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Application Note 57

Product Redesign of Chemical Standards Improves Atrazine and Simazine Stability — Verified by Capillary GC

Supelco routinely monitors its chemical standard products to determine shelf-life quality. Atrazine and simazine, two triazine herbicides included in US EPA Methods 505 and 525, are unstable in methanol. This application note 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.

Key Words

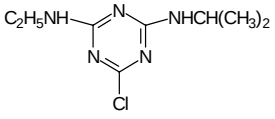
• atrazine • atraton • simazine • simeton

Through routine stability monitoring, Supelco discovered 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.

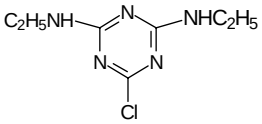
We detected that atrazine and simazine are unstable at 500µg/mL in methanol, the solvent in which these analytes were originally formulated. At room temperature, atrazine reacts to form atraton, while simazine converts to simeton (Figure A).

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

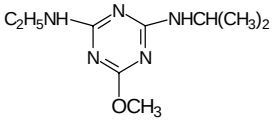
Figure A. Chemical Structures



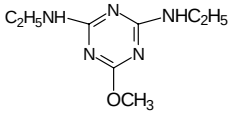
Atrazine
(CAS No. 1912-24-9)



Simazine
(CAS No. 122-34-9)



Atraton
(CAS No. 1610-17-9)



Simeton
(CAS No. 673-04-1)

794-0733,794-0776-0778

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.

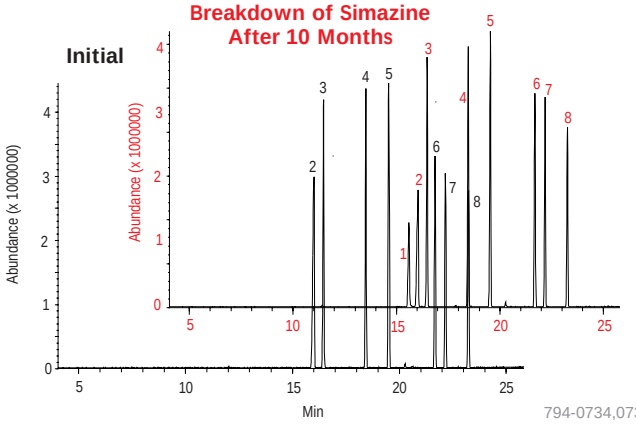
Figure C shows the results of the analyses of atrazine and simazine in methanol. Atrazine showed no sign of reaction until 17 days, and was partially converted to atraton at 24 days. Simazine, on the other hand, had reacted to form simeton between 10 and 17 days, and was completely converted by the 24th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

The reactions of atrazine and simazine with methanol are classic nucleophillic 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.

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**
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



794-0734,0735

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Figure C. Atrazine and Simazine Reactions in Methanol

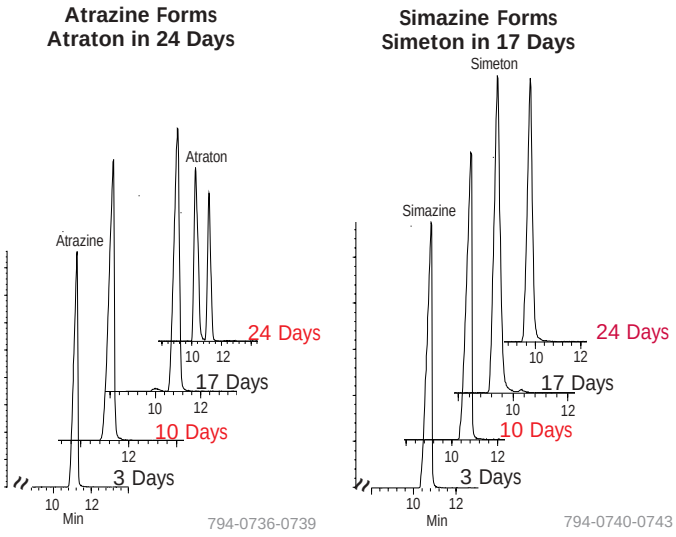
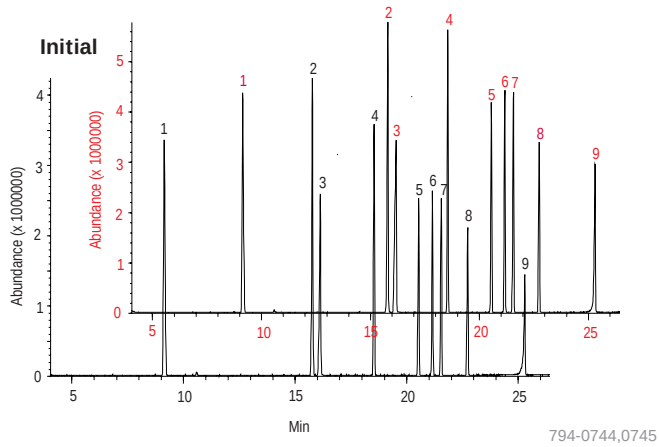


Figure D. Total Ion Chromatograms of EPA 505/525 Update Pesticides Mix B in Acetone

Column: **PTE, 30m x 0.25mm ID, 0.25µm film**
Cat. No.: **24135**
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. 4-7728, 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



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 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 reformulated mix (Cat. No. 4-7728). The other three reformulated 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.

Ordering Information:

Description	Cat. No.
EPA 505/525 Pesticides Mix A	
500µg/mL each component in acetone. Alachlor, Aldrin, γ-BHC (Lindane), Dieldrin, Simazine	
1mL	**47725-U**
EPA 505/525 Update Pesticides Mix A	
500µg/mL each component in acetone. Alachlor, Aldrin, γ-BHC (Lindane), Dieldrin, cis-Nonachlor, trans-Nonachlor, Simazine	
1mL	**47727-U**
EPA 505/525 Pesticides Mix B	
500µg/mL each component in acetone. Atrazine, Endrin, Heptachlor, Heptachlor epoxide (isomer B), Hexachlorobenzene, Hexachloropentadiene, Methoxychlor	
1mL	**47726-U**
EPA 505/525 Update Pesticides Mix B	
500µg/mL each component in acetone. Atrazine, α-Chlordane, γ-Chlordane, Endrin, Heptachlor, Heptachlor epoxide (isomer B), Hexachlorobenzene, Hexachloropentadiene, Methoxychlor	
1mL	**47728-U**

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