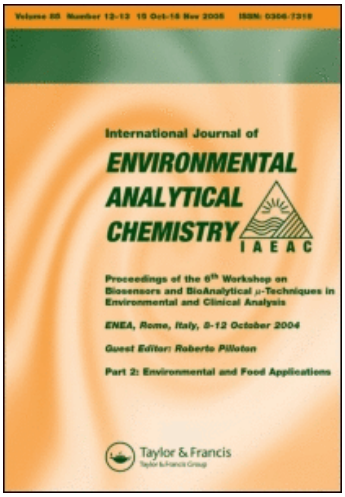

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Trace Naphthalenesulphonates Determination in Natural Water Samples

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TRACE NAPHTHALENESULPHONATES DETERMINATION IN NATURAL WATER SAMPLES

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The presence of sulphonated derivatives of naphthalene was investigated in river, tap and bottled water samples, by means of HPLC with fluorescence detection and GC-MS, after SPE pre-concentration and, in the case of GC-MS analysis, derivatization. These methods showed detection limits in the low ng/L range, and were capable of providing spectroscopic information on the unknown substances, which were of help for assessing the presence of target analytes in the examined samples. In particular, concentrations ranging from 8.9 to 220 ng/L of 2-naphthalenesulphonate were found in samples of the Italian rivers Po and Sangone, and concentrations of this same substance ranging from 6 to 21 ng/L of were found also in the tap water of the city of Torino, part of which is collected from the river Po. The presence of 2-naphthalenesulphonate at concentrations close to the detection limits of both analytical techniques was also suspected in some samples of bottled water.

Keywords: Naphthalenesulphonates; HPLC; GC-MS; natural waters

INTRODUCTION

Sulphonated derivatives of aromatic hydrocarbons are used in the chemical industry as intermediates in the synthesis of pharmaceuticals and dyes. Oligo- and polymeric condensates of naphthalenesulphonates with formaldehyde have found widespread use as plasticisers for concrete. Structure -activity relationship studies revealed no worrying toxicological profile for these substances, while their ecotoxicological properties showed non-uniform patterns. [1] Considering also that they derive from human activities, the environment is reasonably safer without them and their presence in natural waters should be controlled and limited as much as possible. Sulphonated aromatic hydrocarbons have been found in river, sea and underground water as a consequence of industrial activities or due

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to leaching processes occurring in landfills [2–19]. Due to their chemical stability and to their highly hydrophilic character, they can easily propagate through the aquatic environment [20]. Seeing the considerable quantities of sulphonated derivatives of naphthalene used in practice, the possible ubiquitous character of these substances seems worth to be investigated.

Several techniques are applicable for the analysis of aromatic sulphonates in natural waters [21], and most of them are based on HPLC, with either UV or fluorescence detection, although different techniques, including CZE [22], have been applied to the separation of complex mixtures of aromatic sulphonates. The best detection limits lied in the sub-microgram per litre range [19]. To investigate the potential ubiquity in the aquatic environment of naphthalenesulphonates, the need for very sensitive analytical techniques, capable also of unequivocal qualitative identification, was felt. In this study, the presence of mono- and disulphonated naphthalene derivatives at low nanogram per litre levels in river, tap and bottled water was investigated by both ion-pair HPLC with fluorescence detection and GC-MS, this last after converting the analytes into their trifluoroethyl esters. The information obtained from these two analytical techniques was combined in order to take advantage of the complementary peculiarity of each one of them, namely the linear quantitative response of HPLC and the reliable qualitative identification of mass spectrometry. Both techniques required preliminary concentration of water samples, in order to achieve detection limits at ppt levels, which were estimated adequate for this research, and GC-MS analysis required further derivatization for rendering volatile naphthalenesulphonates, which are in-volatile in nature.

EXPERIMENTAL

Reagents and materials

2,2,2-Trifluoroethanol, cetyltrimethylammonium bromide (CTA), Extract Clean RC-C 18, 500 mg cartridges for Solid Phase Extraction (SPE), phosphorus pentachloride and standard naphthalenesulphonates were obtained from Aldrich (Milano, Italy), HPLC grade acetonitrile and analytical grade methanol, ethyl ether, benzene and hexane were purchased from BDH Italia (Milano, Italy). The ultrapure water used for standard solutions and HPLC eluent was produced by means of an Elga-Stat (Elga, High Wycombe, UK) purification apparatus.

