Gas chromatography of the C_1 to C_4 nitroparaffins: Ramp function temperature programming*

In previous work on this problem[1], values of R_{67}, corresponding to the resolution[2] of 2-nitrobutane from 2-methyl-1-nitropropane (representing the most severe test of our data) were 0.80 and 0.64, respectively, for the separation of the C_1 to C_4 nitroparaffins at a constant temperature of 50° and a hydrogen flow rate of 90 ml/min and at a hydrogen flow rate of 60 ml/min when using linear temperature programming at a

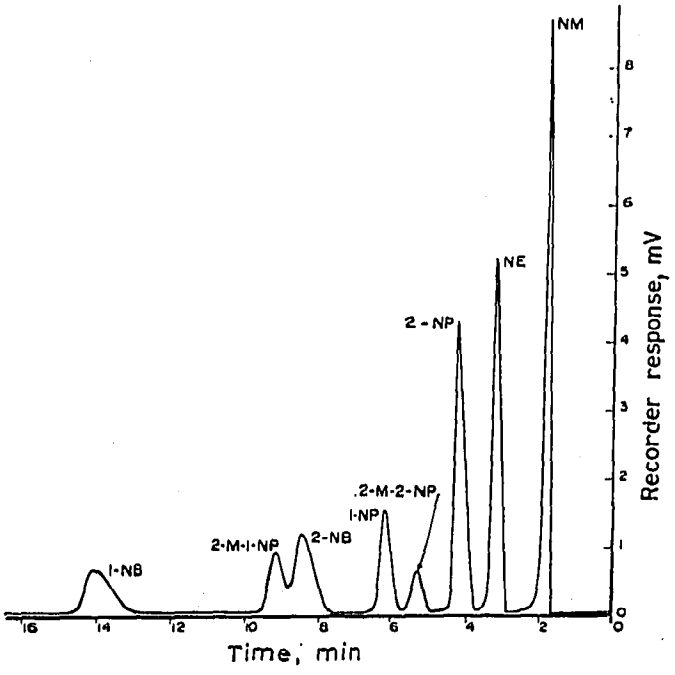

Fig. 1. Optimum isothermal separation of the C_1 to C_4 nitroparaffins. Conditions: 50°; 90 ml H_2/min.

rate of 2.9° per min, starting from 40°. The total optimum isothermal analysis time was 14.8 min as seen in Fig. 1. Under these conditions, excessive leading was observed for the 1-nitrobutane peak. Nitromethane, nitroethane, and 2-nitropropane were eluted in the first 4 min. The crowded condition of the initial portion of the run prohibited using isothermal analysis for the separation of the C_1 to C_4 nitroparaffins in the presence of the C_1 to C_4 oxygenated aliphatics and the oxides of nitrogen and carbon.

Using the optimum linear temperature programming rate, the total analysis time was 18.8 min as seen in Fig. 2. The deciding factors which caused us to reject these operating conditions were the low value of $R_{67} = 0.64$ and the fact that satisfactory calibration curves could not be obtained for direct quantitative analysis. This was even more apparent when using the optimum isothermal operating conditions. It was thought that the combination of an initial constant temperature period followed by linear temperature programming at a high heating rate would greatly

* This work was supported jointly by research grants from the Iowa Engineering Experiment Station and Phillips Petroleum Company.

improve the separation of the nitroparaffins. This work was performed to verify the expected beneficial effects of ramp function temperature programming on the resolution of the nitroparaffins.

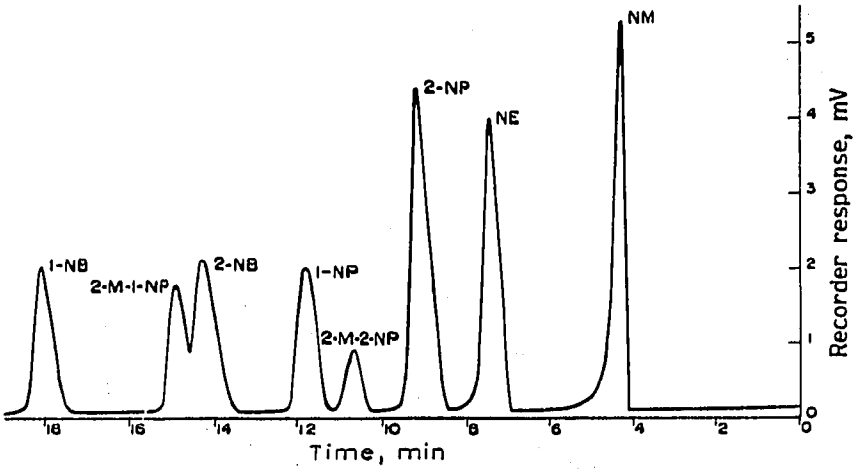

Fig. 2. Optimum linear temperature programmed separation of the C_1 to C_4 nitroparaffins. Conditions: 2.9°/min starting from 40° at time zero; 60 ml H_2/min.

