Journal of Chromatography, 114 (1975) 261–265
© Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 8441

Note

Quantitative determination of tetryl and its degradation products by high-pressure liquid chromatography

MICHAEL G. FAREY and SARAH E. WILSON
Ministry of Defence, Explosives Research and Development Establishment, Waltham Abbey, Essex (Great Britain)

(Received May 28th, 1975)

The stability of N-methyl-N,2,4,6-tetranitroaniline (tetryl) as demonstrated by the vacuum stability test is more than adequate and it can be stored for many years at normal temperatures without detectable decomposition. In use it is usually in contact with other explosives and may be surrounded by considerable quantities of rubbers or plastics; its stability under these circumstances, for example when in contact with lead azide, may be less satisfactory. To investigate this problem, a quantitative method for the determination of tetryl and its degradation products was required.

Previous workers[1-3] have studied the thermal decomposition of tetryl at temperatures at and above its melting point (129°). Dubovitskii *et al.*[3] used conventional liquid chromatography to separate some degradation products and identified them by UV spectroscopy. Yasuda[4] developed a two-dimensional thin-layer chromatography (TLC) method for the separation and identification of a large number of possible degradation products and identified a limited number of them in tetryl heated at 120°.

High-pressure liquid chromatography (HPLC) is ideally suited to the analysis of thermally unstable compounds. The methods described in this article provide fast analysis times with a high degree of resolution and are quantitative and very reproducible.

EXPERIMENTAL

The instrument used was a Waters Ass. ALC 202 liquid chromatograph equipped with a UK6 septumless injector which allowed highly reproducible injections to be made at atmospheric pressure using a Hamilton 701N 10-μl syringe fitted with a Chaney adaptor. A 254-nm UV detector was used, and quantitative results were obtained by measuring the peak areas electronically with a Spectra Physics Autolab System IV computing integrator. Several columns and solvent systems were tried, of these a 30-cm μPorasil (Waters Ass.) column and a cyclohexane–redistilled tetrahydrofuran (93:7) solvent system gave quite a good separation of many of the degradation products but required about 1 h per analysis. Finally, two different chromatographic systems, I and II, were found to be necessary for the complete quantitative analysis of the possible degradation products. This is because picric acid, which has been reported as one of the major thermal decomposition products, is very strongly retained under conditions that favour the separation of the other compounds of interest and it was therefore necessary to determine it separately using a reversed-phase system.

The determination of the possible products 1–10 in Table I was made with system I using a 30-cm × 4.4-mm I.D. stainless-steel µBondapak CN column (Waters Ass.) operated at ambient temperature and a solvent system comprising cyclohexane–chloroform–redistilled tetrahydrofuran (77:20:3), the flow-rate was 2 ml/min at an operating pressure of 1750 p.s.i. The sensitivity of the UV detector was 0.16 absorbance units and at this setting the detection limit of the degradation products was 0.05 µg. The samples of tetryl (30 mg) were dissolved in 3 ml of redistilled tetrahydrofuran for injection and the volume injected was usually 5–10 µl.

After standing for several hours, solutions of some of the degraded samples in tetrahydrofuran appeared to have decomposed; therefore, throughout this work all samples were injected immediately after solution, and the solvent was then removed from the rest of the sample by evaporation in a current of air. This problem was not evident when dealing with solutions of pure compounds for calibration purposes. Using system I, all the degradation products and tetryl are separated within 20 min with capacity factors in the optimum range 0–10. All the compounds are sufficiently well resolved for reproducible peak area measurements to be made with the Autolab System IV integrator. Table I lists the retention times of each compound under the specified conditions and Fig. 1 shows a sample chromatogram of a synthetic mixture of them.

