IDENTIFICATION AND DETERMINATION OF IMPURITIES IN PENTAERYTHRITOL TETRANITRATE

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(Received May 14th, 1970)

SUMMARY

Thin-layer chromatography (TLC) combined with photometry has been used successfully for the simultaneous determination of PETriN, DiPEHN, and TriPEON in PETN samples. The impurities are separated by one-dimensional TLC on Silica Gel G–Zn–sodium sulfanilate plates with an acetone–benzene mixed solvent. When the chromatogram is sprayed with N,N-dimethyl-1-naphthylamine (DMNA)–acetic acid reagent, the separated components are converted to a diazo dye to produce red spots on an off-white background. The intensities of the spots are measured by visible reflectance and are related to concentration by calibration curves. The standard deviations obtained in the analysis of various synthetic mixtures and authentic samples are less than 0.2%. Identification of the impurities is accomplished by their R_G values, measured relative to PETN.

INTRODUCTION

Pentaerythritol tetranitrate (PETN) commonly contains several impurities that can alter its physical and chemical properties. Dipentaerythritol hexanitrate (DiPEHN), for example, can cause a measurable change in the firing characteristic of exploding-bridgewire, PETN detonators. Thus a convenient procedure for identifying and determining the impurities in PETN is of considerable practical interest.

IR spectroscopy and thin-layer chromatography (TLC) are two of the most common techniques used for the analysis of PETN impurities. With IR it is difficult to detect the impurities at low concentration unless some sort of concentration step is incorporated into the procedure[1]. Furthermore, analytical bands become scarce if DiPEHN and tripentaerythritol octanitrate (TriPEON) are both present in the sample. TLC combined with radiometric scanning has been employed successfully to determine the hydrolysis products of tagged PETN, but DiPEHN and TriPEON were not included in the study[2].

TLC is an excellent method for separating mixtures, but the ultimate success of the method lies in the detection method used to locate the separated components.
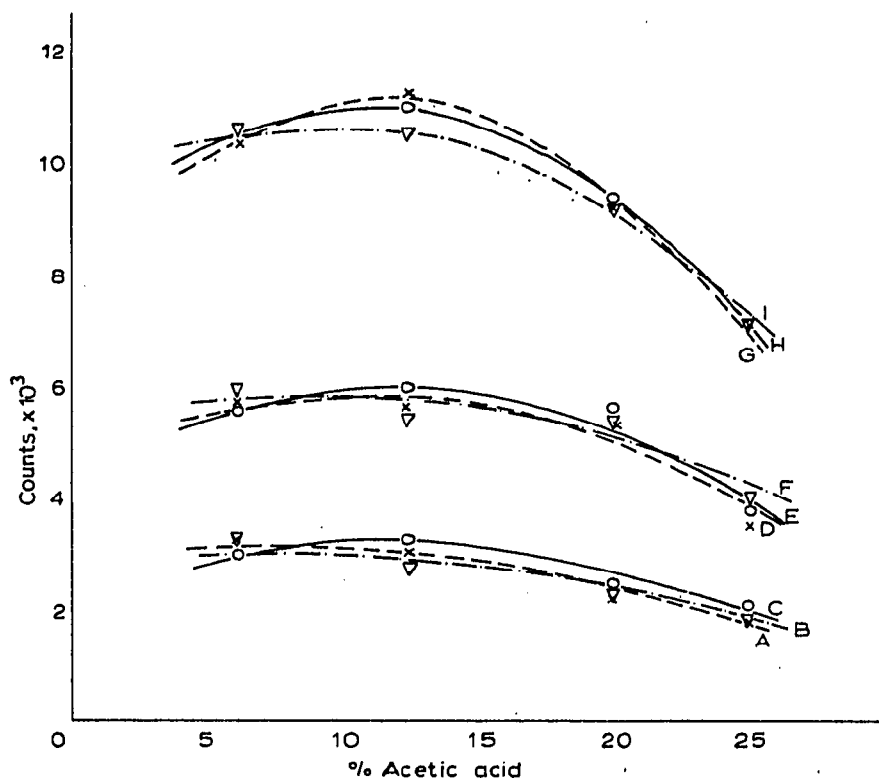
Fig. 1. Effect of acetic acid concentration (vol.%) on the color intensity of the diazo dye; 1% N,N-dimethyl-1-naphthylamine. (————), PETriN; curve C = 2.1 μg; curve E = 4.2 μg; curve H = 8.4 μg. (— — — —), TriPEON; curve A = 2.1 μg; curve D = 4.1 μg; curve G = 8.2 μg. (— · — · —), DiPEHN; curve B = 2.0 μg; curve F = 3.9 μg; curve I = 7.9 μg. Each point represents an average of 2–4 determinations.

