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MEASUREMENT OF PARTIAL PRESSURES IN VACUUM
TECHNOLOGY AND VACUUM PHYSICS

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16. Abstract A few selected problems of partial pressure analysis are discussed: the necessary reciprocal action measurement, condition of the vacuum system, and the need for partial pressure measurement. A description is given of ion sources, ion detection, and separation systems. It is concluded that partial pressure measurements can provide valuable information only when the weaknesses and potential for error of this system are taken into account.			
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Summary

A short review on problems concerning partial pressure measurements is given. First, a number of examples show why and how to use mass spectrometry in the field of pressure measurement. The possible modes of interaction measurement — residual gas composition are discussed. Specific features of the modules ion source, analyzer and ion detection system required for partial pressure analysis are compared.

Introduction

It is not the intention of this article to give a complete survey of all the types of problems for which partial pressure measurement can be used. Several authors [1] have published detailed descriptions of the use of all kinds of simple mass spectrometers, in partial pressure measurement. We will discuss here only a few selected problems of partial pressure analysis: the necessary reciprocal action measurement - condition of the vacuum system, and the urgent need for partial pressure measurement.

Total pressure measurement - partial pressure measurement

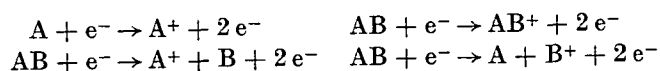
In most cases the need for partial pressure measurement arises when one wishes to obtain not only qualitative information on the total pressure in a vacuum system but also information as "how much of what" one has. Partial pressure measurement at pressures of less than 10^{-4} tors is essentially always done indirectly via ionization of the gas atoms and molecules by electronic impact. Actually one is not measuring the pressure p but the particle density n ; these two values are connected by the relation $p = n \cdot k \cdot T$ (k is the Boltzmann constant, T the absolute temperature). In recent years there has been more and more discussion as to whether or not it would

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make more sense, particularly with respect to better vacuums, to characterize the condition not by the historic measurement of the partial pressure but by measurement of the particle density.

Let us return, however, to ionization. When ionization occurs as the result of electronic impact, the following decomposition schemes are possible:



The decomposition schemes shown represent only the simplest possibilities. In addition to the atom and molecule ions, numerous charged species also occur.

The number I^+ of the ions formed is $I^+ = I^- \cdot l \cdot n \cdot Q$

whereby I^- is the number of colliding electrons, l the length of the electron paths, n the particle density and Q the total ionization cross-section. I^- and l can be kept constant. The number of ions is then proportional to the particle density (i.e. to the pressure) and the ionization cross-section Q . On what does the value of Q depend? Q depends on the energy of the colliding electrons and also the type of gas. The ionization process begins at a minimum acceleration potential that is characteristic for the type of gas, the so-called appearance potential of the electrons. If the electron energy is increased, then the ionization cross-sections rapidly become greater and reach a flat maximum between 50 and 150 eV. After higher energies are reached, the cross-sections become smaller again. In order to achieve as high a yield as possible (i.e. the highest sensitivity), one normally works with electrons from 70 to 100 eV. The different levels of the maximums in this range have only a slight effect. However, the various types of gases make a great deal of difference. If one looks at the total ionization cross-sections of various gases and vapors [2], one finds that the values are distributed over a range of almost two orders of magnitude.

Table 1. Total ionization averages.
 ($Q 10^{16} \text{ cm}^2$, electron energy 75 eV)

He	0,38	H ₂	1,2	H ₂ O	3,0
Ne	0,61	N ₂	2,9	CH ₄	4,6
Ar	3,5	O ₂	2,5	C ₂ H ₆	8,3
Kr	5,2	CO	3,0	n-C ₆ H ₁₄	22,3
Xe	7,3	CO ₂	4,3	C ₆ H ₆	16,9

It follows from the values in the table that in extreme cases the true pressure in a vacuum system may suffer uncertainty by a factor of the order of 50 or 100, if the type of gas is not known. Therefore, normally one gives pressure data as the nitrogen equivalent pressure; i.e. one acts as though all the gases present possess the ionization cross-section of nitrogen. Only if one knows the type of gas, or in the case of gas mixtures, the percentage distribution of the different types of gases, is one in a position to determine the exact total pressure with an ionization vacuum meter. Thus arises by necessity the need for partial pressure analysis. /323

The question of the partial pressure composition is of basic importance in many problems posed in vacuum technique and physics. One needs only to look at the simple technical case of a vacuum system. Which factors determine the equilibrium pressure reached: leaks, or diffusion through the walls, gas exhaust through the walls and fittings, or the final pressure of the pump itself? All these questions can be answered quickly and reliably by means of partial pressure measurement.

