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U.D.C. 543.54:543.549

THE QUANTITATIVE INTERPRETATION OF GAS CHROMATOGRAMS

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I. INTRODUCTION

When attempting a chromatographic analysis, the investigator is faced with three main types of problem. The first group relates to the choice of the best procedures and parameters for the separation process, the second to the identification of the components of the mixture to be analysed, and the third to the quantitative interpretation of the gas chromatograms.

The results of calculations of the concentration of the various constituents from the experimental chromatogram depend on correct choice and accurate measurement of the key parameter of the elution curve (particularly when the peaks are only partially resolved), on correct choice of the method of calculating the concentration, and lastly, on correct evaluation of the sensitivity of the detector towards each of the constituents.

The present review is devoted to a discussion of these problems. It is a continuation of our earlier articles[1,2], which dealt with the choice of separation procedures and with the qualitative analysis of mixtures.

A summary of published correction coefficients and peak areas for various substances and different detectors is given at the end of the review, so as to enable the reader to use these values directly in his experimental work.

Throughout this paper, it will be assumed that a differential detector is used.

II. PARAMETERS OF THE PEAK AND METHODS OF CALCULATION

When a small enough sample is eluted, a distribution of concentrations (called a layer chromatogram) is formed on the sorption layer. Further elution leads to desorption of the wanted constituent. The resulting distribution of concentrations is called an eluate chromatogram.

If the system of detector and recorder used does not distort the curve, the resulting chromatogram differs from the true eluate chromatogram only by a scale factor.

The main parameters of the chromatographic peak (Fig. 1) are[3]:

1. The height h, measured by the length of a perpendicular dropped from the peak maximum to the base line.

2. h', the length of a perpendicular dropped to the base line from the intersection of the tangents to the peak.

3. The width of the peak, which can be measured as the distance between points on the peak at a height of 0.5 ($\mu_{0.5}$), 0.75 ($\mu_{0.75}$), 0.9 ($\mu_{0.9}$), or 1/e (μ_e) of the total peak height,

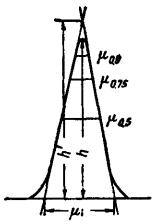


Fig. 1. Parameters of the chromatographic peak.

or alternatively as the distance between the points of inflection (μ_p) or as the intersection (μ_i) on the base line of the tangents at the points of inflection (peak base). It can be readily shown that if the chromatographic peak is sufficiently close to a gaussian distribution curve the following relationships hold between the various μ values:

$$\mu_e = 1.201\mu_{0.5},$$
$$\mu_{0.75} = 0.645\mu_{0.5},$$
$$\mu_{0.8} = 0.392\mu_{0.5},$$
$$\mu_p = 1.540\mu_{0.5},$$
$$\mu_i = 1.700\mu_{0.5}.$$

4. The peak area Q, defined by the outline of the curve and the base line.

5. The retention time t_R, the retention volume V_R, or the corresponding length l on the chromatogram.

The peak height h is related to the concentration of the substance in the sample. If the column is not overloaded with sample, this relationship is linear, provided of course that the response of the detector is directly proportional to the concentration of the substance in the eluate. However, the peak height is appreciably affected by temperature and by the flow rate of the carrier gas; therefore, the peak height should be selected as the quantitative parameter only if the following conditions are satisfied: (1) high reproducibility of sample size; (2) high stability of temperature and carrier flow; (3) no overloading of the column by the sample; (4) operation in the linear region of the detector and of the recording system.

The use of peak heights for calculating the quantitative composition of a mixture is convenient when the components have small retention times and give narrow peaks on the chromatogram. The method is applicable also to incompletely resolved constituents, provided the band maximum of one component is not affected by its neighbours. Calculations based on peak heights are particularly successful in routine analysis, requiring only moderate precision[4-7]. They are especially convenient in chromatography and in capillary chromatography.

In practice, peak areas are more frequently used as the parameter for calculation. There are various methods for measuring peak areas: planimetry, cutting out and weighing the peak, multiplying the height h by the half-width $\mu_{0.5}$, drawing the tangents to the curve at the points of inflection and calculating the area of the resulting triangle, and the use of integrating devices. The choice of method for measuring peak areas should be guided by the features of the particular elution curve.

When using a planimeter the shape of the curve is immaterial, but the method is inconvenient for very small or very large areas. The precision of the calculation depends very much on subjective factors.

The shape of the peak is likewise unimportant when cutting out and weighing, but in this case significant errors can be introduced by lack of uniformity in the paper as well as by the subjective factor.

The measurement of peak areas as the product of the height h and the half-width $\mu_{0.5}$ is convenient and accurate only if the peaks are symmetrical. Errors are again caused by overloading the column with sample, since the relationship $Q = 1.064h\mu_{0.5}$ (which applies to a gaussian distribution) does not hold when the column is overloaded. The method is difficult to use for small areas of negligible height and long retention time, or for large height and small t_R, because the half-width cannot be measured accurately. This method is accurate only when the peaks are adequately resolved.

When the area is measured by multiplying the peak height h' by the base μ_i (triangle method) the accuracy of the measurement is affected by the shape of the curve and by the care with which the tangents are drawn. Obviously, this method should be used only when the sides of the peak are approximately rectilinear.

Assuming that the chromatographic peak is not very different from a normal gaussian curve, the following method for determining the peak area can be suggested[8]. The equation of this curve is of the form

$$y = \frac{Q}{\sqrt{2\pi}\,\mu_{st}} \times e^{-\frac{1}{2}\left(\frac{x}{\mu_{st}}\right)^2}. \quad (1)$$

Here y is the ordinate of the curve, measured at a distance x from the ordinate at the maximum; Q is the area of the peak; μ_{st} is the standard deviation. At the peak maximum, where $x = 0$, $y = h$.

Hence,

$$Q = 2\pi h\mu_{st} = 2.507h\mu_{st}. \quad (2)$$

The height of the peak is measured directly, and the standard deviation can be determined from the width of the peak measured at various heights, thus:

$$\mu = \mu_{st} \quad \text{at } y = 0.882h,$$
$$\mu = 2\mu_{st} \quad \text{at } y = 0.607h,$$
$$\mu = 3\mu_{st} \quad \text{at } y = 0.324h,$$
$$\mu = 4\mu_{st} \quad \text{at } y = 0.134h, \text{ etc.}$$

Often the chromatographic peaks take the form of somewhat distorted gaussian curves. With asymmetric, biased peaks, for which the centres of the width lie on a straight line at all heights, the area can be calculated by Eqn. (2) just as though the peak were symmetrical[8].

It has been shown[8] that the standard deviation is a linear function of the retention time. Hence it is evident, see Eqn. (2), that the peak area can be measured[9] by using the peak height h and the retention time t_R (or the retention volume V_R). It can be readily shown[5] that the quantity hV_R is proportional to the amount of the substance. The half-width of the band, expressed in units of volume, is known to be equal to

$$\omega_{0.5} = 3.33 \times \Gamma_0 \times S\sqrt{\frac{DLx}{\alpha}}, \quad (3)$$

where L and S are the length and cross-section of the column respectively, x is the fraction of free volume, α the linear velocity of the carrier gas calculated for the cross-section of the column, D the effective coefficient of longitudinal diffusion, and Γ_0 the normal Henry coefficient. The retention volume is proportional to the length and cross-section of the column and to the Henry coefficient: $V_R = \Gamma_0 SL$. Cancelling $\Gamma_0 S$ from these two equations we find

$$V_R = \frac{\omega_{0.5}}{3.33}\sqrt{\frac{L\alpha}{Dx}} = A\frac{\omega_{0.5}}{\sqrt{D}}, \quad (4)$$

where

$$A = \frac{\sqrt{L\frac{\alpha}{x}}}{3.33}.$$

It follows that

$$V_R \times h \sim \frac{Q}{\sqrt{D}}. \quad (5)$$

This method is to be preferred to the others, because it is simpler to measure a retention time than the width of a peak. Eqn. (5) shows that the relationship between hV_R and the amount of a substance in the mixture varies from constituent to constituent due to difference in diffusion coefficient [10]. The method can be used successfully when high precision is not required. It should be noted that the method can be applied to overlapping peaks, whose area is often impossible to evaluate by any other method. All that is necessary in this case is to apply a correction to the peak height, depending on the extent of overlapping (see below for the calculation of the peak height correction).

Various integrating devices are used for measuring peak areas [11]. The mechanical integrator introduces errors into the measurement because it has a high inertia and gives few impulses per square millimetre of area, particularly with small areas and shallow peaks. The same disadvantages are found in the electromechanical integrator. The electronic integrator is much more accurate, but it cannot be used when the components of the mixture are not fully resolved. It should also be remembered that large errors may arise from drift of the base line.

Experimental tests of the various methods have been reported by many workers [4,7,11-15]. It has been shown that all methods give an appreciable error when the peak area is less than 50 mm² (15–25% for peak areas of the order of 25 mm²). The largest errors arise when planimeters or mechanical integrators are used, and the best results are obtained in calculations based on the peak height. When the peak area is about 50–100 mm², practically all the methods are liable to a 10% error, and the accuracy of the results can only be improved by averaging a large number of planimetric measurements. With peak areas above 100 mm² the error is 1–3%, irrespectively of the method.

