The Analysis of Pesticides Using Solid Phase Microextraction

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1. Introduction

Contamination of our water supplies by pesticides is a growing concern because of their universal application and persistence in the environment. The focus of this paper is on the analysis of organochlorinated pesticides, and nitrogen containing herbicides that are currently investigated by US EPA methods 507 and 508. Preliminary results for phosphorous containing pesticides are also included.

Currently, aqueous samples are analyzed by either liquid-liquid extraction (LLE),[1-3] or solid phase extraction (SPE).[2-4] Although LLE is a popular technique recommended by the US EPA, it requires large quantities of expensive, toxic solvents that are harmful to the environment. The procedure itself is time consuming , tedious, and often requires pre-concentration of the sample prior to analysis. SPE has increased in popularity as a sample preparation technique because it overcomes a few of the disadvantages encountered with LLE. It is not as time consuming and the method requires less solvent. However, disadvantages include plugging of cartridges, significant background interferences, and poor reproducibility.

Solid phase microextraction (SPME) is a solvent free analytical technique that is significantly faster and simpler than the conventional methods. The SPME device consists of a syringe assembly that serves as a holder for the fiber assembly which is comprised of a needle that protects a small diameter fused silica fiber that has been coated with a liquid polymeric stationary phase. During sampling the coated fiber is directly exposed to the sample or to the headspace above the sample, allowing partitioning of the analytes according to their affinity toward the fiber coating. The analytes are thermally desorbed from the fiber into the hot injector of a Gas Chromatograph (GC) and are subsequently analyzed. The fiber can immediately be used for a succeeding analysis.

2. Experimental

The fibers selected were 1 cm in length and coated with either 100 μm thick poly-dimethylsiloxane, or 85 μm thick polyacrylate. The fibers were conditioned according to the instructions listed by the supplier (Supelco Canada) prior to use. The stock standard mixtures for the different classes of pesticides (Supelco Canada), were diluted to prepare working standards of different concentrations.

Initial analyses were performed with a Varian GC, equipped with a flame ionization detector (FID). Varian 3400 series GCs equipped with a nitrogen phosphorous detector (NPD), or an electron capture detector (ECD) were used for further investigation of the

nitrogen and phosphorous containing pesticides, and organochlorines respectively. Subsequent analyses for both classes of compounds were performed using a Varian Saturn Ion Trap Mass Spectrometric detector (MS). The column for separating the analytes was a PTE-5, 30 m x 0.25 mm with a 0.25 μm thick stationary phase.

Preliminary experiments involved generating time profiles for each analyte, to determine equilibrium times and calculate the partition coefficient (K). Optimization of the extraction conditions by matrix modifications were investigated, to enhance the amount extracted by the fiber coating. This was followed by determining the precision, and the dynamic range of detection. The limits of detection were also determined from the linearity experiments. Finally, the viability of the method was assessed by analyzing real environmental samples.

3. Results and Discussion

Solid phase microextraction is an equilibrium process, that involves the partitioning of analytes from a liquid or gaseous sample into the polymeric phase according to their partition coefficients, K[5]:

$$n_s = \frac{KV_sV_{aq}C_{aq}^{\circ}}{KV_s + V_{aq}} \qquad (1)$$

where n_s is the amount extracted by the fiber coating, V_{aq} and V_s are the volumes of the aqueous phase and stationary phase respectively, and C°_{aq} is the initial concentration of the analytes in the aqueous phase. Equation 1 indicates that the amount of analytes extracted are dependent on both the volume of the stationary phase and the partition coefficient. Likewise the sensitivity and the linear range of the method are also dependent upon these parameters.

The organochlorines fall into a non-polar class with relatively high octanol-water coefficients (K_{ow}),[6] therefore a polydimethylsiloxane polymeric coating has been used for the extractions. The nitrogen-containing pesticides being studied are predominately slightly polar with small K_{ow},[6] thus, extractions were performed with a more polar polyacrylate coating.[7] The polyacrylate coating is also being employed in the preliminary investigation of the phosphorous containing pesticides. Figures 1 and 2 illustrate the successful extraction of pesticides from aqueous media using the two different coated fibers.

The time exposure profiles were generated for each target analyte by plotting the response of the GC in area counts against the exposure time of the fiber to the sample. The equilibration times are listed in Table 1. Since equilibrium times vary for each analyte extraction times of 50, 90, and 45 minutes were selected for the nitrogen-containing, organochlorinated, and organophosphorous pesticides respectively to ensure optimal time and extraction efficiency for the SPME methods.

