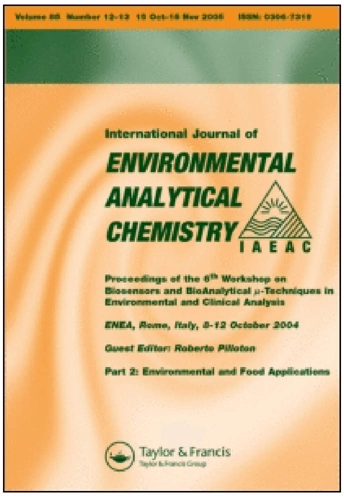
This article was downloaded by:
On: *17 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

HPLC Determination of Sulphonated Melamines-Formaldehyde Condensates (SMFC) and Lignosulphonates (LS) in Drinking and Ground Waters

Giulio Pojana[a]; Claudio Carrer[a]; Filippo Cammarata[a]; Antonio Marcomini[a]; Carlo Crescenzi[b]
[a] Department of Environmental Sciences, University of Venice, Venezia, Italy [b] Department of Chemistry, University "La Sapienza" of Rome, Rome, Italy

Online publication date: 17 September 2010

To cite this Article Pojana, Giulio , Carrer, Claudio , Cammarata, Filippo , Marcomini, Antonio and Crescenzi, Carlo(2003) 'HPLC Determination of Sulphonated Melamines-Formaldehyde Condensates (SMFC) and Lignosulphonates (LS) in Drinking and Ground Waters', International Journal of Environmental Analytical Chemistry, 83: 1, 51 — 63

To link to this Article: DOI: 10.1080/0306731030000104236

URL: http://dx.doi.org/10.1080/0306731030000104236

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Environ. Anal. Chem., Vol. 83, No. 1, pp. 51–63

HPLC DETERMINATION OF SULPHONATED MELAMINES-FORMALDEHYDE CONDENSATES (SMFC) AND LIGNOSULPHONATES (LS) IN DRINKING AND GROUND WATERS

GIULIO POJANA[a], CLAUDIO CARRER[a], FILIPPO CAMMARATA[a], ANTONIO MARCOMINI[a,]* and CARLO CRESCENZI[b]†

[a]*Department of Environmental Sciences, University of Venice, Calle Larga S. Marta 2137, 30123 Venezia, Italy;* [b]*Department of Chemistry, University "La Sapienza" of Rome, Piazzale Aldo Moro 5, I-00185 Rome, Italy*

(Received 27 March 2002; In final form 3 September 2002)

New separation/detection procedures by reversed-phase HPLC coupled with UV and fluorescence detection have been developed for the determination of organic admixtures of the sulphonated melamines-formaldehyde condensates (SMFC) and lignosulphonates (LS) type in environmental samples (drinking and ground waters), as well as in concrete leachates. The developed method permitted to reach detection limits in the 0.05–0.3 µg range (as injected amount). An extraction/enrichment method from the titled environmental samples based on solid-phase-extraction (SPE) has been developed for SMFC by using polystyrene-divinylbenzene (PS-DVB, Envichrom-P) resin as sorbent. SMFC were extracted (recovery: *ca.* 70%) from aqueous samples at starting concentrations down to 10 µg/L. A structural confirmation of SMFC in aqueous samples was established by HPLC/Mass Spectrometry with electrospray interface (HPLC-ESI-MS) by using collision-induced ion fragmentation (in source-CID mode). The developed analytical procedures were applied to the determination of SMFC and LS in commercial blends, in drinking and ground waters, as well as in industrial effluents and liquors from leaching test experiments. Only shorter SMFC and LS components were identified as result of the leaching from concrete specimen.

Keywords: Concrete admixtures; Sulphonated melamines-formaldehyde condensates; Lignosulphonates; SMFC; LS

INTRODUCTION

Sulphonated organic compounds have been produced by industry since the yearly nineteenth century, and they are used nowadays on large scale (> 3 million tons/year) as synthesis intermediates for drugs and textiles (sulphonated benzenes), wetting agents and polymer stabilizers (alkylnaphthalene sulphonates), surfactants (linear alkylbenzene sulphonates, petroleum sulphonates), lubricants (lignosulphonates),

---

*Corresponding author. Fax: +39-041-257-8584. E-mail: marcom@unive.it

† Present address: Department of Analytical Chemistry, Stockholm University, S-10691 Stockholm, Sweden.

ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/0306731031000104236

optical brighteners (stylbene sulphonates), tanning agents (polyphenol sulphonates) and pharmaceuticals (amino and hydroxy naphthalene sulphonates) [1]. Sulphonated compounds are being discovered only recently as ubiquitous contaminants in the aqueous environment [2], triggering an increasing attention by the scientific community and environmental protection agencies on their environmental behavior and fate [3–5].

Polymeric sulphonated organics are used by the concrete industry as admixtures. Admixtures (over 1 000 000 tons/year productions in the EU), both organic and inorganic, are usually added to concrete up to 0.1–2% (w/w), with respect to concrete weight), in order to improve properties of concrete in the fresh state, as workability, or in the hardened state, as durability of structures [6–9]. Concrete admixtures can been divided into accelerators, water reducers, superplasticizers, retardants, air entraining agents, polymer-modifying agents, multifunctional admixtures. The most common organic concrete admixtures are sulphonated polymers as sulphonated naphthalene-formaldehyde condensates (SNFC), lignosulphonates (LS) and sulphonated melamine-formaldehyde condensates (SMFC) [10,11].

