THE QUANTITATIVE DETERMINATION OF HYDROGEN IN GASES, BY GAS CHROMATOGRAPHY WITH HELIUM AS THE CARRIER GAS

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Gas-chromatographic analysis of gaseous mixtures containing hydrogen with helium as carrier gas is easily achieved qualitatively, but an exact quantitative analysis presents some difficulties. Hydrogen has a very high thermal conductivity, higher than other gases used as carriers in gas chromatography (see Table I). Hence the hydrogen peak in a chromatogram obtained with a thermoconductivity detector (thermistors or katharometers) presents an inversion of the polarity. Furthermore it is necessary to apply a correction factor which is greater than the ratio between the conductivity of the hydrogen and the carrier gas. When helium is used and this, for several reasons, is considered the best carrier gas in the majority of cases, the correction factor is very high, causing a considerable error.

TABLE I

THERMAL CONDUCTIVITY OF COMMONLY USED CARRIER GASES

Gas	Thermal conductivity at 0° (cal/cm/sec °C)
H_2	40.0
He	33.6
Ne	10.9
N_2	5.7
Ar	4.0
CO_2	3.4

All these reasons, however, do not completely account for the problems connected with the quantitative determination of hydrogen. The chief difficulty has been, as shown by several authors[1-4], that in gaseous mixtures thermal conductivity is not a linear function dependent on the concentration but shows maxima and minima. For example, the hydrogen–helium curve shows a minimum for low hydrogen concentrations (approximately 8 % H_2) (Fig. 1).

A study of the behaviour of the curve, which is affected by many factors, such as detector temperature, filament temperature, detector type, and flow rate of carrier, is not included in the present work. However, we would like to show that, on increasing the injected amount of hydrogen, the peak is at first positive, and then becomes "M" shaped, with the central "V" of the "M" largely extending on to the negative side

of the recorder (Fig. 2). The correction factor changes considerably and is not linear with respect to the concentration of hydrogen in helium.

Although it is possible to obtain a calibration curve useful from 0 to 100 % of hydrogen, such a plot is only feasible if a detector of known characteristics is used under fixed operational conditions. In addition, the plot requires numerous analyses.
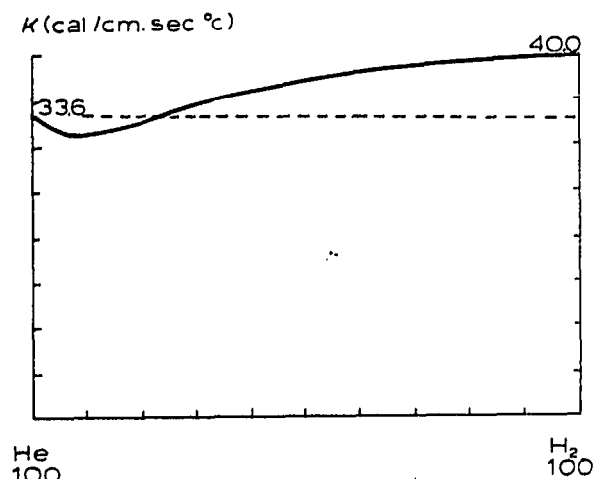
K (cal /cm. sec °c)

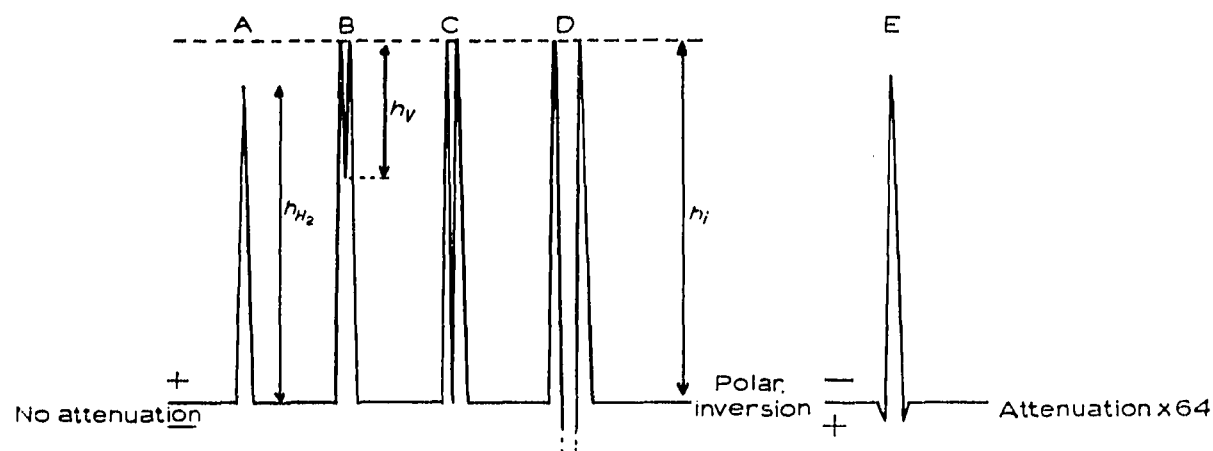Fig. 1. Thermal conductivity of hydrogen–helium mixtures.

