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Short Communication

Instability of tetryl to Soxhlet extraction

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ABSTRACT

The stability of tetryl (N-methyl-N,2,4,6-tetranitroaniline) to Soxhlet extraction with methanol was examined by refluxing tetryl in methanol and extracting a tetryl-contaminated soil using Soxhlet, ultrasonic bath and wrist-action shaker methods. The results indicate that tetryl is unstable to Soxhlet extraction. If wet soils are Soxhlet-extracted with methanol, tetryl hydrolyzes to N-methylpicramide (N-methyl-2,4,6-trinitroaniline). If extracted dry, methanolysis products are formed. Ultrasonic bath extraction with acetonitrile is recommended instead.

INTRODUCTION

Tetryl (N-methyl-N,2,4,6-tetranitroaniline) was used as a common component of USA military high explosives from 1916–1979 [1,2]. While it has been largely replaced by RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) in modern explosives formulations, residues of tetryl have been found at a number of military facilities [3–5]. Concerns about the health effects of tetryl have led to interest in its fate under environmental conditions [6].

Tetryl (Fig. 1a) is a solid at normal environmental temperature and the neat material is known to be thermally unstable at temperatures above 131°C [7]. Tetryl has a water solubility of about 80 mg/l [8] and an estimated octanol–water partition coefficient of 45 [9], indicating it is relatively mobile in the soil and has a potential to contaminate ground water.

Analytical methods for the determination of tetryl and other nitroaromatics and nitramines in environmental samples have generally relied on solvent extraction followed by gas chromatography (GC) with electron-capture detection [10], GC–mass spectrometry (MS) [11], reversed-phase high-performance liquid chromatography (RP-HPLC) [12–14], or supercritical fluid chromatography [15]. Because of the facile thermal conversion of tetryl to N-methylpicramide (Fig. 1b) during GC analysis [11], most routine analyses of tetryl in soil extracts have been conducted using RP-HPLC [16–18].

A comparison of extraction techniques for nitroaromatics and nitramines in soil showed that ultrasonic bath and Soxhlet extraction were superior to other methods examined and approximately equivalent in extraction efficiency, and that acetonitrile was superior to methanol due to its more rapid extraction of nitramines [19]. Tetryl was not studied, but the authors cautioned that thermally labile compounds can be a problem with the Soxhlet method because the extract is maintained at the boiling point of the solution

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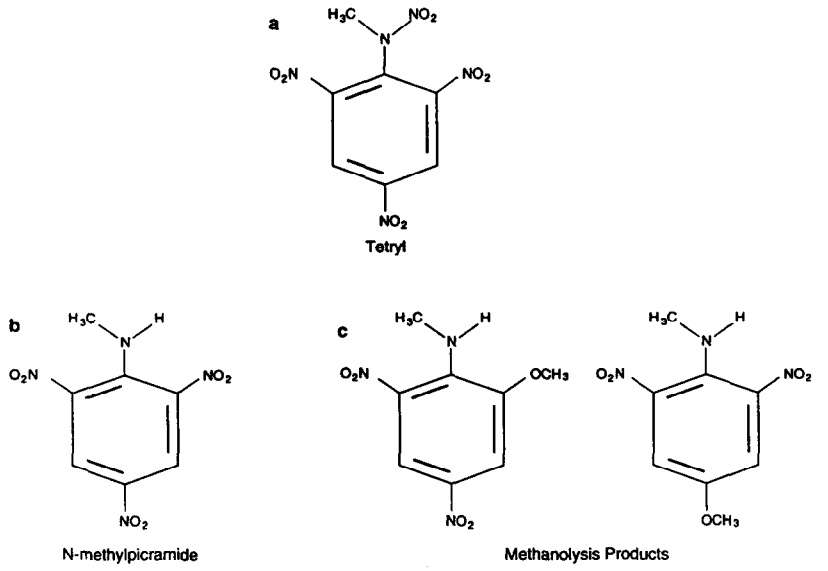

Fig. 1. Molecular structures of (a) tetryl, (b) N-methylpicramide and (c) tetryl methanolysis products.

in the receiver for an extended period. In a collaborative study of the ultrasonic bath extraction method, low recovery of tetryl was traced to high sonic bath temperatures (> 45°C) [20]; for this reason, standard methods based on this procedure now specify that the sonic bath be maintained at or below room temperature [16–18].

