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Analysis of Cement Superplasticizers and Grinding Aids A Literature Survey

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ANALYSIS OF CEMENT SUPERPLASTICIZERS AND GRINDING AIDS - A LITERATURE SURVEY

ABSTRACT

This literature survey reviews the methods for analysis of cement plasticizers and organic grinding aids in cement solutions in preparation of grouts/concrete and methods for determination of plasticizers and grinding aids in groundwater conditions. The survey focuses on three different types of superplasticizers: sulphonated naphthalene condensates, sulphonated melamine condensates and polycarboxylates. There are various organic grinding aids, such as alkanolamines, glycols or phenolic compounds, used in the cement industry. This review is concerned with the following compounds: triethylenetetramine, tetraethylenepentamine, diethanolamine, triethanolamine, triisopropanolamine, ethyleneglycol, diethyleneglycol, aminoethylethanolamine, hydroxyethyl diethylenetriamine and phenol.

Keywords: superplasticizers, grouts, concrete, cement, groundwater, sulphonated naphthalene condensates, sulphonated melamine condensates, polycarboxylates, grinding aids

SEMENTIN ORGAANISTEN LISÄAINEIDEN ANALYSOINTI -KIRJALLISUUSSELVITYS

TIIVISTELMÄ

Työraportissa on selvitetty menetelmiä, joilla voidaan analysoida sementtien valmistuksessa käytettäviä orgaanisia lisäaineita ja seosaineita sementti/vesiliuoksista ja pohjavesistä. Tarkastelun kohteeksi valittiin kolme erityyppistä lisäainetta: sulfonoitu naftaleenikondensaatti, sulfonoitu melamiinikondensaatti ja polykarboksylaattit sekä seosaineista trietyleenitetramiini, tetraetyleenipentamiini, dietanolamiini, trietanolamiini, tri-isopropanoliamiini, etyleeniglykoli, dietyleeniglykoli, aminoetyylietanoli-amiini, hydroksietyylidietyleenitriamiini ja fenoli.

Avainsanat. orgaaninen lisäaine, sulfonoitu naftaleenikondensaatti, sulfonoitu melamiinikondensaatti, polykarboksylaattit, sementti, pohjavesi, seosaineet

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1 INTRODUCTION

Superplasticizers (SP) are compulsory components of concrete or injection grouts in the construction of deep underground repositories for disposal of radioactive waste. One purpose they serve is to fluidise fresh concrete at very low water/cement ratios enabling the production of high performance concrete. Although they are added only at the order of 1-2% of dry cement, their total mass in a repository is considerable. Radionuclides potentially released from a nuclear waste deposit could complex with these admixtures. The effect and contribution of these superplasticizers to the migration of radionuclides is still unresolved.

The determination of chemical additives in cement and concrete, in leaching solutions and in environmental samples is often difficult because the additives are usually present at relatively low concentrations. Furthermore, the additives can often undergo alkaline hydrolysis to form other compounds or precipitate as insoluble calcium salts during preparation of the cement. Thus some portion of the original chemical form of certain additives is absent when the chemical analysis of cement, concrete or leaching solution is performed. Furthermore, some degradation of the additives can also occur. All this can complicate identification and quantification of additives in groundwater.

This literature survey focuses on three different types of superplasticizers: sulphonated naphthalene condensates (PNS), sulphonated melamine condensates (PMS) and polycarboxylates (PC). Commercial admixtures may contain by-products and impurities, but these are not considered here. Also the possible degradation products of admixtures are excluded from this compilation. The analytical methods reported in the literature are reviewed. In addition, the environmental occurrence of these superplasticizers and their laboratory experiments concerning leaching are examined.

Grinding aids are common cement additives, and can consist of several different types of compounds such as alkanolamines, glycols or phenolic compounds. These are used to increase the throughput of cement clinker in the grinding mill. Generally, the concentration range of grinding aids added is from 50 to 500 ppm. After the grinding process the additives might not be any longer in their original chemical form. In addition, grinding aid composition might not consist of mixtures of pure compounds, but rather more complex raw materials (Jeknavorian et al. 1998b).

The grinding aids such as alkanolamines and glycols are also widely used in other kinds of chemical industry, e.g., as corrosion inhibitors, emulsifiers, laundry materials, stabilizers in pharmaceutical productions, dyestuffs and gas purifiers (Holčapek et al. 1999, Mrklas et al. 2003). The wastes containing alkanolamines from these industrial operations are often stored in surface retention pits or landfills, leakage from which has contaminated subsurface soils and groundwater. Elevated concentrations of suggested degradation products, such as ammonia, nitrite and nitrate, have been measured on the contaminated areas (Headley et al. 1999, Davis and Carpenter 1997).

Binding mechanisms for organics in cement are largely unknown. Leaching of grinding aids varies between classes of organic compounds depending on a variety of factors including solubility in water, polarity, presence of functional groups, volatility etc. (Hebatpuria et al. 1985). Open chain polyamines in their protonated form have a strong ability to bind several metal cations and form fairly stable species with organic and inorganic polyanions (De Stefano et al. 2000).

Alkanolamines have high water solubilities and can undergo a wide variety of reactions common to amines and alcohols. (Davis and Carpenter 1997). Their high polarity makes the chromatographic separation of mixtures of alkanolamines difficult and the absence of a chromophore, fluorophore or electroactive group make their detection and quantification challenging. Generally, chemical derivatization is necessary to increase the detection sensitivity and to improve selectivity (Worsfold and Yan 1991). Due to their high water solubility, enrichment of aliphatic amines by liquid-liquid or solid-phase extraction is complicated at the trace level (Sacher et al. 1997).

Most of the reported methods suitable for amines, glycols or phenol analyses are from other industrial applications and not from the cement/concrete industry. However, there have been a number of results reported recently on these materials and also their improved analytical methods (Herterich et al. 2004, Page et al. 2005).

2 SUPERPLASTICIZERS

Superplasticizers are one type of concrete admixtures. They are often negatively charged polymers and are composed of a variety of different molecules. The molecular weight may vary over a wide range from less than 100 to 100 000 g/mol. The composition is in many cases ill-defined and kept secret for proprietary reasons by the manufacturer. The chemical composition from batch to batch may also vary even in the same product of one producer.

Superplasticizers have been mainly based on PNS, PMS or lignosulphates (LS). New generation superplasticizers consist of PC. Pojana et al. (2003) tested commercial mixtures and found a clear difference in oligomeric distribution in PMS mixtures from Switzerland and Italy. The former contained a greater content of longer oligomers (85-87%) than the latter (44-58%). Ruckstuhl et al. (2003) observed in their commercial mixture of PNS 12% monosulphonated monomers, 23% disulphonated monomers and 66% oligomers.

The general molecular structure of admixtures is shown in Figure 2-1. There is a wide range of values reported for the number of oligomers per superplasticizer molecule.

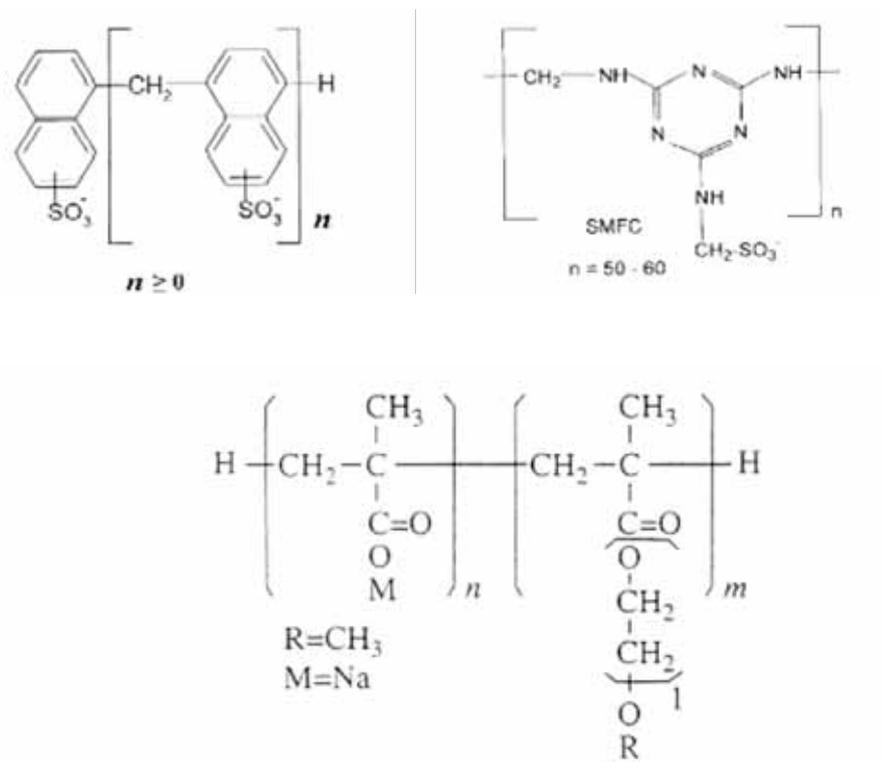


Figure 2-1. The molecular structures of PNS (upper left), PMS (upper right) and PCE (polycarboxylate ester). n , m , l represent the number of monomer unit within the molecule. (From Ruckstuhl 2001, Pojana et al. 2003, Herterich et al. 2004)

2.1 Sulphonated naphthalene condensates (PNS)

PNS is produced by condensation of naphthalenesulphonic acid with formaldehyde. There is no detailed study of the average molecular weight, degree of sulphonation etc. of PNS from different producers. There are some reported weight distributions for PNS. Roy et al. (1983) observed that in their compounds the average molecular weight was approximately 1000 g/mol. On the other hand Andersen et al. (1987) obtained 19 500 g/mol for their compounds. Herb et al. (2000) obtained a very flat distribution between 2000-30 000 g/mol with a small peak below 1000 g/mol.

The distribution of molecular weight indicates that the oligomeric distribution is very different for these admixtures. Ruckstuhl et al. (2002) observed in their technical PNS mixture (Galoryl LH 120) the following monomers: 1-NS, 2-NS, 2,6-NDS, 1,5-NDS, 2,7-NDS, 1,6-NDS, 1,7-NDS and other dimers and trimers. The reported values for the number of oligomers can be divided in two groups: those up to 10 (Ruckstuhl 2001, Yilmaz et al. 1992, Pierre et al. 1988, Pojana et al. 2003) and those from 11 to 20 (Ruckstuhl 2001, Piotte et al. 1995 Wolf et al. 2000). Piotte et al. 1995 suggested that the degree could go up to 90. Miller (1985) detected also branching in PNS. He explained that the branching of the product is controlled by the amount of formaldehyde used in the condensation process.

The elemental composition of one PNS (Mighty 150) has been reported by Mannonen 1996 to contain carbon (50.3 wt%), sulphur (11.3 wt%), hydrogen (3.2 wt%) and sodium (8.9 wt%).

PNS are strong acids, $pK_{as} < 1$, and strongly hydrophilic. They exhibit low octanol-water partition coefficients. Thus they are very highly soluble in water (Ruckstuhl 2001).

2.2 Sulphonated melamine condensates (PMS)

The variation of commercial products, which have been observed in PNS, are similarly present in PMS. Even in the starting material melamine there have been reported differences (Ono et al. 1998). The average molecular weight and molecular weight distribution reported by Cunningham et al. (1989) in their mixture was 1200 to 44 000 g/mol. Andersen et al. (1987) obtained 15 000 g/mol for their compounds. Pojana et al. (2003) have identified oligomers indices of up to 7 in commercial blends and suggested that they can go up to 50-60 and that the structure can be branching.

PMS too are very water soluble (>100 mg/L) with low $\log K_{ow}$ (Pojana et al. 2003).

2.3 Polycarboxylates (PC)

These SP too have wide molecular weight distribution and it is not easy to characterize their chemical structure. Since it is easy to modify only one component of the polymer while keeping rest of the structure the same, there can be a wide range of different mixtures available. The quantity of the carboxylate groups in the principal chain defines

the adsorption power and the consistency of the mortar mixture. Polycarboxylates can have as a backbone chain acrylic or methacrylic polymers.

Yamada et al. (2000) have analysed the chemical structure of PC containing polyethylene (PEO) graft chains (PEO side chains), as well as sulphonic and carboxylic acid groups. Their materials were based on polymethacrylates. The molecular weight average was between $2.2 \cdot 10^4$ to $9.9 \cdot 10^4$ g/mol. The number of carboxylic acid groups per average molecule were 43 to 207, sulphonic acid groups 5 to 31, PEO chains 14 to 66. Borget et al. (2005) characterized the PC of a PMAANa backbone with PEO chains (Sika AG) the molecular weight being 14 100-60 000 g/mol, PEO 68-86 (w/w%), and number of backbone units 80-420.

According to Herterich et al. (2003,2004) their concrete admixtures were based on polycarboxylate esters (PCE) consisting of a polymethacrylic acid backbone, which is partially esterified with polyethylene glycol methylether side chains. Upon contact with cement there is saponification of the PCE. Of the two resulting parts - polymethacrylic acid backbone and free polyethylene glycol (derivate) – only polyethylene glycol (derivate) (an ethoxy compound) is soluble and mobile in aqueous solutions.

The functional groups of PC are weaker acids compared to those of PNS or PMS and also the ratio between mass of molecule to mass of functional groups is higher, therefore they are weaker electrolytes.

3 ANALYSIS OF SUPERPLASTICIZERS

3.1 General aspects

There are several qualitative analytical methods for additives but fewer quantitative ones. They comprise the whole spectrum from unspecified methods to very specific methods, but none of them is superior. Since it is only just from this century that superplasticizers have been analysed in more detail, the methods are still not validated for complex environmental samples.

Most analytical studies have concentrated on PNS while comparatively few concerned PMS; and PC being a new compound in the field its studies have just started. Since SP have imprecisely known compositions, containing possible interfering compounds, standard solutions are scarce, no analytical method is available or methods have to be tested, refined and evaluated before applying them to real samples. Quite recently Reemtsma (2003) published a literature review of analysis methods of polar organic pollutants at the trace level including also PNS. The Appendix presents the analytical approach of NUMO/CRIEPI (Nuclear Waste Management Organization of Japan/Central Research Institute of Electric Power Industry) as applied in their cement leaching studies.

In most cases fractionation or purification of the sample is needed before analysis. When dealing with environmental samples an enrichment of the organic compounds in solution is required. After this the separation and analytical method can be chosen. The analysis can be especially difficult because the additives are usually present at relatively low concentrations. Separation techniques such as size exclusion chromatography (SEC), high performance liquid chromatography (HPLC), gas chromatography (GC) and ion chromatography (IC) can be combined with detection mode UV/VIS, diode array detection (DAD), fluorescence detection (FLD) or mass spectrometry (MS). The resolving power of different separation techniques has been reported to be HPLC>IC>SEC (Rosenberg 2003). For this reason SEC is often used as a clean-up or fractionation technique before more powerful techniques. Some of the methods are used for detecting monomeric compounds and others for also oligomeric ones. The methods allow the detection of residual PNS in aqueous environmental samples in the ng/L to µg/L range (Lange et al. 2005). So far analyses of PMS have been reported only from wastewater, but the reported detection limit for the HPLC/MS method was 5 µg as an injected amount (Pojana et al. 2003). For PC there is only NMR study and no detection limit was reported.

3.2 Extraction and enrichment

Few methods to analyse additives in solid concrete samples have been reported. Earlier a common method was chemical wet-extraction using potassium carbonate followed by UV-VIS spectroscopy, but the type of cement used to fabricate the concrete influenced this. Later pyrolysis-gas chromatography (py-GC) has replaced this (Jeknavorian et al. 1998). Glaus and van Loon (2004) used HCl and NaOH in extraction procedure to determine the PNS in hardened cement paste (HCP) and obtained full recovery. Most

recently nuclear magnetic resonance (NMR) for PC has been used in concrete studies. In these studies it was reported that water extraction was enough (Herterich et al. 2003, 2004). Also a method for suspended samples has been developed by Lange et al. (2005). This means ultrasonic extraction under alkaline conditions, followed by ion-pair HPLC with FLD for the analysis of PNS.

