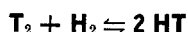
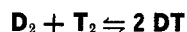
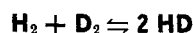


# Quantitative Analysis for the Isotopes of Hydrogen— $H_2$ , HD, HT, $D_2$ , DT, and $T_2$ —by Gas Chromatography

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Total separation of the six isotopic compounds of hydrogen—i.e.,  $H_2$ , HD, HT,  $D_2$ , DT, and  $T_2$ —using a column filled with alumina covered by ferric hydroxide at 77 °K was carried out. The conditions for good separation, symmetrical peaks, and short retention times were studied. After defining the column and, in particular, the treatment of the stationary phase which is made to undergo partial deactivation by carbon dioxide, quantitative analysis for the six compounds was perfected by using a double detection system consisting of a thermistor catharometer and an ionization chamber. The linearity ranges of these two detectors were defined. It is shown that the use of the equilibrium constants:



allows the determination of the isotopic ratios of a mixture of the six compounds by means of the ionization chamber alone. Besides, no calibration is needed for this analysis. The advantages of this method are compared with those of mass spectrometry.

THE SEPERATION of hydrogen isotopes by gas chromatography has been studied for a little less than 10 years. The first workers investigated gas mixtures containing only two isotopes, either hydrogen and tritium (1), or hydrogen and deuterium (2-7). In 1963, Carter and Smith (8) tackled the problem of three isotopes,  $H_2$ - $D_2$ - $T_2$ , and the mixed molecules, HD-HT and DT, but with mixtures in which the tritiated molecules were in the form of traces. King (9), on the other hand, separated five of the six sorts of isotopes on a column more than 7 meters long. In 1964, West and Marston (10, 11) achieved complete separation of six varieties but, as their work was mainly preparative in character, the form of the peaks left much to be desired for purposes of subsequent quantitative analysis. Botter and Cercy (12) handled this problem by capillary chromatography and recently, Conti and Lesimple (13) obtained six entirely separated peaks on a molecular sieve column, but no one had previously attempted quantitative analysis for all of the isotopes of hydrogen combined in the same mixture. This was the object of our study, and for this purpose the actual process

of separation was first improved in order to pass on to quantitative analysis of the chromatograms obtained in this way.

## EXPERIMENTAL

**Apparatus.** In view of the large quantities of tritium handled, the gas chromatograph is installed in a glove box with air ventilation. So as to have easy access to the different elements of the apparatus, it was built by the authors (with the exception of the electronic part) using vacuum-tight "Nupro" bellows valves capable of withstanding pressures of several bars,  $\frac{1}{4}$ -inch and  $\frac{1}{8}$ -inch stainless steel tubes, and Swagelok connections.

The various parts of the gas chromatograph are shown in Figure 1: the cylinder of carrier gas and the purification trap (Molecular Sieve 5A); the inlet system with the calibrated volume,  $V$ ; the column, immersed in a Dewar flask filled with liquid nitrogen (this system is less expensive and simpler than a cryostat); the detection system comprising a Gow-Mac catharometer fitted with two thermistors of 8000  $\Omega$  each, followed by a flow ionization chamber of small volume (2.5 ml) produced by M. Lesimple of C. E. N. Saclay; and a control rack with the electronic part, situated outside the glove box. This part comprises a Gow-Mac stabilized power supply (0-20 mA) connected to the catharometer, a preamplifier of the PCC type supplied by the Ateliers de Montages Electriques and an ACC5 Merlin-Gerin amplifier, both being connected to the ionization chamber. The voltage between the central electrode and the wall of the chamber is 90 V and the leakage resistance can assume two values:  $10^{10}$  and  $10^{11}$   $\Omega$ . The two detectors are connected to a Texas Instrument Servo-Ritter II two-channel recorder and to an Infotronics CRS 100 integrator.

As will be seen later, it is quite possible to work only with the ionization detector, the operation and stabilization of which take only a few minutes.

**Reagents.** Tritium was supplied by the Commissariat a l'Energie Atomique Département des radio-éléments. The other gases used were supplied by Air Liquide: 99% neon; equimolecular  $H_2$ - $D_2$  mixture; hydrogen of quality "U"; and 99.99% carbon dioxide for deactivation.

The molecular sieve used to purify the neon was of Type 5A, had a grain size of 0.3-0.4 mm, and came from Touzart-Matignon as did the activated alumina used as the stationary phase.