LS have been commonly employed until the 1950s as water reducers and plasticizers, while SNFC are typical superplasticizers and dispersants used since mid '70 s. SMFC have been recently introduced as superplasticizers for precast concrete and for applications at low temperature [10]. Currently, plasticizers and superplasticizers are employed to an extent of approximately 30% of all new concrete structures and buildings, and are essential additives for special applications, such as tunnels, bridges and all high-strength and prestressed concrete structures [9].

While SNFC have a well-defined chemical structure, with an average number of 5–10 oligomeric units in the commercial mixtures (Fig. 1A), SMFC exhibit a much higher average number of oligomeric units (usually 50–60), and have a more complex structure, containing both linear and branched isomers, because of the synthetic route involved (Fig. 1B) [1]. Lignosulphonates, whose average mass weight can range between 3000 and $> 100\,000$ Dalton, have even more complex chemical structures, deriving from partial depolimerization and sulphonation of lignin (Fig. 1C). The high variability of lignin (a by-product of cellulose production) composition and the presence of impurities lead LS to be used only for low and mid-quality concrete specimen [12].

Organic concrete admixtures are usually characterized in commercial blends for quality control by UV and IR spectroscopy, Total Organic Carbon (TOC) and Dissolved Organic Carbon (DOC) determination [13]. Only recently specific determination of their average molecular weight by gel permeation chromatography (GPC) and HPLC [14,15] and elucidation of their structure by high-performance liquid chromatography coupled with mass detection (HPLC-MS) have been proposed [15]. Most analytical studies concentrated on SNFC [16,17] while, comparatively, fewer data are available for SMFC and LS. The LS structure has been recently investigated by using Size-Exclusion Chromatography and Gas-Chromatography/Pyrolysis/Mass Spectrometry (GC-PY-MS) [12,18].

As far as toxicology, environmental behavior and life cycle of concrete admixtures are concerned, SMFC and LS were shown to have a lower toxicity (EC50, fish > 500 mg/L), but still they can pose a potential hazard for the aquatic environment because of local high consumption amounts and subsequent potential high mobility up to reaching groundwaters and then, possibly, drinking waters [19,20]. Despite of the high molecular weights, SNFC, SMFC and LS are highly water-soluble polymers (> 100 mg/L) with very low $\log K_{\mathrm{ow}} (< -4)$. Various types of wastewaters, such as

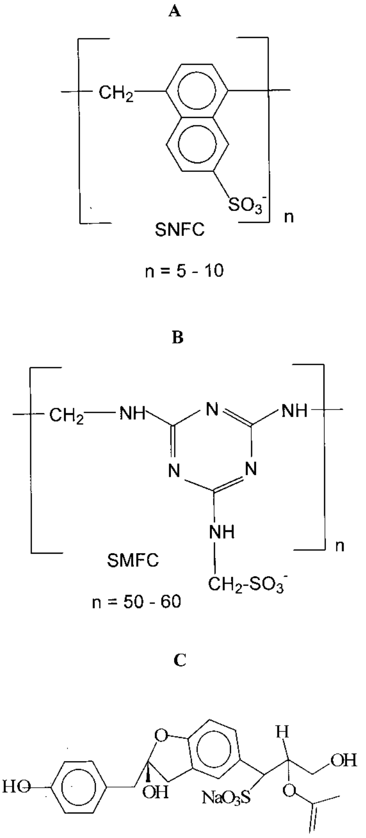


FIGURE 1 Molecular structures of SNFC (A), SMFC (B) and LS (C, one of the possible monomeric structures).

those from admixture and concrete production sites, transportation and concrete use, are supposed to be potential pathways for input of such chemicals into the environment [21,22]. Studies based on aspecific determination indicated that some (5–20% of the total) of added organic admixtures may be released by concrete after hardening in the receiving waters and soils [23,24]. Moreover, shorter SNFC oligomers have been recently identified as ubiquitous contaminants in many river, ground and drinking waters [25].

According to the findings for SNFC, shorter oligomers and isomers of SMFC and LS are also expected to be environmentally relevant for the receiving waters. To the best of our knowledge, no specific analytical methods have been developed for the determination of SMFC and LS in environmental waters. Specific, selective and sensitive methods are in fact a fundamental prerequisite for a reliable assessment of the environmental behavior and life-cycle of such concrete admixtures.

Here we present the results obtained within the EU Project ANACAD (ANalysis and Fate of Concrete ADmixtures) on the determination of concrete admixture of the SMFC and LS type in water samples. Such procedures were applied to the determination of the target compounds in commercial blends, industrial wastewaters and liquors from stability and leaching tests.

EXPERIMENTAL

Reagents and Chemicals

The tested SMFC and LS technical mixtures (40 to >90% declared active material) were kindly provided by the manufacturers. SMFC-CH (40% solution) was from SIKA (Zurich, Switzerland), SMFC-I1 (40% solution) and SMFC-I2 (>90% pure solid powder) were from MAPEI (Milan, Italy). LS-CH was from EH (Germany). LS-1 (40% solution) and LS-2 (>90% pure solid powder) were from MAPEI (Milan, Italy). LS standard mixture was from Aldrich (Milwaukee, WI, USA).