Figure 1 shows a characteristic example. A vaporization system is pumped with a combination of various pumps (turbo-molecular pump, nitrogen-cooled surface and titanium sublimation pump) [3]. The contributions of the various pumps can be seen clearly. It is easy to see that water vapor is pumped by the cold surface, but not air. However, the remaining air is pumped out in the third phase by means of sublimated titanium with a high suction capacity.

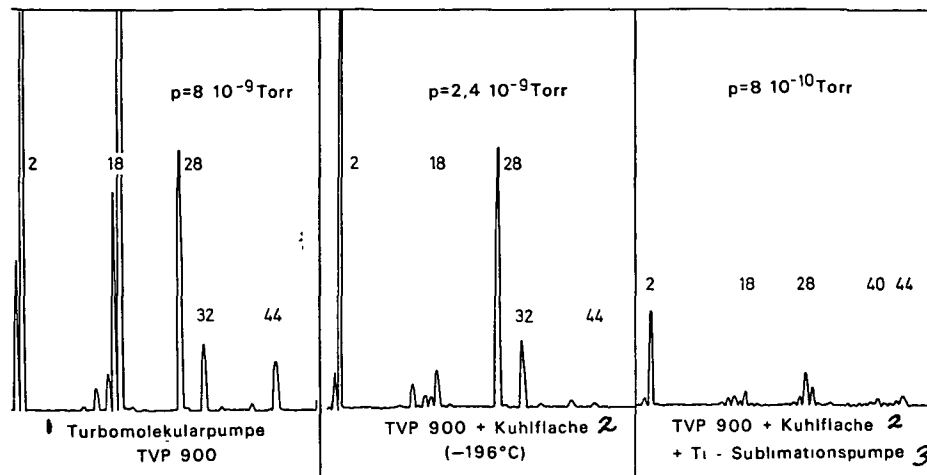


Figure 1. Residual gas composition in a high vacuum vaporization system (BAK 550).

a) turbo-molecular pump, b) supplemented by: cooling surface, -196°C , c) supplemented by: titanium sublimation [3].

Key: 1 turbo-molecular pump; 2 cooling surface; 3 sublimation pump.

In the case of gases pumped by means of the action of ion pumping (ion pumps, ionization vacuum meters), the familiar memory effects may occur. Gases already pumped are partially released again when other gases are admitted. These processes have been studied in particular by Carmichael and Trendelenburg and by Brown and Leck [4]. Figure 2 shows an example from actual practice: how previously pumped argon and hydrogen are released in an ion getter pump when nitrogen is admitted. Total pressure measurement would suppress this effect.

In order to ensure that an oil-free vacuum is produced for ion getter pumps, sorption pumps are frequently used. A molecular sieve cooled by liquid nitrogen is used as the adsorption agent. Vacuums up to 10^{-5} torr are possible with multi-phase pumps. These levels can only be achieved, however, when the pumps do not pump simultaneously, but are switched on and off in sequence and at certain pressures. If one follows the gas composition one can see that, in the case of single-phase pumps (or corresponding parallel operation of several pumps), a considerable percentage of the residual

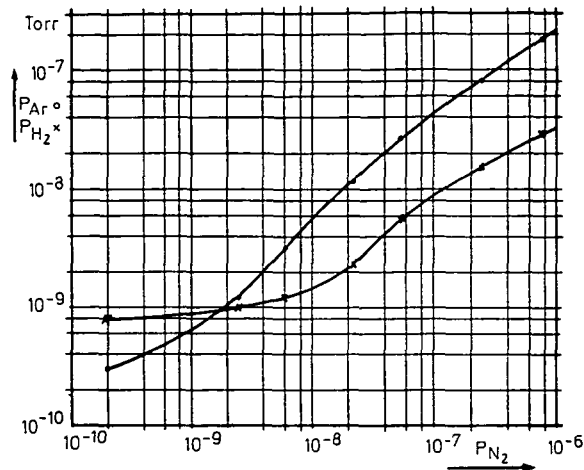


Fig. 2. Memory effect of an ion getter pump when nitrogen is admitted.

gas consists of the light inert gases neon and helium that are present in the air in the [amount] of about $10^{-3}\%$. However, these are gases that are poorly pumped at high pressures by ion getter pumps (starting problems). If one makes sure that general evacuation occurs rapidly up to a few [torr] by means of a sorption pump, which is then switched off, one will thus achieve a clear pumping effect by means of the carry-over effect in the laminar flow between [recipient and pump], even for light inert gases.

