



## DETERMINATION OF CARBON AND HYDROGEN IN HYDROCARBONS BY NEUTRON SCATTERING

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*A method is proposed for the carbon and hydrogen analysis in liquid hydrocarbons, based on the moderation of fast neutrons by the liquid hydrocarbon to be analysed. The method can be adapted to the analysis of mixtures of liquid hydrocarbons flowing in pipes. The error of the determination is of the order of 3 per cent.*

### 1 — INTRODUCTION

The rapid determination of the carbon and hydrogen content in a mixture of liquid hydrocarbons is a problem of special interest in the oil and petrochemical industries, in particular when the mixture of liquid hydrocarbons flows in pipes as part of a continuous process.

For this purpose, the interaction with neutrons has been considered (1), (2), (3), (4), (5), (6).

In some cases a collimated beam of thermal neutrons is used, and the fraction of neutrons transmitted by the sample is measured with a detector of slow neutrons (2), (3).

In other cases a source of fast neutrons and a detector of slow neutrons has been used, the sample to be analysed being used as a moderator (1), (4).

The latter method, which we have used previously (3), (5), is the one employed in the present work.

To solve the problem proposed, it is necessary to find a correlation between the counting rate measured by the detector, in pulses per unit time, and a parameter  $\mu$  characteristic of the mixture to be analysed, which must be a known function of the carbon and hydrogen content.

Previously (5) we found that a good parameter was  $\mu$ , which is defined by the relation:

$$\mu = \xi + \frac{1}{4} \eta = \frac{P\delta}{A_H} + \frac{1}{4} \frac{Q\delta}{A_C} \quad (1.1)$$

with:

$$P + Q = 100 \quad (1.2)$$

where  $\delta$  is the density of the mixture at the temperature of the experiment,  $P$  and  $Q$  are the percentage in weight of hydrogen and carbon in the mixture,  $A_H$  and  $A_C$  are the atomic weights of hydrogen and carbon and therefore  $\xi$  and  $\eta$  are the hydrogen and carbon concentrations in gram-atom per cubic centimeter.

Since the ratio of the scattering cross sections of carbon and hydrogen for most of the energies involved in the

moderation process is  $\frac{1}{4}$ ,  $\mu$  is proportional to the macroscopic cross section, in this energy range.

### 2 — APPARATUS AND EXPERIMENTAL PROCEDURE

In order to reproduce the geometrical conditions of an industrial pipe line, a stainless steel cylindrical

vessel, with 15 cm diameter and 50 cm high was used as the container of the mixture to be analysed. Four different geometries, for the system source-sample-detector, were used.

In three of them (fig. 1) the detector is outside the container, and only the position of the neutron source is changed, to detect the slow neutrons obtained by transmission (c), reflexion (a), or reflexion plus trans-

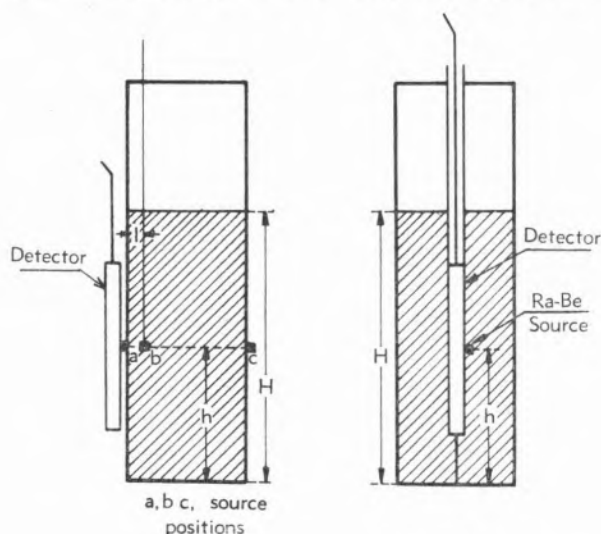


Fig. 1

Fig. 2

mission (b). The fourth geometry (d) corresponds to the use of a probe as seen in fig. 2.

The neutron source is always placed along a radius of the detector cross section at middle height.

A 10 mCi Ra-Be source, and a 12EB40 BF<sub>3</sub> proportional counter, enriched in B<sup>10</sup>, were used in all measurements. In the counting of the pulses delivered by the detector, we used the equipment and conditions described before (5), with the exception of the differentiation time constant.

The counting rates  $A_0$  were obtained by extrapolation to zero voltage of the integral bias curves. For this purpose, a differentiation time constant of 0.8  $\mu$ sec. is more convenient than the value 1.6  $\mu$ sec. used before (5), since the error involved in the extrapolation is smaller.

For a particular geometry, as the slopes of the integral bias curves, in percentage per volt, are constant, the counting rate at a particular discriminator voltage can also be used.

A height of liquid  $H = 2h = 34$  cm was used, which is more than sufficient to give saturation, as far as the activity is concerned.

