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# Determination of Hydrophilic and Amphiphilic Organic Pollutants in the Aquatic Environment

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*Abstract.* Environmental chemists performing monitoring or process-oriented fate and behavior studies on organic micropollutants face the challenge of having to determine low concentrations of problem compounds in complex mixtures and difficult matrices, such as sewage sludge, surface and groundwater. Selective extraction and enrichment help to overcome sensitivity limitations and also to reduce the number of different species in the sample. A subsequent chromatographic separation step, together with analyte-specific detection, finally allows to identify and quantify single analytes in the presence of other organic material. This article describes a selection of analytical development work carried out at EAWAG for the determination of hydrophilic and amphiphilic organic pollutants in the aquatic environment.

## Introduction

Many organic compounds are discharged into the aquatic environment as a consequence of human activities. In order to understand their potential impact on ecosystems, their fate and behavior, as well as their effect on the biota need to be assessed. Experience shows that just monitoring the disappearance of pollutants can lead to misinterpretation of their environmental effect. For instance, alkylphenolpolyethoxylates were used in high quantities as nonionic surfactants in household detergents. On closer inspection it was found that the parent compound was indeed degraded in bioreactors of wastewater treatment plants, but that a highly toxic and persistent transformation product, nonylphenol, was generated [1][2]. In addition to its toxic effect, nonylphenol was recently found to act as an endocrine disruptor [3][4]. Ecotoxicologists are evaluating effects, using a wide variety of test systems, in order to be able to assess the impact of anthropogenic chemicals on ecosystems (see *Escher et al.* [5]). This dual approach of fate and behavior studies and testing for effects allows environmental scientists to predict the potential impact of micropollutants on the ecosystem and intervene at the sources.

Environmental chemicals can be categorized according to a polarity/volatility diagram (*Fig. 1*). Many researchers have focused their studies on relatively volatile and nonpolar pollutants taking advantage of gas chromatography and its sensitive and selective detectors (FID, ECD, NPD, mass spectrometry, see *Table 1*).

Particularly for the aquatic environment, the more polar and hydrophilic substances are highly relevant. In addition, metabolites of biotransformations are usually polar compounds. Therefore, research groups at EAWAG are emphasizing substances well soluble in water such as amphiphilic surfactants, organic complexing agents (NTA, EDTA), phenols, aromatic sulfonates, and others (for an overview see also [6]). *Fig. 1* highlights a selection of polar and amphiphilic analytes which are in focus at EAWAG. Several analytical techniques are employed for the determination of polar and amphiphilic pollutants, as can be seen in *Table 1*. All these activities are under a rigorous scheme of analytical quality assurance and control which is paramount for the determination of trace pollutants. It is crucial to recognize that good quality assurance is also needed in research projects and must not be limited to contract work in analytical chemistry.

The remainder of this article describes a selection of analytical development work carried out at EAWAG for specific case studies. The three cornerstones of organic

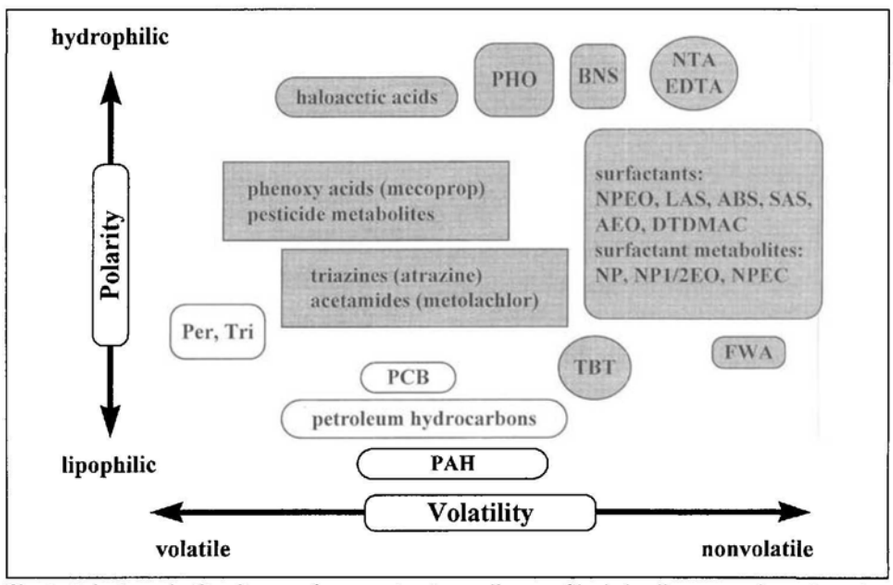


Fig. 1. *Polarity-volatility diagram for organic micropollutants.* Shaded pollutants are investigated at EAWAG. Nonylphenol (NP), nonylphenolpolyethoxylates (NPEO), nonylphenolpolyethoxycarboxylates (NPEC), linear alcohol polyethoxylates (AEO), linear alkylbenzenesulfonates (LAS), secondary alkanesulfonates (SAS), ditallowdimethylammonium chloride (DTDMAC), fluorescent whitening agents (FWA), nitrilotriacetate (NTA), ethylenediaminetetraacetate (EDTA), phosphonates (PHO), benzene- and naphthalenesulfonates (BNS), tributyltin (TBT), perchloroethylene (Per), trichloroethylene (Tri), polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH).

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environmental analysis, extraction/enrichment, separation, and detection will be covered by these examples.

## Enrichment: Effects of the Sample Matrix in Supercritical Fluid Extraction

Analytical scale supercritical fluid extraction (SFE) is an attractive alternative to conventional liquid extraction for the enrichment of organic pollutants from a wide variety of solid samples. For the extraction of polar and ionic organic compounds by SFE, addition of organic modifiers to the supercritical carbon dioxide is often required [7].

