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Gas Chromatography of C1 to C4 Nitroparaffins

Abstract

simple, fast, and accurate method for gas-liquid partition chromatographic analysis for the products of a pilot plant designed for the vapor phase nitration of commercial butanes has been developed. Errors in reproducibility were less than $\pm 0.6\%$ with errors in accuracy less than $\pm 0.5\%$. The substrates used for this separation were Apiezon T grease, Lubriscal stopcock grease, and Wemco C transformer oil.

Disciplines

Catalysis and Reaction Engineering | Other Chemical Engineering | Petroleum Engineering

Comments

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terial was prepared in a standard manner using 33% (w./w.) Armeen SD on 30- to 60-mesh Chromosorb (Johns-Manville) as the stationary liquid phase. This was packed into copper tubing 22 feet long by 1/4-inch outside diameter. The tube was then coiled and used in the instrument. The number of theoretical plates for this column was calculated as being 2100 using *n*-propyl alcohol as the reference standard (2).

Procedure. The sample (mixture of alcohols and water) was injected into the instrument by means of a 0.25-ml. syringe. The chromatograph was maintained under the following conditions:

Gas, helium, 25 p.s.i., 85 ml. per minute.
 Sample size, 0.01 to 0.05 ml.
 Temperature, 88° C.
 Column, 22 ft. long, 1/4-inch diameter.
 Copper tubing filled with 33% Armeen SD on 30- to 60-mesh Chromosorb.

The areas under the peaks of the chromatogram were integrated, using a polar planimeter, and then added and calculated as area per cent. The results corresponded to the weight per cent of the individual compounds in the mixture. The water peak produced a small degree of tailing, making it necessary to extend the tailing side of the water peak to the base line, then calculating the total area under it. The extended area under the tail was calculated as water and was not included in the calculation of the ethyl alcohol peak.

RESULTS AND DISCUSSION

To test the accuracy and precision of

Table II. Retention Time of Alcohols and Water

	Boiling Point, ° C.	Retention Time,* Min.
Water	100.0	6.04
Ethyl alcohol	78.3	10.04
Isopropyl alcohol	82.3	11.88
<i>n</i> -Propyl alcohol	97.2	22.68
<i>sec</i> -Butyl alcohol	99.5	26.24
Isobutyl alcohol	107.9	39.64
<i>n</i> -Butyl alcohol	117.7	51.64

* Measured from air peaks.

this method and to find out if a direct ratio existed between the thermal conductivity responses of the individual components in the analyzed mixture and their respective concentrations, a series of synthetic mixtures were prepared and analyzed. Ethyl, isopropyl, *n*-propyl, *sec*-butyl, *tert*-butyl, and *n*-butyl alcohol were mixed with water in varying concentrations and analyzed.

The results are reported in Table I. Five-carbon alcohols were also resolved on the Armeen SD column, but their retention times were too long to include in this study.

Chromatograms for the analyzed mixtures indicate that all alcohols produce essentially symmetrical peaks (Figure 1), and that only the water fraction exhibits some degree of tailing. This was easily corrected by extending the tailing side of the water peak to the

base line and using the total area under it for the calculation of the water concentration.

The results (Table I) indicate that the determined concentrations of the alcohols and the water were in good agreement with the amounts of those materials present. The precision and accuracy in all cases were within the accepted limits for chromatographic techniques. This indicated that the thermal conductivity response per unit weight (using helium as a reference) was the same and linear with concentration, making correction factors unnecessary.

The retention times (measured from the air peak) for analyzed alcohols and water are reported in Table II. The water fraction appears as the first peak and precedes the alcohols with boiling points below the boiling point of water. This indicates that Armeen SD separates alcohols and water on the basis of their polarity.

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Gas Chromatography of the C₁ to C₄ Nitroparaffins

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► A simple, fast, and accurate method for gas-liquid partition chromatographic analysis for the products of a pilot plant designed for the vapor phase nitration of commercial butanes has been developed. Errors in reproducibility were less than ±0.6% with errors in accuracy less than ±0.5%. The substrates used for this separation were Apiezon T grease, Lubriscal stopcock grease, and Wemco C transformer oil.

