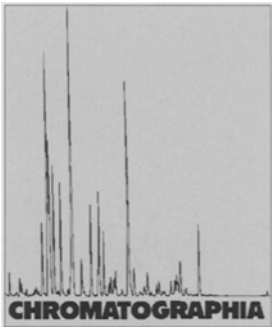
Analysis of Alkyl Sulfonates and Carboxylates Using High Performance Ion Chromatography



2000, *52*, 162–164

H. A. J. M. Bevers[1] / R. Hulst[1,2]*

[1] Department of Chemical Analysis, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
[2] Present address: BioMaDe Foundation, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Key Words

Column liquid chromatography
Ion chromatography
Alkyl sulfonates
Alkyl carboxylates

Summary

A simple and general method for the determination of both C_1–C_{10} alkyl sulfonates and alkyl carboxylates using the same basic methodology, based on High Performance Ion Chromatography, using relatively simple eluent systems allowing fast analysis with both high sensitivity and accuracy is presented.

Introduction

Alkyl sulfonates and alkyl carboxylates (Figure 1) are increasingly important target materials for industrial, pharmaceutical and academic research and application.

Organic sulfur-containing materials and inorganic sulfate (SO_4^{2-}) are often present as contaminants in industrial cleansing baths. Traces of these materials are capable of inducing severe problems like etching of industrial malls and several methods were recently developed to determine both their qualitative and quantitative presence. Most methods developed are capable of determining C_6 and higher alkyl sulfonates excluding the important class of C_1–C_5 alkylated sulfonates [1–4]. Vogt and co-workers [3] developed a method to determine the alkyl sulfonate contents of polluted water using reversed phase chromatography and compared the results with capillary zone electrophoresis (CZE). Detection limits were found to be 0.3 ppm and 4.8 ppm for the HPLC and CZE methods, respectively. Boden and co-workers [5] used CZE to determine the contamination in samples of C_1–C_{10} alkyl sulfonates, whereas Jira and co-workers [6] used chiral and achiral ion pair reagents in combination with cyclodextrines to perform separation of enantiomeric alkyl sulfonates by means of capillary electrophoresis (CE). The method was shown to be applicable to the analysis of C_3–C_8 alkyl sulfonates.

Ion chromatography (IC) appeared to be a promising technique especially for the determination of small(-er) alkylsulfonates, with detection limits expected to be in the lower ppb range. Gjerde and Fritz [7] discussed the potential pitfalls in analyzing anionic sulfonic acids using conductivity detection and suppression, which gives a much better signal to noise ratio compared to unsuppressed detection.

The structurally closely related aliphatic carboxylates are natural products with interesting chemical and pharmaceutical properties. In the literature their analysis is described most frequently together with the analysis of di-carboxylates, hydroxy-carboxylates and unsaturated carboxylates. Gjerde and co-workers [7] described several analytical applications using Ion-exchange chromatography and UV detection. Ion-exclusion chromatography using compressed conductivity detection as well as short column cation exchange in combination with organic modifiers was also used for the analysis of alkyl carboxylates. Tanaka and co-workers [8] also described a method based on the latter technique. De Backer and co-workers [9, 10] analyzed C_1–C_{10} alkyl carboxylates using CZE and were able to detect quantities as low as 100 fmol. C_1–C_{18} Alkyl carboxylates were also analyzed by Desbene and co-workers [11] using CZE and organic co-solvents; quantitative determination proved possible down to 1 ppm. The same methodology is applied in the determination of C_1–C_{10} alkyl sulfonates affording detection limits typically in the 700 ppb range. Ion

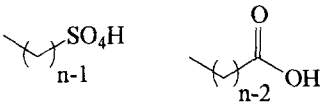


Figure 1. Alkyl sulfonates and carboxylates used in this study.