Quaternary ammonium surfactants show a high affinity for negatively charged surfaces, making these cationic surfactants suitable for industrial applications and as components of consumer products. Ditallowdimethylammonium chloride (DTDMAC), typically containing homologs with alkyl chain lengths of $C_{16}$ and $C_{18}$, have a rather low water solubility and are highly lipophilic (log $K_{ow}$ = 2.69). DTDMAC is enriched in anaerobically digested sewage sludges and anoxic sediments because of its physicochemical properties and its nonbiodegradability in anoxic environments.

DTDMAC was quantitatively extracted from anaerobic digested sludge using 380 atm of supercritical $CO_2$ modified with 30% methanol at 100° [8]. To validate the quantitative SFE conditions, the results were compared to those obtained with a conventional liquid extraction method. Determination of the extracted DTDMAC was performed by normal-phase HPLC with postcolumn ion-pair formation and extraction.

Because of the heterogeneous nature of environmental samples, the analyte-matrix interactions are quite complex. For example, chemicals in a sediment sample may be associated with a variety of inorganic and/or organic active sites, each with different binding strengths. The influence of the sample matrix will be discussed below when describing the extraction of DTDMAC from digested sludges, marine and freshwater sediments.

Taking into account the cationic character of DTDMAC, *p*-toluenesulfonate (*p*TS) was added as a counterion to enhance extraction of native DTDMAC into supercritical $CO_2$ by formation of hydrophobic ion-pair complexes. However, in digested sludges, *p*TS did not show any improvement in extraction efficiency over methanol and, therefore, was not used for extracting DTDMAC from this matrix. High concentrations of anionic surfactants such as linear alkylbenzenesulfonates in digested sewage sludges are assumed to be sufficient to solubilize cationic surfactants in the supercritical $CO_2$ by the formation of ion-pairs. The modifier may act primarily by facilitating the removal of the analyte from the matrix active sites and prevent re-adsorption to the matrix.

In contrast to digested sludge, ion-pair reagents played an important role for the extraction yield with sediments. The influence of the sample matrix was studied by applying SFE to highly polluted surface marine sediments from the urban sewage outfall of Barcelona, Spain. While virtually no native DTDMAC was extracted with pure $CO_2$, addition of modifiers increased the extraction yield of native DTDMAC significantly (*Fig. 2, A*). However, a high percentage of methanol (30%) alone yielded identical extraction efficiencies to those obtained with the ion-pair reagent.

The adsorption of quaternary ammonium compounds to clay material is probably mainly caused by an ion-exchange mechanism, although, because of the high organic carbon (8.4%) of this sediment, a hydrophobic partitioning caused by the aliphatic chain may also play a significant role. In the case of electrostatic interactions, addition of ion-pair reagents may enhance extraction of native DTDMAC into supercritical modified $CO_2$, overcoming the strong electrostatic interactions between DTDMAC and the matrix.

While SFE and a conventional liquid extraction method gave equal DTDMAC concentrations in sludges, the extraction of marine sediments yielded 30% higher DTDMAC values for SFE compared to those obtained by liquid extraction. As sediments are much older than sewage sludges, longer equilibration times would have allowed DTDMAC to migrate to remote and/or stronger binding sites and thus become more resistant to extraction. In contrast, in the liquid extraction method the solvent may not have access to the more remote sites because liquids have lower diffusivities compared to supercritical fluids.

The procedure for the determination of DTDMAC in sediments from lakes and rivers had to be modified further because of high RSDs (= relative standard deviations) (> 50%) when extracting with $CO_2$/30% methanol. The final SFE method involved initial addition of *p*TS and NaCl in methanol/water (3:1) directly onto the sample which was allowed to swell overnight. *Fig. 2, B* shows the effects of ion-pair reagent, swelling time, and electrolyte addition on the extraction yields of DTDMAC from a homogenized sediment from Lake Wohlen, Switzerland. Addition of high concentrations of sodium ions resulted in swelling of the layered clay

Table 1. *Analytical Methods Used for the Determination of Polar and Amphiphilic Pollutants*

| | | | | |
|---|---|---|---|---|
| *Enrichment* | *solid samples*<br>sludge, sediment, soil | | *Soxhlet* extraction<br>supercritical fluid extraction (SFE)<br>accelerated solvent extraction (ASE)<br>microwave-assisted extraction ultrasonication | |
| | *aqueous samples*<br>raw and treated wastewater, natural waters (rivers, lakes, groundwaters), drinking water | | liquid-liquid extraction<br>sublating<br>evaporation<br>ion exchange<br>solid-phase extraction (SPE) with $C_{18}$-silica and graphitized carbon black | |
| *Fractionation*<br>*Cleanup* | liquid chromatography<br>derivatization | | | |
| *Separation* | high-performance liquid chromatography (HPLC)<br>capillary electrophoresis (CE) | | gas chromatography (GC) | |
| *Detection* | UV absorption,<br>– variable wavelength<br>– diode array detection (DAD)<br>UV fluorescence | | flame ionization detector (FID)<br>electron capture detector (ECD)<br>nitrogen phosphorous detector (NPD) | |
| | mass spectrometry (MS)<br>tandem mass spectrometry (MS/MS) | | | |
| | electrospray (ESI)<br>atmospheric pressure chemical ionization (APcI)<br>continuous-flow fast atom bombardment (CF-FAB)<br>particle beam (PB)<br>thermospray (TSP) | | electron ionization (EI)<br>chemical ionization (CI) | |

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structure and together with the addition of an ion-pair reagent increased the extraction yield significantly. In interlayer swelling, the supercritical fluid penetrates the interior of the solid and thus increases the exposure of the matrix to the fluid. Depending on the composition of the clay, more or less swelling will occur.

Extraction conditions that successfully extract an analyte from one sample type may not yield quantitative recovery from a different matrix. Therefore, careful validation of the method is essential when extracting different matrices.