The amount of analyte extracted by the fiber increases when the solubility of the analyte in water decreases. This can be achieved by altering the ionic strength by the addition of salt to the matrix or by adjusting the pH of the water. Figure 3 is an example of the matrix effects determined for the organochlorines. This figure indicates that certain conditions are optimal for different groups of analytes. Similar results are observed for the nitrogen containing pesticides. Although salt or pH increased the amount extracted for some analytes, sub ppt detection limits can still be achieved under neutral conditions. Therefore, most analyses are carried out under neutral conditions.

The reproducibility of the measurements between fibers is greater than 90%, with precision typically below 10% for 7 extractions with a single fiber. All organochlorines analyzed illustrate a linear response within the range of 0.1-100 ng/mL when analyzed by GC/FID and GC/MS, and between the ranges of 0.001-1 ng/mL and 1-100 ng/mL using the GC/ECD. Of the 22 nitrogen containing herbicides analyzed, 21 demonstrate linearity across the range of 0.1-1000 ng/mL, using the GC/FID, GC/NPD, and GC/MS. The detection limits achieved for the chlorinated and nitrogenated pesticides are comparable if not better than those listed in conventional methods 507 and 508.

Commercial wine samples were analyzed for the presence of nitrogen containing herbicides with the GC/MS. Several wine samples were analyzed by the standard addition procedure after initial screening with the method indicated the presence of some herbicides. Nine of the 22 herbicides were found in a white wine sample from the Rhone valley, France. Environmental samples, taken from the Arctic regions of Canada, were analyzed for the presence of organochlorines using GC/ECD. Thirteen of the eighteen chlorinated pesticides under investigation were identified and confirmed by dual column and dual ECD detection and quantified by external calibration.

The SPME technique is a viable, rapid alternative for the quantitative and qualitative analysis of pesticides from aqueous environmental samples. These SPME methods are precise, reproducible and have a wide dynamic linear range. The detection limits obtained are comparable if not better than those required by US EPA methods 507 and 508. The compact nature and simple design of the sampling device along with the elimination of solvent use during sample preparation allows it to be easily adapted for use with an autosampler, and provides an opportunity to perform on-site field sampling studies.

4. Acknowledgments

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5. References

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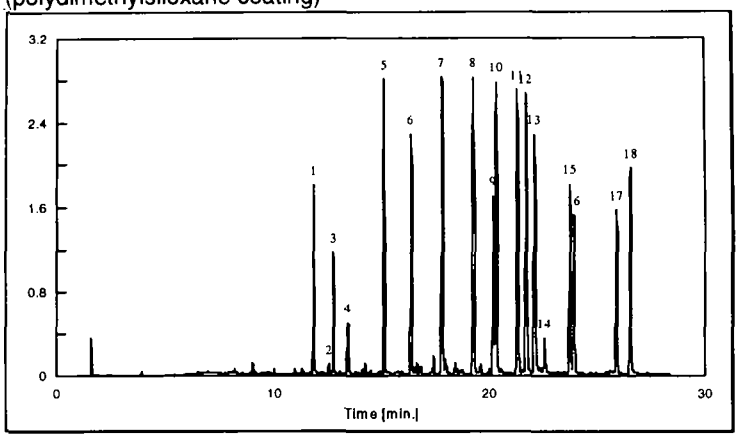
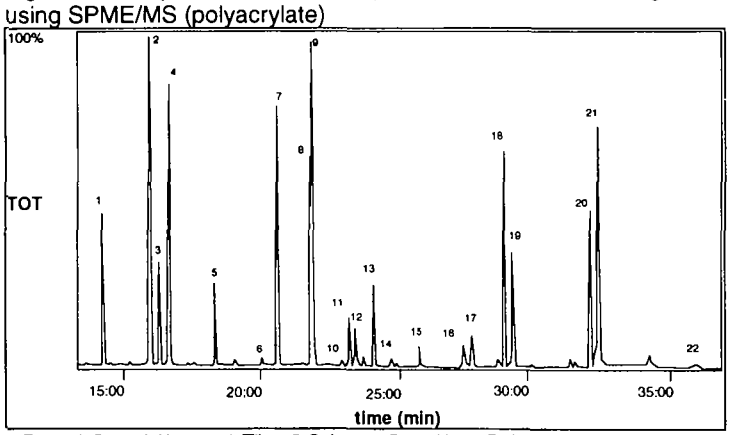
Figure 1: Analysis of a 1 ppb aqueous standard of 18 organochlorines using SPME/ECD (polydimethylsiloxane coating)



