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If you have questions about applying methodology described in this article to a current application, please contact our technical service chemists.

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Atrazine and Simazine — Product Redesign Improves Compound Stability

S. Cole and D. Henderson

Atrazine and simazine, two triazine herbicides included in US EPA Methods 505 and 525, are unstable in methanol. This article describes the Supelco reformulation of four chemical standards containing these analytes, each originally prepared in methanol. Accelerated stability studies demonstrated that the reformulated mixture components are stable in acetone for an equivalent of at least 16 months at 25°C.

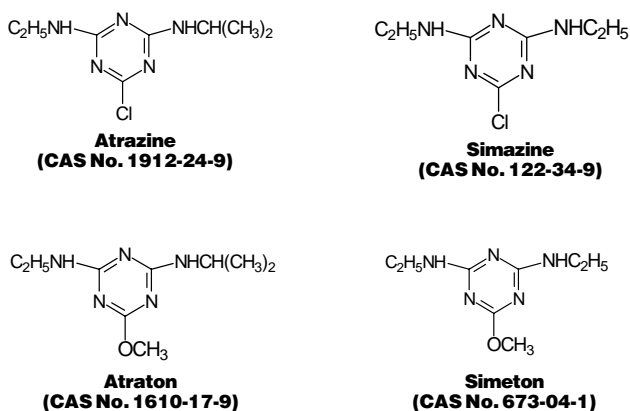
Supelco recently discovered, through routine stability monitoring, a need for the redesign of four chemical standard products. These products included the triazine herbicides atrazine and simazine, target analytes in US Environmental Protection Agency (US EPA) Methods 505 and 525.

We detected that atrazine and simazine are unstable at 500µg/mL in methanol, the solvent in which these analytes were originally formulated. At room temperature, atrazine reacts to form atraton, while simazine converts to simeton (Figure A).

Figure B shows, over a 10-month period, the breakdown of simazine to simeton in a product we subsequently deleted.

To learn more about the stability of atrazine and simazine in solution, we prepared individual solutions of the compounds at 500µg/mL in acetone, methanol:water (90:10 v/v), methanol, and methylene chloride. In each case, the compounds were soluble in the solvent. Each solution was analyzed immediately by GC/MS to establish baseline values, and after 3, 10, 17, and 24 days at 60°C.

Figure A. Chemical Structures



794-0733,794-0776-0778

Figure C shows the results of the analyses of atrazine and simazine in methanol. Atrazine showed no sign of reaction until 17 days, and was partially converted to atraton at 24 days. Simazine, on the other hand, had reacted to form simeton between 10 and 17 days, and was completely converted by the 24th day. Atrazine and simazine were stable in acetone, methylene chloride, and methanol:water.

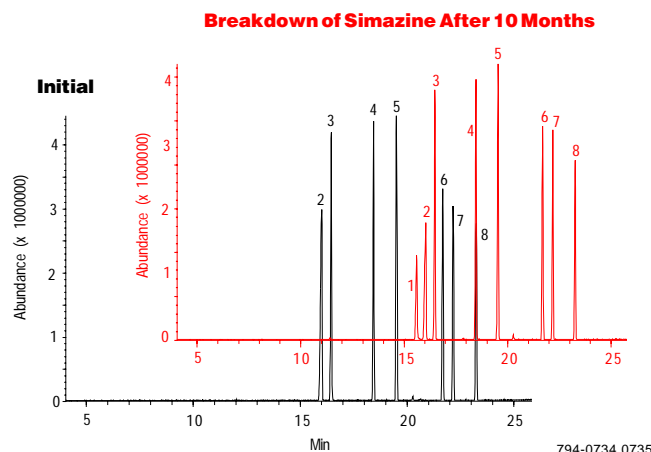
The reactions of atrazine and simazine with methanol are classic nucleophilic displacement reactions, with ring nitrogens strongly activating chlorine-containing carbon atoms for attack by the methoxy group. The differences in the kinetic rates between the two reactions probably are related to activation energy effects and to the difference in molecular structure between atrazine and simazine.

On the basis of stability data, we reformulated the four methanol-based products. We replaced the solvent with acetone and with methanol:water (90:10 v/v), keeping the concentration of each component at 500µg/mL. (See the ordering information for a listing of analytes in these four mixes). Methylene chloride similarly