## Direct Coupling of Enrichment, Derivatization, and Separation

The aqueous phase is important when studying the fate and behavior of anthropogenic compounds in the aquatic environment. Trace analysis of organic compounds in aqueous samples normally requires pre-concentration and/or extraction of the analytes to make them accessible for analytical determination. Among the chromatographic techniques, gas chromatography (GC) is the method of choice with regard to separation efficiency and sensitivity. Yet aqueous samples can not generally be applied directly to GC capillary columns. The analytes have first to be transferred into an organic solvent. Further, many hydrophilic compounds of environmental interest have to be derivatized to become volatile enough for GC analysis. Often the pre-concentration and derivatization steps are tedious and costly work [9]. Obviously automated sample pretreatment combined with automated analysis in one setup is desirable. Enrichment procedures coupled on-line to analytical instruments not only reduce manpower but also result in better reproducibility [10]. Furthermore, the sample volume required for on-line techniques is reduced by the fact, that the total amount of the enriched analytes is transferred to the analytical instrument, whereas only a small fraction of the extract gained from off-line enrichment can be injected into chromatographic apparatus. Within an increasing number of on-line sample pretreatment procedures, solid-phase enrichment (SPE) coupled to HPLC is nowadays quite popular while SPE-GC applications found in the literature are rather scarce [11]. The following analytical method for the quantification of organotin compounds in natural waters demonstrates direct coupling of enrichment, derivatization, and analysis of the aqueous samples using SPE-GC [12].

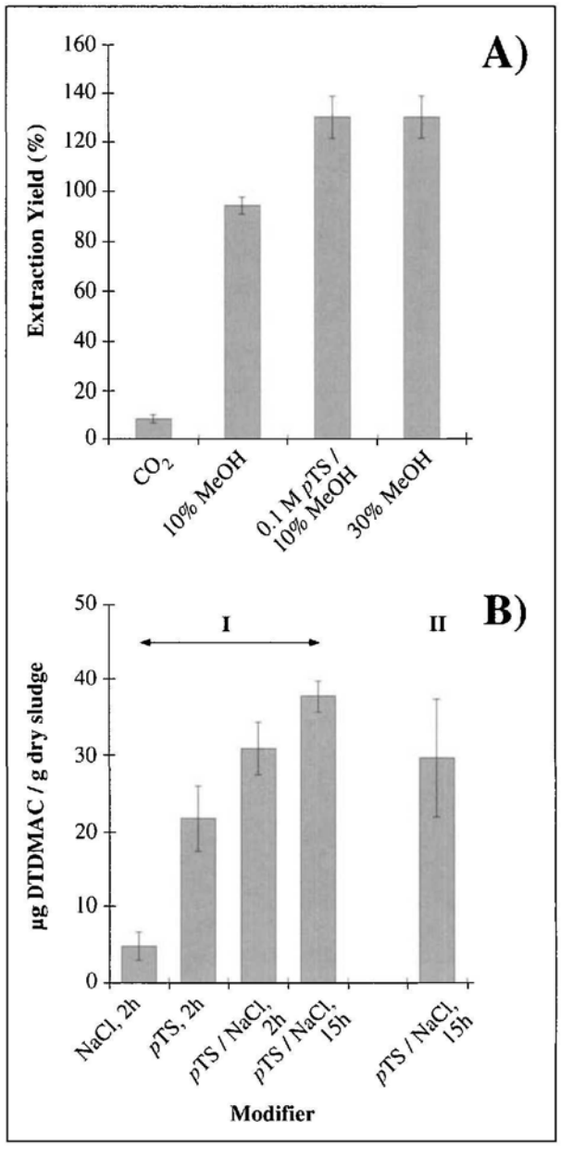


Fig. 2. *Effect of ion-pair reagent and modifier on the extraction yield of DTDMAC. A)* Surficial marine sediment samples. Extraction yields are given relative to the values obtained by liquid extraction. SFE conditions: 100° and 380 atm. *B)* Sediments from Lake Wohlen, Switzerland. Concentrations in µg/g (RSD, $n = 4$). The static extraction was performed at 170 atm (I) instead of 380 atm (II) in order to reduce compaction of the swelled clay sediment during mixing of the ion-pair reagent with the sediment at 100°.

Butyltin and phenyltin compounds are the most widely used organometallic compounds worldwide. Used as, *e.g.* antifoulings, wood preservatives, PVC stabilizers, or agrochemicals, they are of great environmental concern due to their high toxicity and persistence. Tributyltin (TBT), the most toxic substance ever deliberately introduced into natural waters [13], has been used since the 1960s as antifouling agent in underwater paints for boats and aquaculture nets (see also *Escher et al.* [5]). At concentrations as low as 20 ng/l, TBT can inhibit Pacific oyster reproduction and populations of some mollusks decrease dramatically [14] as soon as levels reach 2 ng/l. Further due to their high sorption potential to organic material ($K_{ow} = 10^3$–$10^4$) [15], these compounds accumulate in sediments, sewage sludge, and aquatic organisms. As the toxicity and the environmental fate of organotin compounds is strongly dependent on the number and nature of the substituents, analysis of the parent species as well as of their degradation products is essential.

To study the fate and behavior of mono-, di-, and tributyltin as well as of mono-, di-, and triphenyltin at trace levels in natural waters, a fully automated analytical method for aqueous samples was developed using a liquid chromatography system for solid-phase enrichment (SPE) and derivatization, which was directly coupled to a gas chromatography/mass detector system (GC/MS). All the operations involved were first characterized and validated in off-line mode. *Fig. 3* shows the instrumental setup of the SPE-GC system. Water samples of only 1 ml were pumped through a cartridge packed with graphitized carbon black (GCB) for SPE. The sorbed analytes were then derivatized (ethylated) on-cartridge with an aqueous solution containing $NaBEt_4$. The SPE cartridge was washed with water and methanol. The GCB material was thereafter dry enough for the elution of the derivatized