In the case of vacuum processes the gas composition is often of decisive importance for the optimum functioning of the process. For example, if one ignites niobium in an ultra-high vacuum while adding oxygen [5], the carbon contained in the niobium is oxidized to CO. At predetermined temperatures an optimum level for the oxygen pressure is produced by the diffusion rate of the carbon in the niobium. Since, however, CO is formed at the same time, it is sensible to monitor the partial pressures with the mass spectrometer.

The highest demands are placed on the vacuum in particle accelerators and accumulator rings. For example, the protons need to be kept for long periods (days) in the proton accumulators and also the beam cross-section should be kept as small as possible. This means that residual gas losses resulting from scattering must

be held at a correspondingly low level. Fischer [6] gives data on the mass ratio of Coulomb multi-scattering for proton accumulator rings for the CERN. At the same partial pressures nitrogen contributes 50 times more than hydrogen to multi-scattering and argon 150 times more.

These few arbitrarily chosen examples should serve to document the importance of partial pressure analysis. To give a complete catalog of all the important applications would exceed the scope of this article. We will mention here just a few key words: adsorption-desorption measurement, diffusion analyses, exhaust data, vaporization and molecular beam experiments, gas levels in electron tubes, and, last but not least, the broad field of the physics of the upper atmosphere and space research.

Effects of partial pressure measurement on the state of the vacuum system.

The first question is one that is of basic importance to any measurement: How is the state of the system itself altered by measurement? The objective is not to allow the measurement to change the original state at all if possible, but to measure it in its original and reproducible form, or at least to permit the original state to be reconstructed from the measurement data.

Let us first look at the mass spectrometer as a whole, without going into the individual function elements. Depending on the type of instrument and the form of construction, an additional surface of several 20 to several 100 cm² is added to the vacuum system by the spectrometer. Whether this additional source of gas exhaust, adsorption or desorption has a noticeable effect on the gas level in the system or not depends largely on the type of vacuum system. For example, if one takes a large ultra-high vacuum system with pumps with a high suction capacity, then the contribution of the measurement system can essentially be disregarded.

However, the conditions are quite different in small glass systems. Since their suction capacity is at the most a few liters per second, it is difficult to stop a change from occurring. In this case, de-

spite other limitations, we find that the omegatron works well; it was already used by Alpert and Buritz [7] in the first UHV systems. With its small surface area and the small electron flow required, it is still extremely useful. It is intended not so much for technical application, i.e. for the engineer, as for researchers and laboratory scientists. Two improvements made in the last ten years have contributed significantly to the actuality of the omegatron. Klopfer [8] replaced the customary molybdenum electrodes with electrodes made of precious metal. Gentsch [9] went one step further by providing the electrode system made of platinumiridium with supplementary heaters made of platinumiridium; this meant that the entire measurement system could be operated during measurement at about 400°C, in order to eliminate memory effects.

As an alternative solution we should look at the three-dimensional quadrupole or ion-cage first described ten years ago by Paul, Osberghaus and Fischer [10]. Rettinghaus has shown [11] that with this mass spectrometer partial pressures of up to 10^{-13} torr can be measured. In recent years, Dawson and Whetten at General Electric have worked very hard on the three-dimensional quadrupole. In addition to several effective systems, Dawson, Hedman and Whetten [12] have developed a very simple version of the ion cage made of stainless steel lattice. In spite of the fact that the lattice system was only formed by hand, they achieved a resolution of 75 (relative to half value width) and a detection limit of about 10^{-12} torr. In this instance only the ions from one mass are accumulated. After a predetermined accumulation period (equal to the ionization period), the stable ions are accelerated by a potential impulse from the ion cage into the open multiplier and measured there. During this detection period the emission of electrons is blocked. Thus the X-ray underground in the multiplier resulting from the blocking of the electrons is inhibited. Except for the multiplier used, the measurements taken with this system are entirely comparable with those made with an omegatron. However, the three-dimensional quadrupole does not require any magnet (adjustment problems, magnetic disturbance fields) and can therefore also be built as an immer-

/326

sion model. The twelve-phase multiplier used in these studies can be replaced by a channel multiplier with a much smaller surface area.