Samples

River water samples were collected by means of dark glass bottles, which were washed by dilute sodium hydroxide solution and then carefully rinsed with ultrapure water before sample collection. Cleanliness of bottles was tested prior to the collection of river water samples, by filling one of them with ultrapure water and then analysing its content after one day. The samples were stored at 4°C and pretreated within 24 hours, in order to avoid biodegradation phenomena.

Sample concentration procedure

Preconcentration was performed by eluting 250 mL water samples on silica C18 SPE cartridges, previously conditioned with 2 mL of 0.4% CTA solution [3]. The retained compounds were then recovered with 2 mL methanol, which was then evaporated to 0.5 mL by means of a gentle stream of nitrogen. The extracts were divided in two aliquots: one of them was injected for direct HPLC analysis, and the remaining one was evaporated to dryness before derivatization for GC-MS analysis.

Derivatization procedure

Derivatization of water extracts for GC-MS analysis was effected by converting sulphonic acids into their sulphonyl chlorides by means of phosphorus pentachloride, followed by esterification with trifluoroethanol [23]. 0.25 mL of the extract obtained by the SPE preconcentration procedure was evaporated to dryness and then heated at 100 °C for ten minutes with 100 mg of phosphorus pentachloride, then the mixture was extracted with diethyl ether. This last extract was evaporated to dryness and added with 1 mL of trifluoroethanol at room temperature; the resulting solution was extracted with two aliquots of 1 ml of hexane. This derivatization procedure was found effective on naphthalene- mono- and di- sulphonates, while their hydroxy-, nitro- and amino- derivatives were not detectable with this procedure.

GC-MS

The GC-MS system used in this study was composed by a Hewlett-Packard 5972 gas chromatograph, connected to a 5890 quadrupole mass analyser from the same firm. An HP-5, 30-m capillary column with 0.32 mm i.d. and 0.25 μm film thickness was used with helium carrier gas. The carrier flow rate was maintained constant at 0.6 ml/min.

1 μL of the hexane extract obtained from derivatization was injected in splitless mode by closing the split valve for one minute after the injection. The oven temperature program started from an initial temperature of 90 °C, then it was ramped at a rate of 15 °C/min up to 180 °C, then at a rate of 5 °C/min up to 250 °C. Injection port and transfer line were maintained at 280 °C. 2-chloronaphthalene and docosane were chosen as internal standards.

Electron impact (positive ions) with selected ion monitoring conditions were adopted for maximum sensitivity. The gaschromatogram was divided in time windows corresponding to the investigated compound, and three ions were monitored in each window, in order to achieve high detection sensitivity without sacrificing its selectivity. Ions at m/z 290, 127 and 115 were monitored for the trifluoroethyl esters of mono-naphthalenesulphonates, while 452, 289 and 127 ions were monitored for the esters of naphthalenedisulphonates.

HPLC

HPLC conditions were chosen in order to obtain maximum sensitivity for the target analytes, even sacrificing chromatographic resolution. Analyses were performed by means of a Supelcosil C8, 250 X 4.6 mm, 5 μm silica column, with 55/45 acetonitrile/water eluent, degassed by helium sparging and containing 1 g/L CTA, at room temperature. In order to minimise baseline noise, no buffer was added to the eluent, after observing that, while the elution order of naphthalenesulphonates is influenced by pH, the reproducibility of retention times is not [3]. Fluorimetric detection was effected by means of an Hitachi F4000 spectrophotofluorimeter, equipped with flow cell accessory. Excitation and emission wavelengths for fluorimetric detection were set at 230 and 339 nanometers, respectively. For the qualitative identification of unknown substances, their fluorescence emission and excitation spectra were recorded after stopping the flow during HPLC run. 200 μL of sample solutions were injected to increase sensitivity. This large volume, together with the relatively high organic solvent content of mobile phase, produced co-elution of 1- and 2-naphthalenesulphonate and incomplete separation of naphthalenedisulphonates. Larger resolution of HPLC peaks would have implied longer retention times, with the consequent decrease of peak height and of sensitivity. These limitations were accepted, since unequivocal identification of the analytes was made possible by means of GC-MS analysis and fluorescence spectroscopy, while these two techniques did not provide reliable quantitative information at nanogram per litre levels. The quantitative evaluation of the identified compounds was best performed with HPLC/fluorescence, since the GC-MS response was found to be non linear at the concentrations expected in the real world samples.