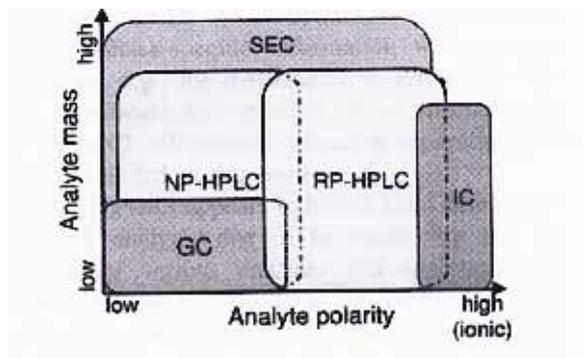


Figure 3-1. Application range of the most important separation techniques as a function of analyte polarity and molecular mass. (From Rosenberg 2003)

The areas where the methods for fractionation are best suited are shown in Figure 3-1. HPLC techniques cover most of cases, SEC being better only for very high molecular masses. The GC and IC methods have limited applicability.

3.2.1 Solid phase extraction (SPE)

Enrichment of additives from low-level samples has been done mainly by solid phase extraction (SPE). C18 (octadecyl-coated silica gel) phases are most frequently used, but C8 (octyl-coated silica gel) is also reported. These have good recoveries for NS. They have been used both for surface and wastewaters. Sometimes a second clean up has been performed on C18 cartridges. In general, C18 can be used for the removal of less polar substances prior to ion-pair extraction.

PNS lack a hydrophobic alkyl chain; therefore their SPE is not straightforward. PNS exhibit no retention on C18 reversed-phased material unless they are paired with an organic cation such as tetraalkylammonium (TAA). Ion-pair formation with tetrabutylammonium (TBA) has been also used. Usually, the ion-pairing agent is added to the aqueous sample prior to extraction. Alternatively, Zerbinati et al. (1994) saturated the solid phase with octyltrimethyl ammonium acetate, thereby producing an anion-exchange column, and loaded the sample afterwards to the column. The ion exchange capacity and the breakthrough volume were unfortunately low. The extraction of polar sulphonates by anion-exchange phase was an unsuitable method. Later Zerbinati et al. (1997) used SPE cartridges loaded with cetyltrimethyl-ammonium bromide (CTAB) for pre-treatment.

Although being a valuable tool for the extraction of aromatic sulphonates from aqueous media, ion-pair SPE suffers from co-extraction of interfering dissolved organic carbon (DOC), limited extraction efficiency for very polar sulphonates and from the poor

recoveries from samples of high contents of inorganic salts. An alternative approach was presented by Altenbach and Giger (1995). They used deactivated charcoal (Carpoback B), which can be used without ion-pairing agents. They concluded that this reduces interference from humic substances.

Loos et al. (2000) studied different SPE materials for extraction of different aromatic sulphonates. LiChrolute EN performed best, but very hydrophilic sulphonates containing more than one negative sulphonate group could not be extracted by any of the tested adsorbents. This means compounds such, as 1,5-NDS, 2,6-NDS and 1,3,6-NTS are not recovered. Lange et al. (2005) used ion-pair extraction of RP-C18 material for enrichment of oligomers of PNS from aqueous samples. The ion-pair agent was tetra butylammonium bromide (TBABr). A new polymeric sorbent, molecularly imprinted polymers (MIP), has been tested for PNS directly from aqueous samples. Unfortunately only 1-NS and 2-NS were tested, but these showed promising results (Caro et al. 2004). MIP allows the reduction of background signal in the chromatogram while still retaining the recoveries of PNS well. Further testing and validation is however needed if all oligomers are to be analysed. MIP is good only for specific compounds and is not suited for less specific polymers.

Pojana et al. (2003) extracted PMS using polystyrene-divinyl-benzene resin (PS-DVB) for which the extraction recovery was at maximum 73% from drinking water at concentration down to 10 μ g/L. There are no other studies of enrichment methods for PMS. No suitable method is reported for PC.

3.3 Separation methods

3.3.1 Size exclusion chromatography (SEC) and ultrafiltration

Size exclusion chromatography (SEC)/gel permeation chromatography is a common fractionation technique for organic polymers. SEC has been used to study the structure of PMS, PNS and PC-type superplasticizers (Borget et al. 2005, Roy et al. 1983, Herb et al. 2000, Yamada et al. 1999). The method is optimal for spherical particles; therefore with SP some exaggeration of the apparent molecular weight is expected, unless one has suitable calibration substances. Both aromatic and ionic groups might favour adsorption and ion exchange interaction with gel and therefore a negative error in the measured molecular weight cannot be excluded fully. Molecular weight can be roughly evaluated by this technique.

Piotte et al. (1995) considered ultrafiltration to be a suitable separation technique for high molecular weight PNS, but for smaller molecules it was inaccurate. In addition to extraction and enrichment SPE is used for clean up of complex samples to increase selectivity of the entire analytical method.

3.3.2 Liquid chromatography (LC)

Liquid chromatography (LC) is the most common technique for separation of SP oligomers, due to the wide application area when analyte polarity and molecular mass

are taken into account. The LC/MS method allows the identification and resolution of co-eluting compounds of different molecular weights.

Molecular weight information can identify predicted compounds with better certainty. When using HPLC the interferences from naturally occurring humic substances is minimized and the detection is more quantitative.

Reversed-phase-ion-pair LC has been the most used method (Piotte et al. 1995, Pojana et al. 2003, Lange et al. 2005). In reverse phase liquid chromatography (RPLC) the eluent pH is recommended to be above the analytes' pK_a -value in order to ensure the dissociation of the acidic groups and strong ion-pair formation (Reemtsma 1996). Increasing counter-ion concentration further intensifies retention. In the case of polysulphonated compounds, counter-ion additionally influences the elution order: if the concentration of the ion-pairing agents is sufficiently high to pair all sulphonated groups, monosulphonates elute first, followed by di- and trisulphonates. Electrolyte concentration further influences the retention. It decreases with increasing electrolyte concentration since its inorganic anion competes with analyte in ion-pairing formation. This has to be considered when aqueous samples with high salt content are analysed directly. The LC column type mostly used in analysing PNS is C18.

Interaction of PNS with reversed-phase columns is too weak to separate them effectively, thus other retention mechanisms using ion-pairing agent have to be exploited. Different ion-pairing agents have been reported (Menzel et al. 2002, Loos et al. 2000, Caro et al. 2004, Stüber and Reemtsma 2004, Storm et al. 1999). The two most commonly used ion-pairing agents are tri-n-butylamine (TBA) and tertiary alkylamine (TEA) (Pocurull et al. 1999, Alonso et al. 2000). However, Pocurull et al. (1999) reported that TBA is not suitable if electrospray ionisation (ESI) is used with MS because it can cause contamination of ESI with additional problems of poor reproducibility and in sensitivity.

HPLC separation C8-column with ion-pair agent tetra methylammonium chloride (TMeCl) was used for MS, and a C18-column used for oligomer-oligomer ion-pairing-reverse-phase separation. A technical mixture was used for quantification in the absence of certified standards (Pojana et al. 2003).

Column temperature has a strong influence on separation. Also slightly higher temperatures, 40-45 °C, have been used in HPLC separations (Altenbach and Giger 1995, Fichtner et al. 1995, Suter et al. 1999, Storm et al. 1999, Stuber and Reemtsma 2003, Wolf et al. 2000, Caro et al. 2004).

Carboxylates may cover a wide range of polarities. Thus chromatographic separation methods for these also vary. The addition of ammoniumacetate can be sufficient to attain retention in RPLC. The introduction of a carbonic acid moiety into the parent molecule renders the compound more hydrophilic and a potential for LC-MS determination (Reemtsma 2003).

One of the main problems in the quantitative analysis of environmental samples using HPLC/ESI/MS is the suppression of the analyte signals in the presence of matrix

components. This poses problems to the calibration technique. Stüber and Reemtsma (2004) made an evaluation of calibration methods in environmental analysis with LC/ESI/MS and concluded that external sample calibration is most suited to compensate matrix effects in moderately loaded waste water samples. Suter et al. (1999) have reported that sulphate salts can be potential source of interference.

For quantification of PNS the following reference compounds have been reported: 1-NS, 2-NS, 1,5-NDS, 1,6-NDS, 1,7-NDS, 2,6-NDS, 2,7-NDS and naphthalene-2-sulphonate-dimer.

HPLC/MS performance can be improved in quantitative analysis using a nanosplitter interface making possible to recover most of sample for further analysis, since only 0.01% of the sample is introduced into the mass spectrometer (Andrews et al. 2004).

3.3.3 Gas chromatography (GC)

For analysis of total amount of PNS in solid concrete Jeknavorian et al. (1998) used pyrolysis-gas chromatography mass spectrometry (py-GC/MS). They studied concrete samples containing PNS-based admixtures. The content of PNS in cement paste and diethylene glycol in cement was determined. This method was applied directly to the solid sample hence no leaching was required. The main pyrolysis product was naphthalene and minor amounts of methylnaphthalene. No interference was observed and a linear relationship of naphthalene response versus SP dosage was obtained. The method is suitable for estimating the amount of PNS-based admixture in concrete.

In general, GC provides higher separation efficiency than HPLC though the application range is narrow (see Figure 3-1). However, the polarity of the sulphonate moiety requires derivatization prior to GC analysis. Derivatives of di- and polysulphonates, however, lack volatility and have even lower thermal stability than monosulphonates. They are thus not amenable to GC separations.

3.3.4 Capillary electrophoresis (CE)

Capillary electrophoresis (CE) for separation of PNS type of superplasticizers was used by Garcia and Henion (1992). The buffer contained 10/90 methanol/water and 1% TEA was utilized to facilitate the electrospray process in MS. The method was tested only for 1-NS.

Under suitable conditions the movement of buffer solution towards the target electrode is caused by a negatively charged capillary wall. Sulphonates are separated by the superposition of electro-osmotic flow (EOF) towards the cathode and their own electrophoretic movement in the reverse direction. The elution order is the reverse of their electrophoretic mobility.

Chen and Ding (2004) developed CE further by introducing a cyclodextrin mediator, which enables separation of positional isomers of PNS. Reversed electrode polarity stacking mode (REPSM) increased the sensitivity of CE. Earlier in pure phosphate and borate buffers, isomeric PNS were only separated into groups and the positional isomers

showed little or no separation. Chen and Ding (2004) tested the method for 1-NS, 2-NS, 1,5-NDS, 1,6-NDS and 2,6-NDS. The method needs further validation with real trace level samples.

Different modes of CE such as capillary zone electrophoresis (CZE), EC and micellar electrokinetic capillary chromatography (MEKC) exist. According to Loos et al. (2000) LC-MS offers higher separation efficiency for PNS than CZE. Angelino et al. (1999) compared the ion pair HPLC to MEKC for 1-NS and 2-NS in industrial waste effluent. According to them MEKC leads to better peak shapes, higher efficiency and lower analysis time, whereas ion pair HPLC has superior sensitivity.

3.3.5 Other separation methods

Anion-exchange chromatography is of limited importance in the analysis of aromatic sulphonates due to its low selectivity (Reemtsma 1996). Kim et al. (1992) used it to study aromatic sulphonates in landfill leachates. Also ion chromatography (IC) has not widely been used.

3.4 Detection and determination methods

Although there are established methods for detection other than MS, the identification of substances not ascribed to a reference compound is impossible which is the major drawback for their application to environmental or other complex samples.

3.4.1 Ionisation techniques and mass spectrometry (MS)

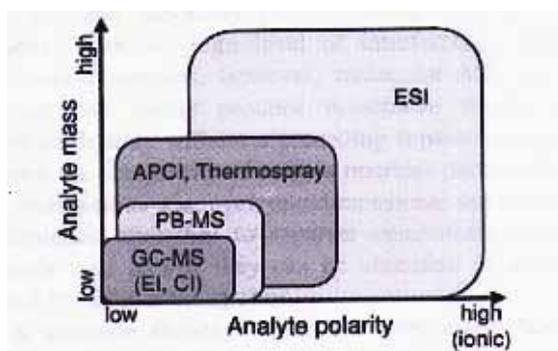


Figure 3-2. Application range of the most important mass spectrometric (ionization) techniques as function of analyte polarity and molecular mass. (From Rosenberg 2003)

Electrospray ionization (ESI) technique has the widest range for mass spectrometric (MS) determinations (Figure 3-2), atmospheric pressure chemical ionization (APCI) being the second widest. ESI is suitable for larger molecules than any other technique. In addition ESI is a softer ionisation technique than APCI therefore less fractionation during ionisation occurs. ESI generates gas phase ions that reflect well the ions actually present in the liquid phase. APCI is an alternative technique for smaller molecules and compounds that do not respond well to electrospray. ESI is suitable for large molecules in fresh water.

API techniques, namely ESI and APCI, rely on the formation of a continuous spray from LC or CE effluents. Ions are formed or pre-existing ions are extracted in an atmospheric pressure ionisation process and transported into the vacuum of the MS. API techniques are suitable for thermally unstable compounds typically separated in the liquid phase. In APCI, in contrast to ESI, solvent evaporation and analyte ionisation are two separated processes, the latter being a chemical ionisation at atmospheric pressure with the mobile phase acts as a reactant gas. APCI normally produces singly-charged ions through the addition or abstraction of a proton (e.g. $(M+H)^+$ and $(M-H)^-$, respectively).

Other ionisation methods, which can be used with MS are EI, ion chromatography (CI), time of flight- matrix-assisted laser desorption ionization (TOF-MALDI), fast atom bombardment (FAB) and atmospheric pressure ionization (API). Two special cases of API techniques are ionspray ionisation and collision-induced dissociation (CID).

Application to SP

PNS and PMS are strongly acidic and suitable for electrospray ionisation (ESI). Carboxylates are weakly acidic, but still within the range of ESI. Considering the range of analyte polarity and molecular mass which is acceptable to ESI it is evident that this technique outperforms even atmospheric pressure chemical ionisation. However, molecular MS techniques can hardly produce reasonable results if applied directly without a preceding separation step.

Negative ionisation is generally more specific and less prone to adduct formation than positive ionisation, since only a minority of substances are able to stabilize negative charges. This is true for sulphur-containing molecules. The addition of alkali ions such as Na^+ in the positive mode or formate or acetate in the negative mode favours ionisation. PNS and PMS have been reported to be detected mainly in negative mode (Suter et al. 1999, Loos et al. 2000, Stüber and Reemtsma 2004). Due to the acidity of PC, ESI-MS in negative mode would be useful for analysis. Too high an ionic strength decreases sensitivity, because the ions in the solvent starts to compete with ions in the analyte.

The molecular ions as well as $(M-SO_2)^-$ and $(M-SO_3H)^-$ are characteristic fragments of aromatic sulphonates in the EI mode. For example 1-NS can be observed in deprotonated molecules $(M-H)^-$ with m/z 207.

Also FAB/MS has been used to analyse aromatic sulphonates and polysulphonates. Zerbinati et al. (1997) used this technique for analysis of PNS. Fast atom bombardment (FAB) produced singly charged molecular ions with negligible fragmentation. FAB-MS/MS provides fragmentation and structural information. The MS/MS fragments were $(m-SO_2)^-$ and SO_3^- .

The high complexity of PMS structure and the presence of multicharged molecules did not allow identification of the characteristic ions for each oligomer, because of the formation of multicharged ions in the ionisation chamber. A qualitative structural determination of PMS could be developed by isolating a characteristic ion fragment of

the monomeric melamine sulphonate structure, obtained by collision at high voltage in the desolvation chamber. Fingerprinting of the presence of PMS-related compounds in aqueous environmental samples is achieved. (Pojana et al. 2003)

The MS discussed here includes all kind of MS and are not described separately. Ion traps are especially suited for structural elucidation, whereas time of flight MS (TOF-MS) with higher mass resolution is ideal for the determination of molecular formulas of unknown compounds and for screening purposes. Further information can be obtained by MS/MS (Reemtsma 2003).

