

INTRODUCTION

The Dangerous Substances Directive (76/464/EC)' lists 132 compounds that have legislated levels in drinking and surface waters, of which, more than 100 are amenable to GC analysis.

The compound groups analysed here represent a wide range of polarities and types, and include benzidines, chloroanilines, chloronitrobenzenes, chloronitroloenes, chlorophenols, chlorotoluidines, OCs, OPs, PAHs, PCBs, phenylureas, triazines and volatile amines. Many of these compound groups will typically have their own dedicated analytical method that requires specific extraction/clean-up and final analysis. Combining these groups into a single method would allow the laboratory to significantly increase sample throughput. A method has previously been published² employing single quadrupole MS using selected ion recording (SIR) for screening of the GC amenable compounds.

SIR allows for targeted screening of a finite number of compounds to be achieved. However, much of the chemical information is discarded so full spectrum techniques are still required in so-called "open" or untargeted screening environments.

To establish a suitable untargeted screening technique there are a number of requirements that would need to be met to extract, detect, locate and identify all components. These include; minimal non-selective sample preparation for a wide range of compound groups with different polarities; simple high resolution GC separation to minimise matrix interference whilst maintaining resolution of critical pairs; and automated peak detection and deconvolution of all components in the sample.

Exact mass time of flight mass spectrometry (TOF-MS) is a full spectrum technique capable of both the targeted and the untargeted screening approaches.

A method is presented here for the targeted screening of 107 GC amenable compounds in surface waters down to the legislated concentration of 0.1 µg/L.

The method will also be extended to include the untargeted screening of other GC amenable compounds in surface waters using automatic peak detection, deconvolution and library searching with exact mass confirmation.

METHODS

Extraction Method

- 200 mL filtered water was adjusted to pH 4.0 with 1 N HCl.
- 500ng I.S. (d5-nitrophenol, 2-fluorobiphenyl, p-terphenyl-d14) added.
- Waters Oasis HLB 60 mg, 3cc SPE cartridge was conditioned with 6 mL dichloromethane, 6 mL acetonitrile and 6 mL water.
- The sample was loaded at approximately 6 mL/min.
- The cartridge was washed with 1 mL water and dried under nitrogen for 20 mins.
- The elution was performed with 2 x 2.5 mL dichloromethane.
- The volume was then adjusted to 0.5 mL under nitrogen at ambient temperature.
- 500ng recovery standard was added (d10-anthracene) for a 400 fold concentration step during the extraction.

GC Method

Agilent 6890N GC with CTC CombiPal autosampler.
Column J & W Scientific DB-17ms 30 m x 0.25 mm i.d. x 0.25 µm film thickness.
Flow rate 1.0 mL/min helium constant flow.
Temp. ramp 40 °C (Hold 1 min)
310 °C @ 15 °C/min (Hold 11 min).
Total run time 30 min.
Injection method Pulsed splitless injection, 1 µL.
4mm i.d. double taper liner.
140 kPa pulse for 1.1 min.

GC-MS Method

Waters GCT Premier TOF-MS.
Ionisation mode Electron impact (EI+).
Source temp. 200 °C.
Electron energy 70 eV.
Trap current 200 µA.
Interface temp. 280 °C.
Mass range 50 and 550 Da.
Acquisition speed 10 spectra / s.
Lock mass 2,4,6-tris-(trifluoromethyl)-1,3,5-triazine
m/z = 284.9949.
Resolution >7000 full width half maximum (FWHM).
Software MassLynx version 4.0
Targetlynx or Chromalynx application managers.

RESULTS AND DISCUSSION

The chromatography was optimised for sensitivity, speed and separation. Baseline resolution was obtained for three critical pairs, 3- and 4-chlorophenol, E and Z mevinphos and o,p'-DDT and p,p'-DDD, using the DB-17ms column. A typical reconstructed ion chromatogram (RIC) for all the pollutants is illustrated in Figure 1.

