

## Quantitation of Nitrogen Dioxide Generated in Propellant and High Explosive by Polarography

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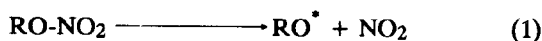
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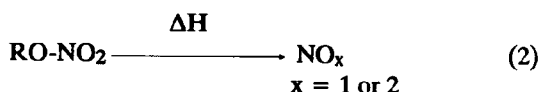
**Summary:** A method for determination of nitrogen dioxide in propellants and high explosives has been developed, based on collection of NO<sub>2</sub> in a cartridge containing Florisil coated with diphenylamine. The nitrogen dioxide reacts with diphenylamine to form N-nitroso and nitrodiphenylamine derivatives which are eluted from the cartridge, analysed by polarography and related to the amount of NO<sub>2</sub> generated in the sample. The utility of this method is exemplified by monitoring NO<sub>2</sub> in some propellants and high explosives subjected to accelerated decomposition at higher temperature.

### Introduction

Already at normal storage temperature, the nitrate esters of single and double base propellants decompose slowly. The initial step in this process is the cleavage of the weak nitrate ester (RO-NO<sub>2</sub>) under formation of nitrogen dioxide and aldehydes as;



An energy of only 150-170 kJ/mol is sufficient to break this bond. The nitrogen dioxide formed during this process can react further with organic materials to form nitrogen oxide and other gases such as N<sub>2</sub>O, CO, CO<sub>2</sub> and H<sub>2</sub>O [1]. This process can be written as;



In presence of air any NO formed can be oxidized to NO<sub>2</sub> which catalyses and hence accelerates the decomposition process. To prevent these reactions, stabilizers are added to the propellant. The function of the stabilizer is to react reasonably fast with the nitrogen dioxide formed before it can catalytically decompose further ester groups. Substances used as stabilizer are diphenylamine and various derivatives of urea [1].

Over the years, different types of stability tests have been developed for the purpose of check-

ing that Ha propellant has been properly stabilized and that it after many years of storage at different temperatures still remained stable.

In our present study we describe a method for the determination of nitrogen dioxide in propellant and high explosives, based on the collection of NO<sub>2</sub> in a cartridge containing Florisil coated with diphenylamine (Fig. 1). The nitrogen dioxide reacts with diphenylamine to form nitroso and nitro derivatives, which are eluted from the cartridge, analysed by polarography and related to the amount of NO<sub>2</sub> generated in the sample.

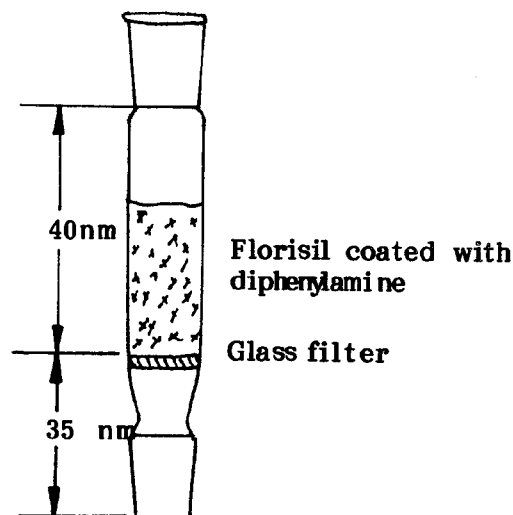


Fig. 1: Cartridge containing Florisil coated with diphenylamine.

*Reactions of diphenylamine*

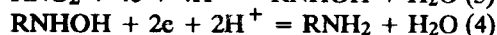
The reaction products in propellants between diphenylamine and the decomposition products of nitrate esters are well known and have been determined by different methods i.e. column chromatography [2], thin-layer chromatography [3], gas chromatography [4], high performance liquid chromatography [5] and differential pulse polarography [6].

The first change in diphenylamine-stabilized propellant is that N-nitrosodiphenylamine, 2-nitrodiphenylamine and 4-nitrodiphenylamine are formed. The same diphenylamine derivatives are also formed in the cartridge used to collect NO<sub>2</sub>, of which the N-nitrosodiphenylamine is the major product. In propellants subjected to higher temperatures even other nitro derivatives of diphenylamine are found. In addition to temperature, the reaction rate is also dependent on whether oxygen is admitted during storage. The acid formed at the decomposition of nitrate esters catalyse the formation of nitroso- and nitrodiphenylamines.

Diphenylamine is oxidized by oxygen in the air to a blue-violet compound called diphenyl-benzidine violet, evidenced by small coloured pigments. This oxidation of diphenylamine has not been taken into account in discussions concerning the reactions of diphenylamine in propellants or in the cartridge used to collect NO<sub>2</sub>.

