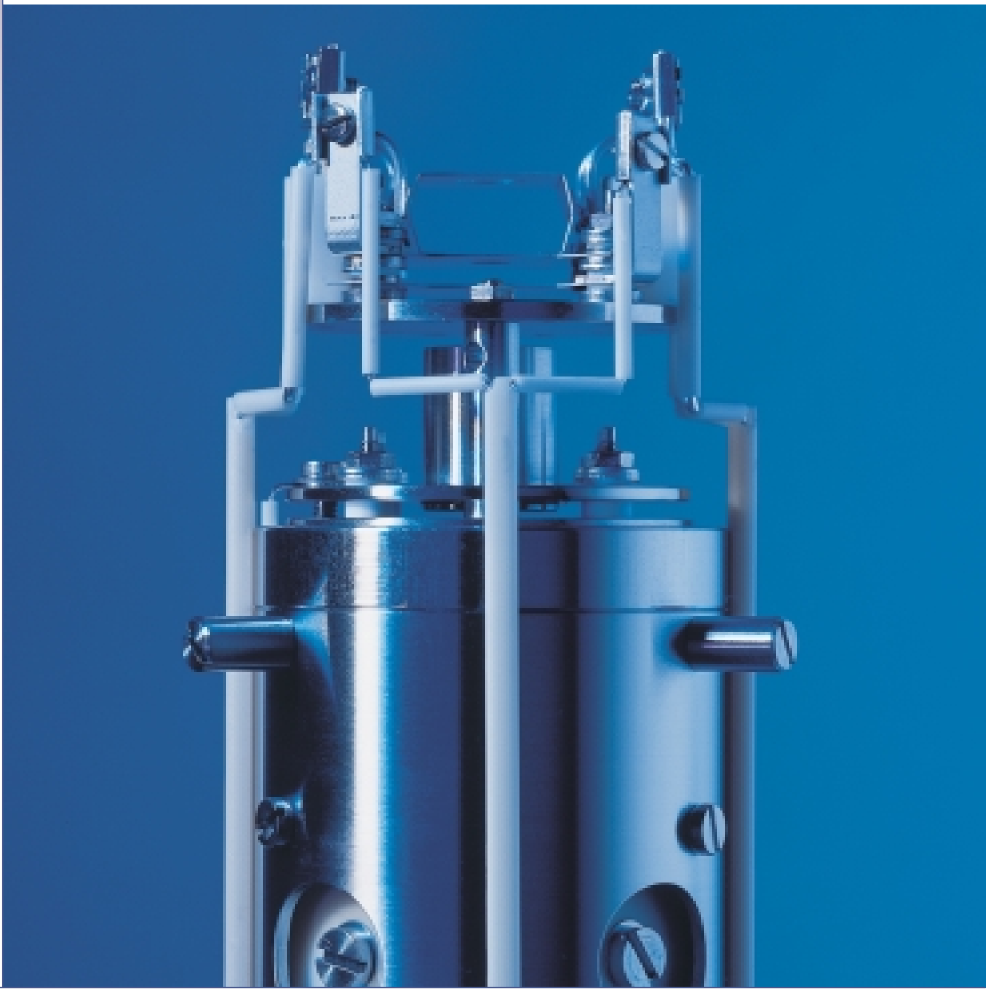


Partial Pressure Measurement in Vacuum Technology

Partial pressure measurement in vacuum technology

1. Introduction

The use of vacuum has over the years become indispensable for many branches of research and process technology. New fields of application will also be opened up in future too. Consequently vacuum technology is steadily gaining in importance. This necessitates constant improvement of the methods employed, e.g. methods of pumping, technology of process installations and the like.

Furthermore the methods of measurement, which are supposed to provide information on the state of a vacuum system, have to satisfy the constantly growing demands. In many cases the information supplied by devices measuring the total pressure may be sufficient. But when it is desirable or necessary to obtain detailed information on phenomena in a vacuum system, this can only be done with the aid of measurements of partial pressure.

Measurement of total pressure by means of ionization gauges yields "nitrogen-equivalent" pressure values: it is assumed that all gases and vapours exhibit the same probability of ionization as nitrogen. From this it follows that a gas possesses that "nitrogen-equivalent" pressure which is indicated by an ionization gauge calibrated for nitrogen. But if the true probabilities of ionization are considered (see Table 11.4.1), it is found, e.g. for helium, that the value is about 6.5 times smaller than that of nitrogen. On the other hand, the probability of ionization of benzene is about 6 times that of nitrogen. Higher hydrocarbons have proportionally higher ionization probabilities. The total pressure measurement in a vacuum system is therefore uncertain to the extent that the nature and proportions of the gases in the vacuum system are not known. This is where partial pressure analysis contributes to complete characterization of a vacuum system. Furthermore, as will be seen from the examples, it is utilized for a large number of measuring, supervisory and process control tasks.

2. Fundamentals

There are several methods for measuring partial pressures. The following discussion will be confined to methods employing mass spectrometers: on the one hand, this is a form of mass spectrometry that has been simplified as far as possible; on the other hand, a number of demands - sometimes very restrictive - are additionally imposed by aspects of vacuum physics.

The aim of this chapter will be to create the prerequisite conditions enabling the operation of a mass spectrometer to be understood (for detailed explanations please consult the relevant literature [1, 2, 3]).

The mass spectrometric partial pressure gauge is also an ionization vacuum-meter, but it is equipped with an additional facility which separates the various kinds of ions generated during the ionization process according to their masslcharge (m/e) ratio, before they are detected. The methods are described and discussed below in the following order: ionization, separation, detection.

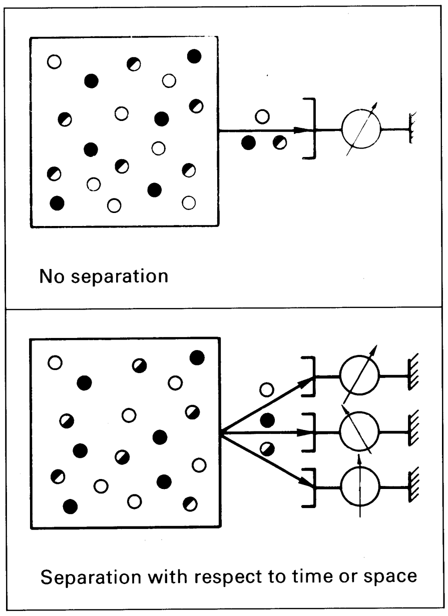


Fig. 1
Principle of measuring partial pressure with a mass spectrometer

2.1 The ionization process

Ionization is that stage of the analytic process which leads to the most drastic alterations in the substances to be analysed [4, 5].

By bombarding the atoms or molecules present in the gaseous phase with low-energy electrons, a small proportion is ionized; ions with single and multiple positive charges are produced. The energy of the impact electrons exerts a marked influence on the number and also on the type of ions that are formed (Fig. 2 and 3).

The ionization process commences at a minimum electron energy (ionization potential). The number of ions formed grows rapidly with increasing energy, reaching a maximum at 50 - 150 eV and then, as the energy continues to increase, slowly decreases again. Apart from the ions with single charge, at higher energies ions with a multiple charge also occur.

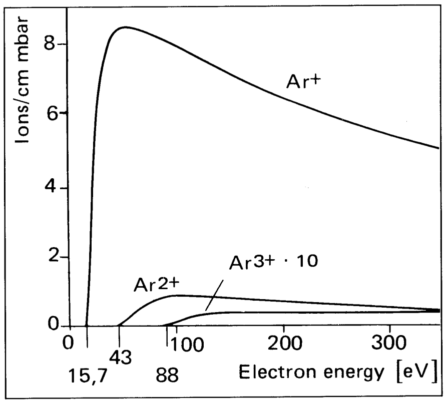


Fig. 2
Ionization by electron impact in terms of the electron energy, shown for argon (Ar)

Since the ion yield - and thus the sensitivity - should be as high as possible, it is usual to employ electron energies of the order of 100 eV. Note, however, that reference data from analytical mass spectrometry are usually recorded at 70 eV.

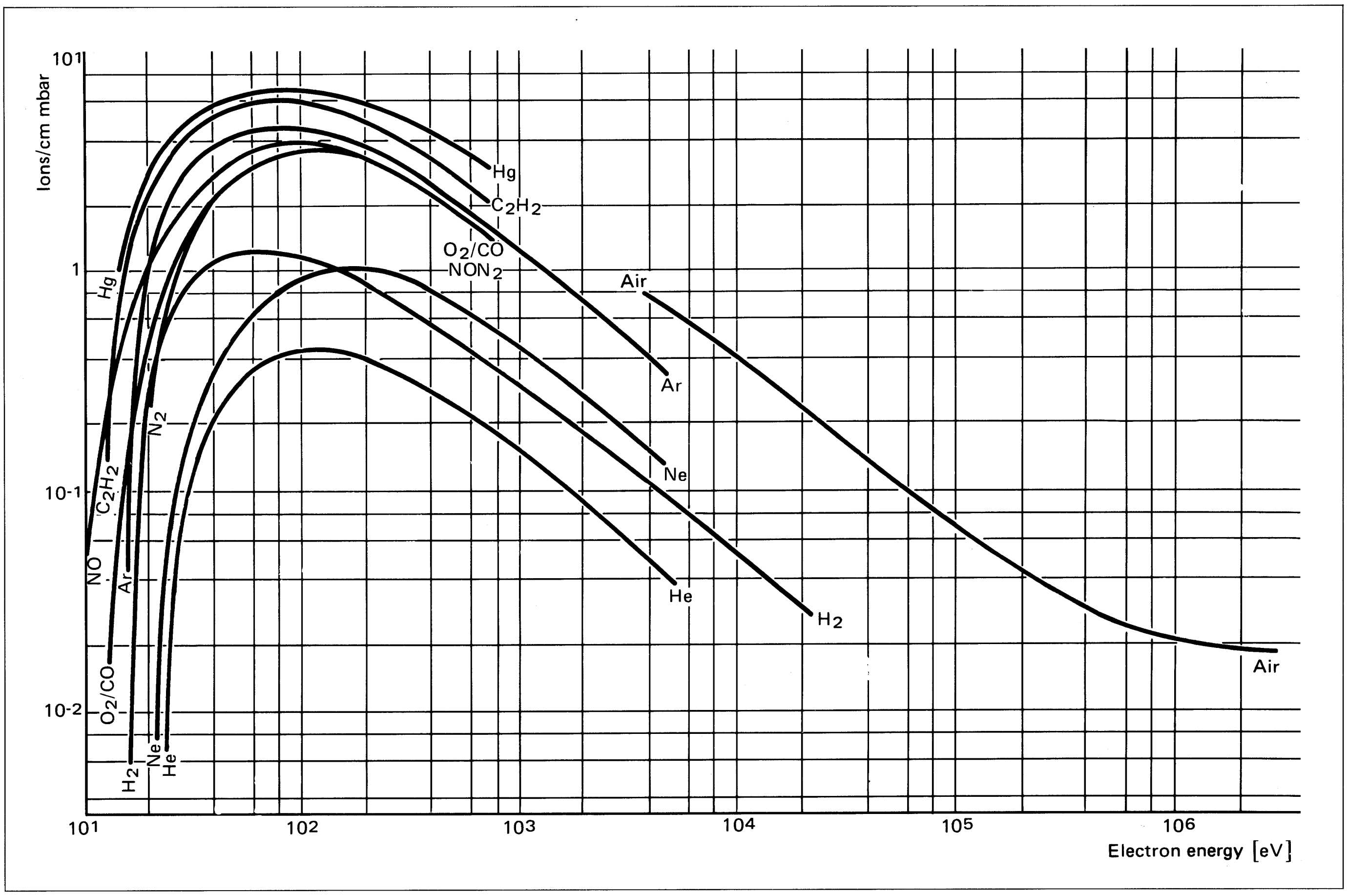


Fig. 3
Ionization by electron impact in terms of the electron energy for different gases

The number of ions produced per unit time, i.e. the ion current i^+, can be calculated from the following relationship:

$$i^+ = i^- \cdot 1 \cdot s \cdot p \text{ [A]}$$

where

i^- = the ionizing electron current [A]
l = length of the mean free path of the electrons in the ionization space [cm]
s = differential ionization [cm^{-1} $mbar^{-1}$]
p = partial pressure of the gas concerned [mbar]

The differential ionization indicates the number of ions produced by one electron on a path of 1 cm at a given gas temperature and a pressure of 1 mbar.

When complex molecules are ionized, the number of possible ion species grows very rapidly with increasing complexity. Apart from the molecular ions with single or multiple charges, fragment ions also occur. This can be illustrated schematically as follows for the simple molecule ABC:

$$\begin{array}{llll} ABC + e^- \rightarrow & ABC^+ & + 2e^- & \\ & ABC^{++} & + 3e^- & \\ & AB^+ & + C & + 2e^- \\ & BC^+ & + A & + 2e^- \\ & A^+ & + BC & + 2e^- \\ & C^+ & + AB & + 2e^- \\ & B^+ & + A & + C + 2e^- \end{array}$$

In addition to the above, it is also possible for others (e.g. rearrangement ions such as AC^+) to be formed. The occurence and relative abnudance of the various ki nds of ions are characteristic of each molecule. If we consider a simple molecule like CO_2, we find from the literature at 70 eV roughly the "cracking pattern" given in Table 11.4.2. Proportions less than 0.01% are not taken into account.

For a number of gases common in vacuum systems, the rough distribution of the fragment ions (cracking pattern) are shown in in Table 11.4.4. The distributions are influenced by various parameters, such as the energy of ionization and the temperature, but also by the properties of the mass analyzer. All intensities are shown relative to the most abundant kind of ion, which in many cases is not identical with the molecular ion. Different isotopes of an element behave in almost the same manner when ionized. The characteristic spectra of a large number of molecules are contained by special data collections [6, 7].

2.2 Ion separation

The separation of the different kinds of ion with respect to space or according to their mass/charge ratio is effected by magnetic and/or electric fields. In the absence of a magnetic field it is necessary to employ electric fields varying with respect to time, mostly with a high frequency, for the mass separation. This is evident from general principles [8].

Magnetic mass spectrometers, which are extensively used in other areas of mass spectrometry, are rarely employed for partial pressure analysis in vacuum technology. The high-frequency quadrupole mass spectrometer is used almost universally as its small size allows it to be inserted direct in the vacuum system. Other types may be indispensable for special applications, e.g. for the detection of rapidly changing phenomena (time-of-flight mass spectrometer) [1, 2, 3, 8].

2.2.1 The quadrupolle mass spectrometer

The quadrupole mass filter was originally proposed by W. Paul [9, 10, 11]. Its basic design is illustrated in Fig. 4. In a high-frequency, quadrupole electric field, which in the ideal case is generated by four hyperbolic rod electrodes a distance of $2r_0$ apart at the tips, it is possible to separate ions according to their mass/charge ratio (m/e) (see Fig. 5). The hyperbolic surfaces are approximated with sufficient accuracy by cylindrical rods of circular cross-section. The voltage between these electrodes is composed of a high-frequency alternating component $V \cos \omega t$ and a superposed direct voltage U.

If ions in the direction of the axis of the field, perpendicular to the plane of the picture, are injected into the separating system, the influence of the high-frequency electric field causes them to oscillate at right-angles to the axis of the field.

The equations of motion of these ions are called Mathieu differential equations, the solutions of which are known and classifiable in two groups. In the first class, the amplitudes of the oscillations remain limited for any length of time. These solutions are referred to as stable. The others – unstable solutions – are charaeterized by a continuous increase in the amplitude.

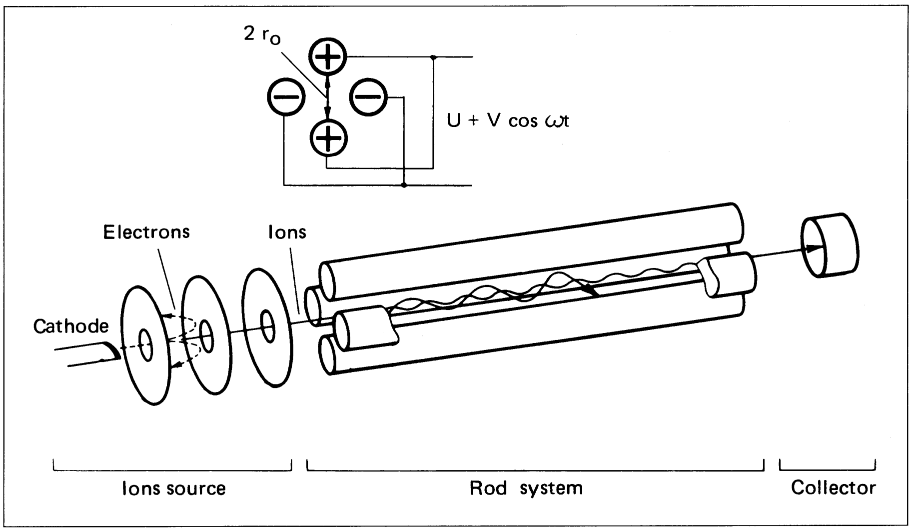
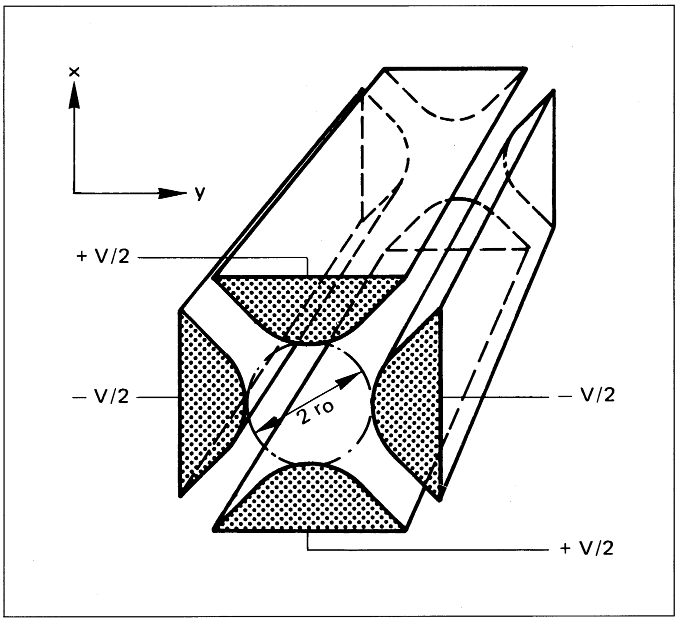


Fig. 4
Structure of a quadropole analyzer



Physically this means that some ions would pass through the mass analyser, while others would strike the rods, be neutralized and pumped away as gas. Here the term "mass filter" is often applied to quadrupoles.

The stability diagram (Fig. 6) shows how the stability of the motion varies with the operational parameters when $q = 2\,eV/m\,r_0^2\,\omega^2$ and $a = 4\,eU/\,m\,r_0^2\,\omega^2$. When the parameters V, U, ω and r_0 are given, only ions of a definite mass, or to be more exact ions of a definite mass interval, are able to pass through the separating field. The amplitudes of oscillation of these ions remain finite and smaller than ro. All other ions are separated out. For "stable" ions the following relationship applies:

$V = 14.4\ m \cdot \nu \cdot r_0^2$ [Volts] $(\nu = \omega / 2\pi)$
(m is the mass number of the stable ions in atomic mass units "amu", V is the amplitude in volts, ν the frequency in MHz and r_0 the field radius in cm), when the ratio U/V is kept just below 0.1678. The "working line" for ions of different mass then intersects the stable region close to its tip.

From the stability relationships it is easy to recognize that the resolving power can be varied by simple electrical means, by altering the ratio U/V, and can thus be readily adapted to suit a particular problem.

If U is set to zero, the quadrupole operates as a high-pass mass filter: At low HF amplitude the ions of nearly all masses move on stable trajectories and jointly strike the detector. This is utilized for measurement of total pressure. Then, with increasing amplitude, beginning with the light masses, ions with increasingly heavy mass become unstable and are thus separated out (”integral spectrum, see Fig. 7).

The mass scan can be effected by varying the frequency ($m \sim 1/\omega^2$) or, as is nearly always done for technical reasons, by varying the voltage ($m \sim V$). In this way a linear mass scale is obtained quite easily.

The ratio U/V can be controlled as a function of the mass in such a way that it is not the resolving power $m/\Delta m$ that remains constant, but the width of the line Δm. This means that the resolving power increases in proportion to the mass number. In practice Δm is made = 1, with the result that adjacent masses are separated throughout the entire mass range, without having unnecessarily large intervals between adjacent masses at low mass numbers.

In spite of the resolution increasing with the mass number, ”mass discrimination” (decrease in transmission with increasing mass number) can be avoided when the rod system of the quadrupole is sufficiently precise and the ion source produces the correct conditions for injection of the ions. But, for higher-order reasons, this second condition cannot always be satisfied.

The property of stability does not depend on the energy of the ions. However, an ion that is only slightly unstable must therefore be given enough time to leave the field, i.e. its axial velocity must not be too high. But the demands for homogeneity of energy of the injected ions remain modest. Hence the quardupole can be equipped with a wide varietey of ion sources (including cold-cathode ion sources).