3.4.2 UV-VIS and diode array detection (DAD)

UV-VIS spectroscopy has earlier been used widely. The method is based on the aromatic cores of molecules absorbing light in a certain wavelength range and the exact position of the absorption maximum is very sensitive to changes in the functional groups attached to this ring (often the method is not sensitive at all to structural changes). But the method is not limited only to aromatic compounds. The measured signal represents the sum of the individual contributions. Since SP are mixtures of different oligomers and the method is not selective enough it is not possible to get information of the distribution of different oligomers in the solution without pre-separation of these oligomers. This can also have an effect on the calibration. The presence of different polymer units in PNS means that there are differences in electronic transitions that give rise to the UV spectra. The spectra are influenced to slightly differing degrees also by the different orientations of the groups such as -OH, SO_3^- , etc. (Bensted 1993). Tetrabutylammonium salts are particularly well suited for UV detection due to their low background absorption (Socher et al. 2001).

There are reports in literature (e.g. Glaus and van Loon 2004) that some interfering substances can seep out from cement particles to water. Earlier UV-VIS measurements we reported to have been sensitive to pH (Spanka and Thielen 1995). Glaus and van Loon (2004) reported that the absorbance of PNS of wavelength 291nm is not sensitive to pH. In the PNS measurement they used TRIS pH-buffer: 2-amino-2-(hydroxymethyl)-1,3-propanediol. However they found a shift in wavelength observed for PNS spectra between sample solution and calibration solutions. This was probably due to the heterogeneity in composition of PNS solutions and the fact that fractions of different molecular weights have different sorption affinities for cement. Wavelength shift is the dominant source of uncertainty. Also nitrate salts induce interferences and must be taken account since some PNS admixtures can have high amount of nitrates.

UV-VIS detection is a relatively robust method for concentration determinations of PNS and not suitable without pronounced separation and purification steps of oligomers and also the use of oligomer based standards. However the method is rapid and efficient for screening purposes.

PNS exhibit a strong absorption band in the UV region (200-300 nm). The wavelength range in detecting PNS has been 215-227 nm (Yilmaz et al. 1993, Pierre et al. 1988) and for PMS 215-218 nm (Pojana et al. 2003, Yilmaz et al. 1993). The UV chromatogram is disturbed by a high background UV absorption, due to humic substances. Therefore, the more selective fluorescence detection (FLD) is preferred for quantifications of PNS.

UV/DAD (diode array detection) has been used for qualitative analysis of PNS combined with FLD for quantitative analysis. Fichtner et al. (1995) measured PNS using DAD at 220 nm, but the background was higher than in FLD.

Loos et al. (2000) compared LC-UV/DAD-MS with CZE and total ion chromatography MS (TIC-MS). The advantage of UV/DAD was that it had narrower peaks than TIC-MS. The LC-DAD-MS offered higher sensitivity than CZE and higher separation efficiency than CE-UV. According to them the limit of detection was ten times higher for SPE-CE-UV than SPE-LC-MS.

3.4.3 Fluorescence detection (FLD)

Ruckstuhl et al. (2001) developed the fluorescence detection (FLD) technique by introducing the synchronous excitation mode. The excitation wavelength was scanned over 200-400 nm while the emission wavelength range was 305-505 nm. The advantage was that in analysis of PNS from environmental samples the additional cleaning and enrichment step could be avoided. Interferences by humic substances and nitrate occurred only at concentrations higher than 1 mg/L C and 10 mg/L NO₃⁻ respectively.

Zerbinati et al. (1994) measured PNS by fluorescence using two couples of excitation/emission wavelengths: 240/330 and 250/455 nm. Lange et al. (2005) used excitation/emission wavelengths of 230/340 nm for monomers and 230/360 nm for oligomers.

Kok et al. (1997) used wave-length-resolved laser-induced fluorescence (LIF) detection with CE for some PNS. PNS were excited at 280 or 325 nm. Since the emission spectra are strongly affected by the type and pattern of substitution, they provide also some structural information. The results agreed with those obtained by HPLC.

Fichtner et al. (1995) compared UV/DAD and FLD techniques when determining PNS and found FLD to be better.

3.4.4 Spectrofluorimetry

Yilmaz et al. (1992) developed a spectrofluorimetric method to study PNS using the excitation wavelength of 291 nm while emission was measured in the range 250-600 nm, centered at 350-354 nm. This method was used for fresh cement-water samples of high pH.

3.4.5 Nuclear magnetic resonance spectroscopy (NMR), infra red spectroscopy (IR), differential thermal analysis (DTA), thermogravimetry (TG) and total organic carbon analysis (TOC)

NMR

The relative relation between the different structural elements is obtained by NMR studies. Herterich et al. (2003,2004) used ¹H NMR combined with GC/MS in the identification and quantification of PNS, PMS and PC compounds present in cement

mortar and concrete and in their leaching solutions. The intensity of signals for ^1H NMR is directly proportional to the concentration of the corresponding protons. The characteristic NMR fingerprints of PNS were $\delta = 7.5\text{-}8.3$ and for PMS $\delta = 3.45\text{-}3.65$ (solvent D_2O). The average molecular weight of PEO side chains and the grafting molar degree in PC can be evaluated by NMR spectroscopy for ^1H (Yamada et al. 2000, Borget et al. 2005).

Miller (1985) used ^{13}C -NMR for detection of branching in PNS. Borget et al. (2005) studied the microstructure of PC by Lorentzian deconvolution of carboxylate and ester peaks obtained by ^{13}C -NMR. The signals relative to the carbonyl functions of acrylic and metacrylic polymers are highly sensitive to the microstructure. PC display two signals: one corresponding to the acid function, the other to ester function. Carboxylic acid peaks are highly sensitive to pH. However, ^{13}C is less suited for quantitative measurements and the low amount of ^{13}C requires a longer analyzing time.

IR combined with DTA and TG

Information about the nature of bonds and functional groups in a compound can be obtained from IR spectra. Yilmaz et al. (1993) used IR, differential thermal analysis (DTA) and thermogravimetry (TG) to study the composition of PNS and PMS and their possible degradation. The characteristic IR absorption bands of PMS were in the range of 1500 cm^{-1} for C-NH-CH, 1335 cm^{-1} for $-\text{CH}_2$, $1190\text{-}1040\text{ cm}^{-1}$ for ionic R-SO_3^- and 810 cm^{-1} for the triazine group in melamine. Absorption bands at 1200 cm^{-1} , 1130 cm^{-1} , 1350 cm^{-1} and 1520 cm^{-1} characterize PNS. Zerbinati et al. (1997) used FTIR for the analysis of possible degradation of PNS and Mannonen (1996) for analysis of the composition of SP in cement paste.

UV-VIS and TOC

Glaus and van Loon (2004) used the total organic carbon (TOC) method to determine the concentration of PNS in cement-water system. This was used in complement with UV-VIS spectroscopy. Measurement of TOC is not a specific method in determining PNS content in solution. TOC results include the amount of SP and the amount of other organic compounds in cement. This gives the upper limit to the amount of SP in cement. Herterich et al. (2003,2004) used also TOC concentrations of the leachates from self compacting concrete (SCC) bodies and Greisser (2002) in his concrete studies. Palmer and Fairhall (1993) studied pore water chemistry of grouts by determining the concentrations of PNS and PMS by TOC.

4 ENVIRONMENTAL STUDIES ON SUPERPLASTICIZERS

There are several studies on the environmental concentrations of superplasticizers, but there is a lack of detailed study on their budget and estimates of leaching amounts especially from concrete structures. The evaluation of budget is difficult since there are in most cases several sources, which make their contribution to the total flow unclear. In addition, before year 2000 typically the total concentrations of superplasticizers have been measured and not the different components, knowledge of which is important because of their different behaviour. The results from literature are collected in Table 4-1. For PNS there are field observations about their leaching and migration in environment, but for PMS less. On the other hand since the PC are quite new admixtures in the concrete industry their environmental occurrence and behaviour have not been reported.

The main sources of these superplasticizers have been industrial (concrete, textile, SP production, etc.), wastewater treatment plants, construction and landfill sites. These environmental studies can give an idea about the behaviour and persistency of different compounds of these admixtures, even though the studies do not handle directly leaching aspects from concrete.

Ruckstuhl et al. (2003) studied the leaching behaviour of PNS from a tunnel construction site of the Swiss Federal Railways. PNS had been used first, but then substituted by PMS. The measurements were made after this change. When fresh cement containing PNS was applied at construction sites in the aquifer, PNS leach out into the ground water. At one site PNS leached to an extent of about 5% of the total applied amount. The maximum concentration found in the ground water was 230 µg/L at a distance of 5-10 m from the construction site. The persistent fraction of the leached PNS was about 20%.

Investigations by Ruckstuhl (2001) and Ruckstuhl et al. (2002,2003) demonstrated that PNS emissions from construction sites into the aquatic environment are rather low. Even under worst case conditions when cement suspensions including PNS were injected into a ground water aquifer for stabilization of the gravel, a mass flux analysis revealed that only 5% of the applied PNS reached the corresponding ground water. The breakthrough period was 320 days. The leached components were the monomers and the oligomers up to the tetramers. Higher condensed oligomers remained immobilized in the cement matrix. Also the tracer experiment with a technical PNS product in a gravel aquifer of the Upper Rhine valley, Germany, demonstrated the low mobility of PNS with three or more NS units in the molecule.

Samples were collected from the textile industry using PNS during clean up of a factory (Ruckstuhl 2001). No mass flux calculations from this were possible to obtain. The product consisted of several mono- and disulphonated monomers and of oligomers up to 17 units. Their relative concentrations reflected the distribution pattern known from superplasticizers. Oligomers with chain lengths of more than 4 units exhibit enhanced adsorption. Most persistent were 1,5-NDS and oligomers.

Lange et al. (2005) studied the PNS concentrations of rivers in Germany. The PNS oligomer concentrations in the aqueous phase decreased with increasing number of naphthalene units. Oligomers with $n > 6$ were detected only sporadically in the water body of the Rhine river. In addition Lange et al. (2005) studied the suspended material, which is the potential source for resorption. In general, persistent NDS and a part of the low molecular PNS fractions up to $n = 5$ have been identified in the water body of European rivers. However, the environmental fate of the higher molecular PNS is so far unknown.

Pojana et al. (2003) have identified some oligomers of PMS in industrial wastewaters. The quantification was based on comparison of the PMS product mixture.

There was one report on experiment of desorption for PC (Jop et al. 1997). In this study polycarboxylic polymer emulsion (50 000-60 000 MW) used in floor finishing was desorbed from domestic sludge following a standard test procedure. CaCl_2 was used as the desorbent twice for 16 hours. K_{des} was 7370, but the standard deviation was high: 6050. The desorption kinetics was slow and levelling was found after 48 hours.

Table 4-1. PNS and PMS (marked in *Italic*) measured in environment according to the literature.

Reference	Site	Sample type	Identified compounds	Compound concentration ($\mu\text{g/L}$ or $\mu\text{g/kg}$) and distance from discharge site (km) in parenthesis
Kok et al. 1997 CE+LIF	Germany	RW Elbe	1,3,5-NTS 1,3,6-NTS	14 (4), 1.5 (475), 1.4 (629) (from Czech border) 31 (4), 3.9 (475), 2.1 (629) (from Czech border)
Menzel et al. 2002 HPLC+UV/DAD+FLD	Landfill site Upper Rhine Valley, Germany	leachate GW	2-NS 1,6-NDS 1,7-NDS 2,7-NDS 2-NS 1,6-NDS 1,7-NDS 2,7-NDS	170 22 22 7.7 29 to 9.5 (~0.35) 6.9 to 8.8 (~0.35) 13 to 4.6 (~0.35) 3.1 to 4.2 (~0.35)
Zerbinati et al. 1994, 1997 HPLC+UV+FAB/MS+spectrofluorimeter	Chemical factory (dyes), Italy Landfill site (chemical industry), Italy	RW Bormida GW (spring normally under RW Bormida)	2-NS 2,7-NDS 1,5-NDS 2-NS 2,7-NDS 1,5-NDS	0.7-17 3.5-15 14-270 558000 1660000 195000
Suter et al. 1999 HPLC+UV+ESI-MS	Landfill sites (mixed) Switzerland	leachate GW	1-NS and 2-NS 1-NS and 2-NS	- -
Wolf et al. 2000	PNS factory, Germany	WW effluent	monomers n=2 n=3	108 77 87

HPLC+UV/DAD +FLD+ESI-MS	Paper mill, Germany	WW	n=4 monomers n=2 n=3 n=4 n=5 n=6	44 2.2 1.7 2.1 2.6 1.0 0.52
		RW Rhine	monomers n=2 n=3 n=4 n=5	2.6 0.86 0.56 0.38 0.10
		BW Rhine	monomers n=2 n=3 n=4 n=5	0.47 0.58 0.34 0.25 0.4
		GW	monomers n=2	0.10 0.15
Crescenzi et al. 2001	Concrete factory, Italy	WW	n=0 n=1 n=2 n=3	0.02 3.2 ~4.3 ~0.3
HPLC+UV+FLD +ESI-MS		GW (below factory)	n=0 n=1	0.05 0.073
		RW Tiber	n=0	0.24

			n=1 n=2 n=3	0.18 0.06 0.011
		RW Piave	n=0 n=1	0.022 0.01
Loos et al. 2000	WW treatment plant, Spain	influent	1-NS 2-NS	75.2 196.9
HPLC+UV/DAD +ESI-MS				
Pocurull et al. 1999	Spain	SW Tarragona	1-NS 2-NS	0.8 0.5
HPLC+ESI-MS				
Storm et al. 1999	Textile factory, Germany	spent dye bath	1-NS, 2-NS, 2,6-NDS, 1,5-NDS, 2,7-NDS, 1,6-NDS, 1,7-NDS	100-2100
HPLC+UV/DAD +ESI-MS		WW	1-NS, 2-NS + 3 different NDS	100-1000
Fichtner et al. 1995	Germany	RW Elbe (5 locations)	2-NS 1,5-NDS 2,6-NDS 2,7-NDS 1,3,6-NTS	0.8-20.8 8.3-47 0.5-1.4 9.4-11.7 40.6-65.2
Riediker et al. 2000	Landfill sites Switzerland	leachate	1-NS 2-NS 1,5-NDS 1,6-NDS 2,7-NDS	<5.8-616 <3.2-1188 <8.3-111 <2.1-397 <2.9-145
HPLC+UV/DAD +FLD+ESI-MS		GW	1-NS	<0.13-17

	WW treatment plant	leachate	2-NS 1,5-NDS 1,6-NDS 2,7-NDS	<0.07-43 <0.1-2 <0.03-12 <0.06-5.7
		effluent	1-NS 2-NS 1,5-NDS 1,6-NDS 2,7-NDS	506-616 1143-1188 <2.5-51 366-397 129-145
		GW	1,5-NDS 1,6-NDS 2,7-NDS	15-22 182-273 88-199 35-74
Ruckstuhl et al. 2002, 2003 HPLC+UV+FLD	Tunnel construction, Switzerland	GW site A (2 weeks after injection)	1-NS 2-NS 2,6-NDS 1,5-NDS 2,7-NDS 1,6-NDS 1,7-NDS dimers trimers	19.4 65.6 6.4 9.1 24 68.8 28.6 10.6 0.25
		GW site A (200 days after injection)	1,5-NDS dimers oligomers	- - -
		GW site B (120 days after injection)	1,5-NDS 1,7-NDS	- -

			dimers oligomers	- -
Lange et al. 1995, 1999, 2005 <hr/> HPLC+UV/DAD +FLD	WW, Germany	WW partial influent	1-NS	250
			2-NS	1700
			1,5-NDS	98
			1,6-NDS	450
			1,7-NDS	230
			2,6-NDS	53
			2,7-NDS	160
			n=1	2900
			n=2	460
			n=3	340
			n=4	240
			n=5	150
			n=6	86
			n=7	74
		WW effluent	1-NS	3.9
			2-NS	25
			1,5-NDS	35
			1,6-NDS	22
			1,7-NDS	92
			2,6-NDS	0.84
			2,7-NDS	57
			n=1	240
			n=2	230
			n=3	160
			n=4	83
			n=5	37
			n=6	14
			n=7	7.5

		RW Kocher	1-NS 2-NS 1,5-NDS 1,6-NDS 1,7-NDS 2,6-NDS 2,7-NDS n=1 n=2 n=3 n=4 n=5 n=6 n=7	0.51 0.5 6.3 2.5 9.7 0.56 6.9 27 49 28 13 5.3 1.8 1.1
		sediment river Kocher	n=3 n=4 n=5 n=6 n=7	4200 36000 73000 51000 46000
<i>Pojana et al. 2003</i>	<i>MS factory</i>	<i>WW</i>	<i>PMS</i>	<i>80000-120000</i>
HPLC+UV+ESI-MS				
Stüber and Reemstma 2004	Tannery factory	WW influent	1-NS 2-NS 2,6-NDS 1,5-NDS 2,7-NDS 1,6-NDS 1,7-NDS	161 1499 23 81 56 93 90
HPLC+UV/DAD+ESI-MS				

		WW effluent	1,5-NDS 2,7-NDS 1,7-NDS	69 48 34
Altenbach and Giger, 1995	Waste treatment plant	WW influent	1-NS 2-NS 2,6-NDS 1,5-NDS 2,7-NDS 1,6-NDS	28 197 5.4 9.4 18 56.7
HPLC+UV		WW effluent	1-NS 2-NS 2,6-NDS 1,5-NDS 2,7-NDS 1,6-NDS	8.9 43 2.1 5.5 6.9 22.2

GW=ground water, WW=wastewater, RW=river water, DW=drinking water, BW=bank water, SW=sea water

5 GRINDING AIDS

In the grinding process, a variety of grinding aids have been used. In Europe different compounds are preferred to those in other countries. Table 5.1 presents the grinding aids and their formulas. There are aliphatic amines such as triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and aminealcohols such as diethanolamine (DEA), triethanolamine (TEA), tri-isopropanolamine (TIPA). Glycol compounds are represented such as ethyleneglycol (EG), diethyleneglycol (DEG). In addition, there are more complex compounds such as aminoethylethanolamine (AEEA) and hydroxyethyl diethylenetriamine (HEDETA). Phenol and phenol-derivates are also used as grinding aids. Other compounds, mentioned in the product data sheets, such as amine acetate, higher polyamines and their hydroxyethyl derivates, are used, but these are undefined in data sheets. Therefore, these compounds are not considered here, only the listed compounds are reviewed and discussed in more detailed.

