Separation and Infrared Analysis of Products from the Nitration of *alpha*-Olefins

HARRY MORGAN, R. M. SHERWOOD, and T. A. WASHALL
The Atlantic Refining Co., Research Center, Glenolden, Pa.

▶ Analytical methods have been developed for the separation and analysis of products obtained from the nitration of *alpha*-olefins with $2NO_2 \rightleftarrows N_2O_4$. Pure C_8 and C_{16} nitro compounds were isolated from nitration products by liquid phase chromatography and solvent crystallization for use as calibrations. Infrared techniques using base-point and inverted matrix methods were devised for the direct analysis of complex mixtures of nitro alcohol, nitro olefin, dinitro paraffin, and nitro nitrates. In addition, an independent, near infrared technique was devised for the determination of nitro alcohol and nitro olefin in complex mixtures. In general, good agreement was obtained between actual and determined values for synthetic mixtures of both C_8 and C_{16} nitro compounds over a relatively wide concentration range.

ALTHOUGH THE LITERATURE on the nitration of olefins is extensive, there are very few references pertaining to the quantitative analysis of complex mixtures of aliphatic nitro compounds. In almost all cases where products from the nitration of olefins were described, yields and compositions reported were based on the results obtained from a separation of the components in the reaction mixture. In many cases, losses were encountered during the separation procedures, intermediate fractions were obtained, and decomposition occurred. Only an approximate or semiquantitative analysis of a complex reaction mixture can be obtained by these procedures.

One of the most extensive spectrometric studies of nitro compounds reported in the literature is the infrared study of Brown (*3*). Although the absorption bands of a large number of pure nitro compounds were reported, the application of infrared techniques to the analysis of complex mixtures was not discussed. Additional infrared data for pure nitro compounds were reported in the work on the synthesis of nitro olefins from olefin–dinitrogen tetroxide adducts by Seifert (*5*). In this work, the concentrations of nitro nitrite and nitro nitrate were determined directly by the internal ratio method (*4*) using the absorption bands at 5.95 and 6.10 microns, respectively. Nitro alcohol was determined from the free OH absorption at 2.78 microns. The concentration of dinitro paraffin was not determined directly by infrared spectrometry either in the crude nitration product or after the conversion of the dinitroparaffin in the product to nitro olefin by treatment with triethylamine.

The object of the work described in this paper was to develop quantitative infrared techniques for analyzing products from the nitration of *alpha*-olefins with $2NO_2 \rightleftarrows N_2O_4$ according to the procedures of Bonetti *et al.* (*2*). Three general techniques were devised: a near infrared method for the determination of nitro alcohol and nitro olefin, an infrared method for the analysis of mixtures of C_8 and C_{16} nitro olefin, dinitro paraffin, nitro nitrate and nitro alcohol using base-point techniques, and an infrared method for the analysis of the same compounds using an inverted matrix technique. Although nitro nitrite was determined in products from the early studies of nitration products, all subsequent techniques were developed for the analysis of hydrolyzed products in which the nitro nitrite was converted to nitro alcohol. Since the compounds needed for calibration were not available commercially, extensive separations were carried out to obtain pure compounds from reaction mixtures.

EXPERIMENTAL

Calibration Compounds. The isolation of pure C_8 nitro compounds from reaction mixtures was effected exclusively by liquid phase chromatography on Davison's Grade 12, 28–200 mesh silica gel. 1-Nitrooctene-1 and 1,2-dinitrooctane were separated from each other and from 1-nitrooctanol-2 by gradient elution with mixtures of benzene and cyclohexane. 1-Nitro-2-methoxyoctane was isolated from a mixture of the nitro ether and nitro alcohol by absorbing the mixture from a benzene solution rather than cyclohexane and subsequently eluting with benzene. In all cases, the nitro alcohol was recovered from the silica gel by desorption with diethyl ether. The elemental analyses and some physical properties of the three C_8 nitro compounds isolated from reaction mixtures are shown in Table I.