For  $H = 34$  cm and for the different hydrocarbons used, the counting rate measured as a function of  $l$ , case (b), show a maximum for values of  $l$  between 1.5 and 5 cm, depending on the hydrocarbon considered, and in agreement with previous results (5).

For this reason, and to avoid errors in geometry, all the transmission plus reflexion measurements were made with the neutron source fixed in a position for which  $l = 2.2$  cm.

### 3 — EXPERIMENTAL RESULTS

The hydrocarbons used, and also their content in carbon and hydrogen, expressed as percentage by weight, are indicated in table 1.

Table 1

Product	P % by weight of hydrogen	Q % by weight of carbon	P + Q
Benzene*	7.743	92.257	100.000
Toluene*	8.753	91.247	100.000
Xylene*	9.495	90.505	100.000
Iso-octane**	15.83	84.12	99.95
n — heptane**	15.99	83.97	99.96
Cumene**	9.69	90.06	99.69
Dypentene**	11.38	85.79	97.17
Cyclohexane**	14.26	85.65	99.91
Methyl-cyclohexane**	14.10	85.72	99.82
Decaline**	12.78	86.92	99.70
Paraffin 1	14.53	85.36	99.89
Paraffin 2	14.04	85.85	99.89
Paraffin 3	13.96	85.93	99.89

\*AnalaR grade products

\*\*Technical grade products

All the analyses were made using a semi-micro combustion technique, with the exception of benzene, toluene and xylene, which we assumed to be pure enough to use the theoretical values. Only carbon and hydrogen were analysed.

For each experiment the temperature of the liquid to be analysed was measured and the density  $\delta$ , necessary to evaluate  $\xi$  and  $\eta$ , was calculated from the curves  $\delta = f(t^\circ C)$ , obtained experimentally for all pure hydrocarbons and mixtures used.

The results obtained for reflexion (b), reflexion plus transmission (c) and with the probe (d), are shown in table 2.

The difference in the values of  $\xi$  and  $\mu$ , for the same product, is a consequence of a difference in the tempe-

Table 2

Product	Reflexion			Reflexion + transmission			Probe		
	$\xi$	$\mu$	$A_0$ c.p.m.	$\xi$	$\mu$	$A_0$ c.p.m.	$\xi$	$\mu$	$A_0$ c.p.m.
Benzene	6.791	8.489	1120	6.714	8.392	2280	6.73	8.41	32400
Toluene	7.564	9.218	1300	7.494	9.133	2660	7.50	9.14	38600
Xylene	8.115	9.738	1460	8.035	9.642	3060	8.05	9.66	45600
Cumene	8.314	9.93	1500	8.25	9.86	3240	8.25	9.86	48400
Dypentene	9.822	11.38	1760	9.75	11.29	3980	9.75	11.29	60100
n-heptane	10.91	12.11	1920	10.83	12.02	4140	10.80	11.99	62400
Iso-octane	10.93	12.15	1920	10.85	12.06	4160	10.81	12.01	61800
Methyl-cyclohexane	10.84	12.22	1950	10.74	12.11	4260	10.74	12.11	64800
Cyclohexane	11.09	12.49	1920	10.96	12.34	4260	10.97	12.28	65800
Decaline	11.11	12.70	2100	11.13	12.72	4700	11.11	12.69	72000
Paraffin 1	11.15	12.52	2060	11.08	12.45	4500	—	—	—
Paraffin 2	11.01	12.42	1940	10.96	12.37	4460	—	—	—
Paraffin 3	10.51	11.87	1840	10.46	11.81	4200	—	—	—

perature when the measurements were made. For each geometry the temperature of all hydrocarbons was constant within  $\pm 1.5^\circ\text{C}$ .

According to our previous results (5), the transmission geometry is of no interest for distances between detector and neutron source of the order of the one used (15 cm).

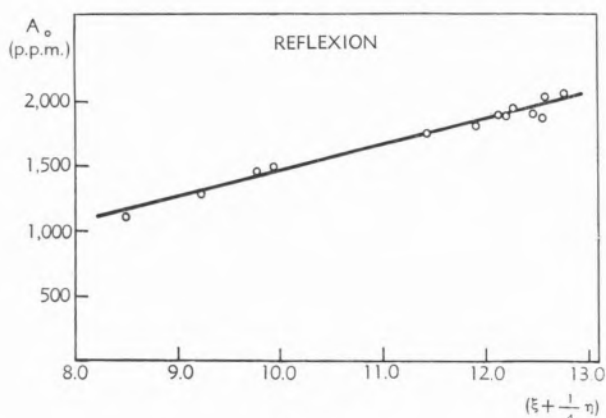


Fig. 3

In fact, when all the hydrocarbons considered are analysed with geometry (c), not only the value of the counting rate (about 450 c. p. m.) but also the sensitivity of the method are very low.

In figs. 3, 4 and 5, the plots of  $A_0$  as a function of  $\mu$  are shown. In all cases the linear correlation is better when we use  $\mu$  instead of  $\xi$ .

