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ANALYSIS OF NITROGEN COMPOUNDS IN LIGHT PETROLEUM PRODUCTS BY ION EXCHANGE FOLLOWED BY GAS CHROMATOGRAPHY WITH A HALL DETECTOR AND MASS SPECTROMETRY

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SUMMARY

Nitrogen compounds, which are poisons for reforming catalysts, are generally present at very low levels (<0.1 ppm) in light petroleum products (b.p. $<180^\circ$) and must be enriched before analysis. An enrichment method by percolation of petroleum products through a column of Amberlyst 15 (H^+) macroporous cation exchanger and subsequent displacement with an alcoholic solution of potassium hydroxide is described. An enrichment factor in the range 2000-3000 (v/v) is obtained for nitrogen compounds with an acidity constant of less than $10^{-5.7}$ ($pK_a > 5.7$). Enriched fractions are separated by gas chromatography on a column of 5% squalane on Chromosorb W (80-100 mesh). Nitrogen compounds are selectively detected using a Hall detector and the individual compounds are identified by mass spectrometry. The total basic nitrogen content of a naphtha studied was 0.012 ppm and thirteen compounds were identified.

INTRODUCTION

The analysis of nitrogen compounds in light petroleum products (b.p. $<180^\circ$) is important in the petroleum industry because reforming catalysts are very sensitive to poisoning by these compounds. However, nitrogen compounds are generally present at very low levels (<0.1 ppm) and must be enriched before analysis. Another problem is that the nitrogen compounds must be identified in order to elucidate the mechanism of catalyst poisoning.

We describe here an enrichment method, the separation of compounds by gas chromatography (GC), subsequent analysis with a Hall detector, which is selective only for nitrogen compounds, and the identification of individual compounds by mass spectrometry (MS).

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EXPERIMENTAL

Ion-exchange resins

Amberlyst 15 was obtained from Rohm & Haas (Philadelphia, Pa., U.S.A.).

Chemicals

All chemicals were obtained from Prolabo (Paris, France).

Gas chromatography

We used an MT 550 gas chromatograph (Techmation, Paris, France) with a glass column (1.5 m \times 1/8 in. I.D.) filled with 5% squalane on Chromosorb W HP (80–100 mesh). The injector temperature was 200° and the oven temperature 110°. Helium was used as the carrier gas at a flow-rate of 12 ml·min⁻¹. The volume injected was 3.5 μ l.

Hall detector

The detector was obtained from Techmation. The reduction oven temperature was 870° and the hydrogen flow-rate 15 ml·min⁻¹. The solvent was water–isopropanol (85:15) at a flow-rate of 4.5 ml·min⁻¹.

Mass spectrometer

We used an AEI MS 30 instrument (AEI Scientific Apparatus, San Diego, Calif., U.S.A.). The separator temperature was 160°, the spectrometer source temperature 250° and the filament current 100 μ A.

RESULTS AND DISCUSSION

Enrichment method

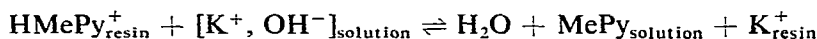
Nitrogen compounds can be classified into two groups according to their basic properties: alkylpyridines with pK_a between 5.7 and 6.8, and weakly basic compounds such as alkylpyrroles, thiazole and pyridones. The most poisonous products for reforming catalysts are the most basic so we used an enrichment method involving percolation through a column of cation exchanger in the H⁺ form^{1,2}. If we represent a basic compound by B it will be retained on the resin by a reaction of the type



Petroleum products have a very low dielectric constant and they do not swell classical ion-exchange resins of the gel type. It is necessary to use macroporous resins which have pores with diameters of hundreds of Ångströms and are filled even by apolar solvents. We used the macroporous cation-exchange resin Amberlyst 15, which contains sulphonate groups. Absorption of nitrogen compounds was studied first with a model compound, 3-methylpyridine, which is the least basic alkylpyridine (pK_a 5.74). We found that the absorption of 3-methylpyridine dissolved in isooctane or in a naphtha at a concentration of 10 ppm was quantitative. We used two columns of length 15 cm and I.D. 4.8 mm, with 20 l of the 3-methylpyridine solution at a

flow-rate of $50 \text{ ml} \cdot \text{h}^{-1}$ (the percolation requires approximately 16 days). More details can be found elsewhere³.

The methylpyridinium cations absorbed by the resin were displaced with a 0.1 M solution of potassium hydroxide in methanol. The reaction



is quantitative from left to right.

A breakthrough front is shown in Fig. 1. 3-Methylpyridine was recovered in a volume of 40 ml and the volume enrichment factor was therefore $20/0.04 = 500$.

