

VAPOR-PHASE BUTANE NITRATION
PRODUCT ANALYSIS BY
PARALLEL COLUMN GAS CHROMATOGRAPHY

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In previous work on this problem^{1,2} an analytical procedure was developed for the analysis of the pure nitroparaffins resulting from the vapor-phase nitration of commercial butane (Phillips Petroleum Co., technical grade) by gas-liquid partition chromatography. This method made use of both constant temperature, linear programmed temperature operation, and ramp function temperature programmed operation of a 6-ft. length of 1/4-in. copper refrigeration tubing packed with a 2:1 mixture by weight of two separate packings, Armeen SD and Apiezon N, each containing 10 g of substrate per 100 g of the -48 + 65 Tyler standard screen fraction of Johns-Manville Type C-22 firebrick. The presence of oxygenated compounds in the product stream from the butane nitrator, chiefly water, formaldehyde, acetaldehyde, and methanol made further work on this problem necessary.

EXPERIMENTAL

Apparatus

The unit used in this work was the F & M Scientific Corp. Model 500A programmed temperature gas chromatograph, modified as previously described¹. The injection port was maintained at 200°. Liquid samples were injected through a self-sealing silicone rubber septum with a 10- μ l Hamilton microsyringe. The carrier gas used in this investigation was helium (minimum purity, 99.98 mole %, The Matheson Co.) which was dried before use by passing through a 12-in. length of 3/8-in. pipe filled with No. 5A Linde molecular sieves installed in the inlet line to the thermal conductivity cell. The flow rate through the reference side of the cell was maintained constant at 30 ml of helium/min, measured at 28°. The flow rate through the columns was also measured at 28° with a calibrated Brooks "Shorate" 150 rotameter, tube No. 1-15-6, stainless steel float. Gas samples for scouting work were collected in 250 ml sample bulbs, fitted with two stopcocks. After the sample was obtained and the stopcocks closed, a rubber serum cap was fitted to the stub end through which the samples were withdrawn (by opening the cock, inserting the needle, sampling,

withdrawing the needle and closing the cock) with a 1-ml gas-tight syringe (Teflon-tipped nylon plunger, Wilkens Instrument and Research). Liquid samples used were 4 μ l. The gas samples used were 200 μ l and 20 μ l. The output signal from the thermal conductivity cell was recorded at a chart speed of 30 in./h on a Bristol Dynamaster Potentiometer, Model 1PH-570.

DISCUSSION

The nitrator product is obtained as a liquid phase and an off-gas. The liquid product is recovered and immediately separated into two layers: an oil layer, containing approximately 80–90 % nitroparaffins, 1–10 % water, 2 % oxygenated organics, and about 2 % dissolved gases; and an aqueous layer containing, in addition to the majority of the water and other oxygenated compounds produced in the reactor, less than 1 % nitroparaffins, 1–2 % dissolved gases (primarily CO₂ and NO₂), and nitric acid.

Oil layer

It was found that linear temperature programming at 2.9°/min, starting at 40°, of the mixed Armeen SD/Apiezon N column, A, was effective in the separation of the nitroparaffins in the oil layer in the presence of small amounts of light hydrocarbon gases, water, and the lower molecular weight alcohols, aldehydes, and ketones. The flow rate used was 60 ml of helium/min. The ratio of substrate to support was 1:10 by weight unless otherwise stated. The very slight tailing of nitromethane, methanol, and water which is typical of this column under all operating conditions, did not affect the precision and accuracy of the analyses.

The columns tested which provided reasonably good separation of the nitroparaffins caused considerable tailing of water, methanol, formaldehyde and acetaldehyde. Those columns which provided good separation for the oxygenated compounds caused leading of the nitroparaffins.

Aqueous layer

Upon mixing the different classes of compounds to form new test mixtures having compositions similar to the expected compositions³ of the oil and aqueous layers, it was found that a column, C, 24 ft. 11 in. long \times 1/4 in. O.D. copper tubing, filled with a packing consisting of 10 g of squalane per 100 g of the —30 + 80 U.S. standard screen fraction of Fluoropak, when operated at 50° at a helium flow of 77 ml/min gave excellent separation of the oxygenated constituents of the aqueous layer. Under these conditions, the nitroparaffins were retarded for 20 min, allowing the aqueous layer analyses to be made on a nitroparaffin-free basis. The first four nitroparaffins (nitromethane through 1-nitropropane) can be determined quantitatively in the squalane column if sufficient time is allowed. 1-Nitropropane has a retention time of 69.5 min under these conditions.

