Determination of Alkylphenols and Alkylphenol Mono- and Diethoxylates in Sewage Sludge by High Speed Gas Chromatography/Mass Spectrometry

Application

Environmental analysis, Sludge analysis

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Abstract

A routine method is described for quantitative determination of 4-nonylphenol (NP), 4-nonylphenol monoethoxylate (NP1EO) and 4-nonylphenol diethoxylate (NP2EO) in sludge samples.

A Soxtec® extraction procedure was used to enrich target compounds from the solid matrix. Quantitative determinations were performed by high speed gas chromatography/mass spectrometry using a short apolar fused silica column. Derivitization allows NP1EO and NP2EO to be analyzed by gas chromatography.

The relative standard deviation was close to 5% for the analysis of 10 different sludges analyzed seven times each. Recoveries were determined for a sludge reference material and were higher than 90%. The experimental limits of quantification were 2, 5, and 5 µg/g of dry matter (µg/g DM), respectively, for NP, NP1EO, and NP2EO.

Good agreement was observed between results obtained with this method and those obtained by our previous method, which used normal-phase liquid chromatography with an aminosilica column. This method was applied to different kinds of sludge collected in France and showed the persistence of these contaminants.

Introduction

Sewage sludge has been used in agriculture for a long time. Since 1986, the use of sewage sludge has been subject to provisions stipulated in EU Directive (86/278/EWG) [1]. Presently under revision, this Directive specifies requirements regarding sludge and soil quality. In contrast to Directive 86/278/EWG now in force, the revised version will cover specific methods for the analysis of sludge and soil. Organic micro-pollutants have been attributed even greater importance in the environment since the toxicity knowledge of refractory organic compounds has grown. Thus, there is a tendency for the European Commission to set up limit values for substances that Europeans generally find undesirable in the environment. Specific compound groups are mentioned in the current version of the revised sludge directive along with limit values (Table 1). Limits are set for: halogenated organic compounds (AOX), linear alkylbenzene sulfonates (LAS), di(2-ethylhexyl)-phthalate (DEHP), nonylphenol and nonylphenol ethoxylates (NPE), polyaromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and polychlorinated dibenzodioxins/dibenzofurans (PCDD/F). From these compound groups, only PAHs and PCBs are included in the current EU Directive (86/278/EWG).

Table 1. Limit Values for Selected Organic Contaminants in Sludge

Compounds	Limit values (mg/kg)
PCBs (Σ of 6 congeners)	0.8
PAHs (Σ of 11 PAHs)	6
AOX	500
DEHP	100
LAS	2600
NP + NP1EO + NP2EO	50
PCDF	100 ng TE/kg

Alkylphenol polyethoxylates (APnEO) represent an important class of nonionic surfactants that are widely used in many detergent formulations both for industrial and household use. Industrial uses include the manufacture of plastics, textiles, paper, and agricultural chemical products (Talmage 1994)[2]. Institutional applications include vehicle cleaning, commercial laundry products, and hard surface cleaners. Personal care products, contraceptives, cosmetics, and household laundry products account for the majority of household applications. Nonylphenol polyethoxylates are nonionic surfactants symbolized by NPnEO where " n " is the number of ethoxy groups, with 2<n<20. A recent study of field degradation of 4-nonylphenol polyethoxylates (Figure 1) has indicated a very complex metabolic behavior. (Stephanou and Giger 1982, Ball, et al., 1989, Maguire 1999) [3, 4, 5]. Laboratory experiments have shown that during biodegradation, the polyethoxylate chain of 4-NPEO is shortened and that NP, NP1EO and NP2EO (which are more hydrophobic and degrade more slowly than parent compounds) are formed as persistent and toxic metabolites in sludge (Ahel and Giger 1994) [6]. Investigation of these compounds in different countries around the world also shows the presence of these compounds (Torben, et al., 1998, Ventura, et.al., 1988, Sheldon, et al., 1989, Rudel, et al., 1998, Fujita, et al., 1996) [7, 8, 9, 10, 11]. NP, NP1EO and NP2EO are found at high concentration in some sewage sludge that may be spread on agricultural lands. Furthermore, NP, NP1EO and NP2EO are considered today as endocrine disrupters (Rudel, et al., 1998) [10].

Environmental investigations carried out over the last decade prompted the development of several specific analytical procedures for the simultaneous determination of NP, NP1EO and NP2EO in environmental samples (Marcomini, et al., 1996) [12]. Non-ionic surfactants are commonly soxhlet extracted using methanol (Mathijs, et al., 1987) [13]. In order to reduce extraction time, supercritical fluid extraction with on-line acylation (Lee, et al., 1997) [14] or with a modifier like methanol (Kreisseler et al., 1997) [15] has been used.