RESULTS AND DISCUSSION

Standard mixtures

After some preliminary analysis of river water samples, 1- and 2-naphthalenesulphonate, in addition to 1,5-, 2,6- and 2,7-naphthalenedisulphonate were chosen as target analytes. The HPLC and GC-MS chromatograms of standard mixtures of these analytes are shown in Figures 1 and 2, respectively.

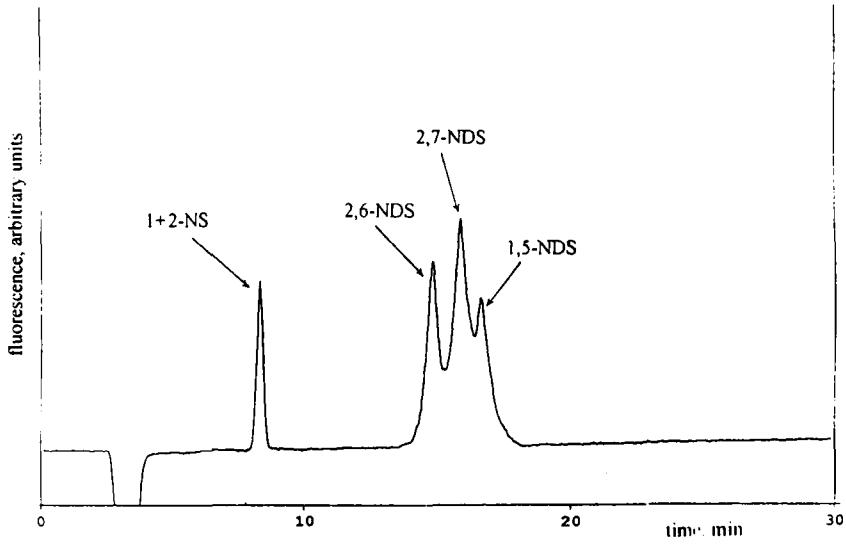

FIGURE 1 HPLC chromatogram of a standard mixture of naphthalenesulphonates. NS : naphthalenesulphonate ; NDS : naphthalenedisulphonate

Detection limits

Detection limits, in water samples, of 1 ng/L for 1- and 2-naphthalenesulphonate, 2,6- and 2,7-naphthalenedisulphonates, and of 4 ng/L for 1,5-naphthalenedisulphonate (S/N=3), were obtained by means of HPLC after preconcentration treatment ; linear response was observed for these substances over three orders of magnitude. Minimum detectable concentrations in the water solution, with GC-MS analysis coupled to preconcentration treatment, of 2 ng/L (S/N=3) for 1- and 2-naphthalenesulphonate, while the minimum detectable quantities ranged from 160 and 500 ng/L for naphthalenedisulphonates. The response of the MS

detector was not linear in the ng/L concentration range, therefore this technique was used for confirming the HPLC identification, but not for quantitative purposes.