Ammonium acetate ($AcNH_4$), tetrabutylammonium chloride (TbuCl), tetramethylammonium chloride (TMeCl), sodium dihydrogen phosphate (NaH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4), all of analytical grade (>99% pure), were from Fluka (Buchs, Switzerland). All sample extracts were stored in 2 mL Teflon capped glass vials (Supelco, Bellefonte, PA, USA).

All organic solvents employed were HPLC grade from Baker (Deventer, Netherlands). Water for chromatographic purposes was purified by a MilliQ system (Millipore, Bedford, MS, USA).

Sample Extraction

The sorbing material used for the solid phase extraction (SPE) was polystyrene-divinylbenzene resin (PS-DVB, Envicrom-P, grain size: 80–160 µm, 0.5 g) supplied by Supelco (Bellefonte, PA, USA). SPE polypropylene cartridges (6 mL), reservoirs (20–60 mL), polyethylene frits and extraction apparatus (Visiprep-SPE-manifold), were from Supelco. Cartridges were conditioned with 10 mL of methanol followed by 20 mL of MilliQ water containing ammonium acetate ($AcNH_4$) 1 mol/L, at a flow rate of approximately 20 mL/min.

Water samples were added with $AcNH_4$ up to 1 mol/L and then passed through the SPE cartridge at a flow rate of *ca.* 20 mL/min. Sample reservoirs were then rinsed with 10 mL of MilliQ water containing $AcNH_4$ 1 mol/L, and this water was passed through SPE cartridges. After drying the cartridges under vacuum for 10 min, the analytes were finally recovered with 12 mL of methanol.

The eluted fractions were concentrated by evaporation in test tubes by heating at 50°C in a sand-bath under a mild air stream. The resulting concentrated extracts were finally transferred into 2 mL screw cap glass vials and evaporated to dryness. Extracts were then redissolved in 100 µL of mobile phase before injection.

Chromatographic Separation and Detection

The chromatographic apparatus consisted of a HP 1050 series liquid chromatograph (Hewlett Packard, Palo Alto, CA, USA) equipped with a mod. 1046A fluorescence detector (Hewlett Packard, flow cell volume: 5 µL) and a mod. 1050 UV–Vis detector (Hewlett Packard, flow cell volume: 8 µL). The samples were injected in a manual 7725 injector (Rheodyne, Rohnert Park, CA, USA) equipped with a 200 µL loop.

Cumulative separations of SMFC and LS were obtained by Ion-Pairing-Reversed-Phase HPLC on a C8-column (Supelco C8, 5 µm, 250 × 4.6 mm) by using a acetonitrile (A) and water (B) both containing TMeCl 0.5 mmol/L and phosphate buffer (pH 6.5) 2.5 mmol/L at a flow rate of 1.0 mL/min.

LS were separated by using a linear gradient elution where the initial mobile phase composition was 20% A, which was increased to 100% in 20 min. SMFC were separated by isocratic elution at 10% A.

Oligomer-by-oligomer separations of SMFC and LS were attained by Ion-Pairing-Reversed-Phase HPLC on a C18-column (Phenomenex Luna C18-2, 5 µm, 250 × 4.6 mm) by using a linear gradient elution by acetonitrile (A) and water (B), both with tetrabutylammonium fluoride (TBuF) 5 mmol/L at a flow rate of 1.0 mL/min. For SMFC the initial mobile phase composition was 30% A, which was increased to 99% in 80 min. For LS, the initial mobile phase composition was 30% A, which was increased to 99% in 120 min.

The elution of SMFC was monitored by UV detection at 218 nm. while LS was monitored by fluorescence detection at: $\lambda_{ex} = 228$ nm, $\lambda_{em} = 320$ nm.

Quantitation

In absence of certified standards for blends and individual oligomers of the tested compounds, the SMFC technical mixture provided by MAPEI (SMFC-I2, purity declared by the producer: >90%) and the LS mixture purchased by Aldrich were used as reference compounds.

Under the experimental conditions adopted for the cumulative separation, the limit of detection (LOD) for SMFC was *ca.* 0.05–0.1 µg (as injected amount), while for LS the LOD was *ca.* 0.1–0.3 µg (as injected amount). Quantitation of SMFC and LS in commercial liquid mixtures, industrial waters, stability and leaching test liquors were based on external standard calibration curves with standard solutions. Generated calibration curves showed linear response–amount relationships ($r^2 > 0.99$) in the 0.1–10 µg range (as injected amount), respectively.

Under oligomer-by-oligomer separation, SMFC and LS exhibited a cumulative LOD of 5 and 10 µg (as injected amount), respectively, with no observed deviation from linearity ($r^2 > 0.98$) for injected amounts up to 100 µg.

The oligomeric distributions of SMFC and LS in commercial mixtures were determined by assuming the same response factor for all oligomers. The displayed values were calculated referring the concentrations of each SMFC and LS oligomer to the sum of the concentrations of all SMFC and LS oligomers, respectively.

HPLC-ESI-MS Analysis

Qualitative analysis of SMFC was performed by means of a VG Platform LC/MS detector (Fisons Instruments, VG Biotech, Milan, Italy). SMFC were separated by HPLC on a C18-column (Alltech Alltima C18, 5 µm, 250 × 4 mm) by using a linear gradient elution by acetonitrile-water, both the TBuF 0.5 mmol/L at a flow rate of 1.0 mL/min. The initial mobile phase composition was 70% acetonitrile, which was increased to 99% in 20 min. The ESI/MS operated in negative ionization mode and selected ion monitoring acquisition mode. Source temperature was 70°C while the skimmer cone voltage was set at 90 V. Investigation was limited to the available standard compounds and leachate samples.

