THE ANALYST
FULL PAPER
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Rapid determination of sulfonated naphthalenes and their formaldehyde condensates in aqueous environmental samples using synchronous excitation fluorimetry

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Received 9th May 2001, Accepted 31st July 2001
First published as an Advance Article on the web 2nd October 2001

Sulfonated naphthalenes and their formaldehyde condensates (SNFC) were determined in aqueous environmental samples by spectrofluorimetry. A clean-up step using n-hexane to extract possibly interfering nonpolar compounds such as naphthalene is the only preparatory procedure. Synchronous excitation mode with a $\Delta\lambda$ of 105 nm allows the determination of SNFC in environmental samples without additional clean-up or analyte enrichment. Interferences by humic acids and nitrate occurred only at concentrations higher than 1 mg C L^{-1} and 10 mg NO_3^- L^{-1}, respectively. The limit of detection was 0.2 μg L^{-1}, the average recovery was 104% and the confidence interval (95% certainty) was 24%. The response factor for the quantitative determination of total SNFC, depending on the distribution of the different SNFC components, was validated for groundwater from two field sites using an HPLC-FD (fluorescence detection) method as a reference method.

Introduction

Sulfonated naphthalenes and their condensates with formaldehyde (SNFC) are widely used in industrial processes.[1] Quantitatively, sulfonated naphthalene products are most extensively used as tanning agents and as plasticizers for concrete, each with a global use of 150 000 tonnes per year.[2] Concrete plasticizers are likely to become more important in the future, since modern concrete technology is based on an increasing use of synthetic organic admixtures.

Sulfonated naphthalenes are strong acids (pK_a values < 1) and exhibit low octanol–water partition coefficients (K_{ow} = −0.94).[3,4] Thus, they are very highly soluble in water. Most of the sulfonated naphthalenes, *e.g.* disulfonated naphthalenes, are only slowly biodegradable.[5,6] Due to these properties they are expected to be highly mobile and persistent in the aquatic environment. Although the toxicity of sulfonated naphthalenes is low (fish toxicity LC_{50} = 100–500 mg L^{-1}),[7,8] they may have some potential environmental impacts. Due to their amphiphilic character, sulfonated naphthalenes may act as remobilizing agents for nonpolar organic contaminants and in addition, unwanted disinfection by products could be formed during drinking water treatment.

The widespread and increasing use combined with the affinity to aquatic environments makes sulfonated naphthalenes a relevant pollutant of natural waters. Several authors reported on the occurrence of sulfonated naphthalenes in rivers and groundwater although their sources were unknown.[9–11] The reported concentrations are shown in Table 1. However, there is no data on the occurrence of formaldehyde condensates in the aquatic environment, even near construction sites, where relatively high concentrations of the condensates, originating from concrete superplasticizers, are expected to be found. This topic gets more important, since the Swiss authorities have issued a provisional SNFC limit of 1 mg L^{-1} for one construction site in a Swiss city where the groundwater serves as a resource for the water supply of the city.

Most presently available methods for the trace determination of sulfonated naphthalenes in aqueous samples focus on monomeric sulfonated naphthalenes. These methods are normally based on solid-phase extraction either with graphitized carbon black[11,12] or with a C18 reversed-phase material using an ion pair reagent,[9,13,14] followed by reversed-phase ion-pair liquid chromatography or capillary electrophoresis[15,16] with UV or fluorescence detection. Some more recent publications report on methods based on mass spectrometric detection.[17–19]

Wolf *et al*. published a method for the quantitative analysis for SNFC in aqueous environmental samples using an enrichment procedure with C18 material and reversed-phase ion-pair liquid chromatography with fluorescence detection.[20] A clean separation of the monomers and the oligomers was achieved. Another method, based on reversed-phase liquid chromatography and detection with mass spectrometry permits the identification and quantification of some monomers (naphthalene-2-sulfonate and naphthalene-1-sulfonate) and the less condensed oligomers (up to the heptamer).[29] Total SNFC in the aqueous phase of fresh cement water was also determined using UV spectrophotometry and spectrofluorimetry, but the selectivity and sensitivity of these methods are not sufficient for environmental samples.[21,22]