Specific gas chromatographic (GC) procedures available for the determination of these compounds are based on GC with flame ionization detection (GC/FID) (Giger, et al., 1984) [16] or mass spectral detection (GC/MS) (Stephanou, 1984)[17]. Methods using high performance liquid chromatography (HPLC) linked to fluorescence detection (Marcomini, et al., 1987) [18] or diode array detection (DAD) (Ahel, et al., 1987, Tanghe, et al., 1998) [19, 20] were reported. Liquid chromatography coupled to mass spectrometry (LC/MS) is an ideal technique for the determination of nonvolatile or labile chemicals in environmental samples. Recently, it has proven to be a useful method for the determination of NP, NP1EO and NP2EO (Castillo, et al., 1997 [21]; Chiron, et al., 2000 [22]). However, its use is limited by the high cost of this instrumentation or its availability in some laboratories.

This application note describes a specific, simple, and reliable procedure for the extraction, enrichment, and derivatization of NP, NP1EO and NP2EO in sewage treatment plant sludge. Separation and detection are by GC/MS using Agilent's 6890/5973 GC/MS system.

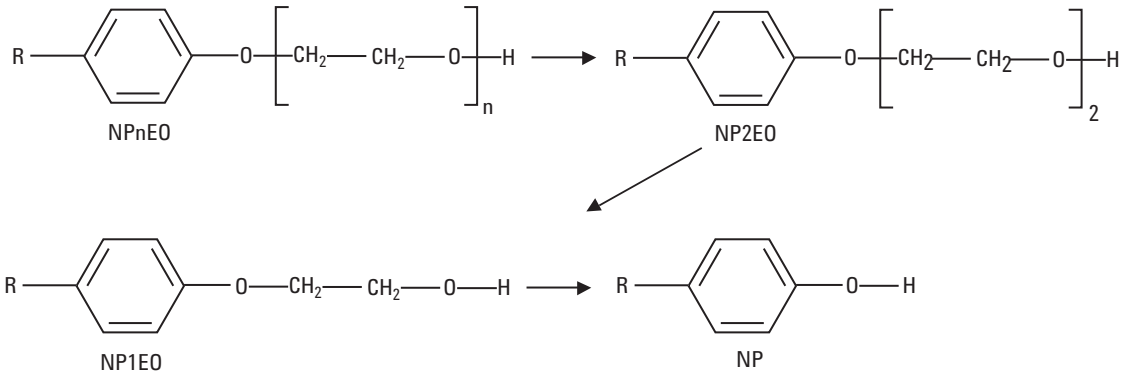

Figure 1. Metabolic pathway of nonylphenol polyethoxylates (NPnEO).

Experimental

Chemicals and Reagents

Hexane and acetone were obtained from Merck (Darmstadt, Germany). The derivatization reagent, Sigma-Sil-A, was purchased from Sigma (Milwaukee, USA). 4-Nonylphenol, 4-nonylphenol mono- and diethoxylates and 4-nonylphenol-d_8 were purchased from Cluzeau (France). Florisil cartridges (1 g, 3 mL) were obtained from Supelco (Bellefonte, USA). Sludge reference material was obtained from LGC Promochem (Molsheim, France).

Stock solutions for 4-nonylphenol, 4-nonylphenol mono- and diethoxylates were prepared in hexane at 300 mg/L. The stock solution of 4-nonylphenol-d_8 was prepared in hexane at 100 mg/L. When stored at 4 °C, the stock solutions were stable for at least six months. Acetic anhydride and BSTFA [N,O-bis (trimethylsilyl)trifluoroacetamide) were purchased from Aldrich (USA).

Sample Collection

Sludge samples were collected in dark glass containers and stored at –80 °C for 24 hours just prior to drying by lyophilization. The lyophilized sludge was ground and only the fraction below 200 µm was analyzed.

Extraction Procedures

One gram of ground lyophilized sludge was Soxtec extracted by 100 mL of hexane (Foss, Nanterre, France). The sample was immersed in hexane for 30 minutes (boiling mode) and then rinsed for 15 minutes (rinsing mode). Concentration of the extract to 1 mL was carried out with a stream of nitrogen using a Turbovap II concentrator (Zymark USA). The concentrated extract was then automatically purified over Florisil using a RapidTrace system (Zymark USA). A loading volume of 1 mL of concentrated extract was applied to a Florisil cartridge at a flow rate of 1 mL/min. The sorbent was rinsed with 5 mL of a hexane/acetone mixture (70/30) and 5 mL of hexane at 10 mL/min. NP, NP1EO and NP2EO were selectively eluted from the cartridge using 5 mL of a hexane/acetone mixture (70/30) at a flow rate of 2 mL/min. Concentration of the purified extract to less than 1 mL was carried out with a stream of nitrogen using a Turbovap LV concentrator (Zymark USA); 20 µL of labelled NP was added just prior to derivatization with 50 µL of Sigma-Sil-A. The extract was left for 30 min in darkness and was then reconstituted to a final volume of 1 mL just prior to analysis.