RESULTS

HPLC Separation

Two approaches were investigated for the HPLC separation of SMFC and LS: a cumulative separation and an oligomer-by-oligomer separation. The cumulative separation can be useful for screening purposes and to increase sensitivity, enhancing signal-to-noise (s–n) ratio for very diluted samples due to the coelution of all isomers and oligomers. The oligomeric separation is instead essential to assess and environmental behavior of the different oligomers and isomers contained in the commercial blends employed by concrete industry and released into the environment.

Typical HPLC separations of SMFC and LS under the conditions suitable for a cumulative separation are reported in Fig. 2. Such separation conditions were applied to the quantitative determination of SMFC and LS in commercial mixtures, which are usually employed as concentrated liquid solutions (*ca.* 40–50%, by weight), both liquid and solid, because they are simpler to be added to fresh concrete. Commercial liquid blends of SMFC and LS resulted to contain (by assuming to have the same oligomeric distribution of reference mixture) approximately 43–49% (molar basis) and 42–52% (molar basis) of active material, respectively. Purity of solid commercial powders of LS ranged between 85 and 100%. Remarkably, under the separation conditions adopted for SMFC, SNFC and LS, that could be copresent in a real water sample

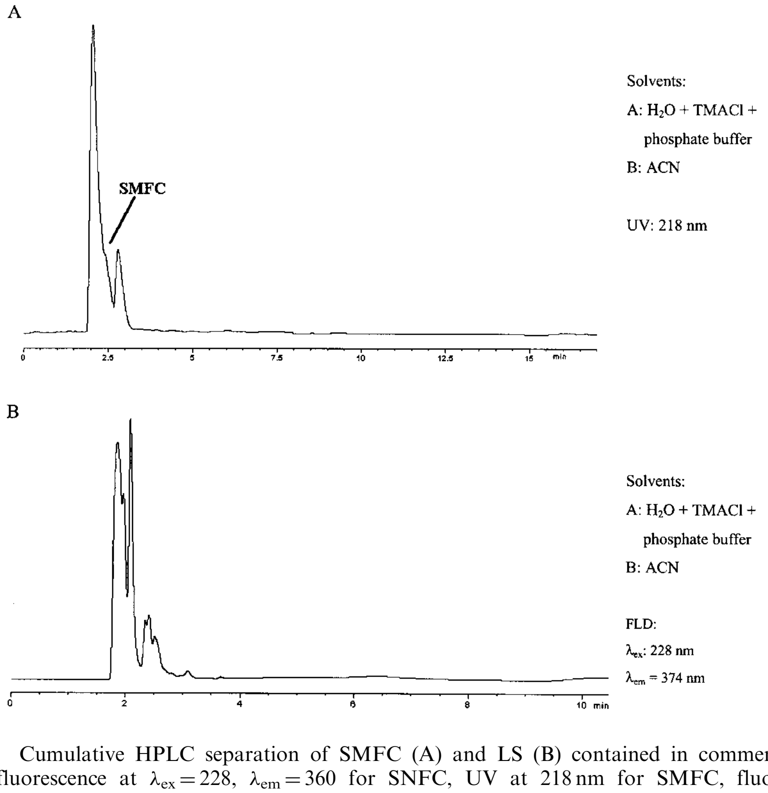


FIGURE 2 Cumulative HPLC separation of SMFC (A) and LS (B) contained in commercial blends. Detection: fluorescence at $\lambda_{ex} = 228$, $\lambda_{em} = 360$ for SNFC, UV at 218 nm for SMFC, fluorescence at $\lambda_{ex} = 228$, $\lambda_{em} = 320$ for LS.

and interfere with SMFC, are retained by the stationary phase (Fig. 3). Moreover, the developed cumulative separation, when applied to spiked drinking water samples, permits to separate analytes from interferences contained in drinking waters (Fig. 4).

Typical oligomer-by-oligomer separations of SMFC and LS commercial blends are presented in Fig. 5. The developed separation permitted to reveal also for LS and SMFC the presence of a series of homologs and isomers similar to that previously recorded for SNFC [14]. Unfortunately, in absence of reference standards for individual oligomers of SMFC and LS, it was not possible to assign a well-defined oligomeric number unit to the signal peaks exhibited by the chromatographic separation. By analogy with the separation exhibited by SNFC under the same chromatographic conditions, shorter oligomers and isomers of SMFC and LS eluted at shorter retention times. As found for SNFC, SMFC longer oligomers were not completely separated, coeluting under a broad peak at 36 min. By assuming for all peaks the same molar response factor under UV detection, an oligomeric distribution of the tested commercial mixtures of SMFC could be estimated (Fig. 6). A clear difference in the