At this point two further mass separation principles are mentioned which are derived from the quadrupole mass filter: the monopole mass spectrometer [12] and the rotationally symmetrical, three-dimensional quadrupole mass spectrometer (or ion trap [11]).

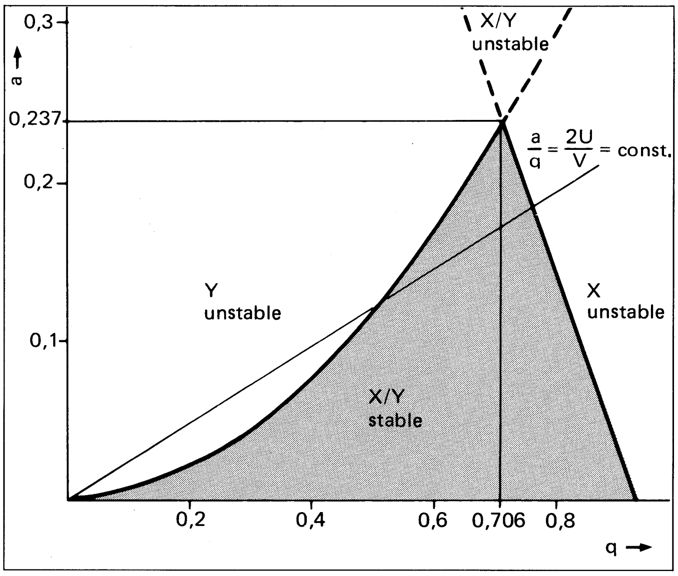


Fig. 6
Stability diagramm of the quadrupole mass filter

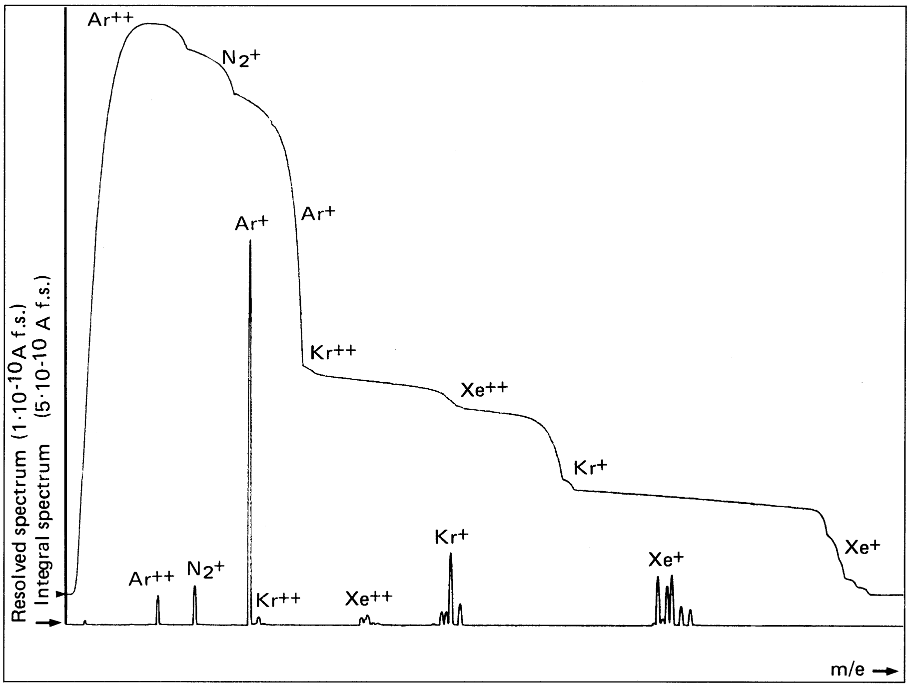


Fig. 7
Resolved and corresponding ”integral” spectrum

2.3 Detection of ions

The ions, separated according to their mass/charge ratio, are detected electrically. The methods of detection vary with the demands on the sensitivity and speed of detection. But, as will be demonstrated, there are fundamental limits.

2.3.1 **Faraday collector**

In the simplest case, which is also the one least affected by systematic errors, the ions strike a collector, where they give up their charge. The current that results is convertedinasensitive, where possible also fast, current-to-voltage converter, to form an output signal proportional to the ion current.

The limit of measurement, for a time constant of some seconds, is about 10^{-16} A. For recording spectra by means of a potentiometer recorder, it is usual to work with time constants down to 30 milliseconds, then the limit of measurement is still below 10^{-14} A.

2.3.2 Secondary electron multiplier (SEM)

If the ion currents are very small indeed, or if the processes take place very quickly, an open SEM is used as an additional amplifying element (Fig. 8).

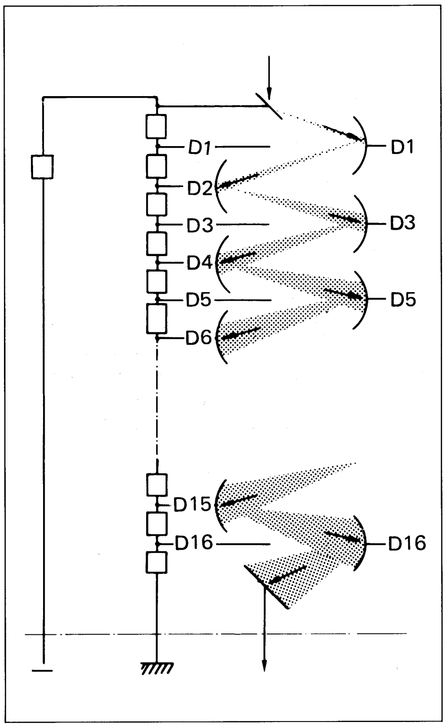


Fig. 8
Principle of a secondary
ectron multiplier

The ions to be detected are further accelerated to some kilo-electron-volts and then strike the "conversion dynode". There they release a number of stages (though the yield of secondary electrons per stage must be greater than one). In this way it is possible to achieve very high current gains from 10^4 to over 10^8. Owing to the high intensity, the succeeding measuring amplifier may be very fast. The highest speed that is reasonable is then limited only by the statistical character of the ion current.

But open SEM does not only have advantages. For quantitative evaluation it also brings uncertainty and possibilities for error. The number of electrons released on the conversion dynode per incident ion depends not only on the ion mass and type of ion (atomic ion, molecular ion, etc.) but also on the ion energy. For the quadrupole the energy of the incident ion roughly corresponds to the operating voltage of the SEM, i.e. max. 3.5 kV this can cause the conversion rate for masses between 100 and 500 to diminish by a factor of 3, for instance.

Furthermore, the state of the surfaces which emit the secondary electrons can change, and with it the output of these electrons. For most cases that occur in practice the SEM exhibits an adequately stable behaviour. For exact quantitative meausrements it may nevertheless be necessary to check the amplification at frequent intervals.

The SEM can be largely freed of these sources of error when it is not operated as a current amplifier (which averages over a definite period of time) but as an "ion counter". The ions generate pulses of short duration which can be quite easily detected individually. The time resolution is of the order of some 10^{-8} seconds. The detection limit is very low: below 1 ion per 10 seconds.

The pulses generated by the individual ions are counted direct or after appropriate standardization, are totalled. In order to keep the counting losses as low as possible, the ion energy (on account of the dependence of the ion/electron conversion rate on the energy) and also the gain of the SEM (over 10^6) should both be sufficiently high. With this method of counting single ions, the extent to which the accuracy is influenced by differences in the ion/electron conversion rate and the SEM gain is much smaller than with current measurement. Difficulties are only encountered at high counting rates (order of magnitude of 10^7) owing pulses overlapping one another in time.

2.3.3 Limits of ion detection

The detection of ions is a statistical process. Ions strike the detector in a random sequence. If a particular accuracy is demanded, and assuming that additional possibilities of errors are ignored, a definite number of events (i.e. single ions) must be measured. For N events the statistical error is given by the following relationship.

Statical error (%) = $100 / \sqrt{N}$

For example, if 100 ions are measured per second (which usually corresponds to a partial pressure between 10^{-13} and 10^{-14} mbar), this results in an error of 10% when the measuring time is one second. This statistical error can only be improved by prolonging the measuring time or increasing the sensitivity (A/mbar).

If the measuring task is not concerned with a rapid process (e.g. measurement of a flash filament, see Fig. 15), the sensitivity of detection or the accuracy of measurement are usually limited by background effects of different nature.

Soft X-rays and other photons and fast or excited neutral particles produce background intensities by releasing electrons in the SEM. At a high total pressure it is also possible for ions of "false" mass to pass through the analyzer to a small extent as a result of scattering.

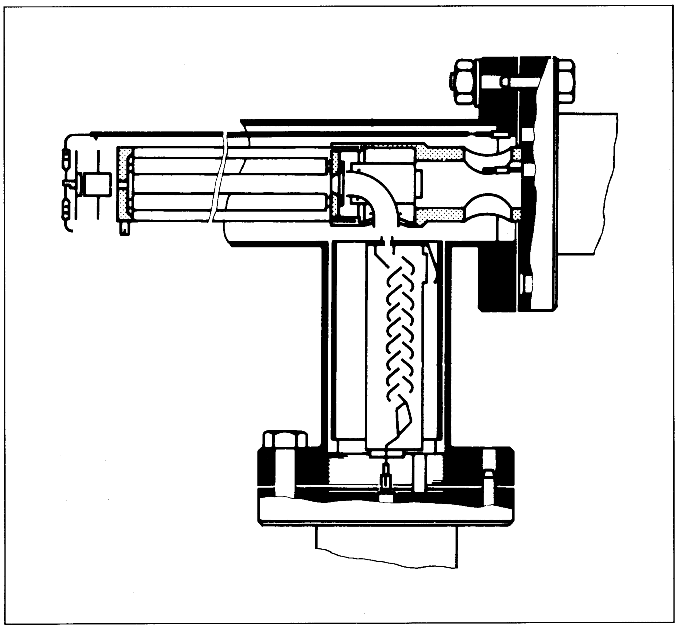


Fig. 9
Quadrupole mass spectrometer with ion deflection between the mass filter and the detector.

In the quadrupole mass filter such effects are encountered on account of the direct line of sight between the inlet and outlet openings. To suppress these effects, the SEM is so arranged that this line of sight is avoided (see Fig. 9). The ions to be detected must then be deflected in a suitable manner, for instance by an electrostatic field, in order that they may strike the SEM. With careful design, such arrangements allow extremely low partial pressures to be determined (below 10^{-15} mbar, see chapter 6) and correspondingly low concentrations (1 : 10^{10}, see chapter 8).

3. Requirements to be satisfied by the mass spectrometer used for partial pressure analysis

In the design and operation of instruments for measuring partial pressures a number of additional demands have to be taken into account. The generally important rule, that the state of the system should not be altered by the measurement, as far as possible, is particularly significant here. In a normal analytical mass spectrometer, on the other hand, the vacuum system is a mere operating medium which, though it has to be taken care of, has little direct influence on the actual analysis as such.

We have to bear in mind that with vacuum applications we have to deal with various systems and a very wide pressure range. These include the balance of the gases in an electron tube and the composition of the atmosphere in a metallurgical vacuum furance – with total pressures from below 10^{-12} mbar to several mbar. If the verification of the purity of process gases is also taken into account, the range extends to atmospheric pressure.

3.1 Mass range

In most cases a mass range from 2 to 100 is sufficient. For ultra high vacuum investigations the range up to 50 can suffice. On the other hand, if investigations are to be carried out on fluids of pumps, a mass range up to about 500 is necessary.

3.2 Resolving power

The resolving power should be high enough to separate adjoining masses at least in a mass range up to 50 ($m/\Delta m_{10\%} = 50$). Here $\Delta m_{10\%}$ means the peak width at 10% of the peak height. For higher masses too it is usually sufficient to have a resolving power of about 50, because normally unit resolution as in organic analysis is not required. So-called ”finger-print” spectra which, for instance, only resolve adjoining CH_2 groups, often provide all the information that is needed (Fig. 19 and 20) because the number of typical compounds to be considered is small, quite apart from non-specific impurities. On the other hand, it may be useful to be able to increase the resolving power (Fig. 30 to 33) for the identification of isotopes or other characteristic distributions.

3.3 Sensitivity

The sensitivity of a mass spectrometer is generally expressed as the ratio of the ion current at the collector to the partial pressure in the ion source. To this the sensitivity of the ion source nd the transmission factor of the separating system also contribute. Both have to be considered jointly because the transmission factor of the separating system is dependent on the entry conditions of the ions: For an ion source of comparatively low sensitivity the transmission factor of the filter may be high if the ions are injected under favourable conditions, so that under certain circumstances a particularly high overall sensitivity is obtained. Usually the sensitivities – say for argon – are between some 10^{-3} and 10^{-5} A/mbar.

3.4 Linearity range

Towards higher pressures the sensitivity of different types of instrument and for different operating conditions decreases at a different rate. This imposes an upper limit on the measuring range. The lower limit is defined bythe detection limit. The linearity limit is somewhere between 10^{-3} and 10^{-5} mbar, but for ”qualitative” measurements it may be quite interesting, while dispensing with pressure proportionality, to record mass spectra above the limit of linearity, for example when the question in point is merely the identification of the type of gas.

3.5 Partial pressure sensitivity

The partial pressure sensitivity is the quotient obtained when the lowest detectable partial pressure is divided by the prevailing total pressure. Various factors contribute towards its limitation: background of scattered ions, ion/molecule reactions, tails of adjacent high peaks, residual gas background on the mass number of interest. The first two problems can be overcome with tandem arrangements combination of separating systems or, in the simplest case, with an additional deflection stage - see Fig. 9 in section 2.3.3, the third by improving the vacuum conditions. There may be numerous reasons for peaktails. Perfect geometry of the separating system is of decisive importance.

3.6 The analyzer

It is not what goes on inside the mass spectrometer that must be assessed but the state of a vacuum system or the course of processes. This has to be taken into account with great care in the design and operation of the analyzer head. Among other things, it means that the analyzer head has to comply with UHV requirements. It should remain as inert as possible, i.e. neither emit nor clean up gases.

These extensive demands, though they cannot be satisfied completely, can be approximately reached when suitable care is taken. For high-vacuum applications it should be possible to bake out the analyzer up to at least 150˚C. In ultra high vacuum bakeout, temperatures up to 400 ˚C are required.

Special attention must be paid to the ion source. For extreme application in UHV it should be possible to outgas it by electron bombardment up to well over 400˚C.

With very caref ul conditioning it is possible to attain outgas rates for the entire analyzer head (with the ion source in operation) in the range of 10^{-10} mbar ls.

3.7 Possible sources of error

The main causes of faulty measurements are to be found in the ion source. Here only a few effects will be described, that may prove particularly serious.

The electron impact ion source normally has a heated cathode, the temperature of which may exceed 2000 K. At such temperatures most gases react. Then some of the gas may vanish (clean-up); on the other hand new gases, formerly not present in the vacuum system, may be produced.

The tungsten, carbon, oxygen cycle is well known. The hot tungsten cathode reacts with the hydrocarbons present and forms W_2C. If, water vapour for instance, is present, it reacts forming CO. In such cases the remedy is to make the cathode of rhenium instead of tungsten. Re does not form any stable carbides. However, it has a comparatively high vapour pressure, which may prove disturbing in sonne applications (Fig. 22 and 23).

The hot cathode also heats up the surroundings. This may give rise to evaporation or desorption effects which alter the original state. The heat developed by the cathode can be considerably reduced by coating with $Th0_2$, this substance being mainly deposited iridium. Such cathodes, even when hot, are insensitive to atmospheric oxygen. LaB_6 emits at even lower temperatures than $Th0_2$, but is sensitive to poisoning and is rarely used.

It has been repeatedly observed that the measuring system with far too low a conductance is connected to the vacuum chamber. The ion source, which is the real measuring point, should, where possible, be immersed in the chamber. Otherwise adsorption and reaction effects may occur not only in the vicinity of the ion source, but also in the connecting duct (Fig. 18). They can seriously affect the result of measurement, especially with condensable or reactive gases or vapours. If an immersed arrangement is not feasible, then at least the connecting duct should be made as wide as possible and kept at elevated temperaure. Though it must be realized that even when this is done, the dependability of a measuring set-up with immersed ion source will not be attained under any circumstance.

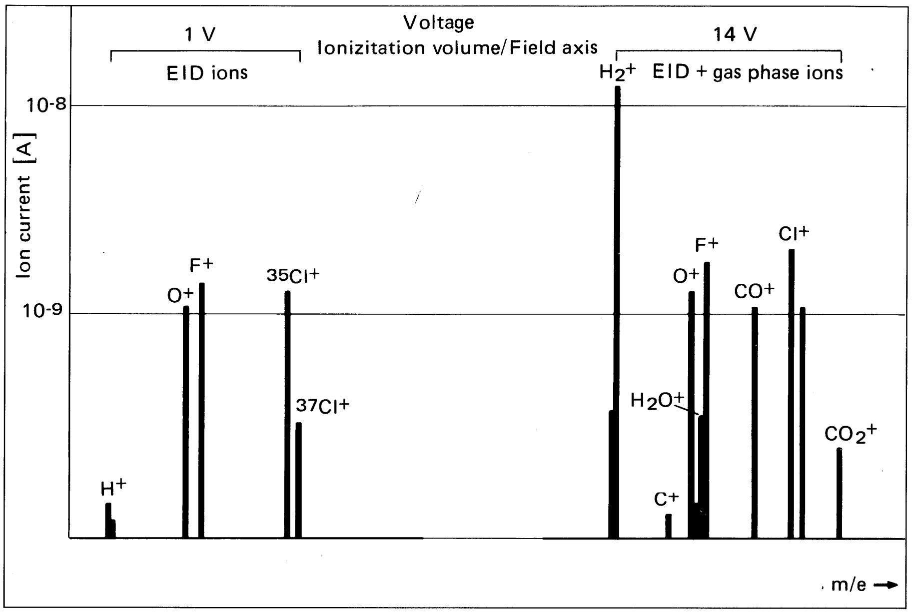


Fig. 10
Illustrating the different behaviors of ions from the gaseous phase and EID ions (electron impact ion desorption).

Adsorption and reaction effects are all the more pronounced, the lower the pressure to be measured is and the more reactive the walls are, i.e. especially under UHV conditions. For further details see chapter 6.

In UHV, additional effects appear, which can often lead to false conclusions, if they are not interpreted with sufficient care. An error that often occurs is caused by electron impact ion desorption [13]. When surfaces are bombarded with electrons, a number of species such as H^+, 0^+, F^+ and Cl^+ are desorbed direct as ions, often with a high yield. Fig. 10 shows an example. These ions, known as EID ions, are released from absorbed layers originating from the history of the UHV apparatus. Usually they have an initial energy of up to a few eV. As the diagram shows, this property can be utilized to distinguish between ions from the gaseous phase. On this account Redhead proposed the "extractor gauge" for total pressure measurements, as it permits good discrimination with respect to ions with initial energy [14].

The quadrupole mass spectrometer can be combined with an ion source operating according to a similar principle. Fig» 11 shows a typical arrangement for measurements under extreme UHV conditions. This ion source also offers the important advantage of being easily degassed by electron bombardment.

As an example of background effects EID is especially significant and it is of considerable importance for the measurement of total pressure. On the other hand, in the mass spectrum the EID ions merely represent an annoying blemish. The masses 1, 16,19, 35, 37, which are typical for EID ions, are of only limited significance for measurement of the residual gas. All gases which contribute to these peaks can also be detected on other masses.

Other sources of error will be discussed in the chapters that follow. The large number of possible errors must not be considered surprising; by their very nature, vacuum measurements are concerned with extremely weak intensities, and it is thus quite obvious that numerous side-effects are bound to be encountered.

Fig. 11
Grid ion source for ultra-high vacuum applications

4. Pressure reduction

For the majority of measuring tasks the total pressure at the point of interest is so low that the mass spectrometer can be connected directly to the chamber, or better still immersed in it (see section 3.7). The upper limit of the pressure is some 10^{-4} mbar.