In a recent study, wet, tetryl-fortified soils were extracted using methanol in a Soxhlet extractor for 48 h [21]. Care was taken to wrap the Soxhlet with aluminum foil to eliminate light. To test the stability of tetryl to Soxhlet extraction, a 15 mg/l solution of tetryl in methanol was refluxed for 48 h and the resulting solution analyzed by gradient elution RP-HPLC. After reflux, although the color of the solution changed from yellow to green (indicating that some tetryl degradation had occurred), a recovery of 82% of unaltered tetryl was reported. Because of the thermal lability of tetryl in GC–MS analysis [11], the conclusion that tetryl was unaltered by this process was based on RP-HPLC retention time using a gradient elution separation.

The objective of this work is to verify the stability of tetryl during Soxhlet extraction relative to its stability in the standard ultrasonic bath method [16–18].

EXPERIMENTAL

Chemicals

Standard analytical reference material (SARM) for tetryl was obtained from the US Army Environmental Center, Aberdeen Proving Ground, MD, USA. Water used in the preparation of HPLC eluent was reagent grade from a Milli-Q Type-1 reagent-grade water system (Millipore, Bedford, MA, USA). Methanol used in the preparation of eluent and for soil extraction was Alltech (Deerfield, IL, USA) HPLC grade. Acetonitrile used for soil extraction and for preparation of eluent was Baker (Phillipsburg, NJ, USA) analyzed HPLC grade. Eluent used for isocratic separations was prepared daily by combining the appropriate volumes of water, acetonitrile and methanol and vacuum filtering through a nylon-66 membrane (0.45 μm) to degas the solvent and remove particulate matter.

Instrumentation

RP-HPLC analyses were obtained on a modular system composed of the following: (1) Spectra-Physics (San Jose, CA, USA) Model 8800 ternary HPLC pump; (2) Spectra-Physics Spectra 100 variable-wavelength UV detector set at 254 nm with a cell path length of 0.6 cm; (3) Hewlett-Packard (Avondale, PA, USA) Model

HP 3393A digital integrator equipped with a Hewlett-Packard Model HP911B disk drive; (4) Linear (Reno, NV, USA) Model 500 strip chart recorder.

RP-HPLC separations

All separations were accomplished on either a Supelco (Bellefonte, PA, USA) LC-18 (octadecyldimethylsilyl) or LC-CN (cyanopropylmethylsilyl) column (25 cm × 4.6 mm, 5 μm particle size, 100 Å pore diameter) using either binary or ternary eluents composed of water, methanol and acetonitrile. The first was the gradient elution separation reported elsewhere [21], where an LC-18 column was eluted with 1.0 ml/min of water–acetonitrile, and the acetonitrile percentage was programmed from 35 to 100% at 1%/min. The second separation was isocratic on LC-18 using water–methanol (1:1) at 1.5 ml/min [13,16–18]. The third separation, also isocratic, was obtained on LC-CN eluted with water–acetonitrile–methanol (65:23:12) [22] at a flow-rate of 1.5 ml/min.

GC–MS analysis

All GC–MS analyses were conducted on an Hewlett-Packard 5992 mass-selective detector. Samples (1 μl) were introduced into the mass-selective detector through a Hewlett-Packard 5890 Series II gas chromatograph operated in the splitless mode. An HP-1 (cross-linked methyl silicone, 12 m × 0.20 mm, 0.33 μm film thickness) column was maintained at 45°C for 2 min and then the oven was temperature-programmed at 20°C/min to 240°C and held for 10 min.