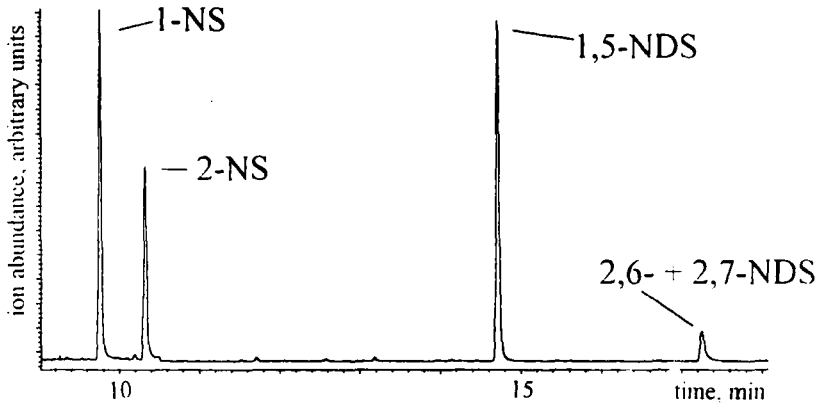

FIGURE 2 GC-MS chromatogram of a standard mixture of the trifluoroethyl esters of naphthalenesulphonates in SIM mode (conditions reported in the GC-MS analysis section). NS : naphthalenesulphonate ; NDS : naphthalenedisulphonate

The analyses of ultrapure and bottled (Perrier) water samples, gave no response either with HPLC or GC-MS analyses. This fact was considered a positive indication of the cleanliness of laboratory glassware and purity of reagents.

Extraction yields

The recoveries of the pre-concentration procedure for 1- and 2-naphthalenesulphonate, as a function of the volume of water treated, were tested by spiking with 50 ng/L concentrations of the analytes, samples of bottled water free from naphthalenesulphonates. An 82 % ($\sigma = 7$ %, $n = 6$) recovery factor was found for sample volumes smaller than 250 mL, while progressively lower extraction yields were observed with larger volumes, as a consequence of the breakthrough of the analytes. For this reason, volumes of 250 mL of real world water samples were pre-treated.

Analysis of real world samples

Water samples of the Italian river Po were analysed. As an example, the HPLC chromatogram obtained for a sample collected in the portion of the river flowing

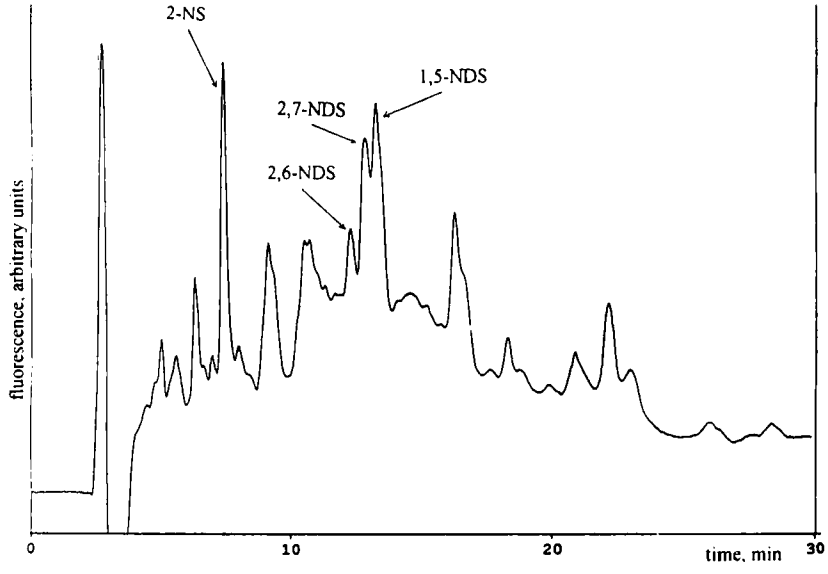

FIGURE 3 HPLC chromatogram of a Po river water sample collected in the urban portion of its stream

through the city of Torino is reported in Figure 3. Some of the peaks had retention times coinciding with those of the target analytes. The fluorescence spectra of the suspected 2-naphthalenesulphonate are reported in Figure 4. As it can be seen, there is a substantial coincidence of the unknown spectra with those of 2-naphthalenesulphonate standard. Also the derivatives of these spectra, which were found very sensitive to the position of the substituents, are reported in Figure 5 for confirmation of the identity of unknown peak. In the GC-MS chromatogram of the extract of the same sample, only the peak of 2-naphthalenesulphonate was observed, but it is to be pointed out that the sensitivity of this technique was from 80 to 250 times lower than that of HPLC, for naphthalene disulphonates, and this fact could explain the absence of naphthalene disulphonates signals from the GC-MS chromatogram. Concentration of 2-naphthalenesulphonate in the urban portion of the river Po water ranged from 17.2 to 220 ng/L in the period from October 9 to November 11, 1997, measured on 15 samples. Peaks probably due to naphthalene disulphonates were observed in HPLC analyses, but not confirmed, by the subsequent GC-MS analysis, in 10 of these samples.