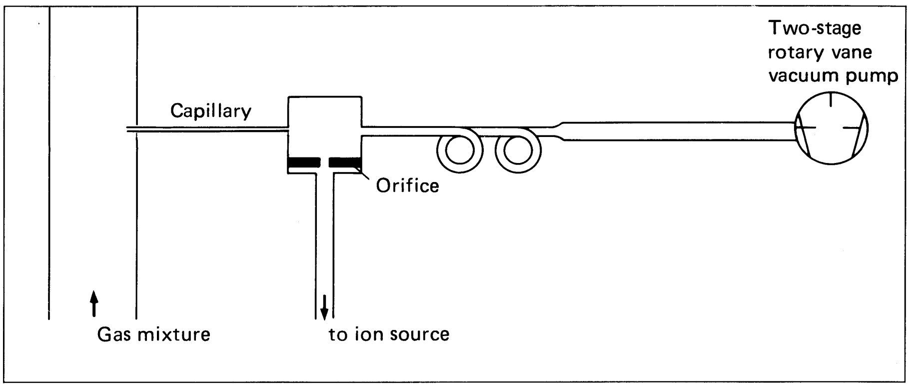


Fig. 12
Two-stage inlet system to avoid mass-dependent changes in concentration

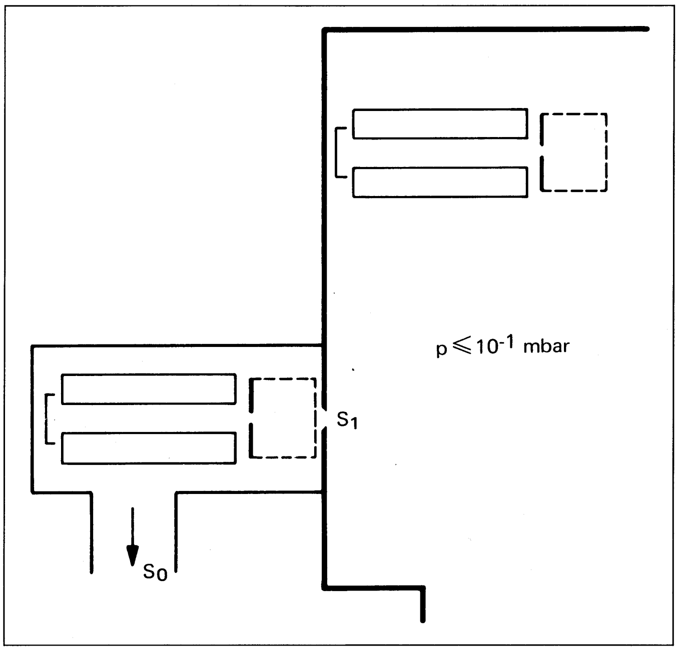


Fig. 13
Single-stage pressure reduction by differential pumping of the measuring system (below).
Normally immersed measuring system without pressure reduction (above).

Many processes, however, such as sputter deposition, plasma etching or ion plating, operate at higher pressures up to several mbar. In this region it is possible to operate with single-stage pressure reduction (Fig. 13).

The working and measuring chambers are thus interconnected through a low conductance S_1, preferably by means of an orifice. The size of S_1, is such that, together with the pumping speed S_0 effective at the location of the ion source, it yields the desired reduction in pressure S_0/S_1.

When the demands on accuracy are more stringent, steps are taken to ensure that S_0 and S_1 behave as strictly molecular conductances (proportional to $1/\sqrt{m}$). For S_0 this means that, under certain circumstances, the pumping speed of the (adequately dimensioned) pump has to be throttled. Small deviations can be taken into account by calibration. But it is expressly warned against using pumps for such applications which, by virtue of their principle, exhibit a pronounced and, furthermore, an unreproducible dependence on the type of gas, such as ion getter pumps. The error that then occurs in measurements cannot always be eliminated, even by calibration.

When the pumping speed is throttled, it is important to ensure that S_0 may not be made too small, for two reasons: The final pressure in the measuring chamber due to its own degassing, i.e. without inflow of process gas, is inversely proportional to S_0 and could consequently be too high. Competing pumping effects - usually depending on the type of gas - such as adsorption on the walls, gas clean-up in the ion source, etc., would have too strong an effect, in proportion, especially when the measuring chamber was conditioned by baking out in order to reduce its own degassing.

To lessen such effects it may be an advantage to allow the gas to be examined to enter the ionization zone directly through an orifice, i.e. as a molecular jet without striking the walls and, at the same time, to allow as high a pumping speed as possible to act directly on the ion source. The high pumping speed reduces the background pressure, while the gas density in the jet is influenced very slightly by the pumping speed.

At pressures appreciably higher than a few mbar (e.g. for analysing the purity of process gases) a two-stage pressure reduction system is employed (Fig. 12). The first stage (capillary and throttled fore pump) is laminar in operation up to the mbar region. From there some of the gas is bled off to the high vacuum region through a conductance as molecular as possible (see above). Each of the pressure stages operates without discrimination provided the two conductances (or pumping speeds) concerned are exactly laminar and molecular, respectively. With a system of this kind gas samples can be continuously extracted and, while doing so, owing to the high gas throughput in the laminar branch, rapid changes can be detected. When the demands on accuracy are less stringent, it is often sufficient to use an adjustable leak valve instead of an expensive two-stage pressure reduction system.

For the sake of completness, mention should also be made of the "genuine" molecular jet systems which provide a sharply defined jet as well as the differentially pumped inlet systems for the direct investigation of ions from plasma, the reaction products from flames, etc. (see chapter 7).

5. Data acquisition and evaluation

Normally a mass spectrometer is operated in such a manner that a definite part of the measuring range is scanned periodically at suitable speed, the data thereby acquired being collected either by means of a recorder or a digital storage device (computer or multi-channel analyzer).

For each single mass number in a spectrum of this nature, relatively little time is available for measurement. Therefore, operation in this manner is only economical when information is desired on all masses to the same extent. But since this is usually not the case, it is advisable to program the mass scan to suit the purpose. In this way one obtains information which, though limited with respect to the mass range, is faster or more accurate.

The largest amount of specific information is acquired when the peaks of interest only are periodically scanned. In this way a maximum of true measuring-time and statistical accuracy are obtained, especially when the measuring time is individually adapted to suit the peak intensity (Fig. 14). Fig. 15 shows "flash desorption" when heating up a tungsten filament in a UHV system. The filament was previously switched off for 20 seconds at a pressure of 10^{-8} mbar In this case H_2^+, CO^+ and the zero intensity were alternately recorded. For this a comparatively simple programming device was used. With modern equipment it is possible to adapt all parameters (e.g. gain, time constant, integration time, etc.) individually for each peak. The greatest scope is attained when the mass spectrometer is connected to a computer in such a way that all parameters can be controlled and, in addition, the incoming measurements are stored and further processed.

One expects that mass spectra will provide qualitative or quantitative details of the composition of partial pressures. But primarily, mass spectra provide nothing but intensities associated with definite mass numbers. The derivation of partial pressures or concentrations from such data involves quite a lot of calibration and computing in complicated cases.

Many of the cases occurring in vacuum technology applications, however, are so simple that the kind of gas can be identified directly on the basis of discrete characteristic masses without having to allowfor mutual interferences. These are (characteristic masses in parentheses): H_2 (2), He (4), CH_4 (15), H_2O (17, 18), N_2 (28), O_2 (32), Ar (40), CO_2 (44) (see Table 4). At high CO_2 concentrations the contribution of the CO^+ fragment to the mass 28 has to be taken into account. If CO is also present, this gives rise to considerable difficulties because N_2 and CO have their main intensities on the same mass. Depending on the ratio - and in the absence of disturbing additives - distinction is possible by means of the masses 12 and 14 (see [15]). Fortunately, CO can usually be neglected in a normal high vacuum. But in contrast it is typical for ultra high vacuum. If other gases than those mentioned above are present in appreciable concentrations, especially organic vapours (solvents, pump oil, lubricants), it is possible for complicated interferences to occur in the spectrum, which may render interpretation difficult or totally impossible. Table 11.4.4 shows the fragment distribution of some common gases of low mass. The measured intensities are linear superpositions of such fragment spectra.

Consequently the interpretation of mass spectra is essentially the solution of systems of linear equations, which in principle can be performed by a computer, provided the individual fragment spectra and calibration factors are known.

In the general field of mass spectrometric analysis the automatic evaluation by computer is being employed to a large extent and, in some cases, with extraordinary success.

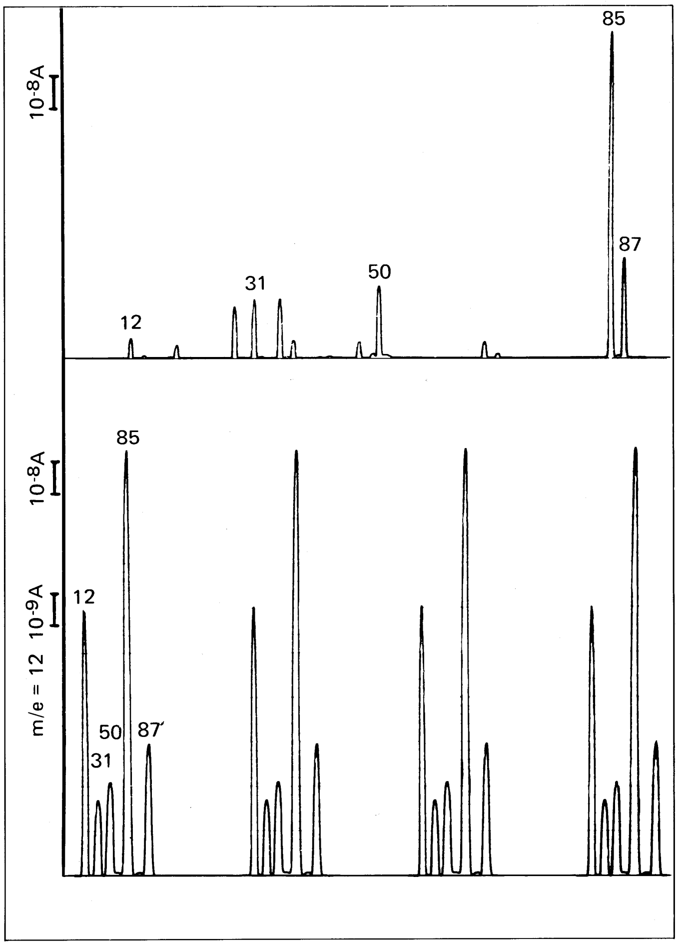


Fig. 14
Programmed mass scan: Compression of a Freon spectrum to the sections that are of interest

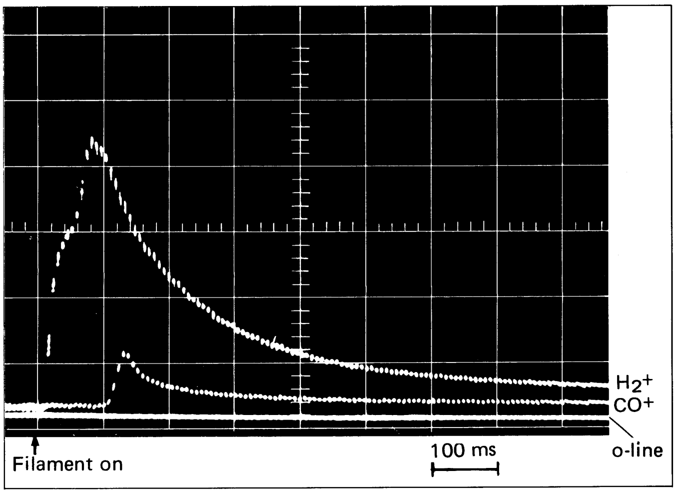


Fig. 15
Desorption phenomenon when the heating filament of a Bayard-Alpert tube is switched on. Rapid cyclic scan of the peaks of interest.

Here, however, attention is drawn to a number of difficulties which could attain special significance for residual gas measurements.

1. Data from the literature can only be regarded as approximate. Fragment distributions are dependent on such factors as:
– Energy of ionization and source temperature, neither of which can always be exactly determined.
– The transmission factor of the analyzer
– Sensitivity of the detector
As a rule individual calibration with test gases is necessary.

2. Depending on the concentrations and fragment distributions, the propagation of error may be so unfavourable that small, inevitable measuring and calibration errors result in large errors when determining the concentrations. (Example: N_2 – CO – CO_2).

3. Reliable calculation of concentrations necessitates prior knowledge of what kinds of gas are involved. No computer program can allow for unforeseen admixtures.

Problems which, in this sense, are considered ”insoluble”, i.e. which cannot be solved with the aid of computer programs, are frequently encountered in residual gas measurements. Contaminations are mostly non specific mixtures, but the mass spectrometer, in the hands of an expert interpreter, is an excellent means of identifying such contaminations. Here computer programs are of little assistance.

The problem of interpreting mass spectra and recognizing the causes on which they are based are dealt with in the succeeding chapters. Anyone who wishes to gain a deeper insight should consult the special literature (see [1, 2, 16] for an initial orientation).

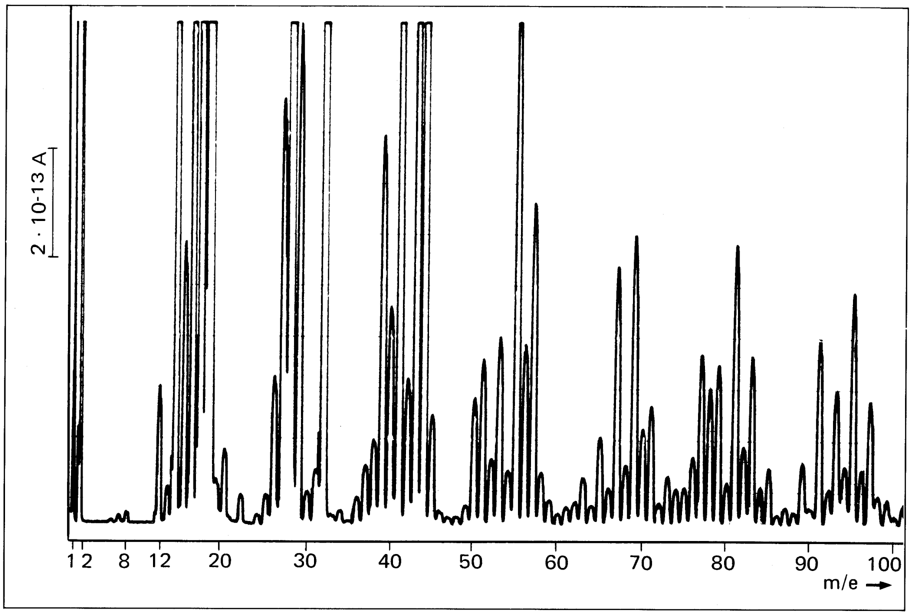


Fig. 16
Residual gas composition in a strongly contaminated vacuum apparatus

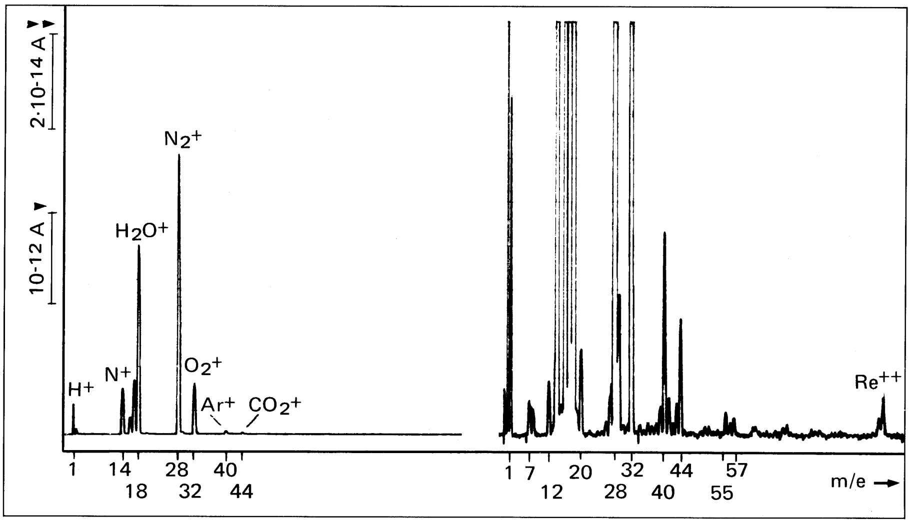


Fig. 17
Residual gas composition in an evaporation coating system equipped with diffusion pump and water baffle. Pumping fluid: Pentaphenylether

6. Residual gas composition in vacuum Systems

The demands for purity in conventional high vacuum systems have increased considerably. It is desired that processes which have been tried out in the laboratory under UHV conditions should be introduced to large-scale production. This imposes strict limits, not only for hydrocarbons, but also to other disturbing gases and vapours specific to the process. (For instance, during the metallization of semiconductor elements with aluminium, O_2, H_2O, H_2 and N_2 are particularly disturbing on account of their harmful effect on the properties of the layer.) In a number of spectra different typical examples of vacuum conditions will be presented. Fig. 16 shows the residual gas composition in a strongly, but indefinitely contaminated chamber. Apart from hydrogen, water vapour, CO_2 and air, which extend considerably beyond the measuring range, the characteristic fragment distribution of hydrocarbon chains can be recognized: Clusters at an average interval of 14 mass units (CH_2). With purely aliphatic hydrocarbons these clusters are especially pronounced (Fig. 33 for n-$C_{14}H_{30}$).

Fig. 17, on the other hand, gives a spectrum of a vacuum system baked out at 90 °C and fitted with Viton seals. It was equipped with a diffusion pump, the fluid being Convalex 10, and with a water-cooled baffle (10 °C). Air and water vapour are the dominating components of the residual gas atmosphere. The total pressure amounts to only $3.5 \cdot 10^{-6}$ mbar and the sum of the partial pressures of all organic impurities is certainly less than 10^{-9} mbar. From such spectra, however, it must not be rashly concluded that the chamber is completely free from the pumping medium. The backstreaming of fluid vapour even

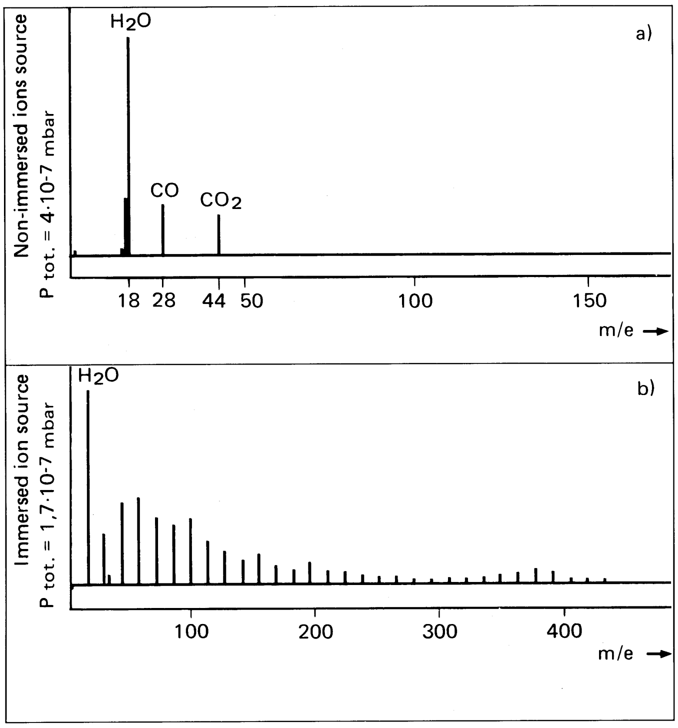


Fig. 18
Validity of the results obtained when using immersed and non-immersed ion sources

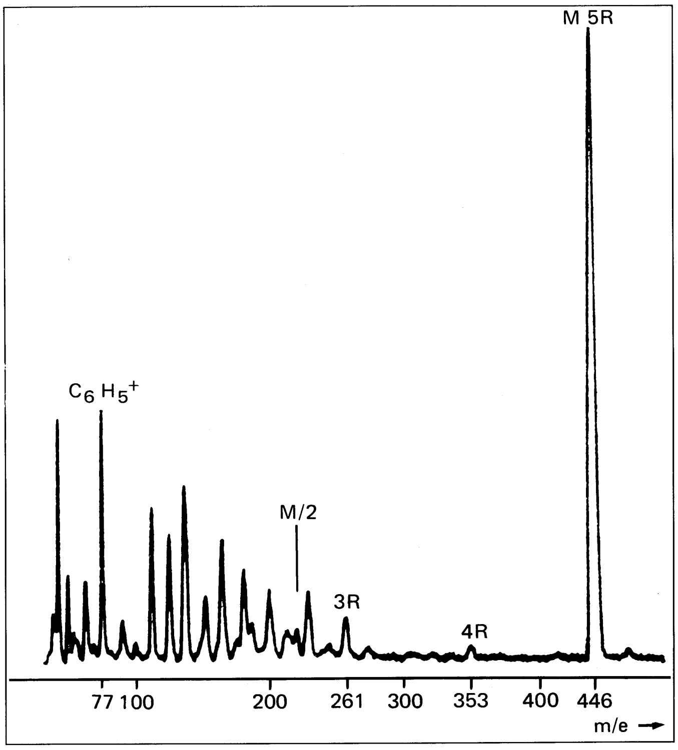


Fig. 19
Pentaphenylether – characteristic spectrum with low resolution

though it may be very small, can result in a gradual accumulation of fluid on the walls. Even if accumulation were very heavy, a pentaphenyl ether such as Convalex 10 or Santovac 5 would still not be found in a spectrum with the sensitivity shown, because its vapour pressure is extremely low at normal temperature.

One must be aware of this if false conclusions are not to be drawn. Whether any oil has been accumulated, and how much, could be determined in the present example by heating the chamber [17].

An essential prerequisite for the detection of oil vapours is that the ion source must be immersed freely in the chamber, as descried in section 3.7. Fig. 18, referring to an example, shows the difference between ion sources that are and are not immersed. The immersed source (Fig. 18a) correctly indicates that the main part of the residual gas in this example is supplied by the pump fluid, Balzers Oil 71. The non-immersed ion source (Fig. 18b) connected with the chamber by a short pipe, in contrast, gave no sign of oil vapour.