Fluorescence spectroscopy is a powerful technique for the determination of low concentrations of fluorescent compounds such as SNFC. Because of its high sensitivity and selectivity, no enrichment of SNFC in non-fluorescent matrices is needed. The selectivity is based on the fact that relatively few compounds show intrinsic fluorescence and that the emission intensity

Table 1 Environmental concentrations of sulfonated naphthalenes

	Concentration/μg L^{-1}		
Analyte[a]	River Rhine[9]	River Bormida[10]	Contaminated groundwater[28]
N15S	3200		2
N27S		3460	5.7
N16S			11.9
N2S		320	34

[a] For abbreviations see Table 3.

 DOI: 10.1039/b104090c

depends on two variables, namely the excitation and emission wavelengths. However, with conventional fluorescence spectroscopy the emission bands are very broad. Narrower bands can be obtained by scanning the excitation and emission wavelengths synchronously.[23] Thus, with the synchronous excitation mode, the selectivity can be increased to such an extent that aqueous environmental and biological samples can be analyzed without prior separation or enrichment.[24]

In this article, we present an analytical method based on fluorescence spectroscopy for the quantitative determination of the total amount of SNFC (monomeric sulfonated naphthalenes and condensates with formaldehyde) in aqueous samples. This technique was developed in order to obtain a readily usable method, which yields reliable quantitative results within a short analysis time. Furthermore, this method can easily be established in laboratories with limited funding, thereby offering an alternative to analytical methods which are becoming more and more sophisticated and expensive. The method was validated using environmental samples. Low detection limits, good accuracy and precision as well as simple handling and instrumentation make this a rapid and robust method ideally suited for routine analyses and hence monitoring of processes affecting the groundwater.

Experimental

Chemicals and materials

Naphthalene-1-/-2-sulfonate (N1S, N2S), naphthalene-1,5-/-1,6-/-2,6-/-2,7-disulfonate (N15S, N16S, N26S, N27S) and diphenylamine-4-sulfonate were obtained from Fluka AG (Buchs, Switzerland), Aldrich (Steinheim, Germany) and TCI (Tokyo, Japan). Naphthalene-1,7-disulfonate (N17S) and the condensed naphthalene-2-sulfonate dimer (8,8′-methylenebis-2-naphthalene sulfonate) were kindly donated by Carmen Wolf, TZW Karlsruhe, Germany. In this report the ″technical SNFC mixture″ refers to Galoryl LH 120 from CFPI Industries (Gennevilliers, France). Tetrabutylammonium bromide (TBABr, puriss.) and formaldehyde solution (37% w/w) were obtained from Fluka AG. Sodium nitrate was from Merck (Darmstadt, Germany) and humic acid (sodium salt) was from EGA-Chemie. n-Hexane (p.a.) was purchased from Merck. HPLC-grade water, acetonitrile (ACN) and methanol (MeOH) (both multisolvent®) were purchased from Scharlau Chemie S. A. (Barcelona, Spain). The C18-material for solid-phase extraction LiChrolute RP-18 (40–63 μm) was from Merck, the 6 mL solid-phase extraction tubes (polypropylene) and polyethylene frits were from Supelco SA (Bellefonte, PA, USA). Cellulose nitrate and regenerated cellulose membrane filters with 0.2 μm pore size were purchased from Sartorius GmbH (Göttingen, Germany).

