

Application

Note
85

Solid Phase Microextraction/Capillary GC Analysis of Nitrogen-Containing Herbicides in Water

SPME (using a polyacrylate-coated fiber), coupled with GC/FID, GC/NPD, or GC/MS, was used to monitor 22 nitrogen-containing herbicides in water at concentrations of 0.1 to 1000ng/mL. Limits of detection were at microgram/liter to sub-nanogram/liter levels; values were precise to within $\pm 2\%$ to $\pm 20\%$.

Key Words:

- nitrogen-containing herbicides • herbicides
- environmental analyses • solid phase microextraction
- SPME

Investigators at the University of Waterloo, where solid phase microextraction[•] was developed, used a polyacrylate-coated SPME fiber to monitor a mixed group of 22 nitrogen-containing herbicides, including thiocarbamates, triazines, nitroanilines, substituted uracils, a substituted amide, an acetanilide, a diphenyl ether, and a triazole, in water samples (1). Responses for flame ionization detection, nitrogen-phosphorus detection, and ion trap mass spectrometry were calculated for each analyte at a minimum of five concentrations. Correlation coefficients for all but 1 of the 22 analytes were greater than 0.99 by linear regression analysis, both when the y intercept was allowed to vary and when the intercept was fixed at zero. Extractions of most of the analytes were precise to within $\pm 2\%$ to $\pm 20\%$, values well within the US EPA requirement of $\pm 30\%$.

The investigators added pesticides at various concentrations to water containing 1g/mL NaCl, introduced 4mL samples into 4.6mL vials, and compared results for SPME extraction times ranging from 10 to 120 minutes, at room temperature, with constant stirring. The addition of salt generally caused an increase in the amount of each analyte extracted, with the exception of the nitroanilines, Goal, and oxadiazon. The effect of pH also was studied. Varying the pH from 4 to 11 had no significant effect on extraction of any of the analytes, but at pH 2 extraction of the nitroanilines and Goal was enhanced. The combination of pH 2 and salt in the sample was effective for extracting most triazines, substituted uracils, and thiocarbamates, but was less effective than salt addition alone. The combination also was detrimental to the extraction of nitroanilines, Goal, and oxadiazon, which were most effectively extracted at neutral pH or at pH 2, without salt. Conditions for GC/MS analysis are shown in Figure A. For GC/FID or GC/NPD the temperature program is 100°C (5 min) to 300°C at 10°C/min, hold 5 min, and the carrier gas flow rate is 1.0mL/min.

Detection limits ranged from 200-19,000ng/liter (FID) to 10-6000ng/liter (NPD) to 0.01-15ng/liter (MS). For almost every analyte, detection was more sensitive by SPME/GC/MS (16 of 16 analytes) or SPME/GC/NPD (13 of 16 analytes) than by the procedures described in US EPA Method 507/508.

Figure A. Nitrogen-Containing Herbicides Extracted from Water

Sample: 4mL (water + 100ng/mL each analyte + 1g/mL NaCl), pH 2, in 4.6mL vial
SPME Fiber: 85 μ m polyacrylate
Cat. No.: 57304 (manual sampling)
Extraction: immersion, ambient, 50 min (constant stirring)
Desorption: 5 min, 230°C
Column: PTE™-5, 30m x 0.25mm ID, 0.25 μ m film
Cat. No.: 24135-U
Oven: 40°C (5 min) to 100°C at 30°C/min, to 275°C at 5°C/min
Carrier: helium, 40cm/sec, set at 40°C
Det.: MS (Ion Trap Manifold: 250°C; Mass Scan Range: m/z = 45-400 at 0.6 sec/scan)
Inj.: splitless, 230°C

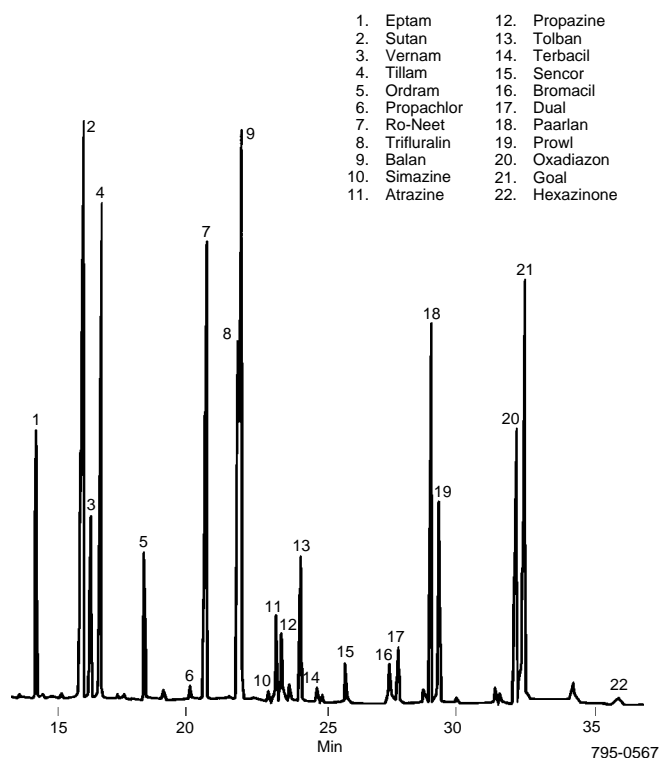


Figure provided by A. Boyd-Boland and J. Pawliszyn, University of Waterloo, Waterloo, Ontario, Canada.

[•]Technology licensed exclusively to Supelco. US patent pending; European patent #0523092.

Ordering Information:

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SPME Fiber Assembly (pkg. of 3)	
7µm polydimethylsiloxane coating	
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For Varian 8100/8200 AutoSampler	57303
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For manual sampling	57300-U
For Varian 8100/8200 AutoSampler	57301
30µm polydimethylsiloxane coating	
For manual sampling	57308
For Varian 8100/8200 AutoSampler	57309
85µm polyacrylate coating	
For manual sampling	57304
For Varian 8100/8200 AutoSampler	57305
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pk. of 25	26364,25
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pk. of 25	26375,25
For Varian GCs (all)	
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pk. of 5	26358,05
pk. of 25	26358,25

*First time users must order both holder and fiber assembly. Holder is reusable indefinitely.

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* Pre-drilled septa reduce septum coring that can cause extraneous peaks.

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995-0250

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SPME Sampling Stand
57333-U

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Clear, 2mL, pk. of 100	27124-U
Amber, 2mL, pk. of 100	27005
Headspace Vials	
Clear, 4mL, pk. of 10	26901
pk. of 100	27136
Amber, 4mL, pk. of 10	26930
pk. of 100	27006
Thermogreen™ LB-2 Septa, Pre-Drilled*	
11mm, pk. of 25	23167
11mm, pk. of 50	23168
9.5mm, pk. of 25	23161
9.5mm, pk. of 50	23162-U

Reference

1. Boyd-Boland, A. and J. Pawliszyn, *Analyst*, **121**:929-938 (1996).

Acknowledgment

This investigation was conducted by Anna Boyd-Boland and Janusz Pawliszyn, University of Waterloo, Waterloo, Ontario, Canada.

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 Prowl—American Cyanimid Co.
 Teflon—E.I. du Pont de Nemours & Co., Inc.

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Note 85

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