Fig. 30 (in chapter 9) shows a resolved spectrum of pentaphenyl ether (Santovac, Convalex) recorded with an "analytical" mass spectrometen Such a spectrum supplies a wealth of information that is of little interest to the person analysing the residual gas. Here it is usually sufficient to record spectra with lower resolution, such as that shown in Fig. 19. Apart from the convenience from the measuring aspect, the information in this case is reduced to what is significant. Such spectra are easy to remember in pictorial form.

Fig. 20 shows a further example, this ́ of a "fingerprint" spectrum of a residual gas in which DC 704 is the main component.

Residual solvents with which, for instance, elastomer gaskets have become saturated also exhibit characteristic spectra (for further details see chapter 9).

Fig. 21 the effect of different methods of pumping can be seen. A large cubic evaporation deposition installation was evacuated with a combination of a turbo-molecular pump, a condensation pump (liquid nitrogen) and a titanium sublimation pump [18].

In UHV, effects resulting from interaction between the gas and the active parts of the measuring apparatus (hot cathodes etc.) and with the walls acquire added significance (see section 3.7). The predominance of the wall effects is truly characteristic of UHV conditions.

"UHV technology" does not simply mean the production of very low pressure but the application of the bakeout procedure or similar effective methods to reduce the gas content on the surface. Such highly degassed surfaces naturally possess an appreciable adsorption capacity and act as powerful pumps whose effect may differ from one place to another and, in addition, depends on the kind of gas. Consequently it is necessary to know that a leak in a highly degassed metal apparatus connot be recognized by the N_2-O_2 distribution characteristic for air. O_2 is often pumped intensively by the walls for quite a long time and therefore cannot be seen in the spectrum. N_2, on the other hand, is often blanketed by CO. To identify a leak it is therefore usual to utilize the masses 14 (N^+) and 40 (Ar^+) instead.

Intensive pumping action at the wall usually leads to pronounced pressure gradients and – depending on the character of the ion source – can sometimes lead to typical beam effects.

Fig. 22 shows the residual gas in a baked-out UHV system with a turbomolecular pump. The total pressure was about $7 \cdot 10^{-10}$ mbar. Here a quadrupole with offset SEM was employed (Fig. 9, section 2.3.3). The spectrum was recorded by counting the individual ions. The counting rate for H^+ was about 10^6 sec^{-1}, the background being less than 10 sec^{-1}, corresponding to a detection limit of some 10^{-15} mbar. A disturbing feature at this sensitivity is the vapour pressure of the rhenium cathode (up to Re^{7+}).

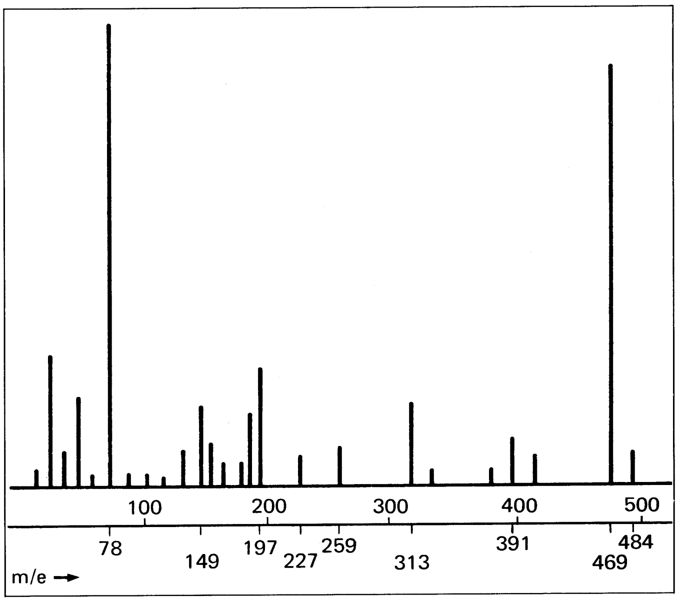


Fig. 20
Residual gas with DC 704 as the main component (low resolution)

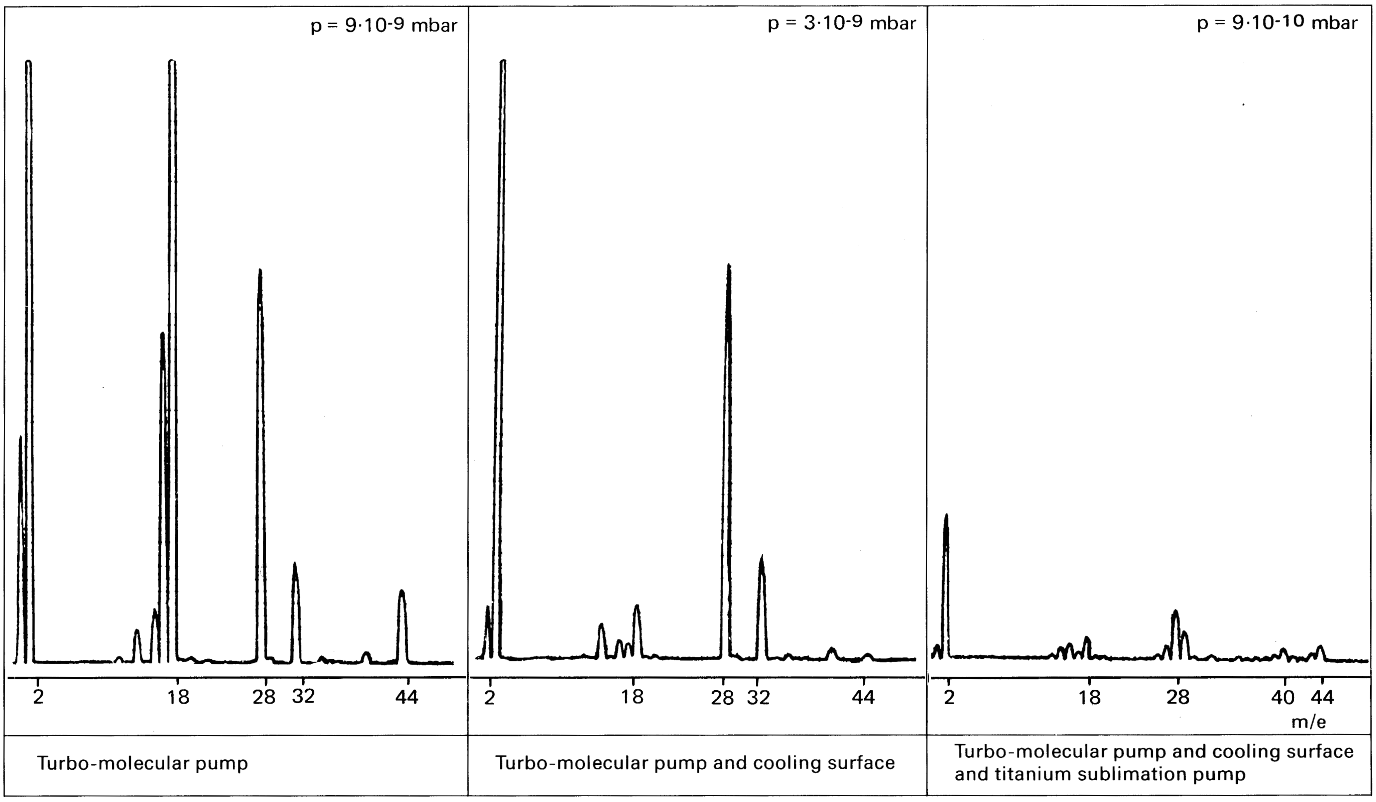


Fig. 21
Showing the difference in the effect of different methods of pumpin

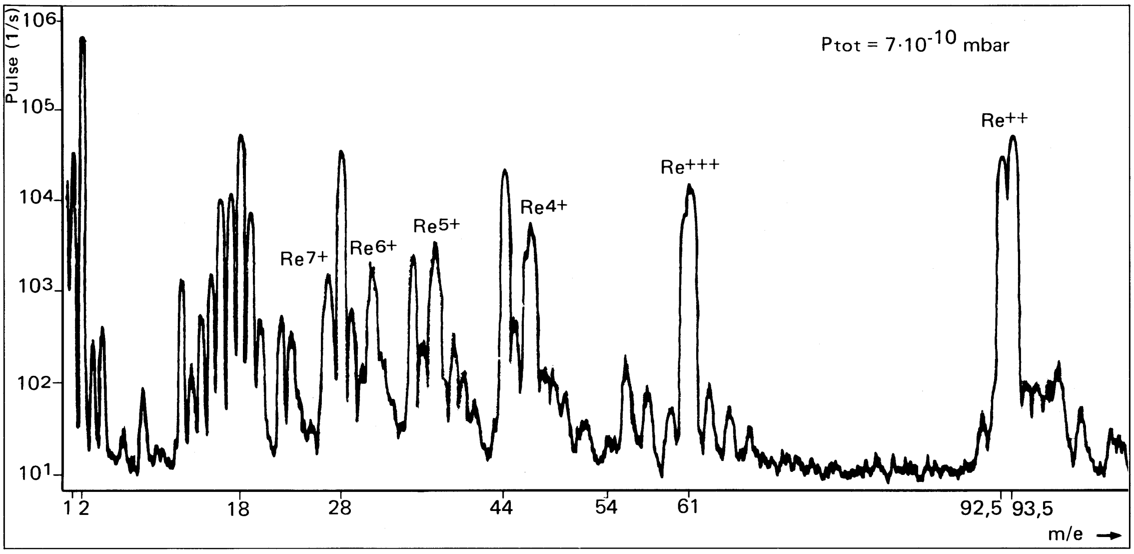


Fig. 22
Residual gas spectrum of a UHV system, individual ion counting, logarithmic plotting

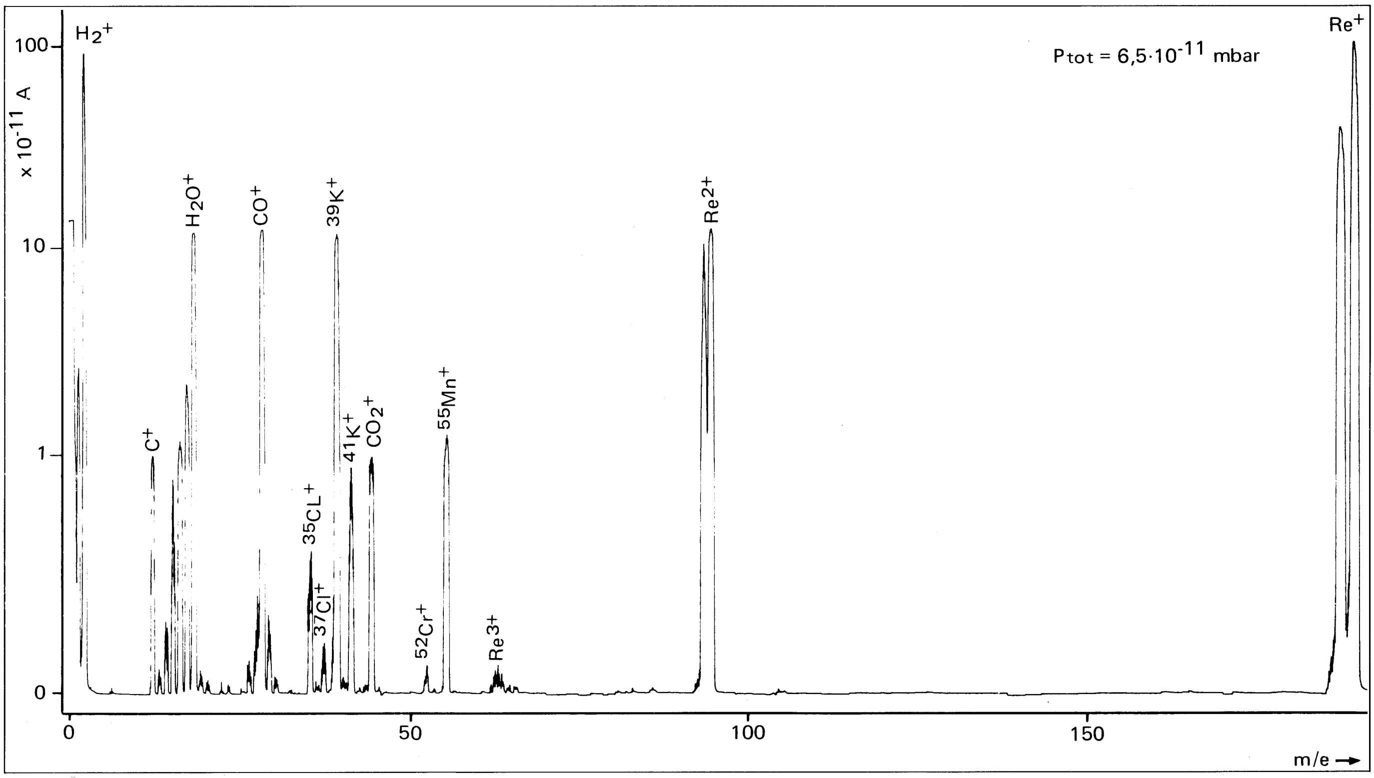


Fig. 23
Residual gas spectrum of a UHV system, including characteristic EID ions

Fig. 23 shows a further example of a UHV spectrum. Here again ions can be recognized which have nothing whatsoever to do with the residual gas in the vacuum system: Re (cathode evaporation), K (impurity), Cl (EID), Mn and Cr (from the stainless steel).

The problems outlined here extend beyond the scope of mere partial pressure analysis: The low vapour pressure of certain pump fluids, seemingly in contradiction to the obviously severe contamination; the consumption of oxygen in the baked-out UHV chambers.

The blame for such effects must be attached to the method of measurement (in contrast to, say, the degassing of an ion source itself), as they are indeed real phenomena which have to be displayed by a good partial pressure measuring apparatus exactly as they are. The measurement of partial pressure is certainly not an end in itself, but merely an aid in the solution of problems in vacuumtechnology. To assess a vacuum system it is not sufficient simply to consider the partial pressures at a definite point in time. Other information, such as the behavior with respect to time and temperature, the background history of the apparatus, knowledge of the materials used, the peculiarities of a process that may be taking place, and so on, must also be included in the assessment.

In any event, the decisive factor is the human expertise which cannot be replaced even by the most intricate measuring apparatus.

7. Measurements with mass spectrometers during evaporation and sputter deposition processes

When producing thin films the mass spectrometer is used in a variety of ways.

Firstly, the balance of the gas in the installation during the various stages of the process is of interest: pumping, out-gassing when heating substrates and evaporation sources, changes due to the glow discharge process, gettering during deposition. In the case of reactive deposition the concentrations can vary considerably in the course of the process and thus adversely affect the correct execution. Fig. 24 shows an example in which the concentration of particular gases has to be kept within close limits.

In such cases the mass spectrometer can be used directly to maintain constant partial pressures. But it cannot be denied that fundamental problems may arise while doing so, similar to those described in the previous chapter: Owing to the enormous gettering effect of the surface, pressure gradients and anisotropies can occur and one must carefully consider how the mass spectrometer shall be arranged in the chamber in order that relevant data may be acquired. Frequently the partial pressure gauge has to be protected against action from the process (e.g. vapour deposition on the ion source). In such cases, the possibility of interference resulting from the protective measures must be very carefully considered.

The working pressures of many processes are so high that pressure reduction is necessary between the mass spectrometer and the chamber. For details please refer to chapter 4.

In plasma processes there is often an interest in extracting ions direct and detecting them by mass spectrometry. Fig. 25 shows a system of this kind, where definite extraction conditions

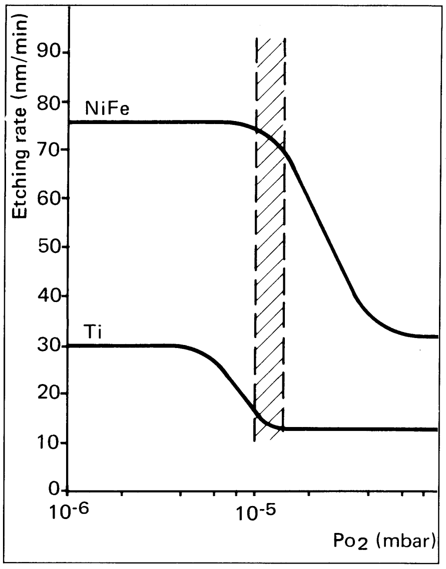


Fig. 24
Example of process control: For an etching process the oxygen partial pressure has o be kept within the hatched band [22]

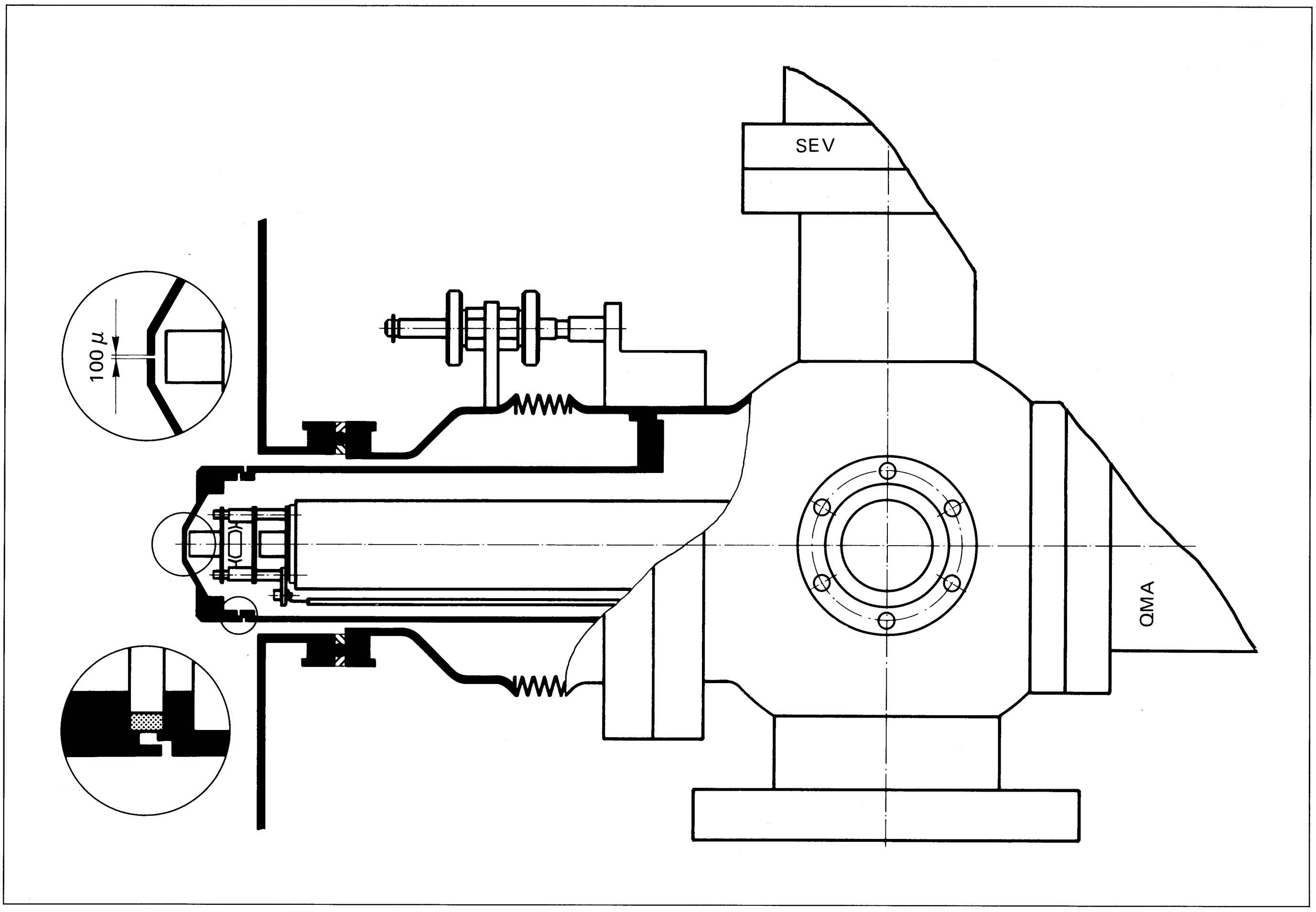


Fig. 25
Plasma monitor for the detection of ions and neutral species from plasmas

have to be adhered to if informative results are to be acquired. Ions are extremely reactive and therefore the fundamental difficulties of the method are far more serious than those of ordinary measurement of partial pressure. As an example, Fig. 26 shows the spectrum of positive ions during sputter deposition of copper The ions of chromium and iron that occur here originate from the holder of the magnetron target (laboratory prototype) and would be most undesirable in a real process [19].

