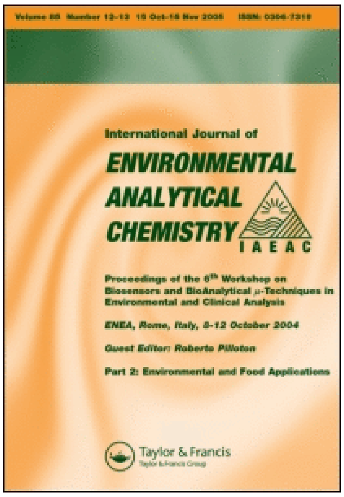

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APPLICATION OF PARTICLE BEAM LC/MS FOR THE ANALYSIS OF WATER FROM PUBLICLY OWNED TREATMENT WORKS

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Effluents from three New Jersey Publicly Owned Treatment Works (POTWs) were analysed for non-volatile organic compounds using particle beam-liquid chromatography/mass spectrometry (PB-LC/MS). The wastewater samples were extracted by XAD-2 resin adsorption methodology. A comparison between the PB-LC/MS analysis and an on-column gas chromatography/mass spectrometry (GC/MS) analysis showed that 46 additional compounds could be detected by PB-LC/MS. Identifications were made either by mass spectral interpretation or by matches with a mass spectral library data base for 19 of the 46 compounds detected only by PB-LC/MS. The majority of contaminants identified were non-ionic surfactants, plasticizers, plastic additives and other various synthetic organic compounds. PB-LC/MS has proven its ability to detect and identify a number of environmental contaminants which on-column GC/MS failed to detect.

INTRODUCTION

Publicly Owned Treatment Works (POTWs) treat sewer waste from domestic, municipal, commercial and industrial inputs. The Resource Conservation Recovery Act (RCRA) and the Domestic Sewer Exclusion state that after an industrial effluent is mixed with domestic sewage, the former is no longer considered a hazardous waste[1]. This exclusion allows industries connected to POTWs to discharge hazardous waste to sewers containing domestic sewage without having to comply with certain RCRA requirements. Discharges from municipal and industrial treatment facilities are monitored for organic priority pollutants by United States Environmental Protection

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Agency (US EPA)[2] standard methods. These methods require the use of gas chromatography/mass spectrometry (GC-MS) techniques for the detection and identification of the organic priority pollutants. The exclusive use of a gas chromatograph for analysis limits the screening of these wastewaters to volatile and semi-volatile compounds and permits compounds that can not pass through a GC intact because of polarity, thermal instability and/or high molecular weight to go undetected. This limitation is significant since the US EPA estimates that only 35% of non-humic materials present in water supplies have been identified[3]. It is believed that liquid chromatography (LC) and liquid chromatography/mass spectrometry (LC/MS) methods will help to identify a large portion of the non-volatile organic chemicals[4].

Until recently, LC/MS instrumentation has predominately produced chemical ionization (CI)-type spectra, which provide molecular weight data but little structural information. Such information has not been very helpful toward identifying unknowns in a complex environmental sample because the fragmentation patterns produced by electron impact ionization (EI) are needed for interpretation and searches in mass spectral library data bases. An LC/MS system incorporating such a source would be more useful for identifying unknown non-volatile and thermally liable compounds in complex environmental samples.

In 1984, Willoughby and Browner introduced a monodisperse aerosol-based interface for LC/MS (MAGIC-LC/MS)[5]. Features of the interface included a monodisperse aerosol, evaporation of solvent, and the use of aerosol-beam gas/solid separators for pressure reduction and solute enrichment. The elimination of the solvent allowed for analyses in both the EI and CI modes. In 1989, Vestal *et al.* described a LC/MS separator capable of using EI[6]. The Vestec Universal Interface operates by using a heated thermospray probe, which nebulizes and partially vaporizes the LC eluent. The majority of the solvent vapour is removed in a heated countercurrent flow gas diffusion separator. Any remaining vapour or carrier gas is removed in a 2-stage momentum separator, leaving only the analyte particles. This system ensures a proper pressure needed for the EI source. Both of these techniques are commonly referred to as Particle Beam LC/MS (PB-LC/MS).