In the work reported here we describe a TLC method for the separation of PETN impurities and a diazotization reaction to detect the components. The impurities are identified by measurement of their relative migration rates (R_G values). For quantitative analysis, the intensities of the developed spots are measured photometrically and related to concentration by means of calibration curves. In this manner pentaerythritol trinitrate (PETriN), DiPEHN, and TriPEON, commonly found in PETN, are determined simultaneously with a single sample.

MATERIALS AND METHODS

Equipment and reagents

Applicator, chromatojar, Silica Gel G, and glass plates (200 × 200 mm) were purchased from Brinkmann Instruments, Inc. Zinc metal dust, AR grade, was from Mallinckrodt Chemical Works. A stock solution of 0.04 M sodium sulfanilate was prepared by dissolving 7.6484 g of sulfanilic acid monohydrate (Matheson, Coleman, and Bell) in about 800 ml of distilled water, neutralizing the solution with dilute sodium hydroxide solution to pH 7, and diluting the solution to 1 l with distilled water. White-label N,N-dimethyl-1-naphthylamine (DMNA) (Eastman Organic Chemical) was distilled at 115–116° and 50 μm pressure. The spray reagent consisted of 5 g of DMNA and 62.5 ml of glacial acetic acid diluted to 500 ml with absolute ethanol.
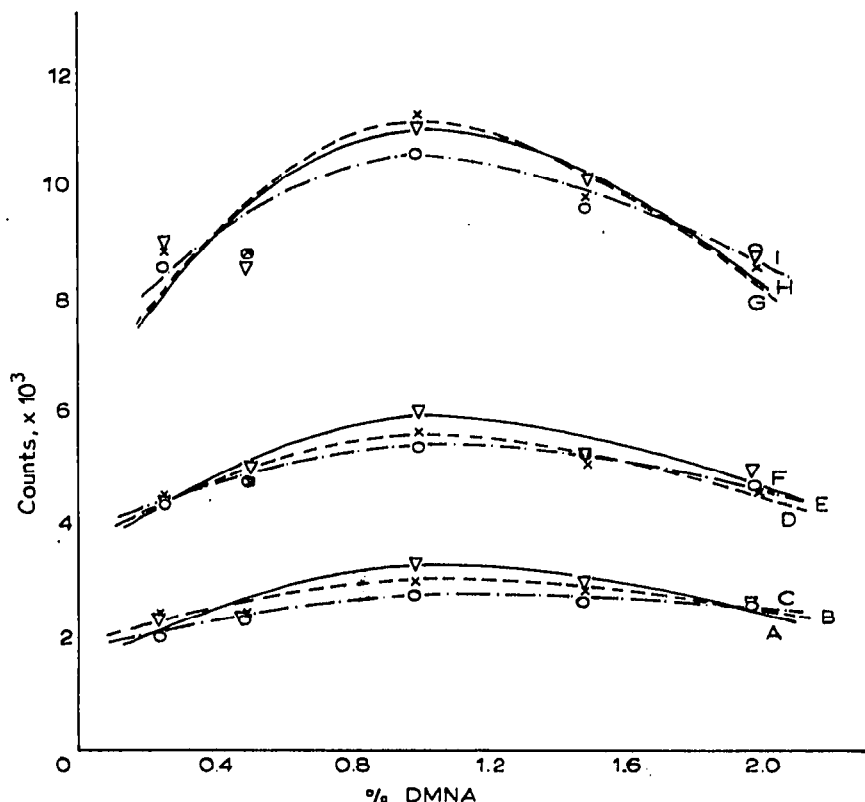
Fig. 2. Effect of DMNA concentration (w/v) on the color intensity of the diazo dye; 12.5 vol.% acetic acid. (———), PETriN; curve A = 2.1 μg; curve F = 4.2 μg; curve H = 8.4 μg. (– – – –), TriPEON; curve B = 2.1 μg; curve D = 4.1 μg; curve G = 8.2 μg. (—·—·—), DiPEHN; curve C = 2.0 μg; curve E = 3.9 μg; curve I = 7.9 μg.