The method was then applied to a naphtha (b.p. $< 180^{\circ}$) without the addition of 3-methylpyridine. We injected on to the resin column (total capacity 4.25 mequiv.) 39.5 l of naphtha at a flow-rate of $45 \text{ ml} \cdot \text{h}^{-1}$, which required 37 days. After washing the column with 10 ml of isooctane, we displaced the basic products with a 0.1 M solution of potassium hydroxide in methanol and the effluent was collected in 2-ml fractions.

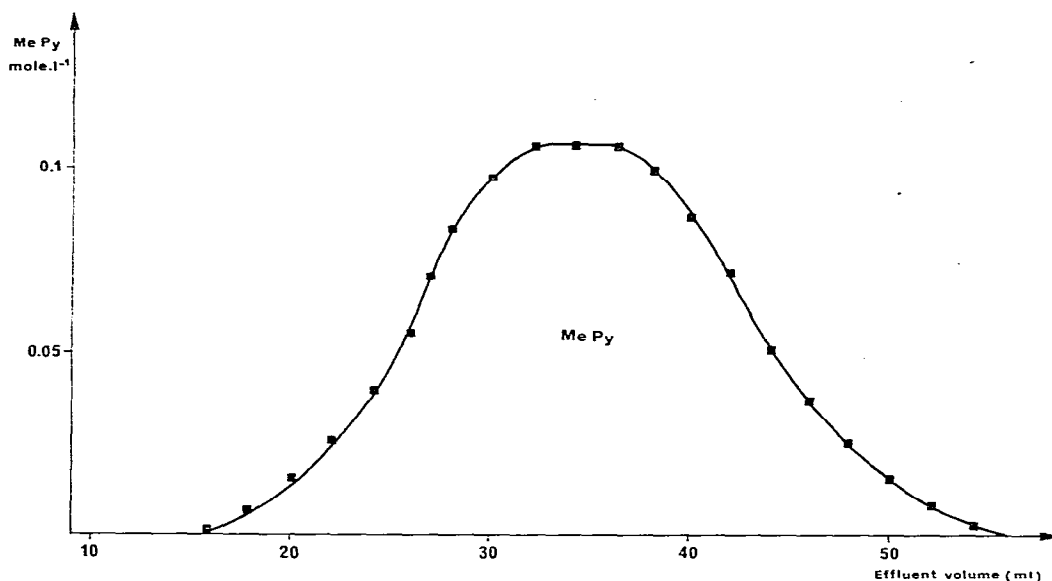


Fig. 1. Breakthrough front of 3-methylpyridine displaced from a column of Amberlyst 15 cation-exchange resin by a 0.1 M solution of potassium hydroxide in methanol. Column, $15 \text{ cm} \times 4.8 \text{ mm}$ I.D.; amount of resin, 0.854 g; total ion-exchange capacity: 3.85 mequiv.

Analysis by GC with a Hall detector and MS

Fractions of the methanolic solution were analysed by GC using a Hall detector and MS.

Hall detector. The principles of operation are as follows⁴. Nitrogen compounds emerging from the chromatographic column are converted into ammonia in an oven at high temperature under a flow of hydrogen using a nickel catalyst. Hydrocarbons are converted into methane, oxygenated products give water, sulphur compounds

give hydrogen sulphide and chlorinated compounds give hydrochloric acid; the latter two compounds are retained in a trap filled with strontium hydroxide. Methane, water and ammonia are carried by helium into a mixture of water and isopropanol (85:15) and the conductivity is measured. Ammonia increases the conductivity of the mixture and is detected by this means. This detector has a very high selectivity, principally for hydrocarbons, methane having a very low solubility and no effect on conductivity. Methanol gives a response just after injection and does not affect the analysis.

This detector was thoroughly studied with pyridine, 3-methyl- and 4-methylpyridine, 2,6-dimethylpyridine, 2,4,6-trimethylpyridine and indole. Calibration graphs are shown in Fig. 2. The linearity is good up to *ca.* 50 ppm of nitrogen. The response is similar for all of the compounds examined in the linear range.

