

SOME STUDIES
ON
MASS SPECTROMETRY

A thesis presented for the degree of

DOCTOR OF PHILOSOPHY

to

The University of Glasgow

by

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CHAPTER ONE

INTRODUCTION

Any short introduction to the ways and means of mass spectroscopy has, almost inevitably, to start with the way instrumentation has developed during the relatively short period since the creation of the first mass spectroscope.

This happened in 1907¹, when J.J.Thomson described his first and now familiar cathode-ray-tube style parabola instrument, and the experiments he had performed with it. The "rays of positive electricity" which he was first to separate according to their charge-to-mass ratios had been discovered in 1886 by E.Goldstein² and by then called "Kanalstrahlen", as they appeared through narrow channels in the cathode of his lamp.

Much important information was gathered by Thomson's instrument and its later and improved versions, about the nature and properties of ionized species from gas discharges. Isotopes of radioactive elements were already known but he discovered evidence of the existence of the first non-radioactive isotopes.¹

In general, a mass spectroscope (otherwise called spectrometer or spectrograph, according to the way charged particles are detected) is an instrument designed to convert a sample into a beam of ions and hence to separate this beam according to mass-to-

-charge ratios. It needs a very high vacuum (10^{-6} torr or higher) and consists essentially of an ion source to form the beam of ions, an analysing system to disperse and resolve the beam into a spectrum and a detecting system to transform the collected beams into a measurable signal.

Ancillary equipment comprises an inlet system which brings a sample (in a suitable form) to be introduced under vacuum into the ion source; a pumping system, generally using mechanical and diffusion or ion pumps; a recorder. Several electrical and electronic systems, more or less sophisticated, are provided to control and measure the various processes and stages involved. The finished product, the mass spectrum, is delivered, usually in the form of a paper chart or a photographic plate.

The later versions of Thomson's instrument used photographic detection. A different design was introduced by Aston^{3,4}, in 1919, photographic detection again being used, as the analysed ion beams were all brought to focus in the same plane. The ions formed in a gas discharge were sorted and focused by passing through consecutive electrostatic and magnetic fields. Those two instruments were the fore runners of the mass spectrographs.

At the same time Dempster⁵ had built the first mass spectro-

meter, of an entirely different design. By bombarding a salt with electrons or by heating it on a metallic filament, ions of low kinetic energy were formed, accelerated through a potential difference and separated by an electromagnet, whose poles were cut in a semicircle.

Aston could measure mass very accurately (1 part in 130 in the first version, up to 2000 in later devices) but the relative peak intensities or abundances on his plates could only be estimated by comparison of the blackening of the lines. In the Dempster instrument, however, electrical detection and measurement were used, at first with a quadrant electrometer, and so accurate relative intensity measurements were possible. This was also much less cumbersome and so most of the early work done in mass spectroscopy was done in mass spectrometers. Hence the reason why the discipline is almost universally called "Mass Spectrometry" nowadays.

In Aston's machine the ion source used was a gas discharge, consequently the ions had great energy spreads. However, by passing through narrow slits they were well collimated in direction and the arrangement of the two fields was such that all ions of the same mass were made to converge (focus) in one point, irrespective of their energies. This effect is called velocity focusing.

In Dempster's machine, with only a magnetic field, velocity focusing is absent but, as can easily be shown, if a slightly divergent beam of identical masses emerges from a point source (slit) it will converge again to a point focus after being deflected 180° of arc. The instrument is said to have direction focusing.

Both Aston's and Dempster's instruments had only single-focusing properties.

These early devices were mostly used to survey and search for stable isotopic species. As the resolution improved it became apparent that isotopic masses departed from integer numbers and the need arose for even higher resolving power to look into this phenomenon more closely. This was achieved with the double-focusing principle, introduced first again in a new instrument by Dempster⁶, in 1935 and, simultaneously, by Bainbridge and Jordan⁷ in 1936. These were double-focusing for one mass only, at the location of the slit.

In Vienna, meanwhile, Mattauch and Herzog⁸ had developed the theory of double-focusing for all masses, and had actually built such an instrument. It is in very wide use still today.

In 1940 Nier⁹ introduced the 60° sector magnetic analyser which has a higher efficiency for the same field strength than the

180° sector. Hipple¹⁰ in 1942 used a 90° sector and modern instruments use one or other of these. Johnson and Nier¹¹ designed a double-focusing machine using a 90° electrostatic analyser followed by a 90° magnetic sector and this design, again, is very widely used today.

Many other specially designed instruments using electrostatic and magnetic deflections have been made with single and double-focusing properties, to first or higher orders of approximation, like the trochoidal mass spectrometer¹², where two mutually orthogonal electric and magnetic fields produce ion paths that are cycloidal.

The great progress that had been achieved during World War II in the field of radar and communications made possible the application of completely new techniques in mass spectrometry, namely pulsed electric fields, in the radio-frequency range. The best known of these new instruments is the time-of-flight mass spectrometer¹³. Ions produced by electron bombardment are drawn from the ion source by a short electric pulse of about 1 μ sec duration, accelerated and set adrift in a long field-free tube. Using suitable voltages and pulse durations in the acceleration stage ions with the same mass but starting at different points can be made to converge in flight, coming to a planar focus. Upwards of 10 000 complete spectra per second may be obtained with these instruments.

Other designs employing radio-frequency techniques are the Bennett¹⁴ and Redhead^{14a} types. Of a different conception but still using radio-frequency, is the quadrupole mass spectrometer, by Paul and co-workers¹⁵. A two-dimensional quadrupolar field is established between four rod-shaped cylindrical electrodes. Two electric fields, one constant the other alternating are superimposed in opposite pairs of rods and a beam of ions is made to undergo oscillations as they travel along the space within the rods. By scanning the fields appropriately a mass spectrum is obtained. This instrument exhibits a high transmission of ions, as no slits are involved.

All these devices have the advantage of dispensing with the use of magnets, always bulky and unwieldy. Using combinations of radio-frequency and magnetic fields the "omegatron"¹⁶ and the "synchrometer"¹⁷ were produced whereby ions are forced to spiral outwards of their place of formation or undertake a circular motion. Mass separation is effected respectively by selective acceleration of ions of a certain mass, which move in resonance with the field or by using the differences in time of flight of the different masses.

Other and more specialized instruments include the coincidence time-of-flight¹⁸; the ingenious and puzzlingly simple energy-to-mass analysers that travel in the nose of satellites¹⁹; the very sophis-

ticated ones built for extra-high resolution²⁰; and others incorporating both positive and negative ion analysis²¹.

In parallel with the accurate measurements of mass, essential for both atomic weight determinations and the establishment of empirical formulas of polyatomic ions, the mass spectrometer has been used extensively to study the energetics of ionization and to measure or compare the intensities of ion beams.

The determination of empirical formulas, chiefly in organic chemistry has become one of the major applications of mass spectrometry since Beynon's²² pioneering works in the field. Organic molecules under electron bombardment often produce complex patterns of ions, stemming from the decomposition of the initial ionized species. These patterns, owing to their two-dimensional diversity, in mass and abundance, are, in general, quite specific for each molecule. Furthermore, it has been found that, to a great extent, the fragmentations follow ground state chemical mechanisms²³. Therefore, many unknown and complex molecules have been studied and their structures elucidated, although the precise laws of breakdown are far from simple. Thus, empirical correlations and analogies are being used, at present, to rationalize the experimental results²³.

Because of the evidence that the initial molecular ion is

able to produce different ion fragments, according to different pathways, a theory to interpret mass spectra as the result of competing, simultaneous decompositions, having different rates, has been developed²⁴. It assumes a time of residence of the primary ions inside the source long enough for the imparted energy to be randomly distributed, through an efficient coupling between electronic and vibrational motion. This should allow for a quasi-equilibrium to become established among the enormous number of energy states that would be present for even small-sized molecules of organic compounds, at the relatively high energies usual in the electron bombardment sources. Reaction rates are then predicted by transition-state kinetics. The theory has been steadily tested and improved²⁵ and seems well enough rooted now to be able in time to yield explanations for the features of complex systems.

As a comparator of ion beam intensities, the mass spectrometer has been used extensively in analysis. Most of the present work will be occupied with this application, therefore no more elaborations will be made at this point.

Amidst all other branches of spectroscopy, mass spectroscopy stands alone (except for the newly-born electron spectroscopy, which may perhaps be said to be its offspring), owing to two main differences.

Firstly ions, contrary to radiation, have electric charges and very substantial masses and so instrument geometries have to be compromises, taking into account space charges and velocity scatter and have always to be computed skilfully so as not to fall too short of the theoretical expectations. Secondly, the instrument is doomed forever to have to "swallow" and "digest" its samples and to have its inside in permanent danger of invasion from the pumping fluids usually employed, both of which, in turn, will coat and spoil the sensitive and carefully designed metallic surfaces (which define the electric potentials) and will otherwise contaminate and be a perpetual source of "background".

It may be safely said that the major breakthroughs in mass spectroscopy have been instrumental: new and ingenious concepts of mass separation; higher orders of ion focusing; ever-increasing mass resolution; new methods of ion production with corresponding novel sources;²⁶ new limits of sensitivity and stability; versatile inlet systems even allowing for coupling with other techniques²⁸; fast and automated acquisition and processing of data;²⁹ etc..

Like the other branches of spectroscopy, mass spectroscopy is an experimental subject. But there are few others where personal dexterity, intuitive feeling and craftsmanship can still play so great a part. The first mass spectrometers were born in the hands of very

capable practical experimentalists, like Thomson, Aston and Dempster. But even in the most modern spectrometers, to obtain the high performances, in both resolution and sensitivity, for which they were intended, or to get the best results in analysis, lengthy and painstaking procedures involving scrupulous cleanliness, source alignments, slit adjustments and magnet shifting have to be sought, mostly in an empirical manner. This is still very much of an art, involving delicate shades of excellence.

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CHAPTER TWO

THE PROBLEM OF CHEMICAL ANALYSIS BY MASS SPECTROMETRY

A. INTRODUCTION

The problems of separation, identification and quantitative analysis of chemical compounds have always been basic in all branches of chemistry, both pure and applied.

Studies of new synthetic methods, identification of components of natural products and control of industrial processes are only a few of the many fields where the analysis of mixtures of varying degree of complexity is of central importance.

Frequently only minute amounts of sample are available, even after many laborious and time consuming stages of preparation and purification. In other instances, as the sampling of reaction vessels for kinetic analysis only small aliquots may be taken to avoid disturbing the concentrations. Therefore, analytical methods that can afford the required answers, using the smallest amounts of material, have been sought and perfected. One of the best among these is, of course, mass spectrometry, which requires only minute quantities of material. Besides its capacity as an analytical instrument, extensive use beginning ¹ more than twenty five years ago, mainly by the petroleum industry, it can be made to yield essential molecular parameters, such as accurate molecular weights and fragmentation pathways .

These latter, in the main, follow chemical patterns, conducive to structure determination.

On the other hand, accuracy in analysis is important in many operations, for instance control of industrial processes where small errors can become very costly. Mass spectrometry has proved to be capable of at least comparable accuracy to many other and more cumbersome techniques.²

It is not surprising, therefore, that the mass spectrometer should have been chosen as a standard analytical instrument for both qualitative and quantitative determinations. Before its outstanding ability for structure determination and qualitative analysis in general became fully realised, it was chiefly used as a quantitative instrument.

Qualitative analysis, however, in the form of compound recognition and structure determination has been, in recent years, more actively pursued than the quantitative aspect.³ This is reflected in the comparatively few studies concerning the analysis of mixtures by mass spectrometry, when compared with the almost unmanageable flood of information regarding structure determinations. The quantitative methods currently used originated and have been kept virtually unchanged in the main for more than twenty five years.

Another factor that has contributed to the lack of deeper exploration of the ability of the mass spectrometer in quantitative analysis has been the relatively recent advent of gas-liquid chromatography (⁴) and its enormous potential for separation of components of very complex mixtures.

The use of the mass spectrometer in analysis has become more and more for identification of the effluent fractions for G.L.C. columns. In many cases, however, retention times for different components of one sample are very nearly the same (⁵) and the corresponding chromatographic peaks are not resolved or only poorly so. In other cases, column "bleeding," i.e. contamination of the effluent with the stationary phase can prove to be a nuisance to the analysis.

There seems, therefore, to be still plenty of room for improvement in the uses of the untapped capacities of the mass spectrometer as a separate analytical instrument on its own merits.

This task can be helped by the widespread use of modern digital computers, that can handle most appropriately the large amounts of data in the form of strings of mass numbers and ion abundances, needed for the performance of analysis by mass

spectrometry ⁶ . The techniques for direct connection of the mass spectral output to a computer have been mainly the result of the search for structural information, as referred to above, but can be profitably used, without any basic alteration, for the quantitative analysis of mixtures. One circumstance that can be very helpful in bringing about a satisfactory answer to the problem is the development of new ionization techniques, which produce much simpler spectra than is usual from normal electron impact. These are photoionization, ⁷ field ionization ⁸ and chemical ionization ⁹ , but at present not enough is known about them to say that sufficient stability and reproducibility of the resultant spectra is obtained by the new processes at this stage of development.

On the other hand, ion formation by low energy electrons, usually only a few volts above the ionization thresholds of the molecules involved, has proved a very useful method, mostly for compound identification in complex mixtures. However, the fact that the electron energies used here correspond to a steep part of the ionization efficiency curves makes it difficult that good reproducibility and accuracy of the quantitative analyses should be obtained.

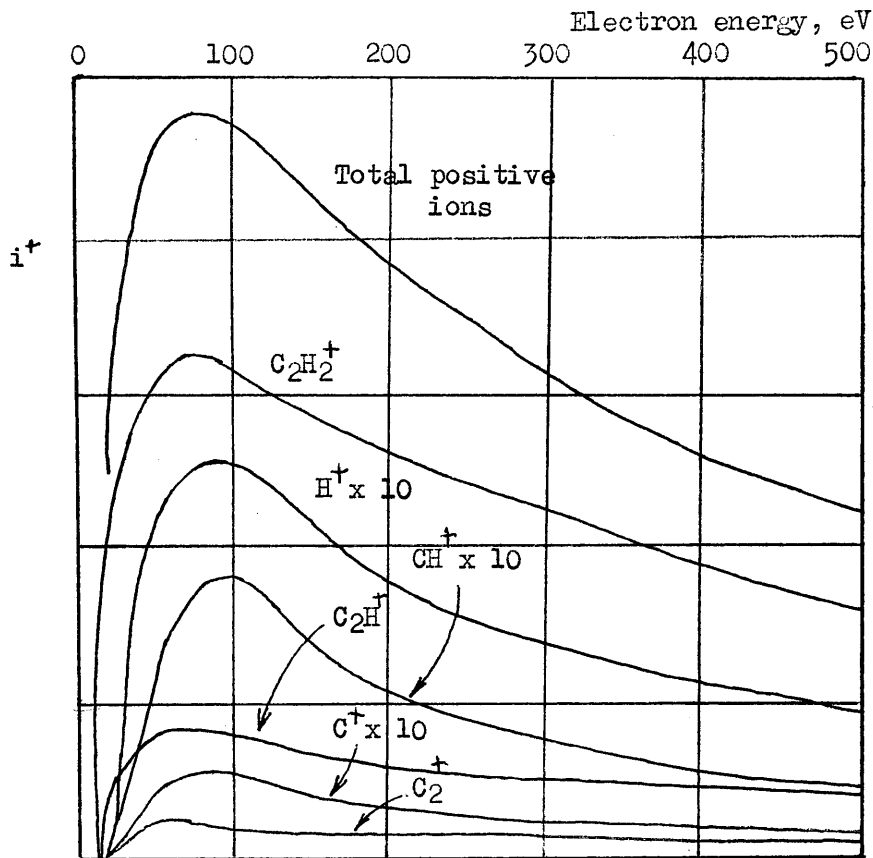


Fig.1 - Ionization efficiency curves for ions of C_2H_2 .¹⁰

The same effect also contributes to the loss of sensitivity that the use of low-energy ionization entails. The sensitivities obtained, for instance, at 9 eV are about two to three orders of magnitude lower than for a 70 eV electron beam¹¹.

In what follows a brief account of the main developments in the use of the mass spectrometer to analyse mixtures will be given, as an introduction to a fresh approach to the problem.

B. REQUIREMENTS FOR THE ANALYSIS

There are some requirements that limit the use of the mass spectrometer for the quantitative analysis of mixtures. The main ones being:

- (1) Inside the mass spectrometer ion source Dalton's law of partial pressures should apply;
- (2) The response of the instrument, in terms of measured ion current, is linear with the partial pressure of each component, inside the ion source;

The combination of these two basic conditions gives the general premise for analysis:

The mass spectra of mixtures, in the pressure ranges normally used, are linear superpositions of the individual mass spectra of the components.

Two other restrictions, of a somewhat lower degree of importance, are:

- (3) The fragmentation patterns of the components should be stable and substantially invariant for small changes in operating conditions;
- (4) The same should apply to the sensitivity co-efficients of the instrument towards the components.

Since inside the ion source only gases are present, condition (1) generally obtains. The instruments are normally designed so that condition (2) is fulfilled, either permanently or adjusting certain parameters. For example, in ion sources of the Nier type ¹², a repeller voltage is used to help the ion withdrawal. This can usually be varied at will for a range of values, the collection of ions being very sensitive to some positions ¹³(Fig 2). It has been found ¹³ that only parts

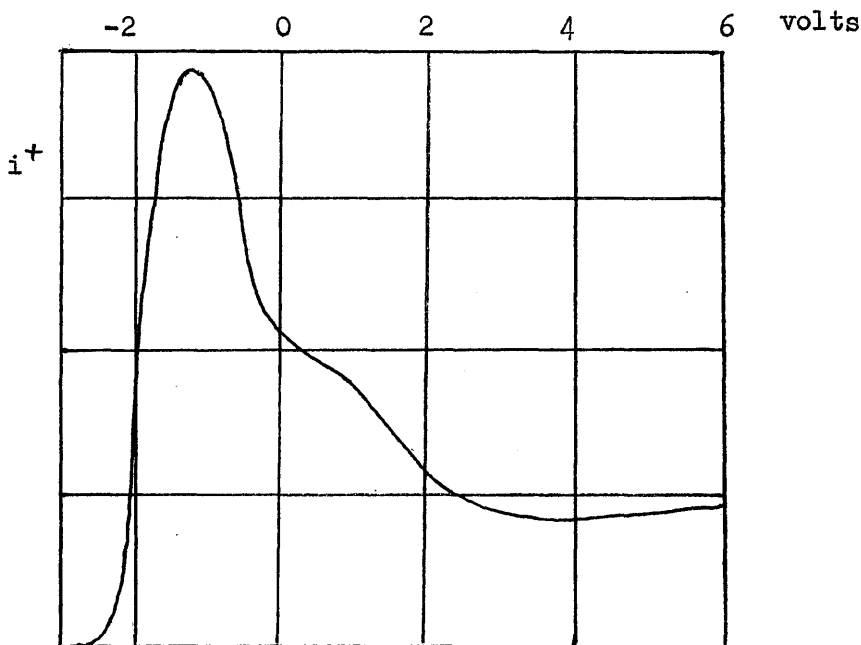


Fig.2 - Dependence of ion beam intensity on repeller potential ¹³.

of this range (usually the second peak of the repeller curve) are suitable for analysis, by keeping to condition (2).

The pressure ranges used inside the ion source have to be low enough in order to avoid ion-molecule collisions, which would distort the fragmentation patterns of the components. Pressures of the order of 10^{-5} torr or lower are usually employed.

However, some interference among compounds is known to occur giving rise to mutual changes in their fragmentation patterns¹⁴. Not a great deal is understood about the causes, but preventive methods have been employed to minimise the effects and so render the cracking patterns stable.

Formerly, conditioning the ion source for several hours with an unsaturated hydrocarbon led to minimal interference in hydrocarbon analysis. Currently, the use of rhenium filaments has greatly overcome this problem.

Once the above requirements are met the general analysis can proceed, along two different routes. The first, involves either the measurements of pressures in the inlet system or the introduction of a constant amount of gas sample always

(e.g. via a dosimeter). The second method makes use of an auxiliary calibration mixture, made up with known amounts of the components. By comparison of its mass spectrum with that of the unknown, the partial pressures in the latter can be found¹⁵.

Both methods make use of matrix algebra throughout and a brief outline of each follows.

C. ANALYSIS USING PRESSURE MEASUREMENTS

In the mass spectrum of a mixture of the n components A,B,C,..N, the ion abundance h_i corresponding to any mass i can be written:

$$h_i = a_i s_A p_A + b_i s_B p_B + \dots + n_i s_N p_N \dots (1)$$

or, more succinctly:

$$h_i = \sum_{j=1}^n a_{ij} s_j p_j \quad (1a)$$

where a_i , b_i , ... n_i (or, in general, a_{ij}) are the relative ion abundances of the components A,B,..N (referred to as j , in general), contributing to mass number i , p_A , p_B , ... p_N are the partial pressures (p_j) of the components, and s_A , s_B , ... s_N are the instrumental sensitivities towards each component (s_j). As the sensitivity factors are constant for all mass numbers of each component spectrum, it is usual to combine the two factors $s_j p_j$ in only one type of factors, x_j , which, for formal convenience, will be henceforth called composites.