THE gas-liquid partition chromatographic separation of aromatic nitroparaffins was recently announced (4). Among the substrates tested and

found acceptable were Apiezon M grease and Silicone DC 710 fluid. The former was easily overloaded, but the latter provided good separations for samples up to 25 μl. in size at 200° C. with a helium flow rate of 20 ml. per minute at column inlet conditions.

The work reported here was done to provide a simple, fast, and accurate method of analysis for the products of a pilot plant designed for the vapor phase nitration of commercial butanes.

EXPERIMENTAL

Apparatus. The chromatographic columns were made of 4.6-mm. internal diameter borosilicate glass tubing and had a packed length of 130

cm. They were surrounded by a 135-cm. long vapor jacket made of 5.1-cm. internal diameter glass tubing. The column assembly, thermal conductivity cell, recorder, and flow control system have been described (1). The recorder range used was 0 to 5 mv.

The packing was prepared by the method of Evans and Willard (2). The solid support was the -48 + 65-mesh Tyler standard screen fraction of crushed Johns-Manville Type C-22 firebrick. A substrate to brick weight ratio of 0.35 was used where dibutyl tartrate or Wemco C transformer oil (Westinghouse Electric Corp.) was used as the substrate. A ratio of 0.10 was used where Apiezon T grease (James G. Biddle Co.) or Lubriscal stopcock grease (A. H. Thomas Co.) was the substrate.

Uniformity of packing was ensured by using an electric vibrator while the columns were filled. A porous plug of glass wool was inserted at either end of the packed section to prevent any solid material from being carried into the thermal conductivity cell or the loss of any packing if the sample injection tee were blown off by a sudden change in supply pressure. Refluxing methanol, water, and isoamyl acetate in the column vapor jacket provided constant operating temperatures of 65.3°, 98.6°, and 127.8° C., respectively.

Materials and Procedure. The nitroparaffins used were supplied by Commercial Solvents Corp. The specifications, as determined by mass spectrographic analysis, are given in Table I. The helium used as the carrier gas in this investigation had a minimum purity of 99.98 mole % (The Matheson Co.).

The instruments were warmed up for 3 hours before the helium was turned on and at this time, the sample injection heater and column vapor jacket were started. The column inlet pressure was adjusted to 1353 mm. of mercury, absolute. The helium rates and column outlet pressures used are given in Table II. The flow rates were measured at column outlet conditions. The apparatus was then allowed to come to thermal equilibrium, as indicated on the recorder chart by a straight horizontal line for 10 minutes. A 20.2- μ l. sample of the test mixture was then injected through a self-sealing rubber serum cap into the column with a microsyringe. The sample injection assembly was kept at approximately 210° C. Injection and vaporization time was less than 2 seconds in all cases.

RESULTS AND DISCUSSION

Several substrates were tested—Apiezon T grease, Lubriscal stopcock grease, and Wemco C transformer oil—and gave satisfactory results. Dibutyl tartrate provided good separation at 65.3° C., but the analysis time was in excess of 50 minutes for nitromethane through 1-nitropropane. At higher column temperatures, this substrate was eluted from the column as indicated by a constantly drifting recorder base line. *N*-methyldiphenylamine, 2,2-diaminoethylamine, tributyl phosphate, and tricresyl phosphate were unsatisfactory as substrates. The retention times, which are reproducible with errors of $\pm 0.6\%$ based upon triplicate analyses, are given for the eight nitroparaffins tested in Table II for five different analysis systems.

Systems *B* and *D* were chosen for quantitative work in which mixtures of known composition were analyzed. Systems *A*, *C*, and *E* resulted in crowded chromatograms where the separation between components was less than 1.5 minutes in several instances. The results from the analyses of several known mixtures containing the four nitro-

Table I. Nitroparaffin Specifications

Nitroparaffin	Symbol	Wt. % Major Constituent	Wt. % Minor Constituents
Nitromethane	NM	99.85	NE, 0.06; 2-NP, 0.09
Nitroethane	NE	99.7	2-NP, 0.3
2-Nitropropane	2-NP	99.9+	...
1-Nitropropane	1-NP	99.9	2-NB) ... 1-NB) 0.1
2-Nitrobutane	2-NB	99.9	...
1-Nitrobutane	1-NB	99.96	...
2-Methyl-1-nitropropane	2-M-1-NP	99.82	...
2-Methyl-2-nitropropane	2-M-2-NP	99.9	...

