

Solid Phase Extraction Provides Interference-Free Samples for Analyzing Triazine Herbicides

Supelclean solid phase extraction tubes provide high, reproducible recovery of triazines from plant extracts and groundwater.

Key Words:

- triazine herbicides • solid phase extraction • groundwater

Although triazine herbicides are widely used to control weeds in food crops, these toxic chemicals generally degrade slowly. They can persist in fields for a year or more after application (1). Therefore, for consumer protection, residual triazines in food plants and groundwater must be accurately monitored.

Chlorophylls, carotenes, and other components of plant extracts frequently interfere with triazine quantification. Sample cleanup through multiple liquid-liquid extractions (2) is time-consuming and frequently fails to yield a pure extract. However, a solid phase extraction (SPE) procedure has been developed for obtaining plant extracts of triazines free of chlorophyll and other interferences. These extracts are suitable for quantifying trace levels of triazines.

Supelclean™ LC-SCX (strong cation exchanger) solid phase extraction tubes isolate simazine, atrazine, and propazine in plant extracts. These compounds are effectively separated from matrix components that would otherwise interfere with the analysis. (For extraction of triazines from fruits and vegetables, see Bulletin 900.)

The procedure is relatively simple. For 20 minutes, shake a mixture of 5g of shredded plant tissue, 4g of anhydrous sodium sulfate, and 20mL of methylene chloride:acetone (4:1). Allow the mixture to stand 1 minute, then aspirate a 2mL aliquot dropwise through a 3mL Supelclean LC-SCX tube previously conditioned with 1mL of methylene chloride. Wash plant pigments and other interferences from the packing with two 2mL aliquots of acetonitrile. Air dry the packing under vacuum for 5 minutes, then pass two 2mL aliquots of water through the tube. Recover the triazines by passing 1.5mL of methanol dropwise through the tube, using a Visiprep™ Solid Phase Extraction Vacuum Manifold*, and collecting the eluate in a 2mL volumetric tube.

To improve HPLC peak shapes, dilute the recovered eluate to 2mL with water. Quantify the triazines by HPLC with UV detection at 254nm. For GC analysis, modify this procedure by eliminating the water wash, eluting the herbicides with 1mL of methanol, and diluting the collected eluate to 1mL with methanol.

To study recovery rates for the three herbicides, we added 2ppm standards of each to grass extracts. Then we prepared and analyzed samples by the procedures described. A 100µL aliquot of each final extract was injected onto a SUPELCOSIL™ LC-8-DB HPLC column (Figure A).

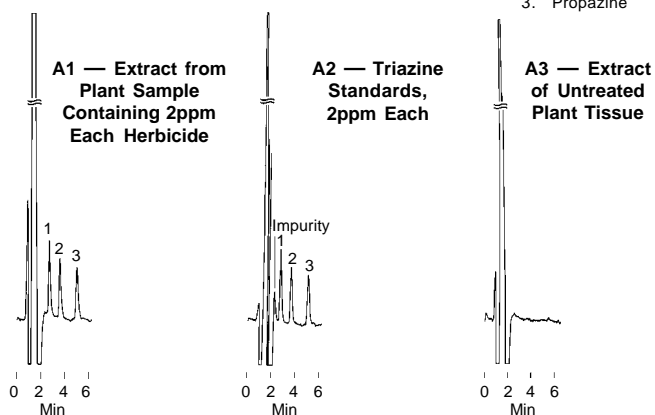
Chromatograms from untreated grass showed that samples obtained by this procedure are free of matrix interferences. For quantification, triazine peak heights in the sample chromatograms were compared with those for 2ppm working standards. Triazine recovery was virtually complete (Table 1).

Supelclean LC-SCX tubes, when used to prepare plant extracts for triazines analysis, remove interfering materials at each of three steps. First, when the sample is added to the tube, nonpolar components pass through the packing while the triazines are quantitatively retained. Subsequent washing with acetonitrile

Figure A. Triazine Pesticides Quantitatively Recovered from Plant Tissue

Sample: 100µL methanol:water (3:1), extracts containing 50ng (A1, A2), or 0ng (A3) each triazine
Extraction Tube: **Supelclean LC-SCX, 3mL tube**
Cat. No.: **57018**
Conditioning: 1mL methylene chloride
Washing: 2 x 2mL acetonitrile, air dry for 5 min, 2 x 2mL water
Elution: 1.5mL methanol (dilute recovered sample to 2mL with water)
Column: **SUPELCOSIL LC-8-DB^{II}, 15cm x 4.6mm, 5µm packing w/ Supelguard™ LC-8-DB, 2cm x 4.6mm**
Cat. No.: **58347**
Temp.: 25°C
Mobile Phase: acetonitrile:water, 45:55
Flow Rate: 1.5mL/min
Pressure: 1392psig
Det.: 254nm UV, 0.08 AUFS