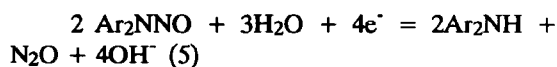
*Polarographic reduction of nitro and nitroso groups*

The saturated aliphatic nitro-compounds are commonly reduced in two stages to amine via hydroxyl amine with 4 and 2 electrones respectively as follows;



The reaction mechanism for the reduction of aromatic nitro- compounds such as nitro derivatives of diphenylamines is more complicated and dependent on the various factors such as the numbers of nitro groups and their position in the aromatic ring, and also the pH of the solution [7]. Under certain test conditions, the reduction of the individual nitro groups in the aromatic polynitro-compounds can be distinguished and it is also possible to prove

the step-by-step reduction to amine via hydroxylamine. N-nitroso-compounds are reduced to amines in acid media (pH 5) but in alkaline solutions the reduction takes place according to the following reaction mechanism:



In differential pulse polarography, a peak is obtained for each nitroso and nitro group. Even for 2,4,4,6-tetranitrodiphenylamine four well-defined and separated peaks are obtained.

Diphenylamine itself is not reduced at a dropping mercury electrode. On the other hand it can be oxidized at a glassy- carbon electrode which has been utilized for analyses [8].

**Results and Discussion**

Three different products have been investigated, namely;

- a) single-base propellant stabilized with 1.1% diphenylamine
- b) single-base propellant stabilized with 0.6% centralite I
- c) single-base propellant stabilized with 0.9% acardite II

The polarographic determination of total nitroso- and nitrodiphenylamine content is best performed with the direct current (DC) technique. The determination are performed in 65% methanol solution in which the solubility of the derivatives is sufficiently high. Linear calibration curves were obtained for both nitroso- and nitrodiphenylamines which showed the validity of the relationship between the peak heights (ip) and the concentrations.

Since N-nitrosodiphenylamine is the major derivative formed and accounted for more than 90% of total nitrogen dioxide generated, it was used as reference substance to evaluate the amount of nitrogen dioxide.

The diffusion current (id) is measured at a potential of -1.10 V at which the diffusion current has reached a constant value (Fig. 2). Fig. 3. shows a differential pulse polarogram for the same sample stored for 150 hrs at 110°C. The peak at a potential of about -1.0 V shows that N-nitrosodiphenylamine

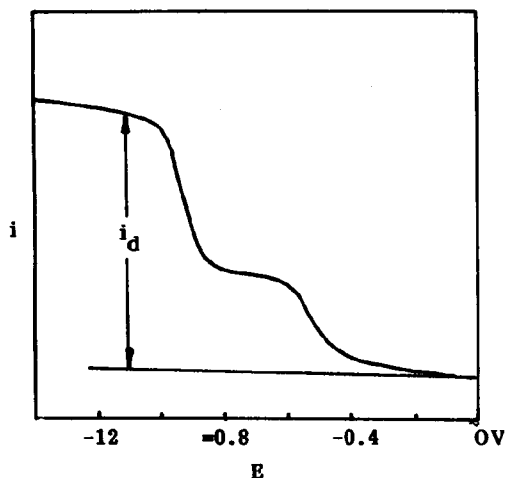


Fig. 2: DC-polarogram from the determination of nitroso- and nitrodiphenylamine derivatives.

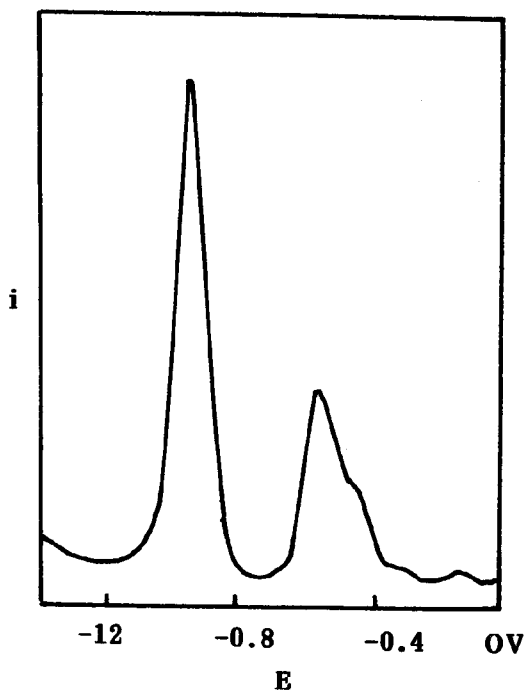


Fig. 3: Differential pulse polarogram from the determination of nitroso- and nitrodiphenylamine derivatives.

is the major derivative formed and the double peak within the potential range of -0.4 and -0.6 V indicates that small amounts of 2-nitrodiphenylamine and 4-nitrodiphenylamine are formed.