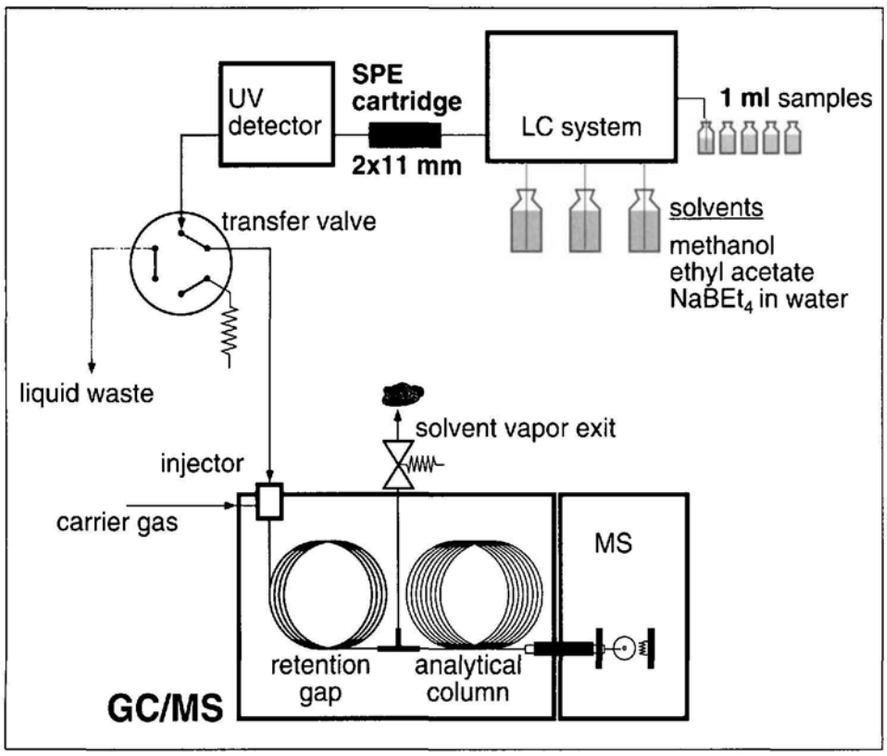


Fig. 3. *Instrumental setup for on-line SPE-GC/MS of organotin compounds.* The LC system is used for on-line enrichment and on-cartridge derivatization. The UV detector, monitoring the liquid line at 244 nm close to the exit of the SPE cartridge, synchronizes the switching of the transfer valve to the GC at the beginning of the elution of ethyl-acetate extract. The solvent vapor of the transferred extract is displaced through the solvent vapor exit valve before GC analysis. Identification and quantification is done using mass-spectrometric detection.

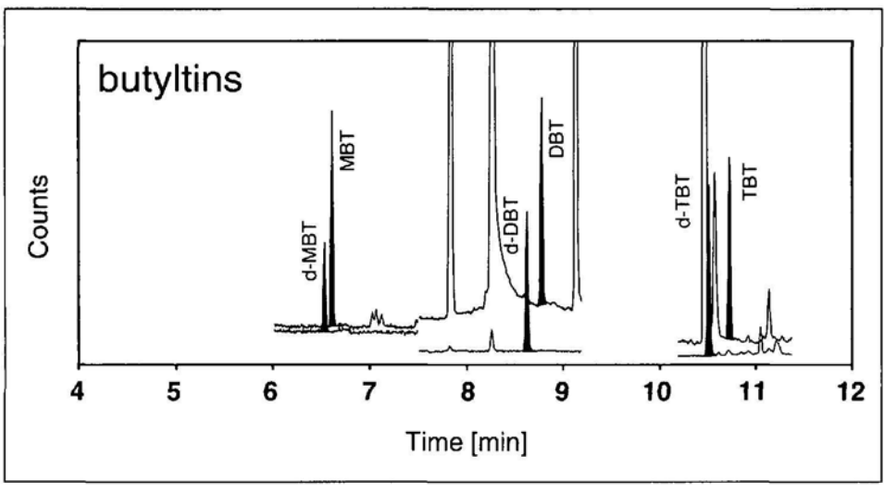


Fig. 4. *Gas chromatogram of ethylated butyltin compounds in a sediment pore-water extract.* Mass-spectrometry detection with single-ion recording of monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), and of their individual deuterated internal standards (d-MBT, d-DBT, d-TBT).

Table 2. *Comparison of the On-Line SPE-GC Method with the Off-Line Procedure.* Average values of the butyl- and phenyltin compounds analyzed are given for surface water ($n = 10$) spiked at levels of 50 ng/l each analyte.

| | off-line procedure | on-line SPE-GC |
|---|---|---|
| relative recovery (%) | 95–104 | 96–102 |
| method detection limit (ng/l) | 3–10 | 0.6–2 |
| relative standard deviation (%) | 2–7 | 2–3 |

organotin compounds with ethyl acetate. The 200-µl extract was directly transferred to an on-line coupled capillary GC (SPE-GC) using a retention gap and partially concurrent evaporation technique. For these techniques, also called large-volume injection, the solvent is introduced into an uncoated GC pre-column (10 m × 0.52 mm) below its boiling point, where a solvent film is formed. The evaporating solvent is then transported by the carrier gas through the solvent vapor exit [16]. After evaporation of 180 µl of ethyl acetate, the solvent vapor exit was closed and separation of the compounds was carried out on an analytical capillary column (25 m × 0.25 mm). For large-volume injections into a GC removal of excess solvent vapor is essential because large amounts of solvent vapor are not transported fast enough through the GC capillary column. This leads to high baseline levels, unreproducible separation, and malfunction of the detector. Identification and quantification was achieved with electron-impact mass-spectrometry detection in the selective ion recording mode.

To reach high accuracy, fully deuterated compounds of each analogous organotin compound were synthesized in our laboratory and used as individual internal standards. The efficiency of the GC separation can be seen in *Fig. 4*. The butyltin compounds not only showed sharp, symmetrical peaks, but also the deuterated compounds were well separated from the analytes. This on-line coupled SPE-GC techniques using just 1 ml of aqueous sample showed method detection limits of < 5 ng/l (RSD < 5%), and relative recoveries determined in, *e.g.*, lake water and seawater were 96–102%. It was compared with the off-line procedure and the two methods were in good agreement (*Table 2*).

This hyphenated application clearly demonstrates the technical feasibility of sample pretreatment coupled directly to the analytical instrument. Yet on-line SPE-GC is not easy to be set up and maintained. However, for several purposes such as, *e.g.* high sample throughput or small sample volumes, the extended evaluation period is well paid off.