The copper columns used had an internal diameter of 4 mm. After filling, they were placed in a primary vacuum for 2 hours before undergoing partial deactivation with carbon dioxide.

**Procedure.** The neon, leaving the cylinder at a pressure of 3 bars, passed through a molecular sieve trap cooled to 77 °K by liquid nitrogen before entering the reference part of the thermal conductivity cell. A regulator,  $R$ , consisting of a needle valve, enabled the carrier-gas flow to be adjusted exactly. The carrier gas then arrived at the inlet system before passing into the column and returning to the catharometer (measuring part). On leaving the latter, it passed through the ionization chamber and then through a soap-bubble flow-meter.

**INLET SYSTEM.** The gaseous specimen in  $E$  is expanded into the calibrated volume,  $V$ ; the latter is then isolated

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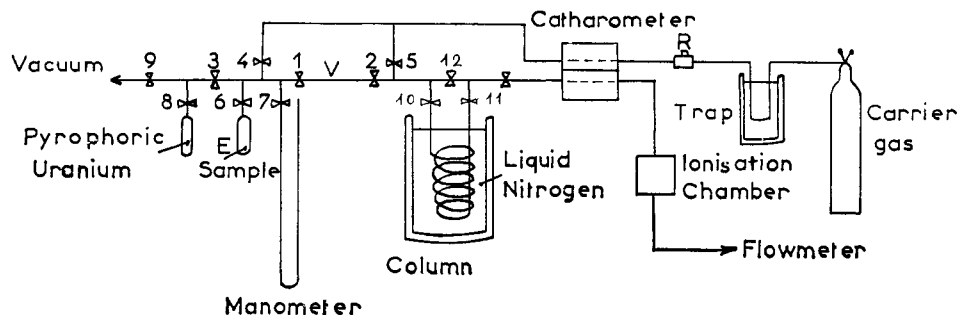


Figure 1. Apparatus

after pressure has been measured. If the gas is rich in tritium, it is recovered by adsorption over a pyrophoric uranium furnace. In the opposite case, the dead volume is evacuated by the vacuum pump.

## RESULTS AND DISCUSSION

The ideal experimental conditions for quantitative analysis of the chromatograms will now be defined.

**Choice of Carrier Gas.** Neon has been used as carrier gas for four reasons: its diffusion coefficient in hydrogen is lower than that of helium; it is slightly adsorbed on the stationary phase, giving peaks with less spread and faster elution; its thermal conductivity is very different from that of hydrogen, whereas that of helium is fairly similar. This last property is the particular advantage of neon and the detector is much more sensitive in consequence (about 20 times); and it gives the opportunity for determining  $^3\text{He}$ .

Hydrogen can be used as carrier gas, but the molecular hydrogen content will be obtained indirectly and the sensitivity of the detector will be similar to that obtained with helium.

**Stationary Phase.** The stationary phase consists of activated alumina treated as described by Moore and Ward (4): it is sieved between 125 and 150 microns and then covered with ferric hydroxide. After drying and activation in vacuum at 220 °C for 24 hours, it is sieved a second time. The column is kept straight during filling, and then is wound into coils 100 mm in diameter. The column is then deactivated with carbon dioxide. This deactivation is very important because it, in fact, determines the quality of separation. If a highly efficient column is desired, one has first to activate strongly the alumina for its specific surface determines the quantity of carbon dioxide which can be adsorbed (100 to 150 mg of  $\text{CO}_2$  per meter of column) and second to fill the column quite compactly and plug its ends carefully to avoid any travelling of the stationary phase. Thus, suitable separation and short retention times may be obtained on a 3-meters-long column as indicated in Figure 2.

This chromatogram combines the necessary conditions for quantitative analysis, namely good resolution, peaks symmetrical enough to rely on measurement of their height, and retention times short enough for several analyses to be made per day.

Tests were carried out on a pure alumina column without any ferric hydroxide treatment in order to confirm separation of the isomers of hydrogen. Extremely intense activation (72 hours in vacuo at 200 °C) is needed to obtain splitting of the hydrogen peak.