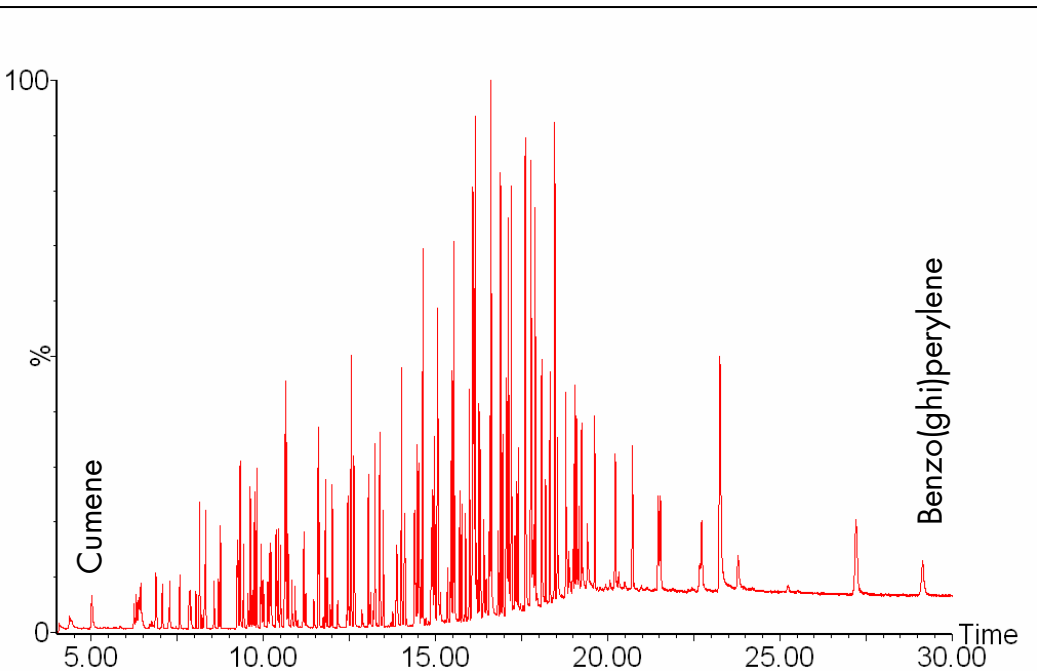


Figure 1. Reconstructed ion chromatogram (RIC) for all pollutants analysed using DB-17ms column.

Targeted Screening Results

The 0.5 µg/L spiked drinking water samples were analysed to determine the recovery for each pollutant using a single SPE sorbent. Table 1 summarises the recoveries achieved from five replicate extractions using the described method.

Overall, the distribution of recoveries for such a wide range of polarities, boiling points, pKa's and water/octanol partition coefficients (Kow) using a single SPE sorbent is excellent.

Mean Recovery	Number of Compounds (%)
70 - 120%	79 (72%)
50 - 70%	9 (8 %)
< 50%	14 (13%)
>120%	8 (7%)

Table 1. Recovery for pollutants spiked at 0.5 µg/L (n = 5) from water.

The limits of detection (LODs) were assessed for confirmation (two exact mass chromatograms per compound) and screening (one exact mass chromatogram per compound). A summary of the instrumental and method LODs is listed in Table 2. All LODs are based upon a peak-to-peak signal to noise (S/N) ratio of 3:1. The instrumental LODs are based upon the lowest concentration standard injection. The method LODs are based upon the average LOD obtained from five replicate extractions of 0.5 µg/L spiked water samples. The LODs reported are excellent for such a wide range of compounds with a single generic extraction method.

		No. of Compounds < 0.1 µg/L	No. of Compounds > 0.1 µg/L
Instrument	Screening	102	1
	Confirmation	101	2
	Screening	101	2
	Confirmation	98	5
Method	Drinking Water	Screening	101
	Surface Water	Screening	101
	Drinking Water	Confirmation	99
	Surface Water	Confirmation	99

Table 2. Summary of the instrumental and method LODs.

For the chlorophenols in Figure 2, the nominal mass chromatogram (A) shows peaks that could lead to interference when using automatic integration. In the exact mass chromatogram (B) the chlorophenols have no interference, improving the selectivity of the method, leading to an increase in the S/N ratio achieved. The mean difference between the nominal mass LOD and exact mass LOD was a factor of six for all the residues in the method.