A study by Northington *et al.* determined that 50 out of 60 environmentally significant compounds, including amines and ureas, could not be detected by GC/MS but responded adequately to PB-LC/MS. They concluded that quantitative analysis could be performed on compounds with linear calibration curves and that semi-quantitative analysis was appropriate for compounds with non-linear calibration curves[7].

This paper will demonstrate how PB-LC/MS was used to identify compounds which went undetected by on-column GC/MS in effluents of three New Jersey POTW's.

METHODOLOGY

Sampling POTW effluent was collected with Manning 3000T (Texas Nuclear Co., Austin, TX) Wastewater Samplers. Three samplers each collected 15 l of wastewater.

The wastewater from the three samplers were composited on site. A 15 l aliquot was taken and kept in darkness at 4°C during sampling, transport and storage. The wastewater samples were extracted within one week of collection.

Two 'field blanks' (distilled de-ionized water is passed through the sampler at the facility site) and one 'lab blank' (distilled de-ionized water not passed through the sampler) were also analyzed.

Sample preparation A 60 cm × 1.0 cm i.d. glass chromatographic column (Kontes, Vineland, NJ) containing 10 g Supelpak-2 (Supelco, Supelco Park, PA), a purified form of Amberlite XAD-2 resin, was connected to a nitrogren-pressurized steel tank containing 10 l of wastewater. The column was conditioned by sequentially washing it with 1 l of HPLC-grade methylene chloride, 1 l of HPLC-grade methanol, and 1 l of HPLC-grade water (Ace Scientific, East Brunswick, NJ). The wastewater was then pumped through the Supelpak-2 column at a flow rate of 10 ml/min. Components were eluted with 1 l of HPLC-grade methylene chloride. The eluate was concentrated to 5 ml in a Kuderna-Danish Evaporator, then to 1 ml under a gentle stream of nitrogren.

Instrumentation conditions PB-LC/MS analyses were performed in the EI mode on a Vestec Model 201 LC/MS (Vestec Corp., Houston, TX), equipped with a Universal Interface. The chromatographic system used was a Kratos Spectroflow 400 Ternary Pumping System (Kratos Analytical, Ramsey, NJ) equipped with a 254 nm UV detector. A 25 cm × 4.6 mm i.d. reversed-phase LC column (Brownlee Labs, Santa Clara, CA) and guard column were used for the LC separations. The Teknivent Vector/One Mass Spectrometry Data System (Teknivent Corp., St. Louis, MO) was used for acquiring and processing data. Mass spectra were searched on a Wiley/National Bureau of Standards (NBS) library data base. The ion source, probe tip and momentum separator temperatures were 265°C, 140°C and 130°C, respectively. The solvent gradient began with 70% 0.0013 M ammonium acetate and 30% methanol and ended with 99% methanol and 1% 0.0013 M ammonium acetate in 80 min. (The aqueous component of the LC mobile phase contains 0.01% ammonium acetate to improve signal sensitivity by improving the transport efficiency of the analyte through the interface[8]). The flow rate was 0.8 ml/min and the scan range was 45–450 amu. The LC injection volume was 24 μl.

Gas chromatography/mass spectrometry (GC/MS) analyses were performed on a Finnigan MAT 8230 High Resolution Mass Spectrometer (Finnigan MAT, San Jose, CA) directly interfaced to a Varian 3400 Capillary Gas Chromatograph (Varian, Sunnyvale, CA). The samples were analyzed by EI to obtain fragmentation and allow correlation with the computerized NBS and Environmental Protection Agency-National Institute of Health (EPA-NIH) data bases. A 30 m long, 0.25 μm film thickness, 0.32 mm i.d. DB-1 fused silica capillary column (J&W Scientific, Folsom, CA) was temperature-programmed from 50°C to 320°C at a rate of 4°C/min with a final hold time of 10 min. The mass spectrometer was operated at injector temperature, 260°C; source temperature, 250°C; electron energy, 70 eV; filament current, 1 mA; scan rate, 1 sec/decade; interscan time, 0.8 sec; masses scanned, 35–550 amu.