**Quantitative Analysis.** One could make a ternary mixture  $\text{H}_2\text{-D}_2\text{-T}_2$  of known composition, equilibrate it, and calculate the concentrations of the six constituents by means of the equilibrium constants. This calculation is not easy, despite

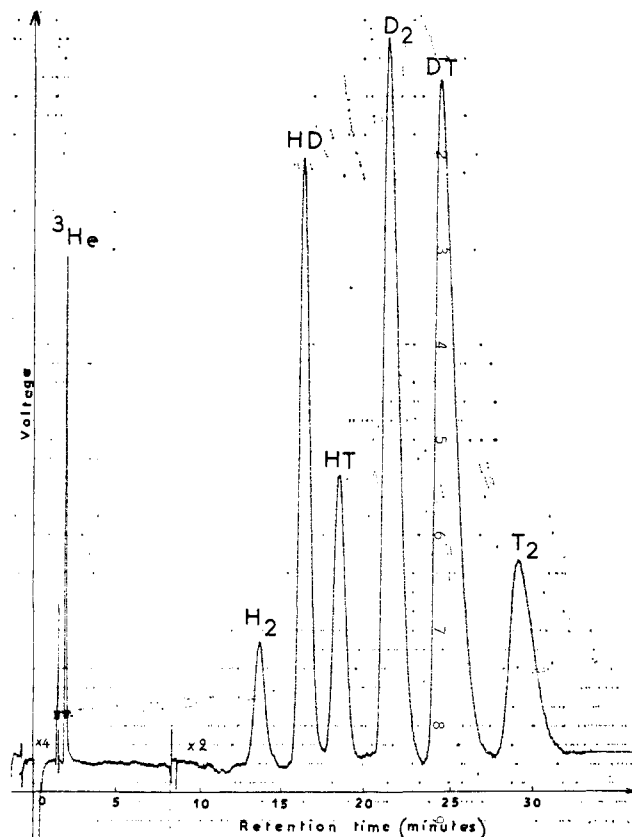


Figure 2. Separation of  $^3\text{He}$ - $\text{H}_2$ - $\text{HD}$ - $\text{HT}$ - $\text{D}_2$ - $\text{DT}$ - $\text{T}_2$  on a 3-meter column

Flow: 200 ml/min

the fact that it involves three equations with three unknowns. Therefore, it is more convenient to undertake a different calibration for each detector.

**IONIZATION CHAMBER.** The response of the ionization chamber is proportional to the intensity of the radiation passing through it. Consequently it is sufficient to have a sample with a known molecular tritium content. To do this, all the impurities are determined by mass spectrometry and gas chromatography, and the tritium content is deduced by difference. For mixtures containing HT, DT, and  $\text{T}_2$  and previously analyzed by mass spectrometry, it was confirmed that, other things being equal, the ratio of the areas of the different peaks depended exclusively on the quantity of tritium. Therefore, the response factor of the chamber is deduced from the measurement of the surface area of the peak of tritium (in microliters of tritium per square millimeter of surface area for example). This factor will be the same for the two other radioactive compounds, HT and DT, to within a factor of 2.

