

MASS SPECTROMETRY

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Radio-frequency Mass Spectrometers and their Application

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I. Introduction

When ions of mass m are accelerated by a voltage U , then their velocity v is given by

$$v = \sqrt{\frac{2eU}{m}} \quad (1)$$

(e = elementary charge).

According to this equation, the velocity is dependent on the mass. Thus, ion separation can be achieved by projecting the ions through electrical fields which are rapidly changed in such a way that only ions of a certain flight speed can pass while the flight is blocked to ions of different flight speed. A further possibility of ion separation is to make the ions oscillate in an electrostatic potential well, i.e. between suitably shaped electrodes to which d.c. or r.f. voltages are applied. The frequencies or amplitudes of these oscillations are dependent on masses.

To sum up, there are two principles: ion separation by time-of-flight (TOF) effects or that by oscillations in a potential well. It should be noted that this is a slightly simplifying statement. It is not always possible to assign a certain type instrument clearly to one or the other of the two categories. Moreover, there are still other possible ways to separate ions by applying electric r.f. fields.

Shown in Fig. 1 are those r.f. spectrometers which are in general use today. Their principles and applications will be discussed here. The instruments marked with (L) are linear, those marked with (M) have circular paths and need consequently, an additional magnet. Linear mass spectrometers are of interest in practice not only because of their lower weight since no magnet is required; other arguments in favour of this type of instrument are the simplicity of construction, the high flexibility, or the fact that with most types the cross-sections of the ion

beams are not confined for ion-optical reasons by narrow object, image or aperture slits. The simplicity of the linear construction permits one to place the analyser close to a reaction chamber which is important for the investigation of rapid chemical reactions such as explosion processes. In some cases, the light linear construction also allows the moving of the entire analyser during the measurement. This could be required for the mass spectrometric detection of molecular beams. Other typical applications are: Partial pressure analyses of residual gases, upper atmosphere studies, identification of free radicals and high-temperature chemistry studies.

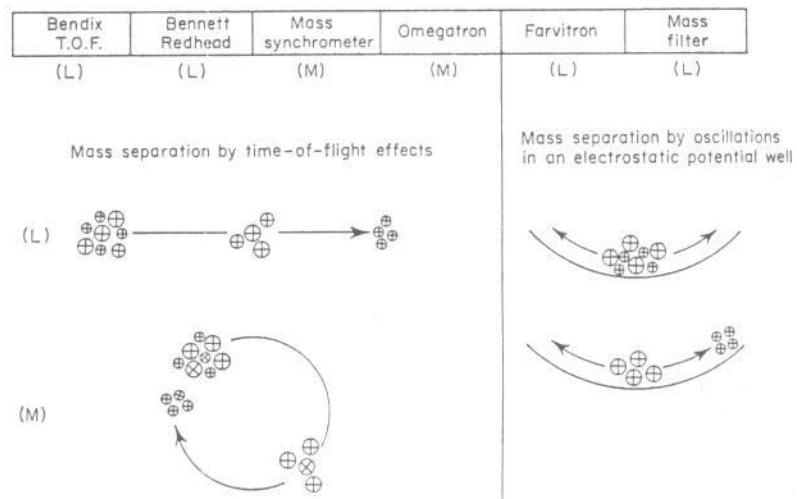


FIG. 1. Various types of r.f. mass spectrometer in general use. L, Instruments with linear ion path; M, instruments with circular ion path (additional magnet required).

A disadvantage of all r.f. instruments as compared to the corresponding sector field mass spectrometers is the more complicated electronic system. Thus, savings in mechanical construction might be offset by increased expenses for the electronic equipment.

Besides the 6 types listed in Fig. 1 there exist quite a few others, which have, however, not gained considerable importance in practical application up to now.

II. Bendix Time-of-flight Mass Spectrometer

The principle, first applied by Cameron and Eggers⁽¹⁾ in 1948, investigated in detail, and considerably improved by Wiley and McLaren⁽²⁾ in 1955, is as follows. The ions produced by electron bombardment are drawn out of the ion source by a short voltage pulse in the μ sec range,

are then accelerated at projected as a bunch through the field-free drift tube of 1-2 m length (Fig. 2). By specific arrangement of the grids in the acceleration region of the ion source and by a draw-out pulse of a suitable value, as Wiley has shown, ions of the same mass but with slight differences in initial position can be made to converge during their flight and reach the collector plane simultaneously. Ions of different mass are separated because the velocity is mass-dependent according to equation (1). Light ions arrive at the end of the drift tube first and then the heavy ones. By means of a secondary electron multiplier and a wide band amplifier, the ion pulses separated according

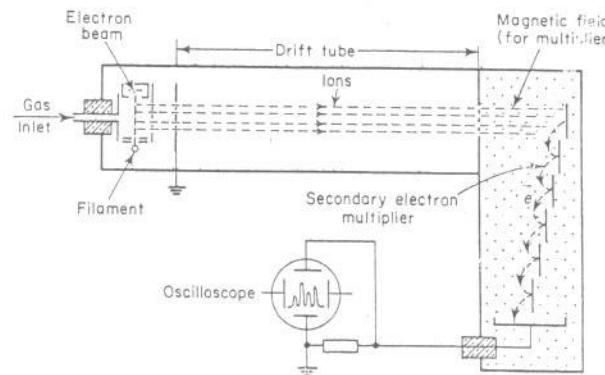


FIG. 2. Schematic view of a Bendix TOF mass spectrometer.

to masses and having a width of about 50 μ sec are amplified and fed to the oscilloscope. The horizontal deflection of the oscilloscope is synchronous with the repetition rate of the ion draw-out pulse. This is usually 10 kc/s so that 10,000 complete mass spectra per second can be obtained on the scope.

