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Note

Analysis of 9,10-dihydroanthracene by capillary gas chromatography for evaluation of transferable hydrogen in heavy oils

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Transferable hydrogen plays an important rôle in coke formation, coal liquefaction, etc. It is established that hydrogen transfer from donors stabilizes the radicals formed in the thermal decomposition reaction of heavy oils. Thus the assessment of the hydrogen-donating ability of heavy oils gives valuable information for the study of these processes.

Several methods are available for assessing the transferable hydrogen[1–9]. One involves the determination of 9,10-dihydroanthracene (DHA) produced by heating anthracene (hydrogen acceptor) and heavy oil, using ^{1}H NMR spectroscopy and an internal standard such as acenaphthene[5] or triphenylmethane (TPM)[6]. In this method, deuterated solvents such as deuterochloroform must be used to prepare the sample solution.

In order to facilitate the whole measuring procedure, we have investigated an analytical method based on capillary gas chromatography, because of its high resolution and the high sensitivity of the flame ionization detector. We will demonstrate its advantage over the ^{1}H NMR method.

EXPERIMENTAL

At first three kinds of simple samples were prepared in order to compare the quantitative results obtainable by the present method with those by the ^{1}H NMR method. DHA, TPM and 1,2,3,4,5,6,7,8-octahydroanthracene (OHA) were weighed accurately and diluted in deuterochloroform.

TPM is the internal standard for the ^{1}H NMR measurement. DHA was determined from a comparison of the peak area of its 9,10-protons (*ca.* 3.9 ppm downfield from tetramethylsilane, TMS) with that of methine proton of TPM (*ca.* 5.5 ppm).

For gas chromatographic (GC) analysis, OHA was adopted as an internal standard. Four kinds of solutions were prepared with DHA, OHA and chloroform in order to obtain a calibration curve for the chromatographic analysis.

Next, three kinds of actual samples were analysed by the two methods. These samples were prepared by almost the same procedure as described in refs. 6, 10. Heating of heavy oil and anthracene (each 0.2 g) was carried out in a sealed stain-

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less-steel tube (35 mm × 10 mm I.D.) in an inert atmosphere (nitrogen). The tube was heated to 400°C at 10°/min by a vertical electric furnace and held at this temperature for 30 min. The resultant product was extracted with *ca.* 8 ml deuterochloroform. Then a 0.5-μm Millipore filter was used to obtain a homogeneous solution, to which accurately weighed amounts of TPM and OHA were added. In general, solutions diluted twice in deuterochloroform was subjected to the ^{1}H NMR measurement, while those diluted four times in chloroform were subjected to GC.

A JNM-FX90Q FT NMR spectrometer (Jeol, Tokyo, Japan) was employed. Accumulation was carried out 200 times for each measurement.

The GC measurements were performed using a GC-9A gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a fused-silica wall-coated open-tubular capillary column (50 m × 0.25 mm I.D.) using OV-1 as liquid phase. The conditions were as follows: carrier gas, helium; flow-rate, 0.6 ml/min; injection port temperature, 300°C; sample size, 0.4–1.0 μl; splitting ratio, 1:50; flame ionization detector; column temperature, 150°C for 40 min, then increased at 15°/min to 270°C and held for 10–20 min. Under these (optimum) conditions the peak of DHA had a retention time of *ca.* 33 min. The temperature increase after 40 min was required for clean-up of the high-boiling, heavy fraction in the sample. This process is not necessary when constructing a calibration curve. The chromatographic data were processed by a Shimadzu Chromatopac C-R2AX.

RESULTS AND DISCUSSION

As is seen from Table I, the present capillary GC method is superior in precision and accuracy to the ^{1}H NMR method.

Figs. 1 and 2 exemplify the ^{1}H NMR measurement and the GC analysis, respectively. Although the actual samples contained many components, DHA was well separated under the analytical conditions stated in the Experimental. Table II shows the results of the analyses of the actual samples. Those obtained by capillary GC were in fair agreement with those by the ^{1}H NMR method. Thus the applicability of capillary GC to the analysis of DHA was demonstrated.

The capillary GC method has some advantages over the ^{1}H NMR method:

(i) It does not require the use of the deuterated solvent.