Following these more general ideas, the individual function elements of the mass spectrometer can now be examined for the possible forms of their effects. The three elements will be mentioned briefly here again: 1. ion production (ion source), 2. separation of ions according to their charge/mass ratio (spatial or temporal), 3. ion measurement. We will not go into the many possible types of mass spectrometers here that can be and are used for partial pressure measurement. All that needs to be said is that, besides the omegatron mass spectrometer, which is used in research and to study the residual gas conditions in electron tubes, in practice it is mainly the various sector field types and the quadrupole mass spectrometer that have taken over. There is no doubt that the ion source exerts by far the greatest effect on the condition of the vacuum system. The separation systems also demonstrate their specific peculiarities, of course, but in general these are reproducible and thus can always be eliminated as an integral component of mass spectrometer measurement. As far as ion measurement is concerned, there are again effects that cannot be controlled directly.

Ion sources

327

Two groups of effects can be distinguished in connection with the ion source: 1. the direct effect on the state of the vacuum resulting from the gas exhaust from the hot cathode, and 2. secondary effects in the ion source that may produce erroneous information on the state of the vacuum system.

Let us look first at point 1. Electrons are emitted from a hot cathode. Rhenium, wolfram-3%-rhenium, wolfram, thorium oxide on iridium, lanthane-hexaboride on rhenium, and oxide cathodes are used as cathode materials. The emission of electrons is highest for rhenium and lowest for oxide cathodes. If the dimensions are otherwise the same, rhenium requires the highest operating temperatures and special oxide cathodes the lowest. The choice of cat-

hode material depends on a number of factors which almost always means that a compromise solution has to be reached. For example, rhenium, with its higher operating temperature, demonstrates a clearly measureable rhenium partial pressure. On the other hand, however, it does not have the property of wolfram of being able to form stable carbides. Wolfram carbide produces good emission levels but it is correspondingly more reactive. If hydrocarbons are present, carbon-free wolfram forms wolfram carbides which then react again in the presence of oxygen or water vapor, forming CO. Thoriated cathodes work at temperatures of 1500°C, while lanthanum-boride and oxide cathodes work at 1000°C and below. However, the last three types mentioned demonstrate other limitations that restrict their range of applications. Some of them are not stable to the entry of air and they also mostly show a background resulting from direct ion emissions.

When deciding the dimensions of the cathode it is also important to select the degree of heat output, as it is almost entirely this output that causes the ion source to heat up. In order to avoid adsorption effects it is sensible to choose the heat output so that the ion source parts are exposed during operation to temperatures of about 200-300°C. However, the operating temperature should always be lower than the heating temperature, so as to prevent excessive outgassing from the ion source. These outgassing effects are especially critical in the case of closed ion sources, as a definite differential pump effect can occur.

What can be anticipated in the future in the field of electron emission? There are a number of suggestions for "cold electron emitters", which have also already been tested in the laboratory. The first group utilizes secondary electron multiplication on surfaces, while the second group makes use of effects of transition layers in semi-conductors. Baumgartner [13] used open secondary electron multipliers as the electron source for a modified Bayard-Alpert tube. The electrons were released by UV light on the first dynode of a CuBe multiplier and then intensified. It was no problem to produce electron beams of 1 mA. However, for mass spectrometer ion sources one requires electron emitters that take up less space and above

/328

all produce higher beam densities. Sprouse and co-workers [14] used a form of construction found in channel multipliers. A quartz capillary 20 mm long with a 2 mm bore and gold contacts on the ends is coated on the inside with a conductive tin oxide layer. A current of several hundred volts is passed along this layer and this produces electron flows up to about 100 μ A. Other methods for cold emitters have also been suggested (Al-Al₂O₃-Au; SiCu_{np} layers). However at present the beam densities achieved and the reliability of the system are not yet high enough to use these types of cathodes in practice.

Let us follow the electrons emitted by the cathode further. After being accelerated and focussed they cross the actual ionization area. There they enter a reciprocal action with the residual gas and form the ions that will then be analyzed.