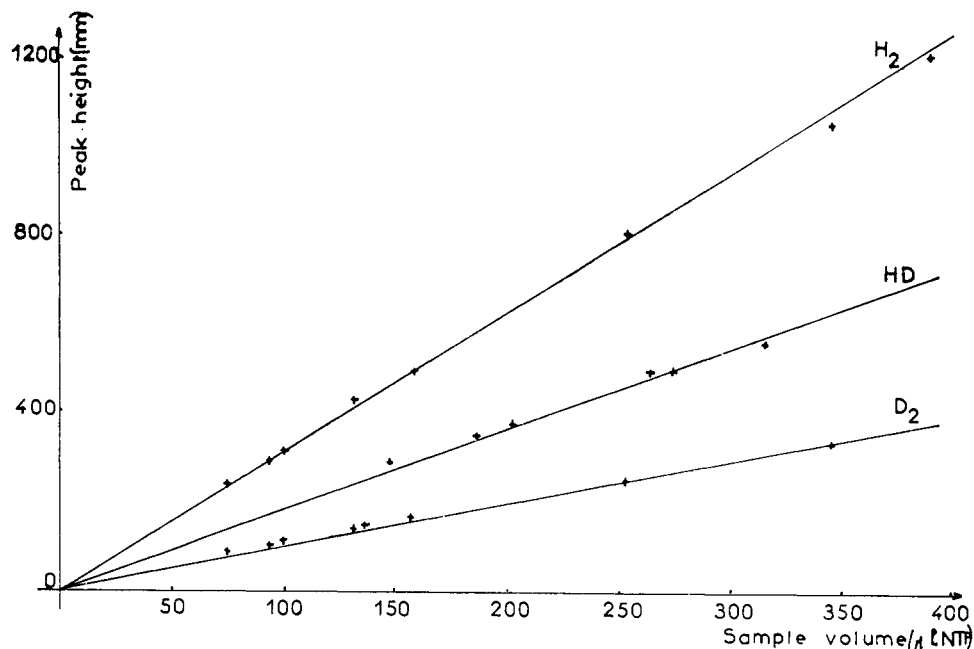


Figure 3. Calibration curves for  $H_2$ ,  $HD$ , and  $D_2$

**CATHAROMETER.** The plotting of the calibration lines for hydrogen, deuterated hydrogen, and deuterium is much more complex because, contrary to what takes place for the tritiated molecules, the response of the detector depends on the nature of the compounds. It is therefore necessary to make three separate calibrations, one for each of the three substances. Although it is possible to obtain hydrogen and deuterium pure enough for the calibration curves to be plotted without ambiguity, the same does not apply to deuterated hydrogen. Not having the latter compound, a hydrogen/deuterium mixture of known composition had to be used for calibration. This mixture was equilibrated by means of a tungsten filament heated to red for 5 minutes.

The concentrations of the different sorts are then governed by the relation:

$$\frac{[HD]^2}{[H_2][D_2]} = K_1(\theta).$$

$K_1$  depending only on temperature  $\theta$ .

For reasons explained later, the equilibrium temperature used was 520 °K, then the value for  $K_1$  was 3.46 (14). For a

mixture initially containing 50% hydrogen and 50% deuterium, the composition after equilibration is therefore as follows:

$$H_2 = 0.257$$

$$D_2 = 0.257$$

$$HD = 0.486.$$

**LINEARITY.** Figure 3 shows the perfectly linear calibration in  $H_2$ ,  $HD$ , and  $D_2$  of the thermal conductivity cell. As the peaks are tapered and symmetrical, only the heights and not the areas were measured. These calibrations remain linear up to quantities of 400  $\mu$ l for each component. Beyond that, it was noticed that the lines curved downward.

Good linearity both for small and large quantities of tritium (up to 150  $\mu$ l STP) was found for the ionization chamber. In this case peak areas were measured.

**LIMITS OF DETECTION.** The detection limits of the catharometer were comprised between 1 and 5  $\mu$ l per 5 mm of peak height (100 mm of scale correspond to 1 mV). It is quite obvious that these limits are infinitely lower for the ionization chamber, which never operated at its maximum sensitivity, since the problem of traces did not concern us. However, it is easy to detect as little as  $10^{-3}$   $\mu$ l of tritium.

(14) P. Pascal, "Nouveau traité de Chimie Minérale" Tome 1 page 924, Masson et Cie, Paris 1956.

Table I. Separation Factors

	This report	(8)	(9)	(10)	(13)
HD/ $H_2$	1.22	1.22	1.13	1.09	1.24
HT/HD	1.13	1.22	1.09	1.10	1.15
$D_2$ /HT	1.16	1.05	1.12	1.05	1.25
DT/ $D_2$	1.15	1.24	...	1.15	1.15
$T_2$ /DT	1.17	1.13	...	1.14	1.16
Length of column in meters	3.00	5.80	7.30	7.30	2.20
Temperature	-196 °C	-196 °C	-196 °C	-196 °C	-156 °C

The separation factors calculated here and those given in reference (13) are obtained from the ratios of the retention times corrected for dead volume, whereas those given in references (8), (9), and (10) are calculated from the retention times taken after injection.

**Table II. Resolution and Number of Theoretical Plates**

		HD/H <sub>2</sub>	HT/HD	D <sub>2</sub> /HT	DT/D <sub>2</sub>	T <sub>2</sub> /DT
<i>R</i>	This re- port (13)	...	1.80 1.56	2.16 2.76	1.75 1.77	2.14 1.78
<i>n</i>	H <sub>2</sub> ...	HD 3800	HT 4200	D <sub>2</sub> 3200	DT 3200	T <sub>2</sub> 3600

**Table III. Calculation of the Equilibrium Constant**

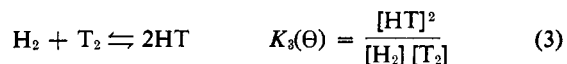
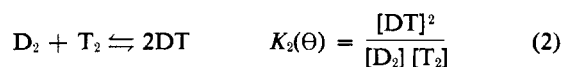
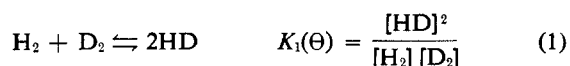
No. of samples	<i>x</i> %	<i>k</i> measured	<i>K</i> <sub>3</sub> calculated
1	2.06	80.0	3.35
2	4.30	36.7	3.27
3	9.40	16.0	3.25