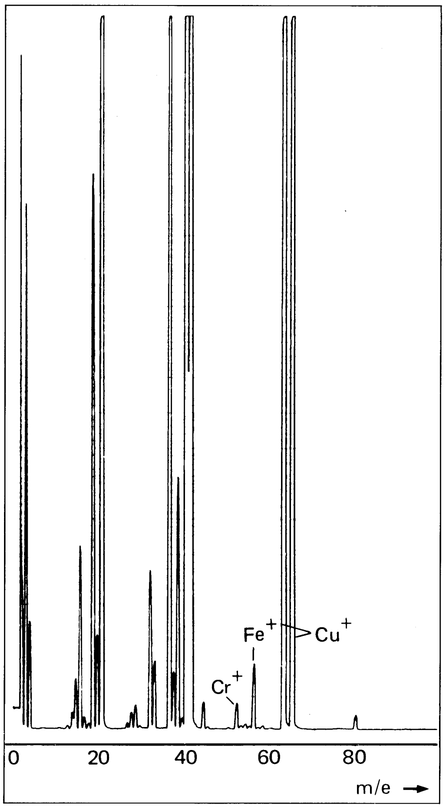


Fig. 26
Spectrum of positive ions from the plasma of a planar magnetron

The plasma monitor illustrated in Fig. 25 is not confined to the detection of ions. The additional electron impact ion source also enables neutral species to be detected, e.g. for direct checking of the composition of the process gas. By opening a bypass it is possible to circumvent the pressure stage so that, for instance, direct measurements of residual gas are possible.

During evaporation deposition processes it is desirable to be able to analyse the evaporating material. This not only allows the composition to be verified, the rate can also be measured or controlled. Of particular interest is the fact that this can be done for several materials evaporated from different sources more or less simultaneously, so that, for instance, alloys may be deposited in definite proportions [20].

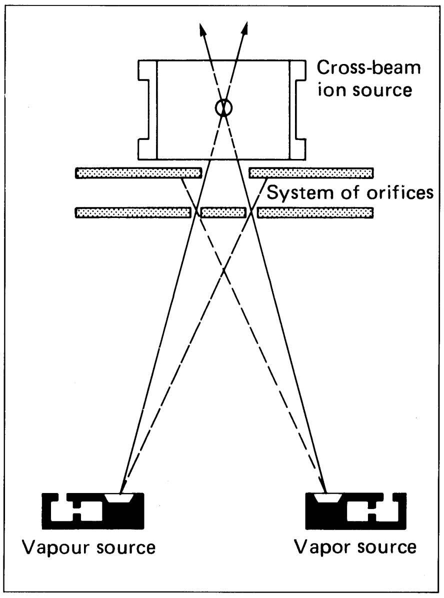


Fig. 27
Quasi-simultaneous control of two evaporation sources by only one mass spectrometer

Fig. 27 shows an ion source modified for this purpose with special orifice arrangements to blank off clearly defined molecular beams which pass directly through the ionization space, without being deposited there and contaminating the ion source.

8. Other applications for mass spectrometry in vacuum technology

Outgassing of materials and components is one of the central problems of vacuum technology. Apparatus is needed with which outgassing can be measured under different conditions, especially at different temperatures. It is impossible to deal at length with all the possible methods here. The absolute outgas rate is usually measured by means of the total pressure measurement at a known pumping speed. The mass spectrometer is used to determine the relative concentrations. Using similar methods, the permeation of gases through materials is investigated.

Another field of application is the analysis of process gases, etc., i.e. gas analysis by mass spectrometry for purpose of vacuum process technology. Here a distinction must be made between two aspects: The high accuracy analysis of mixtures and the high sensitivity analysis of traces.

Mixtures can be analysed with relative accuracies down to some 10^{-4}. But for this the following prerequisite conditions must be fulfilled:
– No unfavourable overlapping in the spectrum (e.g. CO – N_2)
– The concentration of the gas to be determined must not be too low (not much less than 1%)
– Calibration by reference gas mixtures whose composition must be known precisely
– Optimal control of the mass spectrometer, the acquisition and evaluation of data by means of a computer.

Nevertheless, for process gases used in vacuum technology it makes sense only in particular cases to set demands on accuracy of measurement higher than the variation in concentration likely to be encountered during the process as a result of inlet, pumping and reactive effects.

During trace analysis (e.g. doping gas) the demand for accuracy of measurement is less stringent. What is more important here is to ensure that reactive components of low concentration are not lost on their way to the ion source. Hence, for example, great care has to be taken when introducing a mixture of 1 ppm Of O_2 in H_2 to avoid catalytic reactions on the surface of the inlet system, which would result in a complete loss of the O_2. In such cases it is unnecessary to operate the mass spectrometer with a computer, though it may prove convenient for measurement.

The detection limit, given by the sensitivity (in A/mbar) and noise, leaves little to be desired when all facilities for suppressing noise are adopted, especially when the demands on linearity are not strict. Fig. 28 and 29 illustrate what can possibly be achieved, considering the analysis of air as an example. Admittedly, the quality of the air in this case was extremely favourable. The xenon isotope 136 has a concentration of about 8 ppb and here is about 100 times higher than the background noise at a time constant of 1 s, corresponding to a concentration of approx. 0.1 ppb (1 : 10^{10}); (see Fig. 29). With the rare gases nature provides us with an excellent "internal standard".

For such measurements overlapping and secondary effects are all the more disturbing: The isotope ion $^{15}N^{15}N^+$ has a natural abundance of about 13 ppm on mass 30, on which it may be desirable to detect the environmentally harmful gas NO.

If further improvements are desired, other methods of ionization more applicable to specific substances must be sought, or special methods of pre-separation (membranes, chromatographic columns) and inlet (molecular beam) must be applied.

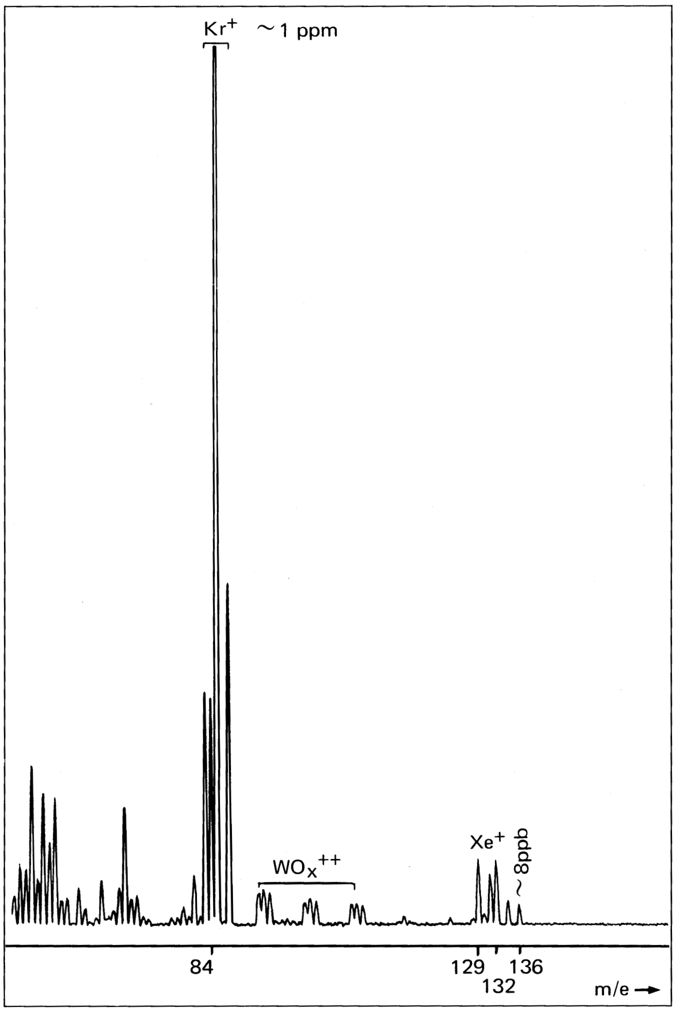


Fig. 28
Detection of natural krypton and xenon in air

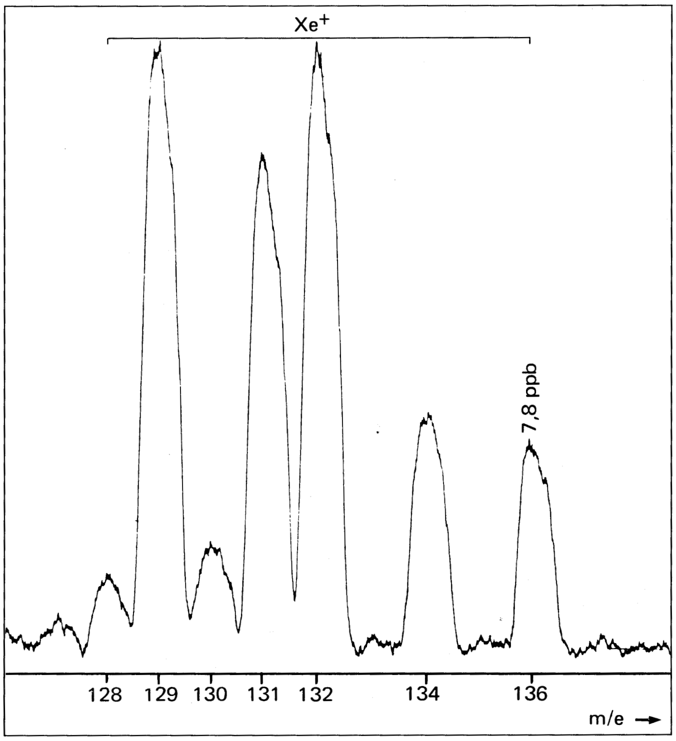


Fig. 29
Spectrum of natural xenon in air with a higher gain, mass scan 30 s/amu time constant 1 s. It is possible to detect about 1% of the xenon isotope 136, i.e. less than 0.1 ppb, dynamic range appr. 1 :10^{10}.

9. Interpretation of results

9.1 Importance of measuring accuracy

It is inherent in vacuum technology that only exceptionally and then in precisely defined cases is it logical and realistic to determine total and partial pressures with high absolute accuracy, despite the fact that the ionization gauge and the mass spectrometer inherently operate very accurately, i.e. the readings of the gas density in the ionization volume are correct. (In gas analysis remarkably high measuring accuracies are obtained using similar mass spectrometers; however, the inlet method employed usually contrast drastically with those required in vacuum technology: molecular beam inlet, etc.).

The better the vacuum, the lower the demands on accuracy have to be set. In low UHV one often has to be satisfied if the order of magnitude is reliably indicated.

It is plausible that the accuracy diminishes, the smaller the intensity to be measured is made. With the extraordinary sensitivity of partial pressure gauges based on mass spectrometry, however, the limits of accuracy are governed to a lesser degree by the natural statistical fluctuations of small signals than by the spread of background and side effects which, even when they do not directly affect the local measuring accuracy of the state in the ionization space, can reduce the validity of the measurement.

In the field of vacuum measurement, especially at UHV, quantifiable statements that can be exactly calculated from the measured values must be replaced by an interpretation which pays less attention to the decimal point than to the overall picture, while paying due heed to all accompanying circumstances.

One must be prepared, for example, to recognize the incompatibility of measured data and the circumstances of measurement, and from this to draw the right conclusions, e.g. that an instrument delivers nonsensical results because the conductance by which it is connected is inadequate. This means that special attention must be paid to the fact that the readings reflect more the characteristics of the vacuum gauge than the state of the vacuum apparatus to be determined.

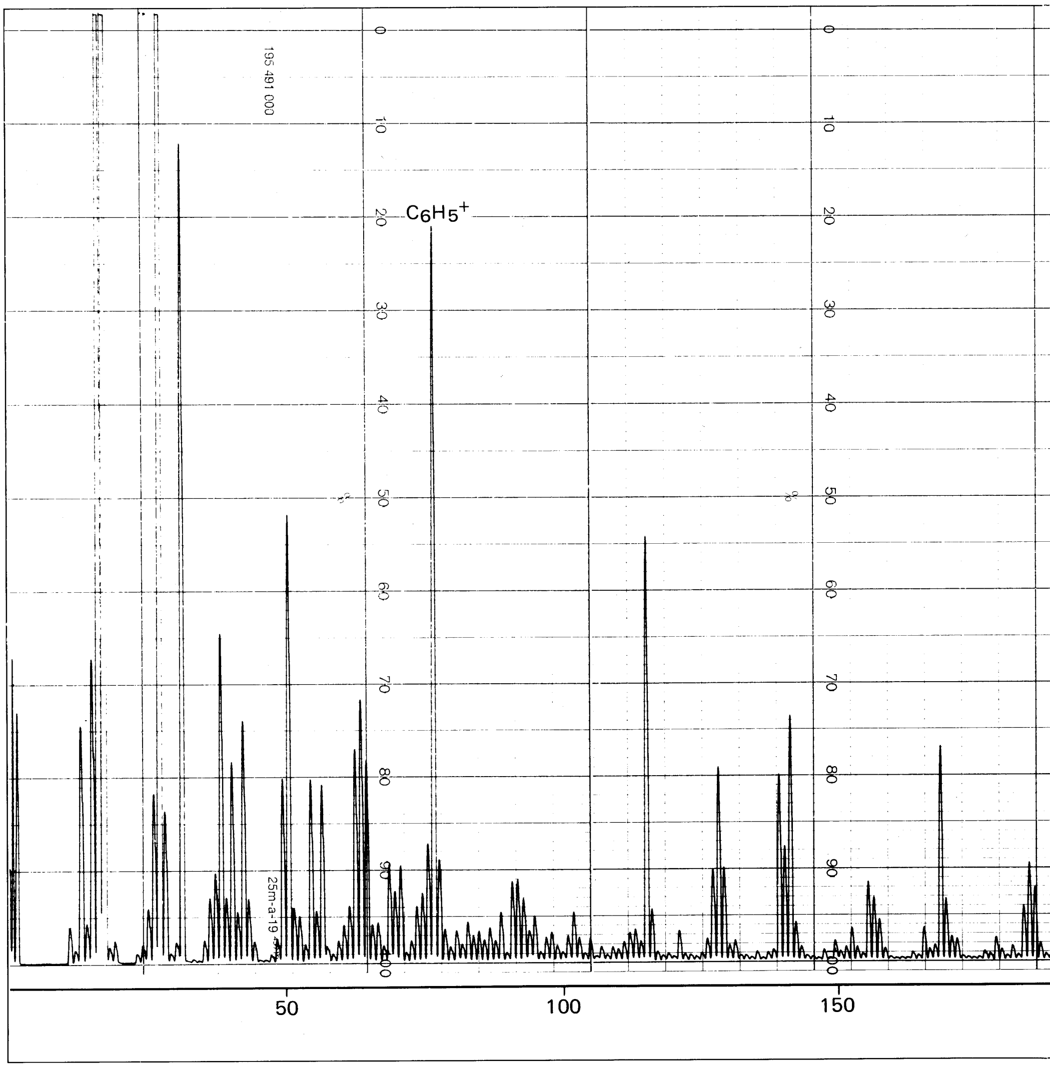


Fig. 30
Pentaphenylether Santovac 5

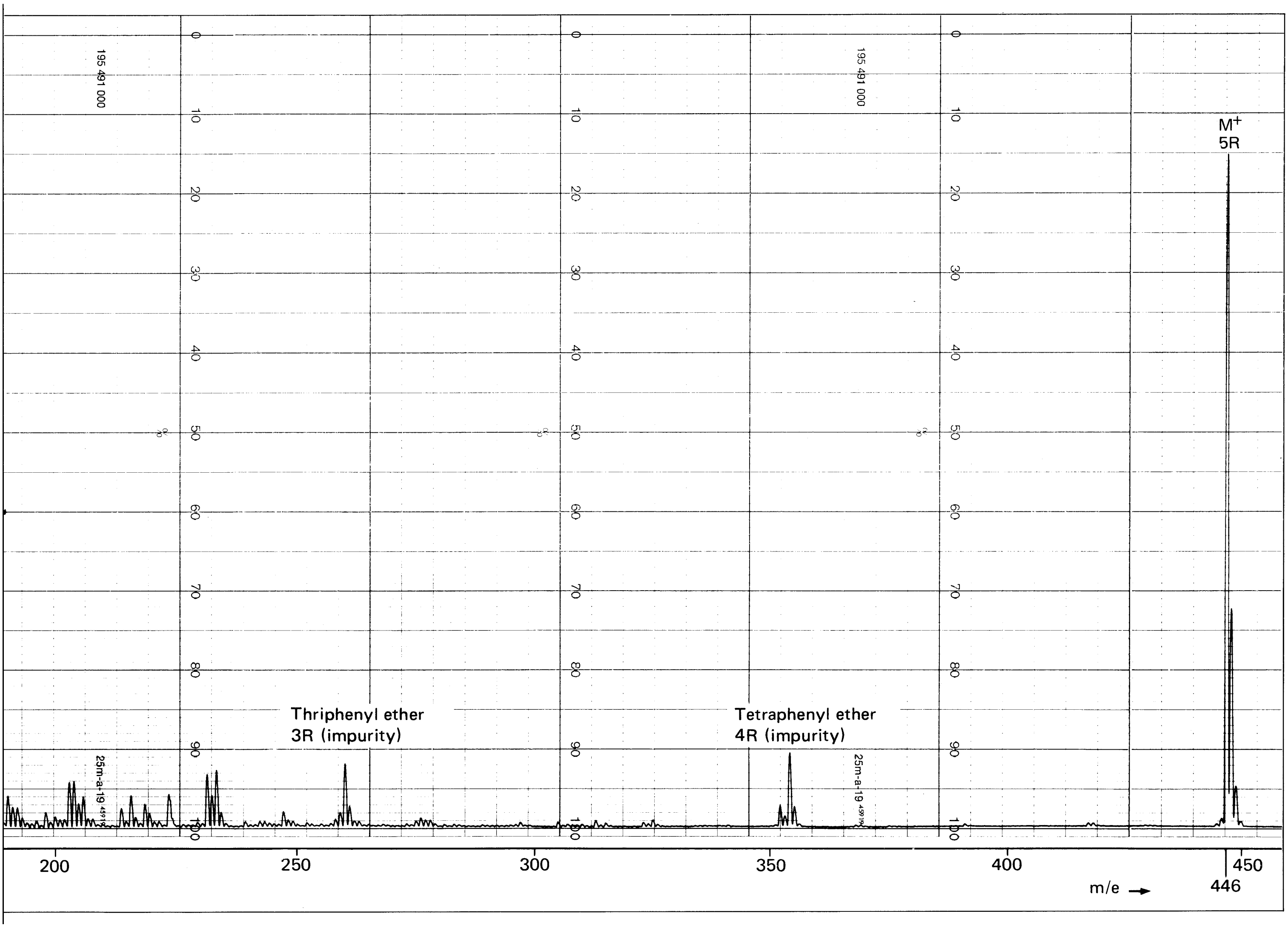
Finally, it must not be overlooked that the measurement of partial pressure is not an end in itself, but merely an aid in the assessment of the state of a vacuum apparatus, its variations and the fundamental causes. If, for example, the measurement shows that too much air is present in the residual gas, it is reasonable to search for the obvious leak and eliminate it, instead of wasting time on a precise determination of the air partial pressure.

9.2 Allowance for additional data and information

When measuring vacua in practice, it is never a question of assessing an isolated spectrum, without any additional information whatsoever. Normally the structure of the apparatus is known (kind of seals, the material used, the type of pump), also its momentary state (total pressure, temperatures) and its history (bake-out temperature and duration, preceding processes, behaviour with respect to time, etc.). This additional knowledge often forms the prerequisite basis for reaching sensible conclusions from the measurements of partial pressure.

Examples:

– The contribution of air obviously visible in Fig. 17 (chapter 6) may be regarded as negligible in view of the very favourable total pressure and because a conventional high vacuum installation employs Viton seals, so that there would be little point in searching for reasons as to whether there really is a leak or whether the phenomenon is due to slow outgassing of an enclosed volume of air (”virtual leak”), especially since the proportion of permeation, already ought to render a perceptible contibution.



– in high vacuum chambers that are not or only moderately baked out, but otherwise perfectly tight, water vapour is generally the dominating residual gas and the main obstacle to the rapid attainment of low pressures.

In a baked-out (e.g. 250 °C), metal-sealed UHV chamber the presence of an undue amount of water vapour would, however, indicate that internal components with a high thermal inertia had not become sufficiently warm.

Very high and only slowly diminishing water vapour partial pressures in chambers that were not baked out may be expected when the walls are coated with hygroscopic material, such as evaporation deposited magnesium fluoride.

However, if the water vapour pressure remains fairly constant at a high level for a long time, it may be assumed that there is another source, such as a leak in a cooling water supply pipe. The behaviour with respect to time is thus a deciding factor in this case. But a non-immersed measuring system may give the false impression of too high a water vapour partial pressure (see section 3.7).

These examples are regarded as sufficient for the purpose.

9.3 Aids to interpretation: Characteristic spectra

As has already been explained a number of times, electron impact ionization in a pure gas does not only produce ions of one mass, but a more or less complicated fragmentation spectrum. Such spectra are characteristic for the particular substance and serve as an important aid to interpretation.

On the other hand, when analysing mixtures such fragment spectra may give rise to overlapping spectra that are difficult to disentangle (see chapter 5). The fragment distributions given in Table 11.4.4, which are important for vacuum technology, naturally represent only a tiny excerpt from the enormous amount of data that exists. There are comprehensive data collections which are of little use to vacuum technologists, with the following exceptions:

- Cornu and Massot [6]
- Stenhagen et al, Vol. 1 [7]
- Spiteller [21]

This volume contains most of the solvents and is very useful for practical purposes.