It was found that in general, substrates which are commonly used^{1,2,4-8} for the separation of water (Armeen SD); alcohols (dibutyl sebacate, 1-decanol, dibutyl phthalate, Carbowax 600 and 1500); aldehydes (Carbowax 20M); and dissolved gases such as CO, CO₂, N₂, O₂, CH₄, C₂H₆, C₃H₈, C₄H₁₀, etc. (squalane, hexamethyldisilazane, activated carbon, activated alumina, silica gel, and a 1:1 mixture by weight of glutaronitrile and propylene carbonate) lose their effectiveness when used for the separation of samples containing compounds from the other classes. This is especially

evident if the liquid partitioning agents have been made up on Type C-22 firebrick or the Johns-Manville acid-washed Chromosorb P. This was also found to be the case when the substrates were prepared using either of the silicone-treated, non-acid-washed Chromosorbs P or W as the support material. When using the silicone-treated Chromosorbs (separately) as the support for the 2:1 Armeen SD/Apiezon N column, water, methanol, ethanol, and acetaldehyde seem to be almost permanently adsorbed, as they did not appear, even after a six-hour wait. This may be of considerable advantage to other researchers who require analyses on a water- and oxygenated-free basis. We have found that the substitution of Fluoropak (Wilkins Instrument and Research) for the Type C-22 firebrick and the Chromosorb P greatly reduces or even eliminates the tailing so often encountered in the analysis of samples containing water by GLPC. However, when this change of support material was tried for the mixed Armeen SD/Apiezon N substrate for the analysis of the nitroparaffins in the oil layer, a decrease in resolving power was observed.

Gas phase

This stream contains primarily *n*-butane, 9–11 mole % NO and NO₂, 2–3 mole % propane, 1.5–2.5 mole % carbon dioxide, and traces of carbon monoxide, methanol, water, and formaldehyde. The gas stream is water saturated. Of the packings tested for the separation of the gas-phase components, the aqueous layer squalane column, C, gave satisfactory quantitative separation of ethane, propane, *n*- and *iso*-butane, carbon dioxide, methanol, acetaldehyde, formaldehyde, and nitromethane through 1-nitropropane when operated at 50° and a helium flow rate of 77 ml/min. Under these conditions, N₂, NO, NO₂ and CO are eluted as a single peak just before CO₂. Operation of this column at 30° and 27 ml helium/min gave quantitative separation of CO and NO, but N₂ and NO₂ still appeared as a single peak. Under these conditions, however, the separations of water, methanol, formaldehyde, and acetaldehyde were unsuitable for quantitative work. The NO₂ and NO were also separated completely by running duplicate samples on a 1/4-in. O.D. column, B, 20 ft. long filled with the —65 + 80 Tyler standard screen fraction of activated charcoal impregnated with 2 parts by weight of squalane per 100 parts of the activated charcoal. Operating conditions were 22° and 66 ml of helium/min.

Hexamethyldisilazane treated Chromosorb P⁶, a 1:1 mixture by weight of glutaronitrile and propylene carbonate, Carbowaxes 600 and 20M, a 1:1 mixture by weight of Armeen SD and Apiezon N, all in the ratio of 10 g substrate per 100 g support; 2 wt. % squalane on activated carbon; 2 wt. % dibutyl sebacate on silica gel; activated carbon; were also tested for the analysis of the off-gas leaving the reactor and were found to be unsatisfactory.

Analytical procedure

The analysis of the nitrator products was broken down as follows. The oil layer samples were analyzed on the Armeen SD/Apiezon N column, A, for the quantitative separation of the nitroparaffins and the oxygenated compounds (Fig. 1, lower chromatogram). The dissolved gases in the oil layer, which appeared as three small incompletely resolved peaks, were separated by running duplicate oil layer samples through the squalane/Fluoropak column, C, (Fig. 1, upper chromatogram), and through the squalane-activated charcoal column, B, (Fig. 2, lower chromatogram).