When all mass numbers are taken into account, the following array obtains:

$$(2) \quad \left\{ \begin{array}{l} h_1 = a_1 x_A + b_1 x_B + \dots + n_1 x_N \\ h_2 = a_2 x_A + b_2 x_B + \dots + n_2 x_N \\ \cdot \quad \quad \cdot \quad \quad \cdot \quad \quad \cdot \\ \cdot \quad \quad \cdot \quad \quad \cdot \quad \quad \cdot \\ \cdot \quad \quad \cdot \quad \quad \cdot \quad \quad \cdot \\ h_{mx} = a_{mw} x_A + b_{mw} x_B + \dots + n_{mw} x_N \end{array} \right.$$

$$(2a) \quad \text{or } h_i = \sum_{j=1}^n a_{ij} x_j \quad (i = 1, 2, \dots, mw)$$

where mw is the mass number of the peak at highest mass present in the spectrum of the mixture.

The relative ion abundances are the result of normalization of the experimental values for the spectrum of each component, usually with respect to the abundance of its base-peak (most abundant peak in each spectrum). They sometimes are normalized through division by the sum of all ion abundances in the spectrum or total ion current. Their relative values are obviously still

the same, although the normalized figures differ in the two methods. The latter method is more used when it is intended to convey an idea of the relative contribution of a given peak or set of peaks for the total spectrum, as opposed to how it compares with the strongest peak.

The sensitivity factor for each pure component is the abundance of a standard peak (usually the strongest or base-peak) per unit of pressure of the gas on the inlet reservoir.

Both the relative abundances and the sensitivity factors for all the mixture components must be known beforehand, by suitable calibration runs. Using matrix algebra notation^(*) we get from (1):

$$\begin{bmatrix} h_1 \\ h_2 \\ \cdot \\ \cdot \\ h_{mw} \end{bmatrix} = \begin{bmatrix} a_1 & b_1 & \dots & n_1 \\ a_2 & b_2 & \dots & n_2 \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ a_{mw} & b_{mw} & \dots & n_{mw} \end{bmatrix} \times \begin{bmatrix} a_A & 0 & \dots & 0 \\ 0 & s_B & \dots & 0 \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & \dots & \cdot \\ 0 & 0 & \dots & s_N \end{bmatrix} \times \begin{bmatrix} p_A \\ p_B \\ \cdot \\ \cdot \\ p_N \end{bmatrix} \quad (3)$$

$$\text{in short} \quad h = ASp \quad (3a)$$

(*) Please see footnote next page.

or, putting sensitivities and pressures together,
as in eq (2):

$$\begin{bmatrix} h_1 \\ h_2 \\ \cdot \\ \cdot \\ \cdot \\ h_{mw} \end{bmatrix} = \begin{bmatrix} a_1 & b_1 & \dots & n_1 \\ a_2 & b_2 & \dots & n_2 \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ a_{mw} & b_{mw} & \dots & n_{mw} \end{bmatrix} \times \begin{bmatrix} x_A \\ x_B \\ \cdot \\ \cdot \\ \cdot \\ x_N \end{bmatrix} \quad (4)$$

In short:

$$h = Ax \quad (5)$$

So, the analytical data in eq. (4) being the set of values of h_i for all masses, the problem is to find the "composite" factors x_i and ultimately the partial pressures, p_A, p_b, \dots, p_N .

(*)

This extension of the notation is used here merely for abbreviating the explanation. A fuller introduction to the use of matrix algebra in mixture analysis is delayed until Chapter 3.

Usually many more masses (equations) than components (unknowns) are present, the problem being, therefore, overdefined. However, owing to the inherent measurement imprecisions involved, a "best" solution is normally sought, through optimization of the system of the m equations in n unknowns. This may be done for instance by the method of least squares, weighted or not, or similar technique. Alternatively, n peaks only may be carefully chosen for the computations, as explained below ¹⁵. Therefore, ultimately, the system reduces to finding the solution for a system of n simultaneous equations in n unknowns and the matrix equation (4) now involves a square matrix A , which can be inverted. The solution is obviously:

$$x = A^{-1} h \quad (6)$$

and the partial pressures will be:

$$p_j = \frac{x_j}{s_j}, \quad (j = A, B, \dots, N) \quad (7)$$

When computational facilities are limited and speed of analysis is essential, certain short-cuts can be used, although some loss of accuracy may be involved. Equations of type (1) may be

chosen, corresponding to mass numbers which are known, from the calibration runs, to contain only contributions of selected components. In this way, the computational stages normally involved in matrix condensation along the main diagonal ¹⁶, customarily used to solve systems of linear equations, is bypassed, and only the regressive substitution stage, giving directly the answers needs to be performed.

Situations where this shorthand procedure might be applied are frequently met with in practice, where mixtures of compounds of different molecular weights are involved. At increasing mass numbers the contributions from the lighter elements of the mixture are lost and the equations become naturally simpler. However, as Barnard ¹⁷ points out, such solutions may bring considerable errors to the analysis, mainly owing to the fact that the use of small peaks in the computations can be rather unreliable.

Another time-saving device is frequently used when, as in industrial plant control, the same type of analysis is done often in a routine basis. Here no loss of accuracy is entailed. From equation (6) it is clear that the inverse

matrix A^{-1} , when the components are always the same, can be computed once, and for all analyses. The computation that remains to be done is the product hA^{-1} each time a new analysis is performed.

Still another short-cut variant of the main method of simultaneous linear equation is that called the "subtraction technique" by Kiser¹⁸. It only uses the unique peaks, i.e. the peaks due only to each component, and, as shown above, this procedure can be inaccurate. Essentially, it consists of subtracting, from the mixture spectrum, the aliquot contributions from each component, in turn, as given by the size of their unique peaks, the respective sensitivities being taken into account. Even if it cannot be applied wholly throughout, this method may be able to simplify greatly the system of linear equations.

Once the answer is obtained in the form of partial pressures from the sensitivity factors, as shown through equations (1-6) a check on accuracy is usually made by comparing the sum of the

resulting partial pressures with the total pressure, as measured in the inlet system, usually with a micromanometer ¹⁹ .

Although the two should theoretically be equal, many factors, such as random changes of sensitivity, interference, preferential adsorption and desorption effects, etc., can cause disparities. Only practice and skilful judgement can determine by what amount the two values may be allowed to differ.

D. ANALYSIS USING A CALIBRATION MIXTURE

The method described above presuppose, not only that the several components of the mixture be known but also that their spectra have been run at measured pressures so that both their fragmentation patterns and the instrumental sensitivities in terms of base-peak abundance per unit of pressure are available to make the analysis. If facilities for pressure measurements are lacking or analysis are made in circumstances that preclude the use of the reservoir inlet system - e.g. when volatility or abundance of sample are low - the following method may be preferable.

It has been shown early ²⁰ that for binary systems their composition could be calculated if a calibration mixture of known composition made with the same components had been run. The problem was thought to have a solution in the general case ^{20,21} but only very recently ²² was this worked out. Here is a brief outline of the solution.

In eq. (1a) the partial pressures p_j can be written in terms of the mole fractions, m_j , for each component, as $\sum p_j = P_c$, then $m_j = \frac{p_j}{P_c}$, P_c being the total pressure for the calibration

mixture.

Eq. (1a) then becomes

$$\sum_{j=1}^n a_{ij} s_j P_c m_j = h_{ic} \quad (8)$$

where h_{ic} is the ion abundance for mass i in the calibration mixture

$$\text{Let } s_j P_c = q_j \quad (9)$$

$$\text{and } a_{ij} m_j = \alpha_{ij} \quad (10)$$

Eq. (1a) is now

$$\sum_{j=1}^n \alpha_{ij} q_j = h_{ic} \quad (i=1,2,\dots,n) \quad (11)$$

$$\text{or } Aq = h_c \quad (12)$$

The solution of which is

$$q = A^{-1} h_c \quad (13)$$

When the unknown mixture is run, the corresponding parameters now are:

P_x , total pressure (unknown)

$$x_j = \frac{p_{jx}}{P_x}, \text{ mole fraction for component } j.$$

p_{jx} , partial pressure for component j .

h_{ix} , ion abundance for mass i

Let the ratio of the total pressures be

$$R = \frac{P_x}{P_c} \quad (14)$$

So, eq. (1a) now assumes the form:

$$\begin{aligned} \sum_{j=1}^n a_{ij} s_j p_{jx} &= \sum_j a_{ij} s_j P_x x_j = \\ &= \sum_j a_{ij} s_j P_c R_{xj} = \\ &= \sum_j a_{ij} q_j R_{xj} = h_{ix} \quad (15) \end{aligned}$$

$$\text{Let } R_{xj} = y_j \quad (16)$$

$$\text{and } a_{ij} q_j = \beta_{ij} \quad (17)$$

Eq. (15) becomes

$$\sum_{j=1}^n \beta_{ij} y_j = h_{ix} \quad (18)$$

or
$$By = h_x \quad (19)$$

which solution is, again:

$$y = B^{-1} h_x \quad (20)$$

Once the y_j are obtained, they can be converted back to the molar fractions x_j :

$$\sum_j y_j = \sum_j R x_j = R \quad (21)$$

and with (10) this gives:

$$x_j = \frac{y_j}{\sum y_j} \quad (22)$$

which is the solution for the general problem. Obviously, the partial pressures for the unknown mixtures can only be derived in terms of the same quantities for the calibration mixture and

as these were not determined only mole fractions are obtained. This is generally, however, all that is required from the analysis.

In this technique, the accuracy of pressure measurements is replaced by the accuracy involved in making up the calibration mixture. It was suggested that the method could be used to evaluate, at least semiquantitatively, the compositions of mixtures introduced via the direct insertion probe, where fractionation, by direct evaporation of a solid or liquid would normally occur. In this case, if the calculated composition of the mixture differs substantially from the calibration standard, a new mixture would be made up, having a composition nearer that of the unknown. An iterative application of this procedure would give a fairly good approximation to the composition sought; for the evaporation conditions prevalent in the source would apply equally to both mixtures.

E. OTHER METHODS OF ANALYSIS BY MASS SPECTROMETRY

Besides the two foregoing methods, which are of general application, some other techniques have been used, with more or less success to the analysis of mixtures.

23 Worth mentioning is the one used by Eden, Burr and Pratt to calculate molecular weights of the components of a mixture. The inlet system of the mass spectrometer itself was used as a fractionating device, by letting the components into the ionization chamber following a purely effusive or molecular regime. The decay rate for the partial pressure (p_j) of each component (j) is proportional to the pressure drop through the molecular leak used, i.e.:

$$-\frac{dp_j}{dt} = c_j (p_j - p_{\infty}) \quad (23)$$

where p_{∞} is the common pressure on the low-pressure side of the leak and, being of the order of 10^{-6} - 10^{-7} torr, may be neglected.

$$\ln p_j^0 / p_j = c_j (t - t_0) \quad (24)$$

where p_j^0 is the partial pressure of component j at time t_0 . If at least one peak at mass i in the mixture spectrum is unique to component j , without interference from the others, equations

(1) and (24) will give:

$$\ln\left(\frac{h_i^0}{h_i}\right) = \ln\left(\frac{p_j^0}{p_j}\right) = c_j (t - t_0) \quad (25)$$

and a plot against time of $\log\left(\frac{h_i^0}{h_i}\right)$, h_i^0 and h_i being respectively

the ion abundances of these unique peaks for each component j , at times t_0 and t , will yield a straight line of slope c_j .

If an internal standard - a compound of known molecular weight - is run at the same time and its behaviour used for comparison, Graham's law gives:

$$c_{\text{standard}} \times \sqrt{\text{m. weight}_{\text{st}}} = c_x \sqrt{\text{m. weight}_x} \quad (26)$$

and as both c_{standard} and c_x are measured from slopes on the graph the molecular weights of the unknown compounds can be deduced. It should be noted that one important feature of this technique is that it provides the number of different compounds present in a mixture by purely physical means, by showing the number of straight lines with different slopes that are obtained.

"Mixed" peaks, which do not follow straight lines are easily distinguishable. For molecular weight determination the method is of only limited usefulness ²⁴ .

Since the introduction by Beynon ²⁵ of the use of high resolution mass spectrometry for compound recognition the qualitative aspect of analysis has been simplified. The assignment on a safe basis of ionic identities to mass spectral peaks has contributed in recognizing single compounds in mixtures. This feature has been exploited by Biemann ^{26,27} in the "element-maps", where tabulations of all peaks of a spectrum in terms of ion identity instead of exact mass number helps to give a visual image of the sample composition.

One technique which uses both high resolution and low electron energy is that introduced by Johnson and Aczel ²⁸ for qualitative analyses of very complex mixtures of hydrocarbons. The complete high-resolution spectrum is recorded in chart form and an interpolation procedure is followed throughout to measure the exact mass of unknown peaks by comparison with those of compounds run simultaneously as internal standards. The unravelling of the spectrum proceeds in stepwise fashion, as the newly determined masses are used as fresh standards. The method lends itself to

automation and computer handling.

The petroleum industry being the main users of the mass spectrometer for analytical purposes, many developments peculiar to hydrocarbon mixtures have taken place. For a good coverage of the subject other sources are recommended ²⁹.

More than ten years ago, Meyerson ³⁰ derived for the first time the spectra of the components of binary mixtures, without prior total separation or detailed knowledge of the identities of the compounds present. The method assumes that the two compounds present possess at least one peak in their mass spectrum unique to each. Two different mixtures of the same compounds are needed for the separation. To discover which peaks are unique to each component the abundance ratios of the peaks at corresponding masses in the two mixtures spectra are listed and the peaks that give the highest and lowest ratios chosen; these peaks contain the least contribution from the other component. The ratio of the abundances in the two mixture spectra of a peak belonging entirely to the fragmentation pattern of a component is found. All the peaks in one of the spectra are multiplied by this ratio so that subtraction of the product from the other, yields the

mass spectrum of one component. A similar procedure gives the spectrum of the other component. If only one component has unique peaks, then only the spectrum of the other may be derived. Meyerson succeeded by this method in separating the pure spectra of benzene and cyclohexane and in identifying persistent impurities in two different samples of n-butyl disulfide, due to butyl sulfide. The method proved capable of distinguishing two different isomers of the sulfide, since each isomer was the contaminant of a different sample.

Also McCormick³¹ has used the same method to separate and identify a mammein homologue of molecular weight 358, present as impurity, in studies of the compounds obtained from Mammeia americana³². The fractionation in this case, was made through thin-layer chromatography.

Again, it was thought that behind the empirical approach of Meyerson a systematic and more general theory might be hidden, that could be made to yield the mass spectra of the components of a mixture starting from several spectra of the same components in different proportions. What follows is the development of such a technique.

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CHAPTER THREE

THE ANALYSIS OF MULTICOMPONENT SYSTEMS WITHOUT PREVIOUS KNOWLEDGE OF COMPOSITION

The analysis of multicomponent systems without previous knowledge of composition is a complex task that requires a systematic approach. This chapter discusses the various methods and techniques used to identify and quantify the components of such systems. The process begins with the collection of data, which may include mass spectra, chromatograms, and other analytical results. These data are then analyzed using a variety of statistical and mathematical tools to determine the most likely composition of the system. The chapter also covers the challenges associated with this type of analysis, such as the presence of unknown components and the need for accurate calibration and validation. Finally, the chapter provides a summary of the key findings and conclusions drawn from the analysis of multicomponent systems without previous knowledge of composition.

A mathematical treatment was developed to deal with the problem of multicomponent systems, without previous knowledge of the number and nature of the components present, and their mass spectra. If applicable to a particular system, this treatment will give, as a solution, the number of components present, their mass spectra, their concentrations and, if desired, the instrumental sensitivities. It requires several mixtures of the same components, in a number greater than that of components. A simple criterion will be given to ensure that this condition has been fulfilled.

The requirement for the method to be applicable is that at least two separate peaks in the spectra of the mixtures should be unique to each component.

This condition may require occasional use of high resolving power to resolve doublets (or multiplets) occurring at nominal

masses. Using additional techniques the problem could still be solved if only one peak is unique to each component; the previously described effusiometric method of Eden *et al.* could be used in this case. Also, if other ionization processes could be used, which would produce simpler spectra than those obtained using electron impact, viz. photoionization ¹, field ionization, ² chemical ionization ³, or low energy electron bombardment, this requirement of two unique peaks to each component would be more easily met. At present not enough is known about some of these techniques to say if there is sufficient stability of the fragmentation patterns and freedom from interference, necessary to analyse mixtures.

The different mixtures to be used may be introduced one at a time in the instrument if available as separate samples or, perhaps in the majority of cases they may be obtained from a single initial sample by means of some fractionating technique, e.g. effusiometry, as described above ⁴, mass separation through the mass spectrometer molecular leak ⁵, differential pumping ⁶, preferential adsorption and desorption ⁷, fraction distillation ⁸ or even by scanning across a non-resolved peak,

flowing out of a G.L.C. column ⁹ .

The problem in its general form is going to be posed, as is clear from what has been said, in terms of a discrete number of items of information made available by the different mixtures involved. This is opposed to another possible approach, whereby a continuous flow of changing data, e.g. from successive sampling of the fractionating system and repetitive running of spectra in the changing conditions is taken for analysis. The latter method would call for a mathematical treatment using differential equations.

As the former is hereby preferred, mostly because we felt that its form is more akin to the normal way mass spectrometry has developed, the problems to solve are mainly in the form of systems of linear equations. Therefore, matrix algebra is used throughout, as this is a long standing practice in mass spectrometry ¹⁰ . Also, it will be readily adaptable for use with a digital computer. In fact, a computer programme has been written to deal with the problem, which will be discussed in Chapter 5 .

THEORETICAL

A. THE NUMBER OF COMPONENTS

For the formal development of what follows we consider a mass spectrum as a vector with as many elements as there are mass numbers, up to the highest present. The elements of the vector are the ion abundances present in the spectrum for each mass number. Some elements may be zero while many others will be significant and if the spectrum belongs to a pure compound, these will form its characteristic fragmentation pattern.

For the \underline{n} compounds A,B,C,...N that will be present in the \underline{l} mixtures to be analysed ($\underline{l} > \underline{n}$), their mass spectra may then be written in vector form ¹¹ :

$$\begin{aligned} \{a\} &= \{ a_1 \ a_2 \ \dots \ a_{ma} \} \\ \{b\} &= \{ b_1 \ b_2 \ \dots \ b_{mb} \} \\ \{n\} &= \{ n_1 \ n_2 \ \dots \ n_{mn} \} \end{aligned} \quad (27)$$

The elements in (27) represent the ion abundances normalized by comparison with an internal reference abundance, usually the base-peak, or the sum of all peaks. The values obtained are therefore dimensionless.

The subscripts form an ordered set containing all the mass numbers to which at least one component makes a significant contribution. They will therefore run from the lowest to the highest mass number found in the mixtures spectra. This latter will be named \underline{m}_w .

Now it is always assumed, when analysing mixtures by mass spectrometry that the fragmentation patterns of the individual components are the result of so many degrees of freedom that they have a true "fingerprint" character which, except in the obvious cases of isomers or very similar molecular structures, are particular to the compound. Without pursuing the matter any further, we will simply assume that the vectors of the set (27) are linearly independent. This means that with any $n - 1$ or fewer of them it is impossible to construct one of the others through multiplication by suitable factors and addition of results (Jacobi operations) ¹².

In other words, it is impossible to find factors $\underline{\alpha}, \underline{\beta}, \dots, \underline{\nu}$, not all zero, such that the expression

$$\underline{\alpha} \{a\} + \underline{\beta} \{b\} + \dots + \underline{\nu} \{n\} = 0 \quad (28)$$

will obtain.

The mass spectrum of any mixture of these n compounds is given by equations (2) or (2a), or in matrix notation, by (4) or (5).

$$h = Ax \quad (5)$$

in which h is the vector spectrum of the mixture, A is the matrix formed with the vectors (27) and x is the vector of the composite factors (product of partial pressures and sensitivities for each component):

$$x_j = s_j p_j, \quad (j=A,B,\dots,N) \quad (29)$$

When the whole set of data formed by the l mixtures is assembled, it may be represented as follows:

Mixtures			Components			Compositions		
I	II	...L	A	B	...N	x_{AI}	x_{AII}	... x_{AL}
h_{1I}	h_{1II}	... h_{1L}	a_1	b_1	... n_1	x_{BI}	x_{BII}	... x_{BL}
h_{2I}	h_{2II}	... h_{2L}	a_2	b_2	... n_2	.	.	.
.
.	h_{iK}	x_{JK}	.
.
h_{mWI}	h_{mWII}	h_{mWL}	a_{mw}	b_{mw}	n_{mw}	x_{NI}	x_{NII}	x_{NL}

or $M = AX$ (30)

In this array h_{iK} stands for the abundance of the i^{th} significant peak of the K^{th} mixture and x_{JK} represents the composite factor corresponding to component J in mixture number K . Matrix M represents the pattern of known mass spectral data concerning the mixtures and matrix X incorporates the quantitative contribution of the components. These connections are more succinctly - although perhaps less clearly - shown on the equivalent equation:

$$h_{ik} = \sum_{j=1}^n a_{ij} x_{jk} \quad (31)$$

with $i = 1, 2, \dots, mw$
 $k = 1, 2, \dots, l$

Now, according to the definition of linear independence, that was mentioned above, the rank of matrix A is n , which is the same as the number of independent components in the system or the number of its degrees of freedom. Thus, for the rank of matrix M not to reduce below n , the rank of X must also be equal to n , implying that the columns of X too must be linearly independent.