Field-contaminated soil

Tetryl-contaminated soil collected at the Nebraska Ordnance Plant, Mead, NE, USA, was used to test various extraction techniques. Soil was air-dried, ground with a mortar and pestle, and mixed thoroughly to obtain as homogeneous a test sample as possible. Because the reported method [21] utilized undried soil, water was added to one test portion (2.0 ml to 10.0 g of soil) prior to Soxhlet extraction to examine the effect of the presence of water on the stability of tetryl during Soxhlet extraction.

RESULTS AND DISCUSSION

Instability of tetryl under reflux conditions

An initial experiment was conducted to examine the stability of tetryl during reflux in methanol reported elsewhere [21]. In this experiment a 2.02 mg/l solution of tetryl was prepared in methanol from a freshly opened bottle, and the solution was refluxed for 48 h in a Soxhlet extractor. The device was wrapped with aluminum foil to eliminate light. A drying tube was attached to the top of the condenser to minimize the incorporation of atmospheric moisture in the methanol during the 48-h reflux. After the extract cooled, a portion was analyzed using the three separations described above. A tetryl standard not subjected to reflux was analyzed as well. Analysis using the gradient elution separation [21] revealed one large peak that eluted at the same retention time as tetryl, a small peak eluting just prior to the retention time of tetryl that was identified as N-methylpicramide, and several other small peaks not present prior to refluxing, which were apparent degradation products caused by the instability of tetryl to reflux conditions (Fig. 2). The apparent recovery of tetryl was 59% compared with 82% reported in the earlier work [21]. However, when this extract was analyzed using an isocratic LC-18 separation [13,16–18], again one large

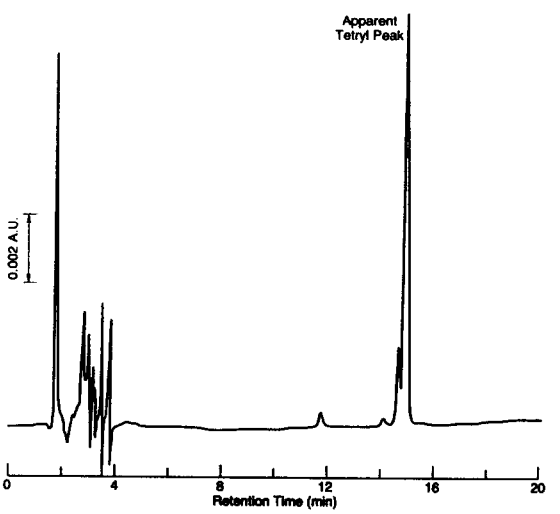

Fig. 2. HPLC chromatogram obtained by gradient elution of an LC-18 column of a tetryl solution refluxed in methanol.

peak was observed, but the retention time was longer than that for tetryl (Fig. 3). Very small peaks were observed at the retention time for tetryl and N-methylpicramide. These results were confirmed using a second isocratic separation on LC-CN [22], which resolved the single major peak observed on LC-18 into two peaks, neither of which had the characteristic retention time of tetryl (Fig. 4). The presence of two major degradation products was confirmed by GC–MS analysis of the extract. These peaks eluted from GC about a minute apart, but had very similar mass spectra. Their mass spectra are consistent with the structures of 2-methoxy-N-methyl-4,6-dinitroaniline and 4-methoxy-N-methyl-2,6-dinitroaniline (Fig. 1c). These compounds may be formed by methanolysis of N-methylpicramide, the initial degradation product of tetryl, or from methanolysis of tetryl followed by loss of the nitramine nitro group during GC–MS analysis in an analogous manner to the loss of NO_2 from tetryl under identical conditions. Thus our results indicate that tetryl is not stable when refluxed in methanol in the dark, even when the solution contains minimal water. These results conflict with those reported elsewhere [21] relative to the stability of tetryl to the reflux conditions typical of Soxhlet extraction.