Table 5-1. Grinding aids

Compound	Abbr.	Formula
Diethanolamine	DEA	$\text{NH}-(\text{CH}_2\text{CH}_2\text{OH})_2$
Triethanolamine	TEA	$(\text{CH}_2\text{CH}_2\text{OH})_3\text{N}$
Triisopropanolamine	TIPA	$[\text{CH}_3\text{CH}(\text{OH})\text{CH}_2]_3\text{N}$
Aminoethylethanolamine	AEEA	$\text{NH}_2-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)-\text{OH}$
Triethylenetetramine	TETA	$\text{NH}_2-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$
Tetraethylenepentamine	TEPA	$\text{NH}_2-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$
Ethyleneglycol	EG	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$
Diethyleneglycol	DEG	$\text{HO}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-\text{OH}$
Hydroxyethyl diethylenetriamine	HEDETA	$\text{NH}_2-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{OH}$
Phenol	-	$\text{C}_6\text{H}_5\text{OH}$

Diethanolamine (DEA), triethanolamine (TEA), triisopropanolamine (TIPA) and aminoethylethanolamine (AEEA)

The commercial formulations of alkanolamines often contain mixtures of mono-, di- and trialkanolamines (Worsfold and Yan 1991). They have the physical and chemical characteristics of both alcohols and amines in one molecule. Diethanolamine and triethanolamine are the simple members of these compounds.

Ethanolamines are used in several industrial applications: in the textile industry, in gas purification processes, as solubilizers for pesticides, as dispersing agents in the application of agricultural chemicals, as emulsifying agents, as catalysts in the production of polyurethanes, in the rubber industry, as corrosion inhibitors, as pigment dispersants and as chemical intermediates for other chemicals products. Isopropanolamine in water is a medium strong base.

Diethanolamine is classified as a hazardous air pollutant (<http://www.scorecard.org/chemicalprofiles/html/diethanolamine.html>). Triethanolamine is used for various reasons in cement industry. Depending on the amount of TEA it behaves differently in the cement production process. At an addition of 0.02% to Portland cement, TEA acts

as a set accelerator, at 0.25% it acts as a mild set retarder, at 0.5% TEA acts as a severe retarder, and at 1% it is a very strong accelerator (Dodson 1990). The acetate of triethanolamine is also one type of grinding aid (Flatt et al. 1998). The mechanism of the action of TEA in cement hydration is not completely understood. TEA is a weak base and in an aqueous phase it is mostly in the molecular state. TEA has the ability to chelate with certain metallic ions such as Fe^{3+} in highly alkaline media (Yilmaz et al. 1993).

Aminoethylethanolamine (AEEA) is one degradation product of ethanol amines (Choy and Meisen 1980). The commercial product of aminoethanolamine can be a pure single compound product instead of the usual mixtures. It is slightly soluble in water (http://www.huntsman.com/performance_products/index.cfm?PageID=1317, <http://www.chemicaland21.com/industrialchem/organic/AMINOETHYLETHANOLAMINE.htm>).

Triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and hydroxyethyl diethylenetriamine (HEDETA)

Ethyleneamines TETA and TEPA are used as asphalt additives, as corrosion inhibitors, as epoxy curing agents in the hydrocarbon purification, as surfactants, as dispersants, as chelating agents, as catalysts, as textile additives and fuel additives (<http://www.Huntsman.com>). The commercial products of TETA and TEPA are often mixtures of alkanamines and not single, pure compounds. TEPA is completely miscible in water and is not biodegradable. Hydroxyethyl-diethylenetriamine (HEDETA) is very soluble in water.

(http://www.delamine.com/SDS_ENG/SDS_TETA_GB.pdf, http://www.huntsman.com/performance_products/index.cfm?PageID=1317, http://www.jetoc.or.jp/HP_SIDS/pdf/files/112-57-2.pdf).

Glycols

Glycols are also used as raw material for the production of plasticizers and polyester resins, humectants, textile lubricants and coupling agents. Large volumes of ethylene glycol are consumed as automobile engine antifreeze/coolant. Diethylene glycol (DEG) is used as a dehydrating agent for natural gas for its hygroscopicity. In addition, glycols are used for the production of alkyl-type resins. Glycol is a dihydric alcohol where two hydroxyl groups are bonded to different carbon atoms; the general formula for glycol is $(\text{CH}_2)_n(\text{OH})_2$. The most important glycol is the simplest, ethylene glycol (EG). Ethyleneglycol and triethyleneglycol (TEG) are biodegraded mainly to acetate, ethanol and ammonium (Mrklas et al. 2003).

Phenols

Phenol is used primarily in the formation of phenolic resins. It is also used in the manufacture of nylon, resins and synthetic fibers, in slimicides, as a disinfectant, as an antiseptic, and in medicinal preparations. Phenol is also formed during the natural decomposition of organic material. Phenol has a limited solubility in water. Phenol and monosubstituted phenols typically have a pK_a in the range 9-11 (Janusa et al. 1993).

The phenol molecule has weak tendencies to lose the H^+ ion from the hydroxyl group, resulting in the highly water-soluble phenolate anion $C_6H_5O^-$. Compared with aliphatic alcohols, phenol shows higher acidity. The properties and behaviour of phenols are affected strongly by its aromatic nature. The group of compounds called phenols cover a wide range of compounds including monohydric, dihydric and polyhydric derivatives of benzene (<http://www.stl-ltd.com/downloads/Phenols.pdf>). Phenols and especially chlorophenolic compounds are environmental pollutants. As a consequence, the safe limit of phenol in drinking water have been stated by the U.S. EPA as well as by the EU.

6 ANALYSIS OF GRINDING AIDS

6.1 General aspects

Grinding aids have been studied scarcely. Therefore, here we also present some methods that have been tested to be suitable for certain low-molecular-mass aliphatic amines, glycols and phenols, but not specifically for the grinding compounds and in cement/concrete matrixes. More specific testes should be done to find the optimal analyzing conditions of these methods.

Amines are difficult to analyze and in most cases they are derivatized before detection. In earlier studies, wet-chemical methods were used for amine analysis (ASTM C465). Grinding aids containing amines were measured by oxidation of the amines to ammonia, followed by nesslerization and colorimetry. A method for ethylene glycol content in Portland cement involved aqueous extraction, conversion of glycol to formaldehyde and reaction with chromotropic acid following the measurement of the product. Acetates of cement additives were measured after phosphoric acid extraction followed by concentration and gas chromatography-analysis (Hime et al. 1966).

The determination of low-molecular-mass amines especially by chromatographic techniques has been documented from various areas including water, air, food and clinical analyses. However, few methods and exact environmental studies have been reported on grinding aids. The low contents of these compounds in environmental samples and, especially, in waters (below the microgram-per-liter level) call for suitable analytical methods (Cobo and Silva 1999). Trace determination of hydrophilic compounds in aqueous matrixes is more difficult than the analyses of hydrophobic compounds. The typical preconcentration steps useful for hydrophobic compounds such as solid phase extraction (SPE) or liquid-liquid extraction (LLE) from water to a nonpolar solvent may fail often because of too low recoveries (Holčápek et al. 1999).

Aliphatic amines

Liquid chromatography (LC) is one of the most frequent techniques for the analysis of aliphatic amines in aqueous media (Moliner Martinez et al. 2004). Because they have low absorptivity, however, their determination requires prior derivatization. Most primary and secondary amines exhibit poor chromatographic performances via direct high performance liquid chromatography (HPLC) approaches. Methods for their determination require a high degree of specificity and sensitivity as they do not exhibit any structural feature that allows detection without derivatization. All existing LC methods for amine determination require at least two steps: separation from potential interferents in the sample and pre- or post-column formation of derivates with better detectability (Sahasrabudhey et al. 1999). The detection methods for secondary amine compounds are more complicated than those for primary amine compounds. Tertiary amine compounds cannot be detected by the derivatization method because of the absence of a hydrogen atom on the nitrogen atom (Niina et al. 2005).

There are major drawbacks in triethylenetetramine (TETA). First, owing to its basicity it is difficult to chromatograph by LC. Second, its detection sensitivity by a UV detector is low because of the lack of UV-absorbing groups (Winkler et al. 1988). Aliphatic amines have been determined by gas chromatography (GC). However, their chromatographic separation is hindered by the polarity of the amine group, which interacts strongly with silane groups and siloxane bridges in the column; this gives rise to asymmetric peaks and decreased sensitivity. Therefore, modifications in the procedures are required. These amines have also been determined by capillary electrophoresis (Santos et al. 2004).

Alkanolamines

Analysis of the alkanolamines and their reaction products is complicated by their tendency to fairly low vapour pressures, decomposition at elevated temperatures and high polarities. Most of the available methods are not suited to trace analysis. The reversed-phase high performance liquid chromatography (RP-HPLC) and ion chromatography (IC) methods are the most applicable to direct analysis since they are compatible with aqueous samples and polar water-soluble analytes. These methods use UV, CL, conductivity or pulsed electrochemical detectors to give the instrumental detection limits of 1 g/L to 40 g/L by direct analysis. Efficient separations have been achieved using organic resin-based ion chromatography (IC) phases in reversed-phase or mixed reversed-phase IC modes in which the ionization of the alkanolamines is suppressed using high pH conditions, and are resolved by a reversed-phase retention mechanism.

While the direct gas chromatography (GC) analysis of aqueous alkanolamine solutions has been demonstrated, most analyses by GC/MS require extraction and/or derivatization of the alkanolamines to improve chromatographic behaviour, detectability or to aid in the determination of the number of hydroxyl groups.

RP-HPLC with thermospray (TSP) interface has been used to detect primary, secondary and tertiary amines in water. Under soft ionization conditions, alkanolamines give intense MH^+ ions with little or no fragmentation, which are well suited for MS/MS analyses (Headley et al. 2002)

Diethanolamines (DEA) have been widely used in the gas processing industry and many analytical methods have been reported for them and their degradation products such as wet chemical techniques, IR and UV spectroscopy and paper- and TLC. However, they all suffer from various disadvantages such as poor accuracy, specificity, reliability and simplicity. Later derivatization and water stripping have been found to improve the methods (Kennard and Meisen 1983). Derivatization was performed with salicyl aldehyde to form Schiff bases followed by separation for GC. Earlier, distillation and titration were used to determine DEA in epoxy resin hardeners (Bauer and Richter 1981, Winkler et al. 1988).

Glycols

Enzymatic, fluorimetric or colorimetric methods for the determination of ethylene glycol (EG) after its oxidation to formaldehyde are nonspecific according to Holčapek

et al. 1999. GC assay is more specific, but problems with peak tailing and carryover effects have been observed (Aarstad et al. 1993, Holčapek et al. 1999). The limits of detection and quantitation of 0.5 and 2 mg/L have been reported respectively for the GC determination of EG and for the GC assay of glycols after phenyl boronate derivatization (Houzé et al. 1993, Holčapek et al. 1999). In addition, glycol analyses of water samples carried out by GC demonstrated interferences due to salt precipitation in inlet ports and resulted in inconsistent quantification (Hong et al. 1999, Mrklas et al. 2003).

Phenols

Total phenol concentration can be determined using colorimetric procedures. These methods can suffer interferences and are more suitable for screening purposes

(<http://www.mfe.govt.nz/publications/hazardous/gas-guide-aug97/gas-3-aug97.pdf>).

Phenols can be directly analysed by GC or LC and detected by FID, MS or electrochemical methods. For derivatization of pentafluorobenzoyl chloride, methyl ethers and acetates prior analysis is common in many standard methods (<http://www.chiron.no/html/phenol2005/phenols.pdf>).

6.2 Extraction, enrichment and derivatization

Owing to the low concentration levels of grinding aids in environmental samples, enrichment is often necessary. Typical liquid-liquid extraction (LLE) is very difficult and time-consuming when the samples are of high polarity and high water solubility such as aliphatic amines (Moliner Martinez et al. 2004, Verdú-Andrés et al. 2001).

Size exclusion chromatography (SEC) has been used in the clean-up and enrichment of low levels of phenols in soil (<http://www.mfe.govt.nz/publications/hazardous/gas-guide-aug97/gas-3-3aug97.pdf>).

6.2.1 Solid-phase extraction (SPE)

Enrichment by liquid-liquid extraction (LLE) has traditionally been the technique of choice for the trace determination of low-molecular-mass amines by GC. On the other hand, when the amines are determined by HPLC or capillary electrophoresis (CE) enriching by SPE has proved a more efficient choice. For the enrichment of these amines different columns and materials have been used (Cobo and Silva 1999). The most common choice is a C18 column.

Meseguer Lloret et al. (2002) used precolumn preconcentration on Bond Elut C18 SPE of low-molecular-mass aliphatic amines in water samples. They studied the precon-

centration conditions. Also Moliner Martinez et al. (2004) and Verdú-Andrés et al. (2001) have used this column for enrichment and purification. Later Mesequer Lloret et al. (2004) used a Bond Elut Varian C18 column. Cobo and Silva (1999) used SPE in an on-line chromatographic system to determine low-molecular-mass amines (aliphatic amines with 1 to 7 carbon atoms) in environmental water. A weakly acidic cation-exchange column IRC-50 was used for preconcentration. Matchett and Brumley (1997) used preconcentration based on SPE of aliphatic amines (C1 to C4) and alkanolamines in water before capillary zone electrophoresis (CZE) analysis.

Nishikawa and Kuwata (1984) collected air samples of amines on SP cartridges Sep-PAK C18 and the collection efficiency was 87-100%. They noticed that the recovery of different amines was somewhat different at extremely low levels.

For phenols, the C18 cartridges and graphitized carbon have been applied (Rodríguez et al. 1997, Tsukagoshi et al. 2002). Rodríguez et al. (1997) concentrated phenols from drinking water with Isolute Env+polystyrene cartridges which allowed 1 L water volumes to be concentrated rapidly with good recoveries. Graphitized carbon was unaffected by the ionic strength of the water sample (Di Corcia et al. 1993).

6.2.2. Derivatization reagents

The main difficulty with the chromatography of grinding aid substances is their detection without chemical derivatization. It is often necessary to increase the detection sensitivity and improve selectivity by derivatization.