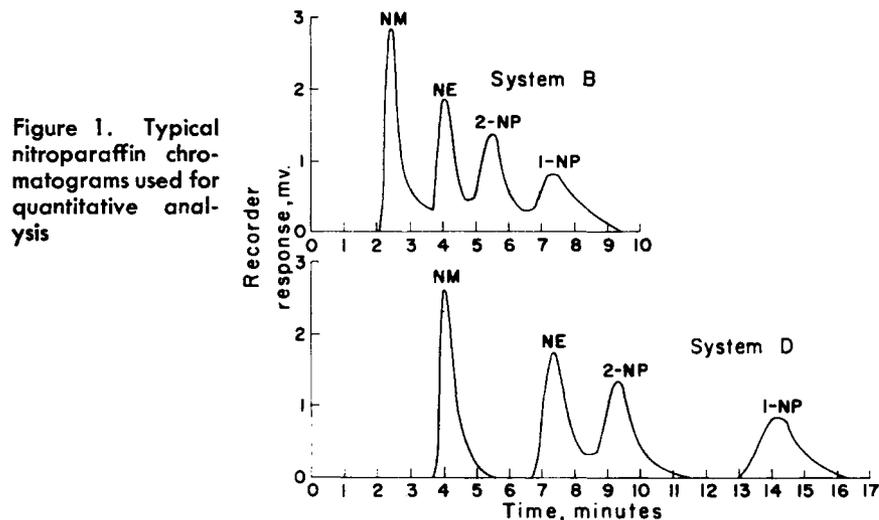


Figure 1. Typical nitroparaffin chromatograms used for quantitative analysis

Table II. Retention Times of C_1 to C_4 Nitroparaffins in Different Systems

Test System	A	B	C	D	E
Temperature, ° C.	127.8	98.6	98.6	65.3	127.8
Flow rate, μ ml./min.	44.6	30.0	30.0	30.0	47.6
Outlet pressure, mm. mercury, abs.	861	969	848	922	962
Substrate	Apiezon T		Lubriscal		Wemco C
Nitroparaffin	Retention Time, Minutes				
NM	1.77	2.38	2.05	4.16	2.25
NE	2.76	4.03	3.22	7.37	2.85
2-NP	3.43	5.42	3.93	9.24	4.54
2-M-2-NP	3.92	6.52	4.74	11.82	4.98
1-NP	4.48	7.32	5.45	14.16	5.85
2-M-1-NP	5.64	10.40	7.35	18.90	8.90
2-NB	6.05	11.34	7.35	20.78	9.83
1-NB	8.08	17.62	10.71	32.65	14.10

* Measured at ambient temperature and pressure.

paraffins of greatest commercial importance are presented in Table III. Mixtures 1, 2, and 3 were prepared from the pure compounds listed in Table I. Mixture 4 was supplied by Commercial Solvents Corp. Typical chromatograms obtained with systems *B* and *D* are shown in Figure 1.

The compositions of the test mixtures were determined directly from the peak areas without correcting the areas for any differences in thermal conductivities between the nitroparaffins. It was determined from six

random samples of chart paper that the error introduced into the analyses by cutting out the peaks and weighing them rather than measuring the areas with a planimeter is negligible, being approximately 0.3 mg. per square inch. Overlapping compounds were separated by drawing a perpendicular line from the point of minimum concentration between the peaks to the base line. The agreement of the gas-liquid partition chromatographic analyses with the known compositions in Table III shows that the peak areas are directly propor-