Isolation of pure C_{16} nitro compounds from reaction mixtures was effected by solvent crystallization and liquid phase chromatography on silica gel. Pure 1-nitrohexadecanol-2 was separated from either C_{16} nitro olefin or dinitroparaffin by solvent crystallization from isooctane. The filtrate was fractionated by liquid phase chromatography to recover pure nitrohexadecene-1 or 1,2-dinitrohexadecane. 1-Nitrohexadecanone-2 and bis-(1-nitro-2-nitrosohexadecane were separated from each other and from nitro alcohol by crystallization from acetone. The bis-(1-nitro-2-nitrosohexadecane was purified further by recrystallization from chloroform while final purification of the nitro

Table I. Elemental Analyses and Physical Properties of Pure C_8 Nitro Compounds Isolated from Reaction Mixtures

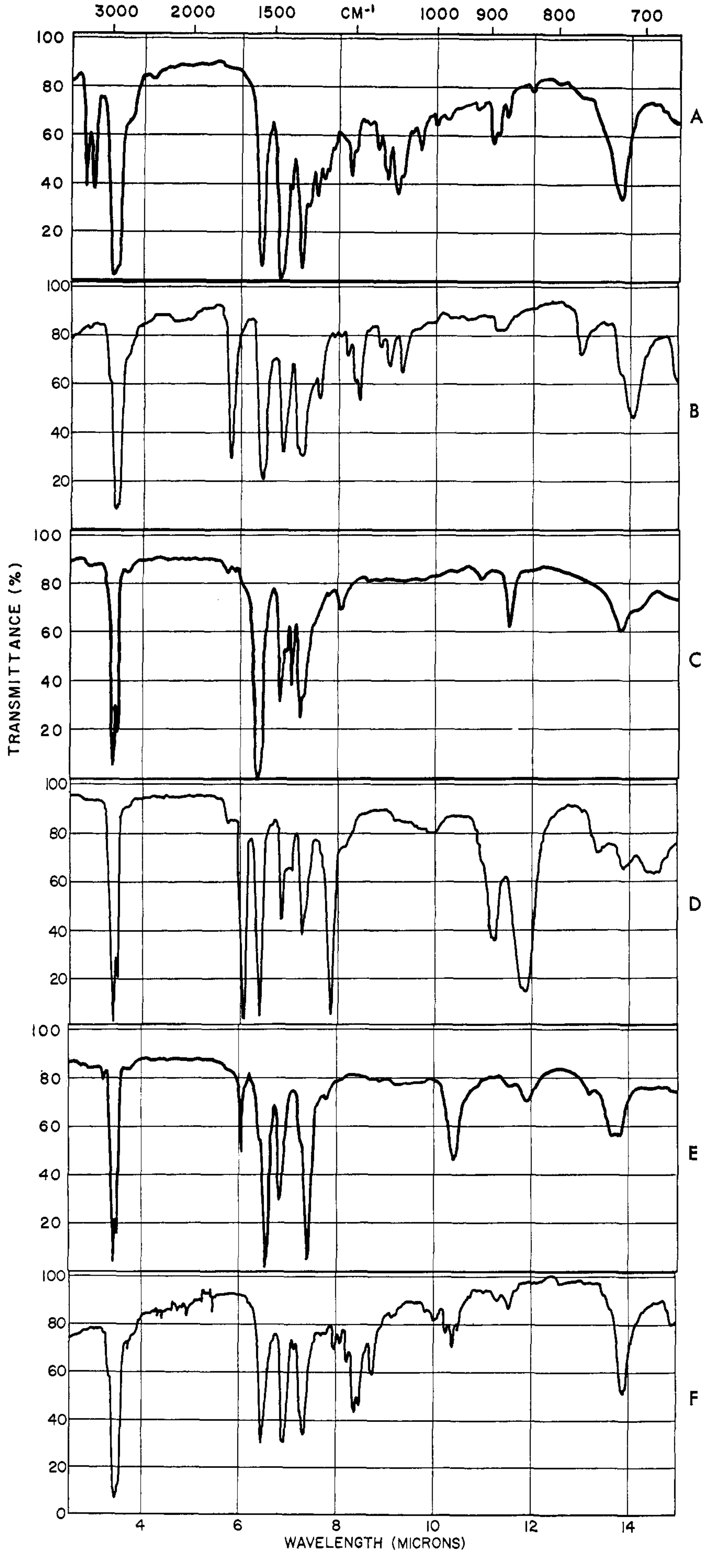
1. Elemental analyses

Compound	Calculated, % C	H	O	N	Determined, % C	H	O	N
1-Nitrooctanol-2	54.9	9.7	27.4	8.0	54.8	9.7	27.2	8.3
1-Nitrooctene-1	61.1	9.6	20.4	8.9	61.0	9.6	20.4	9.0
1,2-Dinitrooctane	47.0	7.9	31.4	13.7	47.2	8.0	31.1	13.7