Instrumental Conditions

The GC/MS system used was an Agilent 6890/5973 MSD (Agilent Technologies, Palo Alto, CA, USA) equipped with a split/splitless inlet heated to 300 °C. The operating conditions were as follows. Using an Agilent 7673 autosampler, 1 µL of the final extract was injected in the splitless mode with the purge vent off for 1 min. Helium carrier gas was run at constant flow (0.3 mL/min). The inlet pressure at 50 °C was 52.2 psi. The compounds were separated on a 20-m × 0.10-mm id × 0.10 µm RTX5 capillary column (Restek USA). The oven was programmed from 50 °C (0 min) to 120 °C at 110 °C/min then at 30 °C/min to 300 °C (5 min). A 6890 oven insert (Part no. G2646-60500) was used in order to reduce the oven volume, allowing the column to heat more quickly, yielding faster separation and faster chromatography. MS detection was achieved in the selected ion monitoring (SIM) mode for quantitative analysis and in scan mode for qualitative analysis. The source was heated at 250 °C, the quadrupole at 150 °C, and the transfer line at 250 °C.

Tuning the Mass Selective Detector (MSD)

For qualitative analysis, the MSD was tuned using the autotune macro. With this macro, the abundances for ions 219 and 502 relative to ion 69 (using PFTBA as calibrant) are typically around 60%–100% and 3%–10%, respectively. For quantitative analysis of derivatized NP, NP1EO, and NP2EO, a target tune was employed using ions 69, 219, and 414. The repeller voltage was set to give an optimum response for ion 219. The target tune resulted in relative abundances (compared to ion 69) of 110% and 10% for ions 219 and 414, respectively. Figure 2 shows the mass spectra of the derivatized target compounds for quantitation. For monitoring ions in the SIM mode, 193, 207, 221, and 292 were chosen for NP, 251, 265, and 336 for NP1EO, and 295, 309, and 380 for NP2EO. The internal standard (ISTD), 4-nonylphenol-d_8, was monitored at *m/z* 300.

Method Validation

The method was validated according to the AFNOR regulation XP T 90-210.

The validation consists in defining:

- The scope of linearity:
  The linearity was determined over seven concentration levels from 2 to 200 µg/L, and was replicated five times. Calibration was done using the ISTD mode with NP-d_8. Linearity is achieved when the correlation coefficient (R) is 0.9990.
- The limit of quantification (LOQ):
  LOQ is validated when the within-batch relative standard deviation (RSD) is under 20% for 10 replicate samples spiked with supposed LOQs.
- The repeatability:
  The repeatability is expressed as a RSD (in %) and is calculated on the basis of three replicates of eight different sludge samples and must be less than 20%.
- The accuracy:
  The accuracy is expressed as recovery (in %) of sludge reference material and must be between 80% and 120%.
- The reproducibility:
  The reproducibility is expressed as a %RSD of a check calibration standard (20 µg/g) and should be under 20%.

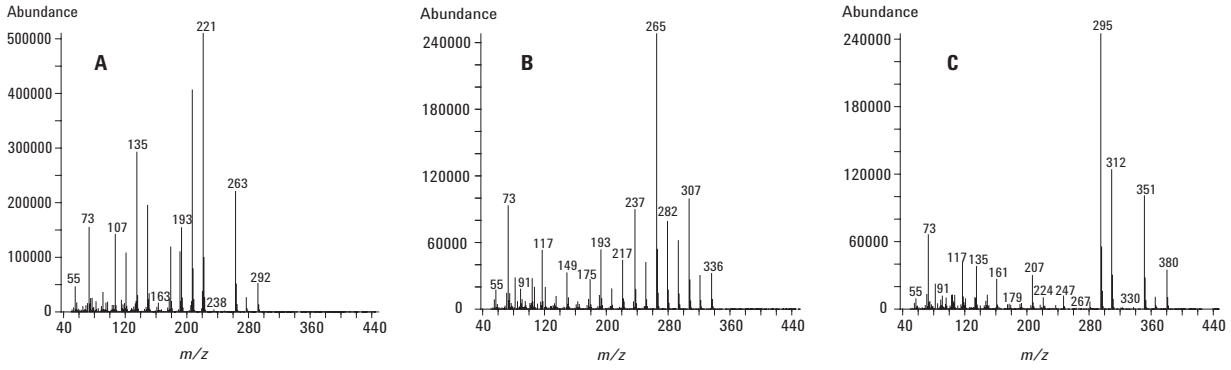

Figure 2. Mass spectra of A) NP, B) NP1EO, and C) NP2EO after derivatization with Sigma-Sil-A under quantitative conditions.