Table III. Analysis of Known Nitroparaffin Mixtures

Component	Added, Wt. %	Found, Wt. %			Av.
		1	2	3	
Mixture 1 ^a					
NM	28.61	28.5	28.6	28.7	28.6
NE	24.03	24.2	23.9	24.0	24.0
2-NP	24.12	24.4	24.7	24.5	24.5
1-NP	23.34	22.9	22.8	22.8	22.8
Mixture 2 ^b					
NM	24.72	24.6	25.0	25.0	24.9
NE	25.63	25.8	25.5	25.4	25.6
2-NP	25.86	25.9	25.9	25.7	25.8
1-NP	23.79	23.8	23.7	23.9	23.8
Mixture 3 ^a					
NM	36.32	36.1	36.5	36.3	36.3
NE	33.19	33.4	33.2	33.1	33.2
2-NP	17.96	18.2	17.8	18.1	18.0
1-NP	12.53	12.3	12.6	12.5	12.5
Mixture 4 ^a					
NM	13.1	13.5	13.6	13.6	13.6
NE	8.4	8.4	8.4	8.4	8.4
2-NP	39.8	39.7	39.7	39.6	39.7
1-NP	38.6	38.4	38.3	38.5	38.4
NB's	0.1

^a System B.^b System D.

tional to weight per cent for nitroparaffins. This method of correlation, as demonstrated by Fredericks and Brooks (3) for the C₂ to C₆ hydrocarbons, was expected to be valid because the two series of compounds are closely related. The errors in reproducibility for these systems were $\pm 0.6\%$ with accompanying errors in accuracy of $\pm 0.5\%$ or less, when used to analyze several four-component mixtures of known composition.

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Polarographic Determination of Titanium in Tantalum and Niobium Concentrates and Ores

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► A rapid polarographic method for the determination of titanium in the range of 0.1 to 5% in tantalum and niobium concentrates and ores is described. The supporting electrolyte is 5.4M sulfuric acid and 0.2M potassium pyrosulfate. No chemical separation is necessary. Tantalum, niobium, iron, tin, manganese, and tungsten do not interfere. Molybdenum gives a reduction wave in the same region as titanium and will interfere if present in appreciable amounts. Vanadium in appreciable amounts shows no evidence of a wave but does enhance the titanium diffusion current. However, these two elements are not normal constituents of tantalum and niobium concentrates and ores.

A SURVEY of the literature showed a lack of simple rapid methods for the determination of titanium in tantalum and niobium concentrates and ores.

The classical gravimetric methods of Schoeller (18) involve complicated and time-consuming separations before a final determination can be made. Oxi-

dation-reduction methods are inapplicable in the presence of niobium which is also reduced by metal and amalgam reductors (6).

Alimarin and Gibalo (2) used solvent extraction with cupferron and isoamyl alcohol. Several extractions had to be made before the separation of titanium was complete. Titanium has also been separated from iron, vanadium, molybdenum, tungsten, zirconium, and niobium by ion exchange (6). Excellent separations are obtained but the procedure is time-consuming.

The colorimetric determination of titanium by means of its complex with hydrogen peroxide is well known. By careful control of the conditions of color development the formation of the analogous complexes of tantalum and niobium may be suppressed. However, the relatively large quantities of iron present in tantalum and niobium ores and concentrates would interfere (17). Carvalho (4) recently described a peroxide method for titanium in ilmenite using differential spectrophotometry. The titanium was separated from the iron present by tannin precipitation before the colorimetric determination. Although the ratio of titanium to ni-

bium was 10 to 1, a correction had to be made for the latter, making the method inapplicable to niobium and tantalum-base materials where the ratio of the two is 60 to 1.

Methods for the determination of niobium and titanium in the presence of each other by the use of their thiocyanate complexes are available (3, 15). However, the critical nature of the conditions of color development makes them unattractive for control purposes.

THEORY

In the search for a suitable supporting electrolyte for the polarographic determination of titanium in tantalum and niobium base materials, certain facts had to be borne in mind. The electrolyte chosen had to form very stable solutions with tantalum and niobium which tend to hydrolyze rather easily. Any hydrolysis would increase the danger of coprecipitation of the small amounts of titanium to be determined.

Vandenbosch (20), after a systematic study, felt that an acid citrate electrolyte at pH 5.5 to 6.0 was the most satisfactory of any of the media investigated for the simultaneous determination of iron(III) and titanium(IV). However,