2. Physical properties

Compound	B.P. (°C. @ 0.5 mm.)	Freezing pt. (°C.)	R.I. @ 20° C.	Density @ 20° C.
1-Nitrooctanol-2	92	−45.[a]	1.45099	1.0180
1-Nitrooctene-1	63	−96.[b]	1.46091	0.9494
1,2-Dinitrooctane	121	−15.[c]	1.45487	1.0962

[a] −44 to −46 (viscous pour or glass).
[b] −93 to −99 (viscous pour or glass).
[c] −14 to −16 (crystals).



◄ Figure 1. Infrared spectra

A. 1-Nitrohexadecanol-2 (in Nujol)
B. 1-Nitrohexadecanone-2 (in Nujol)
C. 1,2-Dinitrohexadecane
D. 1-Nitro-2-hexadecyl nitrate
E. 1-Nitrohexadecene-1
F. Bis-(1-nitro-2-nitrosohexadecane) (in Nujol)

ketone was effected by recrystallization from carbon disulfide and methanol, respectively. The elemental analyses and some of the physical properties of the separated pure C_{16} nitro compounds are tabulated in Table II, while the infrared spectra are shown in Figure 1. For those compounds that were liquid at ambient temperature, the spectra were recorded using liquid films on NaCl plates. For the compounds solid at ambient temperature, Nujol mulls were prepared and the spectra of the mulls were recorded from films on NaCl plates. Using both the pure C_8 and C_{16} nitro compounds isolated from reaction mixtures as calibrations, infrared and near infrared techniques were devised for the analysis of complex mixtures of C_8 and C_{16} nitro compounds.

Near Infrared Method. Calibration curves were constructed using a Beckman, Model DK-1, recording spectrophotometer and 10-cm. quartz cells. A typical near infrared spectrum for a mixture of nitro alcohol and nitro olefin is shown in Figure 2. For the nitro alcohol, the spectrum was scanned from 1.50 microns to 1.35 microns using carbon tetrachloride solutions containing 2–10 mg./ml. of sample *vs.* carbon tetrachloride in the reference cell. The ΔA for each concentration was measured as the difference between the peak of the band at about 1.42 microns and a slight shoulder at 1.39 microns. In the case of the nitro olefin, the spectrum was scanned from 1.75 microns to 1.55 microns using carbon tetrachloride solutions containing 3–25 mg./ml. of sample *vs.* carbon tetrachloride. A base line was constructed across the bank peak at 1.64 microns and the ΔA measured from the base to the peak of the band. In both cases, the solutions were stable and the calibration curves were linear in the concentration ranges investigated.

Base-Point Infrared Method. Calibration curves were constructed for the C_8 nitro compounds using a P-E Model 137 Infracord. The calibrations were made in 1-mm. NaCl cells using CS_2 solutions *vs.* CS_2 in the reference cell. The concentration ranges for each compound calibrated and the base-point positions employed in measuring ΔA are shown in Table III. The calibration solutions for each compound were found to be stable and the ΔA *vs.* concentration plots were linear in the ranges measured. Both nitro alcohol and nitro olefin interfere with the determination for nitro nitrate. However, either one of two procedures may be employed to overcome these interferences: A CS_2 solution of pure nitro alcohol and nitro olefin of the same concentration calculated to be present in the sample may be used as the reference solution or the contribution to the ΔA of the sample at 7.9–8.1 microns by the calculated amount of nitro alcohol and nitro olefin may be determined from the spectra of pure nitro alcohol and nitro olefin and the contribution subtracted from the ΔA of the sample. The second technique is more accurate and is the preferred method. The presence of nitro olefin also interferes with the determination of the dinitro paraffin. The techniques employed for correcting for the contribution of nitro olefin in this case are the same as the two techniques described above. However, the contributions of the nitro olefin are subtracted at the 11.2- to 11.6-micron region where the absorption due to dinitro paraffin is measured. In obtaining calibrations and in actual determinations for dinitro paraffin, the spectrum is scanned from 11.2–12.0 microns with the slit override set at 700. This is required to compensate for the opacity of CS_2 in this region. Although only C_8 nitro compounds are shown in Table III, calibrations were obtained for the corresponding pure C_{16} nitro compounds in the same manner except for the C_{16} nitro olefin. In this case, the ΔA was measured as the difference in absorption between the band maximum at 10.4 microns and the absorption at 10.8 microns instead of 10.0 microns. This eliminates an interference by nitro alcohol that occurs in the analysis of C_{16} mixtures but not in C_8 mixtures.