Comparison of extraction methods for tetryl

An experiment was run to compare the stability of tetryl during Soxhlet extraction with the standard ultrasonic bath procedure using a soil collected at the Nebraska Ordnance Works that was field-contaminated with tetryl. A field-contaminated soil was selected for this study since earlier work indicated a difference in behavior between fortified and field-contaminated soil during extraction [13]. Two subsamples of 10.0 g each were placed in extraction thimbles and refluxed in Soxhlet extractors with methanol in the dark for 48 h, as described elsewhere [21]. Because this procedure uses undried soil, 2.0 ml of reagent-grade water were added to one subsample prior to extraction, and a drying tube was attached to the top of the condenser for the other, as described above. Two additional 2.0-g subsamples of dried soil were also extracted using an ultrasonic bath procedure for 18 h as

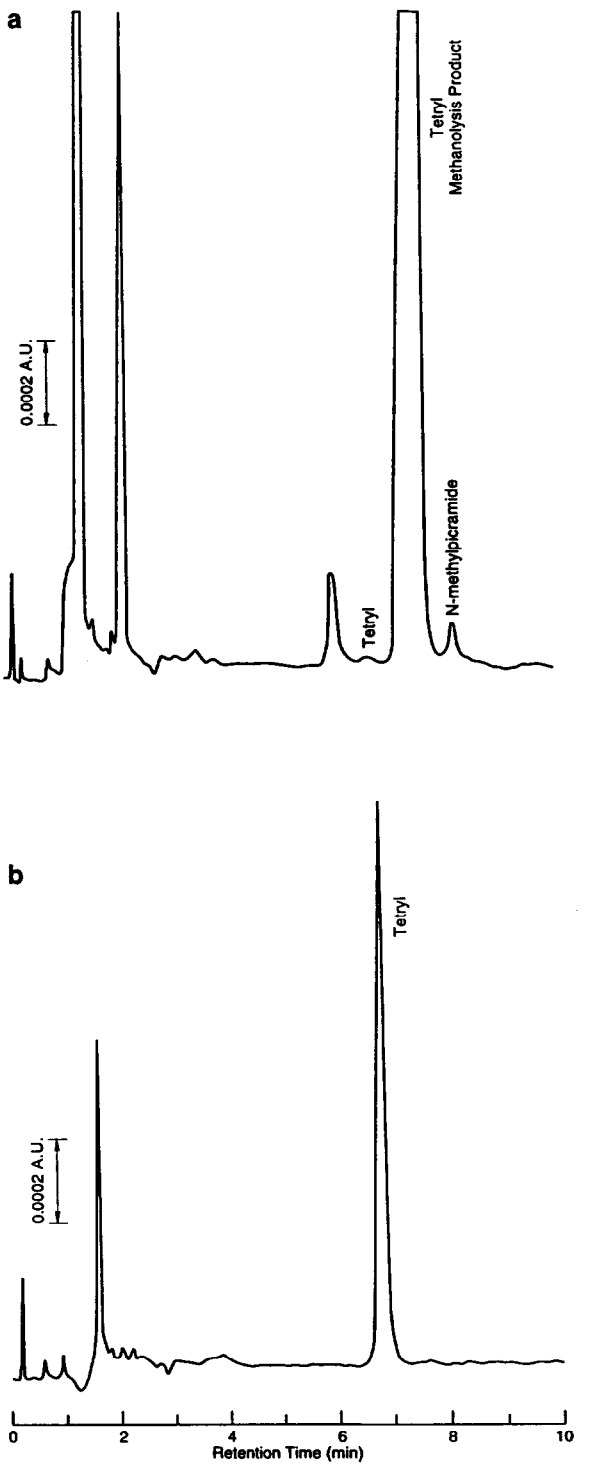

Fig. 3. HPLC chromatograms obtained by isocratic elution of an LC-18 column of (a) a tetryl solution refluxed in methanol and (b) a tetryl standard in methanol.