Determination of the Parameters of Incompletely Resolved Peaks

Incomplete resolution of the constituents of the mixture distorts the shape of the peaks and degrades the precision of quantitative analytical results. When resolution is not complete, allowance must be made for the presence of one component at the band maximum of another component. The total concentration, measured by the peak height on the chromatogram, is

$$C = C_{1,\max}\, e^{-\rho t_R^2} + C_{2,\max} e^{-\rho(\Delta t - t_R)^2}. \quad (6)$$

In this expression ρ is a parameter which characterises the diffuseness of the band, t_R is the retention time of the peak maximum of the second component, Δt is the difference between the retention times of the maxima of the two components.

Starting from Eqn. (6), we can determine the true peak maxima of both components and evaluate the error which arises if the amount of a component is estimated from the apparent height of the peaks found on the chromatogram [16,17].

When the components of a mixture which give symmetrical chromatographic peaks are not fully resolved, the corrected peak heights can be calculated as a function of the extent of overlapping by the method of Stickler and Kovats [17]. Consider, for example, two peaks (Fig. 2) of height h_1 and h_2 whose maxima are a distance Δl apart (measured in units of μ_{st}). The ordinate y of the curve for peak 1 at a distance Δl from the maximum is

$$y = h_1 e^{-\frac{1}{2}\left(\frac{\Delta e}{\mu_{st_1}}\right)^2}, \quad \text{where } h_1 = \frac{Q}{\sqrt{2\pi}\,\mu_{st}}. \quad (7)$$

The corrected height of peak 2, allowing for the effect of peak 1, is given by

$$h_2 = \tilde{h}_2 - h_1 \times e^{-\frac{1}{2}\left(\frac{\Delta l}{\mu_{st_1}}\right)^2}, \quad (8)$$

where $\tilde{h}_2$ is the apparent height of the second peak. The area of peak 2 is then

$$Q = \sqrt{2\pi} h_2 \mu_{st_2} = 2.507 h_2 \mu_{st_2}.$$

In these expressions, μ_{st_1} and μ_{st_2} are the standard deviations of the first and the second peak respectively.

Usually the correction to the peak height is appreciable if Δl is small, and becomes negligible when $\Delta l > 4\mu_{st}$.

When the overlapping peaks are asymmetrical the height correction is obtained as for the case of symmetrical peaks. In general, however, the calculation of the height correction becomes very complicated when asymmetry is present, and involves a number of approximations.

Bartlet and Smith [8] have shown that the two areas corresponding to the individual components can be evaluated with the help of Eqn. (1) even when two substances with similar

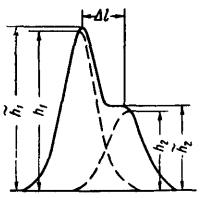


Fig. 2. Symmetrical, partially resolved peaks.

retention volumes give a single broad peak on the chromatogram. These authors used the method[18], and published a plot of the height correction as a function of the distance between the maxima of the overlapping peaks, measured in units of μ_{st}.

Thus, Bartlet and Smith's method gives information on unresolved peaks without any need to choose conditions leading to complete resolution.

Polezzo and Taramasso[19] have proposed a similar method of calculation to give the area of unresolved peaks. They express the corrections to the heights of overlapping peaks in the form

$$a_1 = e^{-\frac{1}{2}\left(\frac{\Delta l}{\mu_{st_1}}\right)^2}, \quad a_2 = e^{-\frac{1}{2}\left(\frac{\Delta l}{\mu_{st_2}}\right)^2}, \tag{9}$$

the corrected peak heights being

$$h_1 = \tilde{h}_1 - h_2 a_2 \text{ and } \tilde{h}_2 = \frac{\tilde{h}_2 - a_1\tilde{h}_1}{1 - c_1 a_2}. \tag{10}$$

In this equation $\tilde{h}_1$ and $\tilde{h}_2$ are the quantities indicated in Fig. 2.

Since μ_{st} is not easy to measure in practice, it is more convenient to express the area of the peak in terms of other quantities.

We know that $\mu_{st} = 0.424\mu_{0.5}$. Hence

$$C_x = C_{max}\exp(-x^2/0.36\mu_{0.5}^2) \text{ or } C_{max} = \frac{C_x}{\exp(-x^2/0.36\mu_{0.5}^2)}, \tag{11}$$

so that the peak area is given by

$$Q = 1.064\, C_{max}\mu_{0.5} = \frac{1.064\, C_{max}\mu_{0.5}}{\exp(-x^2/0.36\mu_{0.5}^2)}. \tag{12}$$

Analogous formulae can be written in terms of $\mu_{0.75}$, $\mu_{0.9}$, etc.

An alternative method for calculating the areas of unresolved peaks, based on the assumption that the gaussian distribution applies in the case of linear sorption isotherms, was put forward by Zhukhovitskii and coworkers[20]. The area corresponding to a given amount of a component of a mixture is calculated using the equation

$$Q = K_\theta h \mu_{0.5}, \tag{13}$$

where K_θ is a coefficient, and μ_θ is the width of the band at the height θh. For θ = 0.5, 0.75, and 0.9 the calculated values of the coefficient K_θ are 1.064, 1.650, and 2.710 respectively. According to the extent to which the components are separated, the value of θ should be chosen so that the width of the peak is unaffected by the neighbouring component. This method was tested, and it was shown that satisfactory results can be obtained at different θ values. However, errors are unavoidable at large θ because μ_{st} is small.

An interesting method of quantitative interpretation in the presence of partially resolved components is described by Serfas[21]. The outline of the chromatographic peak is linearised by using a probability scale as ordinate: the elution curve of two partially resolved peaks then consists of a line showing two rectilinear segments joined by a curve. The true outlines of the individual peaks of the two components are obtained by extrapolating the linear portions.

A theoretical method of calculation for unresolved peaks is given in a paper by Grant and Vaughan[22], in which an equation approximately describing the behaviour of three partly resolved peaks is presented. A method for the analysis of close-boiling compounds is based on this equation: the compounds were mostly isomeric, since compounds of similar boiling points but belonging to different classes can usually be separated by suitable choice of stationary phase. The method is used when the two components 1 and 2 give a single peak on the chromatogram, and their total concentration is known. A third substance is chosen such that the distance between the maximum of its chromatographic peak and the maximum of the peak for (1 + 2) is $\Delta l \simeq 3\mu_{st}$, and its peak area is the same as that of (1 + 2). The chromatogram of such a mixture gives a curve (Fig. 3) from which the quantity $h_{1,2,3(min)}/h_3$ can be evaluated: its value is substantially determined by all three components of the mixture. The concentrations of components 1 and 2 which correspond to this value are read off calibration curves constructed for mixtures of known composition.

Fredericks and Brooks[23] measured the areas of unresolved peaks by dropping a perpendicular from the minimum point to the base line and treating this line as the boundary between the two peaks. Their results were in agreement with the gravimetric composition of the mixture, but the method is unsuitable for asymmetric peaks and also for peaks of widely different size.

Bryce[4] has made an interesting study of the measurement of unresolved peak areas. He examined a mixture of benzene, toluene, and *p*-xylene in the ratio of 2 : 3 : 5, giving peaks of equal height on the chromatogram. Straightforward analysis gives complete separation of the peaks. The peaks of a given component were made to overlap by injecting a second sample, the degree of separation being controlled by the interval between the two sample injections. Perpendiculars dropped from the minimum point, and from the intersection of the tangents to the inner sides of the overlapping peaks, were treated as the peak boundary. The latter method of measuring peak areas gave the more accurate results. If, as a result of incomplete separation, one of the sides cannot be distinguished, the internal tangent is drawn symmetrically to the external tangent with respect to a perpendicular dropped from the peak "maximum" to the base line.

To obtain accurate results in the analysis of impurities whose peaks fall on the diffuse trailing edge of the peak of the main constituent, it is not advisable to use the peak height as a measure of concentration. In this case, the

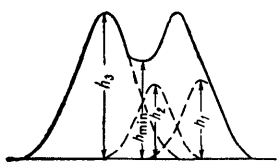


Fig. 3. Incomplete resolution of three components.

peak area is measured[4,24] by extrapolating the tail of the major peak and treating it as the base line of the impurity peak.

III. METHODS FOR CALCULATING THE COMPOSITION OF A MIXTURE FROM THE CHROMATOGRAM PARAMETERS

The precision of the chromatographic method of analysis depends very much on choosing the most rational method for calculating the proportion of each constituent in the mixture for analysis. We showed in the previous Section how a differential chromatogram can be characterised quantitatively in terms of various peak parameters. By varying these parameters, and by choosing the most appropriate method of calculation, the percentage of any component of the mixture can be found.

The main methods of processing gas chromatograms are: the absolute calibration method, the internal normalisation method, and the internal standard method.