The slope of the linear correlation  $A_0 = f(\mu)$ , which is a measure of the sensitivity of the method, increases

in the order reflexion, reflexion plus transmission, and probe, showing that the third geometry is the most sensitive.

The error with which the value of  $\mu$  can be obtained, increases in the order probe, reflexion plus transmission, reflexion, but the order of magnitude is nearly the same in all cases, about 3 %.

The error with which  $P$  is known is always higher, but of the same order of magnitude.

#### 4 — DISCUSSION

While for a static analysis all the geometries considered can be of interest, for a dynamical analysis (hydrocarbons flowing in pipes) only the transmission and reflexion geometries are of practical interest.

According to our present and previous (5) results, for a dynamical analysis, the choice between reflexion and transmission is a function of the diameter of the pipe through which the hydrocarbon flows.

For diameters greater than about 8 cm, the reflexion geometry is the only one to be considered. Between about 6 and 8 cm, the choice of reflexion or transmission seems to be arbitrary. For diameters between 6 and 3 cm only the transmission must be considered. For diameters smaller than 3 cm neither geometry seems to be useful. In these cases the use of the method based on the transmission of a collimated beam of thermal neutrons seems to be advisable.

In order to have a continuous reading of the counting rate, it is necessary to use a ratemeter and a chart recorder instead of a scaler. Once the counting rate is known, the correlation curve  $A_0 = f(\mu)$  gives the value of  $\mu$ , which can be continuously plotted in the chart recorder, once this has been properly calibrated.

As the values of practical importance are  $P$  and  $Q$ , and, from (1.1) and (1.2)

$$P = 1.021 \frac{\mu}{\delta} - 2.128 \quad (4.1)$$

$$Q = 100 - P \quad (4.2)$$

we also need the value of  $\delta$ .

In order to have a continuous reading of the value of  $\delta$ , a system similar to the one used in the determination of  $\mu$  can be used, provided a  $\gamma$  source of appropriate energy is used, instead of a neutron source.

Since the Ra-Be source is also a  $\gamma$  source, it could be of interest to study the possibilities of using the same source for both measurements.

Once the values of  $\mu$  and  $\delta$  are measured continuously, it is also possible to have a third chart recorder which

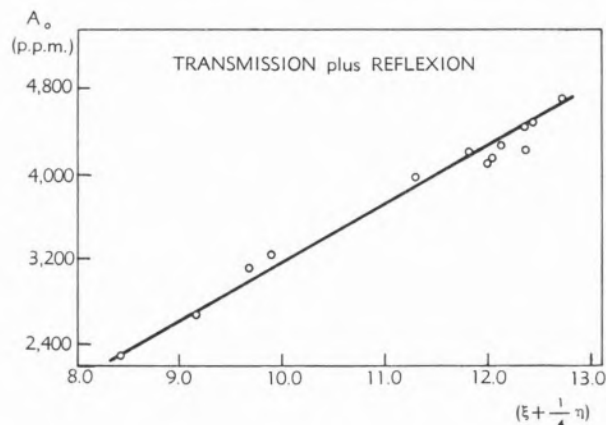


Fig. 4

plots continuously the values of  $P$  and  $Q = 100 - P$  according to the equations (4.1) and (4.2).

Since the major error involved is the error of  $\mu$ , one can expect a mean error in the value of  $P$  not higher than 3 %.

If we are only interested in static analysis, then the conclusions are different. If the amount of sample available is large enough (see fig. 2) the probe method seems to be the best. It is for instance the case with

big deposits where the probe can be immersed. For small amounts it is more convenient to use a transmission

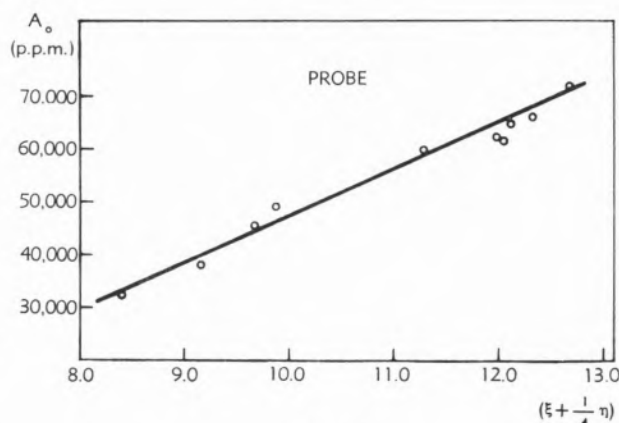


Fig. 5

method (5). For an intermediate amount of sample, the method of reflexion plus transmission can be considered.

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#### RESUMO

Propõe-se um método para dosagem de carbono e hidrogénio em hidrocarbonetos líquidos, baseado na moderação de neutrões rápidos pelo hidrocarboneto líquido a analisar. O método pode utilizar-se para análise de misturas de hidrocarbonetos líquidos em movimento em canalizações. O erro da determinação é da ordem de 3 %.

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