Aliphatic amines

Mesequer Lloret et al. (2002) and Sahasrabuddhey et al. (1999) reviewed the derivatization reagents used for aliphatic amines. In Table 6-2 there is an updated compilation of different derivatization reagents and the studied compounds. Studies concerning air samples are also included. In these studies, the compounds were often collected or removed to a water phase and therefore they are considered suitable methods also for water analyses dealing with grinding aids.

The factors involved in the selection of derivatization reagent are the kind of sample, its structure (primary, secondary or tertiary), its sensitivity and/or selectivity, the detection system and the way in which derivatization is performed before (precolumn), during (on-column) or after (post column) the chromatographic separation (Moliner Martinez et al. 2004, Niina et al. 2005).

Derivatizing reagents commonly used include 5-dimethylaminonaphthalene-1-sulfonyl chloride (dansyl chloride), o-phthalaldehyde (OPA), 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole (NBD-Cl), and 9-fluorenylmethyl chloroformate (FMOC) (You et al. 1999). Reagents such as FMOC, 1,2-naphthoquinone-4-sulfonate (NQS), 3,5-dinitrobenzoyl chloride (DNB-Cl) or dansyl chloride (DNS-Cl) have been proposed for derivatization of amino acids, and primary and secondary amines. With secondary amines there is no reaction with OPA and fluorescamine gives a non-fluorescent product. Many reagents

require high temperatures and a prolonged period for derivatization. Volatility of aliphatic amines may require special handling.

The common OPA reagent offers greater sensitivity and more selectivity, but is limited to primary amines. Reactions with OPA in combination with a thiol such as N-acetylcysteine (NAC) produce a highly fluorescent product in relatively short time.

The principle limitation of OPA derivates is their instability (Moliner Martinez et al. 2004, Verdú-Andrés et al. 2001).

FMOC derivates have good UV adsorptions and very high sensitivities with laser induced fluorescence detection, but the derivatization solution must be extracted away because the excess of derivatization reagent interferes with the separation of amino acid derivates and is detrimental to column performance (You et al. 1999).

Meseguer Lloret et al. (2002) used precolumn preconcentration and derivatization of low-molecular-mass aliphatic amines in water samples with DNS-Cl as derivatization reagent. They studied the chromatographic conditions in detail. Moliner Martinez et al. (2004) used precolumn Bond Elut C18 for extraction and for the preconcentration. For on-line derivatization they used a Hypersil ODS-C18 column.

Sacher et al. (1997) used 2,4-dinitrofluorobenzene (DNFB) and benzenesulfonyl chloride (BSC) for analysis of aliphatic amines by GC/MS. Both derivates have been found to be very stable. These are suitable for primary and secondary amines, but not for tertiary amines.

Aminoalcohols

Primary and secondary aminoalcohols as well as diamines form derivates with DNFB and BSC derivatization agents, but only the amino group reacts (Sacher et al. 1997). The derivates of alcoholamines and diamines with BSC are too polar to be extracted from water by dichloromethane. The 2,4-DNFB derivates of diethanolamine can be extracted, but recovery is poor and the GC separation of the respective compound is incomplete. Diamines can neither be analyzed by derivatization with 2,4-DNFB nor with BSC (Sacher et al. 1997).

Glycols

Holčapek et al. (1999) postulated that derivatization of ethyleneglycol (EG) with benzoyl chloride has several advantages: 1) decreased polarity of the derivates facilitating SPE preconcentration, 2) derivatization of diol groups improves chromatographic behaviour, 3) better detection due to the incorporation of two strong chromophores, 4) increase in the molecular masses of derivates improves the signal to noise ratio with ESI-MS detection. They used the Schotten-Baumann method of the benzoylation of glycols in aqueous solutions.

Phenols

Phenols can be derivatized prior to analysis by pentafluorobenzoyl chloride or bromide or they can be derivatized to methyl ethers or acetates (<http://www.chiron.no/html/phenol2005/phenols.pdf>). Tsukagoshi et al. (2002) derivated phenolic compounds with dansylchloride together with peroxyoxalate. The derivate was detected by chemiluminescence.

6.3 Separation methods

6.3.1 Liquid chromatography (LC)

Amines

Liquid chromatography (LC) and more recently capillary electrophoresis (CE) have been more frequently used than gas chromatography (GC) for the determination of the amines in environmental waters (Cobo and Silva 1999). Most aliphatic amines show poor chromatographic properties in typical LC systems (e.g. under reversed-phase conditions) without derivatization (Verdú-Andrés et al. 2001). Glycols are very polar and would be only weakly retained so that their separation from high concentrations of the inorganic salts in reversed-phase systems would be much more difficult without derivatization (Holčapek et al. 1999). Capillary electrophoresis and gas chromatography have been used in detemining phenols in environmental samples.

The most popular column type is C18 RP and sometimes mixed columns with C8. There are several trade names for these columns. The most recent column choice was Niina et al. (2005) who used a TSK-Gel SP-5PW column in their HPLC system.

Cobo and Silva (1999) used on-line chromatography to determine low-molecular-mass amines (aliphatic amines with 1 to 7 carbon atoms) in environmental water. After elution of the SPE column, the sample was derivatized with DNS-Cl to a C18 Nova-Pak analytical column.

Henriks-Eckerman and Lajjoki (1985) used ion-pair HPLC for analysis of TETA (triethylenetetraimne) and TEPA (tetraethylenepentamine). They used a Spherisorb 5 ODS reversed-phase column. The precision of the method was satisfactory at the concentration of 10 µg/ml or more. Flatt et al. (1998) used reversed phase HPLC to study the acetate of triethanol amine using a RP18 column. The other lower molecular mass amines did not have sufficiently strong interactions to adsorb and could not be identified. Crea et al. (2005) studied the chromatographic behaviour of open-chain polyamines in seawater by HPLC.

Aminoalcohols

Worsfold and Yan (1991) separated ethanolamine, diethanolamine and triethanolamine by ion pair chromatography on an ODS column. The post-column conditions and derivatization were optimized using a flow-injection manifold (FIA). Earlier LaCourse

et al. (1989) used the same separation method, but then used a pulsed amperometric method for detection.

Different ionization methods, APCI (atmospheric pressure chemical ionization) and ESI (electrospray ionization), for MS detection have been used in connection with HPLC. Chua et al. (2006) determined triethanolamine from spiked water and decontamination solutions by LC-MS-ESI using a mixed mode with embedded ion-pairing group Primesep 100 column. The column provides chromatography under reversed phase conditions, which are compatible with ESI-MS. The resolution was greatly improved in comparison to the chromatogram on the C18 column. The TEA was detected at 150 m/z ion and 132, 114, 88 and 70 m/z fragment ions.

Headley et al. (2002) used ion-exchange LC with guard and analytical OmniPack PAX-500 columns for alkanolamines in groundwater. However, one should be aware of possible interferences from glycols and glycolamines, since these contaminants also lose water during collision-induced dissociation (CID). A mass resolution of 1300 for the selection of the (MH^+) ion is generally needed to ensure sufficient discrimination between alkanolamines and glycols that may be present (Headley et al. 2002).

Black and Read (1997) used HPLC-APCI with a HiChrom RPB column packed with C8/C18 and a guard column. They studied triethanolamine and diisopropylaminoethanol from the degradation products of chemical warfare.

Glycols

Benzoyl substituents of low polarity considerably enhance the selectivity of separation of derivatives of individual glycols with respect to the separation of underivatized compounds. Underivatized glycols are very polar and would be only weakly retained so that their separation from high concentrations of inorganic salts in reversed-phase systems would be much more difficult than with their dibenzoyl esters. The salts would interfere not only with ESI-MS but also with UV detection. Holčápek et al. (1999) separated the derivatives in a reversed-phase HPLC system on a Capcell Pack C18 microcolumn.

In principle, it is possible to separate glycol derivatives by HPLC directly in a reaction mixture after derivatization, as the salt would be eluted close to the column dead volume and would not interfere with the determination of glycols. However, the excess of a benzoyl chloride derivatization reagent and the reaction byproducts would be retained more strongly and may interfere with the determination, as their concentration in the reaction mixture could be several orders of magnitude higher than the concentration of the dibenzoylglycols. Therefore, pentane extraction is recommended. The recovery of approximately 40% was reproducible under the conditions used for samples with different concentrations of EG. The incomplete recovery under these conditions necessitated the addition of a suitable internal standard (phenol) before derivatization for a reliable quantitation (Holčápek et al. 1999).

In HPLC separation a Dionex HPIC-AS1 ion exclusion analytical column protected by a NG1 guard column was used for triethyleneglycol separation in biodegradation studies by Mrklas et al. (2003).

Phenols

Achilli et al. (1995) used reversed phase C18 HPLC column with a combined gradient of organic modifier and counter-ion for analysis of phenols in water.

6.3.2 Gas chromatography (GC)

GC of solution samples

Amines

Liquid-liquid extraction (LLE) is usually done before GC (Pietsch et al. 1996). Sacher et al. (1997) used dichloromethane for clean-up extraction and to get the amines to organic media before GC. Nishikawa and Kuwata (1984) reported that amine isomers are difficult to separate by GC.

Sacher et al. (1997) reported detection limits lower than 100 ng/L for primary and secondary aliphatic amines with BSC and 500 ng/L for 2,4-DNFB with GC/MS in surface waters and industrial waste waters. Choy and Meisen (1980) used GC to determine DEA and its degradation products from aqueous solutions. The technique consists of removing water by air stripping, silylating the residue with N,O-bis-(trimethylsilyl)acetamide and separating the silylation products with OV-17 Chromosorb W HP column.

Ng (1984) determined after tert-butyldimethylsilyl (TBDMS) derivatization ethylenediamine, diethylenediamine, triethylenetetramine and tetraethylpentamine by GC-MS. A Chromosorb W HP column was used for separation. The different linear isomers could be differentiated by the peak at 301 m/e present only in the electro ionization (EI) spectra of the trisilylated derivatives of the linear isomers.

For GC-MS analysis the aqueous extractant can be concentrated on dryness and the hydrolysis products converted to trimethylsilyl (TMS) or tert-butyldimethylsilyl (TBDMS) derivatives. Derivatization, particularly to silyl derivatives, can result in a large variability in the apparent recovery, particularly in cases where large amounts of extraneous material are co-extracted or are in the presence of divalent metal ions such as calcium (Black and Read 1997, Black et al. 1994).

A few analyses of amines without derivatization have been performed. Dawodu and Meisen (1993) analysed fresh and chemically degraded alkanolamines in aqueous solutions by GC-FID without derivatization. They separated from gas treatment plant solutions MEA, DEA and TEA in the presence ethylene glycol. The sensitivity range was from 0.01 to 0.05 M.

McCall and Mannone (1975) made analysis of cement pastes for triethanolamine by GC and IR. They suggest that triethanolamine-cement reaction occurred during hydration. They provided only qualitative information.

Glycols

Traditionally, glycol determination can be carried out by GC-FID and HPLC techniques (Mrklas et al. 2003, Holčapek et al. 1999, Houzé et al. 1993). High salt concentrations in water samples may interfere with GC analyses using FID detection (Livesey et al. 1995). Furthermore, carryover and ghost peaks of TEG analyses by GC-FID have been reported (Aarstad et al. 1993).

Sheffield et al. (1987) determined leachability of EG by the EPA extraction procedure using GC for determination. EG was added in organic to cement weight ratios of 1:5, 1:10 and 1:25. EG samples were found to be easily leachable, with > 80% recovery after 28 days by extraction with water.

Phenols

Phenols have been analysed by GC in EPA and ISO methods from different water samples. Low molecular weight alkylphenol etoxylates have been determined by GC-MS and higher molecular weight ones with HPLC. GC combined with FID is used for aquatic solutions (<http://www.chiron.no/html/phenol2005/phenols.pdf>).

Vipulandan and Krishnan (1993) investigated the leaching of solidified phenol-Portland cement mixtures cured for up to 6 months using the Toxicity Characteristic leaching Procedure (TCLP) test recommended by the US EPA. Phenol was solidified with cement at concentrations of 0.5% and 2%. XRD studies and porefluid analyses by GC indicated that the quantity of phenol leached was dependent on the initial phenol concentration and the curing time. In column leach studies by Kolvites and Bishop (1989) phenol was found to be very mobile. The Portland cement pastes were solidified with 4 g/L phenol at a 0.5 liquid to cement ratio. The cement was cured for 3 days and 28 days. Purified water was pumped through the column and the leachate was analyzed by GC.

GC and thermal desorption

Studies of hardened Portland cement mortar, clinkers and concrete paste by Jeknavorian (1999) and Jeknavorian et al. (1998a, 1998b, 1999) suggest that only phenol-based cement grinding aids and glycol-ether shrinkage reducing admixtures (SRA) could be quantitatively measured by simple thermal desorption. *In-situ*-pyrolytic derivatization using BSTFA-TMCS reagent enabled the only qualitative determination of glycols and alkanolamines in Portland cement. Thermal desorption (TD) was performed with the CDS 2000 pyroprobe with insertion into the CDS 1500 interface, and the pyrolysates were chromatographed on a HP-INNOWAX (cross linked polyethylene glycol) column.

Portland cement clinkers were interground with 100-800 ppm by weight of triethanolamine, diethanolamine, diethylene, glycol, propylene glycol and phenol. Most

of the additives tested were recovered at greater than 85% of their originally added concentration. However, the yields were lower in the cases of longer and more intense grinding procedure. The formation of salts or stable complexes was proposed for the explanation of low yields. DEG and TEA were not detected. The BSTFA-TMCS derivatization improved the recovery of the following compounds:

Table 6-2. Derivatization reagents

Reagent	Compound	Detection method	Reference
DNS-Cl + TCPO + H ₂ O ₂	aliphatic amines	CL, UV, FLD	Meseguer Lloret 2004, 2002
DNS-Cl	TETA, TEPA	UV, FLD	Henriks-Eckerman and Laijoki 1985
DNS-Cl	aliphatic amines C=1-7	CL	Cobo and Silva 1999
1)trichloroethyl carbamates 2) 9-fluorenylmethyl carbamates	aliphatic amines	1) GC/MS 2) HPLC/FLD	Pietsch et al. 1996
1) DNFB 2) BSC	prim. & sec. aminoalcohols	GC/MS	Sacher et al. 1997
DNB	aliphatic amines	UV	Verdú-Andrés et al. 2001
FDNB	TETA, DEA	fluoride-selective electrode	Athanasiou-Malaki et al. 1989
fluorescamine	TETA	spectrofluorimetry	Nakano et al. 2002
salicyl aldehyde (Schiff bases)	polyaminoamides and polyamines	SEC	Bauer and Richter 1981
salicyl aldehyde (Schiff bases)	DEA+degradation products	GC, FID	Kennard and Meisen 1983
DOOB	TETA,TEPA,EA, prim. amino groups of higher homologues	UV, fluorimetry	Winkler et al. 1988
TBDMS	TEPA, TETA, ethylenediamine, diethylenedi?amine	GC	Ng 1984
AAHS	several amines and ethylamine, not TEA	spectrofluorimetry	You et al. 1999
NBD-Cl	ethylamine, dimethylamine etc.	spectrofluorimetry	Nishikawa and Kuwata 1984
Benzoyl chloride (Schotten-Baumann)	Glycols	ESI-MS	Holčapek et al.1999
TBDMS, TMS	TEA, diisopropylaminoethanol	HPLC-APCI	Black and Read 1997
phenylthiourea	aliphatic amines.	UV	Sahasrabudhey et al 1999
PSE	TETA		Nakano at al 2002
naphthylacetic anhydride	Polyamines	FLD	Wu and Gaind 1992
m-tolyoul chloride, benzoyl chloride	TEPA, TETA	UV	Duong et al. 1991a,b
trifluoroacetic anhudride	amines with active H	F-19 NMR	Musha and Nagata 1981
OPA-NAC	prim. Aliphatic amines (short chained) amines	UV	Moliner-Martinez et al. 2004 Oguri et al. 1997
BSTFA-TMCS	DEA+degradation products	FID	Choy and Meisen 1980
BSTFA-TMCS	glycols, alkanolamines	Py-GC/MS	Jeknavorian et al.
isothiocyanate	aliphatic amines	UV	Sahasrabuddhey et al. 1999
fluorescein isothiocyanate	aliphatic amines	CE	Brumley and Matchett 1995, Brumley and Kelliher 1997, Dabek-Zlotorzynska and Maruszak 1998
FMOc	aliphatic amines	FLD	Verdú-Andrés et al. 2001
Ru(bpy)3)3 epichlorohydrin	DEA	CL	Niina et al. 2005
pentafluorobenzoyl chloride or bromide	Phenols	GC-FID, GC-ECD	http://www.chiron.no/html/phenol2005/phenols.pdf , ISO method 8165-2 : 1999, EPA method 604

phenol, ethylene glycol (EG), diethylene glycol (DG), propylene glycol (PG), triethanolamine (TEA).

