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INFRARED DETERMINATION OF NITROGEN IN RAW NITROCELLULOSE
AND NITROCELLULOSE CONTAINED IN PROPELLANTS ON
A MACRO AND SEMIMICRO SCALE

by

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January 1972

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I. SUMMARY

The infrared procedure for the determination of nitrogen in raw nitrocellulose has been improved. In the original method 0.31 to 0.32 gram of sample was dissolved in 45 ml of tetrahydrofuran, the solution was weighed, and the infrared peak at 6.0 microns was measured. The calibration curve was prepared by plotting absorbance against mg of nitrogen per gram of solution. The method has the disadvantage that the height of the peak is uniquely affected by the sample weight. In the method proposed in the present paper, the error due to the sample weight is eliminated by using a 0.3000-gram sample and diluting to 50 ml in a volumetric flask. The calibration curve is prepared by plotting absorbance against percent nitrogen in nitrocellulose. The infrared method for nitrogen in nitrocellulose was extended to the semimicro scale by using a 30.0-mg sample and diluting to 5 ml in a volumetric flask. The infrared procedure was also been applied on a macro and semimicro scale to the direct determination of nitrogen in nitrocellulose after a methylene chloride extraction. The amounts of graphite and inorganic salts found in nitrocellulose-base propellants do not interfere with the latter method; however, in weighing out the sample after the methylene chloride extraction, a calculation involving the graphite and inorganic salts must be made, so as to obtain a sample containing 0.3000 gram of nitrocellulose for the macro method or 30.0 mg of nitrocellulose for the semimicro method. The same calibration curve is used for all procedures.

II. RECOMMENDATIONS

It is recommended that procedures described in this report included in the military specification for propellants (MIL-STD-124B).

III. INTRODUCTION

Levitsky and Norwitz (4) proposed a control procedure for the determination of nitrogen in nitrocellulose by infrared. In this procedure 0.31 to 0.32 gram of sample was dissolved in 35 ml of tetrahydrofuran in a glass-stoppered Erlenmeyer flask by allowing to stand overnight, the solution was weighed, and the peak at 6.0 microns was measured. The calibration curve was prepared by carrying samples of nitrocellulose of known nitrogen content through the procedure and plotting absorbance vs mg of nitrogen per gram of solution. The calculation of percent nitrogen in an unknown sample of nitrocellulose was made by the following equation:

$$\% \text{ N in NC} = \frac{\text{mg of N per gram of solution} \times \text{grams of solution}}{\text{grams of NC} \times 10}$$

A round robin group under the chairmanship of Dr. Eugene Burns of Space Technology laboratories evaluated the procedure and found that it was satisfactory (1). Dr. Burns showed that the accuracy could be improved somewhat by preparing a calibration curve each day. In any case, however, the procedure is not as accurate as the nitrometer method and is designed for rapid control work.

In the procedure of Levitsky and Norwitz (4) there is an error caused by the fact that the calibration curve (mg of nitrogen per gram of solution vs absorbance) varies with the sample weight (it is for this reason that 0.31 to 0.32 gram of sample was specified). Clarkson and Robertson (2) stated that this error could be eliminated by correcting all sample weights to a fixed concentration (0.008 gram of nitrocellulose per gram of solution). Some difficulties have been encountered at times with the method of approach suggested by Clarkson and Robertson; therefore, an investigation was undertaken to develop a more direct method for eliminating the error caused by the sample weight. Another aspect of the present investigation was to extend the range of the infrared method for the determination of nitrogen in nitrocellulose to the semimicro scale. Still another aspect was the application of the infrared technique to the direct determination of nitrogen in nitrocellulose contained in propellants, both on the macro and semimicro scale.

IV. STUDY

A. DEVELOPMENT OF IMPROVED PROCEDURES

1. Macro Determination of Nitrogen In Raw Nitrocellulose

The sample weight error in the original method was eliminated by dissolving 0.3000 gram of sample in the tetrahydrofuran and diluting to 50 ml in a volumetric flask. The weighing of this exact weight of nitrocellulose can be conveniently performed by weighing the sample into a tared 30-ml beaker (rather than an Erlenmeyer flask as used in the earlier method (4)). The weighing of an exact amount of nitrocellulose is readily performed since the material is very fluffy.

The accuracy of the original method (4) was further improved by carrying a blank for the tetrahydrofuran through the entire procedure. This compensates for the small amount of water in the tetrahydrofuran which shows some absorption at 6.0 microns. The amount of water in commercial tetrahydrofuran is about 0.02% (3).