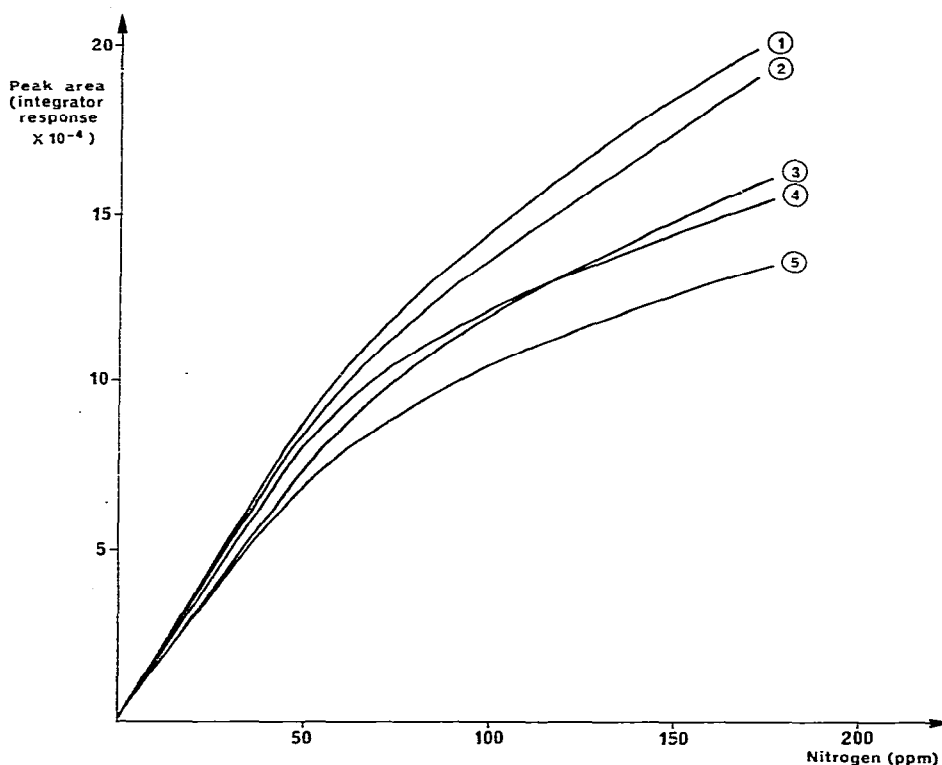


Fig. 2. Calibration graphs for various nitrogen compounds dissolved in isooctane using the Hall detector. 1 = Indole; 2 = 3-methyl- and 4-methylpyridine; 3 = 2,6-dimethylpyridine; 4 = 2,4,6-trimethylpyridine; 5 = pyridine.

The reproducibility was determined by making 15 injections of 3-methylpyridine at a concentration of 23 ppm in isooctane. The relative standard deviation was 1.2% with a confidence limit of 95%.

Various methanolic fractions were analysed by GC with the Hall detector. An example of a chromatogram obtained is given in Fig. 3.

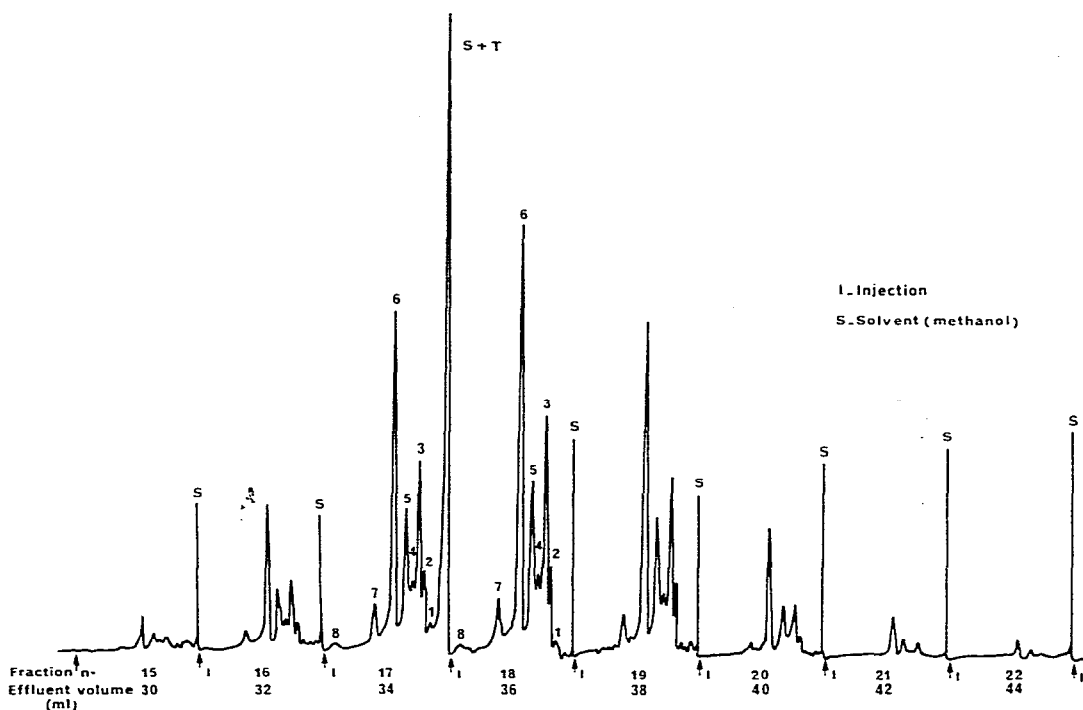


Fig. 3. Chromatograms obtained by Hall detection of a methanolic solution of nitrogen compounds concentrated from naphtha. I indicates the point of injection; S represents the peak given by methanol. Numbers of fractions and corresponding volumes are indicated under the chromatograms. For instance, fraction No. 20 is the fraction obtained between 38 and 40 ml of methanolic solution merging from the Amberlyst 15 column.

