

CHROM. 3445

VAPOR-PHASE BUTANE NITRATION PRODUCT ANALYSIS BY ON-LINE MULTIPLE COLUMN GAS CHROMATOGRAPHY

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(Received February 12th, 1968)

SUMMARY

A reliable on-line gas chromatographic analytical procedure has been developed for the total reaction product of a vapor-phase butane nitrator. The accuracy of the analysis when applied to actual reactor effluent streams is at least ± 2 mole % of the mean of six replications. The method will be of interest generally in the field of hydrocarbon nitration since no other on-line analytical procedure is presently available.

Much of the basic research on the vapor-phase nitration of paraffin hydrocarbons was done before modern analytical techniques were available¹. Recently, however, significant advances in nitration product analysis by gas chromatographic methods have been reported. BETHEA AND ADAMS² developed an approximate analysis and later FEAR AND BURNET³ developed a method for complete quantitative analysis of all significant products from the vapor phase nitration of butane. In both cases, the total reactor effluent was collected, separated into two liquid portions (one an oil and the other a water phase) and two gas portions (one liquified and the other non-condensed) and then analyzed by portion. During the collection and separation steps it was quite likely that chemical interaction continued to some degree so that the final analytical results did not represent the true reactor effluent. In addition to this disadvantage these procedures were very time consuming. It was concluded that an on-line analytical technique capable of analyzing the total reactor effluent was necessary. The purpose of this paper is to report the development of such a method.

CONCEPT

Butane nitration products may be classified into three distinct groups each with unique characteristics. Each group can in turn be separated into its individual components by a particular combination of packing and partitioning agent. The groups are: (1) the nitroparaffins and higher alcohols, (2) water and the oxygenated aliphatics, and (3) the fixed gases and paraffins. The degree of component resolution must assure quantitative results and, because the procedure will be used on-line, the retention time

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must be as short as possible. Assuming that a suitable chromatographic analysis could be developed for each of the three major groups, an effective on-line analysis would then be possible through use of a valving arrangement to carry out each of the three analytical procedures in series.

The general plan was to have a first column operated at a relatively high temperature and flow rate through which the low and middle boilers passed rapidly and only partially resolved. These materials were then sent to a second column operated at a lower temperature and capable of separating these fractions into their individual components. The high boilers were separated by the first column and then vented to prevent contamination of the second column.

APPARATUS

Groups (1) and (2) above, the high and medium boilers, were separated on columns consisting of powdered Teflon packing, marketed under the name Haloport F*, and a partitioning agent of Celanese No. 9 ester*. Ives⁴ had earlier shown that the non-porous surface of the Teflon reduced the possibility of serious water tail and that the ester would quantitatively separate the nitroparaffins and alcohols. Group (3), the gaseous products, were separated on two additional columns, one of silica gel** and one of molecular sieves***. The column characteristics are listed in Table I.

TABLE I

COLUMN CHARACTERISTICS

All columns were 1/4-in. O.D. copper tubing.

Column	Length (ft)	Support	Substrate	Temperature (°C)
I	20	Haloport F	5 wt.% Celanese No. 9	105
II	12	Haloport F	5 wt.% Celanese No. 9	50
III	2		20-25 mesh silica gel	22
IV	6		14-30 mesh, 13X molecular sieves	22

The four columns were connected in series with provisions for bypassing any given column after an initial separation in the first. Two complete chromatographs were required and each had its own supply of helium, the carrier gas used. The first chromatograph was a F & M Scientific Corp. Model 500-A equipped with a 0-1 mV strip chart recorder. The second was a Perkin-Elmer Corp. Model 154-D Vapor Fractometer equipped with a 0-5 mV recorder. Each used a thermal conductivity detector. A schematic flow diagram of the column arrangement is shown in Fig. 1.

The entire effluent from column I passed through the detector of the F & M chromatograph. At a specific time, bypass valve A down stream from the F & M detector was switched to allow the components yet to pass the valve to be vented. These components had been recorded on the first chromatogram and consisted of the

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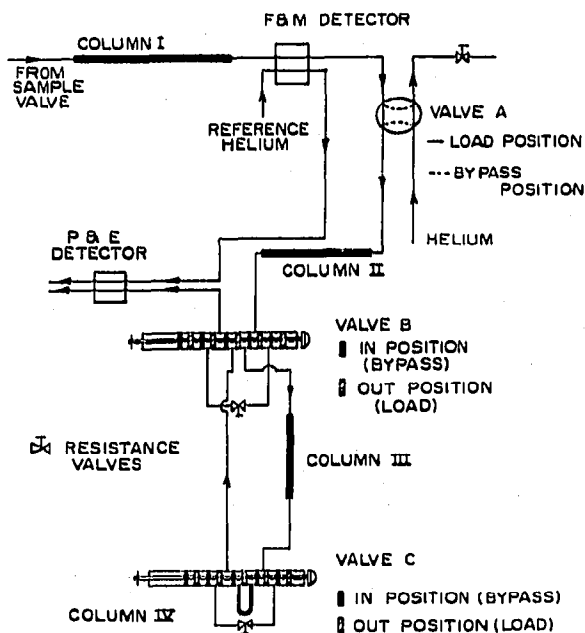


Fig. 1. Schematic flow diagram of chromatographic column arrangement.

high boilers. The low boiling liquids and gases which had passed the valve were separated by the remaining three columns and resolved by the Perkin-Elmer chromatograph.

