Nitrogen Compounds in Petroleum. IV. Distribution Profiles of Nitrogen Compounds in Petroleum by Solid-Liquid Chromatography†

Akira NOMURA,* Yazaemon MORITA, and Yukitoshi KOGURE

Department of Analytical Chemistry, National Chemical Laboratory for Industry, Honmachi, Shibuya-ku, Tokyo 151

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A simple method for the characterization of nitrogen compounds in petroleum products by the investigation of the distribution profiles of nitrogen compounds using stepwise gradient elution on silica gel has been conducted. Samples were charged onto a $8\phi \times 150$ mm glass column containing 3 g of silica gel for column chromatography, followed by 15 ml of hexane to remove the non-polar bulk hydrocarbons from the sample. The eluate collected was removed from the solvent and analyzed for nitrogen, wt % yield and UV absorbance at 220 nm. The same procedure was followed by each 15 ml of 1, 3, 5, 10, 30, 60, 100%(v/v)-THF in hexane eluents. Plots of the nitrogen contents *vs.* the concentration of eluents gave characteristic patterns for petroleum distillates. The crude and residual oils from different geological sources exhibit similar nitrogen distribution profiles. There are two peak values; the peak at 3%-THF increases and that at 30%-THF decreases as the boiling range of the distillate decreases. Nitrogen compounds are distributed uniformly in a wide range of polar components with regard to adsorptivity on silica gel. The method was further applied to the reaction products of quinoline and indole by irradiation with UV light in isooctane (2,2,4-trimethylpentane) solution.

Organic nitrogen compounds in petroleum distillates poison many of the catalysts used in refining processes and cause undesirable deposits, color formation, odor, and poor storage properties. In addition, the nitrogen compounds produce on combustion fairly large amounts of nitrogen oxides (fuel NO_x), one of the sources of air pollution. Further knowledge of these nitrogen compounds should prove useful for the development of processes for their removal and of additives for their control.

Several studies have been made on the nature of nitrogen compounds in petroleum and several separation and identification schemes have been reported. Recently Snyder *et al.*[1-4] systematically studied nitrogen compounds in various petroleum distillates using liquid-solid chromatography combined with UV, IR, and mass spectrometry. Although it is desirable to isolate individual nitrogen compounds from petroleum distillates for the necessary identification by UV, IR, mass spectrometry *etc.*, the isolation is quite difficult in the cases of heavy oils, residual oils, and crude oils, since many nitrogen compounds are present and in small amounts. Therefore it is useful in practice to characterize and classify the nitrogen compounds, not each of them, in crude oil or high-boiling petroleum distillates. Potentiometric titration using perchloric acid has been applied in the characterization of basic nitrogen compounds in petroleum products.[5-8] Linear elution adsorption chromatography[9-12] has been investigated for both basic and non-basic nitrogen compounds by Snyder and Buell, and has proved a useful method for the characterization of nitrogen compounds. In previous papers, a concentration method for nitrogen compounds in various petroleum distillates using a silica gel adsorption technique and a method for the determination of trace nitrogen by Dumas method combined with a silica gel adsorption technique have been presented.[13,14]

This paper describes a simple method for the characterization of nitrogen compounds in petroleum distillates by distribution profiles of nitrogen contents in various petroleum distillates or crude oils using stepwise gradient elution, hexane–tetrahydrofuran (THF) as the eluent on a column of silica gel. The profiles of wt % yield and UV absorbance of eluate have also been determined and compared with the nitrogen contents. This method has been applied in the identification of the reaction products of quinoline and indole by the irradiation with UV light in isooctane solution. The method applies to the analysis of the mechanism in the denitrogenation[16] and characterization of coal liquefaction products and shale oils.

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Experimental

Reagents. Wako's hexane for liquid chromatography was used. Silica gel used was Wako C-200 for column chromatography (pore diameter : 70 Å). Other reagents were of reagent grade.