As before (4), it is recommended that transmittance paper rather than absorbance paper be used for recording the peak. The reason for this recommendation is that in the region of 20% transmittance, transmittance paper can be read more accurately than absorbance paper.

As previously stated, the calibration curve in the original method was prepared by plotting absorbance vs mg of nitrogen per gram of solution (4). Analogously, the calibration curve could be prepared in the present method by plotting absorbance vs mg of nitrogen per ml of solution. However, since a constant weight of sample is used, the calibration curve can be prepared by merely plotting absorbance vs percent nitrogen in nitrocellulose.

For the sake of information, an investigation was made to ascertain the extent to which the sample weight affected the calibration curve obtained by plotting absorbance vs mg of nitrogen per ml of solution. For this investigation, curves were plotted using 0.3000 and 0.2900 gram of sample per 50 ml (Figure 1). It is seen that the weight of sample had a significant effect. The cause of this phenomenon is uncertain.

2. Semimicro Determination of Nitrogen in Raw Nitrocellulose

It was found that the nitrogen content of nitrocellulose can be determined accurately in the semimicro range by infrared by dissolving 30.0 mg of sample in 3 ml of tetrahydrofuran and diluting to 5 ml in a volumetric flask.

3. Macro Determination of Nitrogen in Nitrocellulose Contained in Propellants

The methods that have been previously proposed for the determination of nitrogen in nitrocellulose contained in propellants are troublesome. If the propellant does not contain a significant amount of inorganic material, the determination can be performed by subjecting the propellant to extraction with either methylene chloride, ethyl ether, or 70% acetic acid, drying the residue (nitrocellulose), and determining the nitrogen in a weighed portion by titration (7, 8) or by use of the nitrometer (6). If the propellant contains a significant amount of inorganic materials (graphite, calcium carbonate, barium carbonate, sodium nitrate, potassium nitrate, sodium sulfate, or potassium sulfate), as is usually the case, the method is subject to an error caused by the fact that these inorganic materials are not extracted by the methylene chloride and are included in the weighed sample of nitrocellulose. For a sample containing 13.00% nitrogen and 1.00% of total inorganic material, the error would be -0.13% total nitrogen. This error can be reduced by dissolution of this nitrocellulose in acetone and precipitation with water.

In view of the uncertainties of the above method, an investigation was undertaken to determine the applicability of the infrared method to the direct determination of nitrogen in nitrocellulose.

The first aspect of the investigation was to establish whether the results obtained for nitrogen were additive when samples of nitrocellulose of different nitrogen content were mixed together. This is important because nitrocelluloses of different nitrogen content are often blended together to obtain a composite nitrocellulose of required nitrogen content.

To investigate the above problem, 0.1500 gram of a sample that contained 12.61% nitrogen was mixed with 0.1500 gram of a sample that contained 13.47% nitrogen. The results obtained for nitrogen were 13.01, 13.09, and 13.09% with an average result of 13.06%. The latter result is very close to the theoretical result (13.04%), so it can be concluded that the nitrogen content is additive.

The second aspect of the investigation was the question of interference from graphite, calcium carbonate, barium carbonate, sodium nitrate, potassium nitrate, sodium sulfate, and potassium sulfate. Experiments were carried out whereby 0.0033 gram of each of these substances (equivalent to 1.00% on a 0.3000-gram sample) was suspended in 50 ml of tetrahydrofuran and the absorbance measured at 6.05 microns. In no case was the absorbance different from the absorbance obtained with tetrahydrofuran.

Aside from the question of the interference by increased absorbance, the problem arose as to how to correct for the weight of the inorganic substances, so as to obtain a sample that would contain 0.3000 gram of nitrocellulose. This problem was solved by taking a weight (grams) of residue from the methylene chloride extraction equal to $0.3000 \frac{100-A}{100}$, where A is equal to the total percentage of graphite plus

100
inorganic salts.

4. Semimicro Determination of Nitrogen in Nitrocellulose Contained in Propellants

The semimicro method for the determination of nitrogen in nitrocellulose contained in propellants is the same as the macro method, except that a sample containing 30.0 mg of nitrocellulose is dissolved in 3 ml of tetrahydrofuran and the solution is diluted to 5 ml in a volumetric flask.

It was found that the same calibration curve could be used for all the four methods described in this report.