1. Simazine
2. Atrazine
3. Propazine

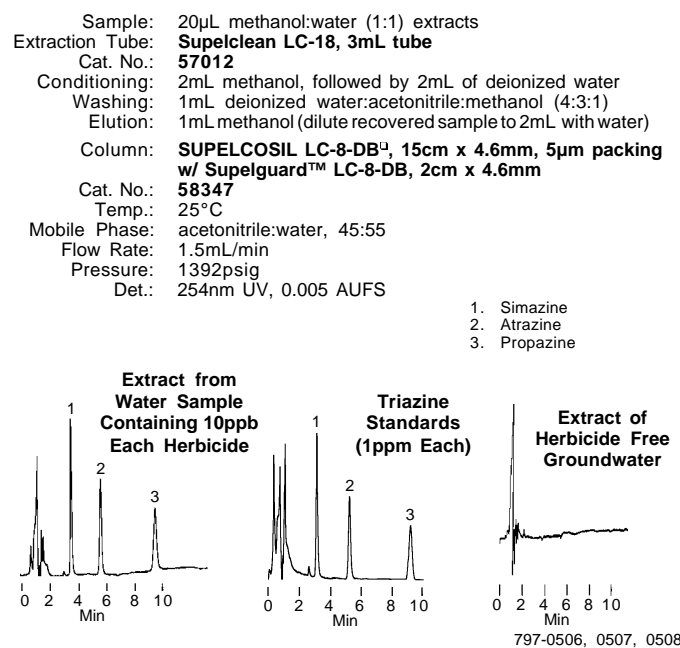


797-0503, 0504, 0505

Table 1. Solid Phase Extraction Completely Recovers Triazine Herbicides from Grass Samples

| | % Recovery | | |
|---------|---------------|---------------|---------------|
| | Simazine | Atrazine | Propazine |
| Trial 1 | 102.3 | 102.1 | 99.0 |
| Trial 2 | 104.7 | 104.3 | 102.4 |
| Trial 3 | 99.0 | 101.3 | 100.0 |
| Mean | 102.0 (± 2.9) | 102.2 (± 1.6) | 100.5 (± 1.8) |

Figure B. Triazine Pesticides Recovered from Groundwater



removes most moderately polar components that were retained with the herbicides. And finally, when the triazines are selectively eluted from the packing in methanol, very polar materials remain behind. The procedure leaves the final sample virtually interference-free (Figure A).

For extraction of triazine herbicides from groundwater, a 3mL Supelclean LC-18 SPE tube is used. The tube is conditioned with 2mL of methanol, followed by 2mL of deionized water. A 20mL sample reservoir is connected to the tube. The sample, consisting of 20mL of the groundwater sample, is passed through the conditioned tube at a slow dropwise rate, using a Visiprep vacuum manifold. Impurities are removed from the packing by washing with 1mL of a deionized water:acetonitrile:methanol (4:3:1) solution. The triazines are then eluted from the packing with 1mL of methanol and collected in a 2mL volumetric flask. The eluant is diluted to the mark with water prior to HPLC analysis (Figure B). The procedure can be easily adapted for GC analysis by thoroughly drying the packing under nitrogen, using a Visidry™ Vacuum Manifold Drying Attachment,* prior to elu-

Table 2. Absolute Recovery of Triazine Herbicides from Groundwater

| Herbicide | % Recovery ± S.D. (n = 3) | | |
|-----------|---------------------------|-------------|------------|
| | 10ppb | 100ppb | 1ppm |
| Simazine | 102 ± 1 | 100 ± 4 | 97.2 ± 0.9 |
| Atrazine | 100 ± 0 | 99.0 ± 10.6 | 94.4 ± 0.7 |
| Propazine | 94.0 ± 11.1 | 92.4 ± 7.4 | 92.4 ± 0.8 |

tion and eliminating the water dilution of the methanol eluant. Recovery of atrazine, propazine, and simazine at concentrations of 10ppb to 1ppm in groundwater was greater than 92% by this procedure (Table 2). (For extraction of acidic, as well as base/neutral pesticides and herbicides, see Application Note 105.)

In addition to the extraction tubes and analytical column for this analysis, we offer a kit of neat triazines for preparing standards. The kit consists of ametryn, atrazine, prometryn, propazine, simazine, simetryn, terbutryn (0.5g each), and prometon (0.1g). We recommend protecting the HPLC column with our guard column kit (2cm x 4.6mm column filled with 5µm packing, column holder, and connecting hardware).

Supelclean LC-SCX solid phase extraction tubes reproducibly isolate triazine herbicides from plant extracts, providing excellent recovery. The procedure is rapid and can be adapted to HPLC or GC analyses.