TABLE I

RETENTION DATA FOR TETRYL AND POSSIBLE DEGRADATION PRODUCTS

Peak No.	*Compound*	*Retention time (sec)*	
		System I	*System II*
1	N-Methyl-2,6-dinitroaniline	165	366
2	2-Nitroaniline	209	158
3	2,4-Dinitroanisole	277	181
4	2,4,6-Trinitroanisole	295	298
5	2,4,6-Trinitrobenzene	326	122
6	N-Methyl-2,4,6-trinitroaniline (methylpicramide)	406	386
7	2,4,6-Trinitroaniline (picramide)	455	198
8	4-Nitroaniline	523	75
9	2,4-Dinitroaniline	618	181
10	N-Methyl-N,2,4-trinitroaniline	781	217
11	N-Methyl-N,2,4,6-tetranitroaniline (tetryl)	1076	249
12	2,4,6-Trinitrophenol (picric acid)	very strongly retained	38

Picric acid was determined with System II using a 60-cm × 2.2-mm I.D. stainless-steel phenyl/Corasil reversed-phase column (Waters Ass.) operated at ambient temperature and a solvent system comprising water–methanol (75:25), degassed prior to use. The flow-rate was 2 ml/min and the operating pressure 1700 p.s.i. The samples (30 mg) were dissolved in 1 ml of methanol and then diluted to 4 ml with distilled water for injection, by this technique baseline disturbances that might affect the area

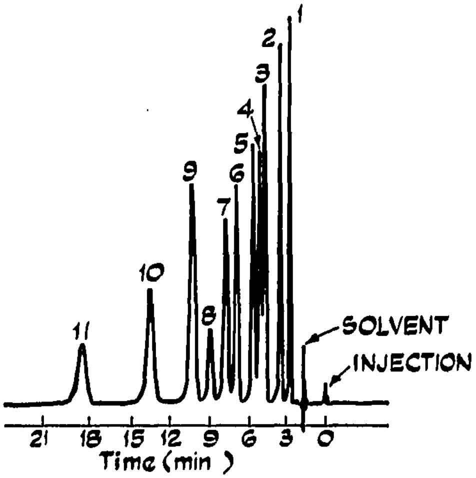

Fig. 1. HPLC separation of compounds 1–11 in Table I using chromatographic system I.

measurement of the picric acid peak, which elutes in only slightly greater than one column volume, were avoided. The samples were centrifuged prior to injection as, although picric acid is quite soluble in the mixed solvent, tetryl is not.

Fig. 2 shows a chromatogram of a mixture of picric acid and the compounds listed in Table I; these are not resolved and are mostly eluted with tetryl as a single peak. Retention times are shown in Table I.

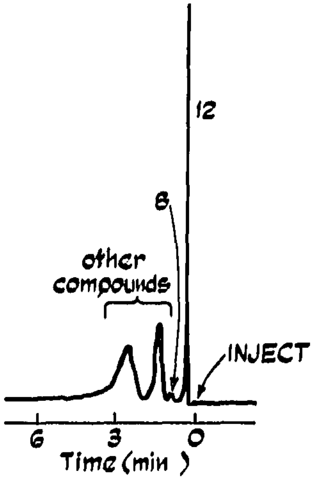

Fig. 2. HPLC separation of picric acid from the other compounds listed in Table I using chromatographic system II.

The detector was calibrated for each compound listed in Table I; plots of detector response *vs.* weight of compound for 2,4,6-trinitroaniline (picramide) and picric acid are shown in Fig. 3. Similar calibration graphs were obtained for each of the other compounds. The reproducibility of the chromatographic methods were