## Determination of Hydrophilic, Non-Aromatic Compounds

Phosphonates are constituents of laundry detergents and industrial cleaners and are used in large amounts for textile and solid-surface cleaning. They have the ability to complex metal ions and prevent

precipitation of insoluble salts. In laundry detergents, they support as so-called builders the washing activity of detergents by preventing precipitation on the laundry through their functioning as threshold agents. In the late 80s, their production has increased to 11000 t per year in Europe and about 10000 t in the USA [17].

Several studies on the biodegradability of organic phosphonates indicate that they are generally persistent [18]. Little is known about the occurrence and fate of phosphonates in the environment because of the lack of sensitive, specific analytical methods for their determination to perform monitoring studies. Recently, an HPLC method has been published on the determination of phosphonates with UV detection at 260 nm after complexation with $Fe^{III}$ [19]. However, not all of the important phosphonates could be determined. The widely used HEDP (1-hydroxyethylene-1,1-diphosphonic acid) elutes in a region with large background signals and cannot be quantified. At EAWAG, we are currently developing analytical methods for the quantification of HEDP. For the application of GC/MS, derivatization is necessary which was found to pose more difficulties than described in [20]. Good preliminary results were achieved for the determination of HEDP by capillary electrophoresis (CE, see *Fig. 5*). HEDP could be detected as its $Fe^{III}$ complex in a spiked wastewater sample. More work is underway to achieve a better detection limit and improve reproducibility.

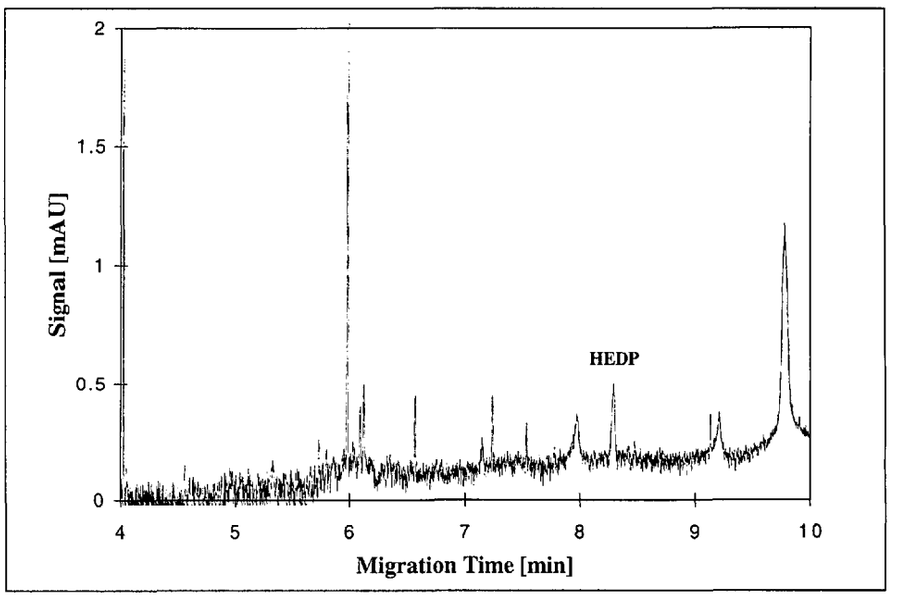


Fig. 5. *Capillary electropherogram of filtered wastewater from the influent of the wastewater treatment plant Zürich Glatt.* Spiked with 50 µM HEDP and 100 µM $Fe^{III}$. HEDP is seen as $Fe^{III}$-HEDP complex at 260 nm. CE electrolyte: 100 mM borate buffer, pH 8.3.

## Selective Detection

There is a wide number of different detection techniques available that can be used after a separation step. This alone shows that the ideal detector, allowing for high sensitivity and selective detection in all cases, still does not exist. The choice of a detector in environmental analytical chemistry depends strongly on ease of use, cost, the need to either be very compound-specific or very generally applicable, but always on its sensitivity.

Mass-specific detection adds structural and molecular-weight information. For instance, a complete determination of all dioxin species would not have been possible without the use of high-resolution mass-spectrometry. The advantage of mass-specific determination is illustrated by the example shown in *Fig. 6*. *Fig. 6, A* shows a negative chemical ionization GC/MS total ion chromatogram, acquired from a linear alkylbenzenesulfonate (LAS) for-