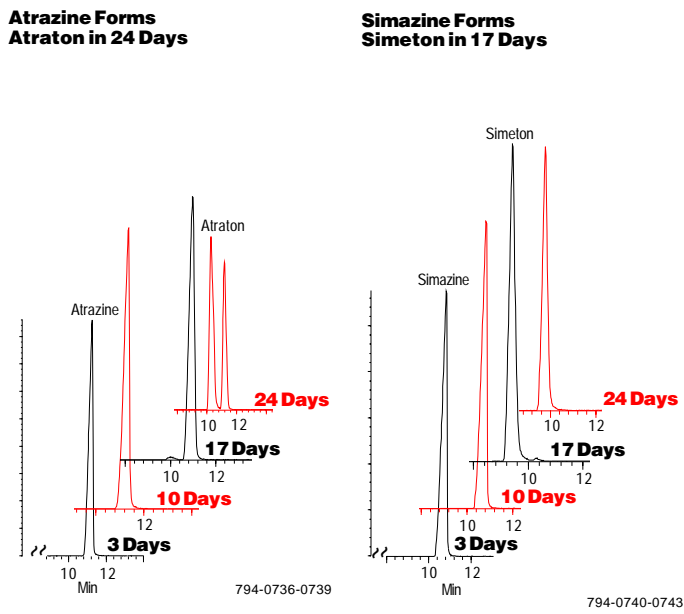
Figure B. Total Ion Chromatograms of EPA 505/525 Update Pesticides Mix A in Methanol

Column: PTE™, 30m x 0.25mm ID, 0.25µm film
 Cat. No.: 24135-U
 Oven: 120°C (4 min) to 300°C at 8°C/min, hold 5 min
 Det.: mass spectrometer, scan 33-500 m/z
 Inj.: 1µL, splitless, 0.35 min valve on

1. Simeton
2. Simazine
3. γ-BHC (Lindane)
4. Alachlor
5. Aldrin
6. trans-Nonachlor
7. Dieldrin
8. cis-Nonachlor

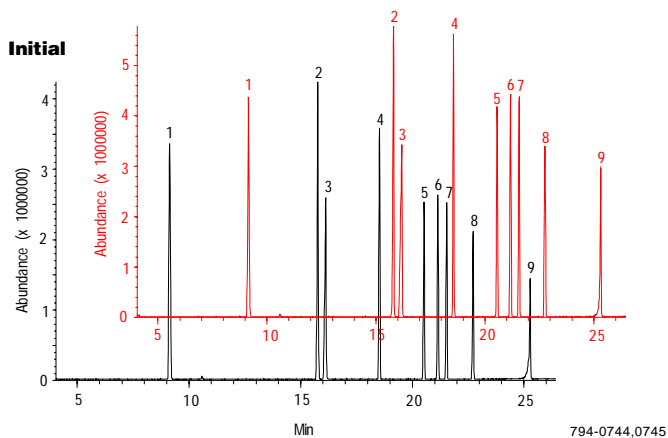


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Figure C. Atrazine and Simazine Reactions in Methanol**Figure D. Total Ion Chromatograms of EPA 505/525 Update Pesticides Mix B in Acetone**

Column: PTE, 30m x 0.25mm ID, 0.25µm film
 Cat. No.: 24135-U
 Oven: 120°C (4 min) to 300°C at 8°C/min, hold 5 min
 Det.: mass spectrometer, scan 33-500 m/z
 Inj.: 1µL Cat. No. 47728, splitless, 0.35 min valve on

1. Hexachloropentadiene
2. Hexachlorobenzene
3. Atrazine
4. Heptachlor
5. Heptachlor epoxide (isomer B)
6. γ-Chlordane
7. α-Chlordane
8. Endrin
9. Methoxychlor

No Reaction of Atrazine to Atraton

yielded stable atrazine and simazine solutions, but we did not use it in reformulating these products on the basis of EPA method requirements. We dropped methanol:water from further study because of solubility problems with two of the products.

The four mixes in acetone were analyzed by GC/MS and subjected to accelerated stability testing at 60°C for 44 days. Samples of each were analyzed after 9, 16, 23, 30, 37, and 44 days. Figure D shows the initial and final (after 44 days) total ion chromatograms of the new Cat. No. 47728-U. The other three new mixes were similarly unchanged after 44 days at 60°C. Storage for 44 days at 60°C is roughly equivalent to storage at 25°C for 16 months.

As a result of these findings, we deleted the four EPA 505/525 pesticides mixes in methanol and replaced them with identical formulations in acetone. Real-time stability studies at room temperature are currently underway.

Ordering Information:**EPA 505/525 Pesticides Mix A**

500µg/mL each component in acetone.

Alachlor	Dieldrin
Aldrin	Simazine
γ-BHC (Lindane)	

1 mL **47725-U**

EPA 505/525 Update Pesticides Mix A

500µg/mL each component in acetone.

Alachlor	cis-Nonachlor
Aldrin	trans-Nonachlor
γ-BHC (Lindane)	Simazine
Dieldrin	

1 mL **47727-U**

EPA 505/525 Pesticides Mix B

500µg/mL each component in acetone.

Atrazine	Hexachlorobenzene
Endrin	Hexachloropentadiene
Heptachlor	Methoxychlor
Heptachlor epoxide (isomer B)	

1 mL **47726-U**

EPA 505/525 Update Pesticides Mix B

500µg/mL each component in acetone.

Atrazine	Heptachlor epoxide (isomer B)
α-Chlordane	Hexachlorobenzene
γ-Chlordane	Hexachloropentadiene
Endrin	Methoxychlor
Heptachlor	

1 mL **47728-U**

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