But what processes occur when the electrons finally land on the receivers or the walls of the ion source? Adsorbed foreign layers may be converted to another adsorption condition, desorbed, cracked or polymerized by the electron bombardment. The last two processes cause contamination of the ion source as a result of conductive or isolating layers. However, in the case of desorption by electrons, the conditions become more complicated, especially in an ultra-high vacuum. A number of species such as H₂, O₂, H₂O, CO, F, Cl, Na and K demonstrate, if they are adsorbed on the surfaces and these surfaces are bombarded with slow electrons, an obvious ion desorption. This means that one has to be very careful when interpreting the spectrum, since not only the desired information from the gas phase of the vacuum system is delivered but also sometimes a considerable amount of adsorption layers. Redhead [15] and Hobson [16] have thoroughly studied the ion desorption effects, particularly in connection with ultra-high vacuum measurement tubes. The following is a greatly simplified but essentially accurate description of the process: In a state of equilibrium an equal amount of gas is desorbed and adsorbed by a surface bombarded with electrons. Some (about 10⁻²) of the desorbed gas is desorbed as positive ions. Then the following is true:

$$I_0^+ = v \cdot s \cdot F \cdot e \frac{Q_0^+}{Q_T^+} \quad I_G^+ = k \cdot I^- \cdot p \quad \frac{Q_0^+}{Q_T^+} \approx \text{const.} \quad v \sim p \quad \frac{I_G^+}{I_0^+} \sim \frac{k \cdot I^-}{s}$$

whereby I_0^+ = the surface ion flow
 v = the impact rate of the gas type used
 s = the probability of adhesion
 F = the surface
 e = the charge
 Q_0^+ = the cross section for ion desorption
 Q_T^+ = cross section for total desorption
 I_G^+ the ion flow from the gas phase
 k = the sensitivity for gas phase ions
 I^- = electron flow
 p = the corresponding partial pressure

It is easy to deduce from the above equation that, if the other conditions remain the same, the ion desorption effect can be kept relatively low by high sensitivity, large electron flow and a low adhesion probability. Davis[17] gives a very impressive example. He measures the residual gas composition in an ultra-high vacuum system using a 90° sector field mass spectrometer. The total pressure is $3 \cdot 10^{-13}$ |torr| and he finds surface ions mainly on the masses 1, (H^+), 10 and 11 (B^+ because of LaB_6), 16 (O^+), 19 (F^+), 23 (Na^+), 35 and 37 (Cl^+) and 39 (K^+). Then the normal ion source was replaced with a magnetron ion source with a hot cathode. Figure 3 shows the mass spectrum at $2 \cdot 10^{-13}$ |torr| together with the "Normal spectrum". Thus the residual gas is composed of H_2 , CO , CO_2 and CH_4 .

/329

Another source that influences the signal-background relationship when measuring ions is the soft X radiation that is released when electrons land on surfaces of the ion source. Particularly when measuring ions with a multiplier, under extreme conditions a direct sight connection between the ion source and the conversion dynode must be avoided (off-axis arrangement of the multiplier).

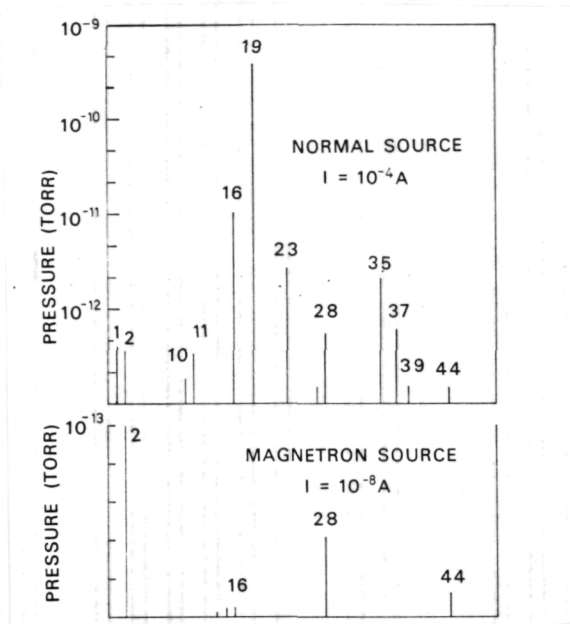
So how should an ion source be designed? Naturally it should first of all demonstrate as high a sensitivity as possible. Relative to its sensitivity, the ion source must always be evaluated in conjunction with the separation system, since ions formed in the ion source that cannot be processed by the separation system

contribute nothing to effective sensitivity. High sensitivity is also a contributing factor for the detection limits and, as was shown above, for the relative contribution made by surface ions. The surface ions can be largely eliminated if one allows a sharply bundled electron beam to hit only those surfaces of the ion source that are arranged in such a way that ions released there cannot get into the entrance opening of the mass spectrometer. Since the surface ions always occur with an initial energy of up to several eV, they appear on the mass scale of direction-focussing mass spectrometers (e.g. sector field) in displaced positions corresponding to their energy and they can thus be identified. In the case of the quadrupole mass spectrometer, which does not demonstrate this energy dependence, Huber and Rettinghaus [18] have shown that the surface ions can be distinguished from the ions from the gas phase as a result of being able to carry out an energy analysis of the ions using the field axis potential of the quadrupole system. If one accepts the surface ions as a necessary evil, they do at least give additional information on the state of the surfaces of the vacuum system.