B. RECOMMENDED METHODS

1. Apparatus

Infrared spectrophotometer. This laboratory used a Perkin-Elmer Model 621 Infrared Spectrophotometer.

0.2-mm sodium chloride cell.

1-ml syringe, Luer Slip, B-D Yale (Arthur H. Thomas Co. No. 9404).

2. Reagents

Tetrahydrofuran, ACS, Fisher Scientific Co. Store in a constant temperature room. Keep covered at all times and dispense the solution from a covered container.

3. Preparation of Calibration Curve

Air-dry 3 or 4 standard samples of nitrocellulose [whose nitrogen content has been accurately determined by the nitrometer method (6)], then dry in a vacuum oven (at 2 to 5 cm of mercury) at 65°C for 4 hours and cool in a desiccator. Weigh 0.3000 gram of the samples into tared 30-ml beakers. Add 35 ml of tetrahydrofuran and immediately cover tightly with aluminum foil which is held in place by rubber bands. Carry along a blank determination. Allow to stand overnight in the room (constant temperature) containing the infrared instrument.

After the overnight standing period, stir with a small stirring rod, wash down and remove the stirring rod, transfer to a 50-ml volumetric flask with tetrahydrofuran, dilute to the mark with tetrahydrofuran, stopper, and shake. Work with only one sample at a time from point of stirring to the dilution in the volumetric flask. Rinse

and fill a 0.2-mm cell with the solution, using a 1-ml syringe. Obtain the spectrum from 5.80 to 6.05 microns (1724 to 1653 cm^{-1}) at a speed of 25 cm^{-1} per minute. Gain, response, and resolution settings should be normal. Suppression setting should be zero.

Observe I_A and I (see Figure 2) and calculate the absorbance as follows: $\text{absorbance} = \log (I_A/I)$. Deduct the blank.

Plot absorbance against percent nitrogen in the nitrocellulose.

The calibration curve should be rechecked occasionally and should be redrawn if a new lot of tetrahydrofuran is used.

4. Procedures

e. Determination of Nitrogen in Raw Nitrocellulose

Macro Method. Dissolve a 0.3000-gram sample in tetrahydrofuran and measure the intensity of the peak at 6.0 microns as described in the preparation of the calibration curve. Calculate the percent nitrogen by referring to the calibration curve.

Semimicro Method. Proceed as for the macro method but weigh a 30.0-mg sample in a tared 5-ml beaker (preferably on a semimicro balance), dissolve in 3 ml of tetrahydrofuran, and dilute to 5 ml in a volumetric flask. Calculate the percent nitrogen by referring to the calibration curve.

b. Determination of Nitrogen in Nitrocellulose Contained in Propellants

Macro Method. Extract 0.5 to 5 grams of sample of the propellant with methylene chloride in the usual manner using a Soxhlet extractor (5). Transfer the residue from the thimble to a weighing dish and dry by heating in a vacuum oven (2 to 5 cm of mercury) for 2 hours.

Calculate the weight of the residue that will contain 0.3000 gram of nitrocellulose as follows:

$$\text{Weight of residue (gram) that will contain 0.3000 gram of NC} = \frac{30}{100 - A}$$

where, A = total percent of graphite plus inorganic salts (carbonates, nitrates, and sulfates) in the propellant.

Weigh the above calculated amount of the residue into a 30-ml beaker, dissolve in tetrahydrofuran, and proceed as described in the macro method in procedure a.

Semimicro Method. Extract approximately 0.1 gram of sample with methylene chloride in the usual manner using a Soxhlet extractor (5).

Calculate the weight of residue that will contain 30.0 mg of nitrocellulose as follows:

$$\text{Weight of residue (mg) that will contain 30.0 mg NC} = \frac{3000}{100 - A}$$

where, A = total percent graphite plus inorganic salts (carbonates, nitrates, and sulfates) in the propellant.

Weigh the above calculated amount of residue in a 5-ml beaker, add 3 ml of tetrahydrofuran, and proceed as described in the semimicro method in procedure a.

C. RESULTS

The results obtained for nitrogen in raw nitrocellulose by the macro and semimicro infrared methods on four samples whose nitrogen content had been established by the nitrometer method are shown in Table I. The macro and semimicro infrared results check the nitrometer results and each other quite well. The average standard deviation of the macro infrared method was 0.037% while the average standard deviation of the semimicro infrared method was 0.046%. The average standard deviation of the original method was 0.093% (4).

