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Tetraethyl pyrophosphate (TEPP) — Formulation Stability and Intervendor Comparison

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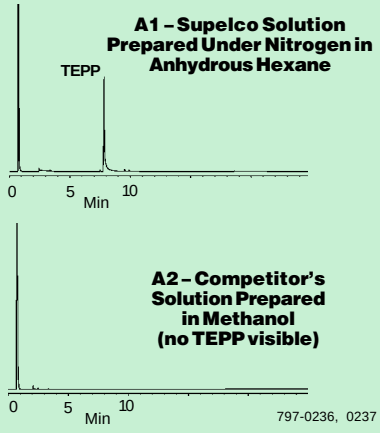
Several years ago, my wife and I were in Jamaica and had the pleasure of meeting a young woman who was in the Peace Corps. She was a veterinarian, assigned to the central part of Jamaica. She had one major frustration: an individual had been selling tetraethyl pyrophosphate (TEPP) to the farmers to kill the flies on the cattle. TEPP was very effective; however, it was also killing the cows. **— Lyle Phifer, President, Chem Service, Inc.**

Tetraethyl pyrophosphate (TEPP, CAS No. 107-49-3), a total-kill pesticide, is hazardous to handle. Fortunately, TEPP is very unstable in 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 of its sensitivity to water, TEPP is difficult to prepare as a stable calibration standard.

Nearly all solvents contain small quantities of water. Hexane, for example, contains about 60ppm water and must be thoroughly dried, 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.

Figure A. Comparison of TEPP Solutions

Column: **SPB-608, 30m x 0.53mm ID x 0.5µm film**
Cat. No.: **25312**
Oven: 100°C to 300° at 10°C/min
Det.: NPD, 320°C
Inj.: 150°C



We prepared a fresh solution of neat TEPP at 1000 µg/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 A1) yielded a TEPP peak at 7.8 minutes. The competitor's product (Figure A2) did not show a TEPP peak. The competitor's product had presumably decomposed in storage to diethyl phosphoric acid.

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 a smaller TEPP peak (Figure B1). Interpretation of the GC/MS fragmentation pattern showed the breakdown peak to be diethyl methylphosphate.
- Decomposition in anhydrous hexane (Figure B2) was minimal. Interpretation of the fragmentation patterns showed this breakdown peak, at 2.5 minutes, to be diethylpyrophosphate (CAS no. 1077-71-7). 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 B3) showed results similar to those in Figure A2. This pattern suggests the formation of a different breakdown product not detectable by GC, possibly the diethyl-phosphoric acid.

Chem Service performed real-time decomposition studies, verifying our findings that different decomposition products are formed, depending on the amount of water present in the solution.

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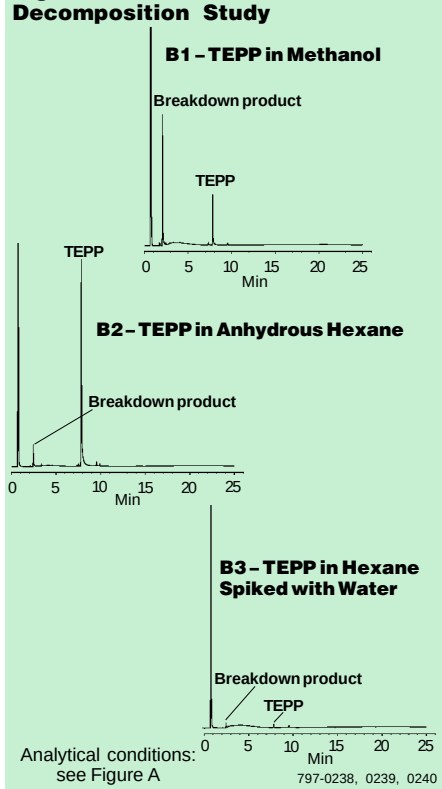
Figure B. Accelerated Decomposition Study



Neat TEPP, packaged and stored under nitrogen, maintains its structural integrity during storage, However, the integrity of TEPP in solution is highly questionable.

Supelco-manufactured products typically include a data-supported expiration date. We know our products are stable because our expiration date is based on real-time data. Additionally, we will not ship products from inventory with less than 6 months of shelf-life remaining.

Ordering Information:

Description	Cat. No.
Tetraethylpyrophosphate	
Neat, 1g	**PS601**
SPB™-608 Capillary Column	
30m x 0.53mm ID, 0.5µm film	**25312**