Results and Discussion

Derivatization Conditions: Optimization

Three kinds of derivatizing reagents were tested during this study -- acetic anhydride, BSTFA [(N,O-bis(trimethylsilyl)trifluoroacetamide], and Sigma-Sil-A which is a 1:3:9 mixture of trimethylchlorosilane (TMCS), hexamethyldisilazane (HMDS ($(CH_3)_3SI$-NH-Si$(CH_3)_3$), and pyridine (see Figure 3).

Acetic anhydride gave only a small response for the target compounds while BSTFA and Sigma-Sil-A gave complete derivatization within 30 minutes. As seen in Figure 4, the BSTFA and Sigma-Sil-A gave the same chromatogram, which contained intense molecular ions for NP, NP1EO and NP2EO. Sigma-Sil-A was chosen for further work because the derivatization occurred at room temperature while BSTFA required heating at 90 °C.

Separation: Optimization

In some studies, capillary column GC procedures were used for the analysis of NPnEO either directly (Giger, 1981) [23] or after conversion into more volatile derivatives (Wahlberg, et al., 1990) [24]. Even though this approach was limited to ethoxylates with one to five ethoxy units, this technique was adopted, instead of HPLC separation because of the higher selectivity of the detector. Instead of a single eluted peak observed for each NPEO in HPLC, the higher resolution of the capillary GC column produced three groups of peaks for derivatized NP, NP1EO and NP2EO resulting from different isomers of the nonyl group. This additional fingerprint information is very useful for the identification of these compounds in a complex matrix such as sludge.