An Agla micrometer syringe was used to deliver aliquots of the sample onto the TLC plates. Stopwatch, 250 ml Kensco atomizer, and a cylinder of nitrogen equipped with pressure reducer valve were used for reagent application. A Nester-Faust Uniscan 900 photometer with Summatic integrator and 10-mV recorder was used for the photometric measurements on the developed spots.

Experimental

Several essential modifications were incorporated into the Uniscan 900. A new base plate, 1/2-in. thick and flat to within 1 mil, was substituted for the original plate. The guide arm for the scanning head was aligned in such a manner that the distance of the scanning head from the thin-layer surface remained constant over a distance of at least 8 in. A micrometer adjustment screw was installed on the scanning head to control precisely the distance between the head and the thin-layer surface. These changes produced a considerable improvement in the performance of the instrument.

The chromatographic conditions were studied for the purpose of developing a method for the complete separation of PETriN, DiPEHN, and TriPEON from PETN. Silica Gel G–Zn–sodium sulfanilate plates activated at 110° for 2, 4, 6, and 16 h were tested with a four-component mixture and with acetone–benzene of varying composition as the mobile phase. The best results were obtained with plates activated at 110° for 16 h and chromatographed with acetone–benzene (4:96).

The color development of each impurity was investigated as a function of acetic acid and DMNA concentrations in the spray reagent. Holding DMNA constant and varying the acetic acid concentration, we found a broad maximum at or near 12.5 vol.% acetic acid for all three impurities (see Fig. 1). By varying the DMNA concentration while maintaining the concentration of acid constant at 12.5 vol.%, we found a maximum in color intensity at 1% DMNA (Fig. 2). From this study we conclude that a spray reagent consisting of 1% DMNA and 12.5% acetic acid in absolute ethanol provides the best compromise for photometric measurements.

Zinc dust in the amount of 0.5 g/30 g of Silica Gel G worked satisfactorily. Increasing the amount of zinc in the thin layer leads to a more rapid color development as well as a more rapid fading of the developed color.

The color stability of the diazo dye was studied. The intensity of the spots remained constant for from 10 to 25 min after the chromatogram has been sprayed. This provides ample time to scan three PETN samples on a single plate.

Preparation of Silica Gel G–Zn–sodium sulfanilate plates. A slurry of 30 g of Silica Gel G and 0.5 g of zinc dust in 65 ml of 0.02 M sodium sulfanilate solution is used to coat five glass plates (8 × 8 in.) by pulling an applicator across the plates at a constant speed. The coated plates are air-dried for 15 min and activated at 110° for 16 h before use.

Procedure. Three samples, each containing 200 μg of PETN, are applied 2 in. apart and 1 in. from the lower edge of an activated plate. The diameter of the sample is maintained at 1/4 in. The plate is developed in 250 ml of acetone–benzene (4:96) for 50 min. It is then air-dried for 5 min and sprayed uniformly with DMNA–acetic acid reagent for 35 sec, using 3 p.s.i. N_2 to propel the reagent. The chromatogram is allowed to develop in the dark for 7 min and is then dried with cold air from a hair dryer. 12 min after the chromatogram has been sprayed, the intensities of the spots are measured by visible reflectance with a dual-channel scanning head. The Summatic integrator of the Nester-Faust photometer, operated manually, registers a number of counts proportional to the intensity of a spot. A previously prepared calibration curve for each component is used to obtain the desired concentrations.

TABLE I

R_G VALUES OF PETN AND IMPURITIES

Compound	R_G value
PETN (ref. compound)	1.00
DiPEHN	0.70
TriPEON	0.47
PETriN	0.24

RESULTS AND DISCUSSION

For identification purpose, the R_G value of each impurity was measured relative to PETN. Table I lists the average values for three measurements.