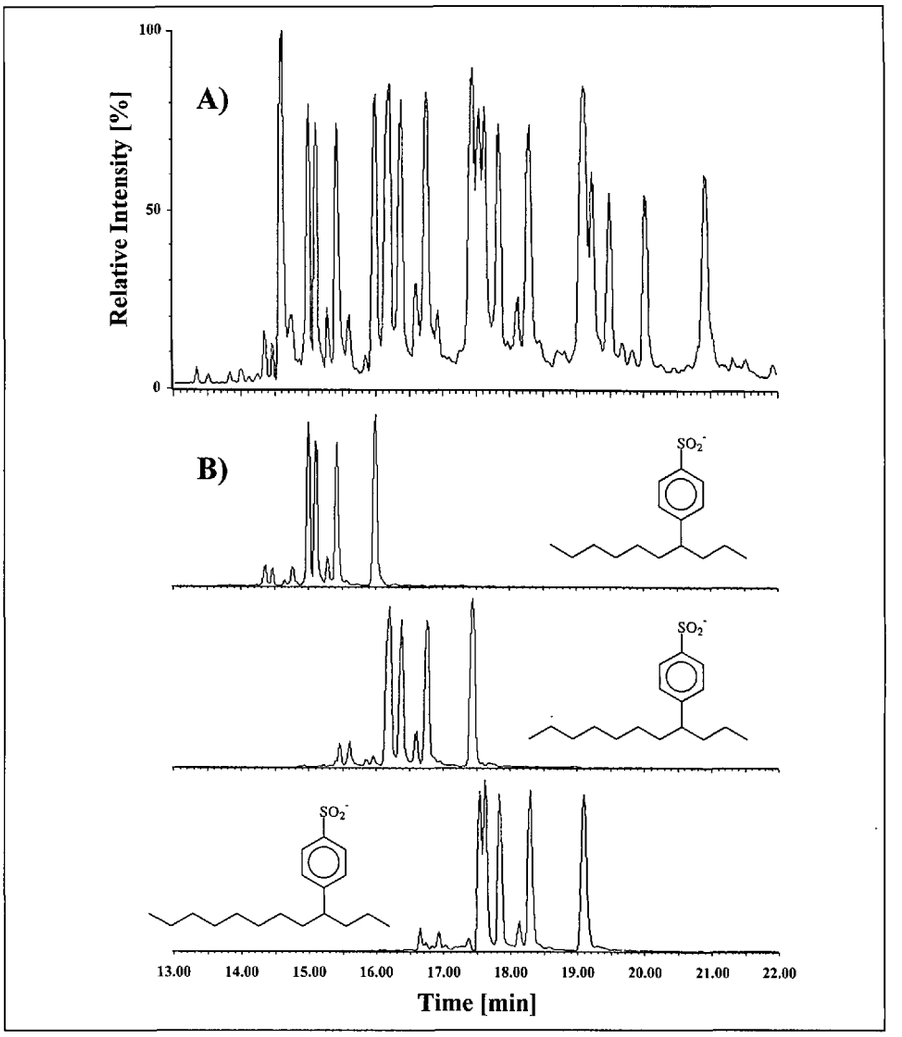


Fig. 6. *GC/MS total chromatograms of a technical LAS mixture. A*) Total ion chromatogram acquired under negative chemical ionization conditions. *B*) Reconstructed negative ion chromatograms using intense fragment ions of the $C_{10}$- (*m/z* 281), $C_{11}$- (*m/z* 295), and $C_{12}$-LAS homologs (*m/z* 309), corresponding to $[M - O\text{–}CH_2\text{–}CF_3]^-$.

mulation. This commonly used anionic surfactant is a mixture of several homologs and isomers. For GC/MS determination, they were derivatized to the corresponding trifluoroethyl esters. The resulting GC trace is similar to what could be expected with GC-FID and proves to be not specific enough to identify and quantify all individual components present, especially since some have overlapping retention times. *Fig. 6, B* shows corresponding reconstructed ion chromatograms of three LAS homologs and their isomers [21][22]. In this case, gas chromatography fractionates according to the position of the aromatic ring system, while mass spectrometry allows to differentiate between the various homologs. This is easily achieved by selecting an intense fragment ion (*m/z* 281 for $C_{10}$-LAS, *m/z* 295 for $C_{11}$-LAS, and *m/z* 309 for $C_{12}$-LAS, respectively), which still contains the intact alkyl chain, in this case the $[M-O-CH_2-CF_3]^-$ ion. By using MS/MS techniques, it is even possible to differentiate between linear and branched (ABS) alkylbenzenesulfonates [21], thus allowing a selective quantitation in, *e.g.*, sediment layers that contain both LAS and ABS.

Other types of aromatic sulfonates are used in a lot of industrial applications and are intermediates for many technical products, such as concrete plasticizers, azo-dyes, and herbicides. 3-Nitrobenzenesulfonate serves as a mild oxidizing agent in the textile industry and *p*-toluenesulfonate is used among other things as catalyst in the production of foundry cores and moulds consisting of sand and furan resin. Naphthalenemono- and -disulfonates are monomers of concrete plasticizers and aminonaphthalenesulfonates are azo-dye components. The high amount of aromatic sulfonates used, combined with the relatively slow biodegradability of some representatives (aromatic sulfonates that have an additional amino, nitro, hydroxy, or sulfo group), is reflected in the fact that they can be found in the ng/l range in surface waters [23]. Aromatic sulfonates are anionic xenobiotica with a high water solubility and a low disposition for bioaccumulation. Therefore, these compounds are very mobile in aquatic systems. Few of the investigated aromatic sulfonates show a low systemic toxicity and they are neither mutagenic nor carcinogenic [24]. Persistent representatives can be used as model compounds for negatively charged organic pollutants with conservative behavior. Solid-phase extraction and ion-pair chromatography combined with UV absorption, fluorescence detection [25], and electrospray mass spectrometry (ESI/MS) have been used to identify and quantify various aromatic sulfonates in leachates from landfills [26]. *Fig. 7* shows HPLC chromatograms of a wastewater extract from a landfill in the canton of Zürich, Switzerland, acquired using three different detectors. The compounds in the 50-fold enriched extract were separated by ion-pair chromatography using tetrabutylammonium (TBA) as counterion (5 mM aqueous TBA hydrogenesulfate, pH 6.5) and methanol as organic modifier. *Fig. 7, A* shows a HPLC/DAD (diode array detection) chromatogram, recorded at 220 nm, a wavelength that most aromatic sulfonates absorb. Using reference compounds, three signals could be assigned, based on their UV absorption spectra and retention times: Naphthalene-1,5-disulfonate (N1,5dS), N2,7dS, and N1,6dS in increasing order of elution. The UV absorption spectrum of the signals at 16:90 (TdS = toluene-disulfonate) and 23:20 min (U3, which stands for unknown 3) were very similar to those of *p*-toluene- and a naphthalenesulfonate, respectively, but could not unequivocally be identified using DAD. *Fig. 7, B* shows the corresponding fluorescence chromatogram acquired with an emission wavelength of 340 nm ($\lambda_{EX}$ = 230 nm). The strong emission at 23:20 min again indicates a naphthalenesulfonate, while the very weak emission at 16:90 min is due to the very high concentration of a benzenesulfonate that shows very poor fluorescence at 340 nm. *Fig. 7, C* finally shows reconstructed ion chromatograms (RIC) acquired using negative-ion electrospray and slightly different chromatographic conditions. The intense trace of mass 492 corresponds to a TdS/TBA cluster with a net negative charge and mass 528 to the corresponding N1,5dS/TBA cluster. The formation of TBA clusters is very typical for aromatic sulfonates, but only disulfonate/TBA clusters can be detected, be-

