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Note

Liquid chromatographic determination of nitroglycerin products in waste waters

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Various techniques have been used for the determination of small amounts of nitrate esters such as trinitroglycerin (NG) in a variety of samples. Included in these are procedures involving spectrophotometry[1–3], polarography[4,5], titrimetry[6], thin-layer chromatography (TLC)[7], and gas chromatography (GC)[8]. Each of these methods has certain limitations ranging from lack of specificity as in the spectrophotometric techniques to low quantitative accuracy as in the TLC method. Also, in most of the techniques, except those involving separation either before or during the course of analysis, there is mutual interference with similar nitrate esters. For some applications, this interference presents no problem; however, we have to determine the amount of both the tri- and dinitroglycerins (DNG) in a variety of samples.

Although GC techniques have been used successfully for the determination of NG at high concentrations, the potential for its decomposition during the course of an analysis makes the method somewhat questionable for the determination of trace quantities.

A technique that has been found to overcome the limitations of the aforementioned techniques is high-pressure liquid chromatography (HPLC). This technique is free from interference from inorganic or other organic nitrates that can cause error in the determination of NG by spectrophotometric or titrimetric methods. The HPLC method is more quantitative than the TLC method, and the nitrate esters are not subject to thermal decomposition as in the GC technique.

EXPERIMENTAL

Apparatus

Separations were performed on a DuPont 830 liquid chromatograph equipped with a 1 m × 2.1 mm precision-bore stainless-steel column packed with 30- to 44-μm Vydac adsorbent. The mobile phase is methylene chloride–hexane (60:40) with a flow-rate of 0.75 ml/min and 450 p.s.i. Sample injection is accomplished with a Hamilton HP305 5-μl syringe. A Hewlett-Packard Model 3370B integrator is used for recording peak areas.

Calibration

The area ratios of sample component (NG, DNG) to internal standard (phthal-

imide) were plotted versus the weight ratios, producing a linear correlation with a zero intercept. The NG used for standards was produced at this facility. The isomeric 1,3- and 1,2-DNGs were prepared according to a nitration procedure developed by Baczuk[9] and chromatographically separated on a 1-in. × 50-cm silica prep column.

Test procedure

Approximately 1 l of the waste water sample is extracted at least three times with methylene chloride. The extracts are combined and placed on a steam bath to evaporate most of the methylene chloride. Care must be taken to prevent evaporation to dryness. The solution is then transferred to a 25-ml volumetric flask, 10 ml of internal standard (phthalimide, 2 mg/ml) is added, and the contents are made up to volume with methylene chloride. For other samples, the NG and DNG are taken into solution with methylene chloride to provide a solution concentration the same as that for water extracts. Because the mobile phase was a mixture of methylene chloride–hexane (60:40), a slight solvent effect on injection of the methylene chloride sample would produce a negative peak at the column dead volume. This negative peak would reset the baseline on the integrator, producing problems in replication. These problems were eliminated by withdrawing 1.5 μl of sample, or standard prepared in methylene chloride, followed by 1.0 μl of spectranalyzed grade hexane. This procedure eliminated the negative solvent peak and replication improved considerably.

RESULTS AND CONCLUSIONS

A HPLC scan for a sample containing NG and the two DNGs is shown in Fig. 1. Phthalimide was selected as the internal standard owing to the inconvenience of preparing and storing the nitrate esters for use as external standards. For determination, the area of both DNGs was summed because only the total amount of DNG was desired.

The precision of the chromatographic portion of the method was determined from replicate injections of a given sample. The data indicated that the coefficient of variation using the internal standard method was approximately 2.8% for NG and 2.6% for DNG.