This requirement, strict as it may seem, simply asks that the relationships between the vectors of the composite factors (and therefore the partial pressures) are not of first degree. This will mean that, for instance in a two-component system, some kind of separation has actually taken place, without further restrictions. In a three-component set of mixture, it is equivalent to saying that the points which represent the system on a Gibb's phase diagram must not fall upon straight lines. Neither must they be coplanar in a tetrahedral representation of a four-component system. And so on.

It also implies that no new information about the system is provided by combining any number of mixtures and treating the combination as a new mixture. This arises from the fact that any intermediate composition \underline{z} obtained in this way, is related linearly to the already available compositions \underline{x} and \underline{y} :

$$\underline{z} = \underline{x} + \lambda \underline{y} \quad (32)$$

Therefore, once separation in the above sense is achieved, the requirement of linear independence is no longer an obstacle and so, by finding the rank of matrix M the number of components becomes known immediately.

The method, as was stated before, makes use of a number \underline{l} of mixtures greater than \underline{n} , the number of components. A simple way of ensuring that this condition has been fulfilled, since the number of components is unknown at this stage is to compute the rank of matrix M after the addition of each new mixture. If a computer is being used to help perform the calculations this could be done easily. The rank will either stay the same or increase by one unit every time, until it reaches the value \underline{n} , and will keep this value for any further additions of new columns to the matrix.

If a continuous method of fractionating a sample is used, like the effusiometric one above, or any other fractional inlet technique such as the one developed by Bokhoven and Theeuwes,⁸ or even sampling across a G.L.C. peak, the peak abundances in the mass spectra may be regarded as continuous functions of time. In the Appendix an alternative treatment using this functional approach is given, such that it may be used and the results still be congruent with the following developments.

B. THE IDENTIFICATION OF PEAKS

Peaks of a mixture spectrum may be unique to one particular component or common to any number of components.

The mathematical model summarized in equation (2) represents the situation as the products of rows of A and columns of X. The abundances h_{iK} thus formed will include contributions from as many components as there are different non-zero elements in the corresponding row i of matrix A.

The next goal will be to assign labels to each peak in the mixture spectra in terms of the components that contribute to it. This is done in order not only to isolate the peaks which are attributable to only one component but also to gather information that will be needed later. The following development might appear to be based on the assumption that both matrices A and M are available. Obviously, only matrix M is available but the considerations will be of a general character and the conclusions drawn will be applicable to the real situation.

Suppose then, that submatrices of A and M are formed side by side by placing rows corresponding to the same mass numbers in

both submatrices, two-by-two, three-by-three, and so on. For instance, the following submatrices containing the rows \underline{i} and \underline{j} may appear:

$$\begin{aligned} &A_{ij} (A;B) \text{ and } M_{ij} (A;B); \\ &A_{ij} (AC;A) \text{ and } M_{ij} (AC;A); \\ &A_{ij} (ABC\dots N; ABC\dots N) \text{ and } M_{ij} (ABC\dots N; ABC\dots N). \end{aligned}$$

The letters in parentheses indicate which components contribute to the two rows \underline{i} and \underline{j} , of both A and M. Thus, in the two submatrices in the second line above, components A and C contribute to rows \underline{i} and component A to rows \underline{j} of both A and M. All submatrices that are formed by rows to which a unique contribution is made by the same component, have the property (common to submatrices A_{ij} and M_{ij}) that their rank is lower than the number of their rows; an illustration will clarify the point.

If the submatrix of A is as follows:

$$A_{ij} (K;K) = \begin{array}{c} \begin{array}{cc} & \begin{array}{c} A \quad B\dots K\dots N \end{array} \\ \begin{bmatrix} 0 & 0\dots x\dots 0 \\ 0 & 0\dots x\dots 0 \end{bmatrix} \end{array} \begin{array}{l} \leftarrow \text{row } \underline{i} \\ \leftarrow \text{row } \underline{j} \end{array} \end{array} \quad (33)$$

i.e. if only component K contributes to the two peaks i and j, then all second-order determinants taken from the submatrix will vanish. Clearly, the same happens to the determinants taken from the corresponding submatrix of M formed with the same two rows, i and j. This implies that in both submatrices the two rows are multiples of each other. So, if the rows of M are taken two-by-two in all possible ways and tested as to which are multiples of one another a certain number of sets of rows will be obtained. The members of each set are the rows contributed by one and the same compound only. This is obviously so because, two rows that are formed by one component only but by a different one each will not be multiples. So, in all other cases there will be at least one determinant of second order which is not null; the rank of the submatrix is therefore two.

The foregoing considerations apply only if for each compound of the mixtures there are at least two unique peaks in their spectra. If less than two unique peaks exist for any of the components, this could only be detected in a later stage of the analysis, when multicomponent peaks are being labelled. We shall not however enter into the details of this case.

In a manner similar to that already presented for second-order submatrices, it is possible to form submatrices of higher order; the remaining rows of A and M are taken three at a time, four at a time, etc., in all possible ways. In the case of three - row submatrices, consider those which happen to be composed of rows such that each of them is contributed to by only two components; furthermore, these two components are the same for the three rows. All such submatrices will have rank equal to two instead of three and so all third-order determinants extracted from them will vanish. And so on.

Perhaps a simpler and more efficient method for labelling the remaining peaks with regard to the components that enter into their composition (after the removal of the rows contributed to by only one component) is to build up submatrices of higher order, starting with two rows, each due uniquely to a different component e.g. A and B, taken from the sets which were obtained in the previous operation. A third row, taken from those remaining in the matrix, is added. Each time a new row is added, which corresponds to a peak in the mixtures formed by the two components A and B, the rank of the third order submatrix drops from three to

two; or, what amounts to the same thing, all third-order determinants formed in this submatrix, vanish. This peak may then be labelled as formed by components A and B (Table I).

All the other two-component peaks are labelled in the same way.

TABLE I

Symbolic representation of two third-order submatrices of M_n . The third row is under test against the other two, contributed by A and B only.^(*)

	A	B	K		A	B	K
$M_{ijk} (A;B;AB) =$	*	0	0	=	*	0	0
row under test \rightarrow	0	*	0	=	0	*	0
row under test \rightarrow	*	*	0	=	0	0	*
(a)				(b)			
row equal to two				row equal to three			

(*) In this table and also in TABLE II the layout is symbolic in the sense that the asterisks stand for the presence of significant contributions from the components A,B,C and K (and the zeros for their absence) to the rows that constitute the submatrices. They do not represent figures as is usually the case.

To find the three-component peaks one can start with any third-order submatrix with rows already labelled as being formed by the same three components be they unique or binary peaks in any combination two-by-two, and then add another row. If this latter is formed by the same three components which contribute to the other "basic" rows the rank again will drop one unit, from four to three, i.e., all the fourth-order determinants formed in the submatrix will vanish (Table II).

TABLE II

Symbolic representation of fourth-order submatrices of M. The fourth row is under test.

$$M_{ijkl} (AB; C; AC; ABC) = \begin{array}{c} \begin{array}{cccc} & A & B & C & K \\ \begin{array}{l} \text{row 1} \\ \text{row 2} \\ \text{row 3} \\ \text{row under test} \end{array} & \begin{bmatrix} \times & \times & 0 & 0 \\ 0 & 0 & \times & 0 \\ \times & 0 & \times & 0 \\ \times & \times & \times & 0 \end{bmatrix} \end{array} \end{array}$$

(a) Rank equal to three.

$$M_{ijkl} (AB; C; AC; ABK) = \begin{array}{c} \begin{array}{cccc} & A & B & C & K \\ \begin{array}{l} \text{row 1} \\ \text{row 2} \\ \text{row 3} \\ \text{row under test} \end{array} & \begin{bmatrix} \times & \times & 0 & 0 \\ 0 & 0 & \times & 0 \\ \times & 0 & \times & 0 \\ \times & \times & 0 & \times \end{bmatrix} \end{array} \end{array}$$

(b) Rank equal to four.

The same procedure is continued for the four-component peaks, five-component peaks, etc., until all peaks in the mixtures spectra are labelled.

Occasionally, errors in the identification of peaks may occur, owing to peculiar properties of the fragmentation patterns of the components. Consider the case, for instance, where at two separate mass numbers, contributed to only by the same two compounds, the peak abundances in the pure compounds' spectra happen to be in the same ratio. More precisely, suppose that at masses m_1 and m_2 compound J has in its spectrum the abundances j_{m1} and j_{m2} , and compound K the abundances k_{m1} and k_{m2} , and that there are no other contributions for the two mass numbers. If, cumulatively, it happens that the relationship

$$\frac{j_{m1}}{j_{m2}} = \frac{k_{m1}}{k_{m2}} \quad (34)$$

should be verified within the experimental errors of measurement or the tolerance range of the calculations, the two peaks would be erroneously taken as belonging to an extra component.

Higher order relationships, among more than two components, would be less likely to occur on a pure probability basis.

C. THE RECOVERY OF THE SPECTRA

The purpose of the next steps will be to find the spectra of the pure components.

For convenience, the arrangement of the spectra of the pure components in the mixtures represented by A, as given by the former steps of the analysis, may be displayed in the form of Table III.

TABLE III

Mass	Component A	Component B	Component C	...	Component N
m_1	X	0	X	...	0
m_2	0	0	X	...	X
m_3	X	X	X	...	0
.
.
.
m_w	0	X	0	...	0

An (0) indicates an ion which is absent from the mass spectrum of any given compound and an (X) refers to the peak abundance of a particular ion for which the actual value has not yet been determined.

The search for the pure spectra may be realized by finding a new matrix, Q, such that, through multiplication by the only known quantity in the problem, namely M, matrix A would be recovered. The required condition is:

$$MQ = A \quad (35)$$

Comparison with equation (30)

$$M = AX \quad (30)$$

will give:

$$MQ = AXQ = A(XQ) \quad (36)$$

It is obvious that, if we are to retrieve A from equation (36), the factor matrix XQ should merely introduce into A (in AXQ) alterations due to multiplicative constants for each of its columns. Only in these circumstances can A be recovered, by

normalization of the columns, in much the same way as crude spectra are normalized. This is equivalent to stating that

$$XQ = K \quad (37)$$

K being a diagonal matrix of order n , formed by any constants k_1, k_2, \dots, k_n , by which A may become multiplied, as stated above.

Combining equations (36) and (37), the result will be:

$$MQ = AK \quad (38)$$

or, in full:

$$\begin{bmatrix} h_{1I} & h_{1II} & \dots & h_{1L} \\ h_{2I} & h_{2II} & \dots & h_{2L} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ h_{mWI} & h_{mWII} & \dots & h_{mWL} \end{bmatrix} \times \begin{bmatrix} x_1 & 1 & \dots & 1 \\ x_2 & 2 & \dots & 2 \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ x_L & L & \dots & L \end{bmatrix} = \begin{bmatrix} k_1 a_1 & k_2 b_1 & \dots & k_n n_1 \\ k_1 a_2 & k_2 b_2 & \dots & k_n n_2 \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ k_1 a_{mw} & k_2 b_{mw} & \dots & k_n n_{mw} \end{bmatrix} \quad (39)$$

To find the desired matrix Q, some equations will be formed, making use of the known positions of the zeros in matrix A (Table III).

Thus, in the formation of the first column of matrix Q , we use the rows of M corresponding to masses to which the first component (A) is known not to contribute, i.e. which correspond to positions in the first column of matrix A where there are zeros. For such a typical mass \underline{i} , we form the equation:

$$h_{iI} \alpha_1 + h_{iII} \alpha_2 + \dots + h_{iL} \alpha_L = 0 \quad (40)$$

Thus, $\underline{L}-1$ such equations, forming a homogeneous system, would be needed to get the set of \underline{L} unknowns $\alpha_1, \alpha_2, \dots, \alpha_L$.

The same would apply to any other column of matrix Q . But, since only \underline{n} of the \underline{L} columns of matrix M are independent, any set of \underline{n} independent columns of M can be used, jointly with a shorter version of matrix Q (we shall denote it by Q') with \underline{n} rows only, namely:

$$Q' = \begin{bmatrix} \alpha_1 & \beta_1 & \dots & \nu_1 \\ \alpha_2 & \beta_2 & & \nu_2 \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \alpha_n & \beta_n & & \nu_n \end{bmatrix} \quad (41)$$

By so doing, the number of equations of type (40) to be used is reduced to $n-1$; as the system is homogeneous, one unknown may be given any arbitrary value. For all other purposes, Q' is equivalent to Q in its functions and it can replace Q in the equations where it appears.

This part of the analysis requires that each component should not have peaks on at least $n-1$ mass numbers to which others contribute. This obviously depends, as before, on the complexity of the system, on the ionization process used and on the similarity of the spectra. Such requirement is, on the whole, less stringent than that of unique peaks.

Also, the internal consistency of the system (40) of linear equations requires the use of a set of peaks for which contributions from all the components - except, of course, the one being sought - are present. In other words, all but one of the constituents of the mixtures must be represented in the reconstruction of each pure spectrum.

For instance, in a four-component system, for the calculation of the second column of matrix Q (corresponding to component B) one would use from matrix M (shortened) those rows labelled "A; AC; AC; CD" or "A; C; CD; C," but neither "A; AD; D; D" nor "A; A; A; D;" for in both cases compound C is missing.

Once all elements of Q' are obtained, the straightforward multiplication of M (shortened) by Q' (equation 38) followed by normalization of the columns of the obtained AK directly gives the spectra of the pure compounds.

The identification of the pure spectra may now be made by the usual methods. It can be studied directly and interpreted for the qualitative analysis ¹³ or may be matched against a bank of spectra; for which the format it is likely to be in at this stage - computer paper or magnetic tape, core memory - may help in eliminating intermediate steps.

Instead of using only one shortened form of matrix M , by taking a number of independent mixtures equal to its rank, it may prove convenient, from the point of view of numerical accuracy, to employ a cyclical procedure, by separately using several shortened

matrices M , taking n independent mixtures each time and submitting the various sets of results to some sort of optimization or statistical treatment, such as by the method of least squares or similar means.

D. THE QUANTITATIVE ANALYSIS

Once in possession of the spectra of the pure compounds the quantitative analysis follows by finding out the partial pressures of the several components in each mixture.

This presupposes pressure measurements at the time each mixture is run in the spectrometer, and this aspect will be dealt with below. Meanwhile, it is easily seen that in order to find the composite factors forming matrix X in (29) or (30) one may use the already determined matrix Q' which will produce the required answer, as seen from equation (42), derived from (37):

$$X = K (Q')^{-1} \quad (42)$$

The factors K are found, after the matrix AK has been normalized and so reduced back to A. Upon multiplication by the inverse of Q', K will produce X.

Q' in equation (41) is a shortened matrix with respect to Q in equation (12), having only n rows instead of L, as required by the inversion procedure. It will not therefore produce the

composite factors for all the mixtures, but only for the n mixtures included in the similarly shortened matrix M. To get the factors for all mixtures, if necessary, new matrices Q' need to be formed successively with all the columns of M, taken n at a time. This would be taken care of automatically if the above cyclical procedure for operating with M is followed. In turn, X, the matrix of the composite factors is in itself a composite matrix, the elements of which are the respective products of the partial pressures and the instrument sensitivity factors for each of the compounds, the sums of partial pressures being the total pressure P_k for each mixture k:

$$x_{jk} = s_j p_{jk} \quad (j = A, B, \dots, N; \quad k = I, II, \dots, L) \quad (43)$$

$$\sum_{j=1}^n p_{jk} = P_k \quad (44)$$

Sensitivities, as was said before, are expressed in units of base-peak abundance (peak height, peak area, chart divisions, digital counts, ion current, etc.) per unit of pressure.

A simple way of finding the partial pressures, to evaluate P , is to consider only those peaks which are unique to each compound and relate the values of their abundances to the total pressures in the sample reservoir.

To show this, and without loss of generality, suppose that in a three-component system masses m_i , m_j and m_k are unique to compounds A, B and C, respectively, as found in the earlier stages of the analysis. Let a_i , b_j and c_k be the corresponding abundances in the standard, normalized spectra and s_1 , s_2 , s_3 the instrumental sensitivities, determined in the usual way, by using the base-peak of each compound. The abundances at these mass numbers in any mixture K of the three substances at partial pressures p_{1K} , p_{2K} , p_{3K} would be given (see equation 1) by:

$$\begin{aligned} h_{iK} &= s_1 p_{1K} a_i \\ h_{jK} &= s_2 p_{2K} b_j \\ h_{kK} &= s_3 p_{3K} c_k \end{aligned} \quad (K = I, II, \dots, L) \quad (49)$$

By comparing each of the different mixtures available with one of the other mixtures, taken as a reference (the first, for

instance), the following equations will result; e.g. for mass \underline{m}_i :

$$h_{iK} = s_1 p_{1K} a_i \quad (50)$$

$$h_{iI} = s_1 p_{1I} a_i \quad (51)$$

$$(K = II, III, \dots, L)$$

Dividing (50) by (51):

$$h_{iK}/h_{iI} = p_{1K}/p_{1I} = R_{1K} \quad (52)$$

Similarly, for masses \underline{m}_j and \underline{m}_k :

$$h_{jK}/h_{jI} = p_{2K}/p_{2I} = R_{2K} \quad (53)$$

$$h_{kK}/h_{kI} = p_{3K}/p_{3I} = R_{3K} \quad (54)$$

$$(for K = II, III, \dots, L)$$

These equations, together with equation (44) yield:

$$\left. \begin{array}{l} P_I = p_{1I} + p_{2I} + p_{3I} \\ P_{II} = R_{1II} p_{1I} + R_{2II} p_{2I} + R_{3II} p_{3I} \\ \cdot \quad \cdot \quad \quad \quad \cdot \quad \quad \quad \cdot \\ \cdot \quad \cdot \quad \quad \quad \cdot \quad \quad \quad \cdot \\ \cdot \quad \cdot \quad \quad \quad \cdot \quad \quad \quad \cdot \\ P_L = R_{1L} p_{1I} + R_{2L} p_{2I} + R_{3L} p_{3I} \end{array} \right\} \quad (55)$$

Solution of this set of \underline{L} linear equations in the three unknowns - p_{1I} , p_{2I} , p_{3I} - gives the partial pressures in all other mixtures by use of equations (52) to (54), unless, as will probably be the case, only the first, the original mixture, is required.

As \underline{L} is greater than \underline{n} , again optimization by a least-squares treatment or an iterative process may be employed to obtain the best solution for system (55).

In the general case, the problem is to find the solution of the matrix equation for the partial pressures p_{iK} in terms

$$\begin{bmatrix} 1 & 1 & \dots & 1 \\ R_{1II} & R_{2II} & \dots & R_{nII} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ R_{1L} & R_{2L} & \dots & R_{nL} \end{bmatrix} \times \begin{bmatrix} p_{1I} \\ p_{2I} \\ \cdot \\ \cdot \\ \cdot \\ p_{nI} \end{bmatrix} = \begin{bmatrix} p_I \\ p_{-II} \\ \cdot \\ \cdot \\ \cdot \\ p_{-L} \end{bmatrix} \quad (50)$$

of the known quantities \underline{R}_{iK} and \underline{P}_K ($i=1,2,\dots,n$; $K=II, III,\dots,L$).

This implies the measurement of the total pressures P_K for each mixture, usually with a micromanometer in the inlet system. Even if these pressure measurements are lacking, a quantitative analysis may still be made, in terms of percentage compositions, provided the same amount of gas sample is taken each time, using a dosimeter. In this case, all elements of the vector on the right-hand side of equation (56) are constant for all mixtures and may be put equal to some arbitrary value, e.g. unity or 100.

This ends the quantitative analysis. The instrumental sensitivities for each of the components, if still wanted, may be obtained by solution of equation (45), for S.

For many mixtures the full analysis will not be needed, the separation and recognition of the molecular species present being the main target. The process may then be stopped at the appropriate stage.

E. APPLICATION

To apply the analytical technique described to real systems is no small task if hand calculations are used. The mathematical problems involved consist mainly of systems of linear equations, and the modern digital computers with their associated and powerful techniques of subroutines or procedures, are well suited for handling this type of problem.

On the other hand, the data produced by the mass spectrometer, in the form of abundances, is subject to errors and fluctuations, that are best dealt with by statistical treatments, like averaging of several experiments, with assessment of maximum errors and standard deviations, etc.

Given, therefore, the desirability of using an automated method of analysis, work was started in two directions:

1. the construction of an analogue - to - digital interface, (digitizer), that is a piece of equipment which would transform the output voltage signal of the mass spectrometer, corresponding to ion abundance into a digital code, which would be then punched in paper tape. At a second phase, a magnetic field sensor, such as an Hall probe, would be introduced in the vicinity of the scanning magnetic field and again the reading converted into a

digital code which would be transformed into an accurate mass, through application of the equation

$$m/e = \frac{B^2 R^2}{2V}$$

The final perforated paper tape (eventually magnetic tape could be used), would have the form of pairs of numbers, for mass and abundance of ionic peaks, as produced by the mass spectrometer output.

2. writing of a computer programme, to handle the experimental data and deal with the mathematical computations.

The electronics workshop of the Department was charged with the first part of the project, while the second part was in charge of the author, with help from Mrs. J. Laycock, and the staff of the Computer Department which is duly and gratefully acknowledged in the proper section.