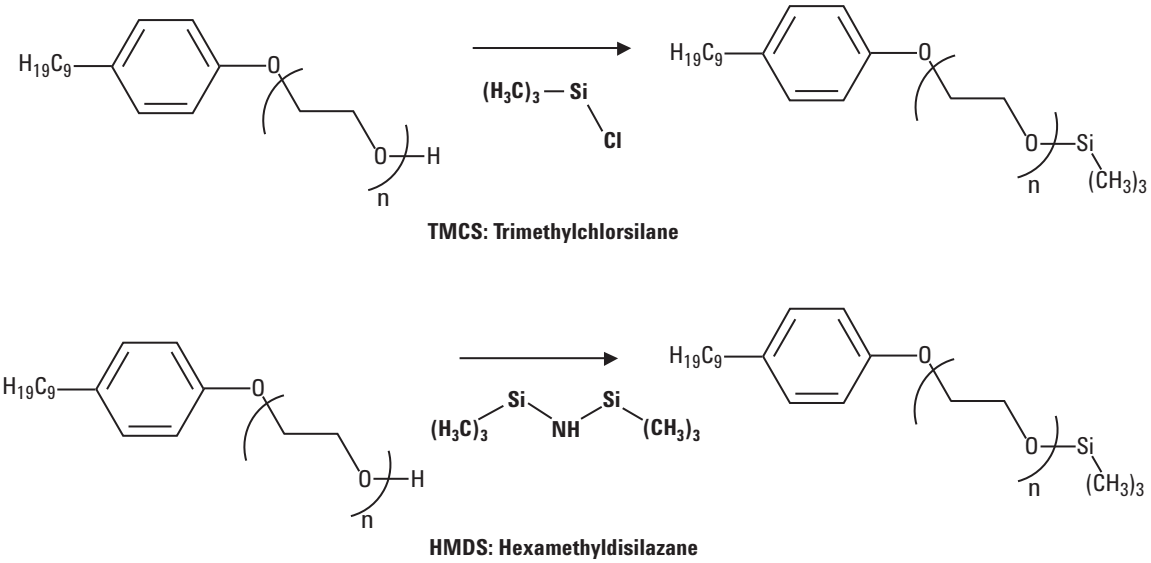

Figure 3. Reaction of Sigma-Sil-A with NPEO

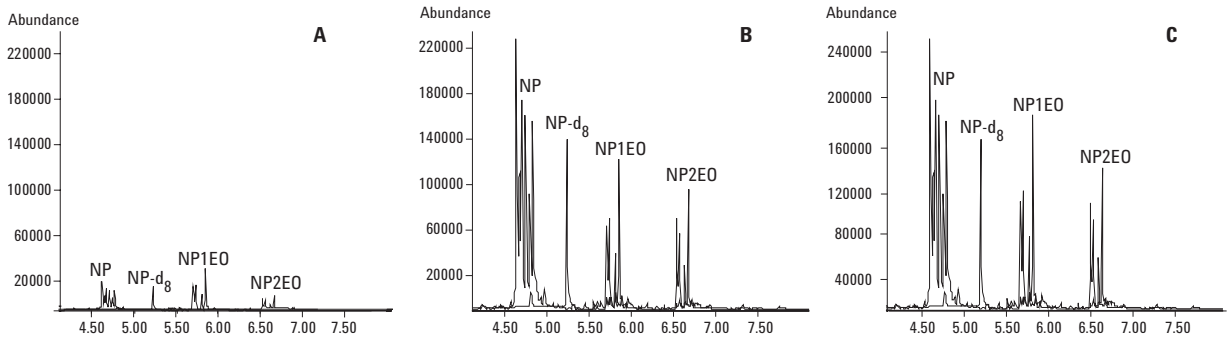

Figure 4. Mixture of NP, NP1EO, NP2EO, and NP-d_8 derivatized with A) acetic anhydride, B) BSTFA, and C) Sigma-Sil A.

There was a desire to improve productivity by reducing the GC run time while maintaining the elution order and selectivity of the analytical column. Exact translation between conventional and high-speed chromatography was achieved by using Agilent's dedicated Method Translation Software (Agilent Technologies, version 2.0.a.c). Using empirical methods, it was impossible to maintain column selectivity.

Full scan GC/MS of derivatized NP, NP1EO and NP2EO shows three groups of peaks with retention times (RTs) from 4.5 to 5 min for NP, 5.6 to 6 min for NP1EO and from 6.5 to 6.8 min for NP2EO (Figure 3). In this case molecular ions were available for quantification. An additional benefit of high-speed chromatography was the increase in sensitivity resulting from the 10-fold reduction in peak width (PW). The first 10 cm of the capillary column had to be removed after each 50 injections.

Purification Conditions: Optimization

Florisil cartridges were used to clean up sludges prior to analysis by GC/MS. The cleanup procedure for NP, NP1EO, and NP2EO was optimized by adding 1 mL of hexane and 1 mL of sludge extract (spiked with 25 µL of the target compounds in hexane) to Florisil cartridges. Various solvents were evaluated for their ability to elute the target compounds quantitatively while separating them from interferences. Previous studies (Benanou, et al., 1999, 2001) [25, 26] showed that 10 mL of hexane allowed one to recover PCBs, hydrocarbons from C6 to C50, some PAHs, and LAS, but not NPEO. An additional 5 mL of a 90/10 hexane/acetone eluted only NP. With this background, different hexane/acetone mixtures (ranging from 90/10 to 50/50) were tested for the elution of all NPEO analogs. Quantitative and qualitative results showed that after discarding the first 10 mL of hexane, a 70/30 hexane/acetone mixture gave the best results. In fact, increasing the proportion of acetone did not improve analyte recovery but dramatically increased the amount of grease in the final extract. Figure 5A illustrates recovery of the NPEO analytes while Figure 5B plots the sum of the total ion chromatogram (TIC) areas as a function of the solvent mixture. The 70/30 hexane/acetone mixture gave the highest recovery of the analytes with the least amount of co-extracted material.

Quantitation of NP, NP1EO and NP2EO

Internal standard calibration was used for quantitation with one labelled congener of the NP mixture (NP-d_8) used as the internal standard (ISTD). Each compound was quantified separately with two or more different ions. In that way, even with interferences, it was possible to quantify the compounds. In such matrices, choosing one quantifying ion and two or more qualifiers is not enough. Calibration curves were prepared between 2 and 200 µg/mL by injecting standards. Table 2 lists the quantifying ions, linearity, RSD, and LOQ.