Fig. 2. Hydrogen peak form for increasing hydrogen concentration.

The three methods reported here are, on the contrary, very rapid but notwithstanding this appreciably accurate. Each of them can be used according to the particular composition of the actual sample. The methods are:

(a) simultaneous calibration with air;
(b) simultaneous calibration with hydrogen;
(c) correction factor determination.

SIMULTANEOUS CALIBRATION WITH AIR

This is the more rapid method, and can be used when the chromatographic column elutes completely all the components of the mixture.

The calibration is made as follows: We calculate the areas of all the peaks, except the hydrogen one, and apply the necessary correction factors. We then inject an amount of air (or pure gas) exactly equal to the volume of the original sample, and calculate, applying the appropriate correction factor, the area of the peak obtained.

The difference between the corrected air peak area and the sum of corrected areas of the actual sample peaks corresponds to the amount of hydrogen in the mixture.

$$S_{H_2} = S_{air} - \Sigma_n S_n$$

The correction factor of air (or pure gas employed) is obviously applied to the hydrogen area. The maximum error of this method is estimated as within $\pm$ 2 % of the amount of hydrogen.

SIMULTANEOUS CALIBRATION WITH HYDROGEN

This method can also be applied when the elution of the components is not complete (*i.e.* when any peak has a very high retention time or is completely absorbed by the stationary phase). For this reason the method is useful in the analysis of very complex mixtures, requiring different columns successively.

The calibration is made as follows: If the hydrogen peak has the shape shown in Fig. 2, (A) or (E), we measure its height, whereas the other peaks are normally calculated by area. If the shape of the hydrogen peak is as in Fig. 2 (B) or (C), we measure the length of the central "V". (It must be emphasized that, with fixed analysis conditions, the "inversion height" is strictly constant, corresponding to a well determined hydrogen/helium ratio in the detector.)

After analysis of sample, a series of mixtures with known amounts of hydrogen, near to the supposed amount in the sample, are injected. A plot of the heights of the obtained peaks, or the lengths of the "V" inversions, against the hydrogen concentration will frequently be a straight line over the restricted range in question. By interpolation it is possible to determine the amount of hydrogen in the actual sample.

For good accuracy it is essential that the analytical conditions for the sample and the reference mixtures are identical, that the sample volume can be reproduced precisely, and that the calibration of the reference mixtures is exact. The last condition would require 100 % pure hydrogen for reference mixtures, which is very difficult to obtain even from electrolysis.

A method has been studied which permits the use of technical hydrogen, containing a small percentage of nitrogen and oxygen. Using hydrogen/air mixtures with the hydrogen concentration increasing to the maximum which can be obtained from the hydrogen source, the height of the hydrogen peak, or the length of the "V" inversion is plotted against the areas of the peaks of the impurity gases. By extrapolation to zero area of impurity, it is possible to determine the height corresponding to 100 % of hydrogen.

We can now calculate a factor f as follows:

$$f = \frac{\text{height of peak of hydrogen available}}{\text{extrapolated height of peak of 100 % pure hydrogen}}$$

By multiplying the values obtained by interpolation of "heights vs. hydrogen concentration" plot by this factor, we can obtain such an accuracy as would have been obtained if 100 % pure hydrogen had been used for reference mixtures (see Fig. 3).
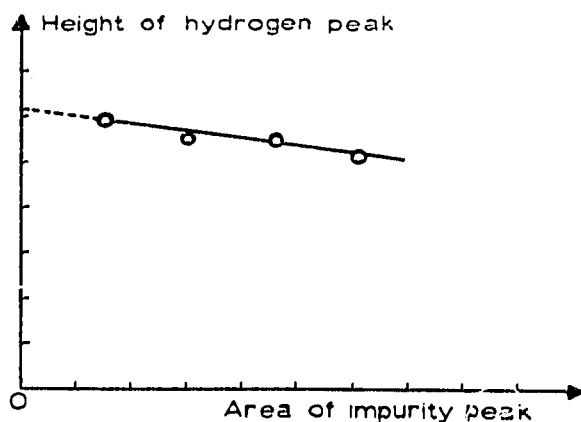

Fig. 3. Determination of height corresponding to pure hydrogen.

