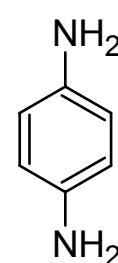


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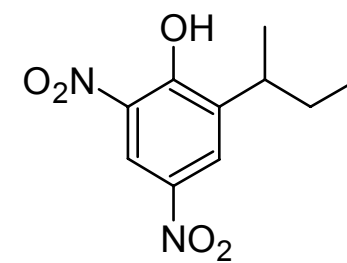
Introduction

The multi-residue GC and GC/MS determination of pollutants in the environment remains a challenge for the analytical laboratory. Acidic compounds, such as phenols, and basic compounds, such as anilines, can usually be extracted using dichloromethane (DCM), but two separate extractions must be performed on the same sample. Consider the protocol for liquid-liquid extraction (LLE) utilized in the US EPA SW 846 method 3550. One extraction is performed at high pH (to recover base/neutrals) and another must be performed on the same sample at low pH (to recover acids). Compared with LLE, solid-phase extraction, (SPE) is a less cumbersome procedure but a similar two pH and two extraction approach must be employed when using traditional reversed-phase sorbents. Moreover, more polar or reactive compounds, such as phenol or phenylenediamine, may not be recovered using either liquid extraction or reversed-phase SPE.

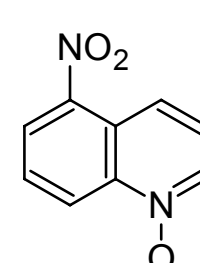
In recent ACS meetings we have reported on SPE methods employing a mixed-mode cation-exchange sorbent for the simultaneous extraction of acidic and basic drugs and pesticides in environmental matrices. Using one sorbent and one extraction step, acidic drugs such as ibuprofen and basic drugs such as phenylpropanolamine were effectively extracted and analyzed at sub µg/L levels. However, these SPE methods were designed to be used with liquid chromatography and atmospheric pressure ionization mass-spectrometry (LC/MS). The solvents utilized in these methods, such as methanol with aqueous ammonia, are not generally suitable for use with gas chromatography. In this study, we have applied the mixed-mode sorbent technology to the analysis of acidic and basic compounds by GC and GC/MS, and have applied the protocol to the analysis of a test mixture containing 33 compounds (acids, bases and neutrals) listed in EPA method 8270C. Structures for a representative acid, base and neutral compound from this list are shown below.



p-phenylenediamine (base)



dinoseb (acid)



4-nitroquinoline-N-oxide (neutral)

Mixed-mode cation-exchange sorbents, such as Oasis® MCX, have not been employed for GC applications because aqueous ammonia or organic amine modifiers have been used for elution of the cationic species. In this study we utilized an SPE eluent prepared from anhydrous ammonia (7 M) in methanol (Aldrich pn. 49,914-5). The eluent used in this study was 10 % of the methanolic ammonia in methylene chloride. This eluent was effective for simultaneous elution of *acids and bases* from the Oasis® MCX sorbent.

