INFRARED METHOD FOR THE DETERMINATION OF NITROGLYCERIN IN DOUBLE BASE PROPELLANT

ALLEN J. SCISM
Department of Chemistry
Southern Illinois University, Carbondale

ABSTRACT. — An infrared method is presented for the determination of nitroglycerin in double base propellant. The method utilizes the 12 micron absorption band of nitroglycerin in order to avoid interference from other propellant ingredients which absorb appreciably at 6.02 and 7.85 microns, the normally used wavelengths for obtaining quantitative data for nitroglycerin. Results by this method are compared to those obtained by the titanous chloride method.

Double base solid propellant consists of the two "base" ingredients nitrocellulose and nitroglycerin in addition to various stabilizers, plasticizers, and ballistic modifiers, depending upon the formulation.

The analysis of this type of propellant usually involves the extraction of the propellant sample by an organic solvent such as methylene chloride ($MeCl_2$). This serves primarily to separate nitroglycerin and other organic components from the nitrocellulose which is not extracted. The quantity of material extracted from the propellant by the $MeCl_2$ extraction serves as a routine check on the propellant and is determined by evaporating the extracted $MeCl_2$ solution to a constant-weight residue. This constant-weight extract can be further analyzed for the individual components contained in it.

The nitroglycerin in the constant-weight extract is often determined by the titanous chloride method (Becker, 1933 and Hirschhorn, 1947). This involves reacting the nitroglycerin with ferrous iron, and titration of the ferric iron produced with a standard titanous chloride ($TiCl_3$) solution. This titrimetric method can be quite time consuming, requires close control of temperature, and must be carried out in an inert atmosphere. The $TiCl_3$ titrant solution must be kept in the dark and under an inert atmosphere. It must be restandardized at each usage or at least every other day.

The infrared study reported here was undertaken in order to develop a more simple and less time consuming method of estimating the nitroglycerin content of double base propellant. It was desirable to work with the constant-weight extract rather than attempting to further separate the nitroglycerin inasmuch as this would be even more time consuming. The use of this extract, however, required that consideration be given to the infrared absorption of the other components present in the extract. Infrared spectra were obtained and studied

for each component of the extract. The infrared spectra of several solvents were also considered in the selection of a suitable solvent system for this method.

Nitroglycerin has three major absorption bands; namely, 6.02, 7.85, and 12.0 microns. Infrared procedures have been developed which employ both the 6.02 and the 7.85 micron absorption bands of nitroglycerin (Castelli, 1954; Schwartzman, 1956; Carol, 1958; and Tippett, 1963). These absorption bands are well suited for quantitative measurement since they are sharp and intense. Neither of these wavelengths could be employed for the system being investigated since there were components of the propellant present in the $MeCl_2$ extract which showed appreciable absorption at both 6.02 and 7.85 microns.

Although the 12 micron absorption band of nitroglycerin is of medium intensity and somewhat broad, it was felt that this band could possibly be used for quantitative measurement. The constant-weight extract could have been redissolved in $MeCl_2$, but this solvent shows very intense absorption in the 12 micron region. Benzene was chosen as the solvent because it shows negligible infrared absorption in the 12 micron region and readily dissolved all the components of the constant-weight extract.

Materials and Methods

Preparation of Standards. For reasons of safety, nitroglycerin is often handled as a 50 per cent solution in ethyl acetate. The nitroglycerin used in this study was available in this form and was treated initially by directing a stream of nitrogen into an open beaker containing the nitroglycerin solution. This removed the major part of the ethyl acetate. Removal of the last of the ethyl acetate was accomplished by placing the nitroglycerin in a vacuum desiccator for several days until constant weight was obtained. As a check on the purity, the refractive index of the nitroglycerin was determined at 15 degrees C. Duplicate determinations were 1.4740 and 1.4739. These values compare well to 1.474 at 15 degrees listed in Merck Index. The material was also assayed by the $TiCl_3$ method. The resulting average of several determinations was 99.0 per cent. The pure nitroglycerin was stored in a plastic beaker in a desiccator and amounts transferred as needed with the aid of a plastic dropper.

Four standard solutions were prepared by dissolving 0.3193, 0.4334, 0.5105, and 0.6142 grams of nitroglycerin in 50 ml of spectrograde benzene. Infrared measurements were taken at each of the three major absorption bands of nitroglycerin and the resulting data appear in Table 1. Plots of concentration versus absorbance showed adherence to Beer's law at each wavelength. Figure 1 shows the agreement of the 12 micron data to a straight line calculated and plotted by the least squares method.

Preparation of Samples. The double base propellant samples studied in this work contained nitroglycerin in the 20 to 30 per cent range. Four-gram samples were weighed out from the turnings produced when wafers of the solid propellant were drilled using a brace and bit. The weighed samples were placed in filter paper packets and the packets were placed in extraction thimbles in Soxhlet extractors. The samples were extracted with $MeCl_2$ and the resulting $MeCl_2$ solutions were evaporated to residues of constant weight. The last stages of the evaporation to constant weight were carried out by placing the samples in a vacuum system.

The constant-weight residues were dissolved in benzene and brought to volume in 100-ml volumetric flasks at 20 degrees C. These solutions were used to obtain to infrared data reported in this work. Portions of these solutions were withdrawn using hypodermic syringes and needles and were transferred to fixed thickness infrared cells with NaCl windows. The two cells used had thicknessses of 0.105 and 0.109 mm. The same cells were used for all determinations reported in this work, the 0.105 mm cell being used to contain the sample solution and the 0.109 mm cell being used to

TABLE 1.—Data for Standard Nitroglycerin Solutions.