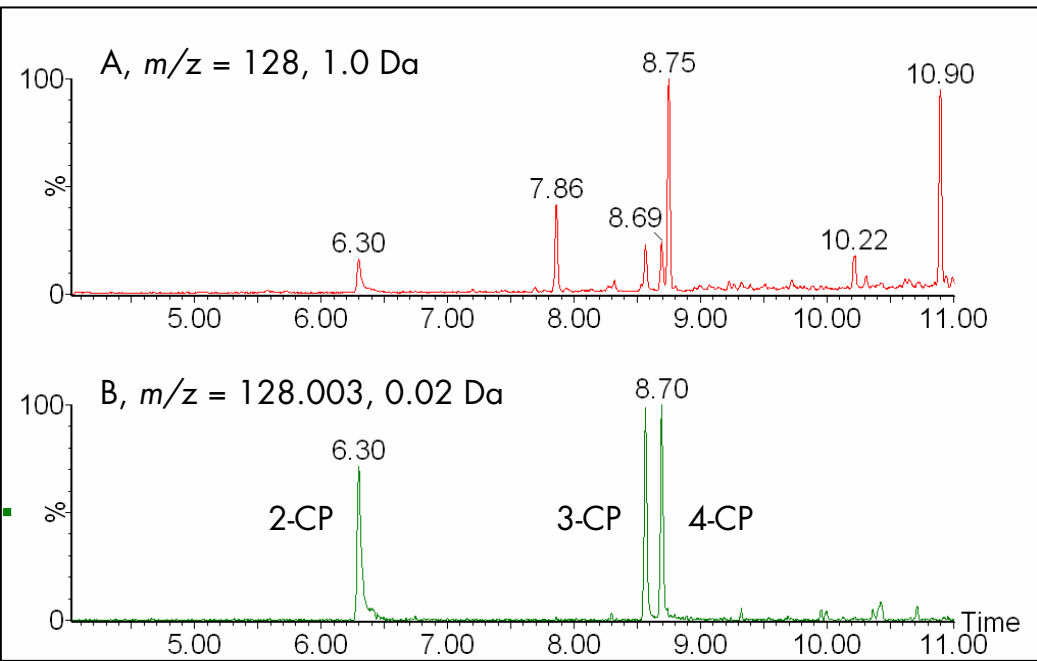


Figure 2. Selectivity offered by nominal mass (A) versus exact mass (B) chromatograms for chlorophenols (0.1 µg/L).

The sensitivity of the method is illustrated in Figure 3, showing that dichlorvos can be confirmed to a level below 0.1 µg/L in surface water. Increasing the number of masses, as in the case of moving from screening to confirmation, does not decrease the sensitivity with TOF.

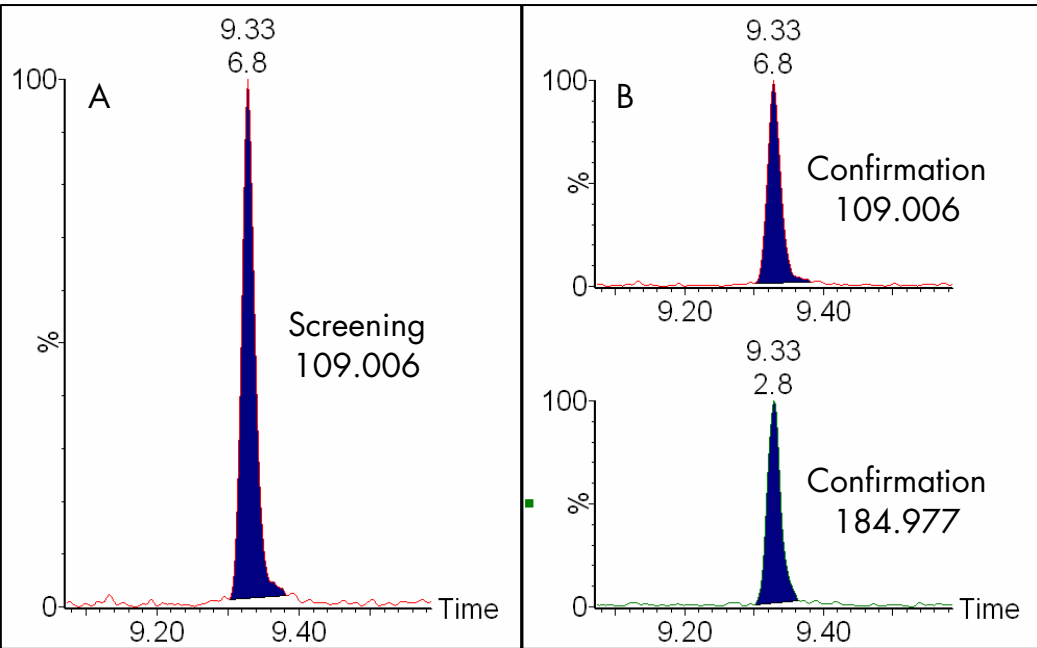


Figure 3. Sensitivity of screening (A) versus confirmation (B) for 0.1 µg/L dichlorvos in surface water.