Another suggestion for avoiding both the effect of the hot cathode and ion desorption and the X-ray effect has been made by Blauth [19]. He proposes a two-chamber ion source in which both the cathode with its focussing electrodes and the electron collector are housed in a separate vacuum system. The electron beam crosses the ionization space through two opposing holes and collides with the residual gas but not with the wall. In this way both effects can be prevented, the reaction on the hot cathode and the formation of surface ions. Of course, the vacuum conditions in the supplementary system have to be at least as good as in the measurement system.

The design and structure of the ion source are further factors that are of great importance for the reliability of the partial pressure measurement. The ionization space should have as open a structure as possible, so that it can rapidly and accurately attain a state of equilibrium with the surrounding atmosphere. A largely closed ionization space can lead such a strong life of its own that no sensible information can be expected from it. This requirement

/330



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Fig. 3. Comparison of residual gas spectra under extreme ultra-high vacuum conditions ($2-3 \cdot 10^{-13}$ tors), a) conventional ion source, b) magnetron ion source [17].

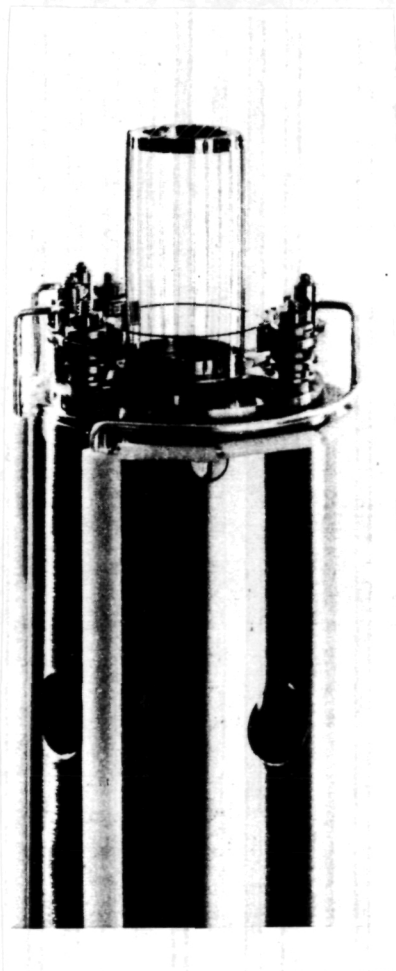


Fig. 4. Quadrupole mass spectrometer with lattice ion source for measurements under extreme UHV conditions.

naturally extends to include the entire ion source. If the ion source is connected to the vacuum system via a connecting pipe, then it is possible, especially in the case of higher molecular vapors, but also with water vapor, that serious falsifications of the actual residual gas composition may be measured as a result of the Blears effect [20] and the pump effect of the ion source. Figure 4 shows a design constructed with consideration given to the points made above - open ion source with lattice structure, which is immersed freely in the vacuum system being studied. This ion source can easily be de-gassed like a Bayard Alpert tube by means of electron bombardment; it shows almost the theoretically possible conductance towards the vacuum system and it possesses the additional property of good discrimination relative to surface ions and X-ray effect.

/331

Separation systems

We will not go into the broad field of separation systems. Only a few brief remarks on the problem of the resolution capacity-sensitivity are needed. In the case of the sector field mass spectrometer with the 60 or 90° diffraction and mass flow by means of variation of the magnetic field force, the conditions are very clear. A given resolution capacity and sensitivity can be achieved with ions that come through the entry aperture out of the ion source within a predetermined angle α to the axis with a permissible energy homogeneity ΔE . The resolution capacity and sensitivity remain constant over the entire measurable mass area. This assertion already has no further unlimited validity if, in the case of a constant magnetic field (permanent magnet) the mass flow occurs by means of variation of the acceleration potential.