Table II summarizes the data obtained on synthetic mixtures and authentic samples. It is evident that the results are excellent, with the standard deviations being

TABLE II

RESULTS OBTAINED ON VARIOUS PETN SAMPLES

Sample	Composition	No. of determinations	PETriN found (%)	Std. dev.	TriPEON found (%)	Std. dev.	DiPEHN found (%)	Std. dev.
Synthetic mixture	PETriN–TriPEON–DiPEHN–PETN (0.3:0.2:0.4:99.1)	6	0.4	0.07	0.3	0.06	0.5	0.08
Synthetic mixture	PETriN–TriPEON–DiPEHN–PETN (0.8:0.8:1.0:97.4)	6	0.8	0.13	0.8	0.18	1.0	0.13
Synthetic mixture	PETriN–TriPEON–DiPEHN–PETN (1.9:1.8:2.2:94.1)	5	2.1	0.07	1.6	0.12	2.2	0.11
Recrystallized mixture	TriPEON–PETN[a] (1:99)	6	<0.1	—	1.0	0.10	—	—
MD-2 recrystallized PETN	—	6	0.2	0.10	<0.1	—	0.7	0.13
Trojan special PETN	—	5	0.2	0.00	—	—	0.2	0.00
PETN, local sample	—	6	<0.1	—	—	—	<0.1	—
DuPont PETN	—	5	<0.1	—	<0.1	—	<0.1	—