The GC injection volume was 1 μl and the samples were injected by an on-column injection technique[9]. Data were acquired and processed using a Finnigan MAT SS300 data system.

Internal standard 1 mg of 4-fluoro-4′-hydroxybenzophenone (Aldrich, Milwaukee, WI) was added to the 1 ml concentrated sample to give a 100 ppb solution based on the original 10 l.

Quantitation Semiquantitative estimates for the concentration of individual pollutants were obtained by peak area comparisons of the internal standard to those of the analytes.

RESULTS AND DISCUSSION

Both the internal standard and the quadrapole tuning compound specified in the US EPA Standard methods, d_{10}-anthracene and decafluorotriphenyl phosphine (DFTPP), respectively, could not be detected by PB-LC/MS because they are too volatile to pass through the Universal Interface and into the mass spectrometer. 4-Fluoro-4′-hydroxybenzophenone was selected as the internal standard and the tuning compound because it gave a good signal-to-noise ratio and a spectrum that could be used for instrument tuning. For tuning purposes, the m/z 121 has a 100% relative intensity, m/z 216 must be at least 25% of the base peak and the m/z 215 ion should be 15% (±5%) of the m/z 216 ion (Figure 1).

The wastewater effluents of three New Jersey POTW's (A,B and C) were analyzed by both on-column GC/MS[10] and PB-LC/MS. A comparison of the two mass spectrometric analyses showed that 165 different compounds were detected by on-column GC/MS, 46 were detected by PB-LC/MS only and 14 by both methods. On-column GC/MS was able to detect a much larger number of compounds than PB-LC/MS because of its greater inherent sensitivity and because many materials are sufficiently volatile to pass through the membrane separator of the Universal Interface instead of into the mass spectrometer.

A summary of those compounds identified by either interpretation or by library matches of PB-LC/MS data is found in Table 1. Some compounds of interest found in the wastewater effluents were phenolphthalein, a cathartic and acid/base indicator; lumichrome, a breakdown product of riboflavin; 3-hydroxy-4-phenyl-quinolinone, an antibiotic substance extracted from *Pencillium viridicatum*; *N*-(4-chlorophenyl)-*N*′-(3,4-dichlorophenyl) urea (triclocarban). The spectra shown in Figures 2 and 3 demonstrate the excellent quality of the EI spectra obtained.

Non-ionic surfactants are a major component of detergents that are discharged into municipal and industrial waste facilities. PB-LC/MS is very sensitive to non-ionic surfactants such as nonylphenol ethoxylates and tertiary octylphenol ethoxylates. While we could detect tertiary octylphenol ethoxylates (2-[1′,1′,3′,3′-tetramethylbutylphenoxy]ethoxy ethanol analogues) up to a molecular weight of 382 (base peak 311) with on-column GC/MS, PB-LC/MS allowed us to detect two higher analogues