**Table IV. Extreme Values of *K*<sub>3</sub> against Uncertainty on *x***

No. of samples	( <i>x</i> - Δ <i>x</i> ) %	( <i>x</i> + Δ <i>x</i> ) %	<i>k</i>	<i>K</i> <sub>3</sub>
1	1.96		80	3.18
1		2.16	80	3.52
2	4.10		36.7	3.10
2		4.50	36.7	3.43
3	9.20		16.0	3.17
3		9.60	16.0	3.33

**Separation Factors  $\alpha$ ; Resolution Factors *R*; Number of Theoretical Plates *n*.** If these results are compared with those obtained by different authors for these same separations, it may be seen that the separation factors  $\alpha$  are approximately the same (Table I). However, the resolution factor  $R = 2dr_2 - dr_1/\omega_2 + \omega_1$  is more illustrative of the separation level because the separation factor keeps the same value whether the column is short or long, and the flow rate slow or fast. So the following values for *R* and *n* were obtained (Table II).

**Equilibrium Constants.** In equilibrium, the concentrations of the six sorts of isotopes are linked by the relations:



The values  $K = f(\Theta)$  are known (14), but different temperatures are used for a mixture equilibrated at high temperature and reduced to ordinary temperature; some authors use the temperature at which the equilibrium is achieved but others consider that the equilibrium regresses and that the temperature of the mixture at the moment of introduction should be used. Use of an ionization chamber as detector is a worthwhile contribution to this difficult problem.

Let us consider an equilibrated mixture H<sub>2</sub>-HT-T<sub>2</sub> obtained from very pure hydrogen and tritium; concentration of the latter was determined after determining the impurities it contained, by calculating:

$$\tau \% = 100 - \Sigma \text{ impurities.}$$

Determination with the ionization chamber ensures that the value  $\tau$  of the concentration falls within the confidence interval allotted to the concentration found by counting. The isotopic composition of the mixture related to one mole is then as follows:

	H <sub>2</sub>	T <sub>2</sub>	HT
Before equilibrium	1 - <i>x</i>	<i>x</i>	0
At equilibrium	1 - <i>x</i> - <i>a</i>	<i>x</i> - <i>a</i>	2 <i>a</i>

The equilibrium constant is given by the relation (3)

$$K_3(\Theta) = \frac{4a^2}{(1 - x - a)(x - a)}$$

To eliminate the influence of random variations from one experiment to another, the value of the equation

$$k = \frac{[\text{T}_2] \text{ at equilibrium}}{[\text{HT}] \text{ at equilibrium}}$$

was utilized—i.e., with the notation used:

$$k = \frac{x - a}{2a}$$

$$\text{then } x = \frac{k(2k + 1) K_3}{2[(1 + kK_3)(k + 1)]}$$

The value of the constant is determined by using a mixture with a known composition *x* such that a large relative variation in *k* and *x* only produces a small relative variation in *K*<sub>3</sub>. Uncertainties in the measurement of *k* are very low with a digital integrator and have little effect on the value of *K*<sub>3</sub>. Calculation indicates that the error on *K*<sub>3</sub> will be minimal when *x* is minimal.

Three sets of experiments with hydrogen-tritium mixtures at a high hydrogen concentration were carried out; the results obtained are given in Table III.

Assuming the uncertainty Δ*x* to be 5%, which is much greater than the actual uncertainty, the resultant error for the value of *K*<sub>3</sub> does not modify the given order of magnitude, as is shown by the values in Table IV.

Under experimental conditions, therefore, the appropriate value for *K*<sub>3</sub> would seem to be about 3.3, which corresponds to an equilibrium temperature of 520 °K. By analogy the same temperature was chosen to determine the other equilibrium constants, *K*<sub>1</sub> and *K*<sub>2</sub>.

**Use of the Results.** UTILIZATION OF THE CATHAROMETER AND THE IONIZATION CHAMBER. In routine analysis the H<sub>2</sub>, HD, and D<sub>2</sub> concentrations are calculated by referring to the catharometer calibration curves, while those of the ionization chamber are used for measuring HT, DT, and T<sub>2</sub>.