Solvent standards were prepared in the concentration range 1 - 500 pg/µL, equivalent to 0.005 – 2.5 µg/L. 2-fluorobiphenyl was used as an internal standard to correct for any volumetric errors. The standards were injected in a typical batch analysis bracketing the drinking and surface water extracts. The resulting data was processed using Waters Targetlynx application manager. The Targetlynx browser for 2-chloro-4-toluidine at a spiked concentration of 0.1 µg/L in surface water is illustrated in Figure 4. Two exact masses are shown for confirmation. 99 residues could be confirmed using this method in surface waters to a concentration of 0.1 µg/L while 101 could be screened to the same concentration.

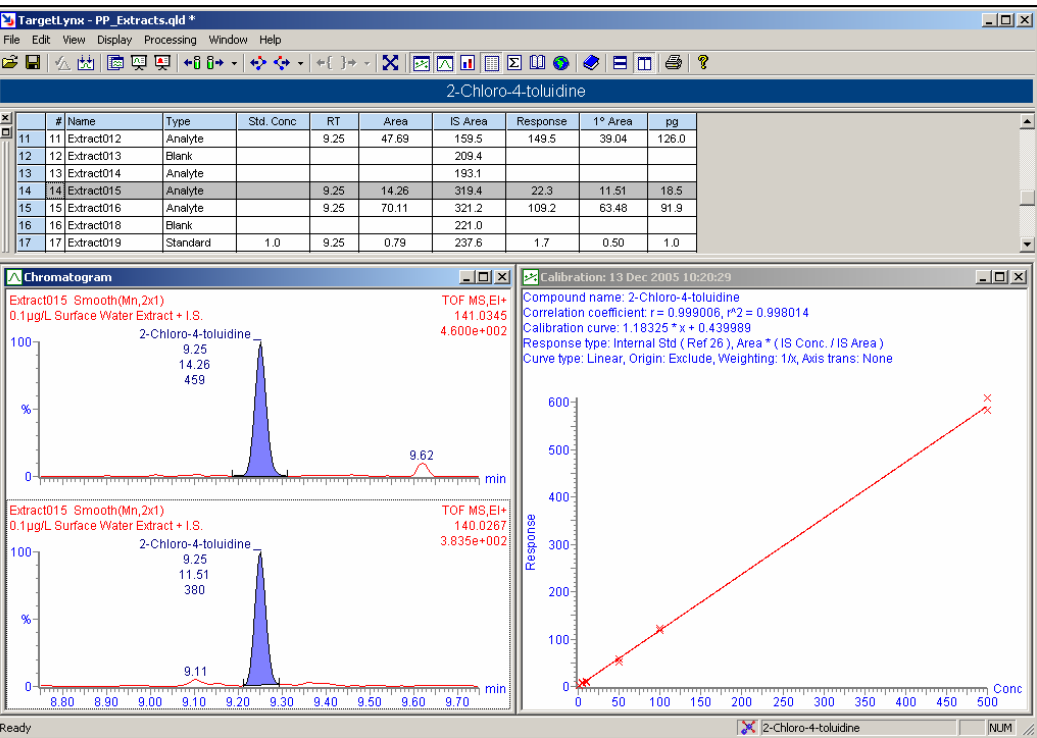


Figure 4. Example Targetlynx browser for 2-chloro-4-toluidine at a concentration of 0.1 µg/L in surface water.

Untargeted Screening Results

In the untargeted screening environment, there may be hundreds of peaks that need to be located, which would be very time consuming if performed manually. In this case, it would be useful to process automatically using a deconvolution package such as Waters Chromalynx application manager.

Chromalynx automatically plots the RICs of the eight most intense ions at any point in the chromatogram. If a peak is found to satisfy user-defined parameters the software will display its deconvoluted mass spectrum. The spectrum can then be submitted to an automatic library search routine with the ability to confirm by exact mass scoring.

Chromalynx processing of the 0.5 µg/L spiked surface water extract located approximately 800 components in the whole chromatogram. 180 pollutants were spiked into the extract, of which, 100 are in the targeted method.