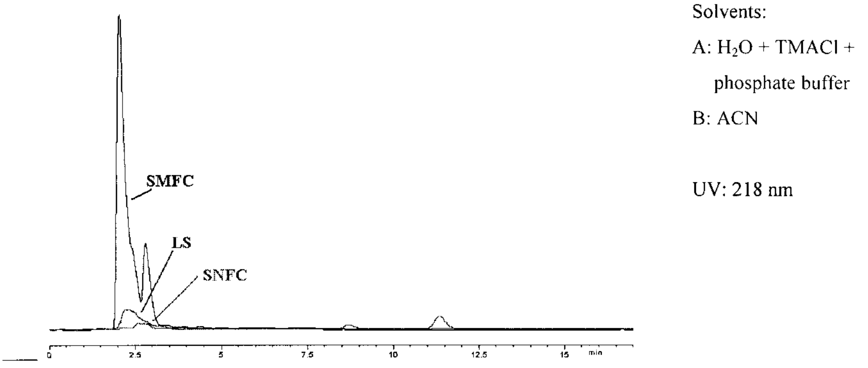


FIGURE 3 Potential interferences from SNFC and LS under cumulative HPLC separation conditions of SMFC. Injected amount: 5 μg for all compounds. UV detection at 218.

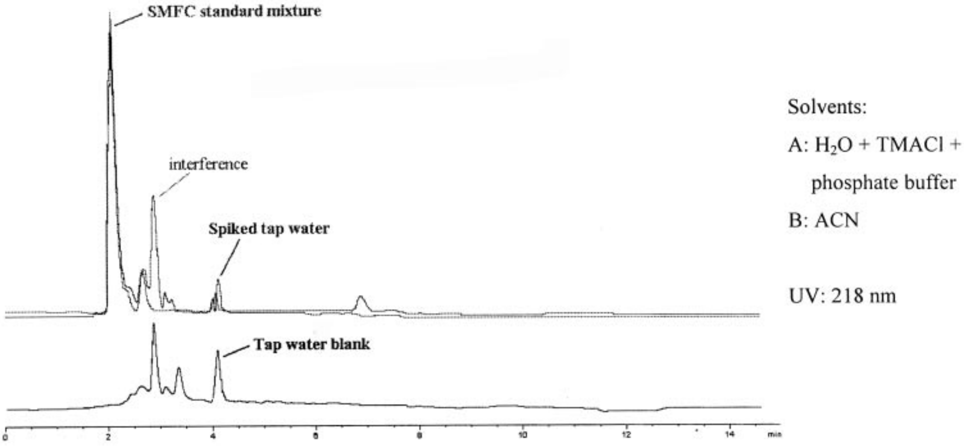


FIGURE 4 Cumulative HPLC separation of SMFC in spiked and unspiked drinking water under the chromatographic conditions adopted. Detection: UV at 218 nm.

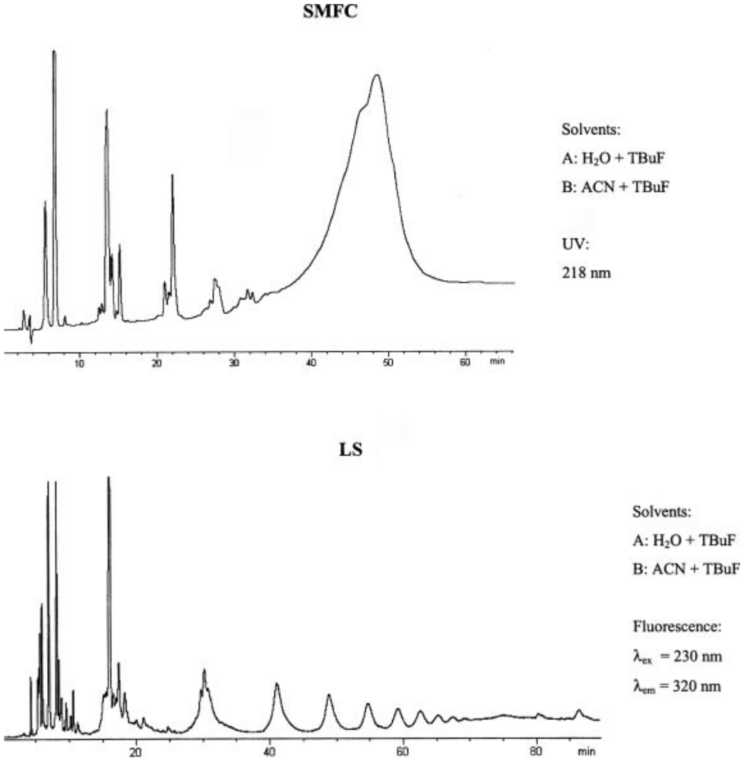


FIGURE 5 Oligomer-by-oligomer HPLC separation of SMFC and LS under the chromatographic conditions adopted. Detection: UV at 218 nm for SMFC, fluorescence at $\lambda_{ex} = 228$, $\lambda_{em} = 320$ for LS.

oligomeric distribution was found for Swiss and Italian SMFC commercial mixtures, the first containing a greater content of longer oligomers (85–87%) than the second one (44–58%).

MS Detection

Admixtures of the LS and SMFC type are complex mixtures characterized by a large number of oligomers and isomers. LS components, moreover, do not have a well-defined molecular weight, because the high variability structure of lignin, rendering MS detection not applicable for their determination in environmental samples.