UTILIZATION OF THE IONIZATION CHAMBER WITH CALIBRATION. However, if an equilibrated mixture is to be analyzed, the only measurement of the three radioactive compounds, which is more sensitive and more accurate, enables the composition of the gas to be found, because the three constants are known. If the concentrations of HT, DT, and T<sub>2</sub>, measured at the ionization chamber are *l*, *m*, and *n*, respectively, the values [H<sub>2</sub>] = *y*, [HD] = *z* and [D<sub>2</sub>] = *t* are deduced from Equations 1, 2, and 3:

$$y = \frac{l^2}{nK_3} \quad z = \frac{l \cdot m}{n} \sqrt{\frac{K_1}{K_2 \cdot K_3}} \quad t = \frac{m^2}{K_2 \cdot n}$$

At 520 °K the equilibrium constants are *K*<sub>1</sub> = 3.64, *K*<sub>2</sub> = 3.93, and *K*<sub>3</sub> = 3.30, respectively.

UTILIZATION OF THE IONIZATION CHAMBER WITHOUT CALIBRATION. Furthermore, if isotopic rather than concentration ratios are taken into account, calibration may be neglected altogether. The mixture is first equilibrated and, in fact, only two data are retained:

—the HT-T<sub>2</sub> peak areas ratio:  $S_{HT}/S_{T_2}$

—the DT-T<sub>2</sub> peak areas ratio:  $S_{DT}/S_{T_2}$

And so it will be possible to calculate the three isotopic ratios  $\frac{H}{H+D+T}$ ,  $\frac{D}{H+D+T}$ , and  $\frac{T}{H+D+T}$  with the help of the following ratios:

$$\frac{[HT]}{[T_2]} = 2 \frac{S_{HT}}{S_{T_2}}$$

$$\frac{[H_2]}{[T_2]} = \frac{4}{K_3} \cdot \left( \frac{S_{HT}}{S_{T_2}} \right)^2$$

$$\frac{[DT]}{[T_2]} = 2 \frac{S_{DT}}{S_{T_2}}$$

$$\frac{[D_2]}{[T_2]} = \frac{4}{K_2} \cdot \left( \frac{S_{DT}}{S_{T_2}} \right)^2$$

$$\frac{[HD]}{[T_2]} = 4 \sqrt{\frac{K_1}{K_2 \cdot K_3}} \cdot \frac{S_{HT}}{S_{T_2}} \cdot \frac{S_{DT}}{S_{T_2}}$$

In these conditions, the catharometer becomes useless and is only switched on for analysis of <sup>3</sup>He.

For the exploitation of the results, a Programma 101 Olivetti is used. After inlet of the magnetic card containing the computer program, one has only to type the three values of the areas of HT, DT, and T<sub>2</sub> and after a few seconds the isotopic ratios are obtained. If the gas contains no impurities, these ratios are equal to the concentrations.

Table V gives the results obtained by means of the two methods of calibration and the results obtained by the previously used standard reference method (mass spectrometry).

This chromatographic method requires only relatively simple equipment; it is quick and gives quantitatively useful results.

Table V. Calculation of the Composition of a Mixture from the Values Given by the Ionization Chamber

	Measured results by referring to the catharometer calibration, %	Calculated results from the values of the ionization chamber, %	Mass spectrometry, %
H <sub>2</sub>	5.8	5.2	5.2
HD	14.6	14.0	13.7
D <sub>2</sub>	10.1	10.4	10.4
HT	19.0	19.2	18.5
DT	29.2	29.6	29.9
T <sub>2</sub>	21.3	21.6	22.3

For routine checks, though the analysis takes longer on the average, we have replaced mass spectrometry by gas-phase chromatography for the following reasons:

The separation of HT-D<sub>2</sub> is not obtained by mass spectrometry unless the resolution of the apparatus is better than 1200 and the results have to be quantitative at this resolution.

Helium-3, which is always present in the mixtures, is easily separated and determined by gas chromatography (helium comes out after 3 minutes), whereas it introduces an additional difficulty in the utilization of mass spectrograms.

Gas chromatography gives more reproducible results.

The operation of the gas chromatograph is more reliable and less delicate than that of the mass spectrometer.

The capital outlay is smaller.

For mixtures with a low hydrogen content, determination of the latter is fairly inaccurate in mass spectrometry.

#### ACKNOWLEDGMENT

The authors thank G. Froment for excellent cooperation.

RECEIVED for review January 18, 1969. Accepted July 16, 1969.