New Solid Phase Extraction Method for Determination of Triazine Herbicides and Metabolites in Aqueous Samples

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ISOLATION OF POLAR SPECIES WITH WATERS PORAPAK™ R_{DX} CARTRIDGES

Atrazine and related triazine herbicides are used in large quantities throughout the world for agricultural pre-emergence weed control. In central United States, for example, millions of kilograms of triazines are applied to crops each year. In these heavy usage areas, surface water supplies are often contaminated by runoff of these substances and their transformation products[1]. Therefore, a number of these compounds are included in the list of drinking water contaminants to be monitored under the Safe Drinking Water Act. There is also significant interest on the part of other agencies, such as the U.S. Geological Survey (USGS), regarding the use and effects of triazine herbicides in the natural environment.

In Europe, where groundwater is utilized for a high proportion of drinking water supplies, the European Community (EC) has established stricter limits than the U.S. EPA. Currently, the U.S. regulated limit for atrazine is 3 µg/L ; the European limit is 0.1 µg/L for atrazine or any individual regulated pesticide, and 0.5 µg/L for overall pesticide usage. As a result of consistently high pesticide occurrence in groundwater levels within agricultural areas, Germany banned the use of atrazine in 1991, and has recommended banning the use of this herbicide throughout the European Community.

Atrazine and simazine, among the more polar pesticides, are compounds now routinely measured in drinking water according to EPA methods 507 and 505[2]. These compounds are included in the class of triazine herbicides, used worldwide for agricultural weed control. For determination of triazine herbicides, detection limits in the part per trillion range are recommended.

Often it is important not only to measure a particular analyte such as atrazine, but also its biological transformation products. For example, environmental researchers studying the effects of widespread atrazine use in the Mississippi River watershed are also interested in studying a number of metabolites[1,3]. Figure 1 shows atrazine and its principle transformation products. Atrazine and its sister compound, triazine, (simazine, propazine) are easily extracted from water using C_{18} silica solid phase extraction (SPE) procedures. However, the more polar metabolites, such as desisopropylatrazine, are not suitable for extraction using C_{18} silica.

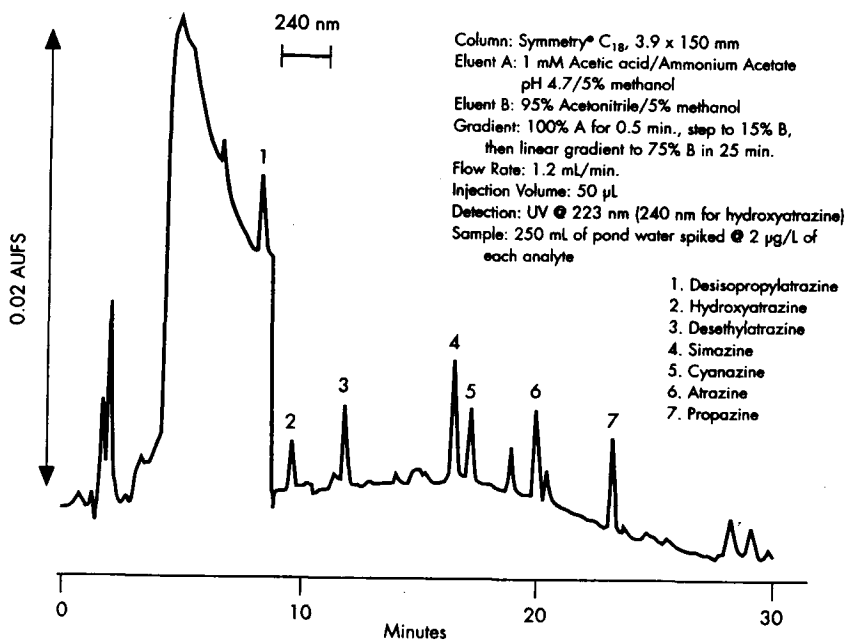
FAST SOLID PHASE EXTRACTION USING PORAPAK R_{DX} SEP-PAK® CARTRIDGES

Porapak R_{DX} solid phase extraction material shows enhanced retention for organic compounds with polar functionalities, unlike traditional C_{18} silica or styrene/divinylbenzene polymeric phases. Sep-Pak cartridges containing Porapak R_{DX} resin were initially developed for the high efficiency extraction of nitroaromatic and nitramine explosives from water[4]. In this research, the Waters Porapak R_{DX} cartridge proved to be a superior SPE device for determination of triazine herbicides and metabolites in aqueous samples. This method has been developed for use with natural waters (surface and groundwater) as well as finished waters (treated municipal drinking water supplies). Samples (up to 1.0 L) are adjusted to pH 7 with phosphate buffer and are eluted through the Waters Sep-Pak cartridge at 10 mL/min. After extraction, the cartridge is eluted using 1:1 methanol/acetonitrile and the resulting extract is analyzed by HPLC/UV using a Waters Symmetry® C_{18} column.