SMFC, in principle, have a well-defined molecular structure with known molecular weights for all individual oligomers and isomers. Unfortunately, attempts to quantify SMFC commercial mixtures by HPLC-ESI-MS were unsuccessful, due to a poor and not reproducible yields of the ionization process when concentrations > 0.5 mmol/L of ion pairing reagents, necessary to obtain an acceptable oligomer-by oligomer chromatographic separation, were used. Vice versa, for concentrations of ion pairing reagents < 0.5 mmol/L, no reproducible chromatographic behavior could be obtained. Moreover, the high complexity of SMFC structure and the presence of multicharged molecules did not allow to identify characteristic ions for each oligomer, because of the formation of multicharged ions in the ionization chamber, differently from the

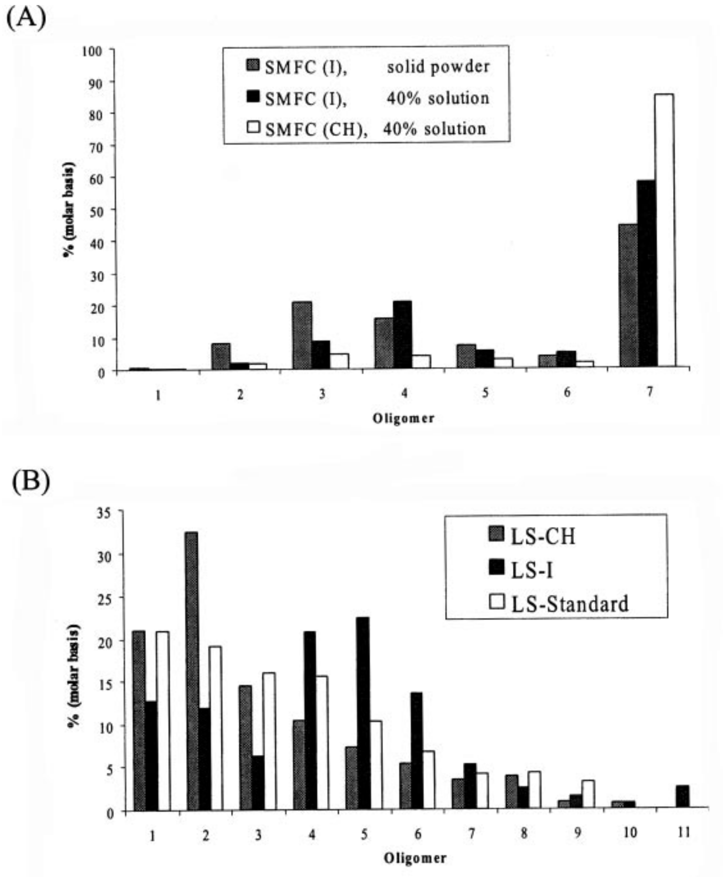


FIGURE 6 Oligomeric distribution (%, molar basis) of SMFC (A) and LS (B) in commercial blends.

findings recently reported for SNFC [16]. In Fig. 7 a typical mass spectrum of a SMFC commercial mixture is reported.

A qualitative structural determination of SMFC could be developed by isolating a characteristic ion fragment of the monomeric melamine sulphonate structure (Fig. 7). Such characteristic ion, obtained by induced collision at high voltage (90 V) in the desolvatation chamber (in source CID spectra), can be used as a ‘finger print’ to qualitatively confirm the presence of SMFC-related compound in aqueous environmental samples.

Extraction–Enrichment

In order to increase sensitivity in the determination of SMFC in diluted water samples, such as ground waters, an extraction–enrichment step was developed. An extraction procedure on polystyrene–divinylbenzene (PS–DVB) recently developed for SNFC [16] was adopted, after minor modifications. SMFC were extracted (max recovery: 73%) from spiked drinking water samples at concentrations down to 10 μg/L. No recovery (approximately 2%) was observed for 1 μg/L spiked samples. A breakthrough

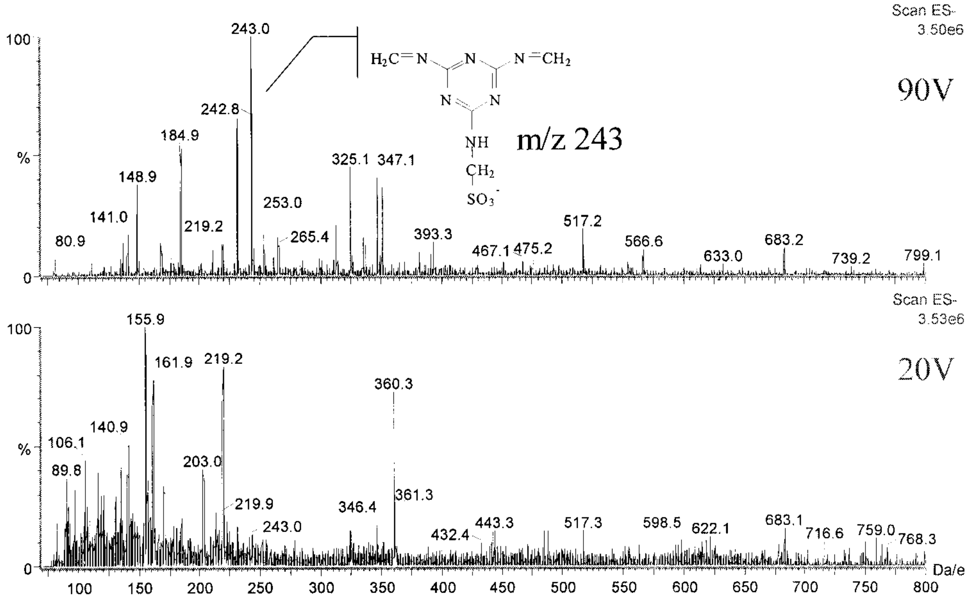


FIGURE 7 Structural confirmation of SMFC by HPLC-ESI-MS.