Inverted Matrix Infrared Method. An infrared method employing inverted matrices (*1*) was developed using a Perkin-Elmer Model 21 spectrophotometer. The infrared data for the pure nitro compounds used as calibrations are shown in Table IV. Inverses were constructed for mixtures containing five different C_8 nitro compounds and for mixtures containing four C_{16} nitro compounds in addition to *n*-hexadecene-1.

RESULTS AND DISCUSSION

Application of the Near Infrared Method. Results obtained from the application of the near infrared method to synthetic mixtures of nitro alcohol and nitro olefin are shown in Table V. Although the concentration range investigated was rather limited, the results indicated that nitro alcohol and nitro olefin can be determined accurately by the near infrared technique. In most cases, both determinations can be made on the same sample dilution. Consequently, the near infrared method proved to be a valuable analytical tool for the rapid examination of those reaction mixtures

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Table II. Elemental Analyses and Physical Properties of Pure C_{16} Nitro Compounds Isolated from Reaction Mixtures

1. Elemental analyses

Compound	Calculated, % C	H	O	N	Determined, % C	H	O	N
1-Nitrohexadecanol-2	66.9	11.5	16.7	4.9	66.6	11.7	16.8	4.9
1-Nitrohexadecene-1	70.4	11.3	13.2	5.1	71.3	11.6	11.8	5.3
1,2-Dinitrohexadecane	60.7	10.1	20.3	8.9	61.0	10.2	20.0	8.8

2. Physical properties

Compound	M.P. (°C.)	R.I. @ 50° C.	Density @ 50° C.
1-Nitrohexadecene-1	19	1.45467	0.9027
1,2-Dinitrohexadecane	30	1.45205	0.9844
1-Nitrohexadecanol-2	48	1.44881	0.9424
1-Nitrohexadecanone-2	93	...	...
Bis-(1-nitro-2-nitrosohexadecane)	105	...	...

Table III. Absorption Bands Employed in Calibrating for the Analysis of Nitro Compounds in Complex Mixtures by Infrared Spectrometry

Instrument: P-E Infracord 137
Cells: 1-mm. NaCl

Compound	Band max. (microns)	Base (microns)	Concn. range (mg./ml.)[a]
1-Nitrooctanol-2	2.74	2.6	1.0–10.0
1-Nitrooctene-1	10.45	10.0	0.5– 6.0
1-Nitro-2-octyl nitrate	7.9	8.1	0.2– 1.3
1,2-Dinitrooctane	11.7	11.2	2.0–15.0

[a] In CS_2 *vs.* CS_2 in reference.