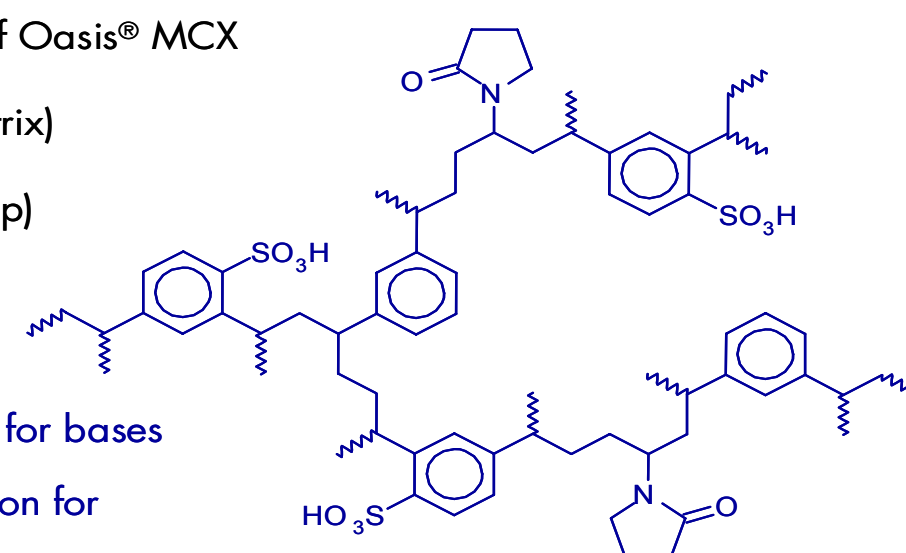
Mixed-Mode Cation EXchanger

Strong sulfonate (-SO₃H) groups bonded to Oasis® HLB copolymer provide cation exchange capacity (1 meq/g)

Sorption Mechanisms of Oasis® MCX

Reversed-Phase
(from the polymeric matrix)

Cation Exchange
(from the sulfonate group)



• mixed-mode retention for bases

• reversed-phase retention for acids and neutrals

Figure 1 shows the relative retention of a typical acid (HA, pKa 4.8), base (BH⁺, pKa 9) and neutral compound as a function of pH on a typical reversed-phase sorbent. At pH 2, there is good retention of the acid and neutral compound with little retention of the base, which is a cation (BH⁺) at low pH. At pH 11, there is good retention of the base and neutral with little retention of the acid, which is an anion (A⁻) at high pH. Consequently, the analyst must perform an extraction at pH 11 to recover the bases and neutrals (base/neutral extraction), then re-extract the sample at pH 2 to recover the acids.

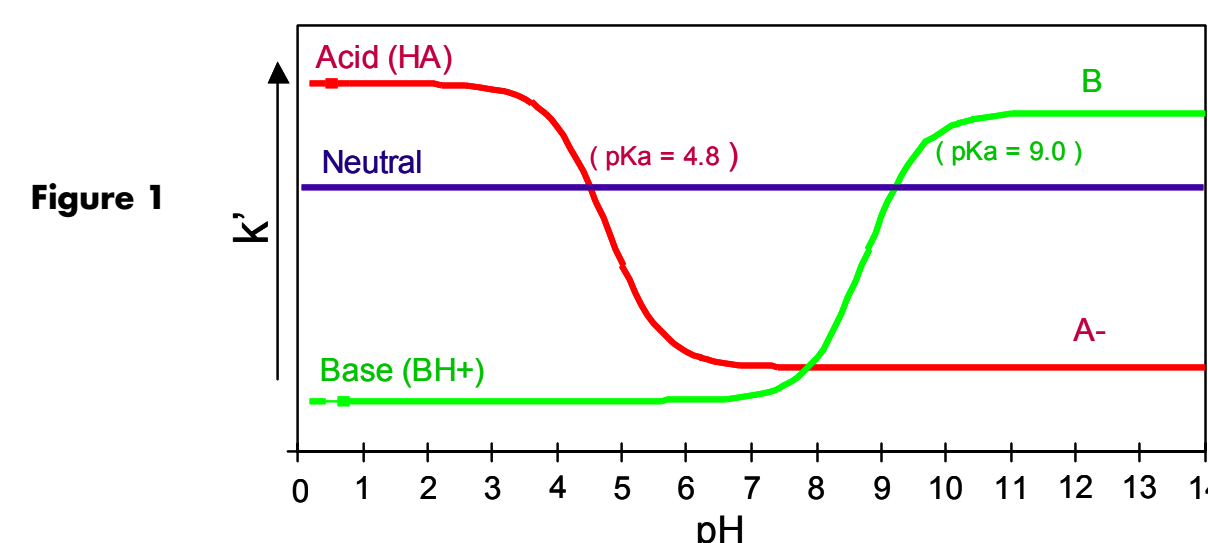
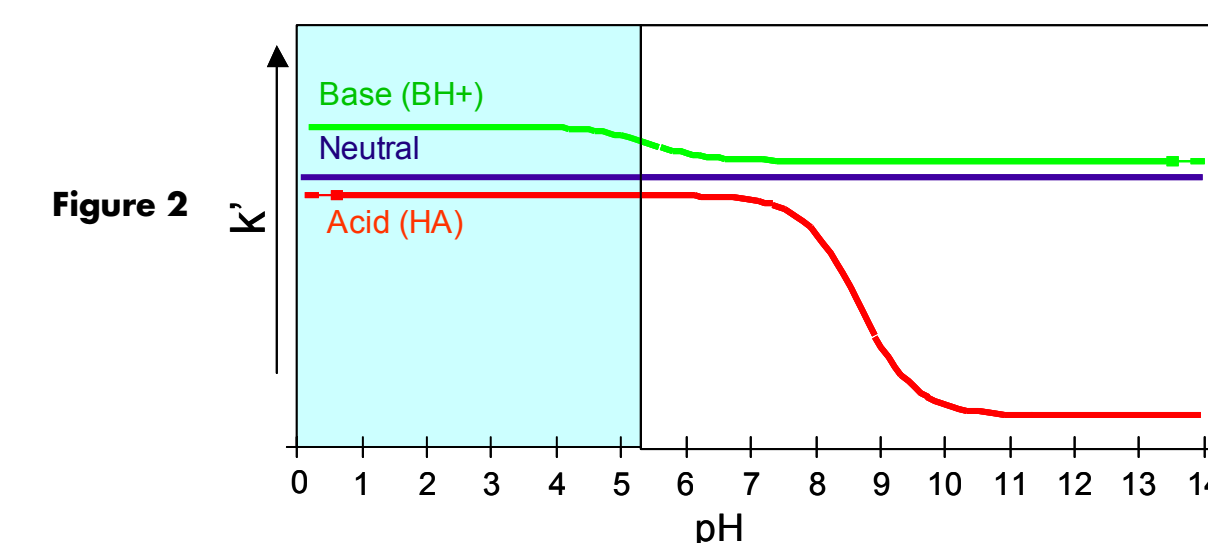