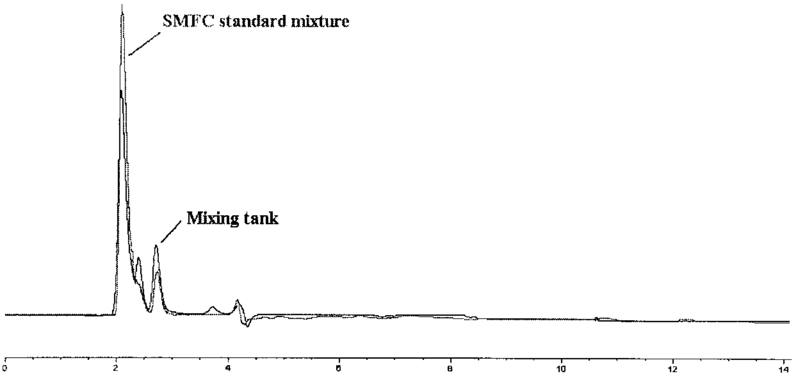
TABLE I Percentages of recovery obtained with SPE by ENVICHROM-P[1] of SMFC from 100 mL and 250 mL of drinking water added with $AcNH_4$ 1 mol/L (triplicate determination, cumulative separation)

Concentration (μg/L)	*Processed volume* (mL)	*Recovery* (%)	*Relative standard deviation* (RSD, %)
100	100	72	5.8
100	250	73	6.0
100	1000	43	6.2
10	250	72	6.7
10	1000	25	9.1
1	250	2	9.2

was moreover observed for >250 mL of processed volume (25–43% recovery). The observed relative standard deviation (RSD) ranged 5.8–9.2% (Table I). Noticeably, no preferential enrichment of selected SMFC oligomers was observed in the enriched extracts, as determined by oligomer-by-oligomer separation.

Applications

The developed separation–detection method was applied to the determination of SMFC and LS in real water samples. Industrial wastewaters collected in a SMFC-manufacturing plant were analyzed by both cumulative and oligomeric separation for screening purposes. The high concentration values exhibited by the samples allowed a determination of analytes by direct injection in the chromatographic system (Fig. 8). The determined concentrations ranged between 80 mg/L in the settling basins and 120 mg/L in the mixing reactors wastes.



Solvents:

A: H_2O + TMACl +
phosphate buffer

B: ACN

UV: 218 nm

FIGURE 8 Cumulative HPLC separation of SMFC contained in an industrial mixing tank. Detection: UV at 218 nm.

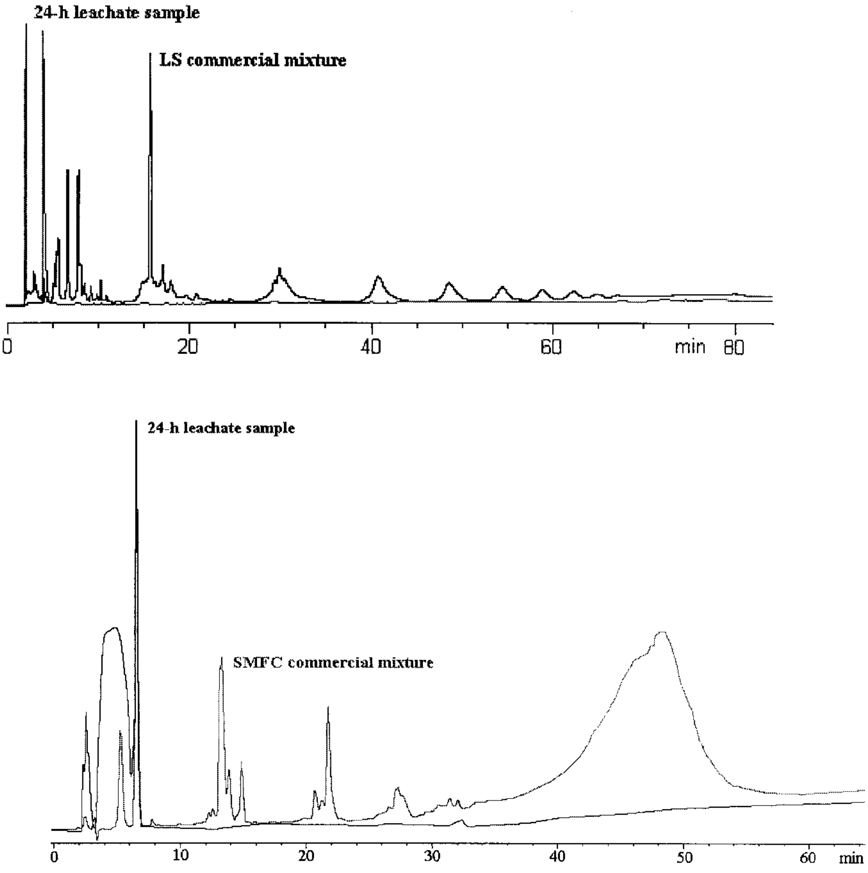


FIGURE 9 Oligomer-by-oligomer HPLC separation of SMFC and LS in liquors from leaching experiments of concrete specimen added with SMFC and LS commercial mixtures, respectively. Detection: UV at 218 nm for SMFC, fluorescence at 228–320 nm for LS.