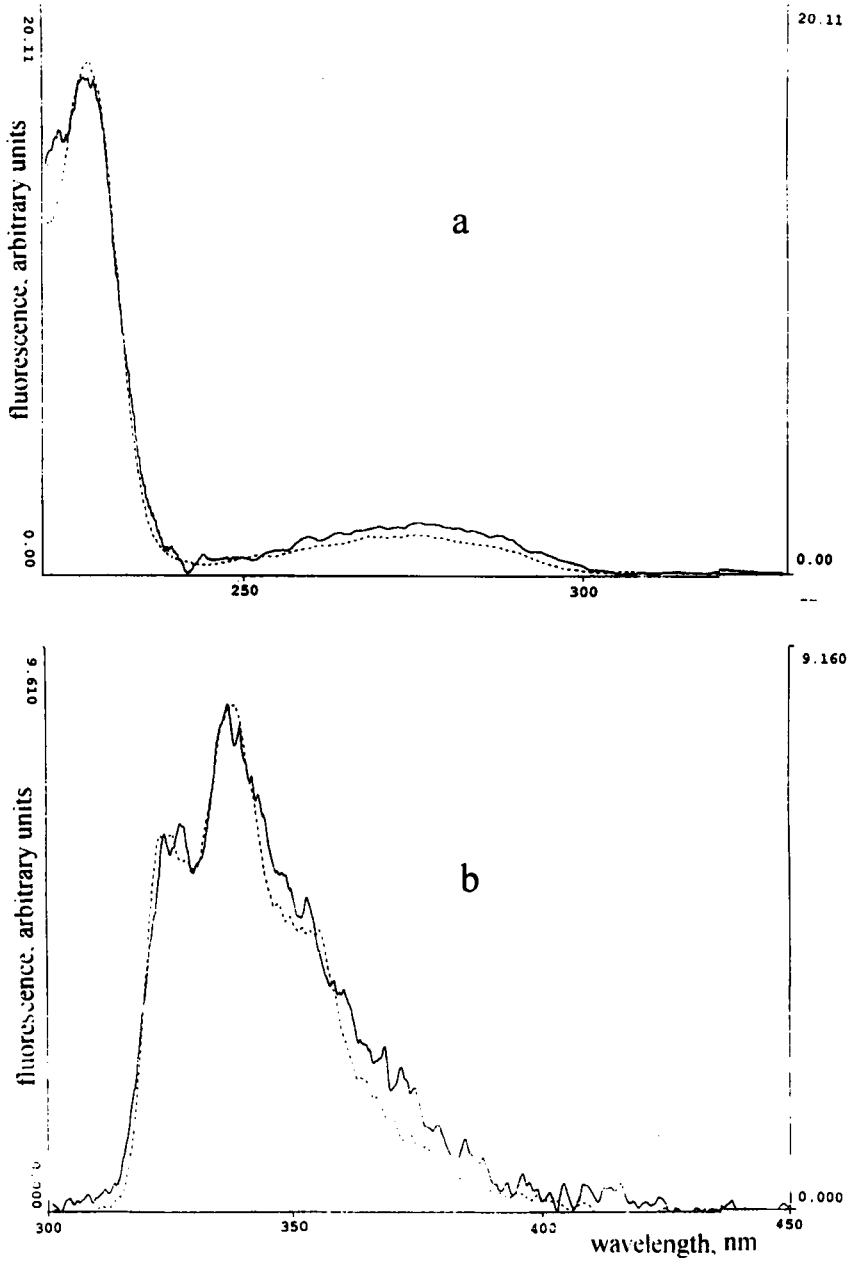

FIGURE 4 Fluorescence excitation (a) and emission (b) spectra of standard 2-NS (dashed line) and suspected 2-NS peak of the chromatogram of Figure 3