1. α-BHC; 2. β-BHC; 3. γ-BHC(Lindane); 4. δ-BHC; 5. Heptachlor; 6. Aldrin; 7. Heptachlor Epoxide; 8. Endosulfan I; 9. Dieldrin; 10. p,p'-DDE; 11. Endrin; 12. Endosulfan II; 13. p,p'-DDD; 14. Endrin Aldehyde; 15. Endosulfan Sulfate; 16. p,p'-DDT; 17. Endrin Ketone; 18. Methoxychlor

Figure 2: Analysis of a 100 ppb aqueous standard of 22 nitrogen containing pesticides using SPME/MS (polyacrylate)



1. Eptam; 2. Sutan; 3. Vernam; 4. Tillam; 5. Ordram; 6. Propachlor; 7. Ro-Neet; 8. Trifluralin; 9. Balan; 10. Simazine; 11. Atrazine; 12. Propazine; 13. Tolban; 14. Terbacil; 15. Sencor; 16. Bromacil; 17. Dual; 18. Paarlan; 19. Prowl; 20. Oxadiazon; 21. Goal; 22. Hexazinone.

Figure 3: Matrix Effects

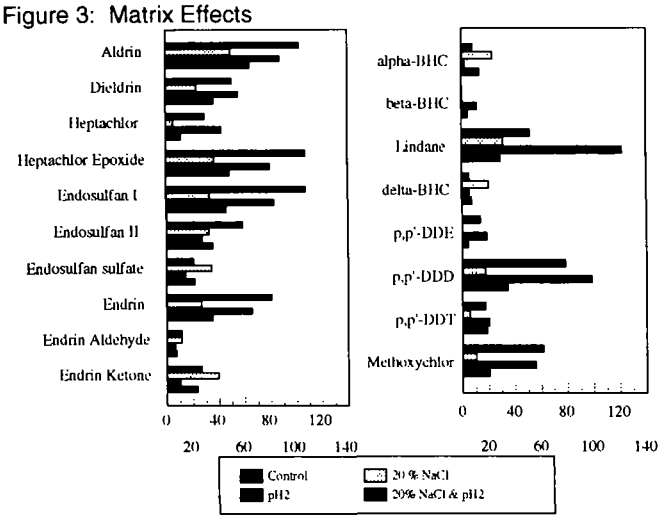


Table 1: Equilibration Times

Pesticides Nitrogen-containing	Equilibration Time (min)
Atrazine	90
Hexazinone	10
Propazine	90-120
Sencor	50-90
Simazine	10
Balan	50-90
Paarlan	50
Prowl	50
Tolban	30
Trifluralin	50
Bromacil	30
Terbacil	50-90
Eptam	90
Ordram	50-90
Ro-Neet	90
Sutan	90
Tillam	90
Vernam	90
Dual	50
Goal	30
Oxadiazon	50
Propachlor	50

Pesticides Organochlorines	Equilibration Time (min)
α-BHC	15
β-BHC	15
Lindane (γ-isomer)	15
δ-BHC	15
Heptachlor	180
Aldrin	180
Heptachlor Epoxide	180
Endosulfan I	45
p,p'-DDE	90
Dieldrin	120
Endrin	120
Endosulfan II	45
p,p'-DDD	180
Endrin Aldehyde	120
Endosulfan Sulfate	45
p,p'-DDT	180
Endrin Ketone	45
Methoxychlor	180

Pesticides Phosphorous-containing	Equilibration Time (min)
O,O,O-triethyl phosphorothiate	40
Dichlorvos	30
Thionazin	40
Ethoprophos	40
Sulfotepp	40
Phorate	40
Dimethoate	25
Diazinon	40
Disulfoton	40
IBP	40
Methyl Parathion	40
Fenchlorphos	15
Bensulide	25
MEP	30
Isoxathion	40
Chlorpyrifos	45
Ethyl Parathion	40
Prothios	25
Famphur	30
EPN	25
Guthion	15