The Absolute Calibration Method

In the analysis of trace constituents, quantitative interpretation is complicated by the special features of the chromatographic separation procedure. Absolute calibration is the most convenient and accurate method, in this case, for calculating the concentration of the components of interest. When using the absolute calibration method, either the height or the area of the peak can serve as the distinguishing parameters recorded on the chromatogram. The method presents rather stringent requirements as regards analytical procedure, and demands considerable skill and accuracy. The absolute calibration method consists in determining the relationship between the height or the area of the peak for a given component, and the amount of the latter, in a sample of given size[3,25-28]. Calibration is usually carried out by analysing a sample of known volume and accurately known composition. The experimental results are used to plot a graph of the peak height or area against the concentration of that component in the sample, and the concentration of the same component in the unknown mixture is obtained directly from the graph. When the calibration curves are straight lines, it is possible to calculate calibration coefficients which apply over wide limits, and the percentage of the compound can be calculated from the expressions

$$P_i = K\frac{Q_i}{g_i}\times 100 \qquad (14)$$

or

$$P_i = K\frac{h_i}{g_i}\times 100, \qquad (15)$$

where Q_i and h_i are the area and height of the peak, g_i the weight of the component, and K the calibration coefficient.

The accuracy of the quantitative results of the absolute calibration method depends first and foremost on the conditions under which the analysis is carried out and on the operating stability of the chromatographic apparatus. Reliable results are obtained only if the calibration and the analysis itself are carried out under identical conditions. Horn and coworkers[29] have given a detailed discussion of the problems arising from the influence of various factors on the height and area of the peak when calculating calibration coefficients. They showed that the correction factor for the peak height is a sensitive function of the amount of substance, whereas the correction factor for the peak area remains practically constant. In order to simplify the calculations, absolute calibration is often based on the height of the peaks, despite its great sensitivity to changes in experimental parameters. In particular, a one-degree change in the temperature of the column, detector, and connecting tubes can cause an error[24] of 2%. Sverak and Reiser[30], in their work on the determination of small quantities of ether in ethylene using a chromatograph with katharometric detection, allowed for a number of parameters in the formula used for quantitative calculations:

$$C_0 = \frac{KQV_\alpha}{v_n z E}, \qquad (16)$$

where C_0 is the concentration of ether (vol.%), v_n the sample volume, Q the peak area, V_α the flow rate of the carrier gas, z the speed of the recorder chart, E the sensitivity of the potentiometer, and K the calibration factor.

It should be noted that calculations with allowance for correction coefficients are justified only as long as the detector response is linear in the concentration of the compound. When this is not true special corrections must be introduced.

The Internal Normalisation Method

The internal normalisation method consists in bringing the sum of all the peak areas on the chromatogram to 100%. Instead of the peak areas, the product of the peak heights and the corresponding retention times of the components may be used. This method affords only the ratio between the amounts of the components whose peaks appear on the chromatogram, and is therefore valid only if all the constituents of the mixture for analysis are fully eluted. It is common practice to normalise corrected peak areas, that is, peak areas to which a correction for detector sensitivity has been applied. In some cases (for example, in the analysis of liquid hydrocarbons using a thermal conductivity detector with hydrogen or helium as the carrier gas, whose thermal conductivity is considerably higher than that of the substance to be analysed), correction coefficients can be ignored to a first approximation[7,31]. However, significantly higher precision is obtained by taking the correction coefficients into account. There is a wide range of publications[7,31-38] on the effect of various factors on peak areas and peak heights. Thus van de Craats[37] examined the problems associated with flow rate and sample size; Dimbat and coworkers[7] studied the effect of temperature and carrier-gas velocity on the parameters of the peak. The latter workers showed that the area of the peak is a function of the flow rate but does not vary with temperature, whereas the height of the peak depends on the temperature but is practically independent of flow rate. For temperature fluctuations of the order of one degree the relative error of peak area measurements is 0.3%. Ray[38] showed that the error caused by this same temperature variation can be as high as 2.4% when peak heights are used for the calculation. With streaming detectors of the flame ionisation type the height of the peak is very sensitive to the rate of flow of the carrier gas, but the area remains practically constant[39]. The time-constant (or inertia) of the system of detector, bridge, and recorder

must be considered when assessing the precision of the calculations. If the width of the peak is decreased by increasing the flow rate or by raising the temperature, the time-constant begins to have a significant effect and to distort the peak[39,40].

It follows from what has been said that the most satisfactory data on the quantitative composition of mixtures are obtained by using various correction coefficients, depending on the chosen method of detection.

In the internal normalisation method, the concentration (in percentage) of the ith component in the mixture to be analysed is calculated by the expression

$$P_i = \frac{K_i Q_i}{\sum_{i=1}^{n} K_i Q_i} \times 100. \qquad (17)$$

To speed up the calculations, some authors advise the use of nomograms[41], computing equipment[42], etc. According to the correction coefficient which was chosen, the concentration of a component found by formula (17) is expressed in weight or molar percentage. These aspects are discussed in greater detail below.

In practice one often has to deal with quite complicated organic mixtures which can only be separated by using multistage analytical procedures. It is obvious that the speed of the carrier gas changes when additional stages are inserted. If the calculation is based on concentration detectors, the corrected peak area should be obtained as the product of the area of the peak, of the correction coefficient, and of the velocity of the carrier gas during elution of the peak in question. Normalisation by multiplying the peak height by the retention time is not adequate in this case. In the analysis of complicated mixtures (petroleum spirit, pyrolysis tar, etc.) Vigdergauz and coworkers[43] used the method of double internal normalisation for quantitatively interpreting the chromatograms obtained at different stages. The first stage of their apparatus is intended to separate narrow fractions in the form of one or several peaks, which are then led to the column of the second stage for more detailed resolution. They showed that the corrected area of the peak of the ith component can be determined from the relationship

$$Q_{\text{corr},i} = \frac{KQ_i'' \sum_{1}^{n} Q_i'}{\sum_{1}^{n} Q_i''}, \qquad (18)$$

where Q_i'' is the area of the ith peak on the chromatogram of the second separation stage, and $\sum_{1}^{n} Q_i'$ and $\sum_{1}^{n} Q_i''$ are the sums of the peak areas corresponding to the fraction transferred to the second separation stage obtained on the chromatogram after the first and after the second stage respectively.

The percentage of the wanted component is calculated by the formula

$$P_i = \frac{Q_{\text{corr},i}}{\sum_{1}^{n} Q_{\text{corr},i}} \times 100. \qquad (19)$$

Conversion of the components at the detector inlet into carbon dioxide, hydrogen, or methane[44-46] is a very interesting method for the quantitative interpretation of gas chromatograms without previous calibration. The authors claim a number of advantages for this method over alternative methods of calculation, and they state that the precision and the reproducibility of the analytical results are higher.

When the gas-density balance (first described by Martin and James in 1956) is used as a detector, preliminary calibration or the experimental determinatin of correction coefficients are again unnecessary, since the signal of this detector depends only on the ratio of molecular weights of the substance being analysed and of the carrier gas[58]. In the analysis of the light fractions of crude oil (up to and including C_7) the measuring error was no more than 1% when a gas-density balance was used[55].

The Internal Standard Method

The internal standard method, first proposed by Ray[38], relies on adding to the mixture for analysis a known amount of a suitable substance to act as a standard: the height or the area of the peak for the wanted component are then compared with those for the standard. This method is widely used both for major constituents and for the analysis of trace impurities[47,55]. The chosen standard should be a substance which is not contained in the mixture for analysis, which is thermally stable at the temperature of the experiment, and which cannot react with any of the constituents of the sample. At the same time, the standard peak should appear on the chromatogram as close as possible to the peaks of the mixture. The percentage of the ith component in the sample can be calculated from the formula

$$P_i = \frac{K_i Q_i}{K_s Q_s} R \times 100, \qquad (20)$$

where K_i and K_s are the correction coefficients for the peak area of the component and of the standard, determined by the sensitivity of the detector, R is the ratio of the weight of internal standard to the weight of the mixture taken for analysis, and Q_i and Q_s are the peak areas of the component and of the standard.

An analogous expression applies to the peak heights. The calibration coefficients are determined by analysing binary mixtures of component and standard. Some workers prefer to plot calibration graphs for all the constituents of the mixture for analysis. Thus, Shlyakhov and coworkers[6], in their analysis of oxygenated hydrocarbons on a capillary column, plotted the ratio of the weight percentage of a given component to that of the standard (on the abscissa axis) against the ratio of the heights of the corresponding peaks (on the ordinate axis). The concentration of every component was determined from these calibration curves, with a mean relative error of 2%. When analysing multicomponent mixtures with a wide range of retention times, more accurate and reproducible results on the quantitative composition are obtained by using several internal standards. Lee and Oliver[56], using two internal standards, estimated small impurities (of the order of tenths of one per cent) of benzene, toluene, and styrene in ethylbenzene to a relative precision of 1–2%. Vlodavets and coworkers[57] used three internal standards for quantitative calculations when developing a method for the chromatographic estimation of acrolein and its dimerisation products.

It is evident from the above examples that the correct choice of method for calculating the composition of a mixture is the key to a successful quantitative analysis.

IV. CALCULATION OF CORRECTION COEFFICIENTS IN QUANTITATIVE CHROMATOGRAPHIC ANALYSIS

The correct quantitative interpretation of chromatograms requires that the law relating the elution curve to the true ratio of components in the mixture should be known. A situation in which equal quantities of the substances to be separated correspond to equal values of the chosen parameter is exceptional in chromatographic practice. One usually has to apply correction coefficients, which make it possible to deal with the calculation as in the simplest case defined above. With these correction coefficients absolute calibration becomes unnecessary, and because of this many workers have examined the problem of evaluating the coefficients using both experimental and theoretical approaches.