0009-5893/00/02 162-03 $ 03.00/0

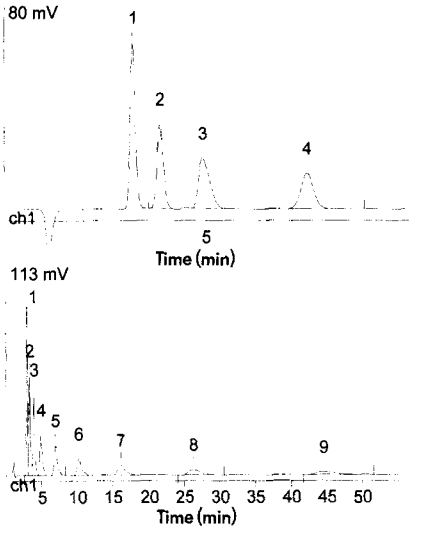


Figure 2. Ion chromatograms of alkyl sulfonates C_1-C_{10} lower ('standard' eluent + 16,8% acetone) and C_1-C_5 upper ('standard') eluent, without C_2), approx. 20 ppm each. Indices refer to eluting order. See text for explanation.

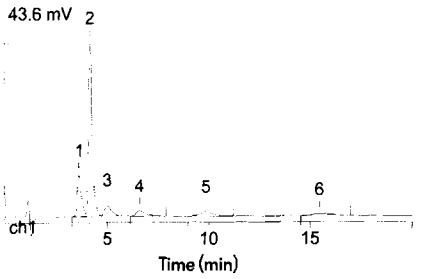


Figure 3. Ion chromatograms of alkyl carboxylates C_1, C_2 and C_5-C_8, approx. 20 ppm each. Indices refer to eluting order. See text for explanation.

exclusion chromatography was used by Ohta and co-workers [12] to analyze C_1-C_{10} alkyl carboxylates by addition of an organic modifier, allowing analysis of quantities in the 3–10 µM range. Chen [13], applying compressed conductivity for detection, used ion chromatography for the determination of (C_1-C_8) alkyl carboxylates. By applying pre-conditioning, detection limits typically in the 0.1 ppm range were feasible. Fisher and co-workers [14] compared ion exchange and ion exclusion methods, whereas several groups [15–20] applied ion chromatography and compressed conductivity for detection.

In this study, a simple and general method for the determination of both alkyl sulfonates and alkyl carboxylates using the same basic methodology is presented based on HPIC using relatively simple eluent systems and allowing fast analysis with both high sensitivity and accuracy.

Table I. R_s values of the alkyl sulfonates as a function of different eluent composition. See text for explanation.

Component (n)	R_s standard eluent n, n + 1	R_s standard eluent +8% acetone, n, n + 1	R_s standard eluent +16.8% acetone, n, n + 1
1	2.56	1.48	1.26
3	2.79	2.02	1.73
4	5.13	3.12	2.15
5	0	3.90	3.40

Table II. Accuracy and detection limits in the determination of alkyl sulfonates using 'standard' eluent and with acetone co-solvent. See text for explanation.

Component (n)	R_t (min) standard eluent, Detection limit (ppb)	R_t (min) standard eluent + 16.8% acetone, Detection Limit (ppb)
1	3.12 ± 0.04 2 ± 0.02	2.92 ± 0.02 25 ± 0.2
3	3.79 ± 0.06 5 ± 0.05	3.27 ± 0.03 15 ± 0.2
4	4.85 ± 0.10 30 ± 0.3	3.87 ± 0.04 20 ± 0.1
5	7.36 ± 0.14 10 ± 0.03	4.90 ± 0.07 20 ± 0.1
6	–	6.88 ± 0.08 30 ± 0.1
7	–	10.19 ± 0.16 25 ± 0.1
8	–	16.07 ± 0.31 20 ± 0.1
9	–	26.50 ± 0.72 125 ± 0.2
10	–	45.37 ± 1.47 150 ± 1

Experimental

Chemicals

$NaHCO_3$, Na_2CO_3 and acetone were purchased from Merck. Alkyl sulfonates and alkyl carboxylates (both as the corresponding mono-sodium salts) were purchased from Fluka. All chemicals were pro analysis grade and used without further purification. MilliQ-water for the preparation of the eluents was used directly.

Equipment

Ion chromatograph Metrohm (Metrohm, Herisau, Switzerland) equipped with a 733 IC Separation Center and 732 IC detector (conductivity) and suppressor and a 709 IC pump system. The separation center contains an injection system with on-line loop. Typically, 50 µL aliquots were injected.