The results obtained for nitrogen in nitrocellulose contained in propellants by the macro and semimicro infrared methods are shown in Table II. There is no accurate method that can be used as a basis of comparison. The macro and semimicro infrared methods check each other well. The average standard deviation of the macro infrared method was 0.028% while the average standard deviation of the semimicro infrared method was 0.022%. The results for both the macro and semimicro infrared methods are within the specification requirements for nitrogen in nitrocellulose contained in propellants.

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VI. TABLES

Table I. Results for Nitrogen in Raw Nitrocellulose
by Infrared Using Macro and Semimicro Methods

<u>Sample</u>	<u>Nitrogen by Nitrometer (%)</u>	<u>Nitrogen by Infrared (%)</u>		
		<u>Macro Method</u>	<u>Semimicro Method</u>	
1	12.58	12.63		
		12.61		
		12.57		
		12.59		
		12.55		
		12.63		
		12.63		
		Avg.	12.60	
		Std. Dev.	0.032	
2	13.47	13.40	13.43	
		13.51	13.50	
		13.49	13.54	
		13.43	13.52	
		13.41		
		13.48		
		13.52		
		Avg.	13.46	13.50
		Std. Dev.	0.049	0.048
3	12.61	12.55	12.57	
		12.50	12.57	
		12.68	12.64	
		12.66	12.62	
		12.65		
		12.65		
		12.56		
		Avg.	12.62	12.60
		Std. Dev.	0.056	0.036
4	13.16	13.15	13.10	
		13.17	13.16	
		13.18	13.23	
		13.15	13.17	
		13.15		
		13.16		
		Avg.	13.16	13.17
		Std. Dev.	0.012	0.054

Table II. Results for Nitrogen in Nitrocellulose
 Contained in Propellants by Infrared
 Using Macro and Semimicro Methods

<u>Sample</u>	<u>Specification Requirement (%)</u>	<u>Nitrogen by Infrared (%)</u>		
		<u>Macro Method</u>	<u>Semimicro Method</u>	
IMR-4895 ^a	13.10 - 13.20	13.15	13.15	
		13.13	13.14	
		13.11	13.13	
		13.18	13.09	
		Avg.	13.14	13.13
		Std. Dev.	0.030	0.026
IMR-4903 ^b	13.10 - 13.20	13.07		
		13.03		
		13.07		
		13.03		
		Avg.	13.05	
		Std. Dev.	0.023	
HPC-1 ^c	13.15 - 13.25	13.25	13.21	
		13.22	13.18	
		13.20	13.14	
		13.24	13.22	
		Avg.	13.23	13.19
		Std. Dev.	0.022	0.031
HPC-14 ^d	13.15 - 13.25	13.09	13.20	
		13.15	13.19	
		13.15	13.20	
		13.17	13.18	
		Avg.	13.14	13.19
		Std. Dev.	0.035	0.010

^a Contains (%): 0.26 graphite, 0.48 potassium sulfate.

^b Contains (%): 0.40 graphite, 0.59 potassium sulfate.

^c Contains (%): 0.29 graphite, 0.70 potassium sulfate.

^d Contains (%): 0.28 graphite, 0.72 potassium sulfate.