The experimental determination of correction coefficients lags behind the rapidly growing number of substances to which chromatographic analysis is being applied. Furthermore, the experimental correction coefficients need to be critically scrutinised: different workers often report vastly different values which are due to subjective factors as well as to differences in the experimental conditions and procedures[31].

A more rational approach is to seek theoretical relationships between the signal of the detector and the physicochemical properties of the substances to be separated. An "ideal" method of processing the results of a chromatographic analysis would involve very complicated corrections for the distortions of the chromatogram introduced both by the column and by the detecting device.

The distortions introduced by the detector can be divided, on the whole, into two groups[59]: (1) those arising from non-linearity of the detector response as a function of the concentration of the wanted substance in the carrier gas, and (2) dynamical perturbations, caused by the rate of change of concentration in the carrier gas, affecting the sensitivity of the detector.

Obviously, correction coefficients can be tabulated for the entire range of concentrations of the wanted substances only if the calibration plot $y = f(c)$ is rectilinear, that is,

$$y = S_i c, \tag{21}$$

where y is the deflection of the recorder pen, c the concentration of the component in question, and S_i the sensitivity of the detector towards that component.

For the first and the second group of distortions, Eqn. (21) becomes, respectively,

$$y = S_0 + S_1 c + S_2 c^2 + S_3 c^3 + \ldots \tag{22}$$

and

$$y = S_1 c + S_2 \frac{dc}{dt} + S_3 \frac{d^2c}{dt^2} + \ldots . \tag{23}$$

Since Eqn. (21) applies only to a limited range of concentrations (lying, as a rule, in the region of low values of c), it is always necessary in practice to estimate the order of magnitude of the error due to non-linearity[60].

A summary of published data on the upper limits of detector linearity is given in Kalmanovskii and Fesenko's paper[40] on detecting devices for gas chromatography.

Among the ways in which the separating part of the apparatus can distort the chromatogram we should list the increase in overall velocity of the flow occurring when the desired component emerges from the column, called the "surge effect" by van de Craats[37]. As a result of this effect, the peak area traced on the chromatogram is smaller than the area corresponding to the measured flow rate.

The author recommends the correction factor

$$f_1 = 1 + \frac{v_s c_s}{100\omega_u} \times \frac{V_2 - V_{gas}}{V_R}, \tag{24}$$

where v_s is the sample size (ml), c_s the concentration of the component in the sample (mole %), ω_u the width of the peak at the base obtained by drawing tangents (ml), V_R the retention volume of the component (ml), and V_{gas} the volume of gas in the column (ml). He also derives a more precise correction factor:

$$f_2 = 1 + 0.7\,\frac{c_{max}}{100 - c_{max}} \times \frac{V_R - V_{gas}}{V_R}, \tag{25}$$

where c_{max} is the concentration corresponding to the peak maximum.

All these errors, most of which are effectively impossible to control, call for the application of corrections for every type of analytical procedure. However, in practical chromatography the corrections are usually confined to coefficients depending only on the principle of operation of the detector and on the nature of the carrier gas and of the wanted component.

We shall now discuss the methods of determining these correction coefficients, which, when multiplied by the peak areas, convert them into the appropriate gravimetric and molar amounts of substance injected into the column.

According to one school of thought[31], the correction coefficients should always convert the chromatographic results into percentage by weight. However, the present writers prefer to use molar correction coefficients in tabulations, because they reflect most clearly the relation between the signal corresponding to a substance and the chemical nature of the substance.

It is easy to show[43] that the molar correction factor for a given component can be readily converted into a gravimetric factor by the relation

$$\frac{K_w}{K_m} = \frac{M_i}{M_{st}}, \tag{26}$$

where K_w is the gravimetric correction coefficient, K_m the molar correction coefficient, M_{st} the molecular weight of the standard (for which $K_w = K_m = 1$), and M_i the molecular weight of the component.

As we have already pointed out, different substances have practically identical correction coefficients only in special cases. These occur, for example, in the analysis of members of a homologous series using katharometric detection and a light carrier gas (helium or hydrogen). The adequacy of this assumption depends, of course, on the analytical precision required. In every other case the correction coefficients are quite different.

Messner and coworkers[61] showed that for a katharometer detector and helium as the carrier gas a strictly linear relationship exists between the molecular weight and the value of $1/K_m$ for the individual members of homologous series of hydrocarbons, the slope of the resulting straight line decreasing as the degree of branching of the hydrocarbon increases. The following rules were established: $1/K_m$ is smaller for cyclic than for normal hydrocarbons; it is smaller for *ortho*-substituted isomers than

for the *meta*- and *para*-isomers; for normal paraffins $1/K_m$ is higher than for any functional derivatives.

Jamieson[62] has examined a large number of organic compounds, and he has confirmed the rule of Messner and coworkers according to which $1/K_m$ decreases as the branching of the hydrocarbon skeleton increases. He has also shown that this rule is not so strictly followed by polyfunctional derivatives (ethers, hydroxy-, alkoxy-, and ketoxy-ethers).

Jamieson, and also other workers[63,64], showed that with alcohols the relative molar correction varies with the square root of the molecular weight. Iogansen and coworkers[65] found that the correction coefficient for hydrocarbons varies with the 2/3 power of the molecular weight.

Nikelly[66] showed that the plot of correction factor against number of carbon atoms (for the case of a katharometer) is curved, the curvature decreasing in the sequence: alkanes, alkenes, alcohols. From the analytical results for a seven-component mixture of alkenes and alcohols, obtained with temperature programming and by using his own correction coefficients, he estimated an error of 2–4% for each of the components. In the same paper it is shown that the correction coefficients are independent of temperature variation during the analysis.

Similar observations are reported by Baumann and Olund[67], who determined the relation between molar corrections and the normal boiling points in a series of sulphides and thiols.

When a flame ionisation detector is used with hydrocarbons and their derivatives a strictly linear relationship is observed between the relative molar correction and the number of carbon atoms[68].

It should be noted that with many detectors there is no simple systematic relation between the signal and the nature of the substance. Typical of these is Grant's emissivity detector[69], for which the correction coefficients depend on the velocity of the carrier gas and on the absolute amount of substance for analysis. Another characteristic of this detector is that the signal depends very much on the class of compound, and is practically constant within a homologous series. Thus[22], the signal for paraffins and halogenated hydrocarbons relative to benzene is 0.14 and 0.15 respectively, whereas for naphthalene the signal is 2.0–3.0.

Thermal Conductivity Detector

Most of the work on correction coefficients, both experimental and theoretical, relates to the thermal conductivity detector. The early workers[70,71] assumed that the results of chromatographic analysis are given in molar percentages: thus, Hausdorff[70] considered that when a katharometer is used in conjunction with a light carrier gas the area under the elution curve is proportional to the number of molecules of the substance, and therefore to its molar percentage.

The question of whether the area under the curve on the recorder gives a better approximation to the weight or to the molar percentage has been discussed in several papers[72–76].

More recent work has shown experimentally that in many cases, particularly in the analysis of hydrocarbon mixtures, the area of the peak of a component expressed as a fraction of the total area for all components gives a better approximation to the weight fraction of the component in the sample. However, in most cases the areas under the curve do not correspond either to weight or to molar percentages. This was clearly demonstrated by van de Craats[37], who measured the relative correction factors for the C_1–C_4 hydrocarbons.

Feish and Engel'gart[72] showed that the correction factors, defined as the peak areas for those hydrocarbons referred to the peak area of n-butane (for equal sample volumes), are equal to the ratio of molecular weights in the zeroth approximation, and to the 3/4 power of the ratio of molecular weights in the first approximation. The first approximation refers to a method in which the standard is chosen to have a molecular weight intermediate between those of the components in the mixture for analysis. In this case the coefficients, calculated as $(M_i/M_{st})^{3/4}$, are approximately the same as those found by van de Craats. At the same time, if the ratio of the areas is taken to the power 4/3 a better approximation to weight percentages is obtained.

The first papers on the determination of correction coefficients were those of Rosie and Grob[34] and Messner and coworkers[61]. Most of the workers who have examined the theoretical aspects of correction coefficients have checked their conclusions against the results of those papers.

Messner and coworkers[61] proposed that the relative molar correction should be expressed in the form

$$\frac{1}{K_M} = A + BM, \qquad (27)$$

where A and B are constants for a given homologous series, and M is the molecular weight.

These workers calculated values of A and B for many classes of organic compounds. Some of their values are tabulated below:

Series	A	B
n-Paraffins	6.7	1.35
Methylparaffins	10.8	1.25
α-Olefins	13.0	1.20
n-Alcohols, primary	34.9	0.808
n-Alcohols, secondary	33.6	0.857
n-Alcohols, tertiary	34.9	0.808
Acetates	37.1	0.841
Ketones	35.9	0.881

These correction coefficients are independent of concentration over a wide range. A tenfold change (from 1.43 to 0.14) in the molar ratio of diisopropyl ether to benzene had practically no effect on the correction factor. In the same paper it is shown that the correction coefficients are independent of the type of katharometer used (thermistor, or hot wire). Furthermore, it was also established that the correction coefficients for helium and hydrogen are unaffected by change in temperature over a wide range. However, in the case of nitrogen, which shows a strong temperature variation of the correction coefficients, standardisation is particularly difficult. This is especially true of the C_2 hydrocarbons, to which the katharometer has practically no sensitivity between 50° and 80°.