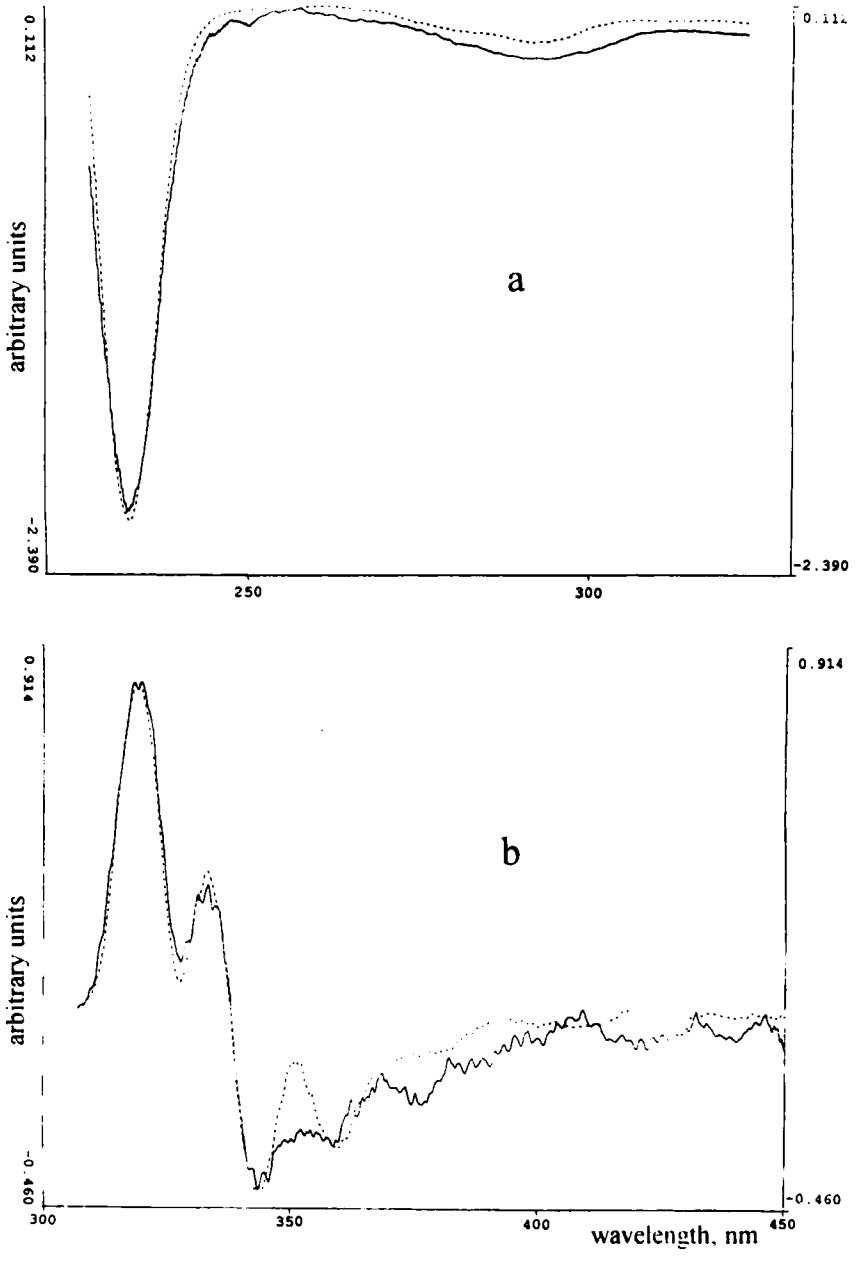

FIGURE 5 First-order derivatives of the spectra reported in Figure 4

The water of four more rivers, Sangone, Dora Riparia, Stura di Lanzo and Varaita, which are tributary of Po river, were analysed. Concentrations ranging from 8.9 to 50 ng/L of 2-naphthalenesulphonate were measured in four samples of the Sangone river, together with the suspected presence of disulphonates, while the water samples of the remaining did not show any measurable content of naphthalenesulphonates.