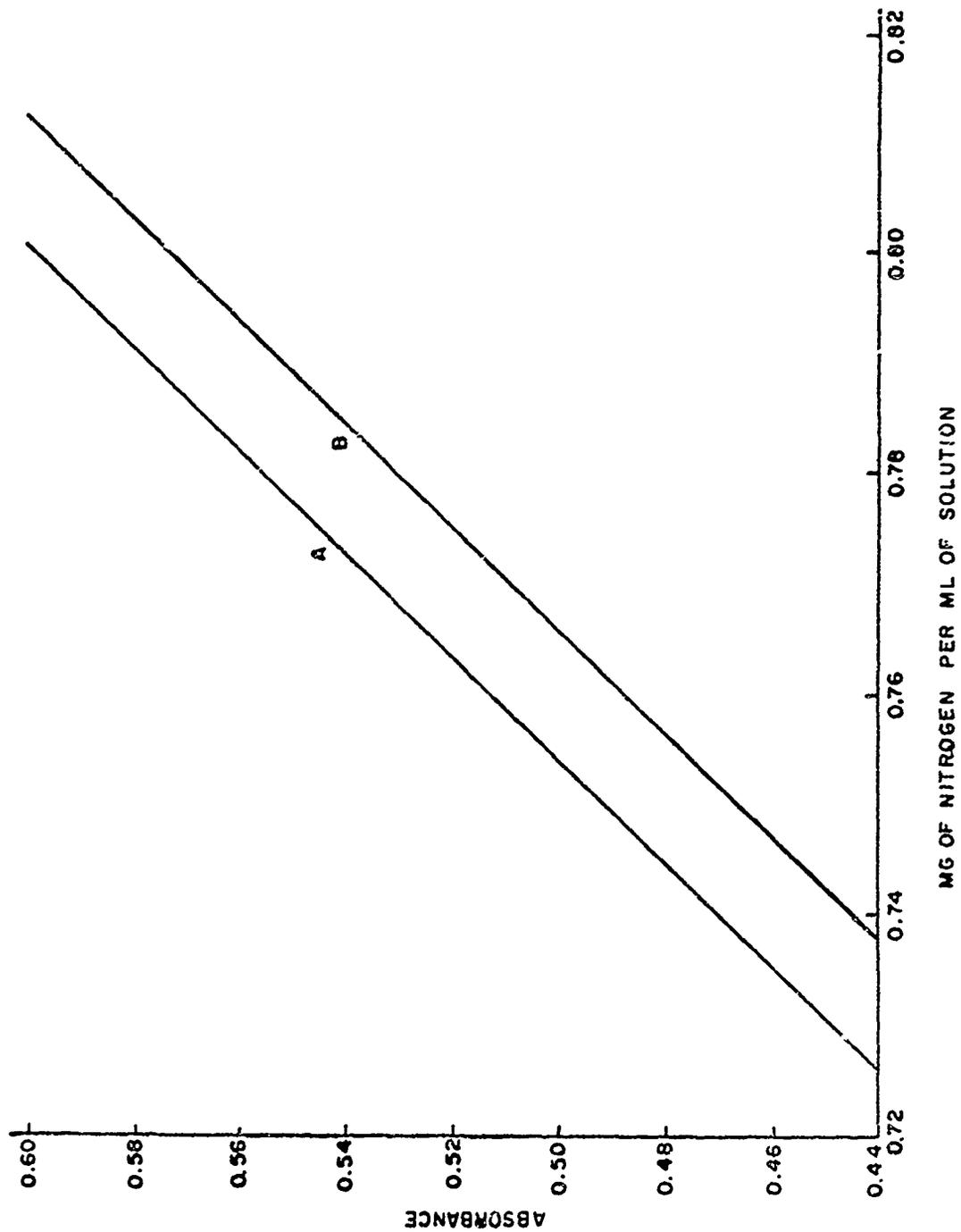


Figure 1. Effect of amount of nitrocellulose on curve obtained by plotting absorbance vs mg of nitrogen per ml of solution

- A. 0.2900 g nitrocellulose
- B. 0.3000 g nitrocellulose

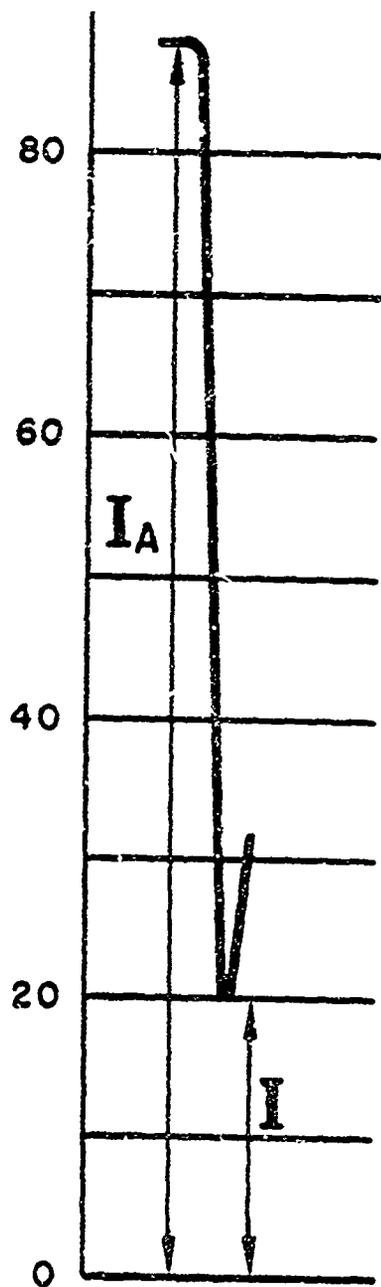


Figure 2. Spectrum of nitrocellulose in tetrahydrofuran from 5.80 to 6.05 microns