Figure 2 shows the retention of the acid, base and neutral compound on a mixed-mode cation-exchange sorbent. At low pH values, the acid and neutral compound are retained by reversed-phase interaction, the base by mixed cation-exchange *and* reversed-phase. The area highlighted in blue represents the pH range with high retention of *both acids and bases*.



SPE Protocol for This Study

Figure 3 shows the general SPE protocol for this study. Prior to analysis, the sample (250 mL) was acidified with HCl and residual chlorine was quenched with sodium thiosulfate. Oasis® MCX cartridges (6 cc, 150mg) were used in this study.

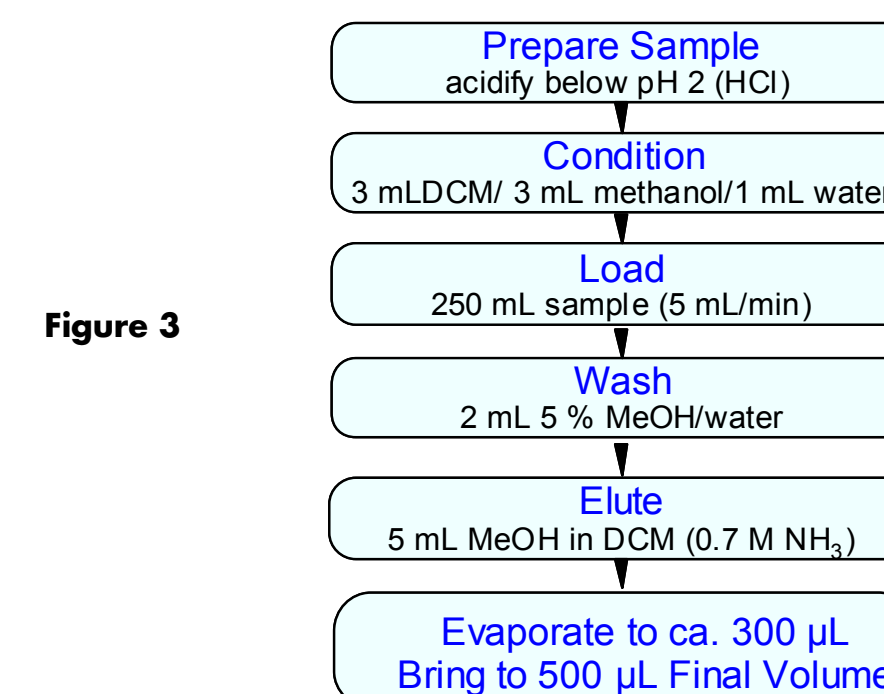


Figure 3

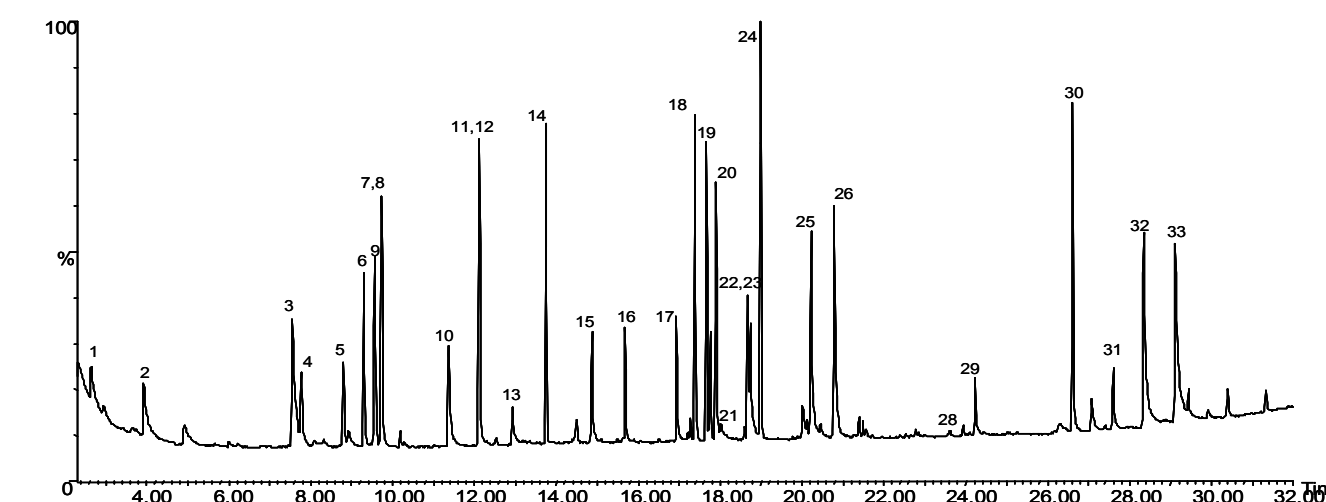
note: the eluent was dried over 4 gm sodium sulfate before the evaporation step

GC/MS and GC/NPD

Figure 4 shows GC/MS and Figure 5 shows GC/NPD chromatograms obtained from a 20 µg/L chlorinated tap water sample.

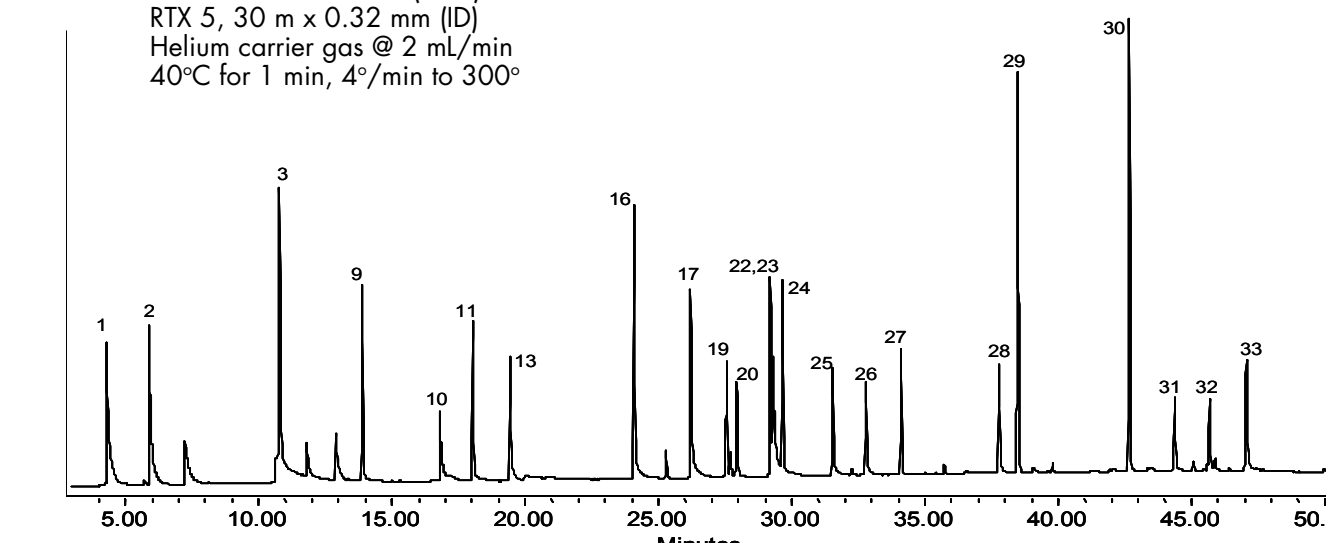
Mass Spectrometer: Waters/Micromass GCT™ with Agilent 6890 GC
RTX 5-MS, 30 m x 0.25 mm (ID)
Helium carrier gas @ 1 mL/min
35°C for 4 minutes, 8°/min, to 300°