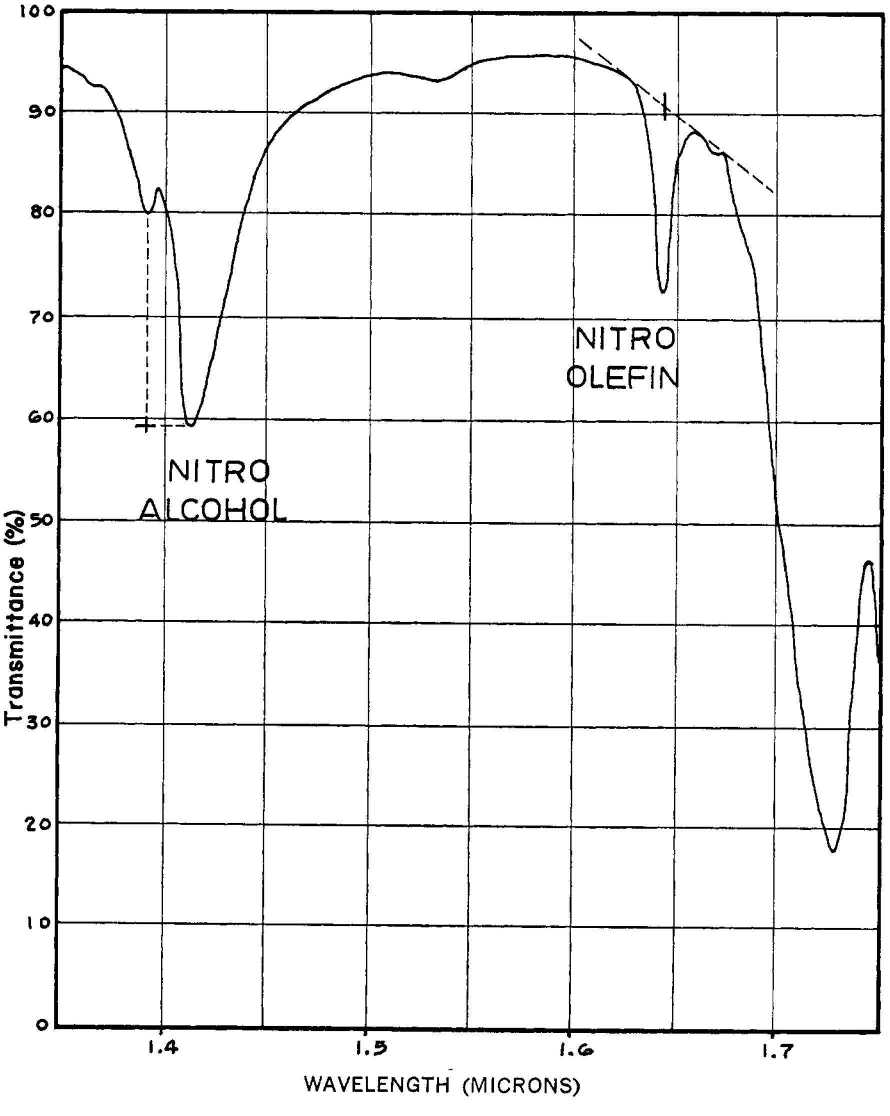

Figure 2. Near infrared spectrum of nitro alcohol and nitro olefin

Table IV. Infrared Data for Pure Nitro Compounds Used as Calibrations for the Inverse Matrix Method of Calculation

	Band position (microns)	Volume absorptivity[a]	Assignment
A. C_8 Nitro compounds			
Compound			
1-Nitrooctanol-2	2.93	2.59	—OH
1-Nitro-2-octyl nitrate	7.83	23.70	*sym*—O—NO_2
1-Nitro-2-methoxyoctane	9.08	10.26	—C—O—C—
1-Nitrooctene-1	10.45	6.27	*Trans* CH=CH
1,2-Dinitrooctane	11.61	2.61	C—N Stretch(?)
B. C_{16} Nitro compounds			
	Band position (microns)	**Absorptivity[b]**	**Assignment**
Compound			
1-Nitrohexadecanol-2	2.90	2.16	—OH
1-Nitro-2-hexadecyl nitrate	7.83	22.25	*sym*—O—NO_2
1-Nitrohexadecene-1	10.45	5.22	*Trans* CH=CH
1,2-Dinitrohexadecane	11.61	2.45	C—N Stretch(?)

[a] Abs. × dilution factor in 0.100-mm. cell.
[b] Abs. × dilution (g./ml.) in 0.156-mm. cell.

Table V. Application of Near Infrared Techniques to the Analysis of C_8 and C_{16} Mixtures of Nitro Olefin and Nitro Alcohol

Instrument: Beckman Model DK-1
Cells: 10-cm. Quartz
Sample concn.: #1–#3 7–10 mg./ml. CCl_4
#4 18 mg./ml. CCl_4

	Mixture	% Component Actual	% Component Determined
#1	1-Nitrooctanol-2	64·0	64·0
	1-Nitrooctene-1	36·0	36·0
		100·0	100·0
#2	1-Nitrooctanol-2	52·0	51·3
	1-Nitrooctene-1	48·0	48·7
		100·0	100·0
#3	1-Nitrooctanol-2	46·4	46·6
	1-Nitrooctene-1	53·6	51·9
		100·0	98·5
#4	1-Nitrohexadecanol-2	65·2	64·8
	1-Nitrohexadecene-1	34·8	34·5
		100·0	99·3

in which nitro alcohol and nitro olefin were the principal products. Since no interferences were observed from other nitration products, the near infrared technique was an excellent referee method for the determination of nitro alcohol and nitro olefin in multi-component nitration products.