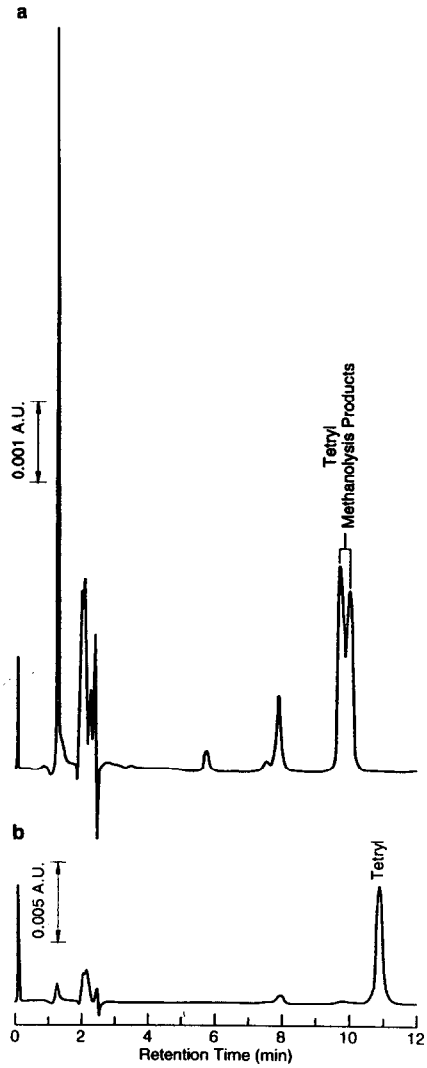

Fig. 4. HPLC chromatograms obtained by isocratic elution of an LC-CN column of (a) a tetryl solution refluxed in methanol and (b) a tetryl standard in methanol.

described elsewhere [13,16–18]. One portion was extracted using methanol and one using acetonitrile. The ultrasonic bath was maintained at or below room temperature to minimize thermal degradation of tetryl [20]. Because the ultrasonic bath procedure also imparts considerable energy into the sample during extraction and could also result in tetryl degradation, two portions of this dried soil were also extracted using a gentler wrist-action shaker procedure. These extractions were also conducted for 18 h at room temperature (about 22°C), one portion using methanol and one using acetonitrile.

The extracts from the Soxhlet, ultrasonic bath and wrist-action shaker were analyzed using the three RP-HPLC separations described above. Fig. 5 presents the chromatograms obtained for the methanol extracts from the Soxhlet, with and without addition of water, and the methanol extract from the ultrasonic bath procedure using the isocratic LC-18 separation. Recovery of tetryl, compared to the methanol extract from the wrist-action shaker, was only 0.2% for the Soxhlet extract of the wet soil and 60% for the Soxhlet extract of dry soil. In addition, the peak area for N-methylpicramide for the extract from the Soxhlet with wet soil was 19 times that found for the wrist-action shaker while the major degradation products from the dry soil were the methanolysis products (Fig. 1c). This behavior is consistent with the hypothesis of Davis and Allen [23], who attributed the conversion of tetryl to N-methylpicramide in refluxing capryl or *n*-butanol to hydrolysis from water present in these alcohols. Thus, the rapid loss of tetryl and immediate production of N-methylpicramide reported elsewhere, when tetryl was spiked onto wet soils and then extracted using the Soxhlet method, were probably artifacts of the Soxhlet extraction procedure [21]. The two chromatograms from extractions using the ultrasonic bath and wrist-action shaker with methanol are nearly identical, showing equivalent recovery of tetryl and a similar pattern of smaller peaks. They are considerably less complicated and qualitatively quite different from the chromatograms from the Soxhlet, particularly the one for wet soil. Chromatograms from the two other separations are consistent with these conclusions.