For various reasons, the "hardware" part of the project has suffered several delays and has never been, to date, operational. Details of the logic structure used can be found elsewhere ¹⁴.

Chapter 5 gives an account of the present state of the computer programme. Its usefulness is at present, limited by the lack of adequate statistical treatment of the mass spectral data. It has, however, been used with simulated data, for testing purposes and to perfect some of the theoretical parts of the analysis.

For the sake of clarifying and in order to demonstrate the several steps involved in the analytical method proposed,

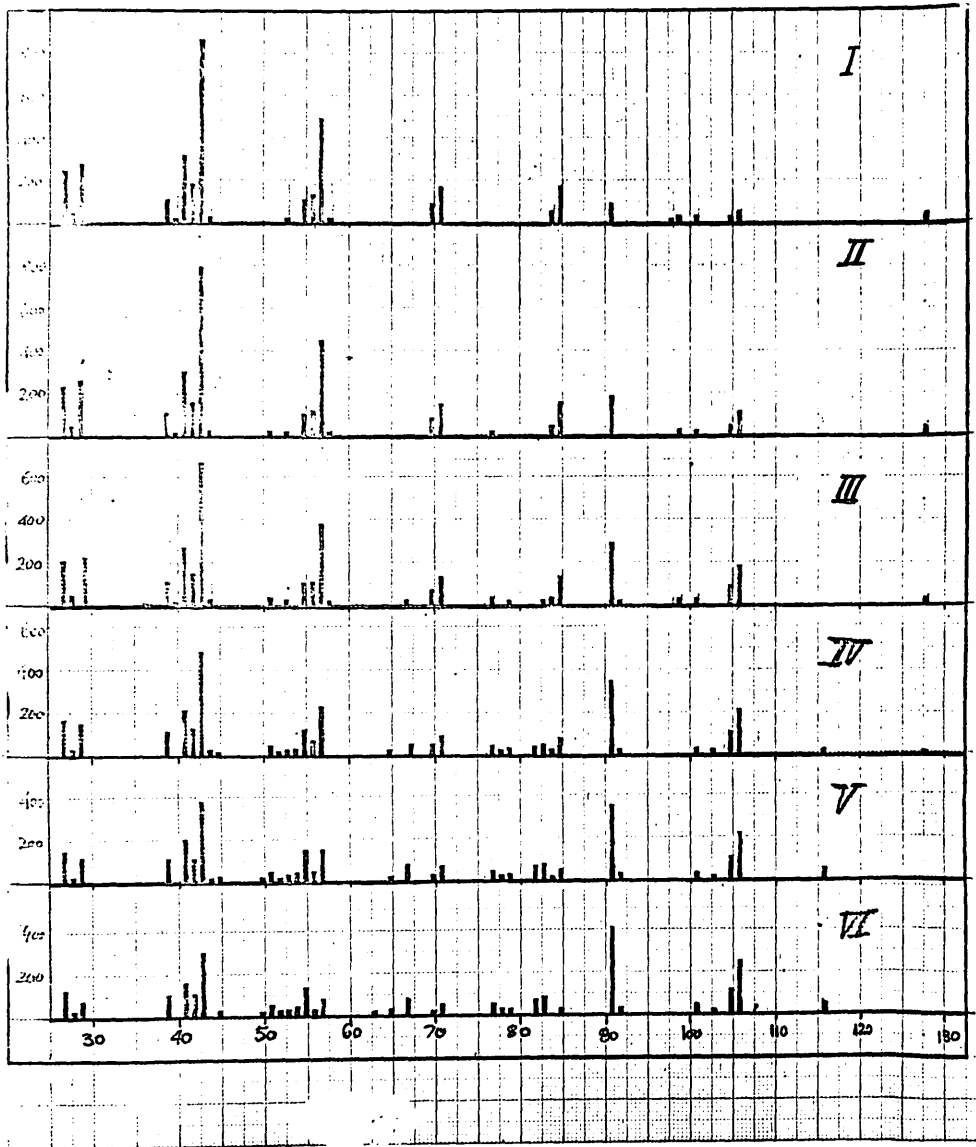


Fig. 3

an worked example is given of a four-component system such as may occur in coal or petroleum samples. It includes a paraffin, a cyclo-alkanethiol, an alkylbenzene and a heterocyclic compound containing oxygen and nitrogen, the mass spectra of which have been taken from published data¹⁵. In this example, the experimental conditions are assumed to have been the same for all the compounds involved. The sensitivities were taken so as to correspond roughly to the different efficiencies against n-butane, as stated by the laboratories concerned. No experimental errors are included in the values associated with the mixtures (which were, themselves, prepared by a separate computer programme), and the results can be regarded as numerically correct.

Six mixtures were used and their line diagrams may be seen in Fig. 3. Only the most abundant peaks are shown, but they are present in full in Table IV.

Number of components

The rank of matrix M, (Table IV), formed with the six spectra, was found by horizontal condensation of the columns, i.e. by multiplying all the peaks of the first mixture by a suitable

TABLE IV

Mass spectra of the six four-component mixtures under analysis

Mass	Mixtures spectra					
	1	2	3	4	5	6
25.0	0.48	0.44	0.42	0.50	0.56	0.58
26.0	17.44	16.46	15.70	16.25	17.21	16.79
26.5	0.04	0.03	0.03	0.04	0.04	0.05
27.0	241.05	227.80	205.63	165.55	152.04	125.48
28.0	52.15	48.31	42.55	34.23	31.18	25.91
29.0	283.51	261.61	222.11	150.04	116.91	77.97
30.0	11.13	10.01	8.71	8.34	7.81	7.98
31.0	2.54	2.21	1.99	2.65	2.76	3.31
32.0	1.10	1.00	1.14	2.01	2.69	2.87
33.0	1.03	1.03	1.77	4.01	6.25	6.26
34.0	0.48	0.48	0.84	1.92	3.00	3.00
35.0	0.28	0.28	0.49	1.12	1.74	1.74
35.5	0.04	0.03	0.03	0.04	0.04	0.05
36.0	0.18	0.17	0.17	0.21	0.26	0.24
37.0	0.96	1.21	1.64	2.26	2.75	2.88
38.0	5.99	7.36	9.18	10.74	11.72	12.30
39.0	112.06	112.67	113.06	107.29	110.70	101.51
40.0	21.50	20.82	19.62	17.20	16.45	14.77
41.0	322.69	300.56	267.54	213.60	202.27	159.66
42.0	180.37	163.89	142.22	126.32	113.57	110.41
43.0	867.03	794.66	672.59	484.31	379.45	296.02
43.5	0.02	0.04	0.06	0.07	0.07	0.08
44.0	35.09	31.88	27.36	22.96	19.88	18.57
45.0	6.01	6.15	9.80	20.50	30.93	31.20
45.5	0.04	0.07	0.12	0.14	0.14	0.16
46.0	0.86	0.93	1.40	2.59	3.76	3.79
46.5	0.01	0.01	0.01	0.01	0.01	0.02
47.0	2.69	2.68	4.63	10.49	16.36	16.35
48.0	0.11	0.11	0.19	0.43	0.67	0.67
48.5	0.01	0.01	0.01	0.01	0.01	0.02
49.0	0.80	1.20	1.81	2.50	2.94	3.18
49.5	0.30	0.26	0.24	0.32	0.33	0.39
50.0	6.48	10.49	15.44	19.17	20.53	22.90
51.0	15.98	26.11	38.11	46.03	48.01	53.95
51.5	0.52	1.04	1.63	1.96	1.96	2.28
52.0	8.04	12.77	18.37	22.12	22.95	25.88
52.5	0.16	0.32	0.49	0.59	0.59	0.69
53.0	19.96	21.90	25.08	28.48	32.10	31.87

Mass

Mixtures spectra

	1	2	3	4	5	6
54.0	16.63	15.78	19.31	32.10	45.61	44.89
55.0	109.43	102.43	103.18	119.80	149.77	136.42
56.0	130.03	119.75	101.03	67.19	50.73	33.34
57.0	492.44	454.52	379.01	228.58	153.51	78.15
58.0	24.08	22.23	19.56	15.60	14.66	11.64
59.0	1.88	1.83	2.78	5.77	8.78	8.76
60.0	2.44	2.44	4.27	9.76	15.25	15.25
61.0	1.53	2.29	3.73	5.93	7.66	8.13
62.0	1.96	3.55	5.47	6.88	7.30	8.28
63.0	5.22	9.55	14.51	17.42	17.68	20.32
64.0	0.91	1.68	2.56	3.09	3.13	3.61
65.0	7.50	12.99	19.37	23.34	24.02	27.30
66.0	1.65	2.18	2.96	3.77	4.32	4.58
67.0	16.07	15.80	24.81	52.39	80.46	79.97
68.0	2.55	2.39	2.73	4.11	5.64	5.48
69.0	17.74	16.40	14.07	9.79	8.11	5.51
70.0	91.09	83.84	70.17	44.83	31.82	19.49
71.0	166.53	152.60	128.89	91.22	71.08	53.55
72.0	9.98	9.11	7.88	6.48	5.80	5.07
73.0	2.39	2.45	3.96	8.33	12.62	12.71
74.0	0.93	1.39	2.19	3.32	4.17	4.45
75.0	1.47	2.64	4.05	5.09	5.41	6.12
76.0	0.65	1.24	1.94	2.45	2.59	2.95
77.0	12.83	23.94	36.69	44.33	45.14	51.97
78.0	6.17	12.18	19.01	23.00	23.21	26.98
79.0	7.97	14.69	22.73	28.34	29.81	33.96
80.0	0.35	0.49	0.75	1.10	1.38	1.46
81.0	2.39	2.35	3.68	7.76	11.91	11.83
82.0	11.10	11.07	19.04	43.07	67.12	67.10
83.0	14.34	14.19	23.20	50.55	78.18	77.89
84.0	47.53	43.93	37.34	24.80	19.41	12.26
85.0	171.23	158.17	132.13	80.10	54.27	28.07
86.0	11.52	10.79	9.30	6.28	4.72	3.26
87.0	0.80	1.03	1.50	2.26	2.90	3.03
88.0	0.03	0.03	0.05	0.11	0.17	0.17
89.0	1.77	3.53	5.52	6.65	6.68	7.78
90.0	0.78	1.56	2.44	2.93	2.93	3.42
91.0	93.27	186.34	291.11	349.27	349.25	407.42

Mass	Mixtures spectra					
	1	2	3	4	5	6
92.0	7.11	14.23	22.23	26.68	26.68	31.13
93.0	0.13	0.18	0.23	0.24	0.23	0.26
95.0	0.22	0.20	0.17	0.10	0.07	0.03
96.0	0.22	0.20	0.17	0.10	0.07	0.03
97.0	3.48	3.21	2.71	1.72	1.27	0.74
98.0	19.66	18.14	15.13	9.17	6.17	3.21
99.0	33.33	30.76	25.64	15.45	10.35	5.26
100.0	9.12	8.06	7.10	8.11	8.02	9.11
101.0	33.51	29.15	26.23	34.84	36.25	43.45
102.0	2.33	2.46	2.72	3.46	3.55	4.21
103.0	5.79	11.47	17.86	21.45	21.45	25.03
104.0	2.61	5.21	8.21	9.78	9.78	11.41
105.0	27.79	55.56	86.83	104.20	104.20	121.57
106.0	57.70	115.37	180.30	216.36	216.36	252.43
107.0	4.30	8.60	13.44	16.13	16.13	18.82
112.0	0.22	0.20	0.17	0.10	0.07	0.03
113.0	1.03	0.95	0.79	0.47	0.32	0.16
114.0	0.44	0.41	0.34	0.20	0.14	0.07
115.0	0.02	0.02	0.03	0.08	0.12	0.12
116.0	8.52	8.52	14.91	34.07	53.24	53.24
117.0	0.62	0.62	1.08	2.48	3.87	3.87
118.0	0.39	0.39	0.68	1.55	2.42	2.42
119.0	0.02	0.02	0.04	0.09	0.15	0.15
125.0	0.15	0.14	0.11	0.07	0.05	0.02
126.0	0.22	0.20	0.17	0.10	0.07	0.03
127.0	0.07	0.07	0.06	0.03	0.02	0.01
128.0	46.78	43.18	35.98	21.59	14.39	7.20
129.0	3.52	3.25	2.71	1.62	1.08	0.54
130.0	0.15	0.14	0.11	0.07	0.05	0.02

factor and subtracting the products from the second mixture. By so doing the first element of the second column is reduced to zero; the same procedure is followed for the third, fourth, fifth and sixth columns. Having reduced the first elements^(*) of the remaining five columns to zero the process was started again with the first significant element of the second column thereby reducing the remaining four elements in the same line to zero. The same was done with the third and fourth columns; at this point it so happens that the fifth and sixth columns have been reduced to zero in all positions. The rank of M is therefore four; it follows that the number of components is also four.

Moreover, the first four mixtures spectra were thus shown to be independent and were used throughout the remaining calculations, without any cyclical procedure, bearing in mind the exact nature of the numerical values.

Another (perhaps simpler) way of finding the number of components would be to start with any second-order regular (rank equal to two) submatrix of M by choosing two rows and adding a third one. Subsequently, the rank is found. If it turns out to be two instead of three replace the added row by one of the

(*) See footnote next page

others left in the matrix. Repeat this until either the rank does go up one unit, in which case higher-order submatrices would be started, or it does not, in which case the rank of M is the highest found for the submatrices. This procedure is suggested because it is developed along lines similar to those used in the steps that follow.

(*) Instead of the natural order of the rows being used for the condensation, the rows (mass numbers) corresponding to the most abundant peaks may be changed to the first positions - provided track is kept of the changes - with a consequent improvement in accuracy.

Identification of peaks

From Table IV it can be seen that the abundances for masses 95, 96, 113, 114, 128 and 129 are multiples of each other, i.e. the ratios between corresponding abundances for any two of these mass numbers are constant for all mixtures. Thus, they must arise from only one component, which we shall call A. Abundances for masses 51.5, 90, 92, 104, 105, 106, 107 must come from another component, B; 34, 35, 60, 116, 117, 118, from C; 31 and 49.5 from D. All the other peaks were labelled by the method which is described in the text.

Recovery of spectra

Based on the pattern of zeros obtained, the following peaks were used to calculate matrix Q' (Table V).

TABLE V

Mass numbers used to construct matrix Q' ,
and their labels

Column of Q'	Masses used	Labels
First	61	BC
	92	B
	102	BD
Second	83	ACD
	99	AD
	128	A
Third	98	AD
	103	BD
	105	B
Fourth	105	BC
	116	AC
	128	B

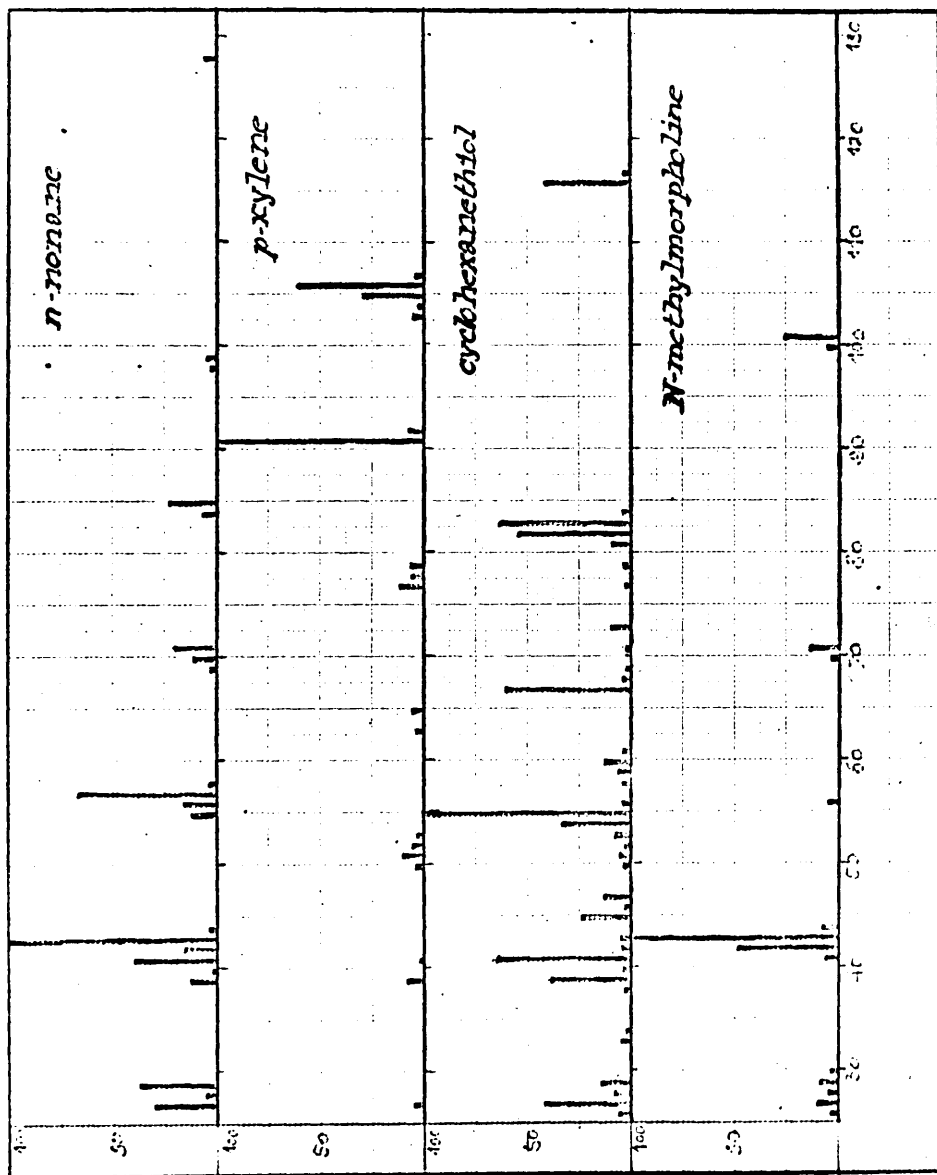


Fig. 4

For instance, to obtain the first column of Q' , the following set of equations was set up and solved:

$$\left\{ \begin{array}{l} h_{61I} x_1 + h_{61II} x_2 + h_{61III} x_3 = h_{61IV} \\ h_{92I} x_1 + h_{92II} x_2 + h_{92III} x_3 = h_{92IV} \\ h_{102I} x_1 + h_{102II} x_2 + h_{102III} x_3 = h_{102IV} \\ (x_4 = -1). \end{array} \right.$$

The solution is: $x_1 = 2.829$; $x_2 = -5.472$; $x_3 = 3.796$; $x_4 = -1$.

Many choices of mass numbers are possible, other than those shown in Table V, and some were actually used to check upon the accuracy of the solution for system (40); the results suggested that, as far as possible, the peaks chosen should be similar in size for better numerical results.

The following matrix Q' resulted:

$$Q' = \begin{bmatrix} 2.829 & 6.077 & 4.758 & 2.728 \\ -5.472 & -9.726 & -9.396 & -5.843 \\ 3.796 & 4.371 & 5.690 & 4.066 \\ -1 & -1 & -1 & -1 \end{bmatrix}$$

and the product MQ' , after normalization of its columns, produced the four pure spectra (Fig. 4), that could be identified as n-nonane, p-xylene, cyclohexanethiol and N-methylmorpholine¹⁵.

Quantitative analysis

For the quantitative analysis, the total pressures of each of the mixtures were put equal to 20.0×10^{-3} torr, at the time they were made.

Product MQ' , before and after normalization, yielded K : $k_1 = 1.7340$, $k_2 = -3.2238$, $k_3 = 0.25534$, $k_4 = -0.28014$, which, together with the inverse of Q' , produced matrix X , by eqn. (42):

$$X = \begin{bmatrix} 7.332 & 6.786 & 5.640 & 3.384 \\ 0.9312 & 1.862 & 2.910 & 3.492 \\ 0.1936 & 0.1936 & 0.3388 & 0.7744 \\ 1.316 & 1.144 & 1.030 & 1.373 \end{bmatrix}$$

Using now both the knowledge about which peaks are unique to which components and the values of the total pressures, the quantitative analysis in terms of partial pressures of the components for the first four mixtures was performed (eqns. 52-56). The results are shown in Table VI.

TABLE VI

Result of the analysis of the four-component mixtures

Components	Mixtures			
	I	II	III	IV
A. n-nonane	13.0	12.0	10.0	6.0
B. p-xylene	1.6	3.2	5.0	6.0
C. cyclohexanethiol	0.8	0.8	1.4	3.2
D. N-methylmorpholine	4.6	4.0	3.6	4.8
Total pressures (10^{-3} torr)	20.0	20.0	20.0	20.0

Finally, the sensitivities were obtained (eqn. 45):
 $s_1 = 56.4$, $s_2 = 58.2$, $s_3 = 24.2$, $s_4 = 28.6$. The other two mixtures were not used but the cyclical procedure as described earlier, would have given their composition, in much the same way.

The computational work involved in the above example took about 14 minutes of computer time (English Electric KDF9 computer), including print-out.

APPENDIX I

If a continuous method of fractionating an original sample is used and is desirable to run mass spectra by consecutively scanning the changing system, a mathematical treatment by using continuous functions may be preferable to the method of discrete samplings used in the text. Here, the ion abundances of the mixture spectra are regarded as continuous functions of time, which could be approximated by any means of curve fitting, for instance a least squares treatment which, eventually, will produce a polynomial function of time.