Column

75 × 4.6 mm Metrosep Anion Dual 2 column (Metrohm, Herisau, Switzerland).

Mobile Phase

Alkyl Sulfonates

$NaHCO_3$ (2 mM)/Na_2CO_3 (1.3 mM) in MilliQ water adjusted to pH 9.6, flow rate 1 mL min^{-1}. Gradient experiments were performed by addition of up to 16.8% acetone (*v/v*) to the eluent; linear increase rate to the desired level of acetone (*v/v*) over a 30 seconds time interval was used typically.

Alkyl Carboxylates

$NaHCO_3$ (1 mM)/Na_2CO_3 (0.65 mM)/ 10% acetone (*v/v*) in MilliQ water adjusted to pH 8, flow rate 1 mL min^{-1}.

Results and Discussion

Alkyl Sulfonates

A mixture of the alkyl sulfonates was prepared by mixing standard solutions of each compound and 50 µL aliquots were injected. Experiments using various eluent compositions were performed, culminating in the use $NaHCO_3$ (2 mM)/Na_2CO_3 (1.3 mM) in MilliQ water adjusted to

Table III. R_s values of the alkyl carboxylates as a function of different eluent composition. See text for explanation.

Component (n)	R_s standard eluent n, n + 1	R_s standard eluent + 5% acetone, n, n + 1	R_s standard eluent + 10% acetone, n, n + 1
2	1.49	1.46	1.55
1	1.96	1.90	1.77
4	1.96	1.90	–
5	2.90	2.49	2.34
6	3.61	3.31	3.57
7	2.76	4.35	3.89
8	0	0	0

pH 9.6 and a flow rate of 1 mL min^{-1}. This setting provided relatively short retention times within the series C_1–C_5 showing appropriate signal shape and separation (Figure 2), whereas under these conditions the separation of C_6–C_{10} became both time consuming and led to (very) broad signals imposing larger errors (Figure 2).

Addition of acetone as (gradient) cosolvent, however, dramatically reduced the retention times without loss of resolution (C_5–C_{10}) and, moreover, yields much better signal shape and hence higher accuracy. Gradient experiments were performed by adding acetone to the 'standard' eluent up to 16.8% (*v/v*); higher amounts cause damage to the column material and were for this reason not applied. The results are collected in Tables I and II.

Clearly, good signal separation is obtained within the series C_1–C_5 by using the 'standard' eluent system, whereas the addition of 8% acetone yields shorter retention especially for the series C_6–C_{10} although with C_{10} these settings led to saturation of the suppressor prior to complete elution of C_{10}. Addition of 16.8% acetone (maximum), however, led to good results both in terms of elution, retention, signal shape and suppression. Using either of the eluents, the separation of C_1 and C_2 was not completely satisfactory as no baseline separation was obtained with our system.

Table II shows the accuracy both with and without the addition of acetone as cosolvent. All the entries yield adequate sensitivity and accuracy for the mixture of C_1–C_{10} indicating that the presence of other sulfonates does not influence the analysis.

Alkyl Carboxylates

A mixture of the alkyl carboxylates was prepared by mixing standard solutions and 50 µL aliquots were injected. Experiments using various eluent compositions were performed, culminating in the use $NaHCO_3$ (1 mM)/Na_2CO_3 (0.65 mM)/ 10% acetone (*v/v*) in MilliQ water adjusted to pH 8 and flow rate of 1 mL min^{-1}. This setting provided relative short retention times within the series C_1–C_8 showing appropriate signal shape and separation (Figure 3).

Using these conditions, separation as well as quantification of C_1, C_2, C_5–C_8 with relative short retention times and appropriate signal shape and signal separation proved possible.

C_3 and C_4 Alkyl carboxylates both have a negative influence on the determination of C_1 due to signal overlap, whereas addition of smaller amounts of acetone yielded better results for C_1 and C_3/C_4 but also led to (very) broad signals for C_7 and C_8 and hence poorer accuracy.