Sample collection and treatment

Two Swiss construction sites were investigated. At field site A, a railroad tunnel of a total length of 9.4 km is being built. The first section of the tunnel is embedded in alluvial material consisting of gravel and sand deposition. Injections with a cement suspension were made over a length of about 400 m to stabilize the gravel around the tunnel. For these injections the cement was fluidized with SNFC, which was partially washed out, due to the groundwater level being above the tunnel. Samples were taken from several piezometers downstream of the construction site at a distance of 25 to 130 m. Field site B is a tunnel construction site for a national highway. A stagnant body of groundwater lies above one part of the tunnel. Cement was injected into the gravel above the tunnel over a length of 150 m in order to stabilize the soil prior to construction. The cement was fluidized with SNFC, some of which partially leached into the groundwater. The groundwater was sampled through three piezometers situated at a distance of about 10 m from the future tunnel.

Groundwater samples from construction site A were collected in amber glass bottles and stored at 4 °C. The samples from construction site B were also collected in amber glass bottles and stabilized on site by adding 1% (v/v) formaldehyde solution.

Synchronous excitation fluorimetry

Highly concentrated samples were diluted with doubly distilled water. 10 mL of sample were extracted in a separatory funnel with an aliquot of n-hexane (10 mL) to remove nonpolar substances, especially naphthalene. The fluorescence signal of the latter interferes with the signal of the sulfonated naphthalenes. The water fraction was then put into a cuvette and degassed for 5 min with nitrogen to remove oxygen, which could quench the signal. The samples were measured immediately with a Perkin Elmer Model LS-3 fluorescence spectrometer (Perkin Elmer, Rotkreuz, Switzerland) with spectral bandwidths of 10 nm. The cuvettes had a light path length of 10 mm and were from Huber & Co. AG, Rheinach, Switzerland. The spectra were acquired and integrated using a program designed on LabVIEW 4.0 for Macintosh from National Instruments, Ennetbaden, Switzerland.

The samples were measured in synchronous scan mode with a $\Delta\lambda$ of 105 nm. The excitation wavelength was scanned from 200–400 nm; the emission wavelength accordingly from 305–505 nm. The attenuation was 0.3 and the scan speed 120 nm min^{-1}.

A naphthalene-2,6-disulfonate solution (4.82 μg L^{-1}) was measured at the beginning and the end of a sample series to correct for intensity changes of the xenon lamp. The measured peak areas of the samples were divided by the average of the fluorescence intensity of the naphthalene-2,6-disulfonate solution before and after measuring the sample series.

For the estimation of the limit of detection a sample with an SNFC concentration below 1 μg L^{-1} was extracted and measured ten times. The limit of detection was calculated as three times the standard deviation of the ten replicates.

The recovery was calculated analyzing a spiked groundwater sample (technical SNFC mixture: 1.75 μg L^{-1}) by four replicate determinations.

The confidence interval was obtained by using the standard deviation of the measurement of a real groundwater sample from field site A (2.1 μg L^{-1}, eight replicates). The standard deviation was multiplied by the Student *t*-factor for 95% certainty.

For the experiments with humic acid, a stock solution of 1 mg mL^{-1} humic acid was prepared. Its DOC (dissolved organic carbon) concentration was 0.5 mg mL^{-1}. The DOC-specific absorption coefficient at a wavelength of 280 nm (a^*) was 4.8 L mg^{-1} m^{-1}.

For the experiments with nitrate a stock solution of 0.15 mg mL^{-1} nitrate was prepared.

HPLC-FD

Environmental samples were prepared and measured according to the procedure developed by Wolf *et al.*,[20] which is a reliable and robust method. A cartridge with 1 g of solid-phase material (LiChrolute) was conditioned with 5 mL of MeOH and 10 mL