Figure 4



HP 5890 Series II GC (NPD)
RTX 5, 30 m x 0.32 mm (ID)
Helium carrier gas @ 2 mL/min
40°C for 1 min, 4°/min to 300°

Figure 5



Results

The results obtained from two types of water are presented below. [Basic](#) compounds were determined using GC/NPD. [Acidic](#) and [neutral](#) compounds were determined using GC/MS.

COMPOUND	% RECOVERY ±RSD (20 µg/L Tap Water)	% RECOVERY (20 µg/L River Water)
1. pyridine	61 (17)	40
2. picoline	77 (16)	47
3. aniline	90 (11)	58
4. phenol	65 (14)	61
5. benzyl alcohol	75 (25)	56
6. o-cresol	91 (8.6)	65
7.8. m,p-cresol	91 (8.9)	65
9. o-toluidine	82 (12)	45
10. phentemine	73 (18)	24
11. chloroaniline	82 (11)	49
12. dichlorophenol	57 (6.2)	40
13. phenylenediamine	93 (15)	nr
14. 2-methylnaphthalene	81 (8.0)	54
15. trichlorophenol	54 (10)	73
16. 2-nitroaniline	95 (7.2)	74
17. 3-nitroaniline	103 (8.5)	81
18. dibenzofuran	80 (5.4)	62
19. 1-aminonaphthalene	87 (5.1)	77
20. 2-aminonaphthalene	88 (8.5)	58
21. tetrachlorophenol	35 (17)	30
22. 2-methyl-5-nitroaniline	104 (6.2)	91
23. 4-nitroaniline	106 (8.7)	104
24. diphenylamine	93 (4.4)	77
25. phenacetin	85 (7.3)	92
26. aminobiphenyl	105 (4.2)	83
27. dinoseb	90 (7.1)	97
28. nitroquinoline oxide	100 (6.5)	87
29. methapyrilene	105 (5.5)	100
30. dimethylaminoazobenzene	100 (3.9)	98
31. dimethylbenzidine	64 (8.9)	20
32. acetamidofluorene	135 (5.4)	130
33. dichlorobenzidine	111 (6.0)	75

pyridine, picoline, aniline and toluidine are not recovered from polymeric reversed-phase sorbents under acidic conditions.

Discussion

For good recovery of compounds 1-9, it is essential to avoid evaporative losses; do not evaporate to dryness.

Recovery of chlorinated phenols was reduced because of interactions with the sodium sulfate in the presence of ammonia. To improve recovery of chlorinated phenols use a two step elution of the cartridge; first elute with 3 mL of 95:5 DCM/methanol, then with 3 mL of 90:10 DCM/methanolic ammonia.

Recovery of some compounds is lower from the high humic content river water (10 mg/L TOC). Since much of the humic material is retained on the sorbent, a 500 mg cartridge is recommended for high humic content samples.

Preliminary experiments indicate that for LOQ below 5 µg/L, a 0.5 L sample should be processed using a 500 mg cartridge, with a final volume of 0.5 mL.