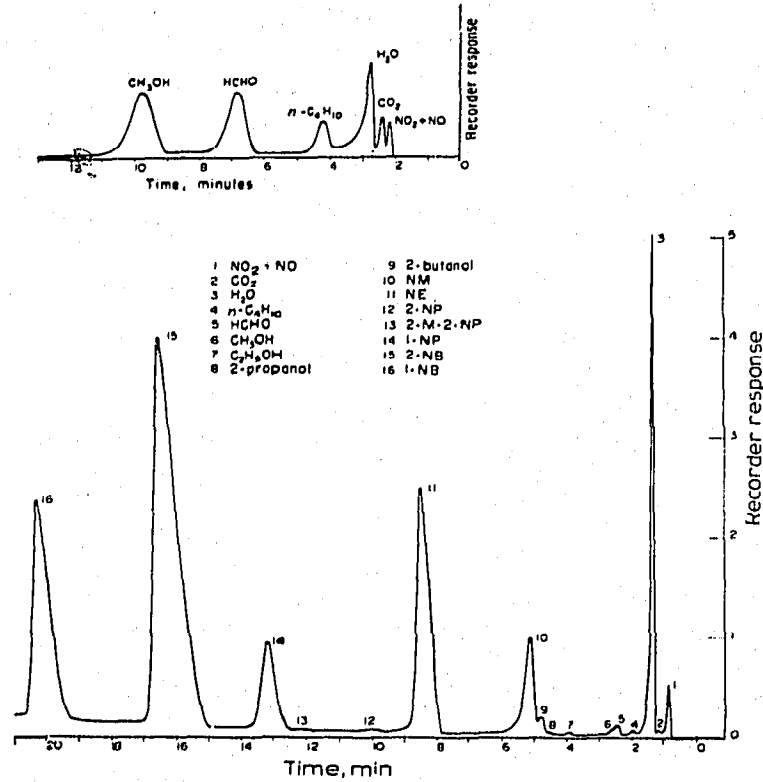


Fig. 1. Chromatograms of the oil layer. Top: Column C: 50°; 77 ml helium/min. Bottom: Column A: linear temperature programmed at 2.9°/min starting from 40°; 60 ml helium/min.

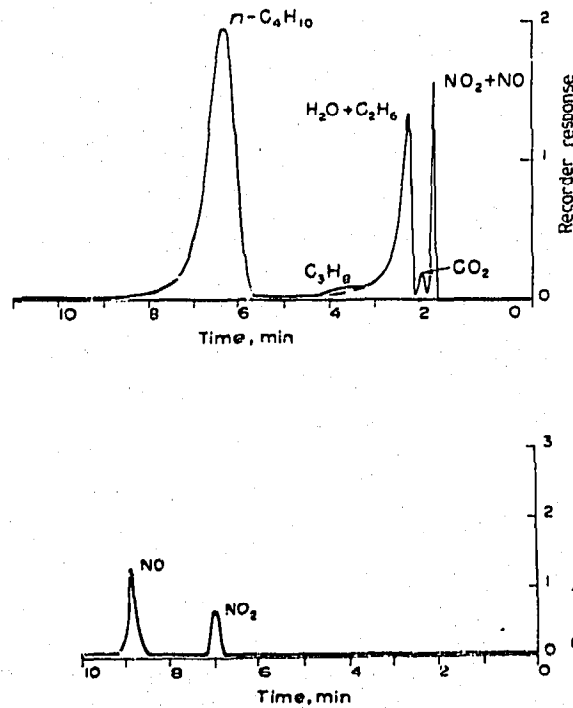


Fig. 2. Chromatograms of the off-gas. Top: Column C: 50°; 77 ml helium/min. Bottom: Column B: 22°; 66 ml helium/min.

The aqueous layer samples were analyzed on the squalane/Fluoropak column, C, at the higher temperature and flow rate to pick out the water, oxygenated compounds, and the nitroparaffins (Fig. 3, upper chromatogram). Duplicate water layer samples were then run through column C at the lower temperature and flow rate (Fig. 3, lower chromatogram), and initially through column B for the analysis of the dissolved gases. This analysis showed that the acidity of the aqueous layer was due almost entirely to the presence of nitric acid. In later runs, an immediate titration with standard base provided the same information as column B.