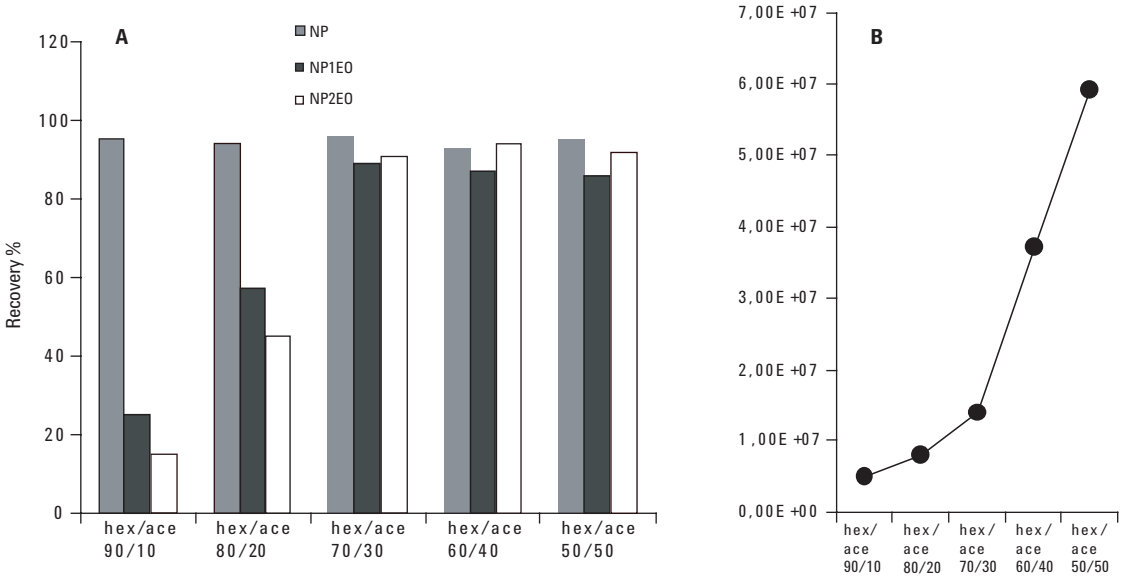

Figure 5. A) Recovery of NP and NPEO analogs after elution with different hexane/acetone mixtures. B) Total peak area of the TIC as a function of the solvent mixture.

Table 2. Calibration Results for the Quantitative Determination of NP, NP1EO, and NP2EO

	Quantifying ions	R^2	RSD%	LOQ µg/g
	192	0.9994	5	
	207	0.9985	12.5	
NP	221	0.9989	3.7	2
	292	0.9997	2.2	
	251	0.9990	3.5	5
NP1EO	265	0.9989	6.2	
	336	0.9999	5.3	
	295	0.9994	5.9	5
NP2EO	309	0.9993	4.8	
	380	0.9996	3.6	

Performance of the Analytical Method and Extraction Optimization

A sludge reference material was used to verify the performance of this method. One g of sludge was introduced into a cellulose thimble with 1 g of sand. The sludge/sand mixture was agitated for 1 min on a vortex mixer and the thimble was then slurried with glass wool. The extraction temperature was 180 °C. A hexane/acetone mixture was chosen instead of pure hexane for complete recovery of NP1EO and NP2EO. By extracting only with hexane, recovery was less than 20%. Soxtec extraction performed with methanol gave satisfactory recovery, but methanol is not amenable to GC analysis. Different hexane/acetone mixtures ranging from 90/10 to 50/50 and different extraction times ranging from 30 to 360 min were tested. Results obtained showed the best compromise was an extraction time of 45 min with a 50/50 hexane/acetone mixture.

The extract was very brown compared to extractions performed with hexane only. The hexane/acetone mixture made it possible to recover NP1EO and NP2EO quantitatively, but many interferences were collected as well (Figure 6). Co-extraction of these polar and mid-polar compounds made it necessary to perform the clean-up twice for some sludge samples. The extraction was improved by adding and thoroughly mixing 1 g of Florisil and 1 g of sand to the sludge just prior the extraction. Analyte recoveries were not diminished by the addition of Florisil to the samples and only one clean-up step was required for all sludge samples.