Application of the Base-Point Infrared Method. The base-point technique using the absorption regions indicated previously was applied to synthetic mixtures of both C_8 and C_{16} nitro compounds. The results shown in Table VI for the analysis of a quaternary mixture of C_8 nitro compounds in addition to a ternary and two binary mixtures of C_{16} nitro compounds indicate that it was possible to analyze mixtures of nitro compounds with a reasonable degree of accuracy. The base-point technique using the Infracord initially was the principal method employed for the analysis of products containing mixtures of nitro alcohol, nitro olefin, nitro nitrate, and dinitro paraffin.

Table VI. Analysis of Synthetic Mixtures of Nitro Compounds by IR Using Base-Point Techniques

Component	% Component Known	% Component Determined	Mean error
1-Nitrooctanol-2	39.5	39.8	+0.3
1-Nitrooctene-1	25.2	25.4	+0.2
1-Nitro-2-octyl nitrate	5.7	6.3	+0.6
1,2-Dinitrooctane	29.6	33.0	+3.4
	100.0	104.5	
1-Nitrohexadecanol-2	24.9	24.6	−0.3
1-Nitrohexadecene-1	20.8	22.1	+1.3
1,2-Dinitrohexadecane	54.3	47.0	−7.3
	100.0	93.7	
1-Nitrohexadecanol-2	55.3	54.8	−0.5
1-Nitrohexadecene-1	44.7	42.3	−2.4
	100.0	97.1	
1-Nitrohexadecanol-2	80.5	81.5	+1.0
1-Nitrohexadecene-1	19.5	19.0	−0.5
	100.0	100.5	

Application of the Inverted Matrix Infrared Method. As the concentration of various components in products from nitration and subsequent treatment of nitration products began to vary considerably, it was found that the base-point technique using the Infracord was lacking in accuracy. This was particularly evident with respect to the determination of dinitro paraffin. To overcome this difficulty, the base-point technique using the Infracord was replaced by the inverted matrix method using a Perkin-Elmer Model 21 spectrophotometer.

Results obtained from the application of the inverted matrix method to the analysis of complex mixtures of C_8 and C_{16} nitro compounds are summarized in Table VII. In the C_8 mixtures, the concentrations of nitro alcohol were varied from approximately 40–90%. The nitro nitrate was determined at the 0–5% level while the concentration of nitro olefin was varied from 0–30% in the synthetic mixtures. The dinitro paraffin was determined at concentrations ranging from 5–40%. The average mean errors for the determination of C_8 nitro alcohol, nitro nitrate, nitro ether, nitro olefin, and dinitro paraffin in the synthetic mixtures were 0.3, 0.6, 0.3, 1.2, and 0.7, respectively.

Similar results were obtained in the analysis of synthetic mixtures of C_{16} compounds containing four nitro compounds and *n*-hexadecene-1. The concentration of nitro alcohol ranged from 30–50% while the concentration of nitro nitrate was varied from 0–10%. Nitro olefin and dinitro paraffin were determined when present in concentrations ranging from 0–43% and 5–70%, respectively. The average mean errors for the determination of C_{16} nitro alcohol, nitro nitrate, nitro olefin, and dinitro paraffin were 0.3, 0.4, 0.8, and 1.5, respectively. In general, the results obtained from the analysis of multi-component C_8 and C_{16} mixtures of nitro compounds indicated that the inverted matrices constructed were reliable and accurate and that they could be applied to the analysis of complex mixtures of similar composition with considerable confidence.

The inverted matrix method was then applied to the routine analysis of products obtained from the nitration of *n*-hexadecene-1. The analyses of four products are shown in Table VIII. The data show that the concentrations of nitro alcohol and nitro nitrate ranged from 30–46% and 0–3%, respectively, while the nitro olefin and dinitro paraffin were present at the 1–4% and 42–73% levels, respectively. Unreacted olefin was absent in runs #2 and #3 but was present in concentrations of 0.3 and 18.6% in runs #1 and #4, respectively.

Table VII. Analysis of Synthetic Mixtures of C_8 and C_{16} Nitro Compounds Using the Inverted Matrix Method

	Vol. % Component							
	#1		#2		#3		#4	
	Actual	Determined	Actual	Determined	Actual	Determined	Actual	Determined
1-Nitrooctanol-2	50.4	50.6	39.4	38.9	79.1	78.8	90.7	90.5
1-Nitro-2-octyl nitrate	4.7	5.8	4.5	5.1	...	0.5	...	0.1
1-Nitro-2-methoxyoctane	4.7	4.2	15.3	15.4	...	...	...	...
1-Nitrooctene-1	30.3	29.3	...	1.0	10.4	8.1	4.6	4.2
1,2-Dinitrooctane	9.9	8.4	40.8	41.6	10.5	10.7	4.7	4.9
	10.0	98.3	100.0	102.0	100.0	98.1	100.0	99.7