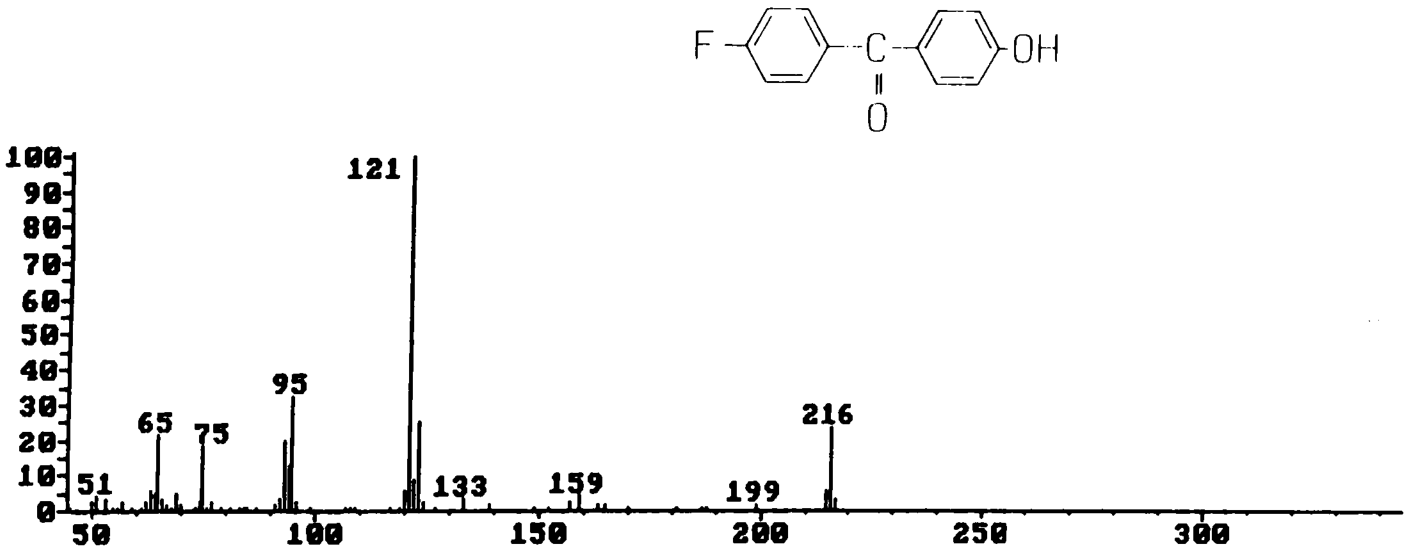

Figure 1 Spectrum of 4-fluoro-4′-hydroxybenzophenone by PB-LC/MS.