Various pyrolysis temperature programs were investigated to maximize the desorption of the additives from the cement. Only trace levels (< 3 ppm) of diethylene glycol could be detected. They suggested that this is due to either irreversible adsorption through the formation of nonvolatile complex, or decomposition of diethylene glycol to other compounds during pyrolysis (Jeknavorian et al. 1998). The polar grinding aid compounds are desorbed with difficulty from cement; these could not be detected directly by pyrolysis

6.3.3 Thin layer chromatography (TLC)

Kalinichenko and Matveeva (1994) determined simultaneously triethylenetetramine (TETA) and tetraethylenepentamine (TEPA) from a spiked solution by spectrophotometry and by thin layer chromatography. Ghos and Whitehouse (1988) used TLC with spectrofluorometer in the determination of primary and secondary amines and amino acids in biological samples.

6.3.4 Other separation methods

Capillary electrophoresis (CE)

Corradini et al. (1995) studied the effects of alkylamines on electro-osmotic flowing (EOF) capillary electrophoresis. They followed the behaviour of triethylamine and triethanolamine in fused-silica capillaries. According to them the differences in the electro-osmotic flow may reflect differences in the adsorbability of closely related alkylamines, which is believed to depend on their specific adsorption energy and molecular size.

Brumley and Matchett (1995, 1997) determined aliphatic amines, such as triethanolamine and diethylamine, in environmental matrices by capillary zone electrophoresis (CZE). In solid phase extraction (SPE) they used SCX cartridges, C18 extraction disks with ion-pairing or cation extraction disks. The studied cation extraction disks gave poor recoveries. The limits of detection (LOD) for triethanolamine and diethylamine were 0.018 mmol and 0.039 mmol, respectively, using laser induced fluorescence detection (LIF) with ex 488 nm and em 520 nm wavelengths. The limitations reported included the derivatization of matrix coextractives and by-products of fluorescein isothiocyanate derivatization for ng and sub-ng amounts of amines. According to the authors, CZE with UV in indirect mode is particularly powerful at being able to detect primary through quaternary amines without derivatization.

Oguri et al. (1997) determined aliphatic amines in raw fish by high performance capillary electrophoresis (HPCE) with on-line mode in capillary derivatization using o-phthalaldehyde (OPA)/N-acetylcysteine (NAC) with fluorescence detection.

Phenols have been analyzed by CE, especially chlorophenolic compounds in environmental waters. The detections have been performed with FLD, DAD, AD and

CL (Arundell et al. 2000, Rodríguez et al. 1997, Wang et al. 2000, Tsukagoshi et al. 2002). Nonaqueous capillary electrophoresis was applied to alleviate electrode fouling compared to aqueous buffers (Luong et al. 1999). Recently microchips have been used to overcome this problem (Wu and Lin 2006). Zeeman and Volgger (1997) used coelectroosmotic capillary electrophoresis with cetyltrimethylammonium bromide as a pseudostationary phase and acetonitrile as an organic modifier to analyze various mixtures of phenolic compounds. Pfeifer et al. (1983) determined directly phenols from industrial waste waters using isotachopheresis (ITP). ITP is an electroseparation technique based on differences of migration velocities of analytes in an electrical field. The detection limit was 0.1 ppm.

Capillary electrochromatography (CEC)

This is a hybrid technique between capillary electrophoresis and capillary HPLC. One of the main problems of CEC is the low sensitivity achieved with its UV detector. By combining CEC with MS, this is overcome as shown by Santos et al. (2004). They studied low-molecular-weight aliphatic amines in surface and tap water by coupling with ESI-MS. The electrophoretic capillary was constructed from a monolithic silica electrochromatographic column bonded with octadecylsilica (ODS) and a fused-silica capillary. One of the most influential parameters was the composition of the sheath liquid, which could affect the performance of the CE separation circuit, the stability of the electrospray, and the ionization process.

Ion chromatography (IC)

Crea et al. (2005) used a Dionex IonPac CS14 cation-exchange column as the analytical column and an IonPac CG14 as a guard column with an ion chromatographic analyzer. The exchanger in these columns was an ethylvinylbenzene, carboxylate-functionalized copolymer. The limits of detection (LOD) were 0.2 $\mu\text{mol/L}$ for TETA and TEPA. The method allows the direct injection of the sample into the analytical column without preliminary separation or pretreatment.

Ion-exchange LC-MS-ESI was used for the determination of selected alkanolamines in wetland vegetation exposed to sour-gas contaminated groundwater (Headley et al. 1999). No further cleanup, preconcentration or derivatization steps were used. Quantification was performed using either selected ion monitoring of the protonated molecular ions (MH^+) or the loss of water transition in product ion scans. Instrumental detection limits were attainable in the picogram range (20-40 pg) for diethanolamine and triethanolamine. The detection limit was a factor of 5 lower than for a conventional ion chromatography method.

Page et al. (2005) did IC analysis of ethanolamine and triethanolamine in concrete/cement paste pore solutions and digests. Characterization was carried out by pulsed amperometry. Dionex analytical and guard columns CS14 and CG14 were applied. The limit of detection (LOD) was 0.5 μM .

Tanaka et al. (1996) used ion-exclusion chromatography of diethanolamine and triethanolamine on an anion-exchange PS-DVB resin in the OH^- form and with HPLC.

The method was suitable for the separation of organic weak bases such as aliphatic amines.

Size exclusion chromatography (SEC)

Bauer and Richter (1981) studied the SEC method to determine polyaminoamides and polyamines (diethylenamine). These reacted with salicylaldehyde to form Schiff bases, which were further separated by SEC. Only primary amino group reacted. Their column was packed with Bio-Beads SX-2. This method was time consuming as it took 16 hours to complete it.

6.4 Detection methods

Generally, amines exhibit very low responses towards common LC detectors such as UV and FLD. Most of the methods used for amine analyses incorporate a derivatization reaction to increase the sensitivity of the analysis (Moliner Martinez et al. 2004).

6.4.1 UV/VIS, DAD and IR

UV/VIS and DAD are common detection techniques to determine the various derivatives of amines, glycols and phenols. However, UV detection is subject to interference from coexisting UV-absorbing organic compounds and this must be taken into account when conclusions are made from complex matrices.

Amines

Sahasrabudhey et al. (1999) detected UV-absorption by ethylamine and diethylamine at 240 nm in analysis of river water, groundwater and tap water. LOD for amines were in the range 0.3-0.6 µg/L. For UV detection monitoring of the DNS-Cl derivatives the 333 nm wavelength has been used (Meseguer Lloret et al. 2002). Henriks-Eckerman and Laijoki (1985) detected dansylated derivatives of TETA and TEPA at 365 nm. Verdú-Andrés et al. (2001) determined the DNB derivatives of aliphatic amines in tap water and river water at 230 nm. The limits of detection were 2-5 µg/L. Flatt et al. (1998) studied acetate of triethanol amine in concrete leachate using UV/DAD after HPLC separation.

Winkler et al. (1988) made a quantitative determination of free primary amines in polymeric hardeners by measuring 2,2-diphenyl-1-oxa-3-oxonia-2-boratanaphthalene (DOOB) derivatives of TETA and TEPA by UV-absorption at 234 nm.

Pauri et al. (1986) used UV to determine the TEA content in the aqueous phase of cement. Yilmaz et al. (1993) criticized the results of Pauri et al. (1986) for the lack of experimental details. Yilmaz et al. (1993) did not observe any UV response from TEA or the complex with ferric ion. Therefore, Yilmaz et al. (1993) developed a method based on the measurement of concentration of TEA-Fe³⁺ complex in high alkaline medium (pH > 12) by polarography and then applied this method to the TEA-3CaO*Al₂O₃-CaSO₄*H₂O-H₂O system.

Kalinichenko and Matveeva (1994) determined simultaneously triethylenetetramine and tetraethylenepentamine from a spiked solution by spectrophotometry and by TLC. They measured the optical density after 1 h at 500 nm and 625 nm. After adding EDTA the optical density was measured after 2 min at 500 nm and after a further 1 min at 625nm.

Nishikawa and Kuwata (1984) derivatized aliphatic amines with NBD-Cl to produce fluorescent substances which were measured by spectrofluorimetry at ex 470 nm and em 530 nm. The apparent fluorescence intensity of the amines reached a maximum within 24 hours and was constant for a week. The detection limits for ethylamine and diethylamine were 0.1 and 5.0 pmol, respectively.

Alcoholamines

Tanaka et al. (1996) detected ethanolamines, diethanolamine and triethanolamine, after HPLC separation by UV at 200 nm. It is well-known that UV detection at 200 nm is subject to interference from coexisting UV-absorbing organic compounds. Therefore conductometry was applied to confirm the UV-measurements. The detection limit for diethanolamine and triethanolamine were 40 μ M and 20 μ M.

Glycols

A method developed by Holčapek et al. (1999) offers a 10-fold improvement to earlier HPLC assay with UV detection after the derivatization of glycols with benzoyl chloride: the LOD is 1 mg/L. As the benzoyl moieties strongly absorb in the UV region, UV detection is suitable for these derivates. The UV detection of EG was performed at the 237 nm wavelength.

Phenols

Hebatpuria et al. (1999) studied the leaching of phenol from cement-based solidified/stabilized hazardous wastes using regenerated activated carbon. The study also included pore-fluid analyses of cement paste containing phenol. Phenol was detected at a wavelength of 270 nm. Even the addition of very low amounts of reactivated carbon efficiently adsorbed most of the phenol and prevented it from leaching. The adsorption was essentially irreversible when the pH was in the range of 7 to 12. Phenol remaining in pore water forms an insoluble complex with calcium ions released from the cement, and is the fraction available for leaching. This part may resolubilize when subjected to acidic leachants.

Rodríguez et al. (1997) used DAD after separation of phenolic compounds from drinking water with capillary electrophoresis. The limits of quantitation were around 0.2 μ g/L at 210 or 230 nm.

Hime et al. (1966) used infrared spectrophotometry for the detection and identification of organic additives in cement and admixtures in hardened concrete. Solvent extraction with chloroform and with HCl-chloroform were used to separate the additive from cement and concrete. The IR spectrum of an organic compound is characteristic of the particular molecule and is therefore useful for qualitative analysis. The spectra of

unknown materials can be compared and identified from an IR spectra library. In order to obtain the IR spectrum of a material present in a cement or concrete specimen, it is first necessary to concentrate the material by extraction. Hime et al. (1966) found various compounds in extractants; unfortunately these were not specified in detail.

McCall and Mannone (1975) did analysis of cement pastes for triethanolamine by GC or IR. They suggest that a triethanolamine-cement reaction occurred during hydration.

6.4.2 Fluorescence detection (FLD)

Meseguer Lloret et al. (2002) used FLD at ex 350 nm and em 530 nm for quantitative determination of low-molecular-mass aliphatic amines.

You et al. (1999) used acridine-9-N-acetyl-N-hydroxysuccinimide (AAHS) for the derivatization of several amines and ethylamine from waste waters. The emission maximum was at 435 nm. For many of the other fluorescence derivates used, such as with 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole (NBD-Cl), there are usually significant solvent effects on their fluorescence parameters. Hence the detection sensitivities for the early-eluted amino acid derivates are lower than for those eluted later. The detection limit for ethylamine was 17-87 fmol and for most amino acids 4.6-36 fmol.

Nakano et al. (2002) used FLD to determine 4-(1-pyrene)butyric acid N-hydroxy-succinimide ester (PSE) derivate of TETA at ex 345 nm and em 480 nm wavelengths. A laser-induced fluorescent detector (LIF) has been used to boost sensitivity in the determination of low-molecular-mass amines. LIF is one of the most sensitive detection methods available for capillary electrophoresis (CE). For alkylamines the detection limit was as low as 1 nM (Dabek-Zlotorzynska and Maruszak 1998). Henriks-Eckerman and Laijoki (1985) detected TETA and TEPA dansylated derivates at ex 341 nm and em 520 nm. The fluorescence detection of dansylated amines was 5 times more sensitive than direct UV-absorption measurement. For the most sensitive detection, the optimum wavelength should be determined separately for each amine of interest.

Brumley and Matchett (1995) determined aliphatic amines in environmental matrices. Derivatizations of triethanolamine and diethylamine were done by fluorescein isothiocyanate. The LOD for triethanolamine and diethylamine were 0.018 mmol and 0.039 mmol, respectively. They used the laser induced fluorescence detection (LIF) with ex 488 nm and em 520 nm. The limitations observed include the derivatization of matrix coextractives and by-products of derivatization for ng and sub-ng amounts of amines.

An indirect fluorescence detection method was studied on chlorophenolic compounds after capillary electrophoresis for spiked samples. The method was rapid compared to conventional ultraviolet detection. The linearity was in the concentration range of 0.8-6.38 mM for a micro glass device and 5-130 μ M for the conventional system (Arundell et al. 2000).

Winkler et al. (1988) made a quantitative determination of free primary amines in polymeric hardeners by measuring 2,2-diphenyl-1-oxa-3-oxonia-2-boratanaphthalene

(DOOB) derivatives of TETA and TEPA with fluorimetric detection at ex 385 nm and em at 470 nm. The details are insufficiently reported.

6.4.3 Flame ionization detection (FID)

Both Kennard and Meisen (1983) and Choy and Meisen (1980) used flame ionization detector in GC of diethanolamine and its degradation products. Concentrations as low as 0.5 wt.% were measured from water solutions. Luther et al. 1998 used GC with FID for analyses of DIPA in sorption experiments of soils, clays and aquifer materials. The detection limit was 5 mg/L.

Traditionally, glycol determination can be carried out by GC-FID and HPLC techniques (Holčapek et al. 1999, Aastad et al. 1993).

Methods for detection phenols from water samples by FID have been reported by the EPA and ISO (<http://www.chiron.no/html/phenol2005/phenols.pdf>).

6.4.4 Chemiluminescence detection (CL)

The most common derivatization reagent applied to amines for chemiluminescence detection is tris(bipyridyl)ruthenium(III)[Ru(bipy)₃]. This compound has been reported for the determination of a variety of nitrogen-containing analytes without derivatization of the analyte. The [Ru(bipy)₃] CL method is highly selective to ternary amines. A sample clean-up step is needed in the solid-support assisted derivatization in order to clean the blank reagent (Meseguer Lloret et al. 2004).

Niina et al. (2005) used postcolumn detection method for compounds having primary, secondary and tertiary amine moieties. The primary and secondary amines were derivatized in ethanol by a reaction with epichlorohydrin having an epoxy moiety in a reaction coil to yield a tertiary amine for subsequent chemiluminescence detection using the [Ru(bipy)₃]³⁺. The detection limit for DEA was 25 pmol and for TEA 40 pmol.

Transition metals such as Fe(III)-, Cu(II)- or Co(II) have been used as catalysts in CL-measurements of alkanolamines (Worsfold and Yan 1991, Yilmaz et al. 1993, Bhatt 1995, Kalinichenko and Matveeva 1994, Kaniansky 1991, 1993, Fisel 1980, Mitsui 1974). From these metals iron(III) has been used most frequently for complexing of amines. Pilipenko et al. (1977) used Mn-catalysis of amino and hydroxyl groups.

Worsfold and Yan (1991) determined ethanolamine, diethanolamine and triethanolamine by their suppressive effect on the Cu(II)- or Co(II)-catalysed CL emission from the luminal reaction. They recommended copper(II) for its slightly superior LOD and reproducibility. The limits of detection for the amines were 0.8, 1.2 and 0.2 nmol, respectively.