If we fix our attention upon any mass number, i , of the continually changing mixture spectrum, $h_i(t)$, and abundances are recorded at times t_0, t_1, \dots, t_r , a polynomy of degree r may be found to fit the dependence of h_i on time:

$$h_i(t) = \alpha_{0i} + \alpha_{1i} t + \alpha_{2i} t^2 + \dots + \alpha_{ri} t^r \quad (a)$$
$$= \sum_{k=1}^r \alpha_{ki} t^k \quad (i = 1, 2, \dots, mw)$$

This is evidently due to the fact that the compositions too are changing with time. So, for component j , its composite

factor may also be written:

$$x_j(t) = \beta_{0j} + \beta_{1j} t + \beta_{2j} t^2 + \dots + \beta_{rj} t^r \quad (b)$$

$$= \sum_{k=1}^r \beta_{kj} t^k \quad (j = 1, 2, \dots, n)$$

The overall situation will be:

$$\begin{bmatrix} h_1(t) \\ \cdot \\ \cdot \\ h_i(t) \\ \cdot \\ \cdot \\ h_{mw}(t) \end{bmatrix} = \begin{bmatrix} a_1 & b_1 & \dots & n_1 \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ a_i & b_i & \dots & n_i \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ a_{mw} & b_{mw} & \dots & n_{mw} \end{bmatrix} X \begin{bmatrix} x_1(t) \\ \cdot \\ \cdot \\ x_j(t) \\ \cdot \\ \cdot \\ x_n(t) \end{bmatrix} \quad (c)$$

or $h(t) = A x(t)$

If a_{ij} is made to stand for the element of matrix A corresponding to mass i of component j , then

$$h_i(t) = a_{i1} x_1 + a_{i2} x_2 + \dots + a_{in} x_n =$$

$$= a_{i1} \sum_{k=1}^r \beta_{k1} t^k + a_{i2} \sum_{k=1}^r \beta_{k2} t^k + \dots$$

$$+ a_{in} \sum_{k=1}^r \beta_{kn} t^k =$$

$$= \sum_{j=1}^n \sum_{k=0}^r a_{ij} \beta_{kj} t^k, \text{ which, by eqn. (a)}$$

will be

$$= \sum_{j=1}^n \alpha_{ki} t^k$$

So, by equating the same powers of t , the solution of the β in terms of the α , will be possible and given by the system:

$$\sum_{j=1}^n a_{ij} \beta_{kj} = \alpha_{ki} \quad (k = 0, 1, \dots, r) \quad (d)$$

These are $r+1$ equations ($r \geq n$) in n unknowns and may be solved by the usual methods, with optimization if necessary, once their coefficients a_{ij} become known.

Again we may represent the system (c) in the new form:

$$\begin{bmatrix} A & B & \dots & N \\ a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ a_{mw1} & a_{mw2} & \dots & a_{mwn} \end{bmatrix} \times \begin{bmatrix} \xrightarrow{\text{time}} \\ \beta_{01} & \beta_{11} & \dots & \beta_{r1} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \beta_{0n} & \beta_{1n} & \dots & \beta_{rn} \end{bmatrix} = \begin{bmatrix} \xrightarrow{\text{time}} \\ \alpha_{01} & \alpha_{11} & \dots & \alpha_{r1} \\ \alpha_{02} & \alpha_{12} & \dots & \alpha_{r2} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \alpha_{0mw} & \alpha_{1mw} & \dots & \alpha_{rmw} \end{bmatrix}$$

or, in short, $AX = M$,

as before, using the method of discrete samplings. One immediate advantage of using this functional treatment rests in the fact that measurement errors, always likely to be present in the isolated and uncorrelated spectra used in the discrete approach, are much more easily detected and "smoothed" out when the successive measurements of the abundances for each peak on the slowly varying mixture are plotted. Any anomalies on the smooth shapes of the continuous curves will be noticeable.

APPENDIX II

During discussions it was pointed out to the author, by Mr. A. QUAYLE, (personal communication), that a simpler treatment of the analysis could be made, which would not require all the information presently necessary. Owing to the lack of time, this suggestion was not pursued further in this work.

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CHAPTER FOUR

THE DESIGN, CONSTRUCTION AND PERFORMANCE
OF A MODIFICATION TO USE THE AEI MS9 MASS
SPECTROMETER SOURCE AT CRYOGENIC TEMPER-
ATURES

A. INTRODUCTION

It has been known for more than 20 years that positive ion fragmentation patterns given by mass spectrometers are sensitive to temperature changes. In 1947 Fox and Hipple ¹ reported that in the mass spectrum of isobutane the $C_4H_{10}^+$ ion peak was almost twice as abundant at 70°C as the $C_4H_9^+$ one, becoming equal to it at approximately 180°C and relatively less abundant at higher temperatures. For other hydrocarbons, mainly branched ones, the variation in ratios could be greater still, as in the case of the parent peak of 2,2,3 - trimethylpentane, which is more than 5 times as large at 175°C than it is at 225°C. Stevenson ² and Berry ³ produced some more examples of this effect, the former offering the first explanations for it: the increases in both kinetic and internal energy of the molecule, associated with the increase in temperature.

The increase in kinetic energy of the molecules results in a decrease in the average number of them present inside the ion chamber, which results in the ion current being proportional to $\frac{1}{\sqrt{T}}$. This effect also accounted for discrimination in the instrument, which was selective against ions formed with initial kinetic energy. Discrimination was proportional to \sqrt{T} , the observed ion current decreasing as $(1 - \alpha \sqrt{T})$, α being a function of the

ion source geometry, field shape, etc. Therefore the overall ion current, as a function of temperature may be expressed for rare gases and simple inorganic molecules, according to Stevenson ², as:

$$i(T) = i_0 \cdot \frac{1 - \alpha \cdot \sqrt{T}}{\sqrt{T}}$$

or,

$$i(T) = i_0 \cdot \frac{1}{\sqrt{T}} - \beta$$

The increase in internal energy results in higher entropy for the system, with corresponding increases in the several rate constants for the competing dissociations from the parent molecular ion species which brings about an overall decrease of the latter, in relation to the fragment ions. effect is (as is to be expected) more pronounced for complex, branched, saturated molecules, than for simple, linear or unsaturated ones.

The experimental results of Berry ³, however, show that the functional relationship between temperature and ion current for simple organic molecules could be expressed, over a limited range of temperatures (80°C to 220°C) as:-

$$\ln \frac{i}{i_0} = -\alpha T + \beta$$

or,

$$i(T) = k i_0 \cdot e^{-\alpha T}$$

in which the law is shown to be exponential instead of hyperbolic as Stevenson's.

The main interest of these early investigators was, however, to study the effects of temperature variations upon the analytical performance of their instruments, by upsetting the fragmentation patterns. Reese, Dibeler and Mohler ⁴, along similar lines, studied the same variations for several hydrocarbons, in the range 50°C to 300°C. They point out that the probability of ionization of a molecule should be independent of temperature, whereas the dissociation of ions into fragments should be temperature sensitive.

Osberghaus, Taubert, and Ehrhardt ^{5, 6} have undertaken more general studies in the temperature range of 200°C to 1000°C, and Cassuto ⁷ in the range - 150°C to 350°C, using specially designed single-focusing instruments. Cassuto has shown that the mass spectra of the rare gases are independent of temperature, as was to be expected being monoatomic species, as were the spectra of simple molecules, such as N₂, O₂ and CO₂, between - 150° and 50°C.

The mass spectra of simple hydrocarbons (ethane, propane and n-pentane) have shown different dependence on temperature, for

the several ion species but, in general, the prediction of Berry, that the more complex the molecule the greater the variation of the molecular ion with temperature was fulfilled. However, it must be pointed out that for neither of the molecules studied was its boiling point included in the temperature range used for such low pressures ($\sim 10^{-6}$ torr). More experimental confirmation was, however, added to the hypothesis that ionization cross-sections are temperature independent, by showing that total ionizations was constant throughout.

No comparable studies of mass spectra at low temperatures have been undertaken to date, in a double-focusing instrument, where mass discrimination does not play such an important part as in single-focusing machines.

On the other hand, low-temperature studies may be considered advantageous from two other points of view:-

a) To get a ratio of temperatures of 1:6 starting at 80°K only the range $80-500^{\circ}\text{K}$ ($-190-227^{\circ}\text{C}$) needs to be covered; whereas the same ratio starting at the usual temperatures of 70°C or higher would need the temperature to be raised to the order of 1900°C . It is easily seen that the lowering of temperatures will be by far more practical.

b) The temperature range may be chosen to include the boiling point of the molecular species under examination, with its determination, at the very low pressures employed normally as a possible aim. Molecular physical constants at such low pressures are scarcely known.

B. INSTRUMENTAL

An early attempt was made to modify the M S 9 source to work at low temperatures. It made use of the alignment holes for the source block, which are only used during assembly. Four metal fingers branched out of a distribution box, placed midway between the base flange and the source block. This is shown in Plate I.

The arrangement was relatively complex and the limitations of the Department's workshop, which lacked facilities for argon-arc welding forced the use of silver-copper eutectic solder (71% Ag - 29% Cu, melt. pt. 778°C) for all the junctions. This proved inadequate under the stresses and strains produced by the wide range of temperatures for which the use of the source was intended, and it often sprang leaks at the soldered joints. When the whole piece, eventually, survived intact under liquid nitrogen cooling, it became evident that the rate of heat transfer was too poor to be of great use: the final temperature, as read by the thermocouple, was never below -100°C - and this design was abandoned altogether.

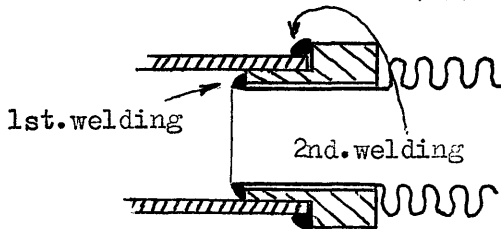
However, some lessons had been learned from it and the next and present model benefitted a great deal from them. Welding

proved to be indispensable and a good metal-to-metal contact essential for a better rate of heat transfer. A much simpler design was thought desirable and was pursued. This took the shape of a cooling finger and is shown in Plates II and III.

A copper bracket (1) is screwed underneath the source block (a stainless steel bracket was used at first but the rate of heat transfer was much lower than with copper, as might be expected). Clearance in the form of two openings was left for the two legs of the ion repeller plate, which protrudes from inside the source.

The collar of this copper bracket embraces the tip of the cooling finger (2), which is made as follows. Two glass-to-Kovar seals (4) were joined together, glass-to-glasswise (5) so as to provide an insulator from the high electric voltage existing on the source block. The resulting seal proved to be quite a good insulator. The resistance between the two Kovar ends of the piece proved to be higher than that between the earthed flange and any of the centre pins of the glass-to-metal seals for the source electric connections. One end of this seal was welded (3) to a stainless steel cap, the other end of which cap was machined to provide a good fit to the inside diameter of the copper bracket. The second Kovar end of the double seal was

joined, by two weldings (3), as shown in Fig. 5 , to a stainless



steel bellows, which would allow for flexibility of the assembly and would absorb the strains due to the cooling cycles in the different metals involved.

Fig.5 - Detail of the weldings.

The lower end of the bellows set was again welded to a small flange made also of stainless steel. This flange, being continuous with the whole finger assembly, could be taken out and replaced by a blank flange in case of need, without having to take out the source flange.

The vacuum seal was provided by a copper gasket, between a ridge and a groove; the latter cut on the main flange. Seven hexagonal screws were used to tighten the seal. A glass tube, 4 mm inside diameter, was introduced up to the tip inside the finger, to carry the coolant, when this struck the top wall and it was forced back between the two cylinder walls. The internal diameters of both the glass and the outside tubes, and the outer diameter of the glass tube were chosen such that the inflow of

coolant was equal to its outflow. The two flows were separated by the use of a heat-exchanger assembly from the Swagelok range of fittings.[‡]

The temperature was taken by a Chromel/Alumel thermocouple, in its usual position, screwed to the body of the ionization chamber steel block. The measurement was by means of a potentiometer bridge at first. After careful calibration⁸ it was made by recording on a pen-and-ink recorder⁹.

As the thermocouple leads were at a potential of 8 kV, to allow the recording of the temperatures, two solutions were possible. Either the DC voltage from the thermocouple could be chopped by a small transistorized circuit so that the resulting AC signal can be isolated from the high DC voltage by means of a transformer, or a pair of condensers, and again rectified (possibly with intermediate amplification); or else the whole recorder could be maintained at the high voltage, in which case the mains supply had also to be raised to the same high voltage, with the necessary safety precautions.

[‡] Supplied by Techmation Ltd., 58 Edgware Way, Edgware, Middlesex, U.K.

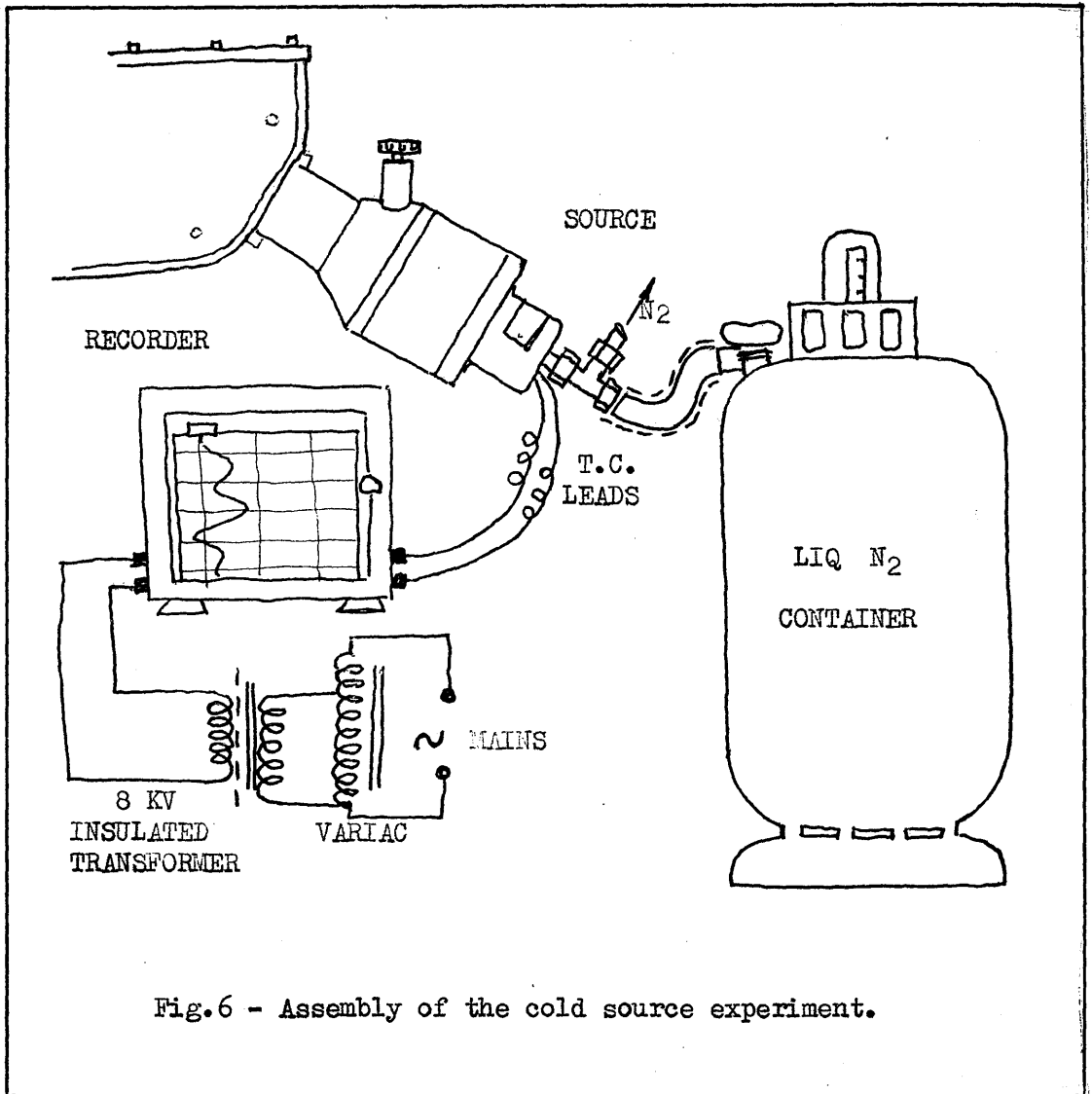


Fig.6 - Assembly of the cold source experiment.

In view of the less skilled work involved, the latter solution was adopted, in spite of the obvious danger it would represent to have such a large piece of equipment as a pen recorder held at a high potential, however well insulated. It is hoped, however, that the other and safer solution could be implemented in the near future. Meanwhile, the arrangement described has worked perfectly, so far. Use was made of an spare set Variac-transformer, insulated for 10 kV.

The coolant is fed straight from a pressurized 260 litre liquid nitrogen container, via a lagged rubber hose with two jubilee clips. The outgoing gas escapes to atmosphere. It is hoped to modify the system so that gravity feeding could be used. This would be less wasteful of the liquid coolant and, together with a more careful thermal insulation a cryostat could be made which would allow for the use of liquid helium and the attainment of still lower temperatures.

A scheme of the whole assembly is presented in Fig 6 .

The rate of cooling varied between experiments, and depended on the metal-to-metal physical contact. Fig. 7 shows the results of a "good" experiment. This is the recorder chart for the

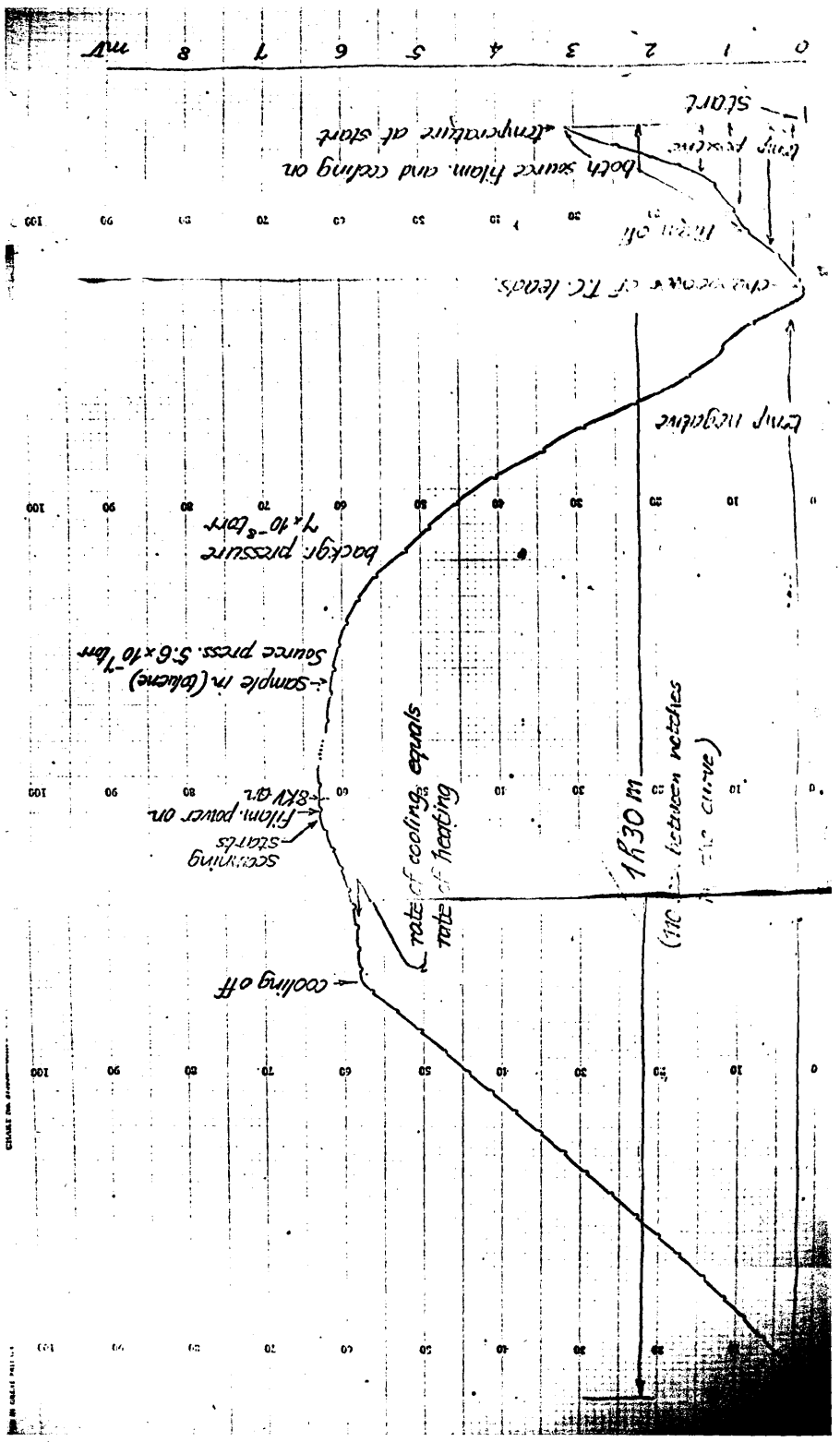


FIG. 7

temperature variation with time. The starting temperature was 95°C (room temperature 19.2°C) and the initial cooling rate - with the filament power going at the same time (about 10W) - was approximately $5.5^{\circ}\text{C}/\text{min}$. It began to tail off at about 48°C , but increased again once the filament power was switched off, so much so that, in the region of -50°C the cooling rate was of the order of $10^{\circ}\text{C}/\text{min}$. This increase must have been due in good part to the different expansion coefficients for steel and copper.[‡] As the temperature lowers the copper bracket, by contracting faster than the tip of the stainless steel finger strengthens the metallic grip. The contact is therefore improved. The same process must operate down to the lowest temperatures. On the other hand, this effect spoils the same contact somewhat, once the materials have been returned to room temperature or higher. For some permanent deformation of the once tight grip remains and the initial start of the cooling

[‡] Copper: 17.7×10^6 ; Stainless steel: order of 11.0×10^6 .
Ratio Cu/St.St. $\cong 1.5$. (values taken from N.A. Lange,
Handbook of Chemistry, 10th ed., 1961, McGraw-Hill).

becomes more difficult for the next experiment.