This method has a maximum error of $\pm$ 1 %, provided that the sampling volume is carefully selected so as to keep the hydrogen peak far from the critical inversion point.

CORRECTION FACTOR DETERMINATION

As we have seen, perfect reproducibility of sample volume is essential for the two above-mentioned methods.

Sometimes this is not possible, for example when the sample is stripped or diluted with carrier gas before injection. In such a case, if the amount of carrier gas introduced in the sample is not exactly known, it is impossible to apply the methods because the carrier is obviously not detected. Nevertheless it is also possible to analyze mixtures containing an unknown percentage of carrier gas, by applying the following technique.

Only one condition must be carefully satisfied: temperature, flow of carrier and detector current must be constant for the analysis and for the determination of the correction factor plot.

Using the method of simultaneous calibration with air (S.C.A.) we determined the hydrogen content in a series of standard mixtures, measuring at the same time the hydrogen peak height or the inversion length. By plotting the height or the inversion length against calculated area S_{H_2} (s.c.a.), we control the linearity of the values obtained (Fig. 4).

One can now calculate the correction factor from the following equation:

$$f_h = \frac{S_{H_2} \text{ (calculated by S.C.A.)}}{h_{H_2} \text{ (measured)}}$$

Plotting these factors against hydrogen peak height or inversion length, we obtain a plot from which, by interpolation, it is possible to find the correction factor corresponding to the amount of hydrogen (Fig. 5). Multiplying this factor by the
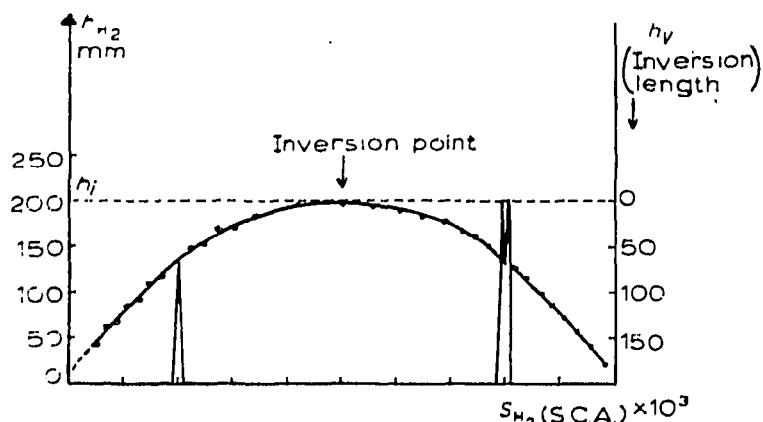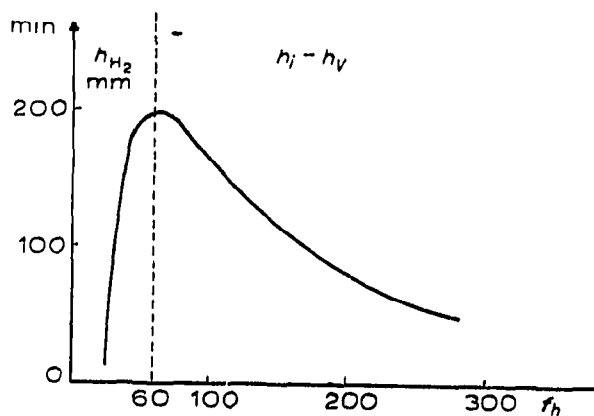
Fig. 4. Plot of hydrogen peak height or inversion length against hydrogen area calculated by means of the simultaneous calibration method.

Fig. 5. Plot of correction factor against peak height or inversion length.

hydrogen peak height and correction factor for the air, we obtain an area proportional to the molar hydrogen concentration. This value can be treated exactly as normally measured peak areas.

The above method is less accurate than the other two, especially for very low hydrogen concentrations. The error can be as large as ± 3 or 4 %, but only this method allows the determination of hydrogen in very complex mixtures, with poor or no reproducibility of the quantity injected.

CONCLUSIONS

The methods described in this paper allow the quantitative analysis of hydrogen in gaseous mixtures when the use of helium as carrier gas is necessary.

The first two methods are rapid and accurate and very useful for routine analysis. The third method is useful for very complex analysis and, if carefully used, is as precise as the other two.

All the methods can be used in other cases where the carrier gas–sample conductivity plot shows such a phenomenon as in the helium–hydrogen case.

SUMMARY

Three methods are described which allow the quantitative analysis of hydrogen in gaseous mixtures, when helium is the carrier gas.

These methods are respectively based on the simultaneous calibration with air, the simultaneous calibration with hydrogen and the determination of the correction factor curve. All the methods can be applied to other carrier gases and samples.

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