a Contains about 0.1% tetrapentaerythritol decanitrate.
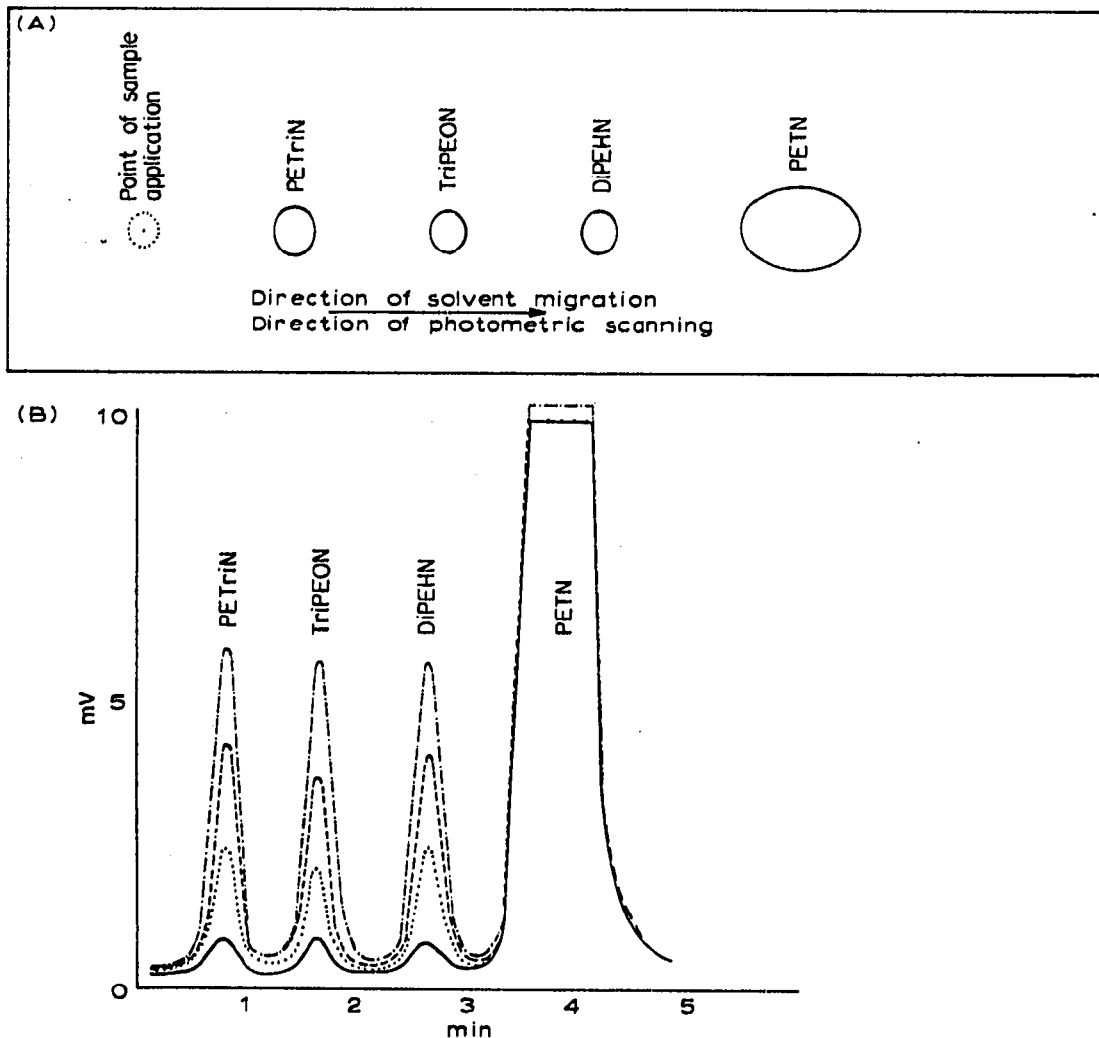
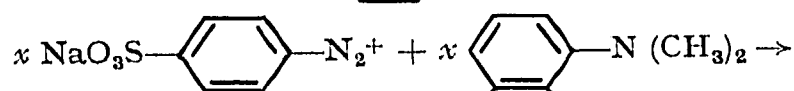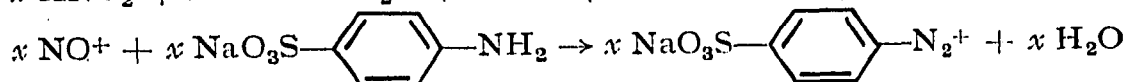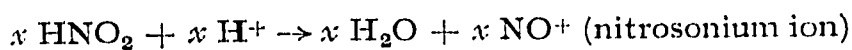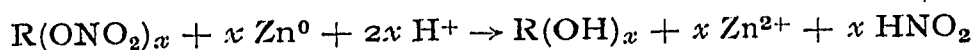Fig. 3. (A) Tracing of a one-dimensional thin-layer chromatogram. Chromatographic conditions: thin layer, Silica Gel G–Zn–sodium sulfanilate activated at 110° for 16 h; solvent, 250 ml of acetone–benzene (4:96); development time, 50 min; development temp., 25°; spray reagent, 1% DMNA and 12.5 vol.% acetic acid in absolute ethanol. (B) Photometric tracings of thin-layer chromatograms. Instrumental settings for Uniscan 900: mode of operation, visible reflectance; scanning head, dual beam; filter, green; no collimator; clearance of scanning head from thin-layer surface, 1/16 in.; slit, 3/4 × 1/16 in.; span, 500; gain, × 100; rate of travel of scanning head, 1.25 in./min. Summatic integrator, operated manually. 10-mV Varian G-14A-1 recorder, recorder speed 0.8 in./min. 200 μg per sample. (————), 0.2% PETriN, 0.2% TriPEON, and 0.2% DiPEHN in PETN; (.........), 1.0% PETriN, 0.9% TriPEON, and 1.0% DiPEHN in PETN; (– – – –), 2.0% PETriN, 1.9% TriPEON, and 2.0% DiPEHN in PETN; (—.—.—), 3.0% PETriN, 3.0% TriPEON, and 3.0% DiPEHN in PETN.

less than 0.2% in all cases. With the exception of MD-2 recrystallized PETN, only small amounts of impurities were found in the various commercial and local samples.

Fig. 3B shows several scans of synthetic mixtures as displayed on a 10-mV recorder. A tracing of a typical chromatogram is shown in Fig. 3A. The horizontal displacement of the components on the recorder tracing is due to the difference in the rates of travel of the scanning head (1.25 in./min) and the recorder (0.8 in./min). However, complete resolution of each peak is obtained on the recorder tracing.