of HPLC-grade water. Samples, with a total volume of 500 mL after the addition of 1 mmol L^{-1} TBABr and 2.5 μg L^{-1} of internal standard (diphenylamine-4-sulfonate), were percolated through the cartridge in about 1 h. The cartridges were dried with ambient air for 1 h under a vacuum and then eluted with 5 mL acetonitrile. The solvent was evaporated with nitrogen, then the dry residues were redissolved in 500 μL of a 4 mmol TBABr aqueous solution and 50 μL were injected onto the HPLC column. Liquid chromatography was performed using an HP 1090L Series II liquid chromatograph (HPLC) equipped with a diode array detector (HP 1090) and a programmable fluorescence detector (FD) (HP 1046) from Hewlett Packard AG (Switzerland). An octadecylsilica column (Hypersil ODS, 5 μm, 250 × 4 mm id) with a precolumn (5 × 4 mm id) was used (Macherey–Nagel AG, Switzerland). The aqueous mobile phase (A) was HPLC-grade water with 4 mM TBABr, which was filtered through a 0.2 μm cellulose nitrate filter. A 25 : 75 mixture of water and acetonitrile with 4 mM TBABr was used as organic modifier (B). Both mobile phases were degassed during 20–30 min by a stream of helium at the start of a measurement series. The following gradient elution was used: 0 min 30% B, 40 min 35% B, 80 min 80% B and 85 min 100% B isocratic to 95 min and back to the initial conditions at 100 min followed by 2 min of equilibration. The flow rate was 0.8 mL min^{-1}, column temperature was held at 40 °C, and the injection volume was 50 μL. The UV-absorption wavelength was 300 and 220 nm with a reference wavelength of 550 nm. The absorption wavelength of the internal standard was 300 nm and the FD excitation wavelength was 230 nm. The acquired emission wavelength was 360 nm, which is the preferable wavelength for the SNFC oligomers. The photomultiplier gain was 9. The cut off filter absorbed the emission wavelengths up to 335 nm. The substances were identified based on their absorption and emission wavelengths and their retention times in the FD chromatogram (see Table 2). The relatively high standard deviation of the retention times is due to the method having a very slow gradient. With the different matrices from the different field sites and with the increasing age of the chromatography column the retention times got an increasing standard deviation. To be sure about the identity of the analyte the samples were spiked with a standard mixture. The concentrations of the individual compounds were estimated by external calibration. The calibration of the dimer can also be used for the other oligomers due to the independence of the response factors (slope of the calibration curve) from the degree of polymerization.[20] The intensity of the FD lamp was monitored with an external FD standard (naphthalene-2,6 disulfonate). For validation of the method, recovery, precision, limit of detection and limit of quantification were determined and compared with the results published by Wolf *et al.*[20] Each environmental sample was enriched and analyzed twice.

Table 2 Retention times and their standard deviation (n = 8) of the SNFC compounds in enriched groundwater samples spiked with the technical SNFC mixture

Compound	Retention time/min
Naphthalene-1-sulfonate	32.87 ± 0.25
Naphthalene-2-sulfonate	35.87 ± 0.24
Naphthalene-2,6-disulfonate	36.85 ± 0.30
Naphthalene-1,5-disulfonate	38.33 ± 0.29
Naphthalene-2,7-disulfonate	40.46 ± 0.31
Naphthalene-1,6-disulfonate	42.27 ± 0.31
Naphthalene-1,7-disulfonate	51.85 ± 0.18
Condensate n = 2	63.16 ± 0.12
Condensate n = 3	68.31 ± 0.15
Condensate n = 4	71.15 ± 0.09
Condensate n = 5	73.27 ± 0.07
Condensate n = 6	74.89 ± 0.08
Condensate n = 7	76.19 ± 0.06

Results and discussion

Method validation

Acquisition with synchronous scan from 305 to 505 nm emission wavelength ($\Delta\lambda$ = 105 nm) gives a fluorescence signal for SNFC with a maximum emission intensity between 330 and 340 nm. Fig. 1 shows the advantages of the synchronous scan acquisition mode. The signal is much narrower than that of the conventional emission spectrum. The probability for interferences with matrix compounds is much smaller and interferences with Rayleigh scattering can be avoided.

One major advantage of this analytical procedure is that a clean-up with hexane is the only preparatory measure, thus reducing the number of steps in the analysis in which analytes may be lost compared to other methods. Recovery experiments yielded an average recovery of 104%. The confidence interval for 95% certainty is 24% in the concentration range of the environmental samples from field site A. The limit of detection is 0.2 μg L^{-1} which is more than three orders of magnitude below the provisional limit for groundwater issued by the Swiss authorities (1 mg L^{-1}).