The minimum temperature attained has been about -190°C , and this consistently, in spite of varying degrees of difficulty in attaining it.

Once at the lowest possible temperature, the high voltage supply is turned on and subsequently, the filament power. After a quick adjustment of the ion beam, the running of mass spectra at the now increasing temperatures is started. Again, if both filament power and cooling are kept running simultaneously, a tailing off occurs at variable temperatures, according to the metal contacts. In the experiment pictured in Fig 7, this plateau was at about -160°C . To have the temperature increase the flow of coolant must be turned off. The increase is then roughly linear, is shown.

Two different procedures could be used to introduce a sample into the ion chamber and run the spectra at different temperatures. Either (i) the sample be introduced early in the process and the successive spectra would be run as the temperature dropped; or (ii) the cooling be allowed to attain the lowest temperatures and only then introduce the sample and run on the way "up."

The two alternatives were tried and the first was shown to be preferable. This was due to several reasons, the chief ones being:

- a) Once the filament power was switched on, to run a spectrum, the rate of cooling was decreased or even stopped. This was rather beneficial to the stabilization of temperature at this point and lent more reliability to the reading of it. On the other hand for a good cooling rate to be restored after this pause took much longer than if the initial rate was kept.
- b) Once the sample was inside the inlet reservoir it was continually bled through the sinter leak into the ion chamber, to be pumped. As this latter was cooling, condensation was taking place on the walls, thus possibly upsetting the source potentials. Making a separate inlet system, which would not contain any leak ¹⁰ would thus be imperative. This solution was thought impractical, and best avoided.

- c) It has been demonstrated ⁴ that the running of spectra at varying temperatures without waiting for equilibrium produced substantially the same results as those obtained when equilibrium was first attained. In any event, the results originally sought could not be expected to yield refined conclusions, as very little is known about the behaviour of mass spectra at these regions and the first experiments were, naturally, exploratory.
- d) It was found that, if a low energy electron beam was used for the ionization, and the filament power was switched off to allow for cooling, switching on again showed that the electronic circuitry was quite unable to reproduce the previous value of the electron energy, without a further fine adjustment. This effect, while insignificant at higher (50 - 70 eV) energies, as only negligible changes in the fragmentation patterns would result, becomes very important at low electron voltages (as shown in Chapter 2).

Thus, method (i) which would mainly avoid cutting the filament power was preferred.

Having, therefore, adopted the first method, viz. starting at low temperatures and working upwards, the successive mass spectra were taken every 10 seconds, having an effective scan time of about 6-7 seconds. This was done by connecting the chart recorder and the oscilloscope, this latter on "slow scan." ¹¹ An advantage of this is that any changes on the spectra are also seen on the oscilloscope screen and action may be taken immediately according to need.

After completion of an experiment, the two recorder outputs - the mass spectrometer and the pen recording of temperature - are compared and temperatures assigned to each mass chart. This is facilitated by the linear character of the temperature increase, as shown in Fig. 7 and the constant periodicity of the mass spectral runs. For a typical experiment, about 120 - 150 charts are taken and measured.

If the measurements are too close in adjacent scans, then only every second or third experimental points are plotted.

C. EXPERIMENTAL RESULTS ON TOLUENE

Some experiments were first made with rare gases only to test the experimental procedures and to verify the constancy of the mass spectra with temperature. The results using the four krypton isotopes of m/e 82, 83, 84 and 86, of relative abundances 11.6, 11.5, 57.0 and 17.3 per cent were specially useful. Within the experimental errors these did provide a control on the abundance measurements of the sample under examination.

Toluene was then chosen for study, firstly owing to the presence, in a narrow mass range, of two large peaks, the molecular ion $C_6H_6CH_3^+$ ($m/e=92$) and the ion of $m/e=91$. The structure of the latter is controversial, being (i) the cycloheptatrienyl¹², (ii) the benzyl ion, or even (iii) an open chain.

There was also a fairly abundant "metastable" ion, at $m/e=90.01$, corresponding to the transition



Second, it would allow this important region of the spectrum to be run very quickly, without an unduly high scan rate and its

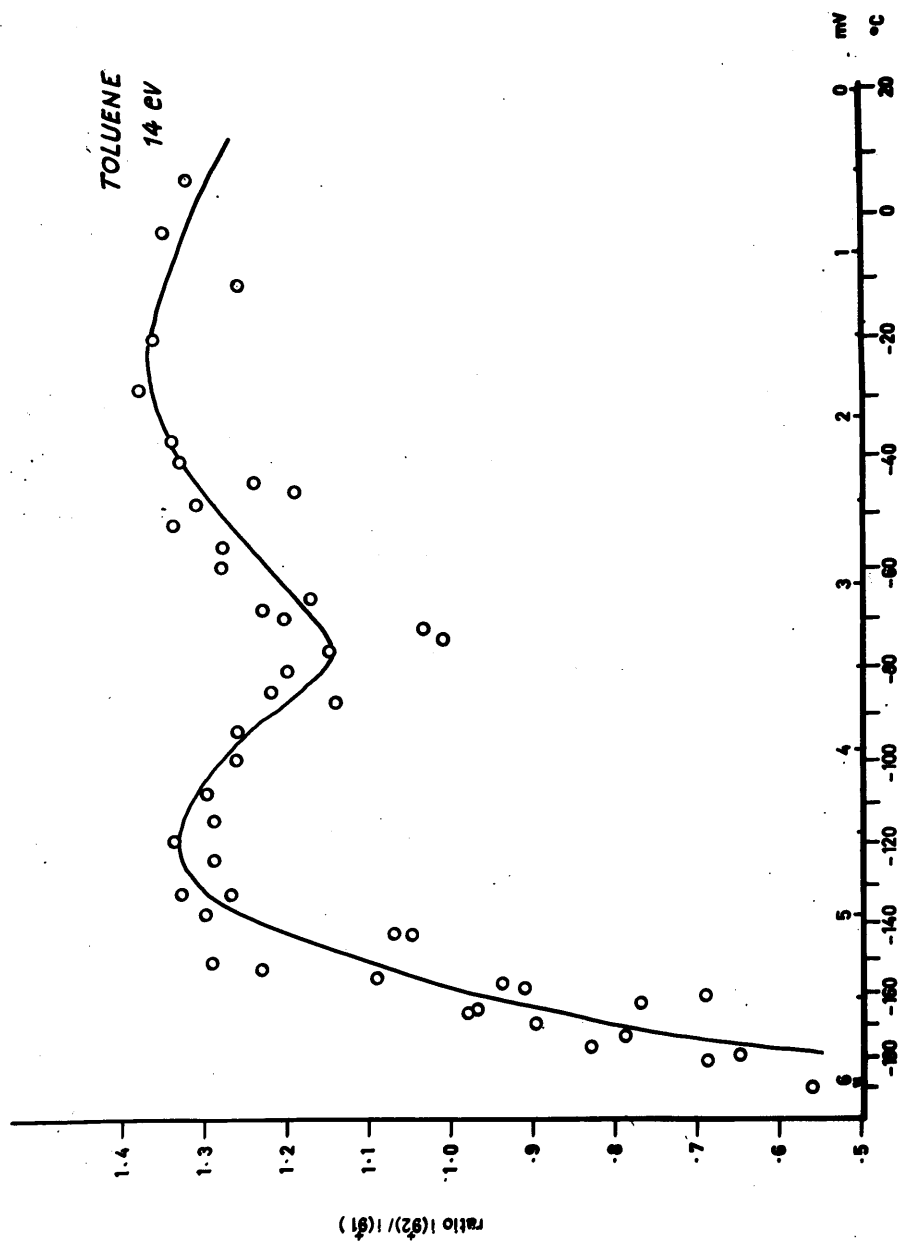


Fig. 8

consequent effect of increasing the statistical fluctuations on the ion beam measurements ¹³ .

A third reason for choosing toluene was the desire to look, at low temperatures, for any structural information about the possible shapes for the 91^+ ion ¹² .

To reduce the complexity of the spectrum even further and with the ultimate aim of curtailing, as far as possible, the energy available to the toluene molecule above its ionization threshold (IP (toluene) = 8.8 eV ¹⁴) a low electron energy of 14 eV (uncorrected) was used for the ionization.

At this energy, the only appreciable peaks on the toluene spectrum were at masses 91, 92 and 93 (isotope) and the "metastable" at $m/e = 90.01$.

The toluene used was of Analar grade, and no impurities or polymerization showed in the mass spectra.

The results of the experiment are shown in Fig. 8 , where the ratio of intensities for masses 92 and 91 are plotted as a function of temperature. Three independent runs were made and, although the actual ordinates of the ratios came out displaced vertically in relation to one another, the general shape of the curve was the same in all three. The reason for the differences

is presumed to be due to the steepness of the ionization efficiency curve, an effect already discussed.

The use of ratios between the two peaks, instead of their abundances stemmed from a desire to avoid absolute pressure measurements, to compensate for the inevitable changes in concentration of molecules in the ion source with temperature. In this way, given a definite rate of formation of molecular ions, to which the abundance of peak at $m/e = 92$ would be proportional, a particular fraction of this species, dependent only on temperature, would give the abundance of the peak at mass 91. The variation of this fraction with temperature would then be the property under study - without unduly complex adjustments for physical absolute conditions. This always assumes, of course, a very low pressure in the ion source, so that ion-molecule interactions may be neglected, to a first approximation.

It will be shown that this does not hold true throughout the whole experiment.

The curve obtained shows a very steep increase from about -180°C with a first maximum at around -120°C , a minimum at -75° and another rather broad maximum at about -20°C , after which it tails off downwards smoothly towards higher temperatures.

One possible explanation for the shape of the curve, making use only of macroscopical physical properties would involve the knowledge of the vapour pressures of toluene at these low pressure regions. This being unknown, a crude estimate was attempted.

From published data ¹⁵ the values of toluene vapour pressure at 10, 100, 1000 and 1500 torr were extrapolated to 10^{-6} torr, a procedure which, although involving considerable risk of gross inaccuracy, was based on the results of Tickner and Lossing ¹⁶ who found that a logarithmic plot of vapour pressures of many hydrocarbons against the inverse of absolute temperature produced essentially straight lines at least down to about 10^{-3} torr. It was, therefore, assumed that (i) the same behaviour would hold for toluene and (ii) the extrapolation could be made.

The values of temperatures for the above vapour pressures (Table VII) falling in a straight line, the extrapolated value will be around -120°C (153°K).

TABLE VII

pressure (torr)	temp. $^{\circ}\text{C}$	temp. $^{\circ}\text{K}$	$1/T \times 10^4$
10	6.36	279.52	35.78
100	51.94	325.10	30.76
1000	120.57	393.73	25.40
1500	136.42	409.58	24.42
extrapolated to 10^{-6}	- 119	154	~ 65

Another estimate was made by using the Antoine equation ¹⁵ :

$$t = \frac{B}{A - \log_{10} P} - C, \text{ where, for toluene:}$$

$$A = 6.95464$$

$$B = 1344.800$$

$$C = 219.482$$

The figure obtained now is -115.7°C , in fair agreement with the first.

This value corresponds to the first maximum in the experimental curve. It corresponds, moreover, to a sudden increase in the source pressure, at the time of the experiment, which resulted in a much stronger ion beam, for some time. At about -90°C the pressure again decreased to the former level. This, too, is seen to correspond almost to the lowest region of the trough in the middle of curve. It is proposed, therefore, that ion-molecule collisions originating from the sudden surge of molecules in the source (in the vapour phase) would account for the increased fragmentation rate of the molecular ion.

As for the very steep slope in the low portion of the curve no exact explanation could be found, apart from the general expectation that, as the temperature decreases and the average

velocities of the molecules decreases as the square root of the temperature (i.e. the velocities decreasing more steeply than the temperature) the residence times of the ions will be much increased. This would produce the net result of, for the same number of molecules, less molecular ions and more fragments formed, as observed.

More work remains to be done to verify if this explanation alone could be held responsible for the whole effect. Another interesting prospect would be to explore further down in the temperature scale, e.g. by using liquid helium, to see what happens to the steeply falling branch of the curve.

To pursue this exploration only minor modifications to the present instrumental arrangements need be introduced.

The field is now opened wide.

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CHAPTER FIVE

ALGOL PROGRAMME FOR THE ANALYSIS
OF MULTICOMPONENT MIXTURES

A. INTRODUCTION

The present programme for mixture analysis was intended as an application of the principles laid down in Chapter III. It is not, at the present stage, adequate for dealing with all experimental data as a good statistical treatment of results must be included. "Theoretical" made-up mixtures that satisfy the requirements for the analysis have been solved by it, producing the number of compounds present and their individual mass spectra.

The part of the programme dealing with the quantitative analysis proved less than adequate and was, therefore, removed. It is hoped to have it replaced by a better treatment in due course.

The programme is at present in an intermediate stage of development. There are several optional testing procedures built into it that should be removed once it is fully developed and tested. Some parts are heavily labelled due to the fact that intensive searches for failures have been made in those areas. These labels can also be discarded later.

Several "tolerance" values have been introduced, which set quite arbitrary limits for errors, both round-off and experimental.

Ultimately it was hoped that these tolerances would be replaced by statistical parameters, with bearing upon the precision and reproducibility of the instrument, scattering of the data around central values, etc.

Again, in a later stage, several long series of steps that recur could be assembled into procedure format, declared ahead of the blocks where they are to be used and called in at the points where needed. This will make for tidiness. Some obvious instances would be: logging in of data, normalization of spectra, comparing abundances, transposing matrix elements, printing out pure spectra, etc.

No claim is made that the best possible or available numerical methods for solving the problems posed were used. Saving of computer time was not a high priority.

The bulk of data is fed into the computer in the form of pairs of numbers: mass number followed by respective abundance, followed by next mass number, etc., within one spectrum. After two strings of 9's to announce spectrum change, the next spectrum (mixture) is logged in, and so on.

The programme is written in KDF9 ALGOL, which does not differ substantially from standard ALGOL-60 ¹. The input-output facilities, however, are local to the system used in Glasgow University and have to be modified to suit any other installation.

B. DESCRIPTION OF THE MAIN STEPS OF THE PROGRAMME

Although several comments are scattered through the ALGOL text, the following succinct description of the programme behaviour is intended to help in the analysis of the layout:

- . Prepares the recipient matrices;
- . Reads the first spectrum;
- . Counts the peaks (k);
- . Allows 2k as maximum number of peaks;
- . Changes over mixture I to second place, to keep it intact throughout;
- . Reads the second spectrum;
- . Compares the masses of the next spectrum (II) with the one (I) which is already in (TOL 1):
 - a) $m_{II} > m_I$
Puts a zero in the corresponding place.
 - b) $m_{II} < m_I$
It is a new peak. Renumbers all the peaks in the first spectrum.
- . If there is a background to be subtracted, it enters as the last spectrum.

- It assumes that the background is constant all through. When the background peaks are fed to the computer, they must read backwards:

Ex: 105 → 100 → 45 →

- The whole background is fed in as a spectrum. But some peaks are given as standards which belong to the background only. The programme scales them down or up to allow for multiplier change, etc.
- Counts how many peaks bigger than TOL there are in each spectrum, to know which spectrum needs to be put first, as this will have peaks at most mass numbers;
- Changes the spectra over:

Ex: 2 ← 1 3 → 4

and the labels as well:

$$R [1] = 2$$

$$R [2] = 1$$

$$R [3] = 3$$

$$R [4] = 4$$

before

$$R [1] = 4$$

$$R [2] = 1$$

$$R [3] = 3$$

$$R [4] = 2$$

after

- Duplicates the matrix:

The new one is HI

The old one is H

- Makes a diagonal condensation (Gauss) starting with element H_{21} of the matrix:

$$H_{21} \times \frac{H_{11}}{H_{21}} - H_{11} \Rightarrow 0 \quad (\text{for } m_1 \text{ in II})$$

- Does the same for all masses:

$$H_{31} \times \frac{H_{11}}{H_{31}} - H_{11} \Rightarrow 0 \quad (\text{for } m_1 \text{ in III})$$

etc.

- If the prospective divisor is $< \text{TOL } 2$ (is a small number) then call it zero and assume is already eliminated. Checks below to see whether all the numbers of the same mass number have been eliminated as well.
 - a) If so, go on to next mass number.
 - b) If not, interchange spectra so that the significant number of this mass comes to the next place. This interchange goes to both matrices HI and H.

	m_1	m_2	m_3		
x_1	*	I
x_2	0	*		II
x_3	0	0		III
x_4	0	0	0	IV

- . If one spectrum turns out to be redundant (all elements zero, most unlikely), it is deleted.
- . Scans along the newly reduced spectrum and counts how many elements are greater than TOL 4.
- . If this number is less than per we can "eliminate" [‡] this spectrum.
- . (Suggestion: In later work, keep the record of this spectrum in H to allow the concentration to be found).
- . Each time a spectrum is declared redundant, the parameter noc (number of compounds) is lowered by 1.
- . Takes account of the spectra thrown away and contracts the matrices.
- . If the found noc is equal to nexp (number of experiments) then prints "INSUFFICIENT DATA."
- . If noc is equal to 1 there is only one compound.
- . Divides all spectra by the first:
 - a) sets up a new vector [L] in which are set the order numbers of the masses, values of which in the first spectra are higher than TOL.
 - b) divides all the spectra by these. Subtract the resultant values for each mass number in every spectra from all the other mass numbers.

[‡] "Eliminate" means "throw away" from both matrices H and HI.