Meseguer Lloret et al. (2004) used chemiluminescence detection of dansyl derivatives of chromatographed and post-column mixed with peroxyoxalate (TCPO) and H₂O₂. The sensitivity was increased from 3 to 75 times with respect to UV detection and from 2 to 10 times with respect to fluorescence detection depending on the amine. Detection

limits were between 0.15 and 0.9 $\mu\text{g/L}$. Cobo and Silva (1999) used an on-line chromatographic system to determine low-molecular-mass amines (aliphatic amines with 1 to 7 carbon atoms) in environmental water. The determination was done using an integrated post-column derivatization-CL unit based on the TCPO- H_2O_2 system. The detection limits were at the ng/L level.

After separation of phenolic compounds by capillary electrophoresis in surface and reused waters Tsukagoshi et al. (2002) used CL detection of derivatized compounds. They used dansyl chloride and peroxyoxalate in derivatization. The detection limits were of the order of 10^{-7} M using glass cuvettes. This was 10 times lower than those obtained by ordinary fluorescence measurement.

6.4.5 Electrochemical methods

Amperometric detection (AD, PAD)

Crea et al. (2005) reported that amperometric detection (AD) of polyamines was independent of possible inorganic species and did not require the chemical pretreatment of natural samples, such as seawater. Pretreatments are generally required in these analyses using UV or conductometric detection. AD permits the use of eluents with high ionic content.

LaCourse et al. (1989) commented that a major shortcoming in amperometric detection at noble metal electrodes has been the loss of activity during anodic detection of organic compounds owing to the adsorption of carbonaceous reaction products on the electrode. They suggest that pulsed amperometric detection (PAD) based on a multistep waveform overcomes this problem by alternating amperometric detection with anodic and cathodic polarizations to clean and reactivate the electrode surfaces. They used an ion-pair chromatography separation method with PAD and obtained 0.13 nmol as the LOD for ethanolamine. Page et al. (2005) did IC-PAD analysis of ethanolamine and triethanolamine in concrete/cement paste pore solutions and digests. The LOD was 0.5 μM .

After HPLC separation glycol compounds can be detected by PAD according to Mrklas et al. (2003). The LOD for triethyleneglycol was 2.12 mg/L .

Since most phenolic compounds are oxidizable at moderate potentials, amperometry can serve as a highly sensitive tool for their detection. Amperometric detection of phenols is commonly prone to surface fouling, due to the formation of inhibitory polymeric films. This passivation problem is not observed when a microchip system is used. Wang et al. (2000) used thick-film amperometric detectors after capillary electrophoresis of spiked river water samples. The detection limit was around 10^{-6} M. Wu and Lin (2006) determined phenol in landfill leachates with end-channel AD after microchip capillary electrophoresis. The limit of detection was 0.4 μM .

Potentiometry

Open chain polyamines such as diethylenetetramine, triethylenetetramine and tetraethylenepentamine in artificial seawater were studied by De Stefano et al. (2000) using potentiometry. They determined the protonation constants for these amines in seawater and observed that the association ability of seawater salt towards amines was quite significant. Athanasiou-Malaki et al. (1989) used a kinetic-potentiometric method for the determination of primary and secondary amines such as TETA and DEA based on monitoring of their reaction with 1-fluoro-2,4-dinitrobenzene (FDNB) by using a fluoride-selective electrode. The linear range was around $(1 \text{ to } 10) \cdot 10^{-4} \text{ M}$.

Conductometry

Tanaka et al. (1996) detected diethanolamine and triethanolamine after HPLC by conductometry. The detection limits for diethanolamine and triethanolamine were 0.007 and 0.017 μM . Krol et al. (1992) used indirect conductivity detection in analyzing alkylamines and alkanolamines after ion chromatographic separation. They attained low $\mu\text{g/L}$ limits.

Voltammetry (SWV)

Menek and Heren (1999, 2000) used a square wave voltammetric technique for quantitative analyses of triethanolamine in cement paste. TEA is not an electroactive matter. But TEA- Fe^{+3} complexes are stable and the voltammogram produced by this complex can be used for the direct determination of TEA.

Polarography

Yilmaz et al. (1993) measured the TEA- Fe^{+3} complex in differential pulse polarographic mode. TEA alone does not give any polarogram. Polarographic measurements are normally carried out using supporting electrolytes. In these studies, the adsorbed amount of TEA by the tricalcium aluminate-gypsum mixture is very small ($\sim 1.5 \text{ mg/g}$ solid phase). They confirmed their results indirectly with atomic absorption spectrophotometry (AAS) measurements.

6.4.6 Mass spectrometry

In cases where chemical background is high, or where concentrations of analyte are very low, tandem MS (MS-MS) offers a more selective technique and structural information for increasing the confidence in identification. Thermospray (TS) ionization is well suited to most low-molecular-mass polar compounds, but the sensitivity for different types of compounds shows a wide variability and decomposition is a problem with thermally labile compounds. Particle beam (PB) with electron beam ionization (EI) has the advantage that mass spectra resembling reference EI spectra are produced, but sensitivity for polar analytes is generally lower than with other techniques, and there are limitations to the percentages of aqueous phases that can be accommodated at normal LC flow-rates. EI is not the best technique for water-soluble polar compounds.

Under soft ionization conditions, alkanolamines give intense protonated molecular ion (MH^+) with little or no fragmentation which is well suited for MS-MS analyses. APCI is commonly applied to non-ionised compounds of low molecular mass (Black and Read 1997, Headley et al. 2002).

Santos et al. (2004) used pressure assisted capillary electrochromatography (pCEC) with MS using an ES/API interface for aliphatic amines in water. On-line coupled flow injection-CE system allows the preliminary clean-up necessary to obtain adequate sensitivity with MS (Santos et al. 2004, Simonet et al. 2003).

Ion-exchange LC-ESI-MS and MS/MS were used for the determination of selected alkanolamines in wetland vegetation exposed to sour-gas contaminated groundwater. Quantification was performed using either selected ion monitoring of the protonated molecular ions (MH^+) or the loss of water transition in product ion scans. Instrumental detection limits were attainable in the picogram range (20-40 pg) for diethanolamine and triethanolamine. The detection limit was a factor of 5 lower than a conventional ion chromatography method (Headley et al. 1999). Identification of the compounds was based on the matches of the ESI-MS, ESI-MS-MS spectra and the retention times against those of the reference standards.

Chua et al. (2006) determined triethanolamine in spiked water and decontamination solutions by LC-ESI-MS. The TEA was detected from 150 m/z ion and 132, 114, 88, 70 m/z fragment ions. Identification of the compounds was based on the matches of the ESI-MS, ESI-MS-MS spectra and the retention times against those of the reference standards.

Black and Read (1997) used HPLC-APCI to study triethanolamine (m/z 150) and diisopropylaminoethanol (m/z 139) from the degradation products of chemical warfare agents. Collision induced dissociation (CID) spectra from MH^+ and high mass fragment ions were listed. It was not possible to compare the limits of detection obtainable with APCI and ES from their data. A disadvantage of ES-MS is the possible occurrence of multiple adduct ions with metal cations in the mass spectra originating from untreated water samples or aqueous extracts of soil (Borrett et al. 1996, Black and Read 1997). Triethanolamine and N-methyldiethanolamine were not separated under conditions used but were easily distinguished by their mass chromatograms. The LOD for triethanolamine standard was 10 ng/ml or 0.2 ng injected.

Sensitive API-MS detection of EG, PG and BG without derivatization would be difficult because their molecular masses are 62, 76 and 90, respectively. The sensitivity of HPLC-API-MS is reduced for compounds with lower molecular weights because of increased noise due to the occurrence of various molecular adducts attributed to the mobile phase. The most abundant ions in the API-MS mass spectra of all dibenzoyl glycol derivatives are the fragment ions $[M + H - C_6H_5COOH]^+$ formed by the loss of benzoic acid from the protonated molecular ions.

Holčapek et al. (1999) reported that the ion of EG with 149 m/z would not be suitable for practical analysis because the ion with the same mass is present in the mass spectra of phthalates, which are very frequent contaminants in various environmental samples.

To avoid possible interferences caused by these contaminants, the intense ions $[M + Na]^+$ and $[M + Na + ACN]^+$ were selected for monitoring of all glycols at the highest signal-to-noise ratio. The LOD for EG was 10-25 $\mu\text{g/L}$ compared with LOD of 1 mg/L in UV methods. They analysed sample solutions containing 100g/L of salts. Normally, ESI-MS cannot cope with such high concentrations of salts due to signal suppression from the ion pairing of the analyte with the counter ion of the salt and frequent contamination of the ion source.

Laser desorption fourier transform mass spectrometry (LD-FTMS) can reportedly detect 150 ppm of TEA and 500 ppm of TIPA that have been interground with cement clinker without any preconcentration step (Cassat et al. 1997a, 1997b, Ohno and Yamamoto 1997, Jeknavorian et al. 1998).

For the qualitative analysis of alcoholamines a coronaspray nebulization and ionization of liquid samples for ion mobility spectrometry (IMS) could be one possible method. Shumate and Hill (1989) used it for detecting triisopropanolamine.

6.4.7 Nuclear magnetic resonance (NMR)

Deuterium NMR spectroscopy has the ability to monitor molecular reorientations over a wide range of reorientation rates. Janusa et al. (1993) studied phenol by ^2H NMR in white Portland cement and pore water. Phenol has a functional group that can react under the basic aqueous conditions that exists during cement matrix formation. For maximum immobilization, deprotonation of the alcohol function and formation of a rigid, insoluble material with tight binding between the phenoxide anion and the cations of the cement matrix is desired. The leachability of phenol has been studied using a 0.5% water-to-cement ratio. Phenol is mainly dissolved in pore waters, thus is poorly immobilized by white Portland cement (at least for cure times up to 1 year). As the cures from 1 month to 1 year, the liquid-like component decreases, but still constitutes a significant fraction (~50%) of phenol at 1 year over a wide range of loading levels.

A number of leaching studies using TCLP tests have shown very high recoveries, and equilibrium leaching procedures afford large leachability indices. With ^{13}C NMR it would be possible to distinguish ionized from nonionized phenol (Janusa et al. 1993).

Herterich et al. (2004) studied and identified ethanolamine and polyethylene glycol in the leaching solutions of different SCC (self-compacting concrete) mixtures by ^1H NMR. They identified these compounds but the quantitation was not included in their report.

7 ENVIRONMENTAL STUDIES ON GRINDING AIDS

Amine compounds play an important role in reactions with sugars or their derivatives, which in natural waters lead to polymerized products containing several amino groups along a linear chain whose composition is very similar to that of the humic water-soluble fraction (De Stefano et al. 2000). Short-chain aliphatic primary amines can be detected in the environment due to the degradation of organic material such as amino acids, proteins or other nitrogen-containing compounds (Moliner Martinez et al. 2004, Sacher et al. 1997). Alkanolamines can react with carbon dioxide and hydrogen sulfide in aqueous solution to form salts. They can also react with nitrosating compounds to form nitrosoamines (Davis and Carpenter 1997).

Amines

Thorough environmental studies on grinding aids have not been reported. The leaching of grinding aids will vary between classes of organic compounds depending on a variety of factors including solubility in water, polarity, presence of functional groups, volatility, etc. (Hebatpuria et al. 1999). The environmental studies that have been reported concerned other low molecular mass aliphatic amines or spiked water samples. De Stefano et al. (2000) studied the speciation and protonation constants and association of open chain polyamines such as TETA and TEPA with the major components of seawater. A monitoring study at concrete batch plants by Environmental Science & Engineering, Inc., found that neither groundwater nor surface water were significantly impacted by plant operations. Unfortunately, they only tested for formaldehyde which was thought to be indicative of other admixture derivatives (Chini and Mbwambo 1996).

Alcoholamines

Davis and Carpenter (1997) reviewed the environmental assessment of alkanolamines. They provide a summary of physical properties, environmental distribution, biodegradation and toxicology. In general, alkanolamines have high water solubilities and low to moderate vapor pressures. Aqueous solutions of the alkanolamines are basic, with pK_a s decreasing with increasing alkyl substitution. Only a small fraction of these materials is expected to sorb to soil or sediments. Alkanolamines have also been shown to be highly susceptible to biodegradation and so are not expected to persist in the environment. Results from numerous studies have shown that these materials undergo rapid biodegradation in soil, surface waters, and waste water treatment plants. Degradation rates for these compounds may vary, with half-lives commonly in the range of 1 day to 2 weeks depending on the length of acclimation period and other environmental factors. These values are based on low octanol-water coefficients and are for nonpolar organic species. However, for polar or ionizable compounds, chemical sorption to soil or sediment can involve other mechanisms thus underestimating the adsorption affinity of alkanolamines. Biodegradation of these compounds is often complete, with carbon dioxide as the dominant degradation product. Degradation can proceed by different paths and with different intermediate products (Davis and Carpenter 1997).

A wide range of laboratory tests have been developed to examine biodegradation of organic chemicals. The OECD has even classified these testing methods. Biodegradation of ethanolamines has been extensively studied in a variety of screening tests to measure ready biodegradability. Although the biochemical oxygen demand tests (BOD) values spanned a wide range, they were routinely greater than 60%. MEA, DEA and TEA undergo extensive biodegradation, as reported routinely when using the OECD tests methods. There have been a few reports from screening and inherent studies examining the biodegradation of the isopropanolamines MIPA, DIPA and TIPA. In addition, there is a little information available on the anaerobic biodegradation of the isopropanolamines (Davis and Carpenter 1997). MIPA have been reported to undergo degradation by anaerobic sludge in a study simulating an anaerobic wastewater system (Chou et al. 1979). Still there are many amine compounds whose behaviour has not been studied and therefore their behaviour in environment is unknown.

The screening and inherent biodegradation tests demonstrate that ethanolamines and isopropanolamines are biodegradable and are not expected to persist in general aerobic environmental compartments. In freshwater systems, low levels of ethanolamines and isopropanolamines have been reported to be change to carbon dioxide (Davis and Carpenter 1997).

Alkanolamines are commonly used in the soil-gas industry during the sweetening process to remove toxic sour gases. Over many years of operation, a number of gas processing facilities have inadvertently released alkanolamines and associated degradation products to subsurface environments with varying degrees of contamination of groundwater and wetland areas. The wastes from operation are often stored in surface retention pits or landfills, leakage from which has contaminated subsurface soils, groundwater and wetland ecosystems. The elevated concentrations of ammonia, nitrite and nitrate are suspected to result from the degradation of alkanolamines. In Canada, the ammonia released into the environment has been a particular concern (Headley et al. 1999, Headley et al. 2002).

Diisopropanolamine (DIPA) has been reported to be sorbed more by clay minerals than by soil organic matter (Luther et al. 1998). Luther et al. (1998) studied the leaching of DIPA into groundwater from landfills and spills at some sour gas processing plant sites in western Canada. The sorbents in these studies included aquifer material from three plant sites, reference montmorillonite and kaolinite, and six soils of various clay and organic matter contents. A decrease in pH from 8.3 to 6.8 produced a slight increase in DIPA adsorption by montmorillonite. X-ray analysis showed that DIPA entered the interlayer space of the mineral. This was predicted as DIPA is a weak base DIPA and so is mostly protonated at the neutral pH of groundwater yielding a positively charged molecule. The DIPA sorption was low for the aquifer materials. The adsorption by kaolinite was much lower than by montmorillonite.

Unlike hydrophobic nonionic organic compounds, the high water solubility and polar nature of DIPA indicated that sorption reactions were likely to include not only partitioning into soil organic matter but in addition other mechanisms that involve hydrogen bonding and ionic interactions with charged soil colloids (clay minerals and oxyhydroxides of Fe, Mn, and Al). In cases where low organic content material was in

question, adsorption by clays may be a significant mechanism controlling the fate of DIPA. The desorption of DIPA from montmorillonite was low relative to its adsorption.