The situation is different, though similar, in the case of the quadrupole mass spectrometer. As in the other case, if certain initial conditions are provided, one can also ensure here that all the ions of a certain e/M shot into the separation field pass this field. Given a predetermined resolution capacity, then a certain sensitivity is present here also. The studies of Brubaker [21] contain a number of examples of experimental confirmation of these facts. Of course, in most practical cases the quadrupole is not

operated at 100% transmission. Even in these instances, the resolution and sensitivity can be kept constant. However, the quadrupole mass spectrometer possesses an additional interesting operation possibility: it is not the resolution capacity $\Delta m/m$ that is kept constant, but the line width Δm , which is far more useful. Then, for example, for $\Delta m = 1$ equidistant, one gets equally wide mass lines over the entire mass area, and not, as is otherwise normally the case, extremely narrow lines and large intermediate spaces for small masses; resolved peaks do not occur until $m = m/\Delta m$. If one records the spectrum at a constant flow rate and $m/\Delta m = 100$, then at mass 10 one gets information only during 10% of the flow period and at mass 1 during only 1% of the time. On the other hand, the conditions with the quadrupole seen in this light, are almost ideal. There is, however, one other disadvantage that one has to accept. Constant Δm means nothing more than a resolution capacity growing proportional to m . If one is not working in the 100% transmission area, then naturally the sensitivity decreases with growing resolution. However, this fact can be adjusted for as a mass-dependent change in transmission.

Ion detection

/332

There is little to be said about the simplest but surest form of ion detection, namely capturing the ions on a Faraday collector and measuring the flow with a sensitive electrometer. At realistic time settings (about 1 sec) flows of 10^{-14} can be measured (at time constants of several 10 seconds, even flows up to several 10^{-16} A). It should be emphasized again that this simple and reliable method of ion detection cannot be recommended strongly enough, especially in vacuum systems where one normally has to analyze slow processes.

If, however, one has very rapid processes or extremely low intensities to measure, then one can use the secondary electron multiplier as an extremely fast and sensitive amplifier. We will not go here into the individual types of multipliers, but more into the principal problems. The method is almost always the same.

The separated ions are re-accelerated (2-30 kV) and then meet a conversion electrode. There they release secondary electrons. These secondary electrons can be processed further in two different ways. Either they are amplified in an open multiplier structure, or they are re-accelerated onto a scintillator, where they release light impulses that are detected by an externally located photomultiplier. The advantage of this second method is that the multiplier itself can be kept under a vacuum. In both cases the amplification is between 10^4 and 10^8 times. The primary ion energy must be high enough to ensure that every arriving ion releases at least one and preferably several secondary electrons. If this is the case, then at the exit of the multiplier one gets one charging impulse per arriving ion. For the further processing of the signals coming out of the multiplier there are again two alternatives. In the simplest case one measures the flow that strikes the collector electrode of the multiplier. One has to adjust for the fact that the number of secondary electrons released per ion on the first dynode depends on the type of ion. One has to take into account several effects that are difficult to control and, if one wants to be certain, one needs to repeat the adjustment periodically. Petermann [22] has published the values for hydrogen, CO and CO₂; these do not fit into the theoretical concept of the process. Lao [23] finds, in his study of a 17-phase copper-beryllium multiplier, that for some of the atomic ions of the periodic system amplification produces only moderate correspondence with the theoretical values. The differences in sensitivity are less than theory predicts.

If one counts the individual ion impulses one can eliminate almost all of the problems described in the last section. The potential impulses generated at the exit of the multiplier by the charging impulse are amplified if necessary by a pre-amplifier. These impulses are then passed to an impulse height discriminator phase, which only passes on impulses above a certain minimum size. By means of further amplification and impulse formation, unit impulses then appear at the exit that can either be counted or can be integrated. As Werner [24] showed, the background can be reduced by the choice of the discriminator threshold.

/333

Table 2. Relative sensitivities of a 17-phase CuBe multiplier for atomic ions of 5.1 keV [23].