As was to be expected, all the workers who studied correction coefficients for katharometers approached the problem by considering changes in thermal conductivity of

the carrier gas as a function of the concentration of the wanted component in the carrier. Keulemans[77] considers that at low concentrations, when the mole fraction (x) of the component in the carrier gas is less than 10^{-2}, the thermal conductivity of the mixture is the sum of the thermal conductivities of the carrier and of the impurity multiplied by the appropriate mole fractions. Then

$$x = \frac{\lambda_1 - \lambda_{12}}{\lambda_1 - \lambda_2}, \quad (28)$$

where λ_1, λ_2, and λ_{12} are the thermal conductivities of the carrier gas, of the wanted component, and of the mixture respectively. Thus, if the signal is proportional to the change in thermal conductivity (λ_1 - λ_{12}), the peak area should lead to an accurate value of the mole fraction when the correction factor $1/(\lambda_1 - \lambda_2)$ is used. However, this is inconsistent with the fact that the area under the elution curve usually corresponds to a weight percentage.

Iogansen[65] takes the same view, and suggests that the molar correction for light hydrocarbons should be calculated by the formula

$$\frac{1}{K_{M_i}} = \frac{\lambda_1 - \lambda_{12}}{\lambda_1 - \lambda_2} \times \sqrt[3]{(M_i/58)^2}, \quad (29)$$

where M is the molecular weight of the wanted hydrocarbon, and 58 the molecular weight of n-butane (taken as standard).

Hinkle and Johnsen[36] propose a correction factor of $\rho^{-2/3}$ to the peak area, where ρ is the vapour density, to give molar percentages. This agrees with Iogansen's conclusion, since

$$\rho = c\left(\frac{\mu c_p}{\lambda}\right)(M)(a)^{-1}, \quad (30)$$

where c is a constant, μ the absolute viscosity, λ the thermal conductivity, c_p and c_v are the specific heats at constant pressure and constant volume, M is the molecular weight, and $a = c_p/c_v$.

Browning and Watts[32] proposed a correction to the peak areas on the basis of the thermal conductivity of the appropriate component. In principle, this correction relies on dividing the peak areas given by the analysis by the thermal conductivities of the corresponding substances, since large peak areas correspond to large thermal conductivities and conversely. Heft has shown[73] that with nitrogen as the carrier gas this correction only makes matters worse.

Littlewood[74], and more recently Mecke and Zirker[75], started from an expression for the thermal conductivity of a mixture derived from the theory of Chapman and Enskog.

Littlewood concluded that the thermal conductivity of the carrier gas, of the component being analysed, and of their mixtures (λ_1, λ_2, and λ_{12} respectively), and also the mole fraction of the component in the carrier gas (x_2), are related to the average diameters of the molecules of the carrier (σ_1) and of the impurity (σ_2) by the expression

$$-\frac{1}{\lambda} \times \frac{d\lambda_{12}}{dx_2} = \frac{\sigma_{12}^2}{\sigma_1^2}, \quad (31)$$

where

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}.$$

To obtain the average molecular diameters needed for the calculation of correction coefficients this worker used some of Rosie and Grob's results on the cross-section of the methyl, methylene, methine, and phenyl groups, and also of the quaternary carbon atom and aromatic hydrogen. Littlewood, on the assumption that the molecular diameter is approximately equal to the sum of the diameters of the constituent elements, calculated correction coefficients (for helium) which were practically indistinguishable from some other results of Rosie and Grob:

Compound	Relative molar correction		Compound	Relative molar correction	
	Rosie and Grob	Littlewood		Rosie and Grob	Littlewood
n-Heptane	143	143	Ethylbenzene	129	135
n-Octane	160	162	o-Xylene	130	132
2-Methylpentane	120	120	p-Xylene	131	132
3-Methylpentane	119	120	Mesitylene	149	148

Mecke and Zirker, who also introduced a correction for the change in molecular diameter under the influence of molecular forces, arrived at the same conclusion.

In keeping with Littlewood's assumption, Mecke and Zirker showed (in the case of normal paraffins) that the ratio of the square of the increment in molecular diameter $\Delta d^2_{CH_2}$ to the increment in molecular weight ΔM_{CH_2} is a constant:

$$\frac{\Delta d^2_{CH_2}}{\Delta M_{CH_2}} = \text{const.} \quad (32)$$

Thus, for the homologous series A–$(CH_2)_n$, where A is a functional group, the square of the average molecular diameter can be calculated by the formula

$$d^2 = d_A^2 + n d^2_{CH_2} = K(A + nM_{CH_2}). \quad (33)$$

The calculation of correction coefficients by the method of Littlewood and of Mecke and Zirker is made much easier by this relationship. The work of these authors is valuable also because it provides an explanation for the observed linear variation of the correction coefficients with molecular weight within a given homologous series, and for the slight deviation from linearity in the first few members (influence of A).

Schmauch and Dinerstein[78], and also Hoffman[79], arrived at their molecular correction coefficients from the classical kinetic theory of monatomic gases. According to the former, the sensitivity of the katharometer (E_0) is related to the thermal conductivity of the carrier gas (λ_1) and to that of the mixture (λ_{12}) by the following expression:

$$E_0 = c\sqrt{\lambda_1}\,\frac{\lambda_1 - \lambda_2}{\lambda_{12}}. \quad (34)$$

To calculate the thermal conductivity of the mixture they applied Vasil'eva's equation

$$\lambda_{12} = \frac{\lambda_1}{1 + A_{12}\left(\frac{1-x}{x}\right)} + \frac{\lambda_2}{1 + A_{21}\left(\frac{x}{1-x}\right)}, \quad (35)$$

where x is the mole fraction, and A_{12} and A_{21} are constants. They conclude that the same correction coefficients can be used over a wide range of concentrations if the difference in thermal conductivity between the substance and the carrier gas is very large (for example, helium or hydrogen carriers, and organic compounds). In other systems, for example, when nitrogen is the carrier and the response is

not linear, a correction is needed for each concentration interval of the test substance.

Hoffman analyses the detector signal into four multiplicative terms: a cell factor, a carrier-gas factor, a molar thermal conductivity change factor, and a concentration factor. From Vasil'eva's equation for the change in molar thermal conductivity, Hoffman obtains

$$F = \frac{\lambda_1 - \lambda_2}{\lambda_{12}\, x} = F_0 + f_x (x \ll 1), \qquad (36)$$

where

$$F_0 = A_{12} - \frac{\lambda}{A_{12}} \text{ and } \lambda = \frac{\lambda_2}{\lambda_1},$$

λ_1 and λ_2 being the thermal conductivities of the pure carrier gas and of the component. Since $x \ll 1$, it follows that $F_0 \simeq F$. The quantity F_0 can be neglected in practice, but the quantity F_{0i}/F_{0st}, corresponding to the relative molar signal, can be calculated if the data needed to calculate the constants in Vasil'eva's equation are available.

The relative molar corrections obtained by Hoffman for nitrogen, helium, and hydrogen agree strikingly well with the corrections determined experimentally, and also with the results of Messner and coworkers[61], and others. Hoffman showed that the second term (effect of the carrier gas) accounts for only 4–13%. He ascribes the peak inversion which is observed when nitrogen is the carrier to negative F_0 values.

Heft[73] explains peak inversion by pointing out that the katharometer response is affected by changes in the specific heat of the mixture of carrier and substance for analysis as well as by thermal conductivity changes. For hydrogen and helium the ratio of these two effects is always much less than unity, whereas for nitrogen the specific heat effect can be much larger than the thermal conductivity effect. This causes cooling of the detector filament, and leads to peak inversion.

As a result of an interesting study of the influence of the specific heat of the components to be analysed on the detector signal, Heft concludes that when nitrogen is used as the carrier gas the areas of the peaks under the elution curve correspond to weight percentages only if one is dealing with members of a homologous series, or with substances having identical specific heats. In all other cases a correction is necessary.

Gas-Density Balance

This detector, as stated above, is the most suitable for quantitative analysis. Phillips and Timms[58] found that the integral signal for the ith substance (a_i) depends on the molecular weight M_i as indicated by the equation

$$Q_i = K g \left(\frac{M_i - M_0}{M_i}\right), \qquad (37)$$

where M_0 is the molecular weight of the carrier gas, g the amount of the substance, and K an apparatus constant.

The relative correction coefficient is then

$$K_B = \frac{(M_{st} - M_0)\, M_i}{M_{st}(M_i - M_0)}. \qquad (38)$$

Thus, for benzene as the standard and hydrogen as the carrier gas, the correction coefficient for the ith compound takes the value

$$K_B = \frac{M_i \times 76}{(M_i - 2) \times 78}. \qquad (39)$$

The main virtue of this detector is that it does not require tabulated and correction factors. When needed, the factors can always be calculated for any unknown substance provided that its molecular weight is known.

Flame Ionisation Detector

At the present time, the flame ionisation detector is one of the most satisfactory devices for quantitative analysis by gas chromatography. It provides results which are independent of temperature and of carrier gas, and a large linear range of signals.

However, relatively little has been published on the use of the flame ionisation detector in the quantitative analysis of real mixtures. This is partly due to the fact that the signal depends very significantly on constructional details of the electrodes, burner geometry, flame temperature, etc.