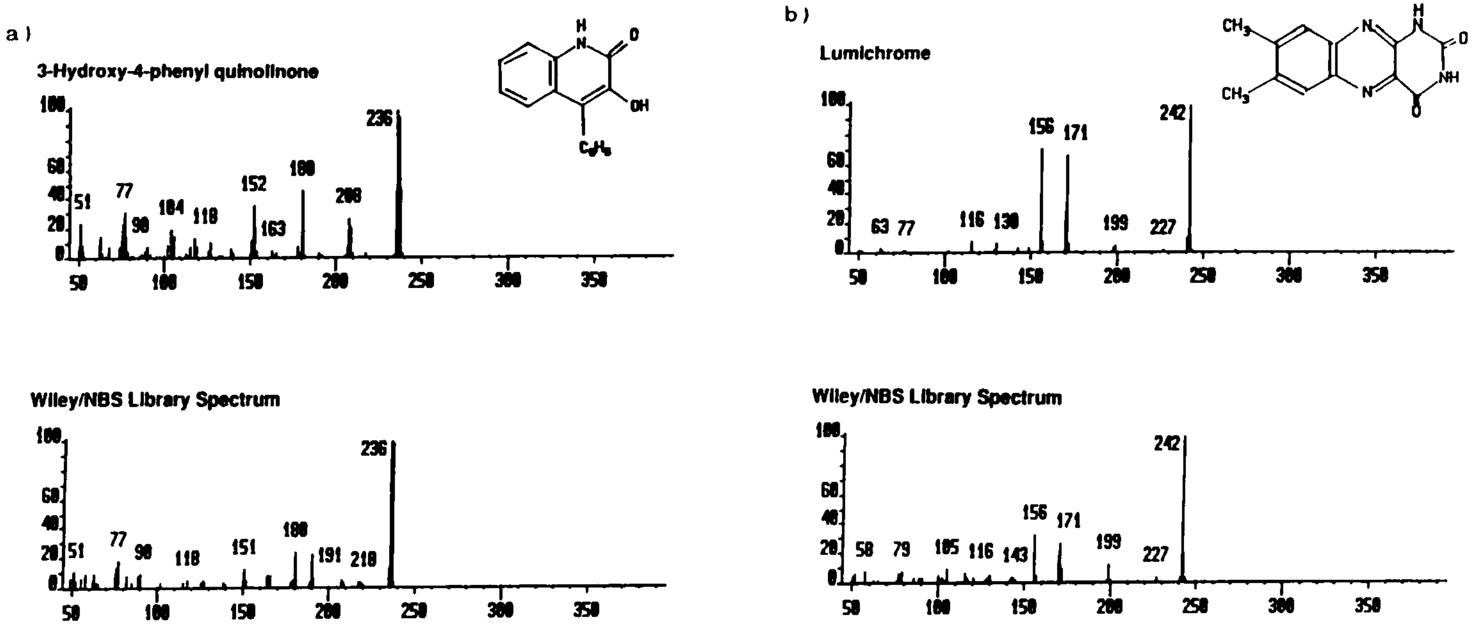

Figure 2 Comparison of spectra obtained by PB-LC/MS with the Wiley/NBS library spectra. (a) 3-hydroxy-4-phenyl quinolinone, (b) lumichrome.