Hawthorne et al. (2005) studied the persistence and biodegradation of monoethanolamine (MEA) and isopropanolamine (IPA) at an abandoned industrial site. Soil and groundwater samples were analyzed from a former chemical processing plant site. The area had been impacted by the accidental releases of these amines. Although the use of the plant had ceased ca. 10 years before MEA concentrations ranging from 400 to 3000 mg/kg and IPA 30 to 120 mg/kg were detected. Even though alkanolamines are miscible in water, transport to groundwater was slow, apparently because they are present in soil as bound cations. Only one groundwater sampling point near the most contaminated soil was polluted. However, ammonia was found in soil and groundwater, and was consistent with the assumption of bacterial degradation of MEA followed by the transport of ammonia to groundwater. The bacterial degradation of MEA in highly contaminated soil was slow: half-life of 30 to 60 days at 10 °C. By contrast, in uncontaminated soil the degradation was rapid for both compounds. The results showed that MEA and IPA can persist for decades in soil at high concentrations (hundreds of mg/kg) without significant migration into groundwater.

Glycols

Staples et al. (2001) reviewed the fate and environmental risks of ethylene glycol. In air, ethylene glycol (EG) reacts with photochemically produced hydroxyl radicals resulting in an atmospheric half-life of 2 days. Staples et al. (2001) showed that EG does not persist in air, surface water, soil or groundwater, and does not bioaccumulate. Several abiotic processes can act to reduce or degrade EG in the environment.

The role of biodegradation as the ultimate fate of EG has been examined in numerous studies, either by using a variety of microbial types and sources of microbes, or by measuring biodegradability. These studies have examined primary and ultimate aerobic biodegradation and anaerobic biodegradation (Dwyer and Tiedje (1983), Evans and David 1974, McGahey and Bouwer 1992). These studies have examined aerobic primary and ultimate biodegradation and anaerobic biodegradation. The extent of biodegradation of EG in tests dependent on factors such as the microorganisms used, the duration of the test, the nutrient level available, and the specific methods. The results of several tests using American Public Health Association (APHA) and Organization of Economic Cooperation and Development (OECD) protocols show that EG undergoes extensive primary and ultimate biodegradation and is considered readily biodegradable (Staples et al. 2001).

Biodegradation of EG has been tested using activated sludge, soil, river water and groundwater. EG was biodegraded extensively in these tests. In river waters, EG was degraded completely in 3 days at 20 °C. At 4 °C, the degradation slowed to over 14 days. In groundwater, 0.1 g/L EG had a half-life of less than one day. The presence of sediment increased the degradation of EG. In sediment, 0.1-1 g/kg EG was aerobically degraded with primary degradation half-lives of 6-17 h. Substantial inhibition of degradation was at 10 g/kg EG. (Staples et al. 2001, Evans and David 1974, McGahey and Bouwer 1992). Dwyer and Tiedje (1983) studied the degradation of EG and

polyethylene glycols using sewage sludge. The rates of degradation were inversely related to the number of ethylene oxide monomers per molecule and ranged from 0.84 to 0.13 mM ethylene oxide units degraded per hour. Howard et al. (1991) modelled the behaviour of EG and estimated the degradation half-lives in various environmental compartments: aerobic half-lives (in surface waters and soil) 2-12 days and anaerobic half-lives (in groundwater 4-24 days) 8-48 days.

Phenols

Different phenol compounds from various sources have been detected in the environment. Following small, single releases, unsubstituted phenol does not remain in the air long. It generally remains in the soil for only 2 to 5 days. It can remain in water for longer than 9 days. Larger or repeated releases of phenol can remain in the air, water and soil for much longer periods of time. Small amounts of phenol may be found in organisms that live in contaminated water (<http://www.atsdr.cdc.gov/tfacts115.html>). Recently, a screening study of various phenol compounds from industrial and household releases to the environment were reported in Sweden. The phenol compounds from the concrete industry were not specified (Remberger et al. 2003).

At room temperature, most phenol in cement is very mobile, even to relatively low loadings, 0.1% by weight, of phenol in cement. This is because the phenoxides are slightly soluble in a highly basic medium such as the pore water in Portland cement (Janusa et al. 1993).

8 SUMMARY

Cement additives

Although the invention and use of superplasticizers is not a new phenomenon, the development of analytical methods to determine their concentration has followed far behind. Earlier analytical methods measured only total concentration of organic carbon as a measure of total concentration of the additive. However, it was noted that this was insufficient because various oligomers behaved differently in the environment. Knowledge of the composition and oligomeric distribution of superplasticizers is required when far-reaching decisions are made.

The environmental concentrations of additives have been low and so analysis of samples requires enrichment. The planned use of SP in concrete and injection grouts also leads to the requirement of enrichment if long-term follow-up is performed. Since superplasticizers have many differently behaving components it is necessary to separate them in analysis. There are several methods for separation of PNS-compounds, but less for PMS and no reports concerning PC. Separation is currently most often done by HPLC using ion-pair reverse phase chromatography.

The separated components have been detected by UV, FLD or MS. Spectrometry can confirm the identification of additive compound. UV or FLD results can quantify the additive, especially with radiometric detector for tracer studies. Recently, soft ionisation methods such as ESI have been applied. NMR techniques have been used especially in PC studies.

PMS and PC have been studied less than PNS due to the lack of available reference compounds for different homologues. PNS and PMS are very water soluble and PC and the PEG (derivate of PC upon contact with cement) are also water soluble. Environmental studies have shown that PNS monomers and oligomers are released and mobile. PEG, part of PC, is also mobile.

- ^1H - and ^{13}C -NMR were shown to be suitable methods for concrete studies of PNS and PC; unfortunately oligomer distributions were not reported. How well and easily these distributions are obtained is unknown.
- For PMS and PC analysis, development is still needed for the quantification procedure in HPLC-MS.
- For PNS there are several methods available, but the analysis of higher oligomers has not been tested sufficiently.
- The lack of reference compounds hampers identification and quantification of oligomers.

Grinding aids

Although organic grinding aids are used in great amounts in the cement industry, there is a limited number of studies concerning their analytical determination and environmental distribution. Several methods have been reported from other industrial applications for the same compounds. Unfortunately, these procedures are tailored for

higher concentrations. There is lack of reported suitable methods for trace level environmental applications.

Organic grinding aids are composed of many different compounds. Their environmental analysis is also posed with difficulties since they can be in very complex mixtures. Usually, attaining the environmental trace level requires preconcentration of these compounds. Sample preparation techniques may include extraction with organic solvents, water, or combination of these and alternatively solid phase extraction.

Various derivatization methods are available to improve chromatographic separations and detection. Several detection methods can be applied depending on the derivatization reagent used and the detection limit required. The most frequently reported methods for separation are HPLC and GC. Direct injection methods using small sample sizes have recently received attention. In the future, analysing procedures will likely center on mass spectrometry combined with different ionization techniques.

There are some reports from studies concerning the environmental pollution due to alkanolamines. Alkanolamines are highly water soluble and therefore can migrate along the water path. They have been shown to be biodegradable, especially under laboratory conditions, but less is known about them under field conditions. Hydroxyethyl diethylenetriamine and aminoethylethanolamine are scarcely studied compounds. There were no reports concerning their analysis in groundwater or in a concrete leaching context. The biodegradation of EG has been examined in numerous studies which state that several abiotic processes can act to reduce or degrade EG in the environment. On the other hand, some aliphatic amines such as tetraethylenepentamine have been reported to be non-biodegradable.

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ABBREVIATIONS

AAHS	acridine-9-N-acetyl-N-hydroxysuccinimide
ACN	acetonitrile
AD	amperometric detection
AEFA	aminoethylethanolamine
APCI	atmospheric pressure chemical ionization
API	atmospheric pressure ionization, namely ESI and APCI
BG	butylene glycol
BSC	benzenesulfonyl chloride
BSTFA-TMCS	N,O-bis(trimethylsilyl)trifluoroacetamide
Carpoback B	deactivated charcoal
CE	capillary electrophoresis
CEC	capillary electrochromatography
CID	collision-induced dissociation
CL	chemiluminescence
CTAB	cetyltrimethyl-ammonium bromide
CZE	capillary zone electrophoresis
C18	octadecyl-coated silica gel
C8	octyl-coated silica gel
CZE	capillary zone electrophoresis
DAD	diode-array detection
DEA	diethanolamine
DEG	diethyleneglycol
DMBA	N,N-dimethyl-n-butylamine
DNB-Cl	3,5-dinitrobenzoyl chloride
DNFB	2,4-dinitrofluorobenzene
DNS-Cl	5-dimethylaminonaphthalene-1-sulfonyl chloride, dansyl chloride
DOC	dissolved organic carbon
DOOB	2,2-diphenyl-1-oxa-3-oxonia-2-boratanaphthalene
DTA	differential thermal analysis
EC	electrochromatography
EG	ethyleneglycol
EI	electron ionization
EOF	electro-osmotic flow
ES	electrospray
ESI	electrospray ionization
FAB	fast atom bombardment
FDNB	1-fluoro-2,4-dinitrobenzene
FIA	flow-injection manifold
FID	flame ionization detection
FLD	fluorescence detection
FMOC	9-fluorenylmethyl chloroformate
FTIR	fourier transform infrared spectrometry
GC	gas chromatography
HCP	hardened cement paste
HEDETA	hydroxyethyl diethylenetriamine
HPCE	high performance capillary electrophoresis

HPLC	high performance liquid chromatography
IC	ion chromatography
IMS	ion mobility spectrometry
IR	infra red spectroscopy
ITP	isotachopheresis
LC	liquid chromatography
LD-FTMS	laser desorption Fourier transform mass spectrometry
LIF	laser induced fluorescence
LLE	liquid-liquid extraction
LOD	limit of detection
LS	lignosulphonate / lignosulphates
MALDI	matrix-assisted laser desorption ionization
MEKC	micellar electrokinetic capillary chromatography
MIP	molecularly imprinted polymers
MS	mass spectrometry
MS/MS	tandem mass spectrometry
NAC	N-acetylcysteine
NBD-Cl	7-chloro-4-nitrobenzo-2-oxa-1,3-diazole
NMR	nuclear magnetic resonance
NQS	1,2-naphthoquinone-4-sulfonate
OPA	o-phthaldialdehyde
PAD	pulsed amperometric detection
PB	particle beam
PC	polycarboxylates
PCE	polycarboxylate ester
pCEC	pressure assisted capillary electrochromatography
PEG	derivate of PC upon contact with cement
PEO	polyethylene
PG	propylene glycol
PMAANa	sodium polymethacrylate
PMS	polymelamine sulphonate
PNS	polynaphthalene sulphonate
PO-CL	peroxyoxalate chemiluminescence
PS-DVB	polystyrene-divinyl-benzene resin
PSE	4-(1-pyrene)butyric acid N-hydroxy-succinimide ester
py-GC/MS	pyrolysis gas chromatography mass spectrometry
REPSM	reversed electrode polarity stacking mode
RP-HPLC	reversed-phase high performance liquid chromatography
SCC	self compacted concrete
SEC	size exclusion chromatography/gel permeation chromatography
SP	superplasticizers
SPE	solid phase extraction
SRA	shrinkage reducing agent
TAA	trialkylamine
TBA	tri-n-butylamine/tetrabutylammonium
TBABr	tetrabutylammonium bromide
TBAF	tetrabutylammonium fluoride
TBAHSO ₄	tetrabutylammonium hydrogen sulphate

TBDMS	tert-butyldimethylsilyl, t-BDMS
TCLP	toxicity characteristic leaching procedure
TCPO	peroxyoxalate
TD	thermal desorption
TEA	volatile tertiary alkylamine
TEG	triethanol glycol
TEPA	tetraethylenepentamine
TETA	triethylenetetramine
TG	thermogravimetry
TIC-MS	total ion chromatography mass spectrometry
TIPA	triisopropanolamine
TLC	thin layer chromatography
TMeCl	tetramethylammonium chloride
TMS	trimethylsilyl
TOC	total organic carbon
TOF-MS	time of flight mass spectrometry
TRIS-buffer	2-amino-2-(hydroxymethyl)-1,3-propanediol
TS	thermospray, TSP
UV/VIS	ultraviolet and visible light detection
1-NS	1-naphthalene sulphonate
2-NS	2-naphthalene sulphonate
2,6-NDS	2,6-naphthalene disulphonate
1,5-NDS	1,5-naphthalene disulphonate
2,7-NDS	2,7-naphthalene disulphonate
1,6-NDS	1,6-naphthalene disulphonate
1,7-NDS	1,7-naphthalene disulphonate
1,3,6-NTS	1,3,6- naphthalene trisulphonate



Dec. 5, 2005

Analytical procedure for leachates from cement compositions

HCC Y. Tanaka

Measurements of organic compounds contained in leachates

1. TOC (Total organic carbon measurement)



If TOC results show several ppm ~ ten several ppm,

→ concentrate leachates (In a case, solidify leachates once and dissolve into certain concentration)

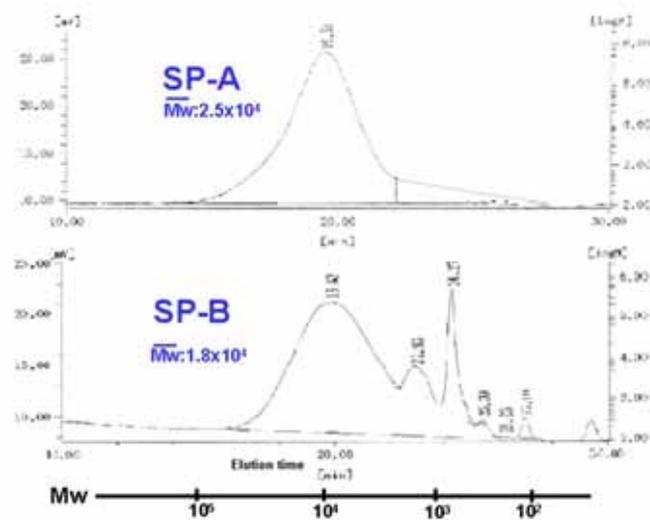
→ go to HPLC-GPC measurements

2. HPLC (High performance liquid chromatography) – GPC (Gel permeation chromatography)

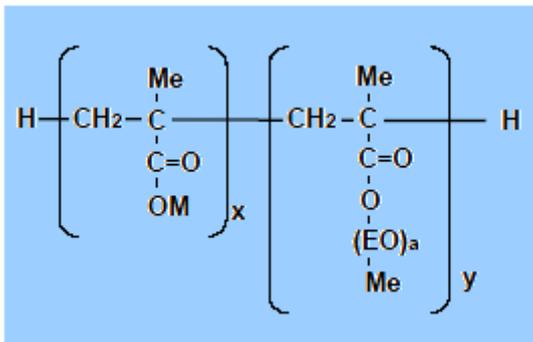


For an example, in the following, comparison of molecular weight distribution of typical PC based superplasticizers are shown, obtained from GPC measurements.

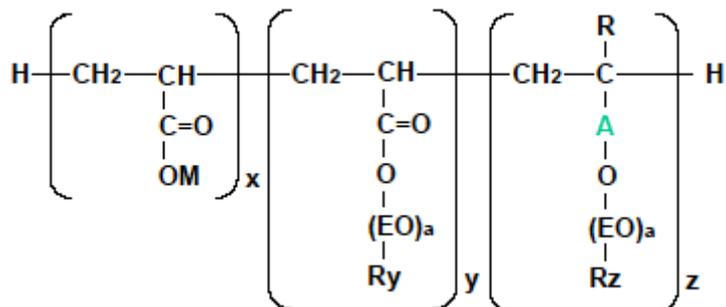
SP-A shows mostly main polymer. This main polymer is an original methacrylate based polycarboxylate polymer. SP-B is one of recent SP which shows main polymer and several components having range of 10^3 - 10^2 molecular weight.



Comparison of molecular weight distribution of typical PC based superplasticizers



Original methacrylate based polycarboxylate polymer



One of recent SP, based on acrylate polymer

From comparing these molecular weight distribution from GPC spectra, components should be mostly or approximately estimated by the person skilled in the art.

If necessary, optional measurements might be conducted.

Options:

3. FT-IR (FT- Infra-red spectroscopy)



4. UV (Visible-UV spectroscopy)

5. Electrophoresis chromatography

2nd Step: Detailed identification of each specific substance

1. Separation by liquid chromatography

2. ¹H FT-NMR (Proton FT-nuclear magnetic resonance spectroscopy)



3. FT-IR

4. ¹³C FT-NMR (C¹³ FT-nuclear magnetic resonance spectroscopy)

5. MS (Mass spectrometry)

6. LC-MS (Liquid chromatography- mass spectrometry)