- If the remainders are all less than TOL 3 (for all the spectra) then the mass number tried is of the same kind as the one used as standard.
- Takes the masses which were found by the standard mass number and strikes them out of [L]. Leaves only the rest of the masses.
- Keeps a separate record of the numbers of the peaks "found" by each mass in turn.
(tr is the parameter that gives the number of masses which have located others of the same kind; if tr < noc in the end of the process, the programme prints a failure message and stops).
- A procedure called SOLVE is used to solve the system of linear equations that would yield the pure spectra. It solves a matrix system of m sets of equations in n unknowns. In this case n = noc (number of compounds) and m = k (number of peaks). Normalization of columns of matrix X given by SOLVE will give the pure spectra.

$$\begin{bmatrix} c_{11} & \dots & c_{1n} \\ & C & \\ c_{r1} & \dots & c_{rn} \end{bmatrix} X \begin{bmatrix} x_{11} & \dots & x_{1m} \\ & X & \\ x_{n1} & \dots & x_{nm} \end{bmatrix} = \begin{bmatrix} r_{11} & \dots & r_{1m} \\ & R & \\ r_{r1} & \dots & r_{rm} \end{bmatrix}$$

C. DATA FORMAT

- true; (or false); - depending upon the wish to have checking tests performed at different points (boolean value for "test")
- I234; 5678; 910; - three sets of figures for
(4 4 3 labelling or any other
digits; digits; digits) identification purposes.
("A1", "B1" and "C1" in the
text)
- nexp; - number of mixture spectra used
- L; - lowest mass number to be considered significant (e.g. 25)
- TOL; }
TOL 1; }
TOL 2; } - tolerance values
TOL 3; } (TOL 2 \leq TOL 4)
TOL 4; }

per;

- percentage of values allowed greater than "TOL 4" (if TOL 4 is high then "per" is set low)

Spectra:

mass;	peak;
(6 digits and no decimal point punched)	(4 digits)

mass;	peak;
.	.
.	.
.	.
.	.
last mass; 999999;	last peak; 9999;

- last reading in each spectrum (last spectrum is the background, if needed)

ns;

- number of standards of background peaks if background is to be subtracted; otherwise, put zero (read masses to be taken as standards with largest mass first)



D. ALGOL · PROGRAMME

ANALYSIS OF MIXTURES

```

begin
comment the input is the set of spectra produced by
  varying the concentrations of the compounds
  present in a given mixture;
real L,TOL1,TOL2,TOL3,w,DIS,b,d,D,sum,y,p,TOL4,TOL,SM;
integer A1,B1,C1,i,nexp,j,k,noc,x,z,nc,l,m,c,q,rr,
  co,r,to,n,s,jo,j1,tr,ri,ns,no,i1,nos,np,j1,pn,
  per,F,FM,FP,FI,FR,FIN,MAX;
boolean test;
array MASS[1:1000],P[1:1000];
integer array R,N[1:20];
library A0,A6,A4;
procedure ZI(i,s); integer i; string s;
  if test then
    begin
      newline(71,1); write(71,FI,i); space(71,3);
      writetext(71,s);
    end ZI;
procedure ZR(r,s); real r; string s;
  if test then
    begin
      newline(71,1); write(71,FR,r); space(71,3);
      writetext(71,s);
    end ZR;
procedure ZB(b,s); boolean b; string s;
  if test then
    begin
      if b then writetext(71,[[c7s]TRUE;[sss]]) else
        writetext(71,[[c6s]FALSE;[3s]]);
      writetext(71,s);
    end ZB;
procedure Z1(A,a,b,s); value a,b; array A;
  integer a,b; string s;
  if test then
    begin
      integer i,m;
      newline(71,1); write(71,FIN,a); write(71,FIN,b);
      space(71,3); writetext(71,s);
      for i := a step 1 until b do
        begin
          m:=i-a; if m+10×10=m then newline(71,1);
          write(71,FR,A[i]);
        end i;
    end Z1;
procedure Z1I(A,a,b,s); value a,b;
  integer array A; integer a,b; string s;

```

```

if test then
  begin
    integer i,m;
    newline(71,1); write(71,FIN,a); write(71,FIN,b);
    space(71,3); writetext(71,s);
    for i := a step 1 until b do
      begin
        m:=i-a;
        if m+10×10=m then newline(71,1);
        write(71,FR,A[i]);
        end i;
      end Z1I;
  procedure Z2(A,a,b,c,d,s); value a,b,c,d;
  array A; integer a,b,c,d; string s;
  if test then
    begin
      integer i,j,k;
      newline(71,1); write(71,FIN,a); write(71,FIN,b);
      space(71,6); write(71,FIN,c); write(71,FIN,d);
      space(71,3); writetext(71,s);
      for i := a step 10 until b do
        begin
          m:=if i+10>b then b else i+9;
          for j := c step 1 until d do
            begin
              newline(71,1);
              for k := i step 1 until m do write(71,FR,A[k,j]);
              end j;
            newline(71,2);
          end i;
        end Z2;
  procedure inter(A,B); real A,B;
  begin
    real ip1;
    ip1:=A; A:=B; B:=ip1;
  end inter;
  procedure Iinter(IA,IB); integer IA,IB;
  begin
    integer ip2;
    ip2:=IA; IA:=IB; IB:=ip2;
  end Iinter;
  open(20); test:=read boolean(20);
  if test then open(71);
  open(70); F:=format([s-nddd;]);
  FI:=format([-ndddd;d]); FR:=format([-d.ddd;-nd;]);
  FIN:=format([-nddd;]); write text(70,[[p2s]MONTEIRO[2c]]);
  write text(70,[[15s]ANALYSIS*OF*MIXTURES[2c]]);
  A1:=read(20); B1:=read(20); C1:=read(20); write(70,F,A1);
  write(70,F,B1); write(70,format([snddd;cc],C1); i:=1;
  nexpt:=read(20); L:=read(20); TOL:=read(20);
  TOL1:=read(20);
  TOL2:=read(20); TOL3:=read(20); TOL4:=read(20); per:=read(20);

```

```

R[1]:=2; R[2]:=1;
for i := 3 step 1 until nexp do R[i]:=1;
pn:=0;
for j := 1 step 1 until 1000 do
L1:   begin
      w:=MASS[j]:=read(20); P[j]:=read(20);
      if (999999.0-w)<10-2 then goto L3;
      if w>32020 then goto L2;
      if w<L or w>18010 and w<18011 or w>27999 and
         w<28010 or w>31970 and w<32020 then goto L1;
L2:   end j ;
L3:   k:=j-1; np:=if k<500 then 2xk else 1000; ZI(k,[k*at*L3]);
      ZI(np,[np*at*L3]); Z1(MASS,1,j,[MASS*at*L3]);
      Z1(P,1,j,[P*at*L3]);
      begin
      comment the largest dimension of the matrix is
         now known to be k .By determining this before
         the dimensions of the matrix are declared,
         storage space is not wasted;
      array H[1:nexp,1:np];
      for j := 1 step 1 until k do H[2,j]:=P[j];
      for i := 1, 3 step 1 until nexp do
      begin
      j:=1;
L4:   w:=read (20);
      if w>32020 then goto L5;
      if w<L or w>18010 and w<18011 or w>27999 and
         w<28010 or w>31970 and w<32020 then
      begin
      DIS:=read (20); goto L4;
      end ;
L5:   if abs (w-MASS[j])>TOL1 then
      begin
      if w>MASS[j] then
      begin
      H[1,j]:=0.0; j:=j+1;
      if j>k then goto L61 else goto L5;
      end missing abundance
      else if w<MASS[j] then
      begin
      k:=k+1;
      for jo := k step -1 until j+1 do
      begin
      j1:=jo-1; MASS[jo]:=MASS[j1];
      for ji := 1 step 1 until i do
      H[ji,jo]:=H[ji,j1];
      end shift down ;
      MASS[j]:=w;
      for ji := 1 step 1 until i-1 do H[ji,j]:=0;

```

```

H[1,j]:=read(20);  j:=j+1;
if j<k then goto L4 else goto L6;
end new mass and abundance appear,
move rest down ;
end
else
begin
H[1,j]:=read (20);  j:=j+1;
if j<k then goto L4 else goto L6;
end mass as before ;
L6:  w:=MASS[j]:=read(20);
L61: if (999999-w)<n-2 then read(20) else
begin
k:=k+1;  H[1,j]:=read(20);
for j1 := 1 step 1 until i-1 do H[j1,j]:=0;
j:=j+1;  goto L6;
end ;
Z1(MASS,1,k,[MASS*after*reading*all*the*data]);
Z2(H,1,nexp,1,k,[H*after*reading*all*the*main*data]);
end ;
per:=kxper/100;  ns:=read(20);
ZI(ns,[ns*number*of*standards*or*background*peaks]);
begin
array SU[1:nexp];
if ns=0 then goto LAB4;
nos:=nexp;
for i := 1 step 1 until nexp do SU[i]:=0;
no:=0;  nexp:=nexp-1;
for i1 := 1 step 1 until ns do
begin
SM:=read(20);
for j := k step -1 until 1 do
begin
if abs(SM-MASS[j])<TOL1 then
begin
for i := 1 step 1 until nexp do
SU[i]:=SU[i]+H[nos,j]/H[1,j];
no:=no+1;
end ;
if no=ns then goto LAB1;
if no=i1 then goto LAB2;
end ;
LAB2:
end read standard background masses SM
and abundances ;
LAB1: for i := 1 step 1 until nexp do
begin
SU[i]:=SU[i]/ns;
for j := 1 step 1 until k do
H[1,j]:=H [1,j]xSU[i]-H[nos,j];

```

```

                end subtract scaled background;
LAB4:  Z2(H,1,nexp,1,k,[H*after*subtracting*background]);
        for i := 1 step 1 until nexp do
            begin
                sum:=0;
LAB6:  for j := 1 step 1 until k do
                    begin
                        p:=H[i,j];
                        if p>TOL then pn:=pn+1;
                        end j ;
LAB7:  N[i]:=pn; pn:=0;
                    end ;
            end ;
LAB8:  close(20);
        Z1I(N,1,nexp,[N*after*LAB8.*N(i)*is*the*number*
of*useful*values*for*experiment*i]);
        begin
            comment this part of the program finds the
            rank of the matrix. this is equal to the
            number of compounds present in the mixture.
            The number of expts. must be at least one
            more than the number of compounds;
            array HI [1:nexp,1:k];
            integer array I[1:nexp];
            comment the original matrix must be
            duplicated as it will be needed at the end
            of the program.The operations are then
            carried out on the duplicate.The parts of
            the original matrix which are found to be
            unnecessary may then be completely discarded;
            MAX:=0;
            for i := 1 step 1 until nexp do
                begin
                    if N[i]>MAX then
                        begin
                            MAX:=N[i];  ji:=i;
                        end ;
                    end ;
                    if ji>1 then
                        begin
                            for j := 1 step 1 until k do inter(H[1,j],H[ji,j]);
                            Iinter(R[1],R[ji]);
                        end ;
                    for i := 1 step 1 until nexp do
                        for j := 1 step 1 until k do HI[i,j]:=H[i,j];
                    I[1]:=1; noc:=nexp; FM:=format([2s-ndddc]);
                    F:=format([2s-ndddd.ddd]);
                    write text(70,[[2s]SUCCESSIVE*STEPS*IN*THE*
                    CONDENSATION*OF*MIXTURE*MATRIX*H[c]FIRST*STEP[c]]);
                    for i := 1 step 1 until noc do

```

```

begin
x:=z:=1; nc:=noc; l:=1+1;
L7: b:=HI[z,x];
  if abs (b)<TOL2 then
    begin
      if z<nc then
        begin
          z:=z+1; goto L7;
        end ;
      if z=nc then
        begin
          if x<nc then
            begin
              x:=x+1; z:=1; goto L7;
            end ;
          end ;
        end ;
      end ;
    if z≠1 then
      begin
        comment if columns in the duplicate
          matrix are interchanged, then the
          corresponding columns in the original
          matrix are interchanged at the same
          time so that finally the correct
          columns of the original matrix will be used;
        for j := 1 step 1 until k do
          begin
            inter (H[i,j],H[z,j]);
            inter (HI[i,j],HI[z,j]);
          end ;
        linter (R[i],R[z]);
      end ;
    for m := 1 step 1 until nc do
      begin
        c:=0; d:=HI[m,x];
        if abs (d)<TOL2 then
          begin
            l[m]:=m;
            if l=m then
              begin
                l:=l+1; goto L8;
              end
            elsefor j := x step 1 until k do
              HI[l,j]:=HI[m,j];
            l:=l+1; goto L8;
          end
        else d:=b/d;
        for j := x step 1 until k do
          begin
            q:=j-x;

```

```

        if  $q \neq 10 \times 10 = q$  then newline(70,1);
        y := HI[1,j] := HI[m,j] x d - HI[1,j];
        write (70,F,y);
        if abs (y) > TOL4 then c := c + 1;
        end ;
    newline(70,3);
    if c < per then
        begin
            I[m] := 0; noc := noc - 1;
        end
        else
            begin
                I[m] := m; l := l + 1;
            end ;
L8:   end ;
        c := 0;
        for q := 1 step 1 until noc do
            begin
                rr := 1 [q];
                if rr = q then
                    begin
                        c := c + 1; goto L9;
                    end
                else if rr = 0 and c < noc then
                    for co := q + 1 step 1 until noc do
                        begin
                            rr := I[co];
                            if rr = 0 then goto E;
                            if rr = co then
                                begin
                                    c := c + 1;
                                    for j := 1 step 1 until k do
                                        H[c,j] := H[co,j];
                                    end ;
                                end ;
E:   end ;
L9:   end ;
        end ;
        if l  $\neq$  noc then writetext (70,[[c]NEXT*STEP***]);
        end ;
    if nexp = noc then
        begin
            write text (70,[[2s]FAIL*INSUFFICIENT*DATA]);
            goto EN;
        end ;
        begin
            write(70,format([nd]),noc);
            writetext (70,[[s]INDEPENDENT*COMPOUNDS[cc]]);
            if noc = 1 then goto EN;
        end ;

```

```

end ;
begin
comment divide all original spectra by the
first one;
integer f;
integer array L[1:k],NR,lg[1:k+2];
array IM[1:noc,1:k+2],H2[1:noc,1:noc];
ji:=1;
array IM1[1:noc,1:k+2],H21[1:r2
ji:=1;
for j := 1 step 1 until k do
begin
if H[1,j]>TOL then ; ji:=ji+1;
begin
HI[1,j]:=1; L[ji]:=j;
end ;
for ji := 1 step 1 until r do
begin
j:=L[ji];
for i := 2 step 1 until nexp do
HI[i,j]:=H[i,j]/H[1,j];
end ;
Z2(HI,1,nexp,1,r,[[c]Matrix*HI*just*after*
division*by*first*spectrum]);
comment since we have assumed that each
compound produces a spectrum with at
least two unique peaks, we can now group
mass numbers which are due to the same
compounds,i.e. pair the rows of HI which
are equal;
to:=1;
writetext(70,[[p]BINARY*GROUPS*OF*MASSES*
FOR*COMPARISON[cc3s]MASSES**]);
for j := 1 step 1 until nexp-1 do
begin
writetext(70,[MIXTURE*NO.]);
write(70,format([nds]),j);
end ;
newline(70,1);
L10: ri:=s:=1; jo:=L[1]; f:=format([ndd]);
write(70,f,jo); writetext(70,[*WITH[c]);
for j := 2 step 1 until r do
begin
c:=0; ji:=L[j];
write(70,format([8sndd]),MASS[ji]);
for i := 2 step 1 until nexp do
begin
D:=HI[i,jo]-HI[i,ji]; write (70,F,D);
if abs(D)>TOL3 then c:=c+1;
end ;

```



```

if c>0 then
  begin
    L[ri]:=ji; ri:=ri+1;
  end ;
if c=0 then
  begin
    s:=s+1; writetext(70,[*UNIQUE*AS]);
    write(70,f,jo);
  end ;
newline(70,1);
end ;
if s>1 then
  begin
    NR[to]:=s; writetext(70,[MASS]);
    write(70,f,jo); writetext(70,[HAS]);
    write(70,f,s-1);
    writetext(70,[*OTHERS*ALIKE[c]]);
    for i := 1 step 1 until nexp do
      y:=IM[i,to]:=HI[i,jo];
    to:=to+1;
  end ;
r:=ri-1;
if r>1 then goto L10;
tr:=to-1; write(70,FM,tr);
writetext(70,[UNICOMPOUND*BLOCKS*FOUND[cc]]);
if tr<noc then
  begin
    write text (70,[[2s]FAIL*LESS*GROUPS*
      THAN*COMPOUNDS]);
    goto EN;
  end ;
if tr=noc then
  begin
    for j := 1 step 1 until noc do lg[j]:=j;
    goto S1;
  end ;
if tr>noc then
  begin
    for j := 1 step 1 until tr do lg[j]:=j;
    for l := noc+1 step 1 until tr do
      begin
        for j := 1 step 1 until noc do
          begin
            if NR[l]>NR[j] then
              be write(70,FM,NR[l]);
              wr I inter(NR[j],NR[l]);
              I Iinter(lg[j],lg[l]);
              Ii write(70,FM,NR[l]);
              wr write(70,FM,NR[j]);
              write(70,FM,NR[l,j]);
          end
        end
      end
  end

```

```

write(70,FM,lg[1]);
write(70,FM,lg[j]);
end ;
end ;
end ;
S1: for j := 1 step 1 until noc do
begin
w:=lg[j];
for i := 1 step 1 until noc do
y:=H2[i,j]:=HI[i,j]:=IM[i,w];
end ;
newline (70,2);
comment the matrix was duplicated so that
calculations may be done on one now, and
on the other later in the program;
begin
comment this part of the program forms
an intermediate matrix, IM, to help
in the calculations of the pure
spectra, using the first mixture;
array X[1:noc,1:noc],D[1:noc];
n:=noc-1;
for j := 1 step 1 until n do
begin
ji:=j+1;
for i := 1 step 1 until n do
w:=IM[j,i]:=HI[ji,noc]-HI[ji,i];
w:=D[j]:=HI[ji,noc]-1;
end ;
comment this new matrix which has been
constructed may now be used to give
the factors from which the first
component may be found;
if n=1 then goto EO;
for j := 1 step 1 until n-1 do
begin
x:=z:=j; l:=j+1;
L11: b:=IM[x,z];
if abs (b)<TOL2 then
begin
if z<n then
begin
z:=z+1; goto L11;
end ;
if z=n then
begin
if x<n then
begin
x:=x+1; z:=1;

```

```

                                end ;
                                end ;
                                end ;
if z≠j then
begin
for i := 1 step 1 until n do
inter(IM[i,z],IM[i,j]);
inter(D[j],D[z]);
end ;
if test then goto L13;
for m := 1 step 1 until n do
begin
d:=IM[x,m];
if abs(d)<TOL2 then goto L12 else d:=b/d;
for i := x step 1 until n do
w:=IM[i,m]:=IM[i,m]×d-IM[i,j];
w:=D[m]:=D[m]×d-D[j];
L12:
end ;
L13:
end ;
EO: sum:=0;
comment calculation of pure spectra;
begin
procedure SOLVE(C,n,R,m,X);
value C,n,R,m; array C,R,X; integer n,m;
begin
integer i,im1,j,jj,k;
real t,modt,p,modp;
array ROWC[1:n],ROWR[1:m];
integer array J[1:n];
for i := 1 step 1 until n do
begin
ROW: p:=modp:=0.0;
for j := 1 step 1 until n do
begin
ROWC[j]:=t:=C[i,j];
modt:=if t<0.0 then -t else t;
if modt>modp then
begin
p:=t; modp:=modt; jj:=j
end found a bigger
end j;
if p=0 then goto fin;
for j := 1 step 1 until n do
C[i,j]:=ROWC[j]:=ROWC[j]/p;
for j := 1 step 1 until m do
R[i,j]:=ROWR[j]:=R[i,j]/p;
J[i]:=jj; im1:=i-1;
for j := 1 step 1 until im1,

```

```

i+1 step 1 until n do
  begin
  t:=C[j,jj];
  for k := 1 step 1 until n do
    C[j,k]:=C[j,k]-ROWC[k]xt;
  for k := 1 step 1 until m do
    R[j,k]:=R[j,k]-ROWR[k]xt
  end j
  end i;
for i := 1 step 1 until n do
  begin
  jj:=J[1];
  for j := 1 step 1 until m do
    X[jj,j]:=R[i,j]
  end i ;
fin:
  end SOLVE;
  Z2(IM,1,n,1,n,[Matrix*IM*before*
  finding*concentrations*by*SOLVE]);
  Z1(D,1,n,[Vector*D*idem]);
  for l := n step -1 until 1 do
  begin
  w:=X[1,1]:=D[1]/IM[1,1]; sum:=sum+w;
  if l=1 then goto E1;
  for m := l-1 step -1 until 1 do
    D[m]:=D[m]-IM[m,1]xw;
  E1:
    end ;
E2: c:=0;
  for j := 1 step 1 until n do
  begin
  w:=X[1,j]; sum:=sum+w;
  if w<0 then c:=c+1;
  end ;
  w:=X[1,noc]:=1-sum;
  comment we must now calculate the
  factors for finding the pure
  spectra in all the mixtures;
  for l := 2 step 1 until noc do
  for j := 1 step 1 until noc do
  begin
  w:=X[1,j]:=H2[1,j]xX[1,j];
  if w<0 then c:=c+1;
  end j ;
  Z2(X,1,noc,1,noc,[Matrix*X*before*SOLVE]);
  Z2(H2,1,noc,1,noc,[Matrix*H2*before*SOLVE]);
  Z2(H,1,noc,1,k,[Matrix*H*before*SOLVE]);
  Z2(HI,1,noc,1,k,[Matrix*HI*before*SOLVE]);
  SOLVE(X,noc,H,k,HI);
  Z2(HI,1,noc,1,k,[Matrix*HI*after*SOLVE]);