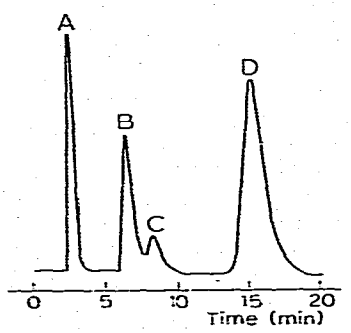

Fig. 1. Liquid chromatographic separation of nitrated glycerin. Column: 1-m × 2.1-mm precision-bore stainless-steel packed with Vidac adsorbent. Mobile phase: Methylene chloride–hexane (60:40) at 0.75 ml/min. Compounds: (A) trinitroglycerin; (B) 1,3-dinitroglycerin; (C) 1,2-dinitroglycerin, and (D) phthalimide.

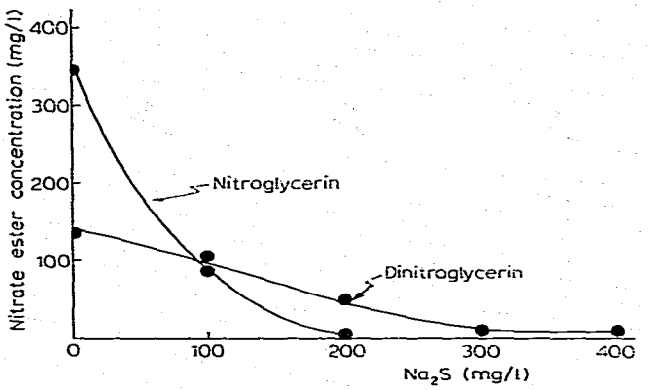

Fig. 2. Effect of sodium sulfide on the decomposition of nitroglycerin wash water.

Concentrations in water samples as low as 10 ppm for NG or DNG were conveniently determined. Analysis of NG purification wash waters showed concentrations up to 1000 ppm of NG and 600 ppm of DNGs. The presence of the relatively high concentrations of the DNGs reflects the higher solubility of this species in water and not the ratio of the concentration of these products to NG in the final nitration product. Thus, during the purification process, which functions primarily to remove residual mineral acids, we have the added benefits of reducing the concentration of DNG in the final product. The mononitroglycerins are not shown on this scan as they were never found in the waste water samples analyzed at this facility, and, therefore, were not considered during the development of a chromatographic method for nitrate esters of glycerin.

The primary use of this procedure has been in the analysis of waste water samples from the NG purification process before and following various techniques which were being considered for the removal of nitrate esters from waste waters. The LC method was used to evaluate the effectiveness of a process for denitrating NG by treatment of waste waters with sodium sulfide. Results of this study are shown graphically in Fig. 2. Denitration of the nitrate esters can be easily monitored as a function of the active denitrating agent's concentration. LC has also been used to monitor oxidation of nitrate esters by ozone treatment as shown in Fig. 3. Data such as these

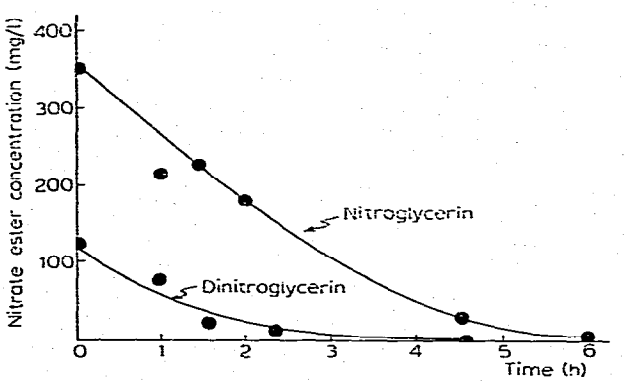

Fig. 3. Effect of ozonolysis time on the decomposition of a nitroglycerin wash water.

are extremely useful in the analysis of waste water samples because they show a high degree of sensitivity and specificity for the various nitrated species necessary to obtain a full understanding of the reactions involved in any pollution abatement scheme. A knowledge of the concentrations of the various nitrated glycerins is especially important because other work at this facility has shown that the dinitro-derivatives are readily bio-degradeable, whereas, NG at moderate to high concentrations is toxic to the bacteria used.

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