

Tetraethyl pyrophosphate (TEPP) — Formulation Stability and Intervendor Comparison

L. Phifer, Chem Service, Inc., West Chester, PA, USA

J. Walbridge, Chemical Standards, Supelco, Bellefonte, PA, USA

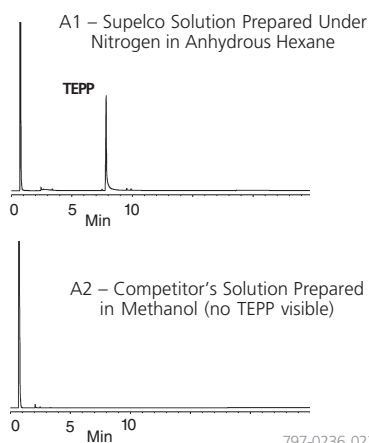
Several years ago, my wife and I were in Jamaica and had the pleasure of meeting a young woman who was in the Peace Corps. She was a veterinarian, assigned to the central part of Jamaica. She had one major frustration: an individual had been selling tetraethyl pyrophosphate (TEPP) to the farmers to kill 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 60 ppm 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, 30 m x 0.53 mm I.D. x 0.5 µm film (25312)
oven: 100 °C to 300 °C at 10 °C/min.
inj.: 150 °C
det.: NPD, 320 °C



797-0236, 0237

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 100 µg/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.

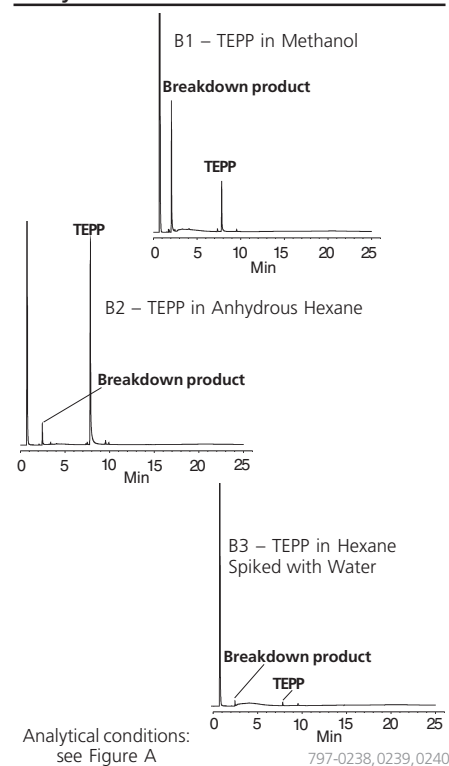
In an accelerated decomposition study, Supelco used neat TEPP to prepare three 1000 µg/mL solutions — in methanol, in anhydrous hexane, and in hexane spiked with water. The samples were heated for 4 days at 60 °C and analyzed by GC-NPD. The study resulted in three different decomposition patterns, each 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 diethylphosphoric 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.

Reprinted from Supelco Reporter, Vol. 16, No. 4, 1997 - T297044.

Figure B. Accelerated Decomposition Study



Analytical conditions: see Figure A
797-0238, 0239, 0240

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, 1 g	PS601
SPB™-608 Capillary Column 30 m x 0.53 mm I.D., 0.5 µm film	25312

SPB and Supelco are trademarks of Sigma-Aldrich Co.
Fused silica columns manufactured under HP US Pat. No. 4,293,415.