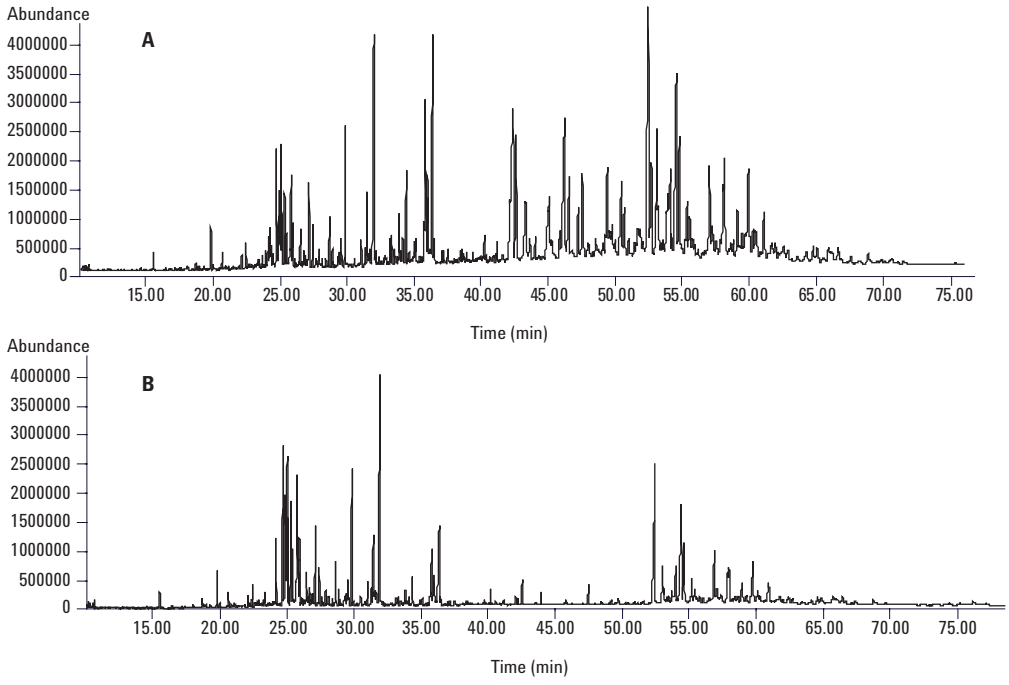

Figure 6. Chromatogram of the same sludge sample A) without addition of silica, and B) with addition of silica during the extraction step.

Table 3 illustrates the recoveries obtained with this method for 10 extractions of the sludge reference material over a 1-week period. Results, expressed in mg/kg DM, are the mean of the results obtained with each quantifying ion. Results obtained with our previous method using Soxtec extraction with methanol (no additional clean up) and normal phase HPLC with fluorescence detection are listed for comparison.

Table 3. Mean Recovery Values and Uncertainties (n = 10) for NP, NP1EO, and NP2EO Determined in Sludge Reference Material

	NP (mg/kg DM)	NP1EO (mg/kg DM)	NP2EO (mg/kg DM)
Certified values	100 ±8.0	5 ±0.9	2 ±0.1
GC/MS mean concentration	102 ±3.4	4.3 ±0.06	2.1 ±0.02
GC/MS recovery %	*102*	*86*	*105*
HPLC/Fluo	87 ±9.1	6.1 ±1.0	2.5 ±0.7
HPLC/Fluo recovery %	*87*	*122*	*125*

Both techniques gave good agreement with the published values for the reference material. All recovery values were higher than 80% showing good performance of the Soxtec extraction method with GC/MS quantitation. However, the uncertainty is greater with HPLC/fluorescence than with GC/MS due to the lack of specificity of this LC detector compared with a mass spectrometric detection.

Sewage Sludge Analysis

This high speed GC/MS method was applied to the analysis of sludge samples from 10 sewage treatment plants (STPs) in France. Each sludge sample was extracted five times and results are shown in Table 4. Results are expressed in mg/kg DM and are a mean of the results obtained with each quantifying ion. Figure 7 shows chromatograms for sludge samples 2 and 5. Some sludge samples were problematic when using the *m/z* 207 ion as the quantifier. Some interference appears due to column bleed, which resulted in a high background at *m/z* 207 around the RTs of NP and NP1EO. In the end, NP was only quantified with ions 193, 221, and 292.

Whatever the sludge sample's origin, the sum of NP, NP1EO, and NP2EO was usually above the limit value of 50 mg/kg DM indicated in the revision of the current regulation. Values ranged from 8.8 to 210 mg/kg DM, with a median value of 91 mg/kg DM. NP2EO showed higher concentrations than NP and NP1EO for most sludge samples. It's contribution to the sum for sludges 1 to 6, ranged from 16% to 80% with a median value of 50% (31 mg/kg DM). These values point out that most of these sludges could not be applied as fertilizer on agricultural land once the EU approves this revision. However, the contamination seems less heavy than that observed in STPs from Switzerland (Ahel, et al., 1994) [6]. The MSD's specificity made it possible to obtain satisfactory SDs for all of these measurements.

Table 4. Determination of NP, NP1EO, and NP2EO in 10 Different Sludge Samples from France

	1	2	3	4	5	6	7	8	9	10
NP	**15.4**	**24.7**	**27.1**	**11.9**	**16.2**	**21.9**	**10**	**12.9**	**8.8**	**38.4**
	±0.6	*± 0.4*	*± 0.7*	*±0.4*	*±0.6*	*±0.7*	*±0.5*	*0.2*	*0.3*	*3.6*
NP1EO	**8.7**	**14.6**	**36.0**	**25.3**	**49.9**	**13.3**	**12**	**12.5**	**<2**	**41.1**
	±0.2	*±0.3*	*±1.1*	*±0.3*	*±0.6*	*±0.8*	*±0.3*	*0.3*		*1*
NP2EO	**90.4**	**40.5**	**12.3**	**152.7**	**143.9**	**85.5**	**21.4**	**<2**	**<2**	**21.8**
	±2.7	*±0.5*	*±0.3*	*±2.4*	*±2.6*	*±1.0*	*±0.4*			*1.2*
Total	**114.5**	**79.8**	**75.3**	**189.9**	**210.0**	**120.7**	**43**	**25.4**	**8.8**	**101.2**
	±3.0	*±0.8*	*±1.5*	*±2.8*	*±3.1*	*±2.0*	*±0.8*	*0.5*	*0.3*	*2.8*