FAST SAMPLE PREPARATION

Using SPE, a 500 mL sample can be processed in one hour—from opening the sample bottle to loading the HPLC system. The cartridge is first preconditioned with 15 mL of methanol followed by 25 mL of reagent water. The sample is then processed at 10 mL/min (if metabolite analysis is required), or

Figure 1: HPLC Chromatogram Obtained from the Spiked Pond Water Experiment.



at up to 20 mL/min (if metabolite analysis is not required). Sample volumes up to 1 liter can be processed for most water samples. After completing the sample enrichment, the residual water is removed by drawing air through the cartridge for a few minutes, and then the cartridge is eluted with 1:1 acetonitrile/methanol. Solid Phase Extraction is fast, easy, and reproducible, requiring less glassware, less time, and most importantly, less solvent, than conventional techniques.

EFFECTIVE OVER A WIDE PH RANGE

Experimental results showed little or no relation between recovery and pH in the 2 to 8.5 range. The recovery experiments documented in this report were obtained from samples buffered to pH 7.0. However, the good recovery shown at pH 2 allows the analyst to utilize Porapak R_{DX} for simultaneous determination of triazines and acidic compounds.

CONVENIENT AND SENSITIVE HPLC ANALYSIS

Porapak R_{DX} Cartridges make it easy for processed samples to be easily prepared for HPLC analysis. After the sample enrichment step is complete, the cartridge is simply eluted with 1:1 acetonitrile/methanol. The subsequent extract is then diluted 1:1 with reagent water and loaded on the HPLC system. No time consuming solvent concentration or drying steps are necessary. The rugged and reliable Symmetry C_{18} analytical column employed for this study was still usable for sub ppb determinations even after 300 injections of extracts from various matrices.

LOW DETECTION LIMITS

According to a procedure recommended by the EPA[5], the detection limit for an analyte may be estimated from the magnitude of the standard deviation in the results obtained from seven or more replicate spiked samples. Based on seven replicates at a spike level of 0.40 µg/L, the detection limit is 0.10 µg/L or lower for all analytes.

HIGH RECOVERY FROM SURFACE WATER

Four replicate 250 mL samples were prepared at a spike level of 2 µg/L using nonfiltered pond water. This was a typical surface water source with considerable particulate matter, biota, and a noticable greenish brown hue of humic or other natural organic matter. The recovery of all analytes was greater than 95%. The results are summarized in Table 1.

Table 1: Recovery of Triazine Herbicides and Metabolites from a Pond Water Source (spike level 2 µg/L, 5 replicates)

Compound	% Recovery	% RSD
Desisopropylatrazine	106	2.8
Hydroxyatrazine	110	11
Desethylatrazine	100	4.3
Simazine	106	4.4
Cyanazine	105	2.5
Atrazine	107	5.4
Propazine	103	1.1

HIGH RECOVERY FROM FINISHED DRINKING WATER

Five replicate 1.0 L samples were prepared at a spike level of 0.4 µg/L using laboratory tap water. Before spiking, each sample was treated with 30 mg of sodium sulfite to remove any residual chlorinating agent. The recovery was 90% or greater for all analytes except for hydroxyatrazine, which had a recovery greater than 85%. The results are summarized in Table 2.

Table 2: Recovery of Triazine Herbicides and Metabolites from a Municipal Drinking Water Source (spike level 0.4 µg/L, 5 replicates)

Compound	% Recovery	% RSD
Desisopropylatrazine	100	6.5 (n=4)
Hydroxyatrazine	86.0	4.9
Desethylatrazine	103	8.1
Simazine	95.5	3.4
Cyanazine	98.0	7.7
Atrazine	97.0	5.6
Propazine	104	2.2

THE BEST SPE METHOD FOR TRIAZINE HERBICIDE ANALYSIS

The Porapak R_{DX} Sep-Pak cartridge effectively extracts parent triazines as well as the most significant metabolites from aqueous samples. With this cartridge, recovery is greater than 95% for atrazine, simazine, cyanazine and propazine, and greater than 90% for desethylatrazine, desisopropylatrazine, and hydroxyatazine. The Porapak R_{DX} Sep-Pak cartridge, a superior polymeric phase cartridge for triazines analysis, is recommended for the solid phase extraction analysis of natural waters and finished drinking waters, with a detection limit below 0.1 µg/L for triazine herbicides and metabolites.

REFERENCES

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