PROCEDURE

The product was sampled for analysis using a Beckman Instruments Inc. sampling valve Model 102396 with a 3 cc sample loop. To prevent condensation in the sampling device, the valve and loop were installed in an insulated aluminum box in which the temperature was maintained at 250°. The sample box was mounted directly on top of the reactor body so that a minimum amount of additional tubing was required to send the sample from the effluent tube to the valve. The sample was picked up by preheated helium in the valve and carried into column I.

The components eluted from column I were recorded with valve A in the load position. After about 7 min, valve A was switched to bypass so that the second supply of helium could carry the gases and low boilers into the remaining columns and the resolved high boilers from column I could be vented. Flow in both systems was thus uninterrupted. Pressures were balanced by adjusting the drop across each needle valve to equal the respective column pressure drop. A chromatogram of a calibration run is shown in Fig. 2.

The gaseous products and low boilers were completely separated on columns II, III, and IV. The gases were loaded on columns III and IV and retained there by pushing valve B in (bypass position) about 4 min after the sample was first introduced. The components from column II were then detected to complete the analysis of all liquid products. A chromatogram showing the medium boiling liquids separated by column II during a calibration run is shown in Fig. 3. The higher boiling gases were also separated by this column and appear as the first three peaks in Fig. 4.

VAPOR-PHASE BUTANE NITRATION PRODUCT ANALYSIS

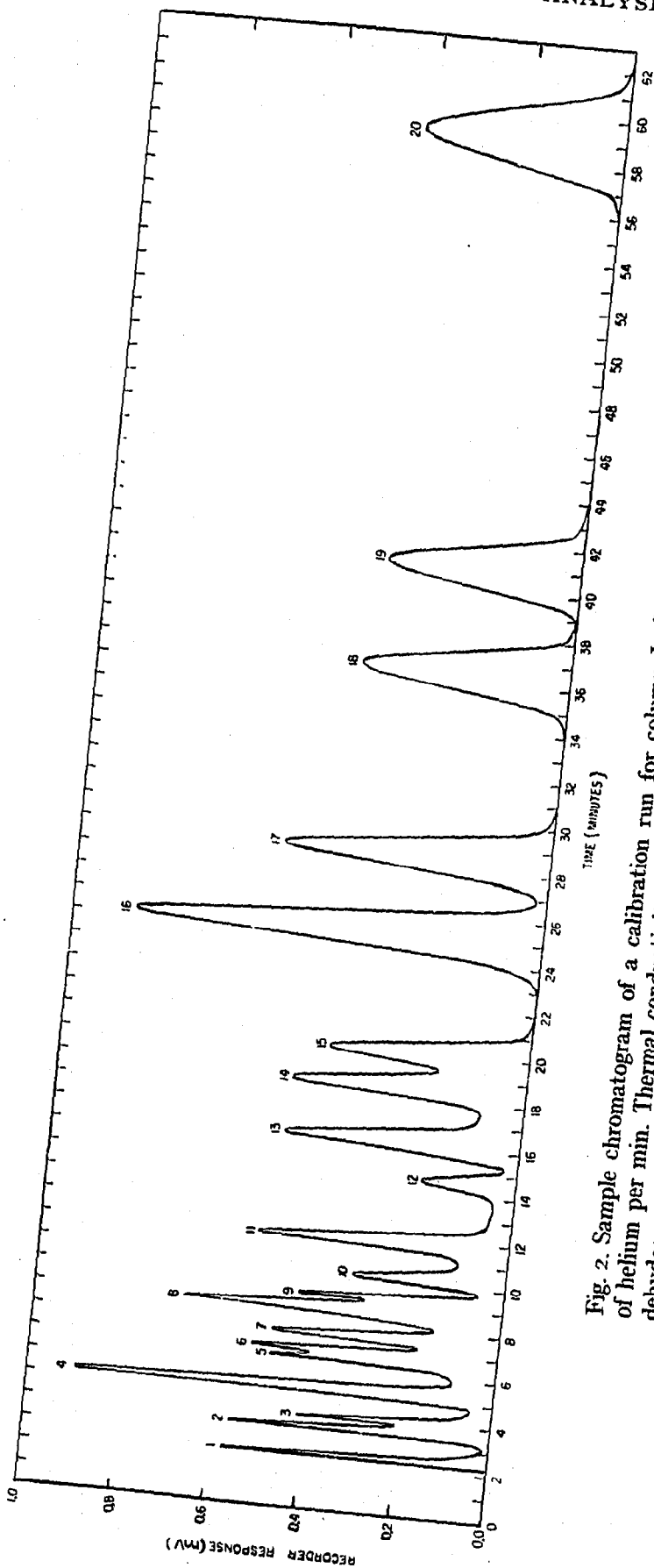


Fig. 2. Sample chromatogram of a calibration run for column I. Conditions: 105° and 55 ml of helium per min. Thermal conductivity detector. 1 = Formaldehyde; 2 = water + acetaldehyde; 3 = methanol; 4 = ethanol + propanal; 5 = 2-propanol; 6 = isobutyraldehyde; 7 = *tert.*-butanol; 8 = *n*-butyraldehyde; 9 = 1-propanol; 10 = nitromethane; 11 = 2-butanol; 12 = isobutyl alcohol; 13 = nitroethane; 14 = 1-butanol; 15 = 2-nitropropane; 16 = 2-methyl-2-nitropropane; 17 = 1-nitropropane; 18 = 2-nitrobutane; 19 = 2-methyl-1-nitropropane; 20 = 1-nitrobutane.

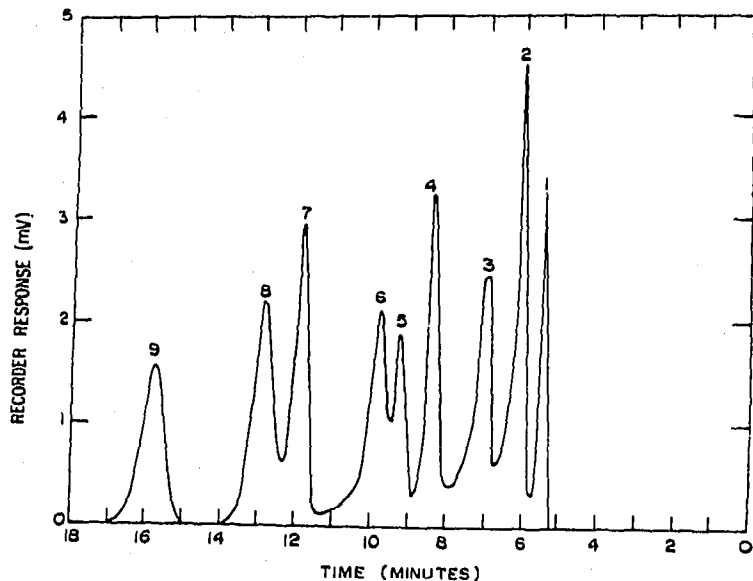


Fig. 3. Sample chromatogram for a calibration run for the medium boiling liquids separated by column II. Conditions: 50° and 55 ml helium per min. Thermal conductivity detector. 1 = Formaldehyde; 2 = acetaldehyde; 3 = water; 4 = methanol; 5 = propanal; 6 = ethanol; 7 = 2-propanol + isobutyraldehyde; 8 = *n*-butyraldehyde; 9 = *tert.*-butanol.

The remaining gaseous components were retained on columns III and IV until all components had eluded from column II. After about 18 min from the original sampling time, valve B was pulled out (load position) for about 2.5 min to allow H_2