Identification of nitrogen compounds. The injection of known nitrogen compounds permits the identification of some compounds by a comparison of their retention times. Other compounds were identified by MS, as follows: 3-methyl- and 4-methylpyridine (peak 1), 2,4-dimethylpyridine (peak 2), 2,3,5- and 2,4,6-trimethylpyridine (peak 3), 2,3,6-trimethylpyridine (peak 4), 2,6-dimethyl-4-ethyl and 2,4-dimethyl-6-ethylpyridine (peak 5), N-ethylaniline (peak 6), 2-methyl-5-ethylpyridine and 4-methyl-3-ethylpyridine (peak 7) and quinoline (peak 8).

Fraction 17, which contains the most nitrogen compounds, also contains an important peak at the beginning of the chromatogram (indicated by S + T in Fig. 3) which corresponds to methanol (S) and to a product of molecular mass 105, formula $C_4H_{11}NS$, with fragments of mass 47, 63 and 65. We think this compound is a product obtained by hydrogenation and ring opening of a methylthiazole during the naphtha hydrotreatment. Snyder⁵ concluded that thiazoles were present in light petroleum products. This peak T was not observed in other fractions.

Nitrogen content. Chromatograms such as those in Fig. 3 permit the determination of the nitrogen content of different fractions and subsequently the calculation of the total nitrogen concentration in naphtha. We obtained a content of 0.012 ppm. The breakthrough front of nitrogen compounds displaced from the Amberlyst 15 resin is shown in Fig. 4. All nitrogen compounds were contained in a volume of 14 ml, and the volume enrichment factor is therefore $39.5/0.014 = 2800$.

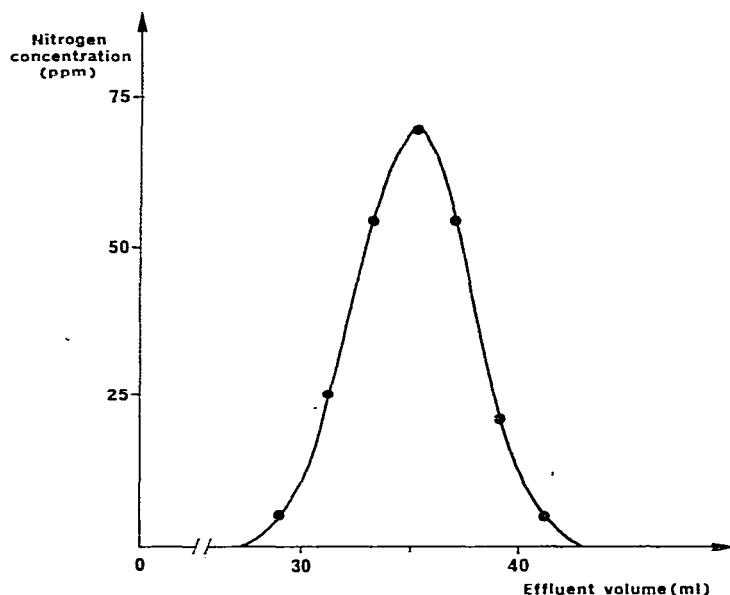


Fig. 4. Breakthrough front of nitrogen compounds displaced from a column of Amberlyst 15 cation-exchange resin by a 0.1 M solution of potassium hydroxide in methanol. Nitrogen content measured by the Hall detector. Characteristics of the column as in Fig. 1.

CONCLUSIONS

Enrichment by percolation through a macroporous cation-exchange resin in the H^+ form permits the concentration of nitrogen compounds present in light petroleum cuts such as naphtha. The nitrogen compounds may then be identified and their concentrations determined by GC with a Hall detector followed by MS.

We obtained for a naphtha a total nitrogen content of 0.012 ppm and identified 13 compounds, principally alkyipyridines, N-ethylaniline, quinoline and the hydrogenation product of a methylthiazole, formula $C_4H_{11}NS$.

The principal drawback of the method is its duration. However, as sensitivity of the Hall detector is about 1 ppm, a volume enrichment factor in the range 2000–3000 permits the volume of naphtha percolating through the resin to be reduced to about 1 l for a naphtha with a nitrogen content of 0.01 ppm. Hence the percolation time is then only 16 h and a complete analysis requires only 1 day.

ACKNOWLEDGEMENTS

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