The development of the red spot on the chromatogram is based on a diazotization reaction; the chemical equations may be written

$$R(ONO_2)_x + x\ Zn^0 + 2x\ H^+ \rightarrow R(OH)_x + x\ Zn^{2+} + x\ HNO_2$$
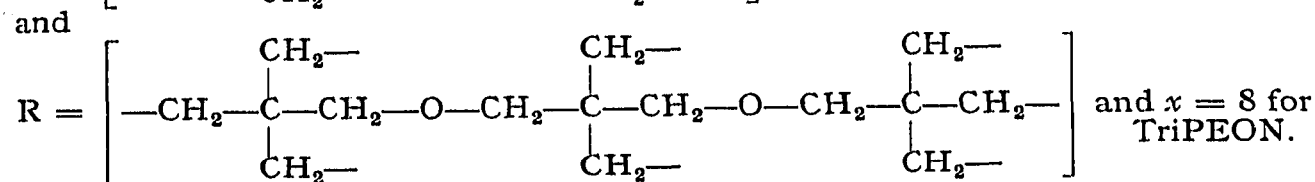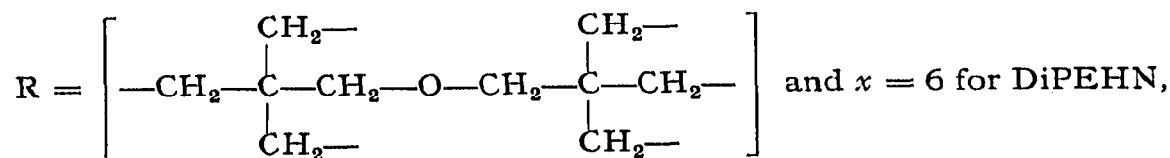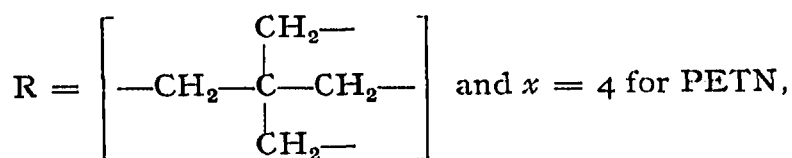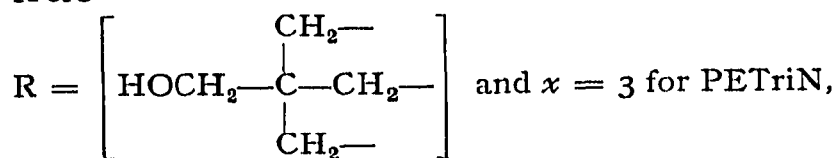
$$x\ HNO_2 + x\ H^+ \rightarrow x\ H_2O + x\ NO^+ \text{ (nitrosonium ion)}$$

$$x\ NO^+ + x\ NaO_3S\!-\!\!\langle\ \rangle\!-\!NH_2 \rightarrow x\ NaO_3S\!-\!\!\langle\ \rangle\!-\!N_2^+ + x\ H_2O$$

$$x\ NaO_3S\!-\!\!\langle\ \rangle\!-\!N_2^+ + x \Big\langle\ \Big\rangle\!-\!N\,(CH_3)_2 \rightarrow$$

$$x\ NaO_3S\!-\!\!\langle\ \rangle\!-\!N\!=\!N\!-\!\Big\langle\ \Big\rangle\!-\!N\,(CH_3)_2 + x\ H^+$$
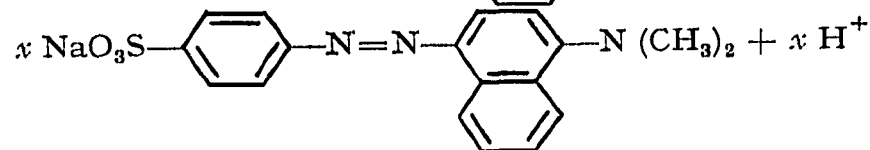
the net result of which is

$$R\,(ONO_2)_x + x\ Zn^0 + 2x\ H^+ + x\ NaO_3S\!-\!\!\langle\ \rangle\!-\!NH_2 + x \Big\langle\ \Big\rangle\!-\!N\,(CH_3)_2 \rightarrow$$

$$R\,(OH)_x + x\ Zn^{2+} + 2x\ H_2O + x\ NaO_3S\!-\!\!\langle\ \rangle\!-\!N\!=\!N\!-\!\Big\langle\ \Big\rangle\!-\!N\,(CH_3)_2$$