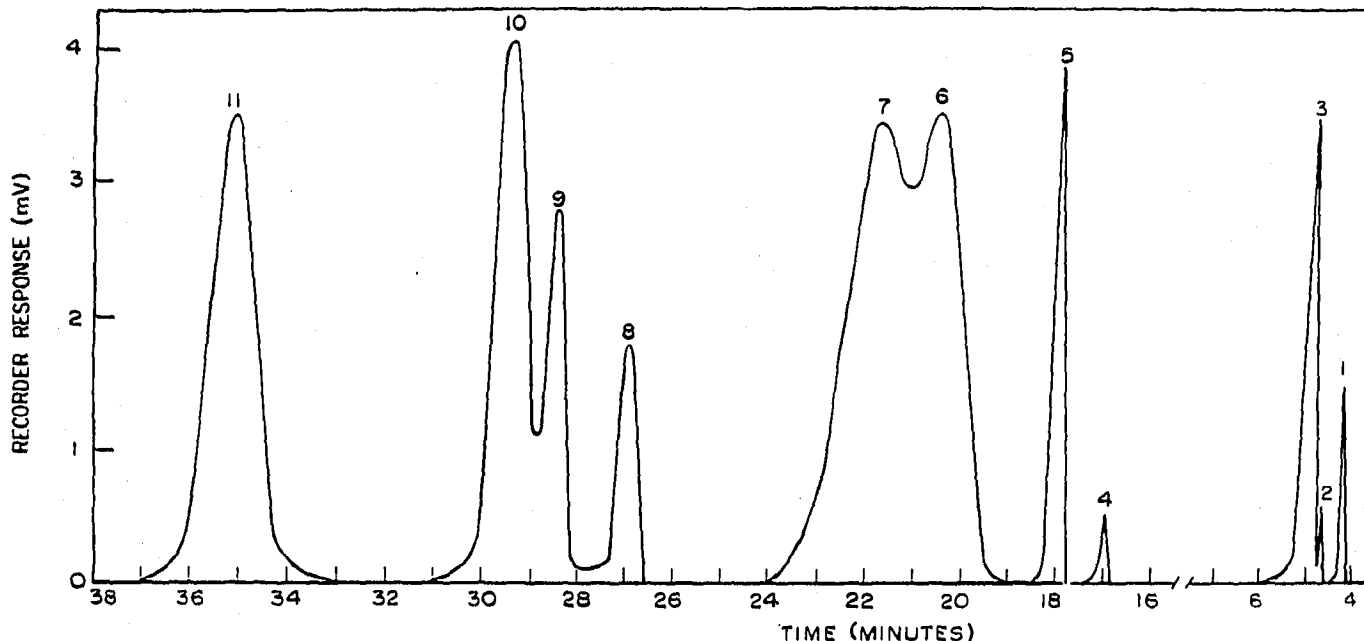


Fig. 4. Sample chromatogram of a calibration run for gases separated by column II and all components from columns III and IV. Conditions: 22° and 55 ml helium per min. Thermal conductivity detector. 1 = Propane; 2 = isobutane; 3 = butane; 4 = hydrogen; 5 = oxygen; 6 = ethane; 7 = carbon dioxide; 8 = nitrogen; 9 = nitric oxide + nitrogen dioxide; 10 = methane; 11 = carbon monoxide.

and O₂ to elude from column IV and be detected (peaks 4 and 5 in Fig. 4) and to allow additional components to load on column IV. At the end of this time, valve C was pushed in (bypass position) and the resolved components from column III were eluded and detected (peaks 6 and 7 in Fig. 4) which required about 7 min. Valve C was then pulled out (load position) to allow the trapped components to elude from column IV and be detected (the remaining peaks in Fig. 4).

The overall procedure required approximately 40 min. The valve switching times are approximate and depend upon the specific carrier gas flow rate and the size and shape of the eluding peaks.

Valves B and C were Loenco, Inc. six-port, push-pull switching valves. All connecting tubing was 1/8-in. O.D. type 304SS.

DISCUSSION

The on-line analysis developed using simulated nitration products (calibration runs) worked very satisfactorily on actual reactor effluents. The results of six replicate runs are presented in Table II.

TABLE II

NITROPARAFFIN DISTRIBUTION RESULTS FOR SIX REPLICATED EXPERIMENTS
Mole % of total nitroparaffins produced.

<i>Component</i>	<i>NM*</i>	<i>NE</i>	<i>1-NP</i>	<i>2-NB</i>	<i>1-NB</i>
Mean value	12.952	23.612	10.659	29.108	23.839
Error mean square	2.952	0.8686	0.1568	9.207	20.05
Standard deviation of the mean	0.7014	0.3804	0.5110	1.239	1.828
<i>t</i> value (90%)	2.015	2.015	2.015	2.015	2.015
90% confidence limits	11.491, 14.317	22.845, 24.379	9.629, 11.689	26.612, 31.604	20.156, 27.522

* Abbreviations: NM = nitromethane; NE = nitroethane; 1-NP = 1-nitropropane; 2-NB = 2-nitrobutane; 1-NB = 1-nitrobutane.

The operating conditions for column I were selected by use of a procedure which optimized on acceptable resolution in a minimum time. As has been previously reported⁵, the effect of tailing on resolution became increasingly evident as analysis times were shortened and maximum column efficiency approached. Any significant tailing led to an unacceptable degree of resolution.

The shape of the individual chromatographic peaks was also influenced strongly by the shape of the sample "plug". In this work it was observed that the sample collection system both induced a tail in the sample before it entered the first column and created a back-mix effect which reduced the plug flow character of the sample. These effects were minimized by making the sample loop as short as possible.

ACKNOWLEDGEMENT

This work was supported by the Engineering Research Institute, Iowa State

University, through funds made available by Commercial Solvents Corporation, Terre Haute, Indiana.

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