The results from the investigations of single-base propellants are summarized in fig. 4. The total loss in weight of each sample has also been determined. From these results it can easily be seen that a total loss in weight of i.e. 2% corresponds to a formation of about 2 mg nitrogen dioxide per 1 g single-base propellant. It can also be seen that a direct relationship applies between the total loss in weight and the formed nitrogen dioxide. The results also indicate that a single-base propellant stabilized with acardite II is more stable than a propellant stabilized with diphenylamine or centralite I. However, note that the propellants contain different amount of the stabilizers.

In conclusion, we have shown that the method has a wide potential and could be applied to field sampling and in determination of  $\text{NO}_2$  in ammunition plants and storage.

### Experimental

#### Apparatus

The polarographic determination were performed with a Metrohm Polarecord E 506 (obtained from Metrohm Ltd., Herisau, Switzerland). All potentials were measured and reported vs. Ag/AgCl electrode (Metrohm EA 427), the scan rate was 2.67 mV/s. The solution were aerated by passing nitrogen through the solutions for 10 minutes before recording the polarograms.

#### Reagents

All chemicals were reagent grade or of equivalent quality. Diphenylamine was purchased from Merck (Darmstadt, Germany). The polarographic determinations were performed in a 65% methanol solution containing 0.1 M ammonium acetate.

#### Cartridge

The cartridge were constructed of borosilicate glass tube with a diameter of 17 mm. The cartridges were equipped with conical ground joints (NS 14) and glass filters (Porosity 2) according to Fig. 1. The cartridges were packed with 2 g 30/60 mesh Florisil (magnesium silicate, Flucka AG) coated with diphenylamine. The coating was done

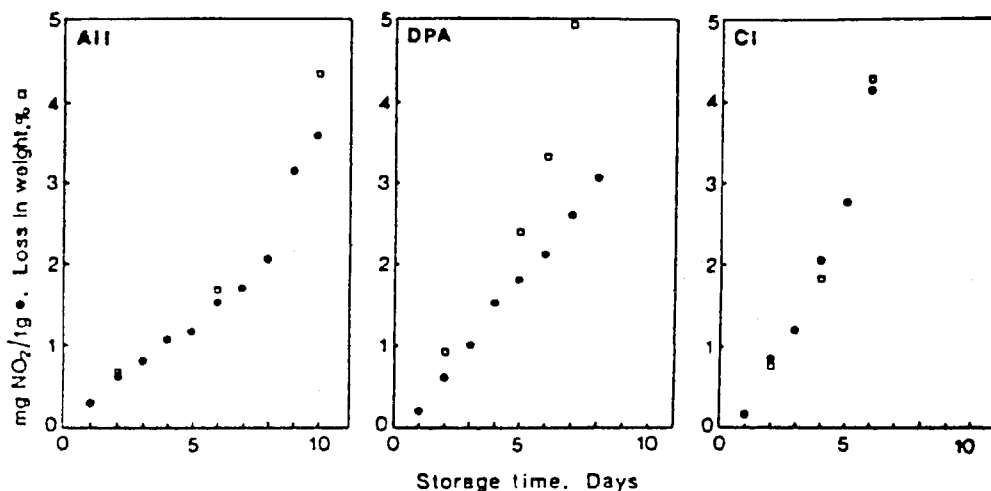


Fig. 4: Results from the determination of loss in weight and NO<sub>2</sub> generated.  
 A II : single base propellant stabilized with 0.9 % acardite II.  
 DPA : single base propellant stabilized with 1.1 % diphenylamine.  
 CI : single base propellant stabilized with 0.6 % centralite I.

by treating 10 g Florisil with 100 ml methylene chloride containing 300 mg diphenylamine. After about 1 hour the CH<sub>2</sub>Cl<sub>2</sub> solvent was slowly volatilized, the coated Florisil was then stored in dark and ready for use in the cartridge.

#### Collection of nitrogen dioxide

4g samples was stored at 110°C in accordance with the Dutch Stability Test [8]. In this test the sample is heated under stadardized conditions. The first 8 hours the test tube should be opened to allow moisture to evaporate. After 8 hours, the cartridge containing coated Florisil is inserted and storage is continued. After every 24 hours a test tube with cartridge is removed and the cartridge is analysed for formed nitroso- and nitro-diphenylamine derivatives.

#### Sample elution and preparation of solution

The cartridges were eluted with methanol and received solutions diluted to 100 ml. For the polarographic determination 20 ml of the clear solutions were diluted with 50 , 5, and 100 ml of

methanol, 1M ammonium acetate and distilled water respectively.

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