Here   (red diazo dye)

$$R = \left[HOCH_2\!-\!\underset{\underset{CH_2-}{|}}{\overset{\overset{CH_2-}{|}}{C}}\!-\!CH_2\!- \right] \text{ and } x = 3 \text{ for PETriN,}$$

$$R = \left[-CH_2\!-\!\underset{\underset{CH_2-}{|}}{\overset{\overset{CH_2-}{|}}{C}}\!-\!CH_2\!- \right] \text{ and } x = 4 \text{ for PETN,}$$

$$R = \left[-CH_2\!-\!\underset{\underset{CH_2-}{|}}{\overset{\overset{CH_2-}{|}}{C}}\!-\!CH_2\!-\!O\!-\!CH_2\!-\!\underset{\underset{CH_2-}{|}}{\overset{\overset{CH_2-}{|}}{C}}\!-\!CH_2\!- \right] \text{ and } x = 6 \text{ for DiPEHN,}$$

and

$$R = \left[-CH_2\!-\!\underset{\underset{CH_2-}{|}}{\overset{\overset{CH_2-}{|}}{C}}\!-\!CH_2\!-\!O\!-\!CH_2\!-\!\underset{\underset{CH_2-}{|}}{\overset{\overset{CH_2-}{|}}{C}}\!-\!CH_2\!-\!O\!-\!CH_2\!-\!\underset{\underset{CH_2-}{|}}{\overset{\overset{CH_2-}{|}}{C}}\!-\!CH_2\!- \right] \text{ and } x = 8 \text{ for TriPEON.}$$
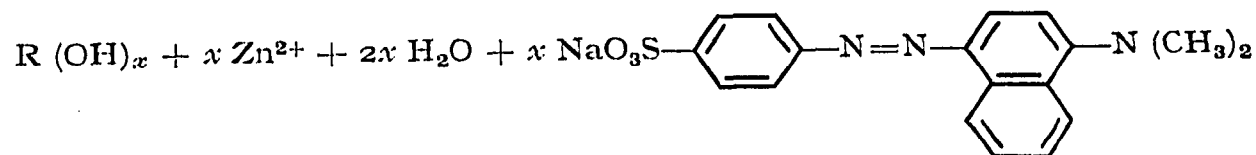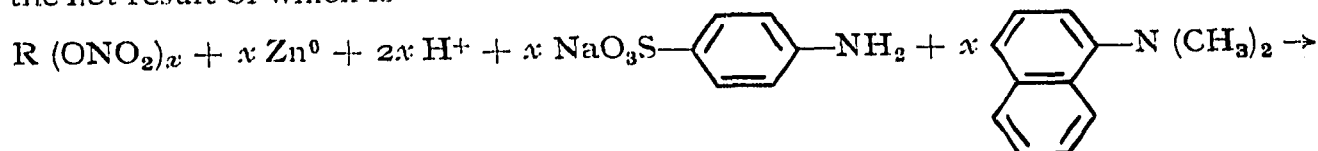
In the absence of the sample, no color is produced on the chromatogram. With sodium nitrite or nitrate, an intense red spot is formed identical to that produced by PETN. Therefore, PETN and its impurities must hydrolyze and produce nitrite ion in the presence of zinc and acetic acid. The formation of nitrosonium ion diazotizes the sodium sulfanilate, and the diazonium ion couples with DMNA to produce the red spots.

The color stability of the diazo dye is superior to that produced by the Griess reagent. The latter utilizes 1-naphthylamine as the coupling agent. The color develops rapidly, but it also fades rapidly, making it unsuitable for quantitative TLC work. DMNA as a coupling agent has been used in the determination of nitrite ion in aqueous solution[3].

The shelf lives of the sodium sulfanilate solution, the spray reagent, and the TLC plates were studied. The sodium sulfanilate solution can be stored for a month, but the spray reagent must be prepared weekly. The activated TLC plates, which are stored in a desiccator, cannot be stored for more than two days, as the color intensity of the spot for a given weight of sample decreases with the age of the plate. All reagents and plates must be stored in the dark.

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