The correction coefficients for the flame ionisation detector are far more sensitive to structural features of the compounds being analysed than are the coefficients for the katharometer[80]

As already pointed out, various authors have obtained a linear relation between the relative molar correction and the number of carbon atoms in the molecule. Altschuller and Clemons[28] showed that the signal of this detector is a linear function of the number of carbon atoms in aromatic hydrocarbons up to C_{10}.

One characteristic of the flame ionisation detector is that carbon atoms linked to oxygen or nitrogen contribute practically nothing to the signal given by the compound being examined[81–85]. This is because such a carbon atom does not take part in the combustion, which is the physicochemical basis of the operation of the flame ionisation detector.

Schomburg[68] found a molar correction coefficient (relative to m-xylene) varying only over the range 0.59–0.65 for a series of carbonate esters of molecular weight between 116 and 172.

Unfortunately, the special features of the flame ionisation detector limit (or even debar) its application in the analysis of some commercially important substances such as the inert gases, hydrogen, oxygen, carbon monoxide, carbon dioxide, and many others[86].

Schomburg warns[68] against the use of the flame ionisation detector in the analysis of substances whose combustion produces a solid deposit in the burner. For example, a solid residue of boron dioxide is formed in the analysis of alkylborons, and makes quantitative analysis impossible.

Ettre and coworkers[82] showed that the correction coefficients for the flame ionisation detector, like those for for the katharometer, can be calculated by Eqn. (27). Those workers, and also Desty and coworkers[87], obtained correction coefficients for very many organic compounds.

Bredel[88] states that the areas of hydrocarbon peaks are related to the retention times and to the number of carbon

atoms in the molecule by the expression

$$Q = t_R(A\,n + B), \tag{40}$$

where the coefficients A and B are different for different types of column. This author suggests that the peak areas should be corrected by dividing them by the product $t_R n$.

Ongkiehong [83] found that in many cases approximate correction coefficients can be calculated without appreciable loss of analytical precision from the formula

$$K_B = \frac{M_i n_{st}}{n_i M_{st}}, \tag{41}$$

where M_i and M_{st} are the molecular weight of the ith compound and that of the standard, and n_i and n_{st} the number of carbon atoms in the molecule of the ith compound and of the standard.

These approximate correction coefficients give particularly good results in the analysis of substances containing different functional groups (alcohols, acids, ether, etc.).

Sternberg and coworkers [89], and also Dewar [90], have correlated the detector signal with the structural properties of the substances being analysed.

β-Ionisation Detector

This very sensitive detector can be used to analyse any compound whose ionisation potential is less than 11.7 eV. One of its characteristics is that the correction coefficients are relatively insensitive to changes in carrier-gas flow and in temperature, and also to the geometry of the apparatus. The integral signal of the β-ionisation detector is proportional to the molecular weight of the substance being analysed, but the recorder deflection is not linear in relation to concentration.

The theory of the β-ionisation detector was first investigated by Lovelock [91]. He showed, by analysing substances belonging to different classes, that the non-linearity of the correction coefficients (relative to pentan-1-ol) as a function of molecular weight varies for substances of different nature. Thus, with the methyl esters of primary fatty acids the correction coefficient decreases sharply with increase of molecular weight up to one hundred, after which it tends to a constant value. A similar behaviour is observed with n-primary alcohols, whereas with ethers and ketones the relative correction coefficient increases sharply over the whole interval of molecular weights (up to 200) which was examined. An increase in the weight correction coefficient with increase in molecular weight was found also in the analysis of non-esterified lower fatty acids [92]. When the molecular weight rises above one hundred the correction coefficient tends to a constant value.

By working with fully halogenated and nitrated hydrocarbons, Lovelock ascribed [93] these anomalies of the β-ionisation detector to the capture of free electrons by suitable groups, such as the carboxyl group, which also explains the results of Böttcher [92] and others.

The formula

$$1/K_M = 2.5 \log n - 1.41, \tag{42}$$

where n is the number of carbon atoms in the molecule, has been suggested for calculating the relative correction factor (with respect to nonanoic acid).

TABLE 1. Molar correction coefficients K_M for the C_1–C_6 hydrocarbons and light gases (relative to n-butane).

Component	Carrier gas: hydrogen		helium			nitrogen
	31, 37*	65	61, 102	103	104	65
Hydrogen	—	—	58.6	—	55.6[d]	—
Helium	2.22	—	—	—	—	—
Nitrogen	1.764	—	2.02	—	—	—
Oxygen	1.955	—	2.12	—	—	—
Carbon monoxide	1.874	—	1.77	—	—	—
Carbon dioxide	1.548	—	2.02	—	—	—
Hydrogen sulphide	—	—	4.48	—	—	—
Methane	2.031	2.27	2.36	—	1.82[d]	—
Acetylene	1.725	2.09	—	—	—	—
Ethylene	1.523	—	1.77	—	1.45[d]	5.0
Ethane	1.436	1.45	1.66	1.663	—	5.3
Allene	1.295	—	—	—	—	—
Cyclopropane	1.225	—	—	—	1.33[d]	—
Methylacetylene	1.265	—	—	—	—	—
Propene	1.236	1.37	1.35	—	1.32[d]	1.43
Propane	1.169	1.23	1.31	1.284	—	1.5
Isobutane	1.030	1.12	1.03	—	—	1.03
Isobutene	1.044	1.02	1.03	—	—	0.91
But-1-ene	1.032	1.14	1.05	—	—	0.91
Buta-1,3-diene	1.085	—	1.06	—	—	—
Buta-1,2-diene	1.047	—	—	—	—	—
n-Butane	1.000[a]	1.00	1.00[b]	1.000[c]	1.00	1.00
trans-But-2-ene	1.021	—	1.00	—	—	0.83
cis-But-2-ene	1.021	—	1.98	—	—	0.83
Ethylacetylene	1.074	—	—	—	—	—
Neopentane	0.922	—	0.85	—	—	—
3-Methylbut-1-ene	—	—	0.86	—	—	—
Isopentane	0.915	—	0.83	—	0.79[d]	0.78
Pent-1-ene	0.911	—	0.86	—	—	0.76
2-Methylbut-1-ene	—	—	0.86	—	—	0.76
n-Pentane	0.888	—	0.80	0.825	0.78[d]	0.76
trans-Pent-2-ene	0.911	—	0.81	—	—	0.76
cis-Pent-2-ene	0.911	—	0.86	—	—	0.76
2-Methylbut-2-ene	—	—	0.88	—	—	0.76
Cyclopentane	—	—	0.87	—	0.81[e]	—
Penta-1,4-diene	—	—	0.81	—	—	—
Cyclopentene	—	—	—	—	0.87[e]	—
Isoprene	0.977	—	—	—	—	—
Hexane	0.809	—	0.70	—	0.57	—

a K_M relative to benzene 1.000
b K_M relative to benzene 1.177
c K_M relative to benzene 1.173
d Measured in the temperature range −4–0°
e Measured at 52°

* These and the corresponding numerals in later Tables indicate literature references (Ed. of Translation).

The correction coefficients for the β-ionisation detector, with argon as the carrier gas, have been calculated by Simmons and coworkers [94] and by Durrett and coworkers [95].

Condon and coworkers [96] determined the weight correction factors (relative to n-butanol) for a number of alcohols.

When a gas not susceptible to metastable ionisation is used as the carrier, the sensitivity of this detector approaches that of the katharometer. Under these conditions the relative weight corrections are easily calculated by the formula

$$K_B = \frac{M_i(\sigma_{st} - \sigma_0)}{(\sigma_i - \sigma_0) M_{st}}, \tag{43}$$

where σ_0, σ_1, and σ_{st} are the ionisation cross-sections of the carrier gas, the wanted compound, and the standard.

Otvos and Stevenson [97] showed that the ionisation cross-sections are additive, and can be calculated from the appropriate increments (which equal 4.16 and 1.00 for carbon and hydrogen respectively).

TABLE 2. Molar correction coefficients K_M for hydrocarbons (relative to benzene).