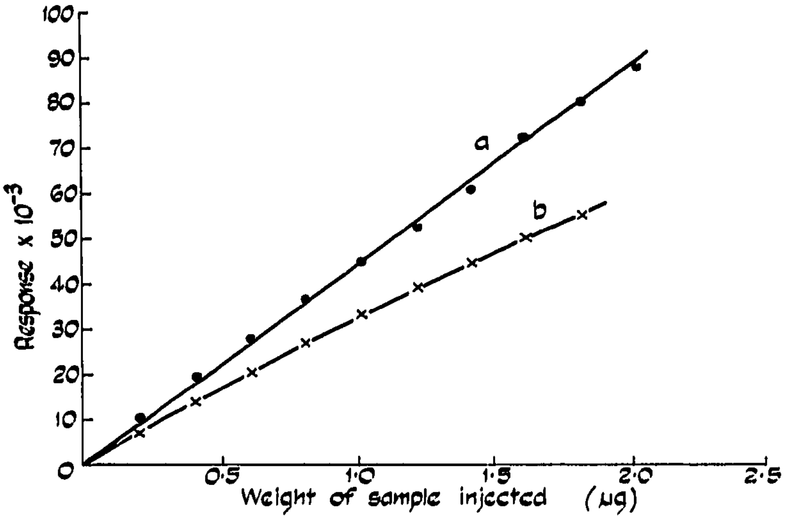

Fig. 3. Calibration plots for (a) 2,4,6-trinitroaniline and (b) picric acid.

determined by making repeated injections of a standard solution of the compounds, the coefficients of variation for each compound determined for a minimum of ten injections are shown in Table II.

TABLE II

REPRODUCIBILITY OF PEAK AREA MEASUREMENTS

Peak No.	*Coefficient of variation (%)*	*Chromatographic system*
1	3.23	I
2	2.18	I
3	1.17	I
4	1.29	I
5	1.09	I
6	1.37	I
7	1.08	I
8	1.49	I
9	1.15	I
10	1.11	I
11	2.82	I
12	0.39	II

Although some of the compounds listed in Table I, notably 2,4,6-trinitroaniline, are reported to be easily hydrolysed to picric acid, repeated analysis of a solution of these compounds in the water–methanol solvent used for system II over a period of 2 h failed to show any increase in the quantity of picric acid present. This 2-h period is more than sufficient for several repeat analyses to be carried out.

RESULTS AND DISCUSSION

The methods were applied to the analysis of a number of samples of tetryl degraded under varying conditions. The results of some of these are shown in Table III and a chromatogram showing the products obtained from a sample heated for 4 weeks at 80° in contact with lead azide is shown in Fig. 4.

TABLE III

ANALYSIS OF DEGRADED TETRYL SAMPLES

Treatment	*Methyl picramide(%)*	*Picramide (%)*	*Picric acid (%)*	*p-Nitroaniline (%)*	*Trinitroanisole (%)*
Tetryl heated alone for 4 weeks at 80°	0.42	—	0.16	—	—
Tetryl heated alone for 4½ days at 120°	0.21	0.01	0.31	—	0.39
Tetryl heated with lead azide for 4 weeks at 80°	2.41	6.70	1.32	0.47	—

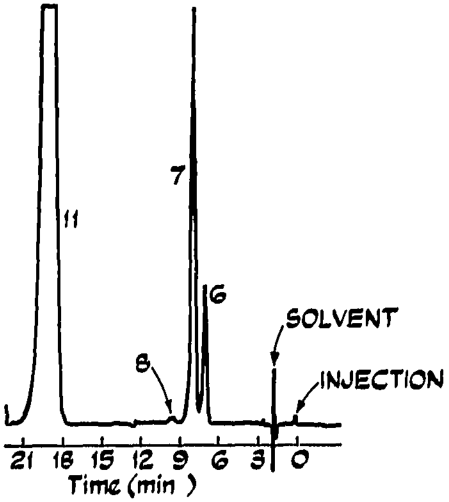

Fig. 4. Chromatogram of tetryl and the decomposition products formed after 4 weeks at 80° in contact with lead azide.

The two-dimensional TLC method of Yasuda[4] was used to confirm the identity of the degradation products found in all samples of heated tetryl. There were no discrepancies between this method and the HPLC methods described above.

REFERENCES

1 R. C. Farmer, *J. Chem. Soc.*, 117 (1920) 1603.
2 C. N. Hinshelwood, *J. Chem. Soc.*, 119 (1921) 721.
3 F. I. Dubovitskii, G. B. Manelis and L. P. Smirnov, *Russ. J. Phys. Chem., (Engl. Transl.)*, 35 (1961) 255.
4 S. K. Yasuda, *J. Chromatogr.*, 50 (1970) 453.