Moving to the blank surface water, a few untargeted pollutants of interest were detected and identified with Chromalynx. An example pollutant was 4-methylbenzenesulfonamide, which is illustrated in Figure 5. Other examples included naphthalene and 1-methylnaphthalene.

Chromalynx automatically performs exact mass scoring of the library search. The formula from the library hit is submitted to elemental composition and the "n" most intense ions are confirmed/rejected by exact mass. Green boxes indicate a good exact mass match, amber boxes indicate a tentative match and red boxes indicate no match.

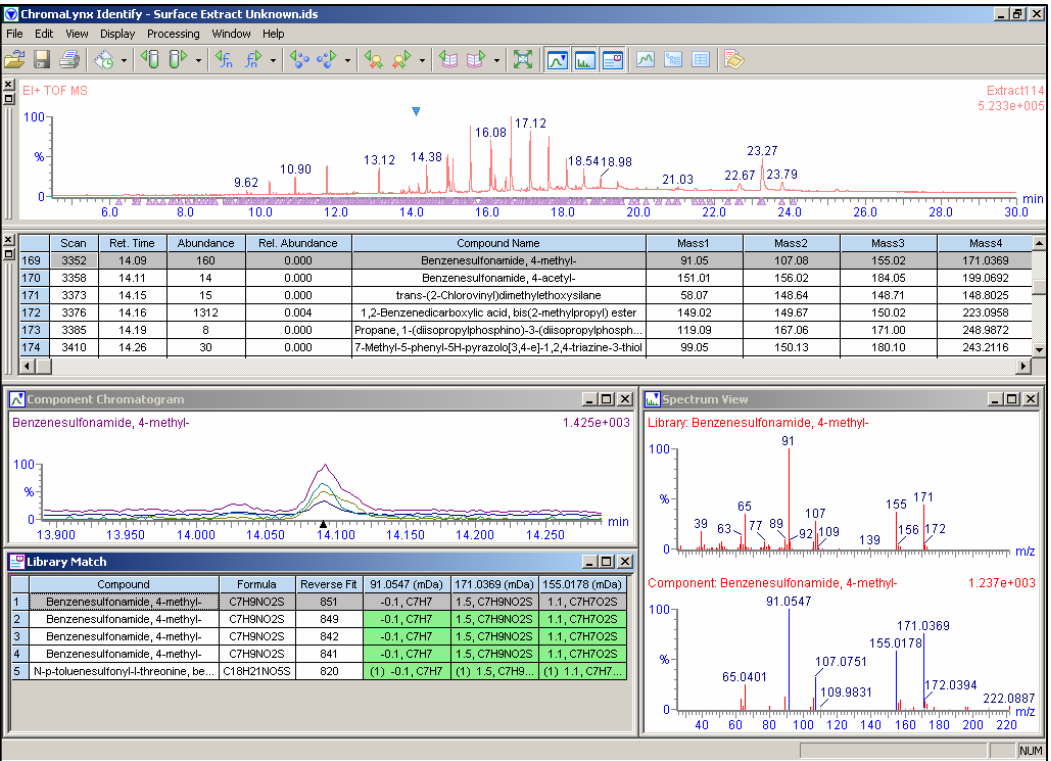


Figure 5. Example Chromalynx browser with exact mass scoring for an untargeted pollutant, 4-methylbenzenesulfonamide, in surface water.

CONCLUSIONS

- A method has been presented for the targeted confirmation of more than 100 priority pollutants using Oasis SPE cartridges and the GCT Premier with the Targetlynx application manager.
- A majority of the pollutants can be confirmed to concentration levels of less than 0.1 µg/L in surface waters.
- Exact mass chromatograms improve the selectivity available, allowing lower LODs to be reached.
- The method can also be extended to larger numbers of residues without loss in sensitivity.
- The full spectrum approach provided by TOF also allows current and historical data to be screened for untargeted residues with the Chromalynx application manager.
- Chromalynx enables automatic peak detection, deconvolution, library searching and exact mass scoring.

References

- Council Directive 76/464/EEC of 4th May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community, Off. J. of the European Communities, **L129** (1976) 23.
- Lacorte, S., Guiffard, I., Fraisse, D. and Barceló D., *Anal. Chem.* **72** (2000) 1430.