Component	Katharometer, carrier gas: hydrogen	helium		nitrogen		Flame ionisation detector		Argon detector	Emissivity detector
	79	79	34, 61	79	62	105	87	94	69
n-Pentane	0.931	0.953	0.95	1.960	—	1.130	—	—	—
Cyclopentane	—	—	1.03	—	—	—	—	0.644	—
2,2-Dimethylbutane	—	—	0.863	—	—	0.920	—	0.456	—
2,3-Dimethylbutane	—	—	0.863	—	—	—	—	0.498	—
2-Methylpentane	—	—	0.834	—	—	—	—	0.535	—
2-Methylpent-1-ene	—	—	—	—	—	0.980	—	—	—
3-Methylpentene	—	—	0.841	—	—	—	—	0.529	—
n-Hexane	0.814	0.834	0.814	1.100	1.041	0.951	0.966	0.55	0.090
Methylcyclopentane	—	—	0.820	—	—	—	—	0.633	—
Benzene	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Cyclohexane	0.954	0.926	0.878	0.925	—	—	1.00	0.647	0.208
2,2-Dimethylpentane	—	—	0.752	—	—	—	—	0.404	—
2,4-Dimethylpentane	—	—	0.775	—	—	—	—	0.441	—
1,1-Dimethylcyclopentane	—	—	0.808	—	—	—	—	0.517	—
2,3-Dimethylpentane	—	—	0.741	—	—	—	—	0.399	—
2-Methylhexane	—	—	0.736	—	—	—	—	0.441	—
2,2,3-Trimethylbutane	—	—	0.775	—	—	—	0.825	—	—
cis-1,3-Dimethylcyclopentane	—	—	—	—	—	—	—	0.566	—
trans-1,3-Dimethylcyclopentane	—	—	—	—	—	—	—	0.561	—
3-Methylhexane	—	—	0.753	—	—	—	—	0.402	—
trans-1,2-Dimethylcyclopentane	—	—	—	—	—	—	—	0.570	—
3-Ethylpentane	—	—	0.764	—	—	—	—	—	—
n-Heptane	0.741	0.710	0.700	0.807	0.807	0.823	0.850	0.465	0.110
cis-1,2-Dimethylcyclopentane	—	—	—	—	—	—	—	0.507	—
Methylcyclohexane	—	—	0.834	—	—	0.847	0.914	0.514	0.017
Ethylcyclopentane	—	—	0.794	—	—	—	—	0.471	—
Toluene	0.863	0.863	0.863	0.863	0.827	—	0.966	1.012	1.100
2,2,4-Trimethylpentane	—	—	—	—	—	—	0.685	0.35	—
1,1,3-Trimethylcyclopentane	—	—	—	—	—	—	—	0.473	—
1,1,2-Trimethylcyclopentane	—	—	—	—	—	—	—	0.382	—
2,5-Dimethylhexane	—	—	—	—	—	—	—	0.338	—
1,2,4-Trimethylcyclopentane (*cis-trans-cis*)	—	—	0.735	—	—	—	—	0.413	—
2,4-Dimethylhexane	—	—	—	—	—	—	—	0.350	—
2,2,3-Trimethylheptane	—	—	—	—	—	—	—	0.297	—
2,3,4-Trimethylpentane	—	—	—	—	—	0.722	—	0.345	—
2,3,3-Trimethylpentane	—	—	—	—	—	—	—	0.284	—
1,2,4-Trimethylcyclopentane (*cis-cis-trans*)	—	—	0.700	—	—	—	—	0.403	—
2-Methylheptane	—	—	—	—	—	—	—	0.348	—
n-Octane	0.657	0.614	0.626	0.654	—	—	0.76	—	0.089
1,2-Dimethylcyclohexane	—	—	—	—	—	—	—	—	0.016
1,3,5-Trimethylbenzene	—	—	—	—	0.600	—	—	—	0.830
1,2,4-Trimethylbenzene	—	—	0.666	—	0.645	—	—	—	0.768
t-Butylbenzene	—	—	—	—	0.556	—	—	—	—
s-Butylbenzene	—	—	0.633	—	0.547	—	—	—	—
4-Isopropyl-1-methylbenzene	—	—	—	—	0.556	—	—	—	—
n-Butylbenzene	—	—	—	—	0.518	—	—	—	—
1,2,4,5-Tetramethylbenzene	—	—	—	—	0.553	—	—	—	—
1,2,3,5-Tetramethylbenzene	—	—	—	—	0.556	—	—	—	—
n-Decane									
Biphenyl	—	—	0.503	—	—	—	—	—	0.092
Naphthalene	—	—	—	—	—	—	—	—	1.237
2-Methylnaphthalene	—	—	—	—	—	—	—	—	1.714
Camphene	—	—	—	—	—	—	—	—	0.96
α-Pinene	—	—	—	—	0.70	—	—	—	—
β-Pinene	—	—	—	—	0.76	—	—	—	—
Limonene	—	—	—	—	0.77	—	—	—	—
Myrcene	—	—	—	—	0.67	—	—	—	—
Ethylcyclohexane	—	—	—	—	0.68	—	—	—	—
Ethylbenzene	—	—	0.690	—	—	—	0.817	—	—
p-Xylene	—	—	0.775	—	0.695	0.766	0.914	—	—
m-Xylene	—	—	0.764	—	0.690	0.766	—	—	0.800
2,2,5-Trimethylhexane	—	—	0.764	—	0.700	—	—	—	0.760
2,2,4-Trimethylhexane	—	—	—	—	—	—	—	0.319	—
2,3,5-Trimethylhexane	—	—	—	—	—	—	—	0.323	—
2,2,3-Trimethylhexane	—	—	—	—	—	—	—	0.327	—
2,3,3-Trimethylhexane	—	—	—	—	—	—	—	0.323	—
2,2,3,3-Tetramethylpentane	—	—	—	—	—	—	—	0.319	—
	—	—	—	—	—	—	—	0.312	—
n-Nonane	0.542	—	0.565	0.486	0.550	0.65	—	—	—
Isopropylbenzene	—	—	0.705	—	0.620	—	—	—	—
n-Propylbenzene	—	—	0.690	—	—	—	—	—	—
4-Ethyl-1-methylbenzene	—	—	0.666	—	—	—	—	—	—

Combustion Tube

The quantitative interpretation of gas chromatograms is made easier if a combustion tube is provided as an attachment to the detector. When the components are converted into carbon dioxide or methane, the weight coefficients are readily calculated by formula (41):

$$K_B = \frac{M_i n_{st}}{n_i M_{st}},$$

where n_i is the number of carbon atoms in the molecule of the ith component. For benzene as the standard,

$$K_B = \frac{M_i}{n_i} \times 0.077.$$

These correction coefficients are independent of the type of detector and of the nature of the carrier gas.

Other Detectors

Information has been published on the correction coefficients of other detectors. Wirth[98] and Bredel[99] have shown that the relative molar correction coefficient for the flame temperature detector is the ratio of the heats of combustion. With other detectors there appears to be no simple systematic relationship between the signal and the nature of the substance for analysis[100,101].

TABLE 3. Molar correction coefficients K_M for oxygenated compounds (relative to benzene). Katharometer detector.

Component	Carrier gas: helium		nitrogen	Component	Carrier gas: helium		nitrogen
	61	31	62		61	31	62
Alcohols				Pentan-2-one	—	—	1.03
Water	0.476	0.365	—	Pentane-3-one	0.909	—	1.02
Methanol	1.818	1.593	5.26	2-Methylpentan-4-one	—	—	0.86
Ethanol	1.384	1.214	2.96	3,3-Dimethylbutan-2-one	0.846	—	0.91
Prop-2-en-1-ol	—	—	2.00	Hexan-2-one	—	—	0.85
Propan-2-ol	1.174	—	2.04	2-Methylpent-2-en-4-one	—	—	0.88
Propan-1-ol	1.200	1.048	1.75	Heptan-2-one	0.752	—	0.74
Methylpropan-2-ol	1.054	—	—	Methylheptanone	—	—	0.69
Butan-2-ol	1.033	—	1.39	Octan-2-one	0.679	—	0.62
Methylpropan-1-ol	—	—	1.25	Methyl phenyl ketone	—	—	0.69
Butan-1-ol	1.054	0.924	1.15	Nonan-2-one	—	—	0.55
2-Methylbutan-3-ol	0.942	—	—	Isophorone	—	—	0.74
Pentan-3-ol	0.916	—	—	Decan-2-one	—	—	0.49
Pentan-2-ol	0.918	—	—	Menthanone	—	—	0.73
2-Methylbutan-4-ol	0.933	—	—	Camphor	—	—	0.74
Pentan-1-ol	0.942	0.826	0.88	Undecan-2-one	—	—	0.44
Hexan-1-ol	0.849	0.744	0.73	β-Ionone	—	—	0.43
Cyclohexanol	—	—	1.09	γ-Ionone	—	—	0.40
Heptan-1-ol	0.773	0.678	0.60	*Ethers*			
Phenylmethanol	—	—	0.82	Diethyl	0.912	—	1.22
Octan-1-ol	—	—	0.52	Butyl methyl	—	—	0.98
Nonan-1-ol	—	—	0.46	Diisopropyl	0.768	—	0.86
Decan-1-ol	—	—	0.40	Di-n-propyl	0.761	—	0.78
Citronellol	—	—	0.47	Butyl methyl	—	—	0.99
Geraniol	—	—	0.48	Butyl ethyl	0.768	—	0.81
Linalool	—	—	0.49	Butyl propyl	—	—	0.68
Menthol	—	—	0.73	Di-n-butyl	0.625	—	0.59
α-Terpineol	—	—	0.68	Dipentyl	0.545	—	—
Laurol	—	—	0.40	Furan	—	—	1.30
Myristol	—	—	0.31	Tetrahydrofuran	—	—	1.04
Stearol	—	—	0.22	1,4-Dioxan	—	—	0.99
Palmitol	—	—	0.26	Tetrahydropyran	—	—	0.96
Ketones				2-Methylfuran	—	—	1.02
Propanone	1.162	—	1.54	2,5-Dimethylfuran	—	—	0.83
Butanone	1.020	—	1.25				
2-Methylbutan-3-one	—	—	1.05				

TABLE 4. Molar correction coefficients K_M for esters (with respect to benzene). Katharometer detector.