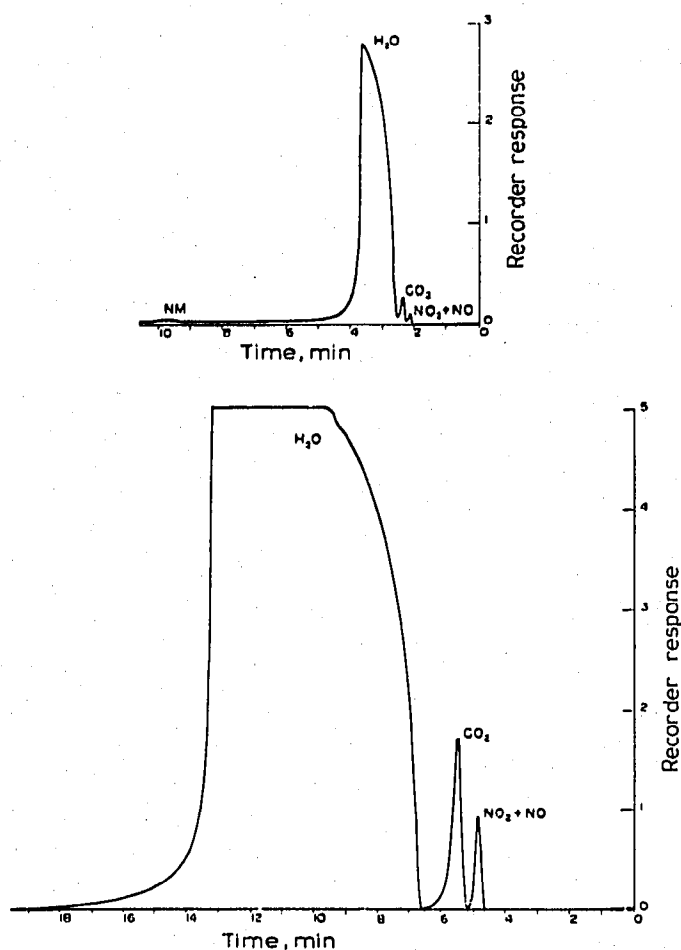


Fig. 3. Chromatograms of the aqueous layer. Top: Column C: 50° ; 77 ml helium/min. Bottom: Column C: 30° ; 27 ml helium/min.

The off-gas samples were analyzed in column C at the higher temperature and flow rate (Fig. 2, upper chromatogram), for water, nitroparaffins, and oxygenated aliphatics and at the lower temperature and flow rate for CO_2 , oxides of nitrogen, ethane, propane, and *n*-butane (Fig. 4). Duplicate samples were analyzed in column B (Fig. 2), for the $\text{NO}-\text{NO}_2$ split.

In all cases, the supplementary analyses (oil layer samples in columns B and C, off-gas and aqueous layer samples in column B and under both sets of conditions in column C) for each product stream were made to obtain quantitative analyses of overlapping or crowded peaks. The peak areas from these supplementary analyses

were used as a basis of partitioning the areas of the primary analysis. For example, the upper chromatogram of Fig. 1 shows the separation of the first 6 components of a typical oil layer sample (lower chromatogram is from column A). The areas from the

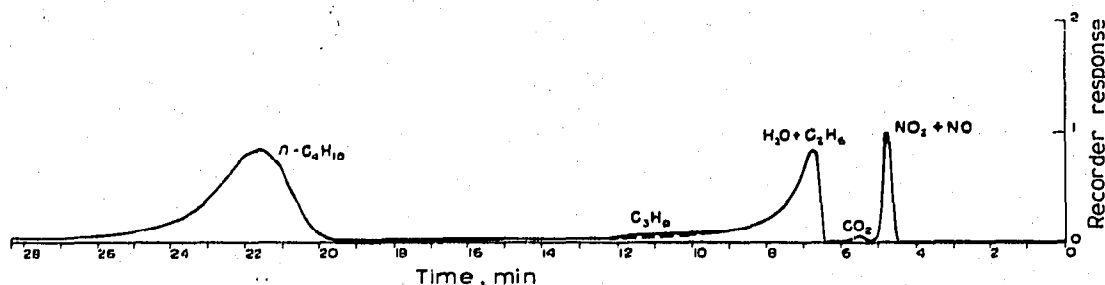


Fig. 4. Chromatogram of the off-gas. Column C: 30°; 27 ml helium/min.

methanol and formaldehyde peaks in the upper chromatogram were used to partition the total area under peaks 5 and 6 in the lower chromatogram. A similar technique was used for any other crowded or overlapping peaks. This procedure appears to be quite reproducible and precise when tested against known, gravimetrically-prepared test mixtures. These results can best be summarized by Table I which shows the procedure followed for routine analysis.