Apparatus. Hitachi type 356 double beam spectrophotometer was used to obtain UV absorbance. Nitrogen contents were obtained by either Kjeldahl method[15] or microcoulometric titration (Mitsubishi Kasei Model TN-01). Toshiba H400-PQ high pressure mercury lamp was used for the UV irradiation.

Procedure. Silica gel (3 g) for column chromatography was packed in a $8\phi \times 150$ mm glass column with a quartz wool plug at one end by the dry packing technique in tapping manner. The filled column (approximately 10 cm in length) was capped with quartz wool. The sample containing the nitrogen compounds (approximately 1 mg as N), diluted with isooctane, if necessary, was added into a separating funnel used as both a sample and eluent reservoir which was attached to the top of the column. A vacuum was applied and the sample was charged into the column by opening the stopcock of the reservoir. After loading of the sample, 15 ml of hexane was added to remove the non-polar bulk hydrocarbons from the sample, leaving all polar components including the nitrogen compounds adsorbed on the silica gel. An eluent flow rate of 5 ml/min or less was maintained through the elution. The eluate was collected in a suction bottle and solvent removed over a water bath. Quartz wool with solid components (asphaltenes) was removed from the column. The eluent was changed from hexane to 1%(v/v)-THF in hexane (15 ml) and the same procedure performed, followed

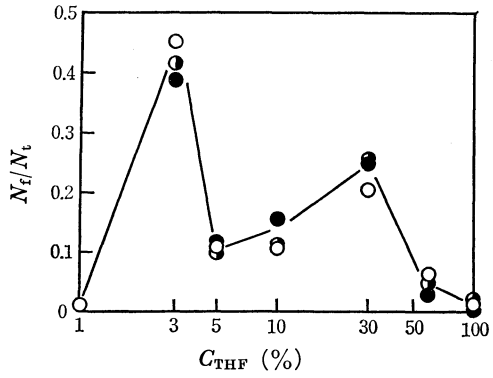

Fig. 1. Distribution profiles of nitrogen contents in crude oils. C_{THF}: Concentration of THF in hexane, N_f/N_t: relative nitrogen ratio (N_f: nitrogen in fraction, N_t: total nitrogen), ○: Kurokawa (Japan), ●: Duri (Indonesia), ◑: Shori (China).

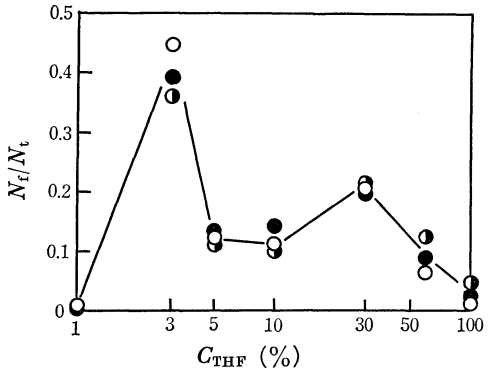

Fig. 2. Distribution profiles of nitrogen contents in residual oils. ○: Kurokawa (Japan), ●: Iranian light (Iran), ◑: Arabian heavy (Saudi Arabia).

by 15 ml of 3, 5, 10, 60, 100% (v/v)-THF in hexane eluents. Each fraction removed from the solvent was weighed and a portion used for the determination of the nitrogen content and another dissolved in THF for the determination of UV absorbance.

Results and Discussion

The silica gel pore diameter used for adsorption and separation of petroleum distillates with a wide boiling range has been investigated in detail previously.[13] A pore diameter ranging from 60 to 100 Å proved to be suitable. The silica gel used here was Wako gel C-200 with a pore diameter of 70 Å. The hexane–THF eluent system was selected because THF is one of the best solvents for petroleum and also the low boiling temperature enables simpler fractionation.

Distribution Profiles of Crude and Residual Oils. The distribution profiles for the nitrogen contents in three different geological crude and residual oils are shown in Figs. 1 and 2, respectively. The three different oils, both crude and residual, show almost the same patterns with regard to nitrogen content, and the patterns of the crude and residual oils are also the same, while the absolute nitrogen contents for each petroleum differ. The similarity in pattern between the crude and residual oils is expected since most nitrogen compounds exist in high-boiling distillates.