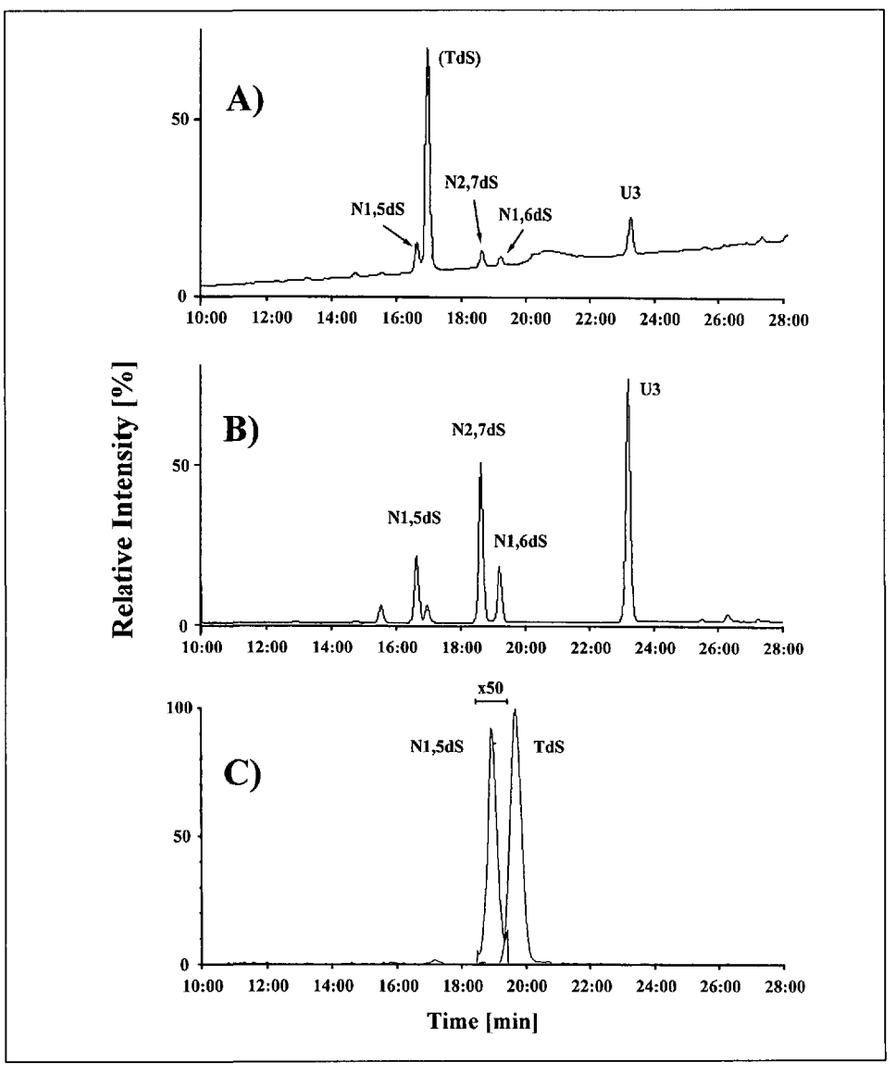


Fig. 7. *Extract from a wastewater of a landfill.* Ion-pair HPLC using a 5 mM tetrabutylammonium (TBA) hydrogensulfate (pH 5)/methanol gradient with UV (*A*, 220 nm), fluorescence (*B*, $\lambda_{EX}$ = 230 nm, $\lambda_{EM}$ = 340 nm), and mass-spectrometric detection (*C*, *m/z* 492 and 528). See text for details.

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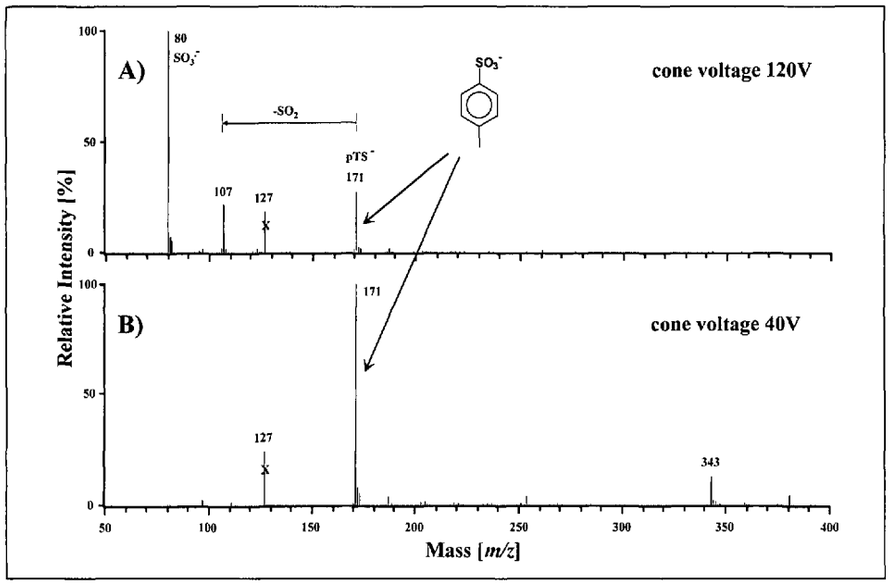


Fig. 8. p-*Toluenesulfonate spectra acquired with two different cone voltage settings.* See text for details.

cause of the uncharged nature of a monosulfonate/TBA cluster. As could be deduced from UV/DAD and fluorescence data, and is again seen in the RIC traces, TdS is present in very high concentration, while the N1,5dS are barely above the detection limit for ESI/MS (note the magnification factor of 50). This poor sensitivity could be improved by approximately a factor of 100, if single-ion monitoring data were acquired. However, one big advantage of ESI/MS is that structural information is available. By adjusting the interface parameters in such a way that charged ions will collide with neutral gas molecules, fragmentation can be induced. *Fig. 8* shows two spectra of *p*-toluenesulfonate acquired using two different cone voltage settings. Spectrum *B* was acquired under mild condition, so that no fragmentation is visible and the deprotonated molecule corresponds to the most intense signal. Under these mild conditions, even a dimeric cluster of *p*TS is visible at mass 343 corresponding to $[p\text{TS} + p\text{TS} - \text{H}]^-$. The ion *m/z* 127 corresponds to iodide, a leftover from the instrument calibration using CsI. Spectrum *A*, on the other hand, shows loss of $SO_2$ and formation of deprotonated methylphenol at mass 107. Toluenedisulfonate seen in *Fig. 7* could be identified in the same manner.