The presence of certain compounds (hydrogen, nitrogen, oxygen, methane, alkenes, alkynes) which might be expected in the product streams was ruled out by

TABLE I
PROCEDURE FOR PRODUCT ANALYSIS BY GLPC

Use	Column	Flow rate ^a	Temperature (°C)	Compounds separated quantitatively
Oil	A ^b	60	L.T.P. ^c	NP's, H ₂ O, oxygenated aliphatics ^d , C ₂ H ₆ , C ₃ H ₈ , n-C ₄ H ₁₀ , iso-C ₄ H ₁₀ , CO ₂ , CO + NO + NO ₂ + N ₂
Oil	B ^e	66	22	CO, HCHO, NO ₂ + N ₂ , N ₂ O ₄ , NO
Oil	C ^f	77	50	C ₂ H ₆ , C ₃ H ₈ , n-C ₄ H ₁₀ , iso-C ₄ H ₁₀ , CO ₂ , NO ₂ , NO + CO
Off-gas	B ^e	66	22	CO, HCHO, NO ₂ + N ₂ , N ₂ O ₄ , NO
Off-gas	C ^f	27	30	CO ₂ , NO ₂ + N ₂ , H ₂ O + C ₂ H ₆ , C ₃ H ₈ , C ₄ H ₁₀
Off-gas	C ^f	77	50	H ₂ O + C ₂ H ₆ , oxygenated aliphatics ^d , NM, NE, 2-NP, 2-M-2-NP, 1-NP, NO ₂ , CO ₂
Aqueous	B ^e	66	22	CO, HCHO, NO ₂ + N ₂ , N ₂ O ₄ , NO
Aqueous	C ^f	27	30	CO ₂ , NO ₂ + N ₂ , H ₂ O + C ₂ H ₆ , C ₃ H ₈ , C ₄ H ₁₀
Aqueous	C ^f	77	50	H ₂ O + C ₂ H ₆ , oxygenated aliphatics ^d , NM, NE, 2-NP, 2-M-2-NP, 1-NP, NO ₂ , CO ₂

Abbreviations: NM = nitromethane; NE = nitroethane; 1-NP = 1-nitropropane; 2-NP = 2-nitropropane; 2-M-1-NP = 2-methyl-1-nitropropane; 2-M-2-NP = 2-methyl-2-nitropropane.

^a ml helium/min measured at 28°, atmospheric pressure.

^b Column A: a 2:1 weight mixture of Armeen SD and Apiezon N, each 10/100 on C-22, —48 + 65 Tyler standard mesh, 1/4 in. O.D. × 6 ft.

^c L.T.P.: Linear temperature programming at 2.9°/min starting from 40°.

^d Includes all C₁ to C₄ RCHO, ROH, ROR', RCOOR', and RR'C=O.

^e Column B: 2/100, squalane on activated charcoal, —65 + 80 Tyler standard mesh, 1/4 in. O.D. × 20 ft.

^f Column C: 10/100, squalane on Fluoropak, —30 + 80 U.S. standard mesh, 1/4 in. O.D. × 24 ft. 11 in.