- The book on "Mass Spectrometry" issued by Kienitz [2] also contains a number of important spectra for vacuum technology.

Figures 18,19, 20, 30, and 32 show characteristic spectra of pumping fluids and lubricants for vacuum pumps. As exampie for an aliphatic hydrocarbon, Fig. 33 shows the spectrum of n-$C_{14}H_{30}$. Very evident are the characteristic clusters of peaks spaced 14 mass units apart, corresponding to the removal of one or more CH_2 groups during the ionization process. Oils for backing pumps and some diffusion pumps (Balzers oil 71) are mixtures of such aliphatic hydrocarbons, though with a higher molecular weight (Fig. 18).

In addition to these many organic vapours contain aliphaticfragments of different length. That is why characteristic clusters at the CH_2 interval can occur even with quite nonspecific contaminants. It is expressly warned against drawing hurried conclusions regarding the presence of backing-pump oil from the mere presence of individual fragments, e.g. with the masses 39, 41, 43, 55 and 57.

Table 11.4.3. provides information on the probable nature and origin of certain "key fragments" which are important in vacuum technology.

It must be borne in mind that the intensity distribution in the fragment spectrum is influenced by a number of parameters, such as temperature, electron energy, mass dependence on the transmission factor of the mass filter, the detection sensitivity of the SEM, etc. It is not always possible to keep these influences exactly under control.

All these limitations, however, do not alter the fact that such fragment spectra – considered pictorially – remain characteristic, regardless of certain quantitative shifts which only in rare cases distort the picture past recognition.

The complexity of the fragment spectra is determined not only by the distribution of the fragments, but also to a large extent by the natural distribution of the isotopes. The measured isotope distribution, in contrast to the fragment distribution, is at the most influenced very slightly by the ionization conditions.

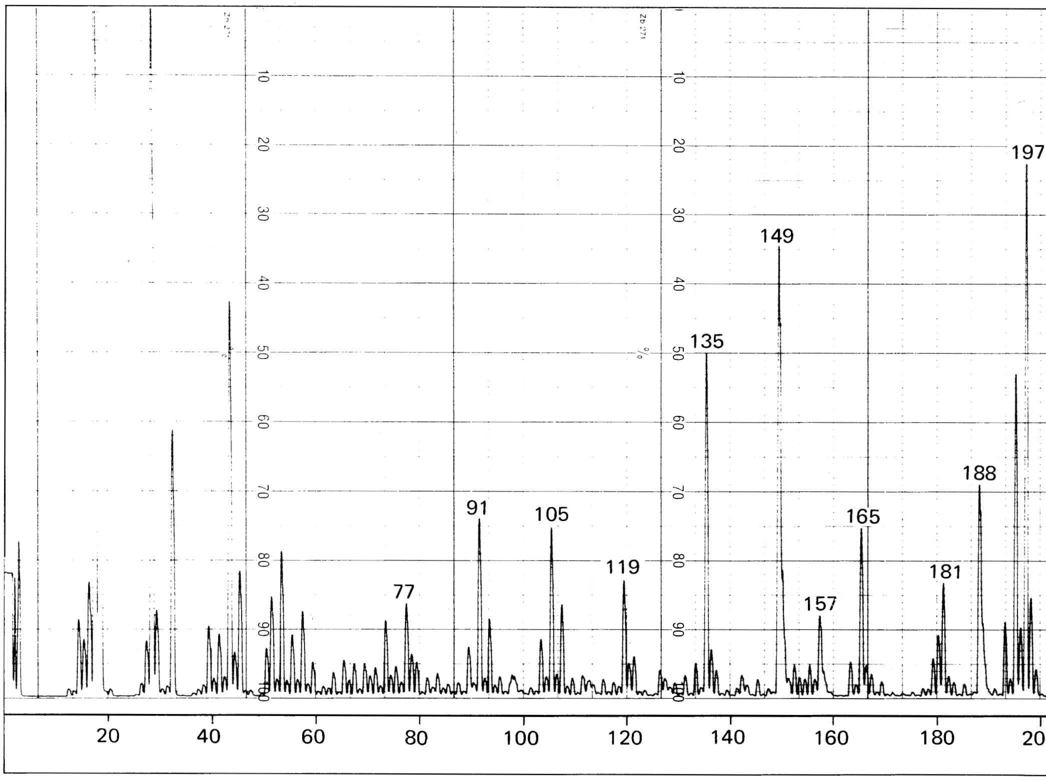


Fig. 31
Silicone oil DC 704

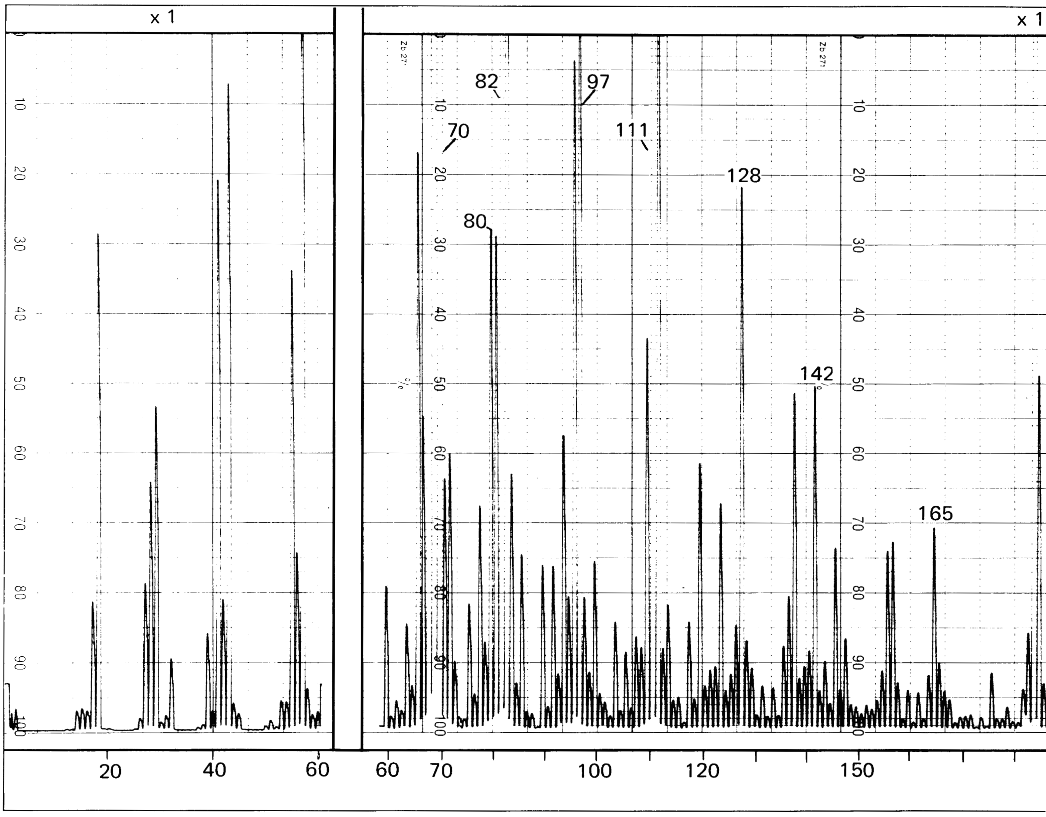
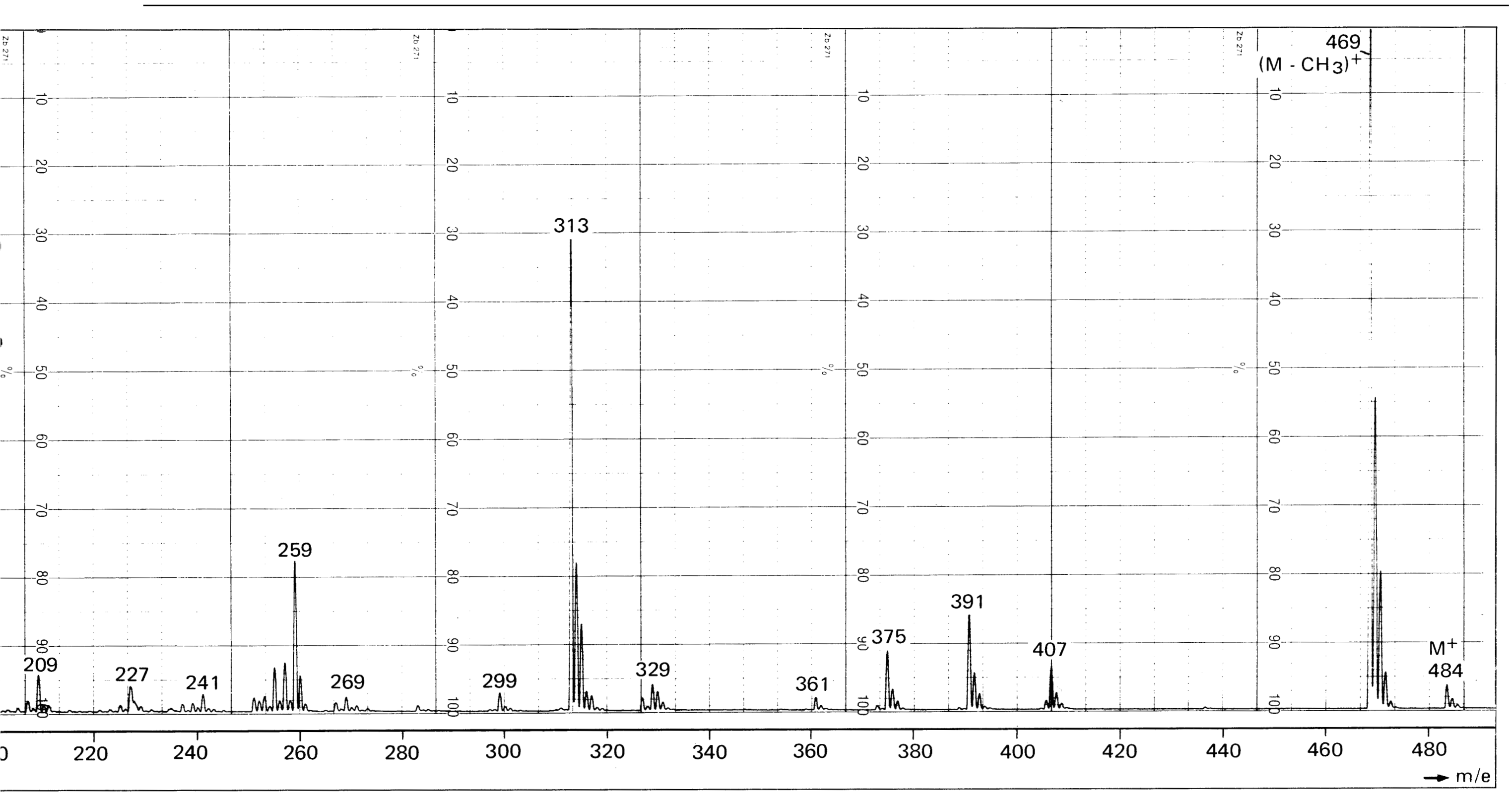
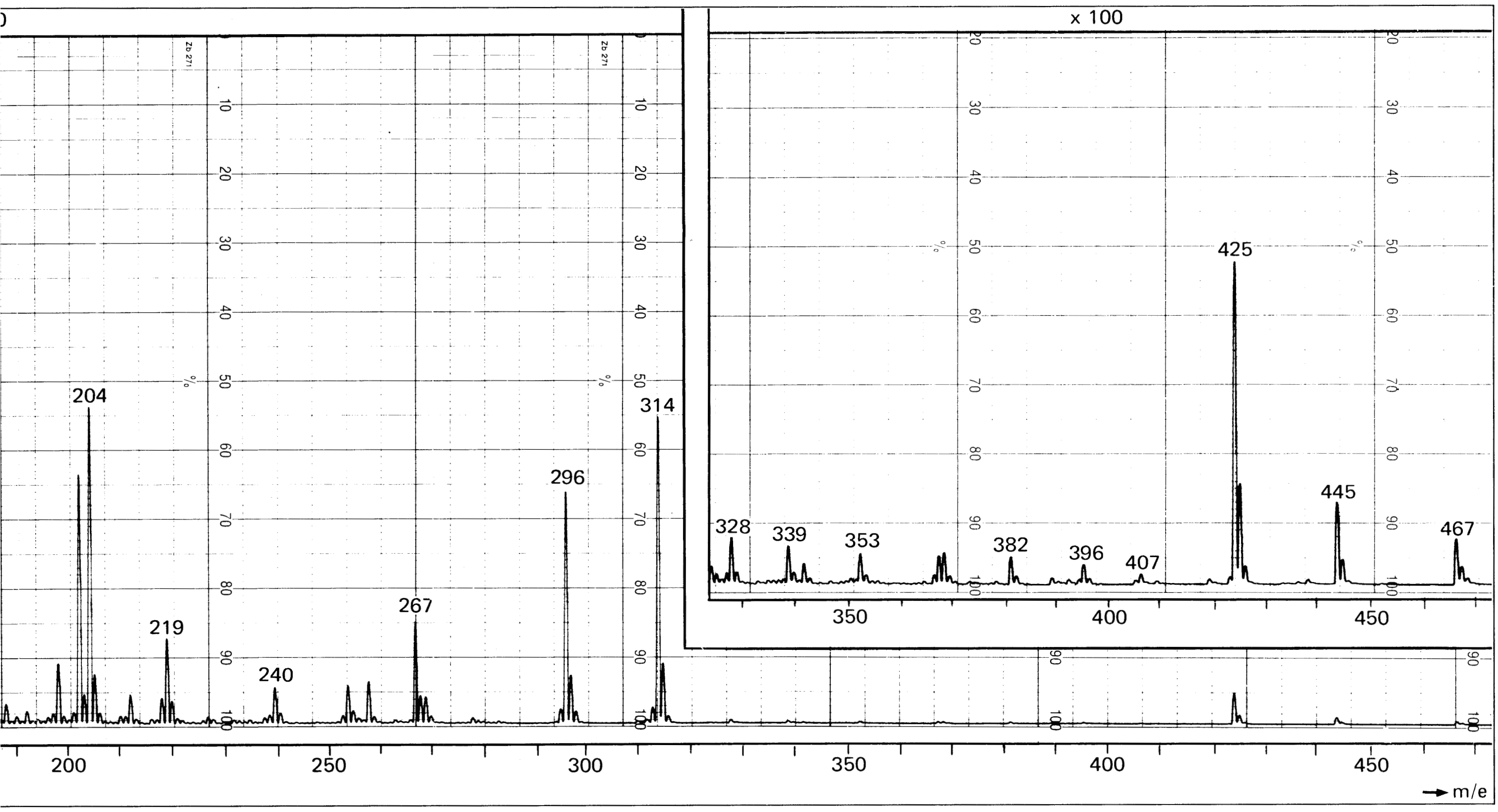


Fig- 32
Turbo-molecular pump oil T 12


209
227
241
259
269
299
313
329
361
375
391
407
469
(M - CH$_3$)$^+$
M$^+$
484
Zb 271
%
10
20
30
40
50
60
70
80
90
100
220
240
260
280
300
320
340
360
380
400
420
440
460
480
m/e


x 100
204
219
240
267
296
314
328
339
353
382
396
407
425
445
467
Zb 271
%
10
20
30
40
50
60
70
80
90
100
200
250
300
350
400
450
m/e

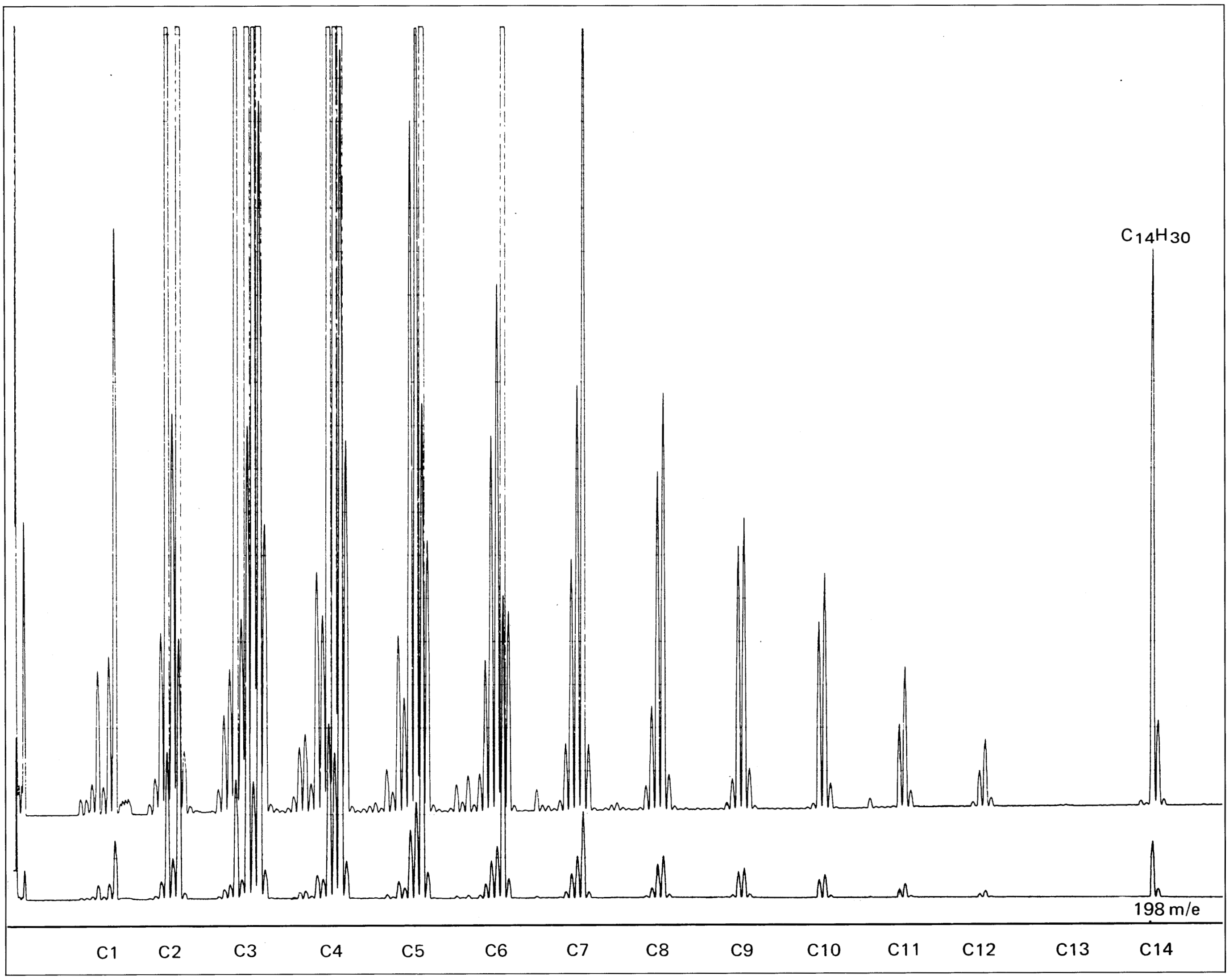


Fig. 33
Aliphatic hydrocarbon n-$C_{14}H_{30}$

Consequently, isotope distributions are a sure aid to interpretation. Tables of natural isotope distribution are to be found in [11] and [2] for example. It is useful to remember some of the most important distributions.

Often the spectrum contains groups of peaks which, on account of the intensity distribution, are necessarily identified as isotopes of a definite element. But the measured mass numbers are sometimes higher than that of the isotopes because compounds are involved. From this it is possible to derive the constituent elements in such compounds.

When dealing with compounds of different elements, all of which have a pronounced isotope distribution, the resultant distribution can be rather complex. In the event that the constituents are identical, there are tables available from which the resultant distributions can be found [2].

10. Summary

This concise survey aims at providing an overview of the basic principles and applications of vacuum measurements employing mass spectrometry, as well as the sources of error and the difficulties likely to be encountered.

Every effort has been made not to omit any important aspect.

The examles quoted are all closely related to practice and were chosen so as to give an impression of the variety and extent of the field. The notes on interpretation of the results of measurement are also meant to be regarded as examples.

Anyone wishing to gain a deeper insight is advised to consult the special literature. But nothing promotes familiarization better than one's own experience.

11. Interpretation of spectra

11.1 Evaluation of spectra

The quantitative evaluation of an unknown spectrum can prove to be a time-consuming task involving a great deal of computing work. When dealing with vacuum problems the conditions found will not be unduly complicated and quite usable results may be obtained without spectra having to be broken down into all their constituent parts.

To avoid going beyond the scope of this brochure, only a simplified example of the evaluation of mass spectra will be referred to here. This is often done according to the relationship:

$$C_n = \frac{I^+_n}{S_n} \text{ [mbar]} \qquad (1)$$

where

C_n = the partial pressure of the component n [mbar]
I_n = ion current as measured for component n [A]
S_n = the sensitivity for a corresponding gas [A/mbar]

Since electron impact ionization of a given molecule produces different kinds of ions, the sensitivity can be referred to a given peak or to the sum of the fragment ions. Table 11.4.8 gives the absolute sensitivities of the mass spectrometer QMG 112 for different gases. The figures are shown for the basic peak as well as for the sum of all fragment ions.