Analysis of tap and bottled water samples

Samples of the tap water of the following Italian cities : Torino, Bardonecchia, Milano and Tortona, were collected and analysed. Naphthalenesulphonates were found only in the tap water of the city of Turin, which is partly collected from the river Po. Concentrations ranging from 6 to 21 ng/L of 2-naphthalenesulphonate were found in the 12 samples analysed.

Samples often different bottled water were analysed. Seven of them were suspected to contain very small concentrations of 2-naphthalenesulphonate, at concentrations ranging from 1 to 2.8 ng/L. Due to the very low intensity of the fluorescence signal, the S/N ratio was unfavourable for the identification by means of fluorescence spectra. On the other hand, also GC-MS analysis was incapable of detecting such small concentrations, and thus of giving any confirmation. The HPLC chromatogram obtained from a mineral water sample where 2-naphthalenesulphonate is possibly present at an estimated concentration of 2.2 ng/L is reported in Figure 6.

CONCLUSIONS

The presence of sulphonated derivatives of naphthalene was investigated in water samples of river, tap and bottled water, by means of two independent, very sensitive and very selective techniques, namely HPLC with fluorescence detection and GC-MS, after SPE preconcentration and, in the case of GC-MS analysis, derivatization. These methods showed detection limits in the low ng/L range, and were capable of providing spectroscopic information on the unknown substances, which were of help for assessing the presence of target analytes in the examined samples. On the other hand, these analytical procedures satisfied only in part the requirements for screening procedures, since their selectivity and the relatively low sensitivity of GC-MS with respect to naphthalene disulphonates limited their use to the screening of naphthalene monosulphonates.

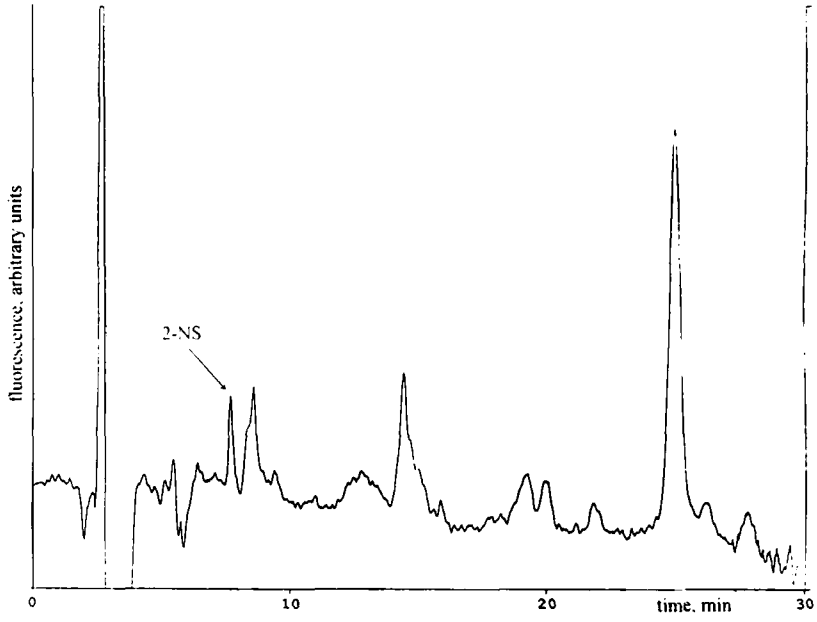

FIGURE 6 HPLC chromatogram of mineral water (Rocchetta)

In particular, 2-naphthalenesulphonate was found at ng/L concentrations in samples of the Italian rivers Po and Sangone and in the tap water of the city of Torino, part of which is collected from the river Po. Analyses performed on samples of tap water coming from different cities showed no presence of naphthalenesulphonates. The presence of 2-naphthalenesulphonate at concentrations close to the detection limits of both analytical techniques was suspected in some samples of bottled water, while some other did not show any detectable amount. These data indicate that naphthalene monosulphonates can be present in various water matrixes, although their ubiquitous character seems rather unlikely on the basis of the results of this study. Further investigation on their diffusion in the aqueous environment should be done in order to ascertain their origin or provenance.

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