In Tables III and IV results obtained using these experimental settings are shown. All entries show good sensitivity and accuracy comparable with the corresponding sulfonates.

Conclusions

We have shown that by using the settings as described, both alkyl sulfonates and alkyl carboxylates can be analyzed easily, quickly and with high sensitivity and accuracy for this increasingly important class of materials. Further research will focus on the (enantio)-separation of the corresponding branched materials.

References

[1] Maki, S.A.; Wangsa, J.; Danielson, N.D. *Anal. Chem.* **1992**, *64*, 583–589.

[2] Smedes, F.; Kraak, J.C.; Werkhoven-Goewie, C.F.; Brinkman, U.A.; Frei, R.W. *J. Chromatogr.* **1982**, *247*, 123–132.

[3] Vogt, C.; Heinig, K.; Langer, B.; Mattusch, J.; Werner, G. *Fresenius' J. Anal. Chem.* **1995**, *352* (5), 508–514.

Table IV. Accuracy and detection limits in the determination of alkyl carboxylates using 'standard' eluent/10% acetone. See text for explanation.

Component (n)	R_t (min) standard eluent + 10% acetone, Detection limit (ppb)
2	3.58 ± 0.14 40 ± 0.3
1	4.13 ± 0.16 2 ± 0.1
5	4.91 ± 0.20 50 ± 1
6	6.46 ± 0.23 145 ± 1
7	9.72 ± 0.60 90 ± 0.6
8	15.36 ± 0.60 160 ± 2

[4] Jiang, S.X.; Liu, X. *J. Liq. Chromatogr. Relat. Technol.* **1997**, *20* (13), 2053–2061.

[5] Boden, J.; Feige, K.; Meyer, B. *Chromatographia* **1997**, *45*, 116–120.

[6] Jira, T.; Bunke, A.; Karbaum, A. *J. Chromatogr. A.* **1998**, *798* (1–2), 281–288.

[7] Gjerde, D.T.; Fritz, J.S. In *Ion Chromatography*: Hüthig, Ed., Verlag Heidelberg, Basel, New York, **1987**.

[8] Tanaka, K.; Ohta, K.; Fritz, J.S. *J. Chromatogr. A.* **1997**, *770* (1–2), 211–218.

[9] De Backer, B.L.; Nagels, L.J. *Biomed. Chromatogr.* **1995**, *9* (6), 257–258.

[10] De Backer, B.L.; Nagels, L.J. *Anal. Chem.* **1996**, *68* (24), 4441–4445.

[11] Desbene, A.M.; Morin, C.J.; Mofaddel, N.L.; Groult, R.S. *J. Chromatogr. A.* **1995**, *716* (1–2), 279–290.

[12] Ohta, K.; Tanaka, K.; Haddad, P.R. *J. Chromatogr. A.* **1996**, *739* (1–2), 359–365.

[13] Chen, J. *J. Chromatogr. A.* **1996**, *736* (1–2), 273–280.

[14] Fisher, K.; Chodura, A.; Kotalik, J.; Bieniek, D.; Kettrup, A. *J. Chromatogr. A.* **1997**, *770* (1–2), 229–241.

[15] Qi, H.; Wang, H.N.; Wang, J. *Fenxi Ceshi Xuebao* **1998**, *17* (2), 62–65.

[16] Kuo, C.-Y. *J. Chromatogr. A.* **1998**, *804* (1–2), 265–272.

[17] Souza, S.R.; Tavares, M.F.M.; de Carvalho, L.R.F. *J. Chromatogr. A.* **1998**, *796* (2), 335–346.

[18] Xu, N.; Vandegrift, S.; Fine, D.D.; Sewell, G.W. *Environ. Toxicol. Chem.* **1997**, *16* (11), 2242–2248.

[19] Zhu, Y.; Zhang, X.D.; Niu, W.J. *Mikrochim. Acta* **1997**, *127* (3–4), 189–194.

[20] Medved, A.L.; Ivanov, A.A.; Shpigun, O.A. *Zh. Anal. Khim.* **1996**, *51* (10), 1055–1063.

Received: Jan 21, 2000
Revised manuscript received: Mar 23, 2000
Accepted: May 2, 2000