Influence of matrix

The robustness of the method towards possible matrix components such as humic acids and nitrate was thoroughly investigated. Humic acids can potentially enhance the fluorescence signal of a sample, because they show some fluorescence. Using the synchronous scan method the fluorescence of humic acids does not interfere with the SNFC fluorescence.[25] However, humic acids show an inner filter effect. In order to quantify this effect, a SNFC standard solution (30 μg L^{-1} technical SNFC mixture in doubly distilled water) was measured at different concentrations of humic acids. The threshold concentration which had an impact on the fluorescence of SNFC was between 0.5 and 1 mg C L^{-1} (Fig. 2). Furthermore, the clean-up had no influence on the SNFC fluorescence, because humic acids are not well extracted by n-hexane. In this study, humic acids could be neglected because humic acid concentrations in Swiss groundwaters are generally below 1 mg L^{-1}. Furthermore, the DOC-specific absorption coefficient at wavelength 280 nm (a^*) of dissolved organic matter in Swiss natural waters is 1.5 to 5 times lower than the one of pure humic acid.[26]

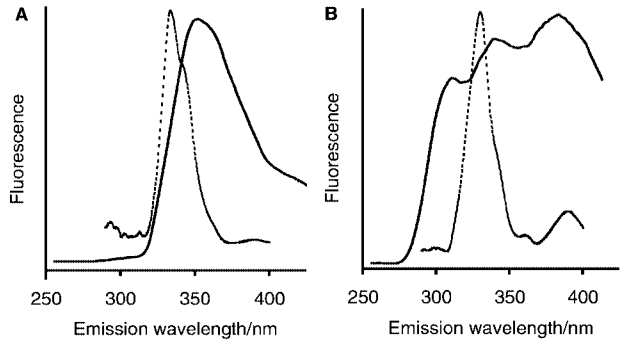

Fig. 1 (A): Emission (λ_{ex} = 230 nm) and synchronous scan spectrum ($\Delta\lambda$ = 105 nm, broken line) of total SNFC (technical mixture) in aqueous solution.($\Delta\lambda$ = 105 nm) (B) Environmental sample with SNFC contamination measured with conventional fluorimetry (λ_{ex} = 230 nm) and with synchronous scan mode ($\Delta\lambda$ = 105 nm, broken line). The signal of the conventional fluorimetry shows interferences by the matrix. With the synchronous scan signal no interferences occur. The difference between the synchronous scan signal of A and B is due to the different relative concentration of the SNFC components in the technical mixture and the environmental sample.

Nitrate also shows an inner filter effect for the wavelength range used for SNFC measurements. The average concentration of nitrate in the groundwater of the field sites was around 15 mg L^{-1}. In order to check the influence of nitrate, a SNFC standard solution (30 µg L^{-1} technical SNFC mixture in doubly distilled water) was spiked with different nitrate concentrations. Only a slight effect at concentrations below 10 mg L^{-1} could be observed (Fig. 2). However, at concentrations higher than 10 mg L^{-1} the fluorescence was increasingly filtered out.

When comparing the influence of humic acid and nitrate on the SNFC fluorescence, it can be observed that the slope of the decrease of the fluorescence intensity with humic acid is steeper. This is due to the broad absorption band of humic acids covering the whole spectral range which suppresses the SNFC fluorescence over the whole signal. The effect of nitrate is minor, because the significant absorption band of nitrate is much narrower with the maximum at 220 nm and interferes only with the first part of the SNFC signal.

No pH-effect on the fluorescence of SNFC could be observed. This can be explained by the very low pK_a of the sulfonic acid groups (< 1), which excludes protonation. Furthermore, the pH of environmental samples is usually around 7 or can be adjusted if needed.