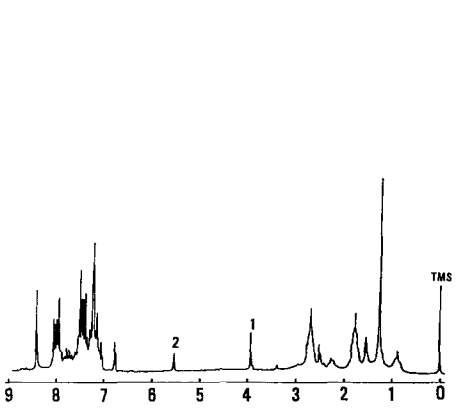
(ii) A large volume of solvent can be used to extract the product obtained

TABLE I

COMPARISON BETWEEN THE ^{1}H NMR AND CAPILLARY GAS CHROMATOGRAPHIC (CGC) METHODS

Sample	*Weighed amount of DHA (g)*	*Found (g)*	
		*NMR**	*CGC*
a	0.2165	0.2247 (0.0036)	0.2169 (0.0001)
b	0.1057	0.1085 (0.0026)	0.1064 (0.0011)
c	0.0533	0.0543 (0.0008)	0.0530 (0.0001)

* Each value is the mean of three determinations; the value in parentheses is the standard deviation.



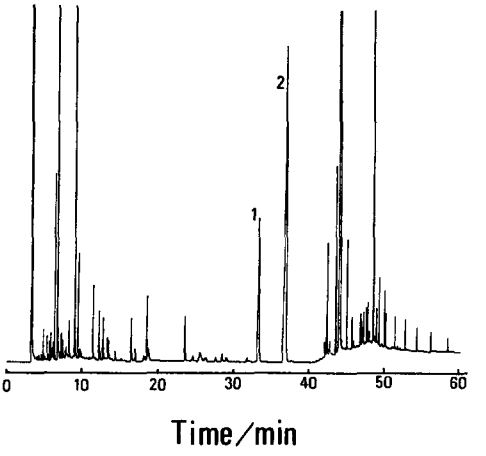


Fig. 1. ^{1}H NMR spectrum for sample 2 in Table II. Peaks: 1 (3.94 ppm) = 9,10-protons of DHA; 2 (5.55 ppm) = methine proton of TPM.

Fig. 2. Chromatogram of sample 2 in Table II. Peaks: 1 (33.31 min) = DHA; 2 (36.88 min) = OHA.

after heating and the sample solution can be subjected to analysis without concentration, *i.e.*, in very low concentration.

(iii) The amount of sample is very small.

(iv) It seems possible to assess the trace amount of transferable hydrogen in the heavy oils, which may be difficult by the ^{1}H NMR method.

(v) The handling and conditioning of the instrument are very easy.

The advantages ii–iv are attributable to the high sensitivity of the flame ionization detector.

On the other hand, the present method has some problems:

(i) The measurement is time-consuming.

(ii) The peak of the internal standard may overlap with another peak arising from a component of the sample.

(iii) In some cases it may be difficult to separate the peak of DHA completely from the peaks of the other components.

TABLE II

DETERMINATION OF DHA IN ACTUAL SAMPLES BY THE ^{1}H NMR AND CAPILLARY GAS CHROMATOGRAPHIC (CGC) METHODS

*Sample**	*NMR*	*CGC*
1	0.0818 (0.0014)**	0.0811 (0.0005)
2	0.0925 (0.0027)	0.0897 (0.0003)
3	0.1193 (0.0032)	0.1179 (0.0005)

* The oils used for the heat treatment with anthracene are petroleum residue for sample 1, middle coal liquid for sample 2 and heavy coal liquid for sample 3.

** The unit is gram DHA per gram oil. Each value is the mean of three determinations, with the standard deviation in parentheses.

Problem ii can be resolved by selecting a suitable internal standard. Even if the peak of the internal standard overlaps with another small peak, the analytical error can be minimized by adding sufficient of the internal standard that the overlapped area becomes small compared with the peak area of the internal standard. The third problem did not occur with the samples we examined.

The method presented is expected to be very useful for the evaluation of transferable hydrogen in heavy oils since it has no complications in contrast with the ^1H NMR method and the results obtained are reliable.

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