the use of certain columns which are most satisfactory for qualitative work. Hydrogen and methane can be qualitatively separated from the other components expected to be present in the oil and off-gas samples in a 1/4-in. O.D. column 4 ft. long filled with a packing consisting of 5 g of squalane per 100 g of the -65 + 80 Tyler standard screen fraction of reagent grade silica gel. When the oil layer and off-gas samples were analyzed in this column at 0° and a helium flow rate of 5 ml/min, no hydrogen or methane was found. The off-gas samples were also analyzed at 30° in a 1/4-in. O.D. column 10 ft. 5 in. long filled with the -65 + 80 Tyler standard screen fraction of activated carbon using hydrogen at a pressure of 11 p.s.i.g. at a flow rate of 84 ml/min. Neither oxygen nor nitrogen was found. The absence of alkenes and alkynes in the oil and gaseous products was demonstrated when those samples were analyzed at 0° and a helium flow rate of 20 ml/min (measured at 28°) in a 1/4-in. O.D. column filled with a mixture of equal parts by weight of two separate packings, glutaronitrile and propylene carbonate, each containing 10 g of substrate per 100 g of the -80 + 100 U.S. standard screen fraction of non-acid-washed, silicone-treated Type C-22 Johns-Manville firebrick. Since these compounds were not present in the samples taken from several of the nitrator runs at different conditions, no further attempts were made to develop quantitative separations for them.

The limits of accuracy and reproducibility for any given component in columns A and C were $\pm 2\%$ of the true value of that component when calibrated against known gravimetric samples containing that component, *i.e.* nitroethane in Table II would be between 16.5 and 17.1 wt. %. The GLPC analyses were obtained by measuring the

TABLE II
ANALYSIS OF REACTION PRODUCTS FROM MOLTEN SALT BUTANE NITRATOR*

	Oil layer	Aqueous layer	Off-gas**
NO	—	—	8.6
NO ₂	1.0	0.4	0.9
CO	—	—	—
CO ₂	0.2	1.5	1.0
H ₂ O	9.8	98.1	—
C ₃ H ₈	—	—	2.1
n-C ₄ H ₁₀	0.2	100.0	86.4
HCHO	0.3	—	—
			100.0
CH ₃ OH	0.2	—	—
C ₂ H ₅ OH	0.2	—	—
CH ₃ CH(OH)CH ₃	0.1	—	—
CH ₃ CH(OH)CH ₂ CH ₃	0.7	—	—
NM	4.7	—	—
NE	16.8	—	—
2-NP	trace	—	—
2-M-2-NP	0.1	—	—
1-NP	4.2	—	—
2-NB	45.7	—	—
2-M-1-NP	—	—	—
1-NB	15.8	—	—
	100.0	—	—

* All analyses are in weight %.

** Off-gas analysis is on a water-free basis.

TABLE III
MATERIAL BALANCES AROUND MOLTEN SALT BUTANE NITRATOR
(gram-atoms/h)

Substance	In	Out			Total	% Accounted for
		Oil layer	Aqueous layer	Off-gas		
C	31.240	1.532	0.060	26.905	28.497	91.22
N	2.160	0.472	0.202	1.333	2.007	92.88

peak areas with a Model K2-1 integrator (Disc Instruments, Inc.). Working with known volumes of pure gases, column B was found to have similar limits. The purity of the compounds used for calibration was the highest normally available. The nitro-paraffin samples (minimum purity, 99.8 mole %) were kindly supplied by Commercial Solvents Corp.

The analysis of the products from a typical nitration run made at a butane flow rate of 6.181 SCFH using 178.5 ml/h of 12.10 N nitric acid and a molten salt temperature of 785° F is shown in Table II. The input and output material balances are shown in Table III. Closing a material balance within $\pm 20\%$ is considered quite satisfactory for developmental work of this type. Deviations from perfect (*i.e.* 100%) material balances may be attributed to product loss during sampling, product deterioration between sampling and analysis, admitted errors in analysis, and certain unavoidable operating losses. However, the fact that the carbon and nitrogen material balances consistently check within ± 7 to 9% and are both of the same order of magnitude is a strong inducement for their acceptance and use for scale-up from an engineering point of view.

From this work, it was concluded that a gas chromatographic analysis technique has been developed which will routinely give adequate quantitative analysis for the reaction products from the vapor-phase nitration of commercial butane. A full report concerning the construction and operation of the nitrator will be made in the near future.

SUMMARY

A routine gas chromatographic analytical procedure has been developed for the reaction products of a vapor-phase butane nitrator. Replicate samples are used in 3 columns to give satisfactory quantitative separation of the C₁ to C₄ mononitroparaffins, alcohols, aldehydes, C₁ to C₄ paraffins, and NO, NO₂, CO, CO₂, all in the presence of water. Accuracy and precision are at least $\pm 2\%$ of the true value of any component. Carbon and nitrogen material balances of approximately 92% are obtained.

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