The methanolysis products discussed in our reflux experiments were also observed, although to a much lesser degree, in the methanol extracts from the ultrasonic bath and wrist-action shaker. As expected, these peaks do not appear in either acetonitrile extract. Instability of tetryl in methanol solution has been observed elsewhere [24], although the products were not reported. Because extracts are often held for many days prior to determination, we recommend the use

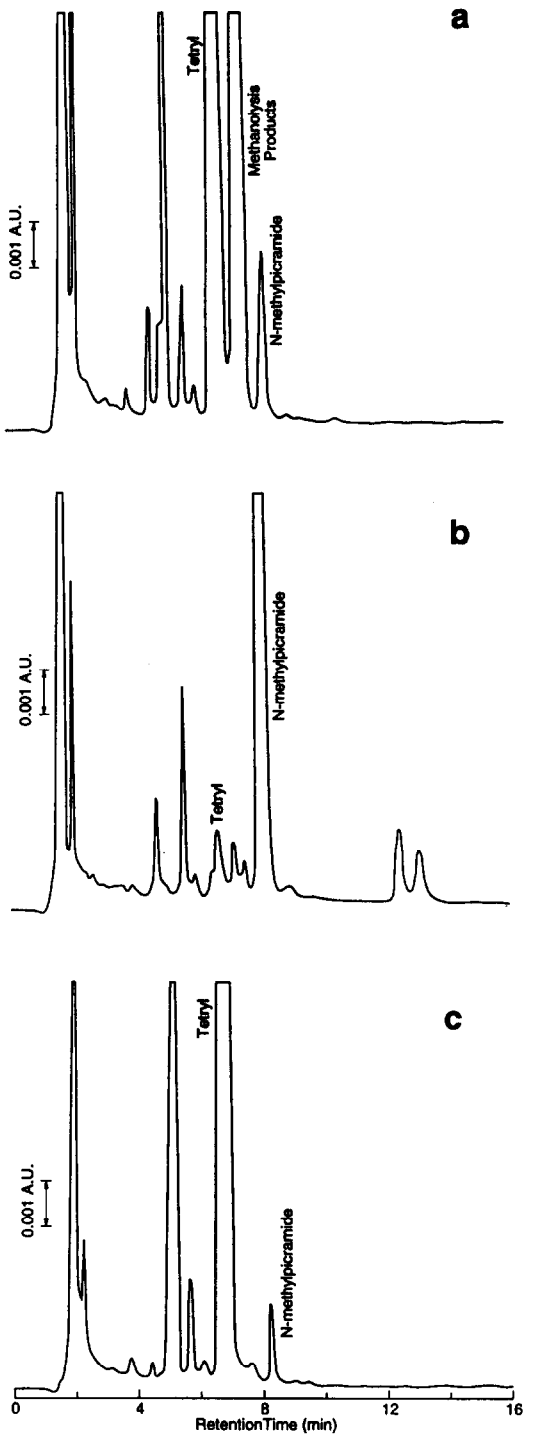

Fig. 5. HPLC chromatograms obtained by isocratic elution of an LC-18 column of extracts of a tetryl contaminated soil. (a) Soxhlet: dry soil (methanol); (b) Soxhlet: wet soil (methanol); (c) ultrasonic bath (methanol).

of acetonitrile rather than methanol for extraction of tetryl-contaminated soils.

CONCLUSIONS

The results of this study indicate that tetryl is not stable to Soxhlet extraction with methanol, particularly for undried soils, and we recommend ultrasonic bath extraction with acetonitrile. Tetryl's instability during Soxhlet extraction casts doubt on the validity of the conclusions presented elsewhere [21] relative to the kinetics of transformation of tetryl in soil and their identification of microbiological transformation products. Research is needed to determine the fate of tetryl in the environment, as was evident from the observation of large concentrations of tetryl remaining in soils contaminated with tetryl many years ago and the presence of a variety of unknown environmental transformation products in the extracts of these field-contaminated soils. The results of this study also demonstrate the need to use second column confirmation when analyte identification is accomplished by RP-HPLC retention time alone.

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