Experimental

The apparatus, flow control system, and test mixture have already been described[1]. The column used for this work was the Armeen SD-Apiezon N column used previously. The duration of the initial constant temperature period was tested at levels of 2, 4, 6, 8, 10, 12 and 15 min followed by linear temperature programming at levels of 2.9, 4.0, 5.6, 7.9, 11.0 and 15.0° per min. Two sets of replicate analyses were made at random within each heating rate group using a 4-μl sample of the test mixture for each run. Additional replicates were made at random over the ranges of the entire experiment. These additional runs showed that there were no changes in the characteristics of the column with time and that the experimental conditions and retention times could be reproduced within $\pm$ 1 %.

Results

It has been found that ramp function temperature programming is preferable for the analysis of the products resulting from the vapor-phase nitration of commercial butane. In addition to the nitroparaffins* (primarily NM, NE, 1-NP, 2-NB and 1-NB), water, formaldehyde, acetaldehyde, methanol, ethanol, and some nitric acid are present in the nitrator product stream. The use of ramp function temperature programming allows part of the analysis to be made at a constant temperature, 40°, where there is no overlapping of the lower nitroparaffin peaks with the peaks of the oxygenated compounds present in the product stream. The higher molecular weight nitroparaffins will be initially retarded during the constant temperature period and then speeded up and greatly sharpened by the change in their partition coefficients

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

due to the higher temperature during the linear temperature programmed portion of each run. The result is a chromatogram of evenly spaced, sharp peaks, Fig. 3. The optimum operating conditions, as determined by the "box" method of data collection, are a 10 min isothermal period at 40° followed by linear temperature programming

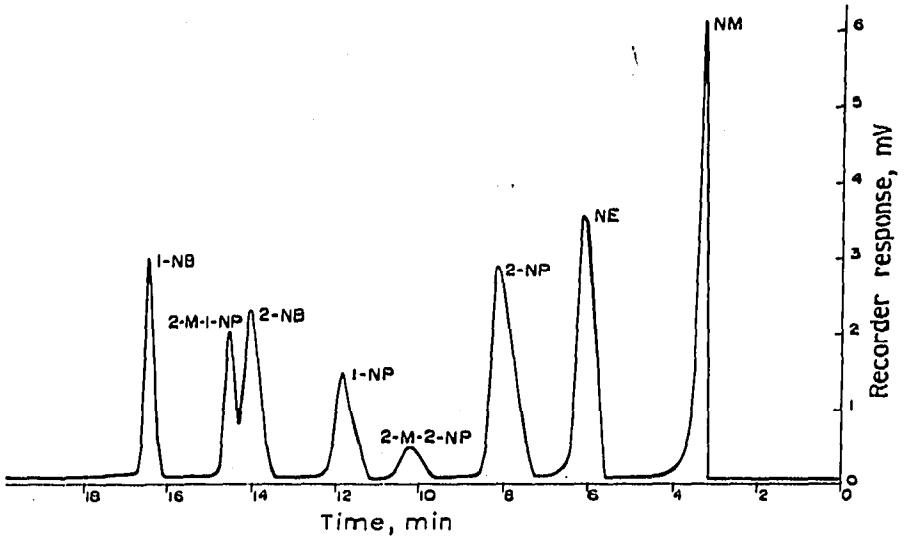

Fig. 3. Optimum ramp function separation of the C_1 to C_4 nitroparaffins. Conditions: 40° for 10 min followed by linear temperature programming at 11°/min; 60 ml H_2/min.

at a heating rate of 11°/min. Under these conditions, both the accuracy and precision of the analyses were ± 0.5 wt. % as determined from multiple replicate runs using known, gravimetrically prepared samples of the pure nitroparaffins. The oxygenated compounds were then added gravimetrically with the N–P mixture and tested in a similar fashion. Under the optimum conditions, values of R_{45} and R_{67} were, respectively, 1.80 and 0.73. It is concluded that the use of ramp function temperature programming for the analysis of the C_1 to C_4 nitroparaffins increases the resolution, R_{67}, by almost 15 % with an increase in the analysis time from the best conditions previously obtained of less than 2 min.

Chemical Engineering Department, Iowa State University, Ames, Iowa — R. M. BETHEA
and
Miami Valley Laboratories, Procter and Gamble Company, Cincinnati, Ohio (U.S.A.) — F. S. ADAMS, JR.

[1] R. M. BETHEA AND F. S. ADAMS, *Anal. Chem.*, 33 (1961) 832.
[2] W. L. JONES AND R. KIESELBACH, *Anal. Chem.*, 30 (1958) 1590.

Received January 5th, 1962