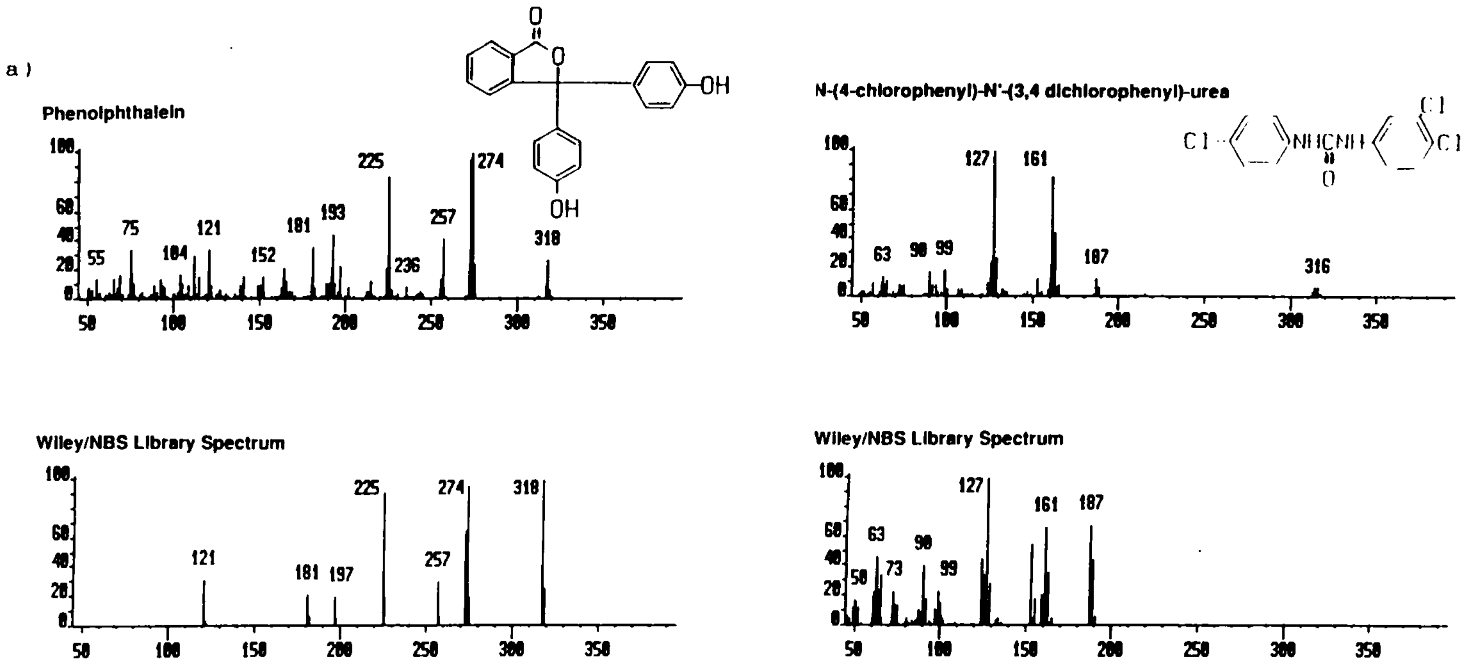

Figure 3 Comparison of spectra obtained by PB-LC/MS with the Wiley/NBS library spectra. (a) phenolphthalein, (b) N-(4-chlorophenyl)-N′-(3,4-dichlorophenyl)-urea.

Table 1 Chemicals tentatively identified by PB-LC/MS in POTW effluent of facilities A, B and C.

Chemical name	*CAS No.**	*Concentration (ppb)*		
		A	*B*	*C*
2-(4-Hydroxyphenyl)methyl phenol	2467-03-0			31
Dichloro-2-(4-hydroxyphenyl)methyl phenol				13
4-Methoxy-7-methyl-(5H)-furobenzopyranone	82-57-5	3		
Alkylated hydroxytoluene analog			5	
Alkylated hydroxytoluene analog			5	
Bis phenol A	80-05-7		25	8
3-Hydroxy-4-phenyl-(1H)-quinolinone	129-24-8			93
Hydroxyphenyl quinolinone analog				18
Brominated hydroxyphenyl quinolinone				3
Triclocarban	101-20-2	6	2	
3,7-dihydro-3,7-dimethyl-(1H)-purinedione	83-67-0			1
Phenolphthalein	77-09-8	1		
Lumichrome	1086-80-2	4		23
Nonylphenol tetraethoxylate + 2 isomers		40	1	
Nonylphenol pentaethoxylate			12	
2-(2-[2-(2-[2-(1′,1′,3′,3′-tetramethylbutylphenoxy)-ethoxy]ethoxy)ethoxy]ethoxy)ethanol		1	3	
2-[2-(2-[2-(2-[2-(1′,1′,3′,3′-tetramethylbutylphenoxy)-ethoxy]ethoxy)ethoxy]ethoxy)ethoxy]ethanol		1		

* Chemical Abstracts Identification Number.

Table 2 Pollutant concentration values for on-columne GC/MS vs. PB-LC/MS.

Facility	*Chemical name*	*On-column Gc/MS (ppb)*	*PB-LC/MS (ppb)*
A	Caffeine	1	1
	Butylbenzene sulfonamide	7	7
	Triphenylphosphine oxide	0.3	1
	Tris(butoxyethyl) phosphate	6	29
	Di-2-ethylhexyl phthalate	6	2
B	Butylbenzene sulfonamide	11	2
	Triphenylphosphine oxide	ND	2
	Tris(butoxyethyl) phosphate	2	4
	Di-2-ethylhexyl phthalate	14	8
C	Caffeine	5	4
	Butylbenzene sulfonamide	9	3
	Triphenylphosphine oxide	15	138
	Tris(butoxyethyl) phosphate	4	10
	Di-2-ethylhexyl phthalate	8	2

ND = not detected.