The developed separation–detection procedures were applied also to the specific determination of SMFC and LS released during standardized leaching tests performed on crushed concrete specimen added with SMFC and LS admixtures. Oligomer-by-oligomer separations of leaching test liquors permitted to reveal that only shorter oligomers of SMFC and LS are released from concrete (Fig. 9), as recently reported for SNFC [17], while longer oligomers and isomers are strongly retained into concrete matrix. Such compounds are supposed to be the most relevant components in the aquatic environment after release from concrete structures. Such results are important for a correct assessment of the environmental impact of such concrete admixtures.

CONCLUDING REMARKS

The combination of oligomeric and cumulative separation by reversed-phase HPLC, as well as the coupling of UV and fluorescence detection, allowed the identification of SMFC and LS concrete admixtures in commercial blends as well as in selected aqueous samples of environmental concern. The obtained results permitted to reveal that released components from leaching tests are composed only by few shorter components of the original admixtures added to the concrete. Further work in progress is focusing on the biodegradation behavior of such admixtures.

Acknowledgments

This work was supported by European Community (ANACAD project, ENV4-CT97-0474). The authors gratefully thank Dr Michael Ochs (BMG Engineering ltd, Schlieren, Switzerland) for providing leachate liquors and grab water samples.

References

[1] O. Lindner, *Ullman's Encyclopedia of Industrial Chemistry, 5th*, Vol. A3, pp. 507–537. VHC Verlagsgesellschaft, Wenheim (1991).
[2] O. Zerbinati, G. Ostacoli, D. Gastaldi and V. Zelano, *J. Chromatogr.*, **640**, 231–240 (1993).
[3] F.T. Lange, M. Wenz and H.J. Brauch, *J. High Resol. Chromatogr.*, **18**, 243–249 (1995).
[4] H. Greim, J. Ahlers, R. Bias, B. Brocker, H. Hollander, H.P. Gelbke, H.J. Klimisch, I. Mangelsdorf. A. Paetz, N. Scong, G. Stropp, R. Vogel, C. Weber, K. Ziegler-Skylakakis and E. Bayer, *Chemosphere*, **28**, 2203–2236 (1994).
[5] B. Altenbach and W. Giger, *Anal. Chem.*, **67**, 2325–2329 (1995).
[6] J.G. Cabrera and C.J. Lynsdale, *L'industria Italiana del Cemento.*, **23**, 532–541 (1996).
[7] F. Faroug, J. Szwabowski and S. Wild, *J. Mater. Civ. Eng.*, **20**, 151–157 (1999).
[8] A.A. Jeknavorian, L. Jardine, D.C. Darwin and A. Kerkar, *Cem. Res. Prog.*, 119–147 (1994).
[9] P.C. Aitcin, *Mater. Sci. Concr.,* **32**, 477–511 (1998).
[10] V. Dodson, *Concrete Admixtures*. Van Nostrand Reinhold, New York (1990).
[11] V.S. Ramachandran, *Il Cemento*, **28**, 11–24 (1993).
[12] N.G. Lewis and W.Q. Yean, *J. Chromatogr.*, **331**, 419–424 (1985).
[13] J. Bensted, *Il Cemento*, **25**, 151–158 (1993).
[14] M. Piotte, F. Bossanyi, F. Perreault and A. Jolicoeur, *J. Chromatogr.*, **704**, 377–385 (1995).
[15] G. Ferrari, T. Cerulli, P. Clemente and M. Dragoni, *Am. Concr. Inst.*, **173**, 869–892 (1997).
[16] C. Crescenzi, A. Di Corcia, A. Marcomini, G. Pojana and R. Samperi, *J. Chromatogr. A*, **923**, 97–105 (2001).
[17] C. Wolf, T. Storm, F.T. Lange, T.J. Reemtsma, H. Brauch, S.H. Eberle and M. Jekel, *Anal. Chem.*, **72**, 5466–5473 (2000).
[18] E.R.E. Van de Hage, W.M.G.M. Van Loon and J.J. Boon, *J. Chromatogr.*, **634**, 263–271 (1993).

[19] Concrete admixtures and the environment. Industrieverband Bachemie Holzschutzmittel E.V., Farnkfurt/Main, Germany, 1996.

[20] Fachverband Schweizerischer Hersteller von Betonzusatzmitteln (FSHBZ): “Betonzusatzmitteln und Umwelt-Klare Fragen, klare Atworten”, 1997.

[21] G. Spanka and G. Thielen, *Beton*, **45**, 320–327 (1995).

[22] S. Dedier, Ph. D. Thesis. Swiss Federal Institute of Technology, Zurich (1997).

[23] R.J. Flatt, Y.F. Houst, P. Bowen, H. Hofmann, J. Widmer, U. Sulser, U. Maeder and T.A. Burge, *Am*., *Concr*. *Inst*., **173**, 743–762 (1997).

[24] H. Uchikawa, T. Sone and D. Sawaki, *World Cement Research and Development*, 70–76 (1997).

[25] F.T. Lange, C. Redin, H.J. Branch and S.H. Eberle, *Vom Wasser*, **90**, 121–134 (1998).