	Wt. % Component							
	#1		#2		#3		#4	
	Actual	Determined	Actual	Determined	Actual	Determined	Actual	Determined
1-Nitrohexadecanol-2	50.0	49.8	35.0	35.3	52.5	52.2	29.7	29.5
1-Nitro-2-hexadecyl nitrate	10.0	10.3	5.0	4.8	...	1.0	...	(−1.2)
1-Nitrohexadecene-1	...	(−3.1)	15.0	15.9	42.7	42.1	...	(−1.9)
Hexadecene-1	...	(−1.1)	30.0	28.8	...	(−0.3)	...	(−1.2)
1,2-Dinitrohexadecene	40.0	40.9	15.0	16.3	4.8	6.0	70.3	72.8
	100.0	101.0	100.0	101.1	100.0	101.3	100.0	102.3

Experience from the application of the inverted matrix method on a routine basis indicated that for greatest accuracy and reliability certain precautions had to be observed. The reliability of results were checked once every two days by analyzing the synthetic mixtures. In general, inaccurate analyses result from one or both of 2 major difficulties. First, when large amounts of impurities are present, as evidenced by poor or unusual material balances, the impurities must be removed or a new inverse calculated if the impurity is available as a pure compound for calibration purposes. Secondly, degradation of the NaCl cells causes changes in the background absorption which results in inaccuracies since the inverted matrix technique is a total absorption method. To correct for cell degradation, the cells have to be recalibrated with the synthetic mixtures or be replaced by new cells. Cell sizes have to be kept approximately the same because of different background absorptions. For example, 0.100-mm. cells cannot be used interchangeably with 0.150-mm. cells. When these precautions were taken, the inverted matrix method was found to be both accurate and reliable for the routine analysis of nitration products.

Table VIII. Application of the Inverted Matrix Method to the Analysis of Products from the Nitration of Hexadecene-1

	Component wt. %						
Run #	NA	NN	NO	DNP	HD	C═O	Total
1	46.3	2.0	3.9	42.2	0.3	0.48	94.7
2	45.7	3.3	2.0	44.2	...	0.42	95.2
3	30.3	0.3	1.2	72.6	...	0.16	104.4
4	34.9	2.9	4.0	38.2	18.6	0.03	98.6

NA = 1-Nitrohexadecanol-2
NO = 1-Nitrohexadecene-1
NN = 1-Nitro-2-hexadecyl nitrate
DNP = 1,2-Dinitrohexadecane
HD = *n*-Hexadecene-1

CONCLUSIONS

Each of the three techniques described above have certain advantages and disadvantages. Consequently, any one of the three methods may be preferred for a particular application. The near infrared method can be employed only for the determination of nitro alcohol and nitro olefin. However, when these two nitro compounds comprise the major components in a product, the near infrared technique is a relatively accurate and rapid method for routine analysis. The base-point technique using the Infracord is generally suitable for the analysis of multi-component products in which the nature and the quantity of unknown by-products is likely to vary considerably. However, as indicated earlier, this method may not be the most suitable technique where a very high degree of accuracy is required, particularly in the determination of dinitro paraffin. As the results from the analysis of synthetic mixtures indicated, the inverted matrix method was the most accurate of the three techniques described for the analysis of nitration products. Since this technique is a total absorption method, its accuracy is likely to be affected more seriously than the base-point technique by the presence of variable quantities of unknown components. However, in cases where the nature of the impurities is known, the inverted matrix method is an accurate and reliable technique for the routine analysis of multi-component products.

LITERATURE CITED

(1) Bauman, R. P., "Absorption Spectroscopy," Wiley, New York, 1962.
(2) Bonetti, G. A., Michalski, C., Rosenthal, R., DeSavigny, C. B., Division of Petroleum Chemistry, 150th Meeting, ACS, Atlantic City, September 1965.
(3) Brown, J. F., Jr., *J. Am. Chem. Soc.* **77**, 6341 (1955).
(4) Cristol, S. J., Seifert, W. K., Soloway, S. B., *Ibid.*, **82**, 2351 (1960).
(5) Seifert, W. K., *J. Org. Chem.* **28**, 125 (1963).

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