—	—	—	H ¹	0,669	He ⁴	0,997			
C ¹²	1,036	N ¹⁴	1,164	O ¹⁶	1,224	F ¹⁹	1,083	Ne ²⁰	1,226
Si ²⁸	0,909	P ³¹	0,940	S ³²	0,926	Cl ³⁵	0,951	Ar ⁴⁰	1,000
Ge ⁷²	0,590	Ag ⁷⁵	0,578	Se ⁷⁶	0,675	Br ⁷⁹	0,626	Kr ⁸⁴	0,733
Sn ¹¹⁶	0,524	Sb ¹²¹	0,494	—	—	I ¹²⁷	0,567	Xe ¹²⁹	0,650
Pb ²⁰⁶	0,400	—	—	—	—	—	—	—	—

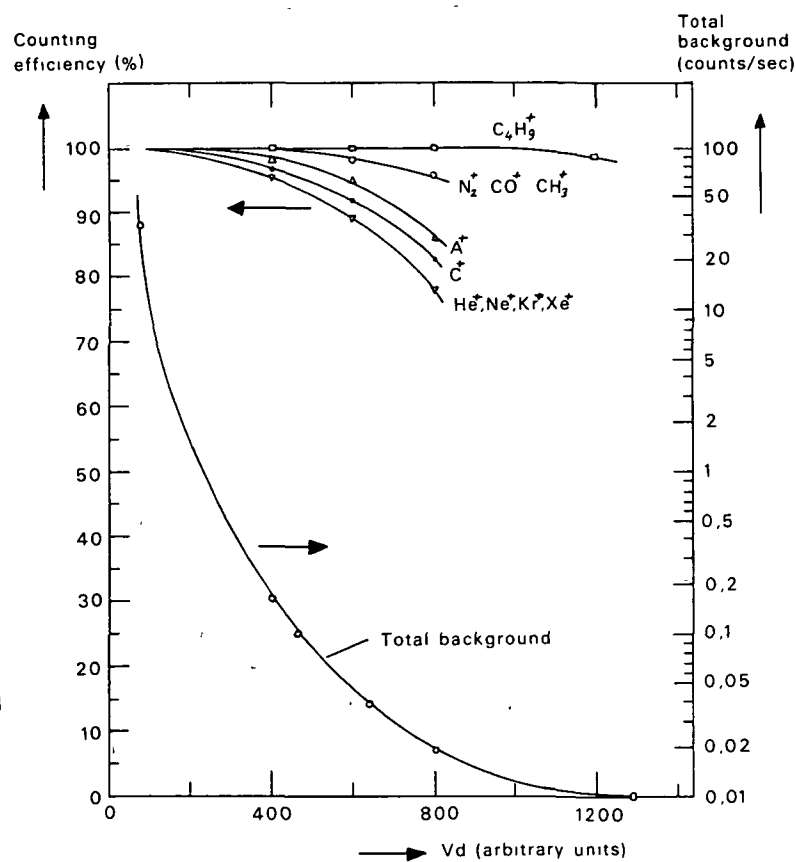


Fig. 5. Counting efficiency and background for an ion-electron converter [24].

Sometimes, however, some counting losses have to be accepted. When ions are being counted, a change in the multiplier amplification is much less noticeable than when the multiplier is being used in normal operation. In this way one can achieve stable conditions for ion measurement. After higher intensities ion counting is mostly limited by electronic dead times. Normally the highest one can go is to counting rates of several MHz. But this corresponds already to ion flows of 10^{-12} and does not represent any further problem for direct flow measurement.

At the conclusion of this section mention should be made of statistical error. It is known that the percentage statistical error is $100/N$, N being the number of occurrences. If one looks at a partial pressure of 10^{-12} torr, a sensitivity of 10^{-4} A/torr and a measurement time of 1 second, then the statistical error will be 4%. At 10 msec it will already be 40%. This means that when measuring very small pressures one needs to take into account the possible statistical error. Improvement of the detection method does not help here, only increasing the measurement time or achieving the highest possible yield from the ion source, which has already been mentioned in the chapter on ion sources.

Conclusion

Finally the question should be discussed: Up to what pressures is partial pressure measurement sensible? The current status of technology has made it possible to measure partial pressures of 10^{-16} torr and even lower, with correspondingly laborious measurement procedures and long measurement times. These extreme values are only of interest, however, for molecular experiments. Naturally measurement provides information on the conditions in the ionization area. However, the question immediately arises as to whether this value is representative of the state of the entire vacuum system. This can certainly not be answered unequivocally, for an isotropic distribution of the residual gases is definitely no longer assured in vacuum systems that operate at pressures below 10^{-9} torr and where processes normally take place. One needs to take into account local gas sources as well as local and selective pump effects. This

essential limitation does not, of course, result from any possible restrictions of the effectiveness of the partial pressure analyzer, but it should be taken into account when one is interpreting the results.

In summary, it can be said that partial pressure measurement can provide valuable and necessary information on the condition of a vacuum system and the processes taking place in it, as long as one is familiar with the weaknesses and potential for error of this measurement system.

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/335

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