Using ESI/MS, the unknown compound U3 could be identified as a NdS. Only the positions of the functional groups of U3 and TdS still need to be determined.

In conclusion, fluorescence detection is by far the most sensitive technique, provided the analyte molecule shows fluorescence at all. UV/DAD allows identification of unknown compounds, if reference material is available. ESI/MS, on the other hand, shows the lowest sensitivity in full scan mode, but gives molecular weight and structural information.

## Concluding Remarks and Outlook

The work presented in this article shows that organic analysis for environmental investigations is indeed a challenge, especially when dealing with polar and ionic compounds. For instance, extraction efficiencies can change greatly, when applying an established method to a different type of matrix, as could be shown for DTDMAC extracted from digested sludges and various sediments.

This is also true in a more general way. The developing of new analytical techniques is always time-consuming and requires extensive validation. This could be nicely demonstrated for the analysis of organotin compounds using hyphenated techniques. In an other example, the determination of all environmentally relevant phosphonates using GC/MS or HPLC proved to be very difficult. In this case, capillary electrophoresis turned out to be a promising tool, even though the sensitivity obtainable is still quite low. Similar sensitivity problems are given, when using LC/MS. However, the additional mass-specific information allows identification of unknown compounds, that would otherwise not easily be possible. In conclusion we can say that even though a wide variety of analytical techniques is available today, very often one approach does not solve all the problems.

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[1] M. Ahel, T. Conrad, W. Giger, *Environ. Sci. Technol.* **1987**, *21*, 697.
[2] H.A. Ball, M. Reinhard, P.L. McCarty, *Environ. Sci. Technol.* **1989**, *23*, 951.
[3] A.M. Soto, H. Justicia, J.W. Wray, C. Sonnenschein, *Environ. Health Persp.* **1991**, *92*, 167.
[4] S. Jobling, J.P. Sumpter, *Aquat. Toxicol.* **1993**, *27*, 361.
[5] B.I. Escher, R. Behra, R.I.L. Eggen, K. Fent, *Chimia* **1997**, *51*, 915.
[6] W. Giger, *Chimia* **1997**, *51*, 729.
[7] J.A. Field, D.J. Miller, T.M. Field, S.B. Hawthorne, W. Giger, *Anal. Chem.* **1992**, *64*, 3161.
[8] P. Fernández, A.C. Alder, M.J.-F. Suter, W. Giger, *Anal. Chem.* **1996**, *68*, 921.
[9] I. Liska, *J. Chromatogr., A* **1993**, *665*, 163.
[10] H.G.J. Mol, H.G.M. Janssen, C.A. Cramers, J.J. Vreuls, U.A.T. Brinkman, *J. Chromatogr., A* **1995**, *703*, 277.
[11] E. Ballesteros, M. Gallego, M. Valcarcel, *Environ. Sci. Technol.* **1996**, *30*, 2071.
[12] M. Berg, S.R. Müller, U. Dommann, C.G. Arnold, R.P. Schwarzenbach, Proc. 21th International Symposium on Chromatography, Stuttgart, Germany, 1996, p. 333.
[13] E.D. Goldberg, *Environment* **1986**, *28*, 17.
[14] G.W. Bryan, P.E. Gibbs, G. Hummerstone, G.R. Burt, *J. Mar. Biol. Ass. UK* **1986**, *66*, 611.
[15] C.G. Arnold, A. Weidenhaupt, M.M. David, S.R. Müller, S.B. Haderlein, R.P. Schwarzenbach, *Environ. Sci. Technol.* **1997**, *31*, 2596.
[16] K. Grob, 'On-line Coupled LC-GC', Huethig, Heidelberg, 1991.
[17] W.E. Gledhill, T.C.J. Feijtel, 'Environmental properties and safety assessment of organic phosphonates used for detergent and water treatment applications', in 'The Handbook of Environmental Chemistry', Ed. O. Hutzinger, Springer Verlag, Berlin, Heidelberg, 1992 Vol. 3, Part F.
[18] B. Horstmann, A. Grohmann, *Vom Wasser* **1988**, *70*, 163.
[19] B. Nowack, *J. Chromatogr. A* **1997**, *773*, 139.
[20] J. Klinger, F. Sacher, H.-J. Brauch, D. Maier, *Acta Hydrochim. Hydrobio.* **1997**, *25*, 79.
[21] M.J.-F. Suter, R. Reiser, W. Giger, *J. Mass Spectrom.* **1996**, *31*, 357.
[22] R. Reiser, Ph. D. Thesis, ETHZ, 1997.
[23] S. Riediker, Ph. D. Thesis, ETHZ, in preparation.
[24] H. Greim, J. Ahlers, R. Bias, B. Broecker, H. Hollander, H.-P. Gelbke, H.-J. Klimisch, I. Mangelsdorf, A. Paetz, N. Schön, G. Stropp, R. Vogel, C. Weber, K. Ziegler-Skylakakis, E. Bayer, *Chemosphere* **1994**, *28*, 2203.
[25] B. Altenbach, W. Giger, *Anal. Chem.* **1995**, *67*, 2325.
[26] M.J.-F. Suter, S. Riediker, W. Giger, 'Proceedings of the 44th ASMS Conference on Mass Spectrometry and Allied Topics', May 12–6, 1996, Portland Oregon, 160.