Sample	Concentration	Absorbance		
	(g/100 ml)	6.02μ	7.85μ	12.0μ
1	.6386	.627	.369	.225
2	.8668	.820	.493	.291
3	1.0210	.885	.560	.337
4	1.2284	1.000	.670	.399

contain the reference benzene solution. The instrument used for this work was a Perkin Elmer Model 21 infrared spectrophotometer.

Data Collection and Treatment. The method of obtaining infrared measurements involved recording only the peak being studied rather than the entire spectrum. To record the peak, a point of low absorbance (a valley) was chosen adjacent to the peak. The 100% adjust control on the instrument was set such that the pen was aligned at zero absorbance at the chosen starting wavelength. The peak was then recorded. This procedure was repeated several times for each peak in order to obtain a good average value of the absorbance for the solution at that wavelength. This method allows one to obtain several absorbance values in the time normally required to record an entire spectrum. The spectrum may be rapidly scanned to the area of interest and then a number of absorbance values may be recorded for the peak in question for any number of solutions.

The plot shown in Figure 1 served as a standard working curve for the 12 micron peak of nitroglycerin. The concentrations shown in Figure 1 are in terms of grams per 100 ml of solution although the actual standard solutions were prepared in 50 ml of benzene as described previously. This was done so that the absorbances and concentrations of the standards would correlate directly with those of the samples.

The absorbance of each sample at 12 microns was determined and the corresponding concentration of nitroglycerin in grams per 100 ml was read directly from the standard curve. The percentage of nitroglycerin in the sample was then calculated by this simple relationship.

$$\text{Per Cent Nitroglycerin} = \frac{\text{Concentration (g/100 ml)} \times 100}{\text{Sample Weight}}$$

RESULTS AND DISCUSSION

The data from the standard nitroglycerin solutions showed adherence to Beer's law at the 12 micron absorption band. This indicated that the 12 micron band should be suitable for the quantitative estimation of nitroglycerin in the concentration

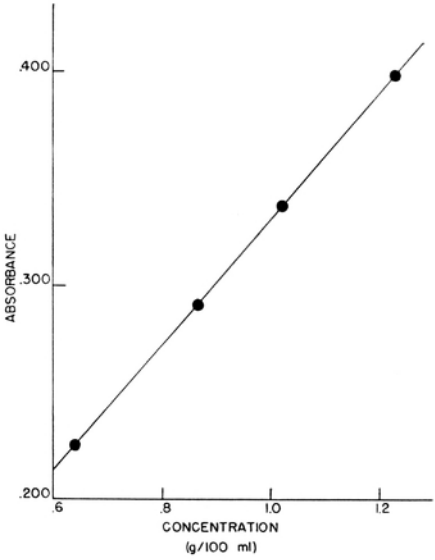

FIGURE 1. — Least Squares Evaluation of Data From Standard Nitroglycerin Solutions Using the 12 Micron Absorption Band.

TABLE 2.—Nitroglycerin Content of Double Base Propellant: Comparison of Infrared and $TiCl_3$ Methods.

Sample	A	Per Cent Nitroglycerin	
		IR Method	$TiCl_3$ Method
1	.306	22.9	23.1
2	.300	22.3	22.5
3	.301	22.4	22.8
4	.345	26.2	26.3
5	.322	24.2	24.1
6	.301	22.4	22.4
7	.358	27.2	26.5
8	.334	25.2	25.0
9	.338	25.6	25.0
10	.347	26.4	25.8
11	.310	23.2	22.3
12	.335	25.3	24.4
13	.325	24.5	24.5
14	.330	24.9	23.6
15	.314	23.5	22.4
16	.359	27.1	25.8
17	.338	25.6	24.8
18	.325	24.5	23.8
19	.310	23.2	23.2
20	.337	25.4	24.3
21	.317	23.8	22.6
22	.301	22.4	22.7
23	.330	24.9	23.8
24	.315	23.6	23.3
25	.324	24.4	24.6

range covered by the standard solutions.

The data obtained from 25 propellant samples appears in Table 2. The values for the per cent nitroglycerin found by the infrared method are compared to those found by the $TiCl_3$ method. Relatively good agreement exists between the two methods.

This work indicates that the 12 micron absorption band of nitroglycerin can be used for the quantitative estimation of nitroglycerin in solutions where the normally used absorption bands (6.02 and 7.85 microns) are masked by other infrared absorbing substances.

ACKNOWLEDGMENT

The author wishes to thank the Olin Mathieson Chemical Corporation for permission to publish this work.

LITERATURE CITED

BECKER, W. W. 1933. Volumetric determination of nitroglycerol and of nitroglycerol and dinitrotoluene in admixture. Ind. Eng. Chem., Alan. Ed 5: 152-154.

CAROL, J. 1958. Report on analysis of drugs by infrared spectrophotometry: Atropine sulfate tablets and nitroglycerin tablets. J. Assoc. Offic. Agr. Chemists 41:504-505.

CASTELLI, A., M. HALIK, W. FREDERICKS, and F. PRISTERA. 1954. Simple, rapid infrared method for the determination of nitroglycerin, triacetin, and 2-nitrodiphenylamine in casting solvent. U.S. Dept. Com., Office Tech. Serv. P B Rept. 157,666, 21 pp.

HIRSCHHORN, I. S. 1947. Rapid determination of nitroglycerin and ethyl centralite in rocket propellant powder. Anal. Chem. 19: 880-882.

SCHWARTZMAN, G. 1956. Analysis of nitroglycerin tablets by infrared spectrophotometry. J. Assoc. Offic. Agr. Chemists 39: 254-255.

TIPPETT, C. F. 1963. The application of infrared spectroscopy to the examination of nitroglycerin explosives. Med. Sci. Law 3: 282-288.

Manuscript received July 27, 1968.