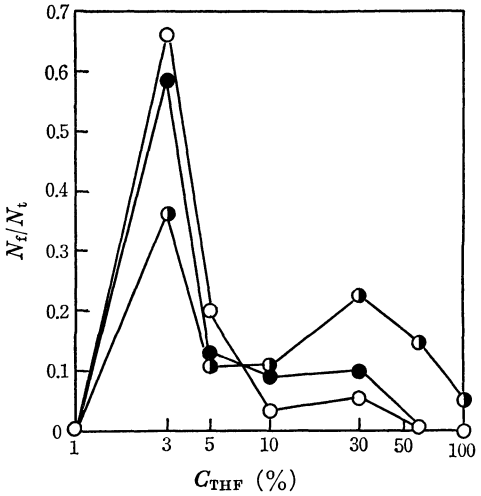

Fig. 3. Distribution profiles of nitrogen contents in different distillates.
Boiling range; ○: 170—340 °C, ●: 340—520 °C, ◑: 520 °C— tower bottom.

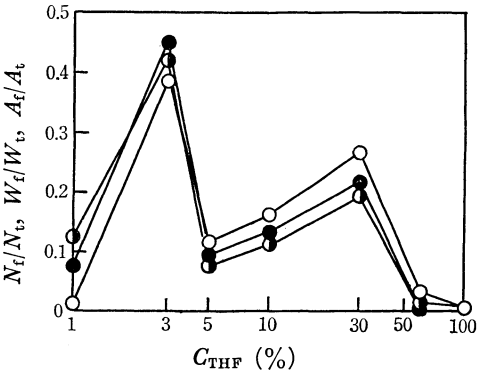

Fig. 4. Distribution profiles of polar components in crude oil. W_f/W_t: Relative weight ratio (W_f: weight of fraction, W_t: total weight), A_f/A_t: relative absorbance ratio (A_f: absorbance of fraction, A_t: total absorbance), ○: nitrogen, ●: weight, ◑: UV absorbance at 220 nm.

The two peak values (at 3 and 30%-THF eluents) are characteristic of crude and residual oils and the pattern is thought characteristic of all high-boiling distillates regardless of the fact that they come from different geological sources.

Distribution Profiles of Different Distillates. Distribution profiles for the nitrogen contents in three different distillates (boiling range : 170—340 °C, 340—520 °C, 520 °C— tower bottom) from the same sample of crude oil are shown in Fig. 3. As the boiling range of the distillate decreases, the nitrogen content at 3%-THF increases and that at 30%-THF decreases. This tendency is similar to the distillates from other crude oils. By examining the distribution profiles, the approximate boiling range can be estimated.

Distribution Profiles of Polar Components. Polar components in petroleum such as oxygen and sulfur compounds (except nitrogen compounds) are also adsorbed on silica gel and eluted with hexane–THF eluent. The relationship between the nitrogen compounds and polar compounds was investigated with

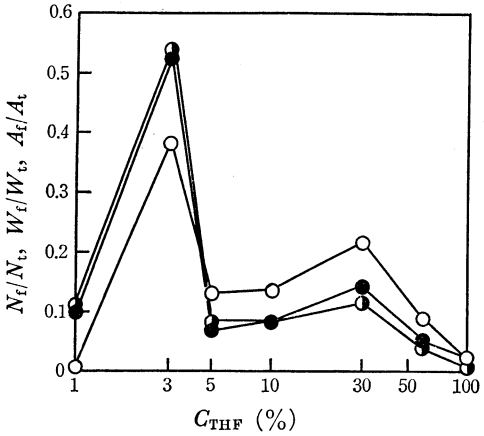

Fig. 5. Distribution profiles of polar components in residual oil. ○: Nitrogen, ●: weight, ◑: UV absorbance at 220 nm.

regard to nitrogen content, wt % yield and UV absorbance in THF at 220 nm. Since practically all fractions eluted with more than 3% THF concentration have a UV absorbance plateau between 215 and 230 nm, the absorbance at 220 nm was selected to characterize the polar components. Figures 4 and 5 indicate the relationship for crude and residual oils, respectively. The other crude and residual oils investigated exhibited similar relationships. Nitrogen compounds are considered to be distributed rather uniformly in a wide range of polar components with regard to adsorptivity on silica gel because of the good correlation among the three distribution profiles.