When comparing tables or line spectra or when using the given sensitivities, it should be remembered that spectrometers from the same product range yield similar, but not identical values. The latter are influenced by the momentary state of the analyzer (contamination), the set resolving power (transmission factor) and the parameters of the ion source.

Example:

How high are the partial pressures of water vapour, nitrogen and oxygen from the spectrum in Fig. 34?

The solution is obtained with the aid of equation 1.

$$p_{HOH} = \frac{10\cdot10^{-11}\text{ A (ion current from m/e = 18)}}{2\cdot10^{-4}\text{ A/mbar (value from Table 11.4.8)}} = 5\cdot10^{-7}\text{ mbar}$$

$$p_{N_2} = \frac{10\cdot10^{-11}\text{ A (ion current from m/e = 28)}}{2\cdot10^{-4}\text{ A/mbar}} = 5\cdot10^{-7}\text{ mbar}$$

$$p_{O_2} = \frac{2\cdot10^{-11}\text{A (ion current from m/e = 32)}}{1.4\cdot10^{-4}\text{ A/mbar}} = 1.4\cdot10^{-7}\text{ mbar}$$

Since the pressure of N_2/O_2 and Ar indicate an air leak, the percentage ratio of N_2 to O_2 will now be calculated.

$p_{N_2} + p_{O_2} = 5\cdot10^{-7}$ mbar $+ 1.4\cdot10^{-7}$ mbar $= 6.4\cdot10^{-7}$ mbar

$$\%N_2 = \frac{5\cdot10^{-7}\text{ mbar}}{6.4\cdot10^{-7}\text{ mbar}}\cdot100 = 78.12\%$$

$$\%O_2 = \frac{1.4\cdot10^{-7}\text{ mbar}}{6.4\cdot10^{-7}\text{ mbar}}\cdot100 = 21.8\%$$

Comparison with Table 11.4.7 shows good agreement. An air leak is obviously involved.

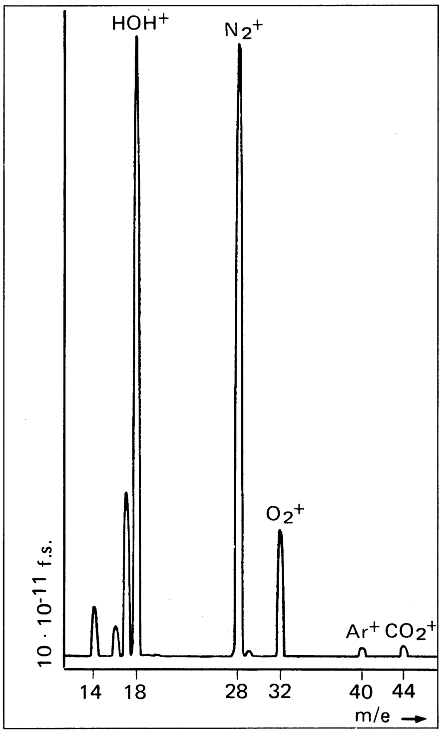


Fig. 34
Air leak in a vacuum system that was not baked out

When appreciating the results of the foregoing example it should be noted that the spectrum and the sensitivity values were not recorded with the same spectrometer, but in different installations at different times. If quantitative analyses have to be performed, the mass spectrometer should be periodically checked with a standard substance (e.g. air). This check will indicate whether there is any discrepancy from the original calibration, so that it can be taken into account in the evaluation.

11.2 Calibration

The sensitivity S of a partial pressure measuring apparatus based on a mass spectrometer is the quotient given by the ion current I^+ (A) measured at the collector and the partial pressure p (mbar) of the reference gas in the ion source.

Therefore, for calibration the true pressure in the sensitive zone of the ion source has to be determined. With open ion sources, such as the axial or grid ion source, the pressure may be measured in the vicintiy of the ion source without distorting the results.

There are various methods that can be used for measuring the pressure
1. Using gauge heads dependent on the type of gas (e.g. Balzers IMR 125 or IMR 132)
2. Using pressure measuring devices independent of the type of gas
- direct measurement with a spinning rotor gauge
- independent measurement with a capacitance manometer

Fig. 35 illustrates the set-up for calibration. The calibrating gas at a pressure of p_0 is fed from the storage vessel V_0 through orifice L_0 to the ion source of the mass spectrometer. Depending on the conductance L_1 of the orifice, a pressure p_1 is obtained in the ion source space V_1. If there is no orifice between the ion source and the pump, the effective pumping capacity of the pump for the gas in question must be known in advance.

Since calibration is mainly effected with pure gases, an ionization gauge head dependent on the type of gas may be used to determine p_1. The reading is usually in terms of nitrogen equivalent.

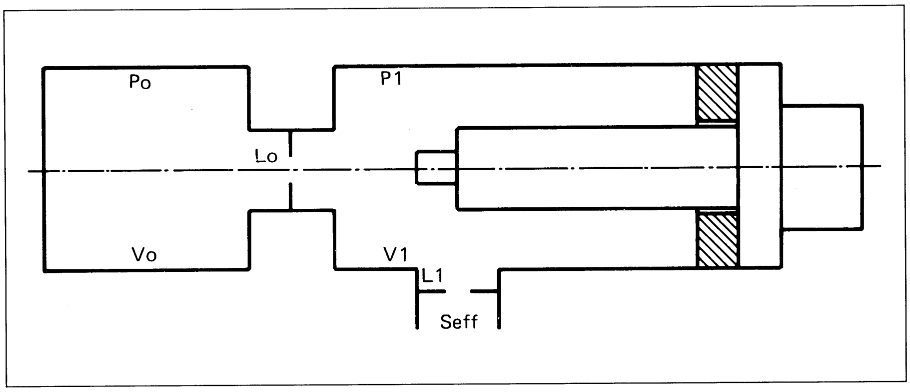


Fig. 35
Set-up for calibrating a mass spectrometer

With the correction factor for the gas n concerned, the true pressure is calculated. For this method the orifice L_0 can be replaced by a gas feed valve (e.g. Balzers UIDV 035). In this case orifice L_1 can be dispensed with.

The correction of the pressure reading is unnecessary when a spinning rotor gauge is used.

With capacitive pressure recorders the pressure p_1 cannot be measured directly with sufficient accuracy. Here the indirect method has to be chosen. In this case the pressure p_0 is measured, from which p_1 is derived in the following manner:

$$p_1 = \frac{Q}{L_1} = (p_0 - p_1)\frac{L_0}{L_1} \qquad (1)$$

when $p_1 \ll p_0$ eq. (1) simplifies to

$$p_1 = p_0 \frac{L_0}{L_1} \qquad (2)$$

The sensitivity S for the gas n is then given by:

$$S_n = \frac{I^+_n}{P_{1n}} = \frac{I^+_n L_1}{P_0 L_0} \text{ [A/mbar]} \qquad (3)$$

Q = inlet rate [mbar l/s]
L = conductance of the orifice [l/s]

The orifice L_0 and L_1 are selected such that at a pressure of 0.5 to 1 mbar in the gas storage vessel, a pressure between $5 \cdot 10^{-6}$ and 10^{-5} is attained in the ion source space. This satisfies the condition $p_1 \ll p_0$. The pressure in the region between 0.5 and 1 mbar can be determined easily and exactly by means of the capacitance manometer. To eliminate the influence of the pump, L_1 should be small with respect to the pumping capacity of the pump. The basic pressure before the gas inlet must be 2 to 3 orders of magnitude smaller than the gas pressure p_1, thus eliminating background influences. For some gases calibrating leaks may be acquired. This enables the pressure measurement to be done away with. The size of the leak (mbar l/s) is then substituted for Q in equation (1).

11.3 Reference spectra

A large number of spectra are contained in spectral catalogs. The spectra of the pure substances are standardized and the fragment with the highest intensity made equal to 100 and designated the base peak. Comparing the recorded spectrum with the catalog usually enables the substance to be identified. However, in practice "pure spectra" are seldom encountered, most being spectra of mixtures, which can give rise to some difficulties in interpretation. By means of the tables of the relative ion currents of fragment ions (Table 11.4.4) and the key fragment ions (Table 11.4.3) the vacuum expert should succeed in finding the appropriate substances in the majority of cases.

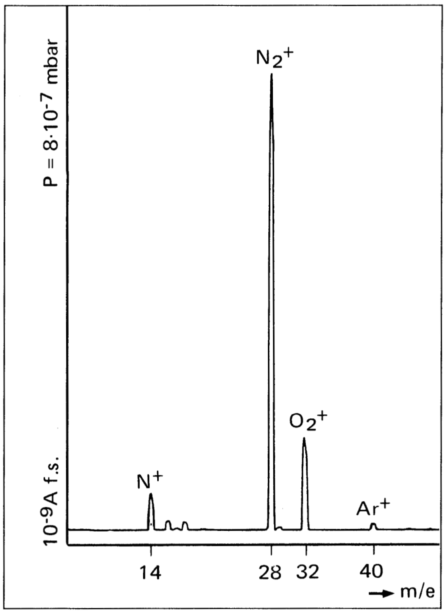


Fig. 36
Air

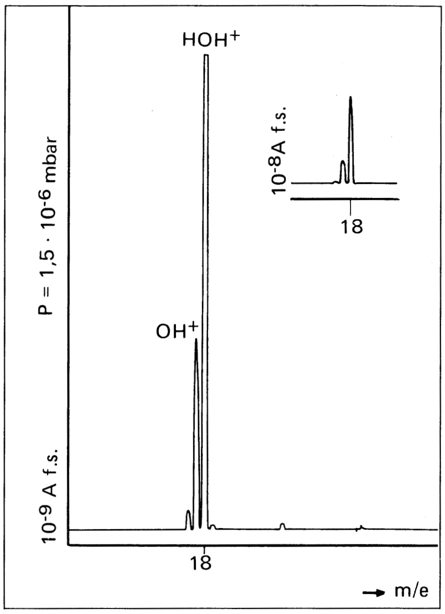


Fig. 37
Water vapour

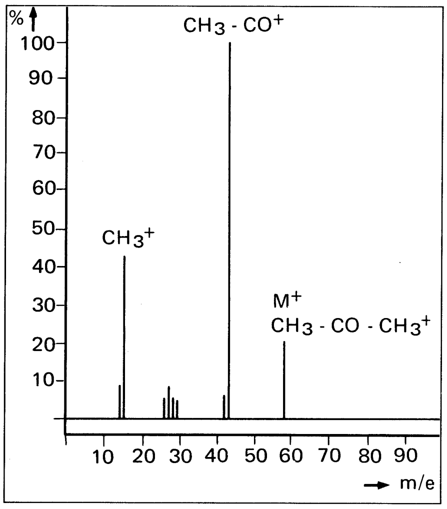


Fig. 38
Acetone

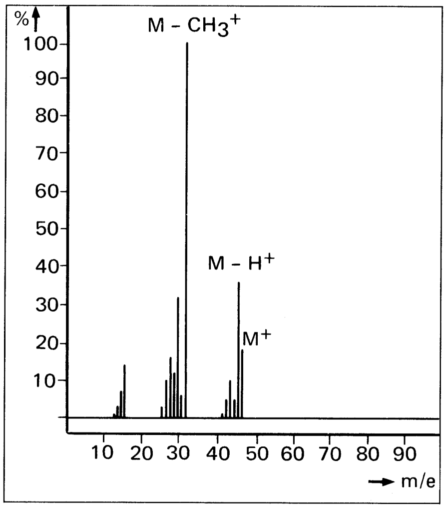


Fig. 39
Ethanol

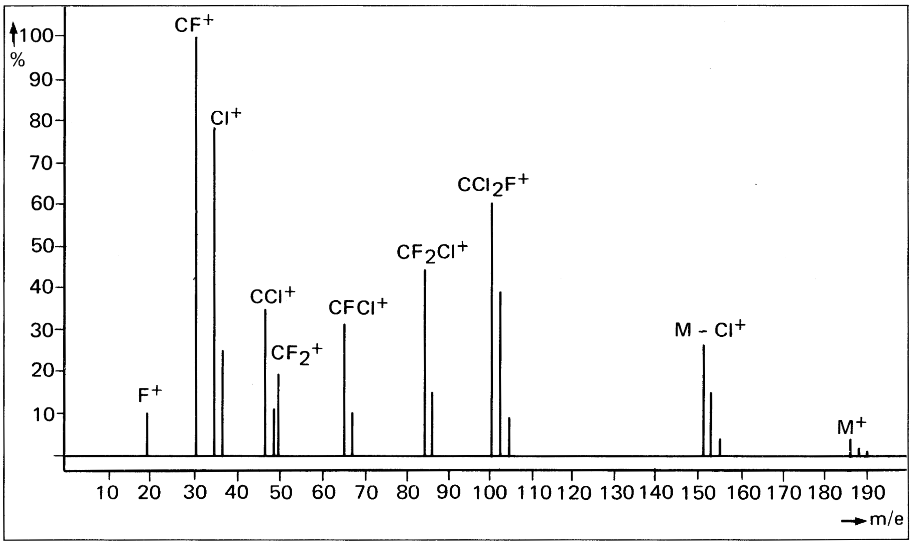


Fig. 40
Freon TF $CF_2Cl - CCl_2F$

11.4 Tables

11.4.1 Relative probabilities of ionization

referred to nitrogen, appr. 100 eV electron energy

He	0,15
Ne	0,30
D_2	0,35
H_2	0,44
Air	1,0
N_2	1,0
O_2	1,0
H_2O	1,0
CO	1,05
Ar	1,2
NO	1,2
NH_3	1,3
HF	1,4
CO_2	1,4
HCl	1,6
N_2O	1,7
Kr	1,0
SO_2	2,1
SF_6	2,3
Xe	2,4
CH_4	1,6
C_2H_6	2,6
C_3H_8	3,7
C_4H_{10}	4,9
n-C_5H_{12}	6,0
C_6H_{14}	6,6
C_6H_6	5,9
C_6H_5Cl	7,0
$C_6H_5CH_3$	6,8
$C_6H_4(CH_3)_2$	7,8
CH_3OH	1,8
CH_3Cl	3,1
CH_2Cl_2	3,7
$CHCl_3$	4,8
CCl_4	6,0
CCl_2F_2	2,7
C_2H_5OH	3,6
C_2H_5Cl	4,0

11.4.2 Mass spectrum of CO_2

at 70 eV electron energy

m/e	Intensity	Ion
12	2,46	$^{12}C^+$
16	6,24	$^{16}O^+$
22	1,78	$^{12}C^{16}O_2^{++}$
28	6,55	$^{12}C^{16}O^+$
29	0,06	$^{13}C^{16}O^+$
44	100,00	$^{12}C^{16}O_2^+$
45	1,16	$^{13}C^{16}O_2^+$
46	0,41	$^{12}C^{16}O^{18}O^+$

11.4.3 Key fragment ions

Mass number	Key fragments		
1	H^+		
2	H_2^+	(He^{++})	
4	He^+		
6	C^{++}		
7	N^{++}		
8	O^{++}		
12	C^+		
13	CH^+		
14	N^+	CH_2^+	CO^{++}
15	CH_3^+	NH^+	
16	O^+	CH_4^+	NH_2^+
17	OH^+	NH_3^+	
18	H_2O^+		
19	F^+	H_3O^+	
20	HF^+	$^{20}NE^+$	Ar^{++}
22	CO_2^+	$^{22}NE^+$	
24	C_2+		
26	$C_2H_2^+$		
27	$C_2H_3^+$		
28	N_2	$C_2H_4^+$	CO^+
29	$C_2H_5^+$	$^{15}N^{14}N^+$	
30	$C_2H_6^+$	NO^+	
31	CF^+	CH_2OH^+	
32	O_2^+	$^{32}S^+$	
34	$H_2{}^{32}S^+$	$^{34}S^+$	$^{18}O^{16}O^+$
35	$^{35}Cl^+$		
36	$H^{35}Cl^+$	$^{36}Ar^+$	
37	$^{37}Cl^+$	C_3H^+	
38	$H^{37}Cl^+$	$C_3H_2^+$	$^{38}Ar^+$
39	$C_3H_3^+$	$^{39}K^+$	
40	Ar^+	$C_3H_4^+$	
41	$C_3H_5^+$	$^{41}K^+$	
42	$C_3H_6^+$		
43	$C_3H_7^+$	CH_3CO^+	
44	$C_3H_8^+$	CO_2^+	N_2O^+
45	$C_2H_5O^+$ (Alcohol)		
46	NO_2^+	$C_2H_5OH^+$	
48	SO^+		
50	CF^+		
55	$C_4H_7^+$		
57	$C_4H_9^+$		
58	$(CH_3)_2\ CO^+$ (Aceton)		
64	SO_2^+		
69	CF_3^+		
77	$C_6H_5^+$ (Phenyl)		
78	$C_6H_6^+$ (Benzol)		
85	$C^{35}ClF_2^+$ (Freon)		
87	$C^{37}ClF_2^+$ (Freon)		
92,5	$^{185}Re^{++}$		
93,5	$^{187}Re^{++}$		
101	$C^{35}Cl_2F^+$ (Freon)		
103	$C^{35}Cl^{37}ClF^+$ (Freon)		
105	$C^{37}Cl_2F^+$ (Freon)		
130	$C_2HCl_3^+$ (Trichlor)		
132	$C_2HCl_3^+$ (Trichlor)		
134	$C_2HCl_3^+$ (Trichlor)		
136	$C_2HCl_3^+$ (Trichlor)		

Mass number	Key fragments
149	Phthalic ester (Softening agent)
151	$C_2{}^{35}Cl_2F_3^+$ (Freon)
153	$C_2{}^{35}Cl^{37}ClF_3^+$ (Freon)
155	$C_2{}^{37}Cl_2F_3^+$ (Freon)
182	W^+
183	W^+
184	W^+
185	Re^+
186	W^+
187	Re^+

11.4.4 **Relative ion currents of fragment ions**

90 eV energy of ionization

Mass number	H2	He	CH4	H2O	Ne	N2	CO	C2H6	O2	Ar	CO2	C3H8
1	3		16,5	2,4				9,6				5,0
2	**100**											
3		**100**										
12			3,0				6,3	0,7			9,7	0,6
13			7,8					1,2				0,9
14			16,0			14	0,8	3,3				2,3
15			85,0					4,7				7,2
16			**100**	1,8			2,8		18		16,0	
17			1,2	26								
18				**100**								
20					**100**					22,6		
22					10,2						2,1	
25								3,8				0,8
26								22,2				9,8
27								33,4				43,5
28						**100**	**100**	**100**			13,0	61,0
29						0,7	1,2	20,0				**100**
30								22,2				21,7
31												
32									**100**			
34									0,4			
36										0,34		
37												4,6
38										0,06		6,7
39												20,2
40										**100**		2,6
41												15,0
42												4,8
43												22,8
44											**100**	24,0
45											1,2	0,8

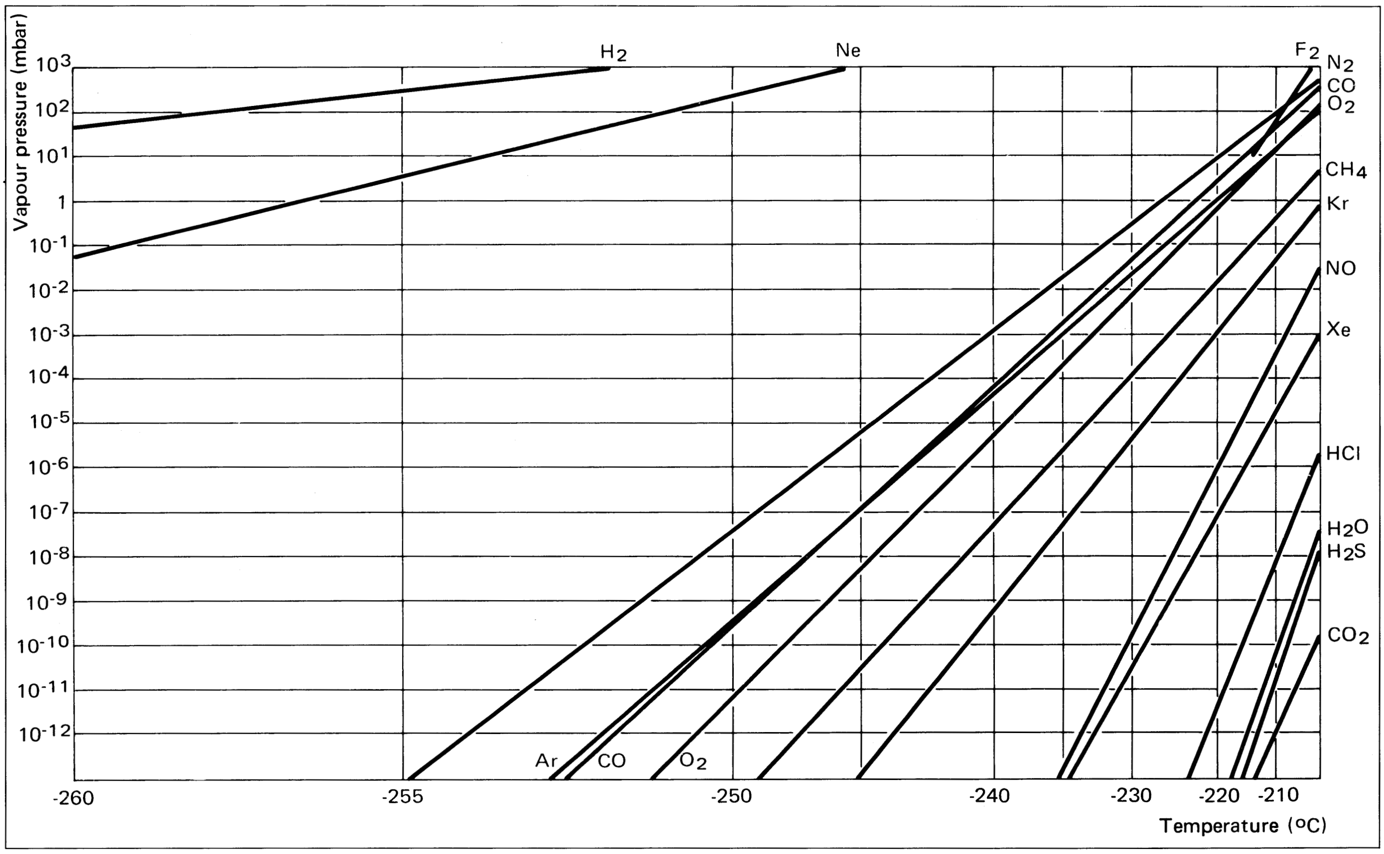
11.4.5 **Table of naturally occuring isotopes**