Optimization of the quantitation

The crucial requirement for measuring the total SNFC content of a sample with fluorescence spectroscopy is that all SNFC components have the same fluorescence properties and thus can be summarized by one single fluorescence peak. With the developed synchronous excitation fluorimetry all monomeric SNFC compounds and the dimer, as the representative of all oligomers, showed a signal with a maximum fluorescence intensity between 330 and 340 nm. However, there were some differences in the response factors (*i.e.* slope of the calibration curves). Table 3 shows that N2S was the most fluorescent monomer and therefore has the highest response factor. The response factors of N2S and N15S, the least fluorescent monomer, differed by a factor of 2.8.

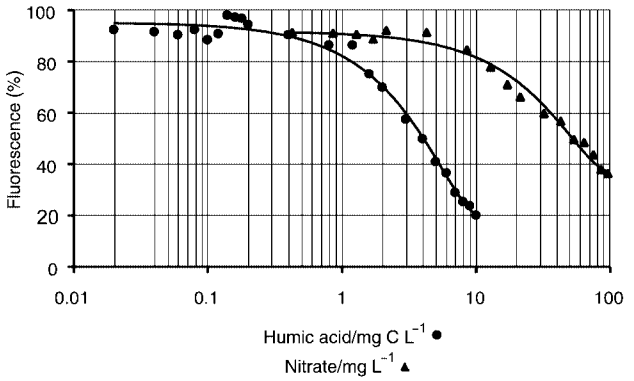

Fig. 2 Influence of humic acid concentration, expressed as organic carbon concentration (●), and nitrate concentration (▲) on the fluorescence of SNFC.

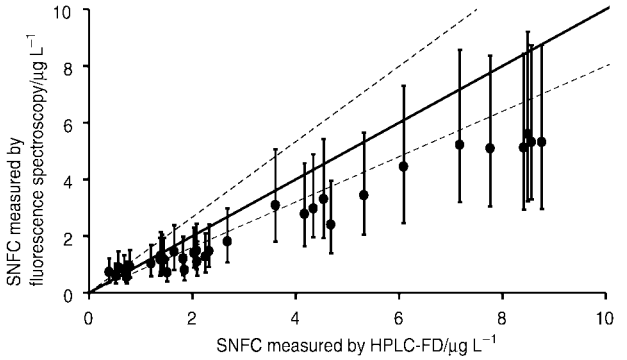

Fig. 3 Correlation of SNFC concentrations in groundwater samples from field site A measured by fluorescence spectroscopy and HPLC-FD. The quantification with an average response factor is not accurate (●). With an accurate quantification method the values should have a slope of 1 (black line). The vertical error bars represent the ranges calculated by the ″best-worst-case-scenario″. Considering the confidence interval (±26%) of the HPLC-FD method (---), the HPLC-FD results are within the range of the ″best-worst-case-scenario″.

The variable response factors of the different SNFC components hampered an accurate quantification, because the ratio of the various SNFC components in environmental samples varies. It was observed that the different physico-chemical properties and biodegradability have an influence on the behavior of the different SNFC components in the aquatic environment (see below), leading to different relative concentrations in comparison to the technical mixture. Thus, using an average response factor or the response factor of the technical mixture is not an optimal solution.

First, attempts to quantify total SNFC were made with a ″best-worst-case-scenario″. By assuming that either the whole fluorescence signal comes from the compound with the highest response (N2S) or from the compound with the lowest response (N15S) (see Table 3) it is inferred that the true value lies between the two extremes. In order to verify this assumption, 37 groundwater samples from piezometers of field site A with an unknown ratio of the SNFC components were analyzed by both the synchronous excitation fluorimetry method and the precise HPLC-FD method[20] (see Experimental). Fig. 3 shows the ranges of the ″best-worst-case-scenario″ compared with the values from the HPLC-FD measurements. In all cases the HPLC-FD values are within the range obtained from the ″best-worst-case-scenario″, when considering the confidence interval of the HPLC-FD method (±26%). The accuracy of the fluorescence spectroscopy measurements itself has to be considered as high due to the good correlation of the SNFC concentration range obtained by fluorescence spectroscopy and the exact SNFC concentrations obtained by HPLC-FD, which leads to the conclusion that matrix effects (see above) and cross-interferences were negligible. Thus, false negative or false positive results as known from screening tests are no problem with this method when not measuring below the quantification limit.