Ordering Information:

| Description | Cat. No. |
|--|----------|
| Supelclean LC-SCX Solid Phase Extraction Tubes, 3mL | 57018 |
| Supelclean LC-18 Solid Phase Extraction Tubes, 3mL | 57012 |
| Reservoirs, 20mL | 57021 |
| Adapters for sample reservoirs | 57020-U |
| SUPELCOSIL LC-8-DB ³ Column, 15cm x 4.6mm | 58347 |
| Supelguard LC-8-DB Guard Column Kit 2cm x 4.6mm cartridge column, column holder, hardware for connecting to 1/16" tubing | 59553 |
| Supelguard LC-8-DB Guard Columns, pk. of 2 | 59563 |
| Neat Triazines Kit | 49092 |
| Visiprep Vacuum Manifold | 57030-U |
| Visidry Vacuum Manifold Drying Attachment | 57100-U |

- ³DB — Deactivated for basic compounds.
- * US Pat. Nos. D.289,861; 4,810,471; other patents pending.
- US Pat. No. 4,810,471; other patents pending.

References

- Burnside, O.C., *et al.*, Weed Sci., **19**: 290 (1971).
 - Ramsteiner, K., *et al.*, JAOAC, **57**: 192 (1974).
- References not available from Supelco.

Trademarks

SUPELCOSIL, Supelclean, Supelguard, Visidry, Visiprep — Sigma-Aldrich Co.

Note 127

For more information, or current prices, contact your nearest Supelco subsidiary listed below. To obtain further contact information, visit our website (www.sigma-aldrich.com), see the Supelco catalog, or contact Supelco, Bellefonte, PA 16823-0048 USA.

ARGENTINA - Sigma-Aldrich de Argentina, S.A. - Buenos Aires 1119 AUSTRALIA - Sigma-Aldrich Pty. Ltd. - Castle Hill NSW 2154 AUSTRIA - Sigma-Aldrich Handels GmbH - A-1110 Wien
 BELGIUM - Sigma-Aldrich N.V./S.A. - B-2880 Bornem BRAZIL - Sigma-Aldrich Quimica Brasil Ltda. - 01239-010 São Paulo, SP CANADA - Sigma-Aldrich Canada, Ltd. - 2149 Winston Park Dr., Oakville, ON L6H 6J8
 CZECH REPUBLIC - Sigma-Aldrich s.r.o. - 186 00 Praha 8 DENMARK - Sigma-Aldrich Denmark A/S - DK-2665 Vallensbaek Strand FINLAND - Sigma-Aldrich Finland/YA-Kemia Oy - FIN-00700 Helsinki
 FRANCE - Sigma-Aldrich Chimie - 38297 Saint-Quentin-Fallavier Cedex GERMANY - Sigma-Aldrich Chemie GmbH - D-82041 Deisenhofen GREECE - Sigma-Aldrich (o.m.) Ltd. - Ilioupoli 16346, Athens
 HUNGARY - Sigma-Aldrich Kft. - H-1067 Budapest INDIA - Sigma-Aldrich Co. - Bangalore 560 048 IRELAND - Sigma-Aldrich Ireland Ltd. - Dublin 24 ISRAEL - Sigma Israel Chemicals Ltd. - Rehovot 76100
 ITALY - Sigma-Aldrich s.r.l. - 20151 Milano JAPAN - Sigma-Aldrich Japan K.K. - Chuo-ku, Tokyo 103 KOREA - Sigma-Aldrich Korea - Seoul MALAYSIA - Sigma-Aldrich (M) Sdn. Bhd. - Selangor
 MEXICO - Sigma-Aldrich Química S.A. de C.V. - 50200 Toluca NETHERLANDS - Sigma-Aldrich Chemie BV - 3330 AA Zwijndrecht NORWAY - Sigma-Aldrich Norway - Torshov - N-0401 Oslo
 POLAND - Sigma-Aldrich Sp. z o.o. - 61-663 Poznań PORTUGAL - Sigma-Aldrich Quimica, S.A. - Sintra 2710 RUSSIA - Sigma-Aldrich Russia - Moscow 103062 SINGAPORE - Sigma-Aldrich Pte. Ltd.
 SOUTH AFRICA - Sigma-Aldrich (pty) Ltd. - Jet Park 1459 SPAIN - Sigma-Aldrich Quimica, S.A. - 28100 Alcobendas, Madrid SWEDEN - Sigma-Aldrich Sweden AB - 135 70 Stockholm
 SWITZERLAND - Supelco - CH-9471 Buchs UNITED KINGDOM - Sigma-Aldrich Company Ltd. - Poole, Dorset BH12 4QH
 UNITED STATES - Supelco - Supelco Park - Bellefonte, PA 16823-0048 - Phone 800-247-6628 or 814-359-3441 - Fax 800-447-3044 or 814-359-3044 - email:supelco@sial.com

H

Supelco is a member of the Sigma-Aldrich family. Supelco products are sold through Sigma-Aldrich, Inc. Sigma-Aldrich warrants that its products conform to the information contained in this and other Sigma-Aldrich publications. Purchaser must determine the suitability of the product for a particular use. Additional terms and conditions may apply. Please see the reverse side of the invoice or packing slip.

BIB