# Application Note 137

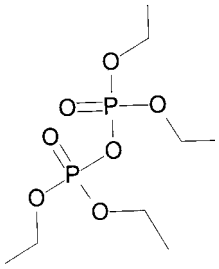
# Formulation Stability and Intervendor Comparison of Tetraethylpyrophosphate (TEPP) and Analysis by GC

***Supelco and Chem Service Inc. conducted independent studies to monitor the decomposition of TEPP in solution. The real-time study made by Chem Service supported the findings in Supelco's accelerated study that different decomposition products are formed, depending on the amount of water present in the solution.***

**Key Words:**
- TEPP
- tetraethylpyrophosphate
- diethyl phosphoric acid

Tetraethylpyrophosphate (TEPP, Figure A) is a total-kill pesticide that is very hazardous to handle. Fortunately, TEPP (CAS No. 107-49-3) is very unstable in the presence of water (a half-life of about 7 hours at pH 7 and 25°C), and its decomposition product, diethyl phosphoric acid (CAS No. 598-02-7), is relatively non-hazardous. Because it is sensitive to water, TEPP is difficult to prepare as a stable calibration standard.

**Figure A. Tetraethylpyrophosphate**



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Nearly all solvents contain small quantities of water. Hexane, for example, contains about 60ppm water and must be dried thoroughly, even for short-term use. A TEPP solution should be prepared entirely under nitrogen in a dry solvent, such as in a nitrogen-filled glovebag.

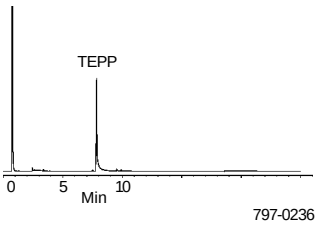
We prepared a fresh solution of neat TEPP at 1000µg/mL in anhydrous hexane. We also used a commercial supplier's stock TEPP solution in 100µg/mL methanol as received. We manipulated both solutions in a nitrogen glove box, and assayed them by GC/NPD (nitrogen-phosphorous detector) and GC/MS (mass spectrometry). The fresh anhydrous Supelco™ solution (Figure B1) yielded a TEPP peak at 7.8 minutes. The competitor's product (Figure B2) did not show a TEPP peak. The product had presumably decomposed in storage to diethyl phosphoric acid.

The TEPP identification was verified against the HPPEST library and the NBS75K library. Interestingly, the TEPP fragmentation patterns shown by the two libraries differed. We ultimately determined that the fragmentation pattern shown by the HPPEST library was correct (Figure C1). The NBS75K library fragment pattern (Figure C2) was that of diethyl pyrophosphate (CAS No. 1077-71-7).

**Figure B. Comparison of TEPP Solutions**

Column: **SPB-608, 30m x 0.53mm ID x 0.5µm film**
Cat. No.: **25312**
Oven: 40°C to 300° at 10°C/min
Det.: nitrogen-phosphate detector, 320°C
Inj.: 150°C

**B1 – Supelco Solution Prepared Under Nitrogen in Anhydrous Hexane**




**B2 – Competitor's Solution Prepared in Methanol (no TEPP visible)**

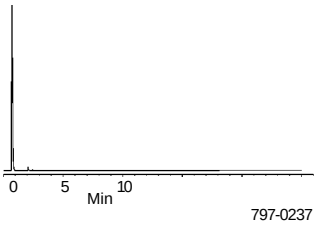



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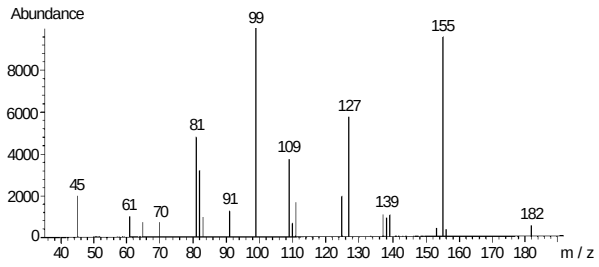
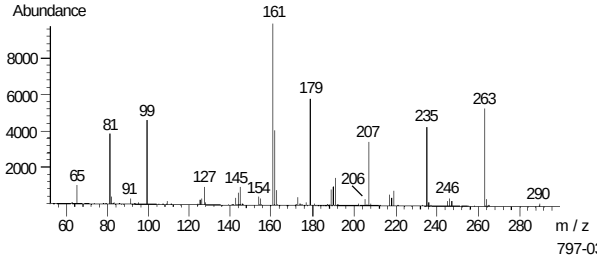
**Figure C. Fragmentation Patterns**

