L^{-1} SO_4^{2-} + 200 mg L^{-1} NO_3^- and in water. Prior to the chromatographic analyses, the calibration standards were steam distilled. Also, undistilled calibration standards prepared in water were used. Three replicates were carried out. The results are shown in Table 1. The standard deviations were shown only for the sensitivity values. All correlation coefficients were good (>0.99). The sensitivities obtained for formic and acetic acids in the undistilled calibration solutions prepared in water were higher than those found for these acids in other calibration curves, whereas for propionic acid, the sensitivity obtained in distilled calibration solutions containing 1% m/v NaCl was lower than those found in other calibration curves. On the other hand, all sensitivities obtained for butyric acid were similar. Also, all sensitivities obtained for each acid in distilled calibration solutions containing 15% and 30% m/v NaCl were similar (test-*t*, 95% confidence level). As the purpose of this study was to develop a method to analyze hypersaline waters, the 30% m/v NaCl solution was selected to prepare the calibration standards.

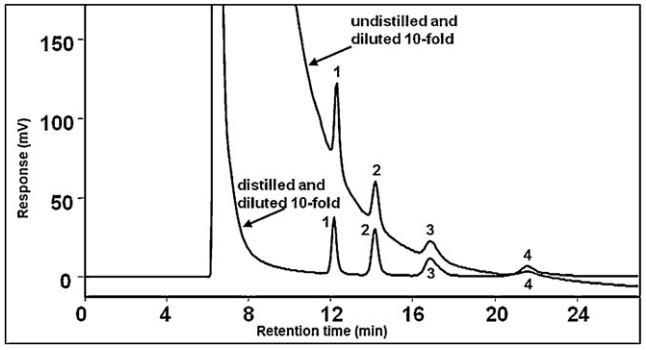

Fig. 1. Chromatograms of the AS solutions prepared according to Section 2.2, after distillation + 10-fold dilution (procedure described in Section 2.3) and undistilled + 10-fold dilution. Peaks 1, 2, 3 and 4 are related to formate, acetate, propionate and butyrate, respectively. Chromatographic conditions are described in Section 2.1.

3.2. Analytical results

The figures of merit for the determination of formic, acetic, propionic and butyric acids in hypersaline waters are presented in Table 2. The limits of detection (LOD) were calculated from the equation LOD = $3S_{BL}/b$, where S_{BL} was the standard deviation of 10 blank concentration measurements and b was the slope of the calibration curve. The obtained LODs were 0.2, 0.5, 0.3 and 1.5 mg L^{-1} for formic, acetic, propionic and butyric acids, respectively. The limits of quantification (LOQ = $10S_{BL}/b$) were 0.7, 1.7, 1.0 and 5.0 mg L^{-1} for formic, acetic, propionic and butyric acids, respectively. The hypersaline produced water samples from the pre-salt layer were analyzed by Mohr's method, and showed high concentrations of NaCl (*ca.* 19% m/v). In order to evaluate matrix interference, recovery tests were carried out. The produced waters were spiked with 40 mg L^{-1} of each analyte and then, steam distilled. The experiment was carried out in triplicate. As the acetate concentrations were relatively high, aliquots of the solution contained in the 50 mL polypropylene flask (Section 2.3) were diluted 5-fold before IEC analyses. Table 3 shows that the formic, propionic and butyric acid concentrations were lower than the LODs. Only acetic acid was found in the samples (391–420 mg L^{-1}). The high acetic acid concentrations found in these produced waters are consistent with the literature [1,3,4]. Good recoveries (99–108%) were obtained for all acids, indicating that the proposed method is accurate.

4. Conclusions

The obtained results demonstrated that steam distillation was an efficient sample pretreatment for determination of carboxylic acids in hypersaline waters containing up to 30% m/v of NaCl by IEC. The proposed method is accurate and precise. Detection limits of 0.2, 0.5, 0.3 and 1.5 mg L^{-1} were obtained for formic, acetic, propionic and butyric acids, respectively.

Acknowledgements

This work is part of the first author's M.Sc. thesis presented at Universidade Federal do Rio de Janeiro – UFRJ, who had a scholarship from CAPES. The authors acknowledge Suely Apati from PETROBRAS/CENPES for providing the water samples.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.12.032.

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