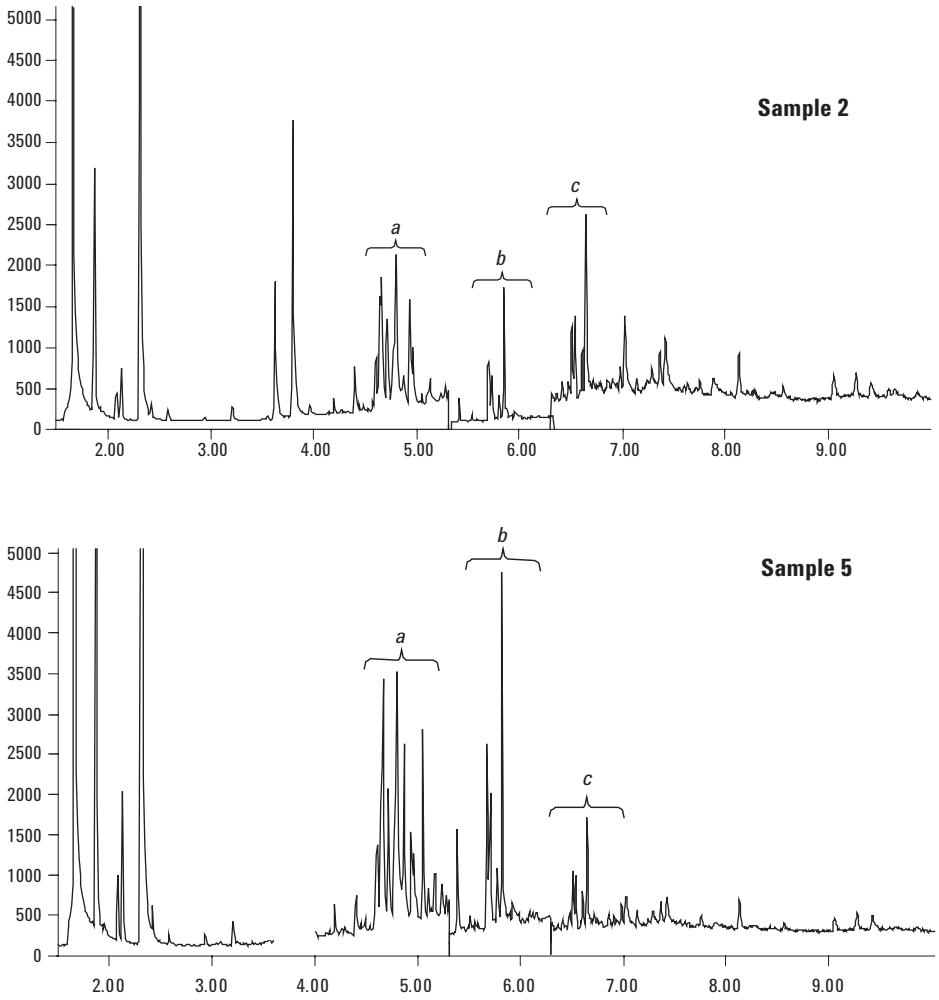

Figure 7. Chromatograms of sludge samples 2 and 5. a) NP, b) NP1EO, c) NP2EO.

Conclusion

High-speed GC/MS enabled rapid determination of NP, NP1EO and NP2EO in sludge samples. The Agilent 6890 GC was able to separate the NP, NP1EO and NP2EO congener groups into three sets of peaks, instead of a single peak for each group as was observed when using HPLC.

DLs were improved by working in the SIM mode and by reducing peak widths with the 0.10-mm id GC column. The LOQs achieved with this method were 2, 5, and 5 mg/kg DM for NP, NP1EO, and NP2EO, respectively. RSDs were under 7%. Soxtec extraction followed by Florisil cleanup resulted in recovery values above 80% in all cases.

Results for 10 typical sludge samples show that, in most cases, the sum of NP, NP1EO, and NP2EO is above the anticipated regulatory value of 50 mg/kg DM. Further work on NPEO will include analysis of the same species in wastewater for a better understanding of their fate during sludge treatment.

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