Column: **SPB-608, 30m x 0.53mm ID x 0.5µm film**
Cat. No.: **25312**
Oven: 40°C to 300° at 10°C/min
Det.: nitrogen-phosphate detector, 320°C
Inj.: 150°C

**C1 – HPPEST Library Pattern of TEPP**




**C2 – NBS75K Library Pattern Determined to be Diethyl pyrophosphate**

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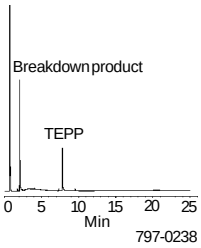
To verify the decomposition products in methanol solution, Supelco and Chem Service Inc. designed several decomposition studies. In an accelerated decomposition study, Supelco used neat TEPP to prepare three 1000µg/mL solutions — in methanol, in anhydrous hexane, and in hexane spiked with water. The samples were heated for 4 days at 60°C and analyzed by GC/NPD. The study resulted in three different decomposition patterns, each with varying phosphorous-containing peaks.

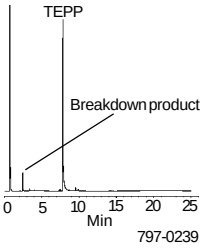
- The decomposition in methanol (<0.01% water) yielded a large breakdown peak at 2 minutes, followed by the smaller TEPP peak (Figure D1). Interpretation of the GC/MS fragmentation pattern showed the breakdown peak to be diethyl methylphosphate.
- Decomposition in anhydrous hexane (Figure D2) was minimal. Interpretation of the fragmentation patterns showed this breakdown peak, at 2.5 minutes, to be diethyl pyrophosphate. TEPP decomposition in anhydrous hexane was less than that in methanol, and yielded a different breakdown product.
- The decomposition in hexane spiked with water (Figure D3 ) showed results similar to those in Figure B2. This pattern suggests the formation of a different breakdown product not detectable by GC, possibly the diethyl phosphoric acid.

## Figure D. Accelerated Decomposition Study

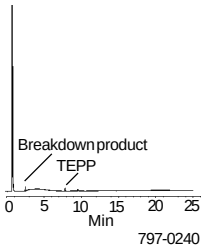
**D1 – TEPP in Methanol**




**D2 – TEPP in Anhydrous Hexane**




**D3 – TEPP in Hexane Spiked with Water**




Analytical conditions: see Figure B

Chem Service performed real-time decomposition studies, verifying our findings that different decomposition products are formed. Chem Service prepared solutions from neat TEPP in methanol and in methanol spiked with water. The samples were analyzed by GC/MS. TEPP was still present in the sample but at a reduced concentration. The two unknown peaks detected in the commercial methanol solution and in the accelerated study were reproduced in the real-time study. The early peak in the Chem Service study occured at about 3 minutes, giving a fragmentation pattern interpreted as diethylmethyl phosphate. A second peak, about 30 seconds later, gave a fragmentation pattern interpreted as diethyl pyrophosphate.

The studies suggest different decomposition paths depending on solvent and on the amount of water present in the solution. Neat TEPP, packaged and stored under nitrogen, maintains its structural integrity during storage. However, the integrity of TEPP in solution is highly questionable.

## Ordering Information:

| Description | Cat. No. |
|---|---|
| **Tetraethylpyrophosphate** | |
| Neat, 1g | **PS601** |
| **SPB™-608 Fused Silica Capillary Column** | |
| 30m x 0.53mm ID, 0.5µm film | **25312** |
| **PTE™-5 Fused Silica Capillary Column** | |
| 30m x 0.53mm ID, 0.25µm film | **24135-U** |

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