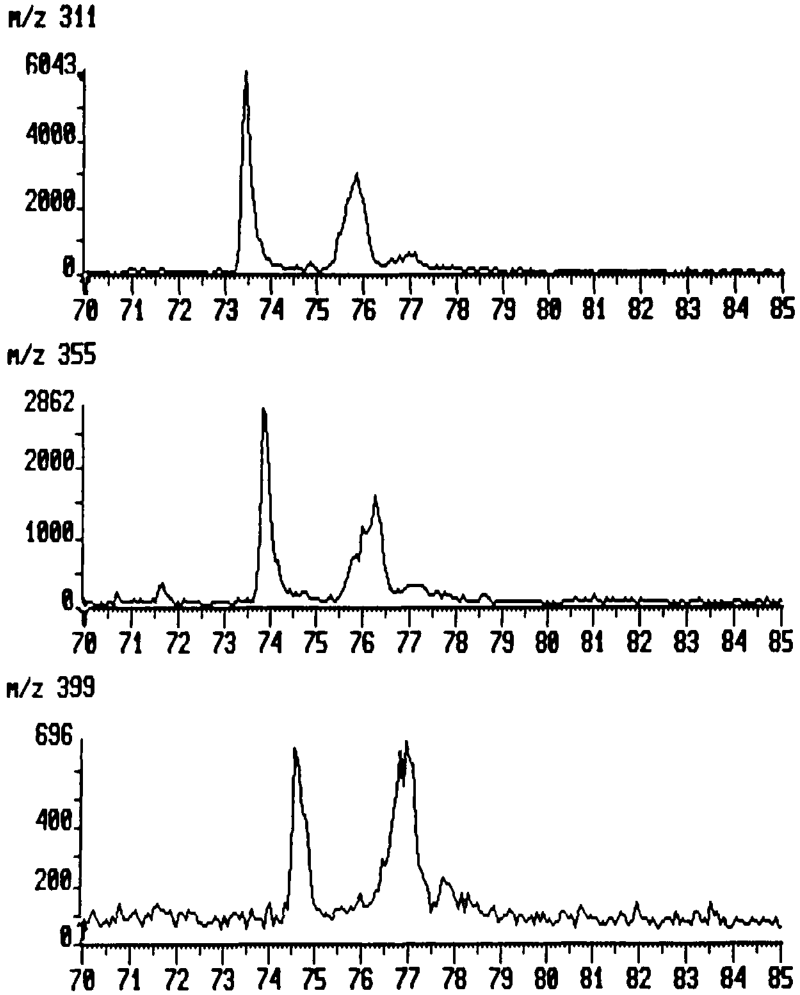

Figure 4 Selected mass chromatograms of ions present in an octylphenol and nonylphenol ethoxylate mixture.

of tertiary octylphenol ethoxylates of molecular weights 426 and 470 (characteristic ions of 355 and 399, respectively) as shown in Figure 4. Nonylphenol ethoxylates have been detected up to molecular weight 440, whereas on-column GC/MS could detect only a few analogues up to a molecular weight of 308. The fragmentation patterns and relative intensity of fragment ions of tertiary octylphenol ethoxylates and nonylphenol ethoxylates have been reported by Stephanou *et al.*[11] and Giger *et al.*[12], respectively.

The concentrations of compounds detected by both on-column GC/MS and PB-LC/MS are compared in Table 2. The majority of the values are very similar but some compounds appear to be more sensitive towards one technique or the other. When comparing the two techniques, one must remember that LC/MS is similar to packed-column GC with peaks eluting in 20 sec to 1 min. On the other hand, capillary GC peaks elute in a few seconds providing a strong signal-to-noise ratio. Therefore, the sensitivity for some compounds can be approximately 20-fold less by LC/MS than by GC/MS. This loss in sensitivity is compensated for by injecting 20–50 times as much material in LC/MS. Behymer *et al.*[8] theorize that co-elution effects may increase the sensitivities of some compounds in PB-LC/MS. It is believed that the co-eluent is acting similarly to ammonium acetate in the mobile phase by enhancing the formation of particles.

Plasticizers and plastic additives (di-2-ethylhexyl phthalate, tris(butoxyethyl) phosphate, triphenylphosphine oxide and butylbenzene sulfonamide) were found in the POTW effluents using either GC/MS or LC/MS. These compounds have been previously found in industrial wastewater[13] and finished drinking water[14]. The quinolinone analogues are thought to originate from a pharmaceutical or chemical manufacturer while the remaining synthetic organic compounds could not be assigned to any specific industry.

PB-LC/MS has proven its ability to detect and identify a number of environmental contaminants which would remain undetected by on-column GC/MS. These studies demonstrate the need for the PB-LC/MS technique in conjunction with GC/MS to allow for a thorough analysis of complex environmental samples.

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