In order to obtain specific values instead of concentration ranges when using fluorescence spectroscopy, which would

Table 3 Calibration curves for the synchronous excitation fluorescence method obtained from linear regression. The response factor is defined as the slope of the calibration curve

Compound	Range/ µg L^{-1}	Response factor (area units)/ µg L^{-1}	Correlation coefficient
Naphthalene-1-sulfonate (N1S)	1.5–7.4	4.31	0.998
Naphthalene-2-sulfonate (N2S)	0.9–6.2	5.46	0.999
Naphthalene-1,5-disulfonate (N15S)	2.0–10.0	1.95	1.000
Naphthalene-1,6-disulfonate (N16S)	1.0–5.0	2.20	0.997
Naphthalene-1,7-disulfonate (N17S)	0.7–2.1	3.32	0.995
Naphthalene-2,6-disulfonate (N26S)	0.6–4.5	3.77	0.999
Naphthalene-2,7-disulfonate (N27S)	0.9–4.5	3.09	0.993
Technical SNFC mixture	1.1–5.8	3.09	0.996
Dimer	0.6–1.9	4.50	0.996
Field site A	1–35	2.14	0.989
Field site B	1–50	4.22	0.983

correlate well with the HPLC data, the processes causing changes in the composition of the SNFC compounds in groundwater must be evaluated. The HPLC-FD chromatogram (Fig. 4, Trace I) shows the distribution pattern of the monomeric sulfonated naphthalenes and their formaldehyde condensates in the technical mixture. For the monomers the same pattern was found in the samples from field site B, where the samples were taken close to the injection site (Trace II). However, the distribution pattern of the monomers in the samples of field site A (Trace III) differed from the one in the technical mixture, *i.e.* only the monomers N15S and N17S are found. The groundwater from field site A was sampled 30 to 100 m downstream of the construction site. The groundwater needs a migration time between 1 to 3 months for this distance. Biodegradation can take place during this period and sorption is possible as well. This results in a typical distribution composed of only the monomers N15S and N17S, which can be explained by their persistence.[6,27] Even after several months, they can still be found in the groundwater. The low response factor of N15S has a substantial impact on the overall response factor for the quantification of the samples from field site A. This is contrary to the groundwater from field site B, where the contribution of the N15S fluorescence to the overall response factor is only minor.

In the case of the condensates the analysis of field samples with the HPLC-FD method showed that the more highly condensed oligomers are not leached from the cement. In the samples from field site B, oligomers up to $n = 4$ were detected (not visible in Fig. 4 because of the scale), while in the samples of field site A mostly dimeric condensates were found at a distance of 30 to 100 m (during the first 3 months after the start of injections). The distribution of the condensates in the samples of the two field sites had no major effect on the measured fluorescence because all condensates have a similar response factor.

The above-mentioned observations from the field studies have to be considered while developing a method for the SNFC quantification in environmental samples. It was decided to fit two response factors based on the samples from the two field sites (see Fig. 5). Field site A gave a good fit with a response factor that can be expressed as 1.095 times the response factor of N15S. The optimum fit for field site B was obtained with 2.165 times the response factor of N15S. The curves have a correlation coefficient of 0.989 for A and 0.983 for B, respectively. With these fitted response factors good results were obtained during the whole sampling periods (12 and 6 months for field site A and B, respectively).

In order to apply the presented method to other field sites, the response factor needs to be estimated or determined by HPLC-FD. The estimation can be made based on the migration time in the aquifer, with field sites A and B representing the two extreme cases. With this additional information satisfactory results can be expected. Alternatively, a reliable confidence interval can be calculated using the ″best-worst-case-scenario″.