Application to Irradiated Products. The proposed method for the characterization of petroleum distillates was applied to the reaction products of quinoline and indole by irradiation with UV light in isooctane solution. Many reagents involving nitrogen have been examined in order to obtain standard samples for the calibration of the instrument determining nitrogen in petroleum. During the process heterocyclic nitrogen compounds were irradiated with UV light and the distribution profiles of nitrogen contents in the products were examined, the results of which are shown in Figs. 6 and 7 for quinoline and indole, respectively. Before irradiation most quinoline and indole are eluted with 10%- and 5%-THF, respectively, so the profiles are represented by single peak without a shoulder. The pattern of quinoline changed as the time of irradiation increased, and after 3 h the pattern of the products became similar to that for a typical crude oil. The pattern for indole remained rather unchanged after irradiation. It should not be concluded from the results that nitrogen compounds in crude oil are similar to the irradiated products of quinoline but the proposed method has been shown useful for the characterization of complicated products.

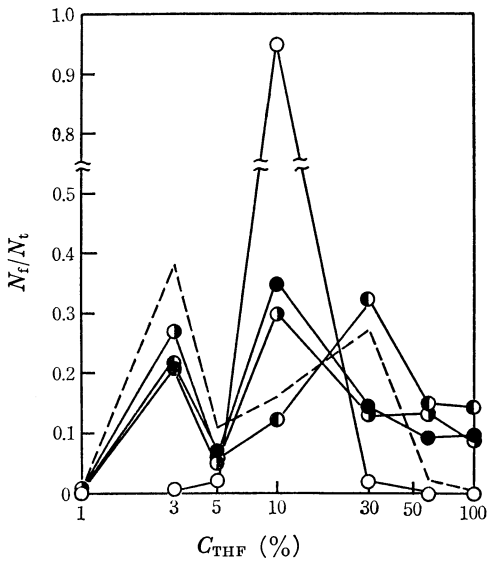

Fig. 6. Distribution profiles of nitrogen contents in quinoline irradiated with UV light.
Irradiating time; ○: 0 h, ●: 0.5 h, ◑: 1 h, ◐: 3 h, ----: distribution profile of typical crude oil.

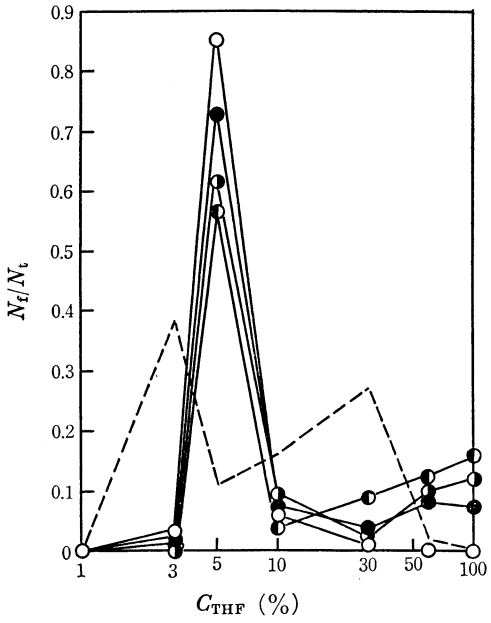

Fig. 7. Distribution profiles of nitrogen contents in indole irradiated with UV light.
Irradiating time; ○: 0 h, ●: 0.5 h, ◑: 1 h, ◐: 3 h, ----: distribution profile of typical crude oil.

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