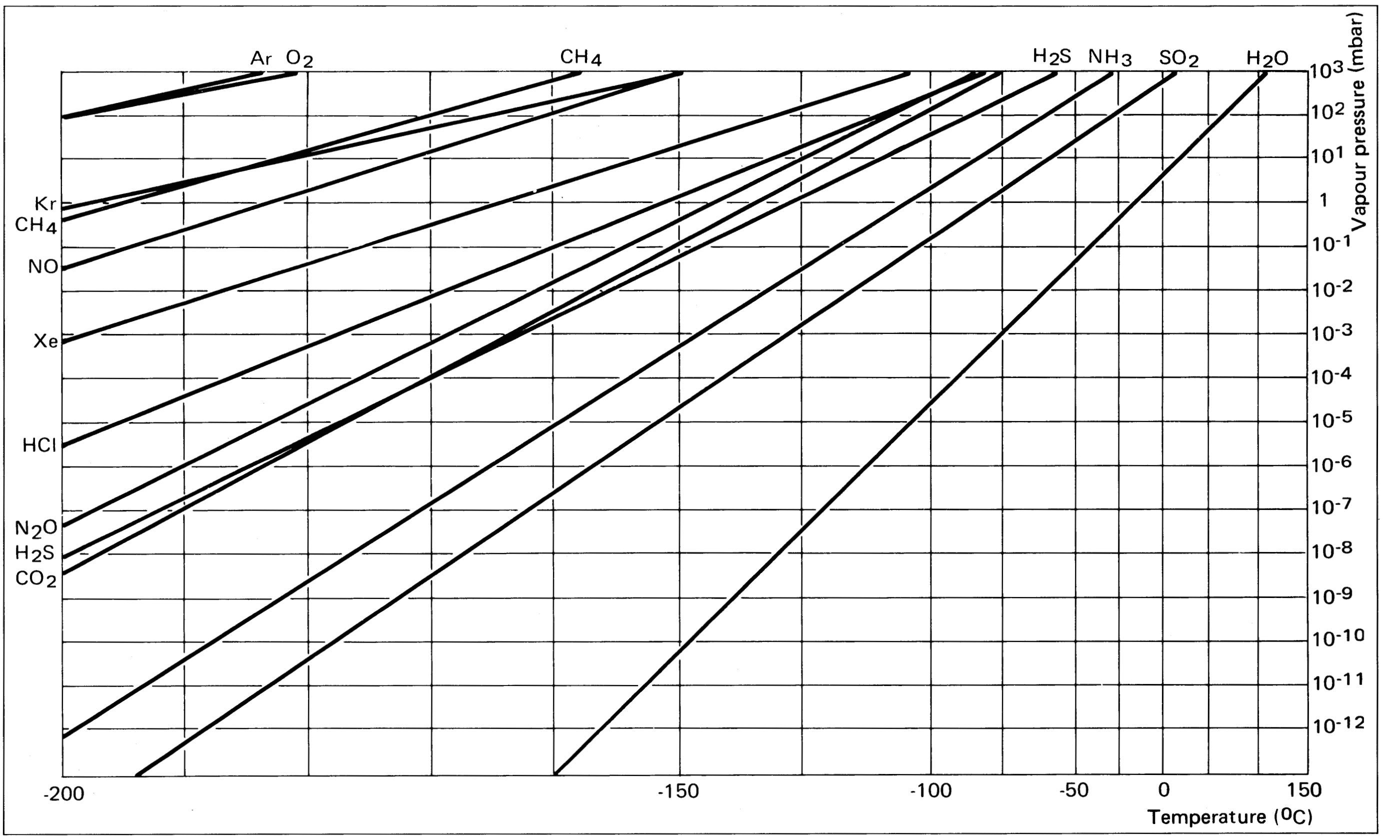
Atomic number	Element	Chem. symbol	Mass number	Relative abundance [%]
1	Hydrogen	H	1	99,985
		D	2	0,01492
2	Helium	He	3	0,000137
			4	99,999863
3	Lithium	Li	6	7,42
			7	92,58
4	Beryllium	Be	9	100
5	Boron	B	10	19,61
			11	80,39
6	Carbon	C	12	98,893
			13	1,107
7	Nitrogen	N	14	99,6337
			15	0,3663
8	Oxygen	O	16	99,759
			17	0,0374
			18	0,2039
9	Fluorine	F	19	100
10	Neon	Ne	20	90,92
			21	0,26
			22	8,82
11	Sodium	Na	23	100
12	Magnesium	Mg	24	78,70
			25	10,13
			26	11,17
13	Aluminium	Al	27	100
14	Silicon	Si	28	92,21
			29	4,70
			30	3,09
15	Phosphorus	P	31	100
16	Sulfur	S	32	95,0
			33	0,76
			34	4,22
17	Chlorine	Cl	35	75,53
			37	24,47
18	Argon	Ar	36	0,337
			38	0,063
			40	99,600
19	Potassiom	K	39	93,1
			40	0,0118
			41	6,88
20	Calcium	Ca	40	96,97
			42	0,64
			43	0,15
			44	2,06
			46	0,003
			48	0,18
21	Scandium	Sc	45	100

Atomic number	Element	Chem. symbol	Mass number	Relative abundance [%]
22	Titanium	Ti	46	7,93
			47	7,28
			48	73,94
			49	5,51
			50	5,34
23	Vanadium	V	50	0,24
			51	99,76
24	Chrome	Cr	50	4,31
			52	83,76
			53	9,55
			54	2,38
25	Manganese	Mn	55	100
26	Iron	Fe	54	5,82
			56	91,66
			57	2,19
			58	0,33
27	Cobalt	Co	59	100
28	Nickel	Ni	58	67,88
			60	26,23
			61	1,19
			62	3,66
			64	1,08
29	Copper	Cu	63	69,09
			65	30,91
30	Zinc	Zn	64	48,89
			66	27,81
			67	4,11
			68	18,57
			70	0,62
31	Gallium	Ga	69	60,4
			71	39,6
32	Germanium	Ge	70	20,52
			72	27,43
			73	7,76
			74	36,54
			76	7,76
33	Arsenic	As	75	100
34	Selenium	Se	74	0,87
			76	9,02
			77	7,58
			78	23,52
			80	49,82
			82	9,19
35	Bromine	Br	79	50,54
			81	49,46
36	Krypton	Kr	78	0,35
			80	2,27
			82	11,56
			83	11,55
			84	56,90
			86	17,37
37	Rubidium	Rb	85	72,15
			87	27,85
38	Strontium	Sr	84	0,56
			86	9,86
			87	7,02
			88	82,56
39	Yttrium	Y	89	100
40	Zirconium	Zr	90	51,46
			91	11,23
			92	17,11
			94	17,40
			96	2,80
41	Niobium	Nb	93	100
42	Molybdenum	Mo	92	15,84
			94	9,04
			95	15,72
			96	16,53
			97	9,46
			98	23,78
			100	9,63
43	Technetium	Tc	–	–
44	Ruthenium	Ru	96	5,51
			98	1,87
			99	12,72
			100	12,62
			101	17,07
			102	31,61
			104	18,58
45	Rhodium	Rh	103	100
46	Palladium	Pd	102	0,96
			104	10,97
			105	22,23
			106	27,33
			108	26,71
			110	11,81
47	Silver	Ag	107	51,35
			109	48,65
48	Cadmium	Cd	106	1,22
			108	0,875
			110	12,39
			111	12,75
			112	24,07
			113	12,26
			114	28,86
			116	7,58
49	Indium	In	113	4,28
			115	95,72
50	Tin	Sn	112	0,96
			114	0,66
			115	0,35
			116	14,30
			117	7,61
			118	24,03
			119	8,58
			120	32,85
			122	4,72
			124	5,94
51	Anthimony	Sb	121	57,25
			123	42,75
52	Tellurium	Te	120	0,09
			122	2,46
			123	0,87
			124	4,61
			125	6,99
			126	18,71
			128	31,79
			130	34,48
53	Iodine	J	127	100
54	Xenon	Xe	124	0,09
			126	0,09
			128	1,92
			129	26,44
			130	4,08
			131	21,18
			132	26,89
			134	10,44
			136	8,87

Atomic number	Element	Chem. symbol	Mass number	Relative abundance [%]
55	Cesium	Cs	133	100
56	Barium	Ba	130	0,10
			132	0,09
			134	2,42
			135	6,59
			136	7,81
			137	11,32
			138	71,66
57	Lanthanum	La	138	0,09
			139	99,91
58	Cerium	Ce	136	0,19
			138	0,25
			140	88,48
			142	11,07
59	Praeseodymium	Pr	141	100
60	Neodymium	Nd	142	27,11
			143	12,17
			144	23,85
			145	8,30
			146	17,22
			148	5,73
			150	5,62
61	Promethium	Pm	–	–
62	Samarium	Sm	144	3,09
			147	14,97
			148	11,24
			149	13,83
			150	7,44
			152	26,72
			154	22,71
63	Europium	Eu	151	47,82
			153	52,18
64	Gadolinium	Gd	152	0,20
			154	2,15
			155	14,73
			156	20,47
			157	15,68
			158	24,87
			160	21,90
65	Terbium	Tb	159	100
66	Dysprosium	Dy	156	0,05
			158	0,09
			160	2,29
			161	18,88
			162	25,53
			163	24,97
			164	28,18
67	Holmium	Ho	165	100
68	Erbium	Er	162	0,14
			164	1,56
			166	33,41
			167	22,94
			168	27,07
			170	14,88
69	Thulium	Tm	169	100
70	Ytterbium	Yb	168	0,14
			170	3,03
			171	14,31
			172	21,82
			173	16,13
			174	31,84
			176	12,73
71	Luthetium	Lu	175	97,41
			176	2,59
72	Hafnium	Hf	174	0,18
			176	5,20
			177	18,50
			178	27,14
			179	13,75
			180	35,24
73	Tantalum	Ta	180	0,01
			181	99,99
74	Tugsten	W	180	0,13
			182	26,41
			183	14,40
			184	30,64
			186	28,41
75	Rhenium	Re	185	37,07
			187	62,93
76	Osmium	Os	184	0,02
			186	1,59
			187	1,64
			188	13,3
			189	16,1
			190	26,4
			192	41,0
77	Iridium	Ir	191	37,3
			193	62,7
78	Platinum	Pt	190	0,01
			192	0,78
			194	32,9
			195	33,8
			196	25,3
			198	7,21
79	Gold	Au	197	100
80	Mercury	Hg	196	0,15
			198	10,02
			199	16,84
			200	23,13
			201	13,22
			202	29,80
			204	6,85
81	Thallium	Ti	203	29,50
			205	70,50
82	Lead	Pb	204	1,48
			206	23,6
			207	22,6
			208	52,3
83	Bismuth	Bi	209	100
84	Polonium	Po		
85	Astatine	At		
86	Radon	Rn		
87	Francium	Fr		
88	Radium	Ra		
89	Actinum	Ac		
90	Thorium	Th	232	100
91	Protactnium	Pa		
92	Uranium	U	234	0,0056
			235	0,7205
			238	99,2739

11.4.6 **Curves of vapor pressure**





11.4.7 **Composition of atmospheric air**

The relative humidity is usually listed separately for a given temperature. For periodic checking of the mass spectrometer it is convenient to use air (main components). To demonstrate the limit of detection and the detectable partial pressures, the rare gases (He, Xe and Kr) are often used with entry of air.

	Percent by weight	**Percent by volume (x 10 = pressure [mbar])**	
N_2	76,5	78,1	
O_2	23,0	20,9	
Ar	1,29	0,93	
Co_2	0,04	0,03	Main components
Ne	$1{,}2 \cdot 10^{-3}$	$1{,}8 \cdot 10^{-3}$	
He	$7 \cdot 10^{-5}$	$5{,}2 \cdot 10^{-4}$	
Kr	$3 \cdot 10^{-4}$	$1{,}1 \cdot 10^{-4}$	
Xe	$4 \cdot 10^{-5}$	$8{,}7 \cdot 10^{-6}$	Rare gases
Ch_4			
H_2			Together appr. 2 ppm
N_2O			for mass spectrometry of minor significance

11.4.8 **Sensitivity for QMA 120**

Gas	**Mass number of base peak**	**Total sensitivity for base peak x 10^{-5} [A/mbar]**	**sum of fragment ions x 10^{-5} [A/mbar]**
He	4	6,4	–
Ne	20	6,4	7,2
Ar	40	24	34
Kr	84	6,8	17
H_2	2	13	–
N_2	28	20	23
CO	28	20	22
O_2	32	14	16
CO_2	44	13	19
CH_4	16	28	54
C_2H_6	28	34	68
C_3H_8	29	26	74
C_4H_{10} (n)	43	22	74
C_4H_{10} (iso)	43	24	68
H_2O	18	20	26

11.4.9 **Natural constants**

Velocity of light in vacuum	$c = 2{,}997925 \cdot 10^{8}\ \mathrm{m} \cdot \mathrm{s}^{-1}$
Acceleration due to gravity (standard value)	$g = 9{,}80665\ \mathrm{m} \cdot \mathrm{s}^{-2}$
Avogadro's constant	$N_A = 6{,}0221 \cdot 10^{23}\ \mathrm{mol}^{-1}$
Electron charge	$e = 1{,}6022 \cdot 10^{-19}\ \mathrm{C}$
Faraday's constant	$F = N_A e = 96485\ \mathrm{C} \cdot \mathrm{mol}^{-1}$
Planck's constant	$h = 6{,}6262 \cdot 10^{-34}\ \mathrm{J} \cdot \mathrm{s}$
Boltzmann's constant	$k = 1{,}3806 \cdot 10^{-23}\ \mathrm{J} \cdot \mathrm{K}^{-1}$
Universal gas constant	$R = kN_A = 8{,}3143\ \mathrm{J} \cdot \mathrm{K}^{-1}\ \mathrm{mol}^{-1}$
Absolute zero	T_0 = O K or $\delta_0 = –273{,}15$ °C
Normal molar volume of an ideal gas (0 °C and 1013 mbar)	$V_{molar.0} = 0{,}022414\ \mathrm{m}^3 \cdot \mathrm{mol}^{-1}$
Atomic mass unit	$1\ \mathrm{u} = 10^{-3}\ \mathrm{kg\ mol}^{-1} \cdot 1/N_A = 1{,}66055 \cdot 10^{-27}\ \mathrm{kg}$
Rest mass of	
Electron	$m_e = 9{,}1095 \cdot 10^{-31}\ \mathrm{kg} = 0{,}548580 \cdot 10^{-3}\ \mathrm{u}$
Proton	$m_p = 1{,}6726 \cdot 10^{-27}\ \mathrm{kg} = 1{,}007277\ \mathrm{u}$
Neutron	$m_n = 1{,}6749 \cdot 10^{-27}\ \mathrm{kg} = 1{,}008665\ \mathrm{u}$
Deuteron	$m_d = 3{,}3436 \cdot 10^{-27}\ \mathrm{kg} = 2{,}013554\ \mathrm{u}$
Alpha particle	$m_\alpha = 6{,}6447 \cdot 10^{-27}\ \mathrm{kg} = 4{,}001506\ \mathrm{u}$
Hydrogen atom	$m_H = 1{,}6735 \cdot 10^{-27}\ \mathrm{kg} = 1{,}007825\ \mathrm{u}$
Helium atom	$m_{He} = 6{,}6465 \cdot 10^{-27}\ \mathrm{kg} = 4{,}002603\ \mathrm{u}$
Mass ratio proton/electron	$m_p/m_e = 1836$
Specific charge of	
Electron	$e/m_e = 1{,}7588 \cdot 10^{11}\ \mathrm{A} \cdot \mathrm{s} \cdot \mathrm{kg}^{-1}$
Proton	$e/m_p = 9{,}5788 \cdot 10^{7}\ \mathrm{A} \cdot \mathrm{s} \cdot \mathrm{kg}^{-1}$
Rest energy of	
Electron	$m_e c^2 = 0{,}5110\ \mathrm{MeV}$
Proton	$m_p c^2 = 938{,}3\ \mathrm{MeV}$
Compton wavelength of electron	$\lambda_c = 2{,}4263 \cdot 10^{-12}\ \mathrm{m}$

11.4.10 **Densities of some gases** at 1013 mbar and 0 °C [g/l]

Hydrogen	0,0899
Helium	0,1785
Ammonia	0,7714
Nitrogen	1,2505
Air	1,2929
Town gas	0,65
Oxygen	1,4290
Carbon dioxide	1,4290
Chlorine	3,2140

12. Bibliography

[1] C. Brunnée und H. Voshage: Massenspektrometrie, Verlag Thiemig KG. München (1964)

[2] H. Kienitz: Massenspektrometrie, Verlag Chemie GmbH, Weinheim / Bergstrasse (1968)

[3] D. Prince: Dynamic Mass Spectrometry, Vol. 2, Heyden & Son Ltd., London (1971)

[4] H.S.W. Massey and E.H.S. Burhop: Electronic and Ionic Impact Phenomena, Vol. 1, University Press, Oxford (1969)

[5] R.I. Reed: Ion Production by Electron Impact, Academic Press, London (1962)

[6] A. Cornu and R. Massot: Compilation of Mass Spectral Data, Heyden & Son Ltd., London (1966) (and Supplements)

[7] E. Stenhagen, S. Abrahamsson and F.W. Mc Lafferty: Registry of Mass Spectral Data, John Wiley & Sons, New York (1974)

[8] E.W. Blauth: Dynamic Mass Spectrometers, Elsevier, Amsterdam (1966)

[9] W. Paul und H. Steinwedel, Z. Naturforschung 80 (1953) 448

[10] W. Paul, H.P. Reinhard und U. v. Zahn: Z. Phys. 152 (1958) 143

[11] P. Dawson: Quadrupole Mass Spectrometry, Elsevier, Amsterdam (1976)

[12] U. v. Zahn: Rev. Sci. Instrum. 34 (1963) 1

[13] P.A. Redhead, J.P. Hobson and E.V. Kornelsen: The Physical Basis of Ultrahigh Vacuum, Chapman & Hall, London (1968)

[14] P.A. Redhead: J. Vac. Sci. and Technol. 3 (1966) 173

[15] H. Eppler: Bestimmung von CO und N_2, Fachbericht BK 800 006 DD, Balzers AG, Balzers, Liechtenstein

[16] G. Spiteller: Massenspektrometrische Strukturanalyse organischer Verbindungen, Verlag Chemie, Weinheim/Bergstrasse (1966)

[17] G. Rettinghaus und W.K. Huber: Backstreaming in diffusion pump systems, Vacuum 24 (1974) 249

[18] F. Gaydou and W.K. Huber: Coating Plant for Thin Film Production under clean vacuum conditions, Report 27, Balzers AG, Balzers, Liechtenstein

[19] K. Höfler: Proc. 5th Int. Coll. on Plasma and Sputtering (CIP 82), Nizza 1982, special issue of "Le Vide, les Couches Minces" (1982)

[20] W.K. Huber, U. Wegmann and L. Wellerdieck: Proc. 8th Int. Vac. Congress, Cannes 1980, special issue of "Le Vide, les Couches Minces" Vol.2 (1980) 542

[21] M. Spiteler und G. Spiteler: Massenspektrensammlung von Lösungsmitteln, Verunreinigungen, Säulenbelegmaterialien und einfachen aliphatischen Verbindungen, Springer Verlag, Wien/New York (1973)

[22] R.W. Dennison, Solid State Techn. 23.9 (1980)