Component	Carrier gas		Component	Carrier gas
	helium 61	nitrogen 62		nitrogen 62
Methyl formate	–	1.43	n-Butyl propionate	0.58
Ethyl formate	–	1.09	Methyl 1-chloropropionate	0.66
Isopropyl formate	–	0.94	Methyl 2-chloropropionate	0.60
n-Propyl formate	–	0.88	Ethyl 1-chloropropionate	0.59
Allyl formate	–	0.95	Ethyl 2-chloropropionate	0.52
Isobutyl formate	–	0.77	Methyl pyruvate	0.99
s-Butyl formate	–	0.79	Ethyl pyruvate	0.82
n-Butyl formate	–	0.74	Methyl crotonate	0.79
2-Chloroethyl formate	–	0.72	Ethyl crotonate	0.67
Ethyl acetate	0.901	0.84	Isopropyl crotonate	0.61
Isopropyl acetate	0.826	0.75	n-Propyl crotonate	0.58
n-Propyl acetate	0.812	0.75	Methyl isobutyrate	0.77
Allyl acetate	–	0.78	Ethyl isobutyrate	0.67
t-Butyl acetate	–	0.72	Isopropyl isobutyrate	0.61
Isobutyl acetate	0.743	0.64	n-Propyl isobutyrate	0.59
s-Butyl acetate	–	0.68	s-Butyl isobutyrate	0.58
Isopentyl acetate	0.69	0.56	Isobutyl isobutyrate	0.55
n-Hexyl acetate	–	0.50	n-Butyl isobutyrate	0.54
n-Heptyl acetate	0.587	0.42	Methyl n-butyrate	0.74
n-Octyl acetate	–	0.36	Ethyl n-butyrate	0.65
Decyl acetate	–	0.31	Allyl n-butyrate	0.60
Geranyl acetate	–	0.33	Isopropyl n-butyrate	0.59
Lauryl acetate	–	0.27	n-Propyl n-butyrate	0.57
Myristyl acetate	–	0.23	s-Butyl n-butyrate	0.54
Stearyl acetate	–	0.19	Isobutyl n-butyrate	0.52
Palmityl acetate	–	0.21	n-Butyl n-butyrate	0.51
2-Acetoxyethanol	–	1.00	Methyl n-valerate	0.63
Methyl methoxyacetate	–	0.82	Ethyl n-valerate	0.56
Ethyl methoxyacetate	–	0.69	Methyl n-hexoate	0.56
Methyl ethoxyacetate	–	0.68	Methyl heptoate	0.50
2-Methoxyethyl acetate	–	0.66	Methyl octoate	0.42
Ethyl ethoxyacetate	–	0.59	Methyl nonoate	0.36
2-Ethoxyethyl acetate	–	0.57	Methyl decoate	0.32
Methyl acetoacetate	–	0.69	Methyl laurate	0.28
Ethyl acetoacetate	–	0.61	Methyl myristate	0.25
Methyl chloroacetate	–	0.71	Methyl palmitate	0.22
Ethyl chloroacetate	–	0.60	Methyl stearate	0.20
n-Propyl chloroacetate	–	0.53	Methyl eicosanoate	0.18
Methyl propionate	–	0.88	Ethyl glycollate	1.04
Ethyl propionate	–	0.75	Methyl lactate	1.200
Allyl propionate	–	0.68	Ethyl lactate	0.93
n-Propyl propionate	–	0.64		
Isobutyl propionate	–	0.58		
s-Butyl propionate	–	0.60		

TABLE 5. Molar correction coefficients K_M for acetals (relative to benzene). Katharometer detector, nitrogen carrier [62].

Component	K_M	Component	K_M
Dimethoxyethane	1.28	Diisopropoxyethane	0.63
Diethoxymethane	0.94	Di-n-butoxymethane	0.52
Dimethoxypropane	0.96	Diisobutoxymethane	0.55
Diethoxyethane	0.80	Di-n-propoxypropane	0.51
Di-n-propoxymethane	0.68	Diisopropoxypropane	0.56
Diisopropoxymethane	0.74	Di-n-butoxyethane	0.47
Diethoxypropane	0.74	Diisobutoxyethane	0.49
Di-n-propoxyethane	0.59		

TABLE 6. Molar correction coefficients K_M for phenols and their ethers (relative to benzene). Katharometer detector, nitrogen carrier [62].

Component	K_M	Component	K_M
Phenol	1.16	*o*-Chlorophenol	0.67
o-Cresol	0.94	*m*-Chlorophenol	0.60
m-Cresol	0.86	*p*-Chlorophenol	0.60
p-Cresol	0.87	4-Chloro-2-methylphenol	0.56
2-Ethylphenol	0.73	4-Chloro-3-methylphenol	0.55
4-Ethylphenol	0.66	Anisole	0.84
2,6-Dimethylphenol	0.73	Phenetole	0.66
2,4-Dimethylphenol	0.68	*o*-Cresyl methyl ether	0.75
2,3-Dimethylphenol	0.72	*m*-Cresyl methyl ether	0.67
2,5-Dimethylphenol	0.69	*p*-Cresyl methyl ether	0.68
3,4-Dimethylphenol	0.69	*o*-Cresyl ethyl ether	0.62
3,5-Dimethylphenol	0.65	*m*-Cresyl ethyl ether	0.55
3-Methyl-5-ethylphenol	0.53	*p*-Cresyl ethyl ether	0.54
2,4,5-Trimethylphenol	0.60	*o*-Chloroanisole	0.55
2,3,5-Trimethylphenol	0.60	*m*-Chloroanisole	0.49
2,4,6-Trimethylphenol	0.60	*p*-Chloroanisole	0.49

TABLE 7. Molar correction coefficients K_M for alcohols (relative to propan-1-ol). Katharometer detector, helium carrier [64].

Component	K_M	Component	K_M
Methanol	0.222	2-Methylbutan-1-ol	0.756
Ethanol	0.135	3-Methylbutan-2-ol	0.606
Propan-2-ol	0.962	2-Methylbutan-2-ol	0.649
Propan-1-ol	1.00	Pentan-3-ol	0.725
Methylpropan-2-ol	0.787	Pentan-2-ol	0.641
Butan-2-ol	0.833	Pentan-1-ol	0.685
Methylpropan-1-ol	0.538	2-Methylpentan-2-ol	0.629
Butan-1-ol	0.787	Hexan-2-ol	0.629

TABLE 8. Molar correction coefficients K_M for aliphatic acids (relative to nonanoic acid). Argon detector [92].

Component	K_M
Butyric acid	11.11
Valeric acid	2.86
Hexanoic acid	1.89
Heptanoic acid	1.35
Octanoic acid	1.16
Nonanoic acid	1.00
Decanoic acid	0.92

TABLE 9. Molar correction coefficients K_M for alcohols (relative to butan-1-ol). Argon detector [80].

Component	K_M
Propan-1-ol	1.86
Methylpropan-2-ol	2.17
Butan-2-ol	1.37
Methylpropan-1-ol	1.12
Pentan-1-ol	0.93
Hexan-1-ol	0.66

TABLE 10. Molar correction coefficients K_M for phenols and pyridines (relative to benzene). Emissivity detector [31,69].

Component	K_M	Component	K_M
Phenol	0.656	Pyridine	0.306
o-Cresol	0.565	2-Methylpyridine	0.344
m-Cresol	0.675	2,6-Dimethylpyridine	0.313

TABLE 11. Molar correction coefficients K_M for halogenated aromatic hydrocarbons, nitro-compounds[62], thiols, and sulphides[67] (relative to benzene). Katharometer detector.

Component	Carrier gas: nitrogen	Component	Carrier gas: helium
Halogen compounds		*Thiols*	
Chlorobenzene	0.66	Ethanethiol	1.78
o-Chlorotoluene	0.58	Propane-2-thiol	1.64
m-Chlorotoluene	0.52	Propane-1-thiol	1.52
p-Chlorotoluene	0.52	2-Methylpropane-2-thiol	1.42
Benzyl chloride	0.53	2-Methylpropane-1-thiol	1.37
Bromobenzene	0.51	Butane-2-thiol	1.42
o-Bromotoluene	0.49	Butane-1-thiol	1.47
m-Bromotoluene	0.44	Pentane-1-thiol	1.51
p-Bromotoluene	0.43	*Sulphides*	
Nitro-compounds		Dimethyl sulphide	1.14
Nitromethane	1.47	Ethyl methyl sulphide	0.99
Nitroethane	1.16	Diethyl sulphide	0.83
Nitropropane	0.93	t-Butyl methyl sulphide	0.82
		Ethyl isopropyl sulphide	0.79
		Ethyl propyl sulphide	0.91
		Thiacyclopentane	0.94

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THE USE OF ION-EXCHANGE CHROMATOGRAPHY FOR STUDYING THE STATE OF IONS OF HIGH-VALENCY ELEMENTS IN SOLUTION

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I. INTRODUCTION

Advances in the chemistry and technology of the rarer elements have set research workers a number of problems involving investigations into the state of ions from high-valency elements in solution. Generally, such ions cannot exist in the free state in aqueous solutions, owing to their relatively high ionic potential, and undergo hydrolysis or form complexes with various ligands; the formation of hydrolysed polymeric species is also characteristic of these ions.

The state of ions of high-valency elements greatly affects their reactivity with various reagents and the composition of the reaction products. This is of particular importance in analytical chemistry and in the hydrometallurgical processing of ores where one requires to separate metals, to isolate them from solution, and to obtain compounds or reaction products having a specific composition.