```

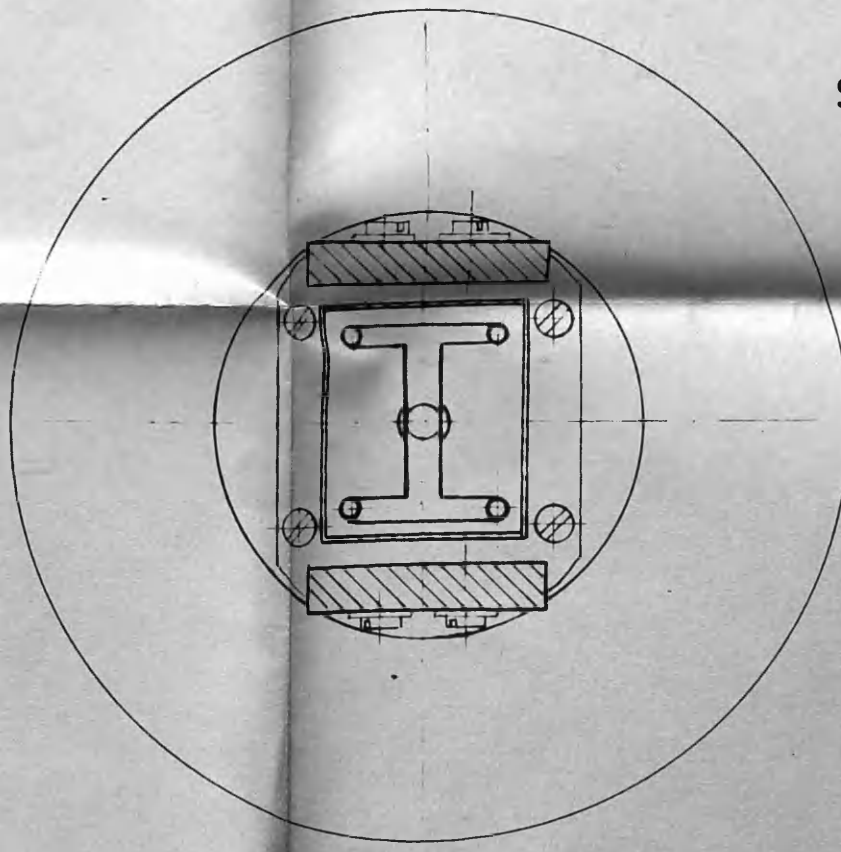
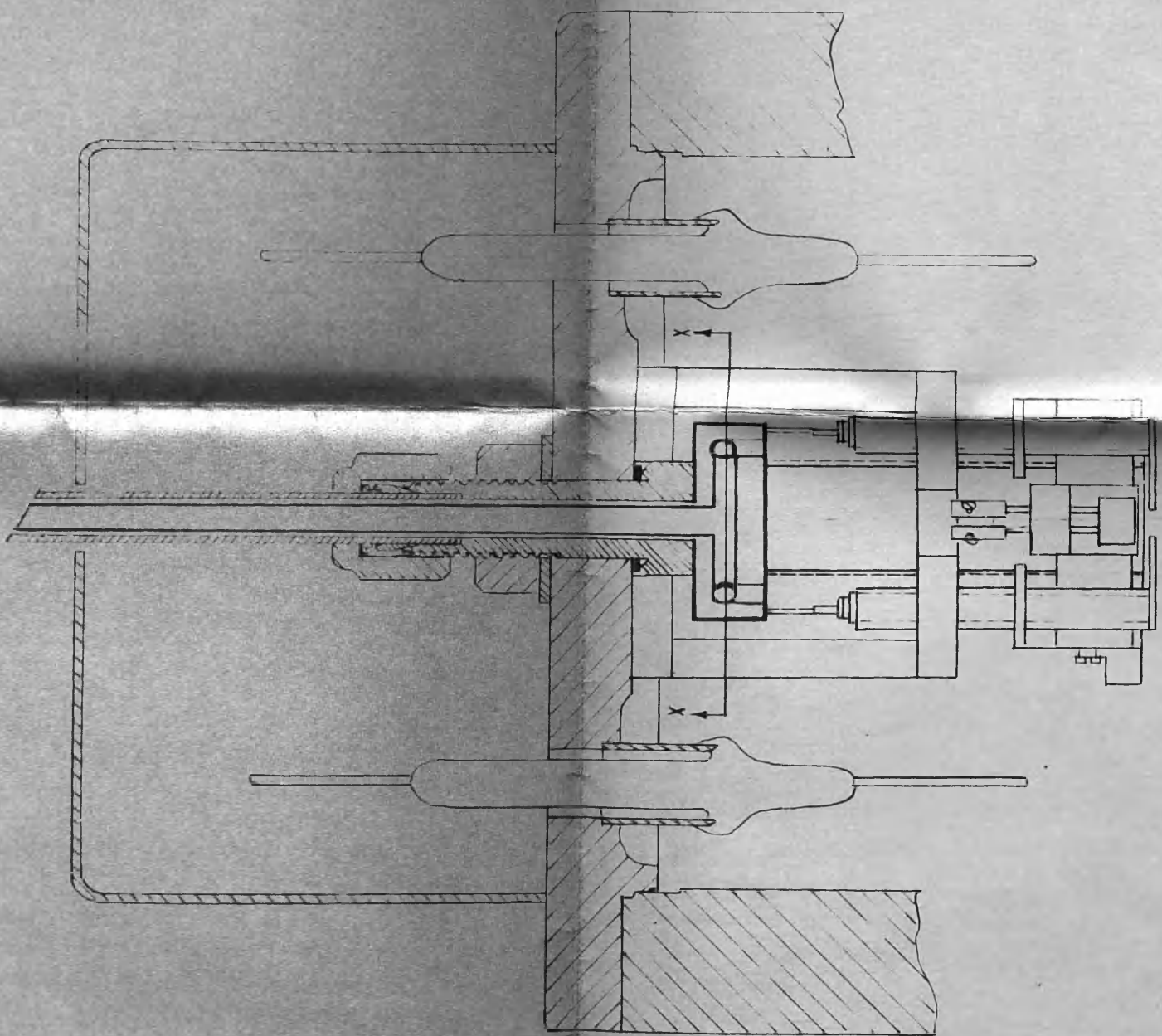
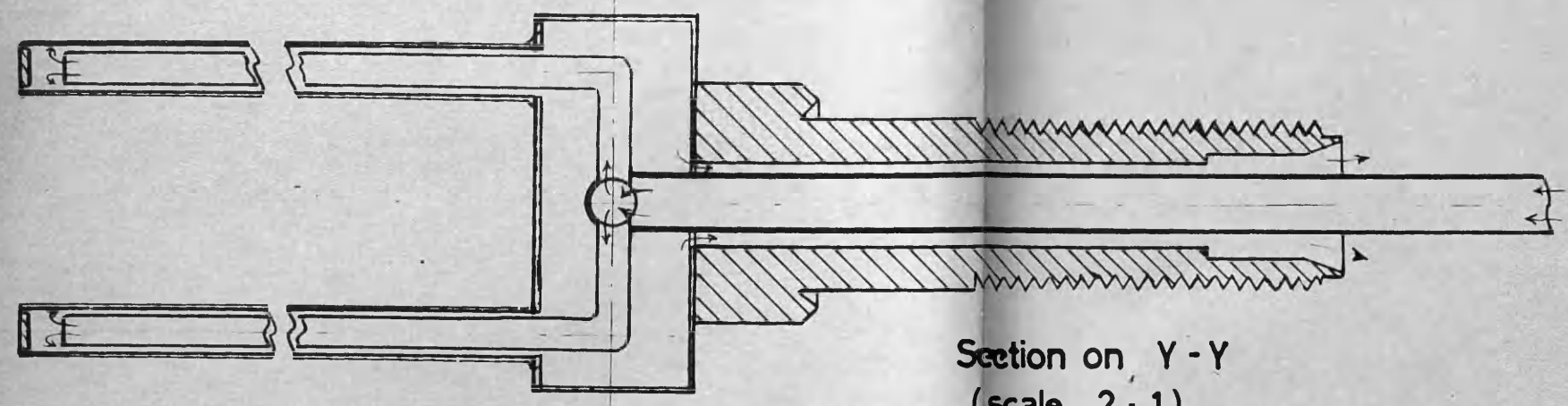
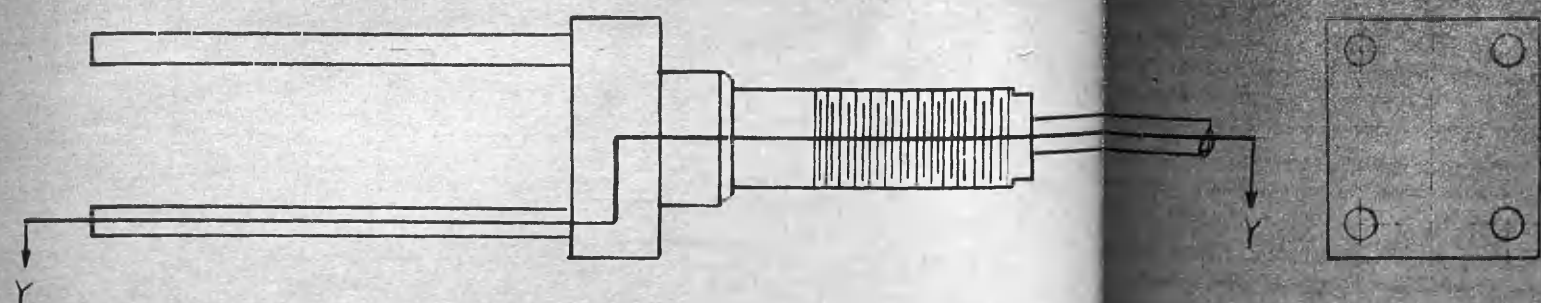
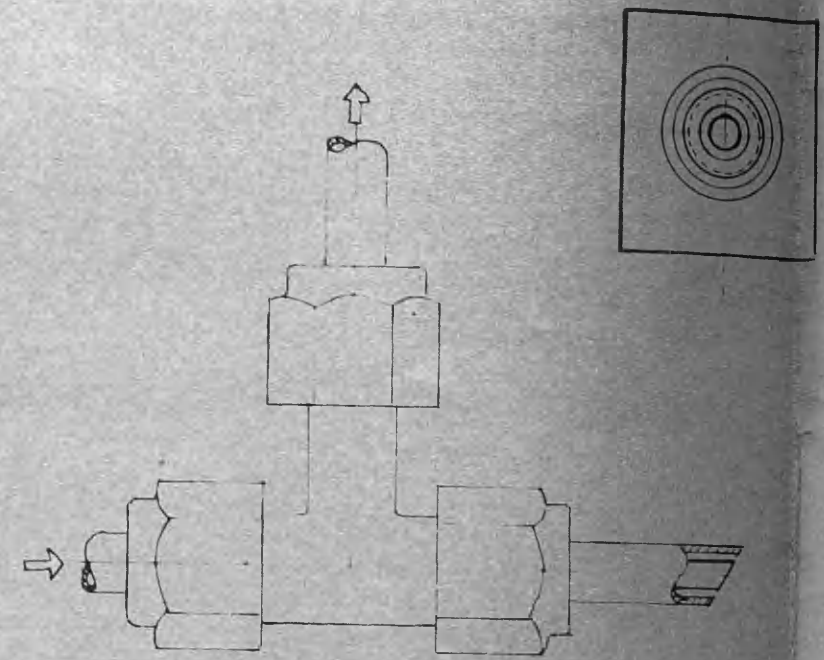
```

end ;
comment The final part of this program
is the normalisation of the pure spectra;
begin
real g,sc1;
integer FH;
write text(70,[[15s]NORMALISED*PURE*
SPECTRA[2c]]);
F:=format([snddd.dddc;]);
FM:=format([3sndd.ddd]);
FH:=format([6sndd.dd]);
FP:=format([6s-d.ddddd,-ndc]);
write text(70,[[4s]MASS[4s]
NORMALISED*PEAK[4s]APPROX*
PERCENT.*TOTAL*CURRENT[2c]]);
for i := 1 step 1 until noc do
begin
sum:=g:=0;
write text (70,[[2c]SPECTRUM]);
write(70,F,i);
for j := 1 step 1 until k do
begin
w:=HI[i,j]; sum:=sum+w;
g:=if abs(w)>abs(g) then w else g;
end ;
sc1:=100/g;
for j := 1 step 1 until k do
begin
write(70,FM,MASS[j]); w:=HI[i,j];
write(70,FH,abs(w*sc1));
write(70,FP,if w<0 then -w else w);
end ;
write text(70,[[c6s]TOTAL*CURRENT]);
write(70,FP,sum);
end ;
end ;
end ;
end ;
end ;
close(70);
if test then close (71);
EN:
end→

```

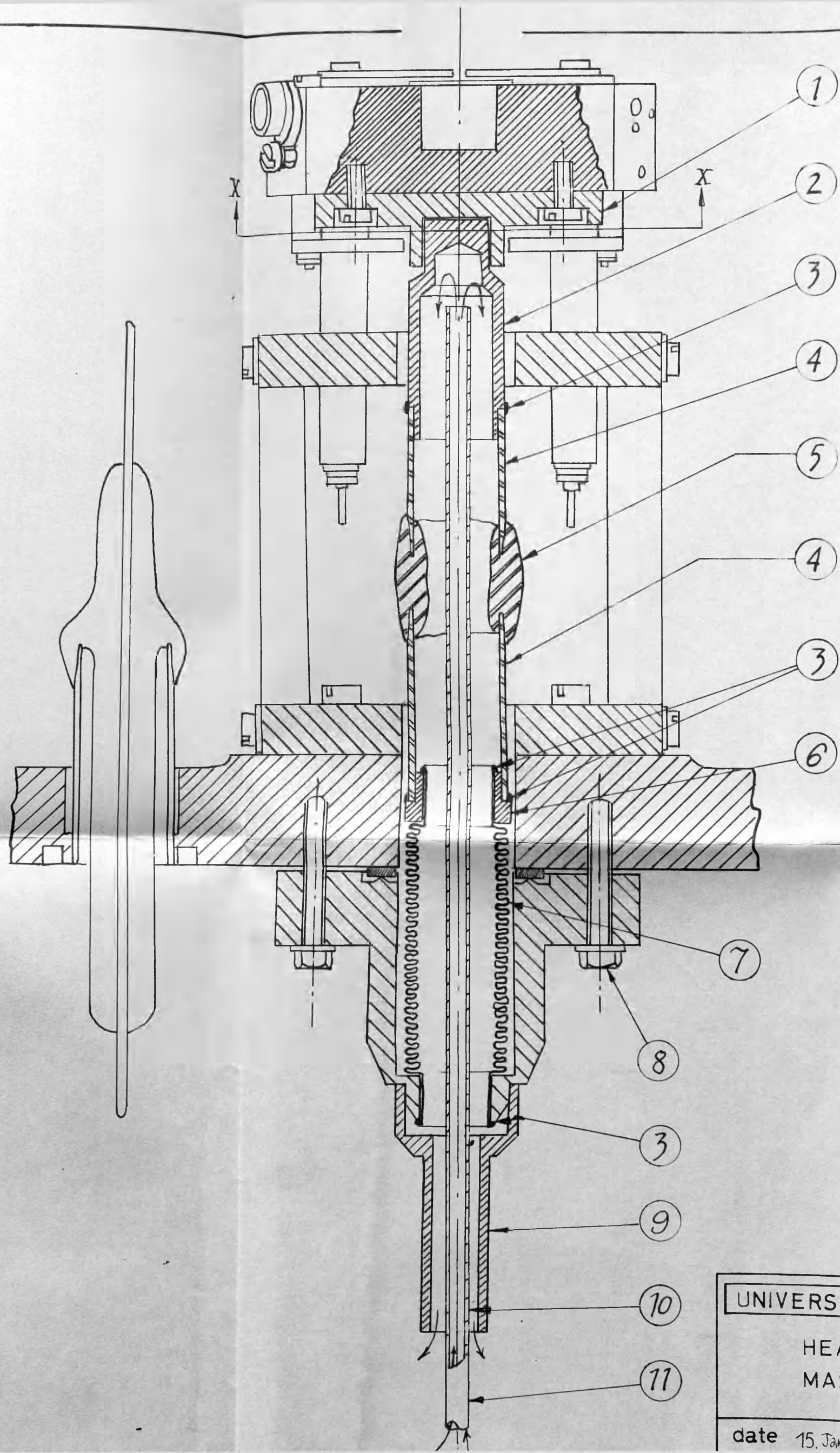
REFERENCE

1. NAUR, P. (ed.), Revised Report on the Algorithmic Language ALGOL 60, The Computer Journal, (1963).



Section on X-X

UNIVERSITY of GLASGOW - Chemistry Department		
HEAT EXCHANGER FOR M-S-9 MASS SPECTROMETER SOURCE		
date 15. Oct. 68	SCALE FULL SIZE	drawn <i>L. Fraser Monteiro</i>

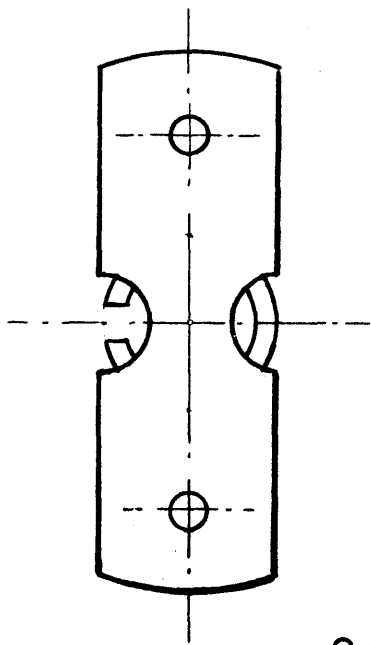


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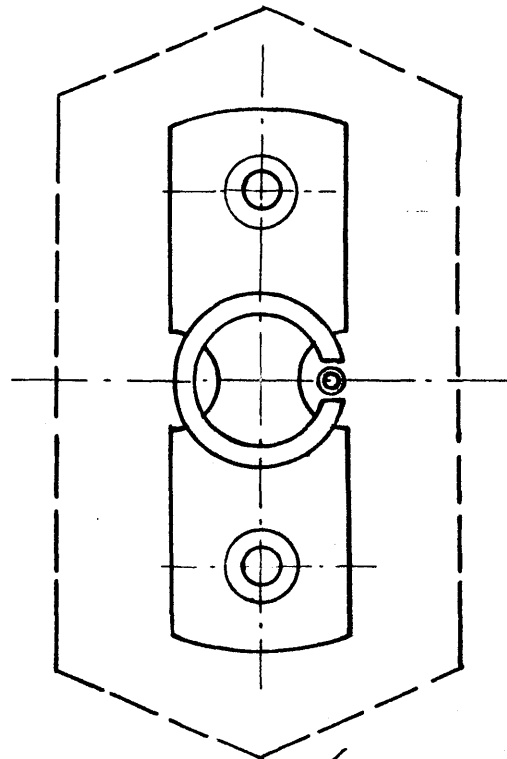
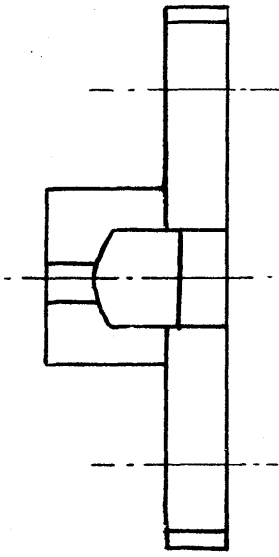
HEAT EXCHANGER FOR M.S.9
 MASS SPECTROMETER SOURCE Mk. II

date 15. Jan 69 scale 2:1 drawn *L. F. Monteiro*

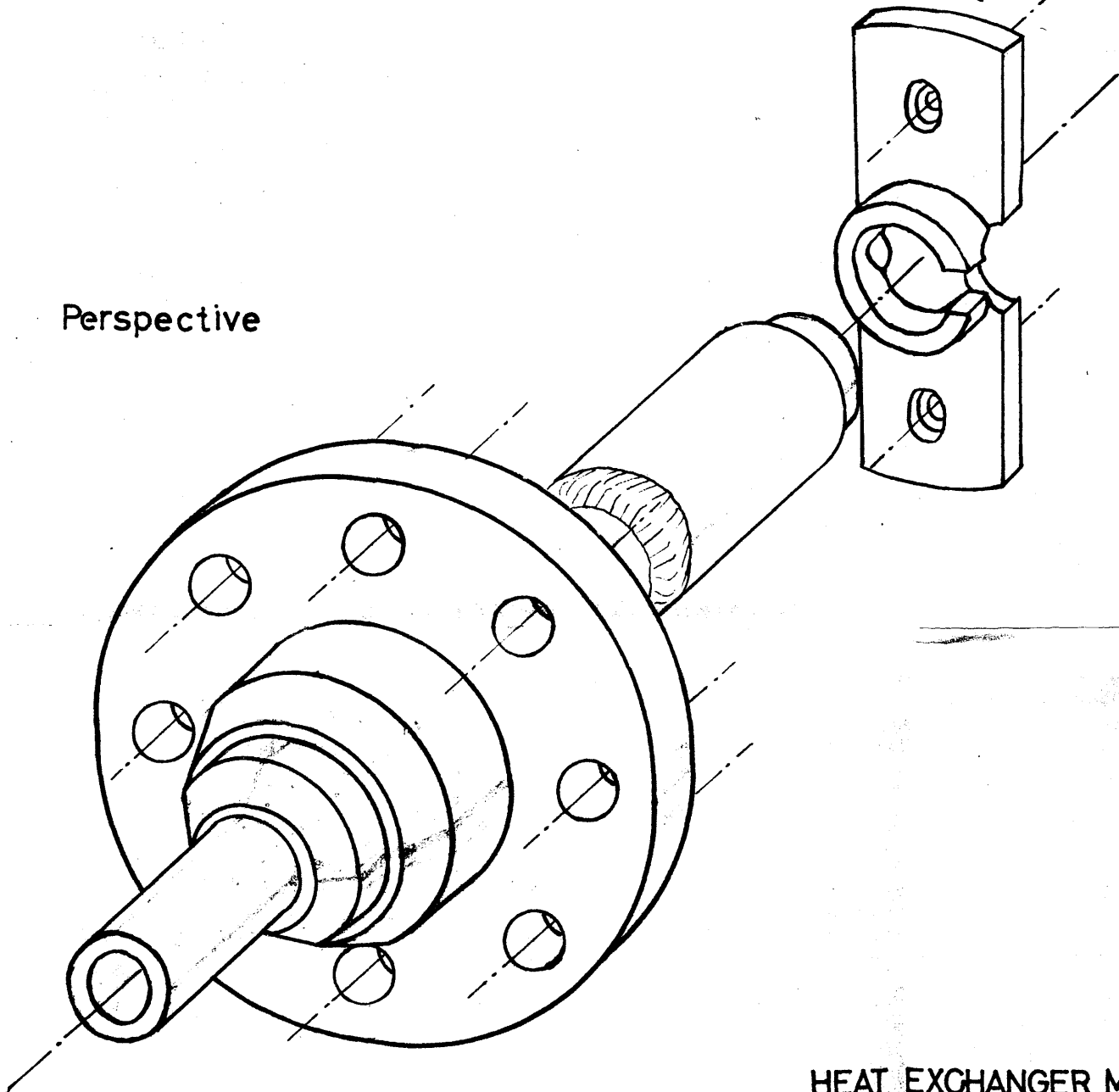
Section on X-X



Copper bracket



Perspective



HEAT EXCHANGER Mk-II