Conclusions

The presented method demonstrates that organic compounds can be determined in complex matrices without sophisticated equipment and time-consuming sample preparation steps. The described method can be implemented in laboratories with only limited resources. Furthermore, results are obtained in less than half an hour. The detection limit reaches far below the provisional limit for SNFC in groundwater, which has been issued by the Swiss authorities. Thus, this method can easily be used to obtain quantitative results in exploratory screening studies.

Acknowledgements

This work was supported in part by the ″Stiftung für den angewandten Betonbau″ of the Swiss cement industry. The authors thank the Swiss Federal Railways and the ″Baudepartement des Kantons Aargau″ for good collaboration, C. Wolf (TZW, Karlsruhe) for providing us with standards and all kinds of support, S. Canonica (EAWAG) for sharing his knowledge on fluorescence spectroscopy with us and Ph. Périsset (EAWAG) for helping to install the hardware for data acquisition. A. Alder, M. Berg, S. Canonica, P. Hartmann (all from EAWAG) and F. Jacobs (TFB, Wildegg) are greatly acknowledged for reviewing the manuscript.

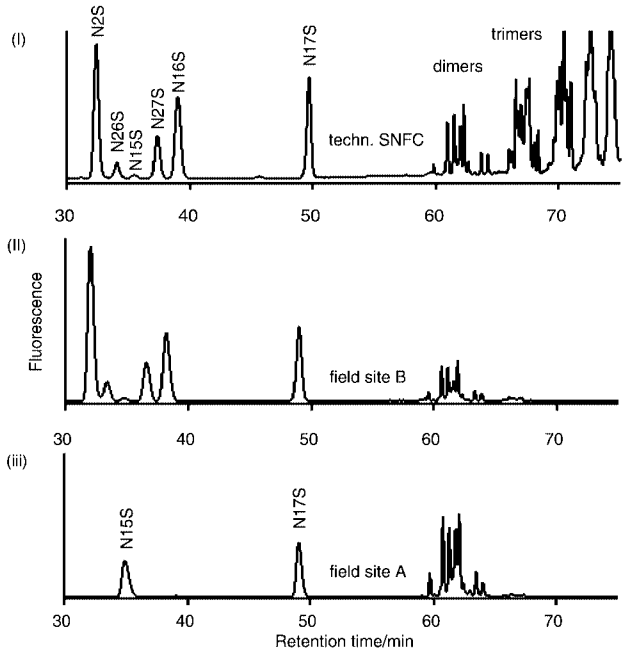

Fig. 4 Chromatograms reflecting the distribution of sulfonated naphthalene monomers and their formaldehyde condensates in different samples: (I) technical SNFC-mixture, (II) groundwater from field site B, (III) groundwater from field site A. The slight differences in the retention times of the monomers in the different samples are due to the very long run time. For abbreviations see Table 3.

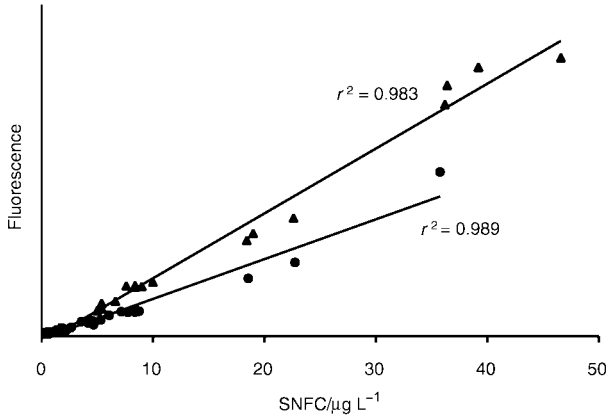

Fig. 5 The response factors for the field site A and B were obtained by plotting the fluorescence intensity from fluorescence spectroscopy as a function of the SNFC-concentration from the HPLC-FD measurements. The response factors for field site A (●) and B (▲) were calculated from the slope of the trendlines.

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