To use a pen and ink recorder, the ion pulses must be integrated with an analogue output system. In this system, an electronic gate to the integrator is opened briefly, after a certain time-of-flight characteristic of a certain ion mass. The entire spectrum can be scanned by shifting the gate on the time axis according to the different flight times of the various masses. By using a multiplier with several outputs, e.g. six, the simultaneous recording of six different components is readily effected.

Some details with respect to ion production are interesting. Until 1962, the ion source of this instrument was usually so operated that first an ion bunch was produced by a very short electron pulse of 0.25 μ sec duration. Lately, Studier⁽³⁾ has demonstrated that operation with a continuous electron beam is also possible. The continuously produced ions are trapped in the ionization chamber by the negative space charge of the electrons until they are accelerated by the draw-out

pulse. Since, in this method of operation, one has continuous ionization (instead of an ionization of $0.25 \mu\text{sec}$ duration as before), a considerable increase of sensitivity could be achieved.

The performance data of an instrument with a drift tube of 1.80 m length are: resolution $M/\Delta M \approx 300$; mass range up to 1500 u; detection limit 10^{-12} torr. The characteristic advantages of such TOF instruments are: The extraordinarily high recording speed, the flexibility

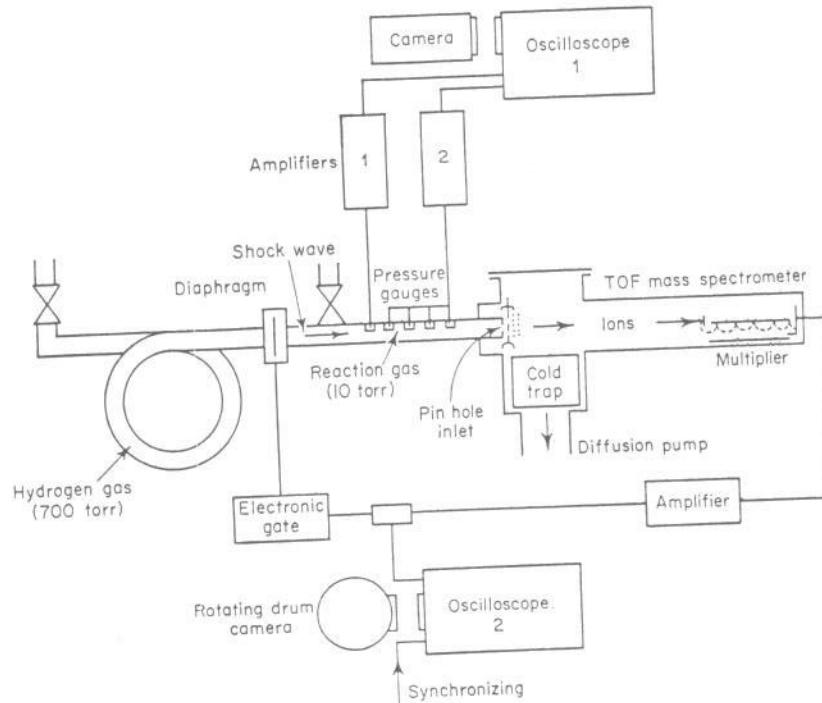


FIG. 3. Arrangement of Bradley and Kistiakowsky⁽⁴⁾ for study of reactions in shock waves.

and the simple mechanical construction. The ion source region is easily accessible so that molecular beam devices can be connected. With respect to measuring accuracy, sector field mass spectrometers are superior to TOF instruments.

These TOF instruments are widely used for studies in the field of chemical physics. Figure 3 shows the experimental arrangement of Bradley and Kistiakowsky⁽⁴⁾ for the investigation of rapid reactions in shock waves. The shock tube contains the reaction gas, N_2O in this case, under a pressure of about 10 torr. After piercing of the membrane which closes the shock tube, the hydrogen gas which is in the left tube under atmospheric pressure will expand, and a shock wave will be

formed. On the front of the reflected shock wave a high temperature is generated which leads to thermal decomposition of the N_2O . The reaction products enter through a pinhole inlet into the ion source of the spectrometer and can be analysed every $100 \mu\text{sec}$, i.e. with a frequency of 10 kc/s. To the analyser tube a pumping system of very high suction capacity is connected to obtain a small time constant for the

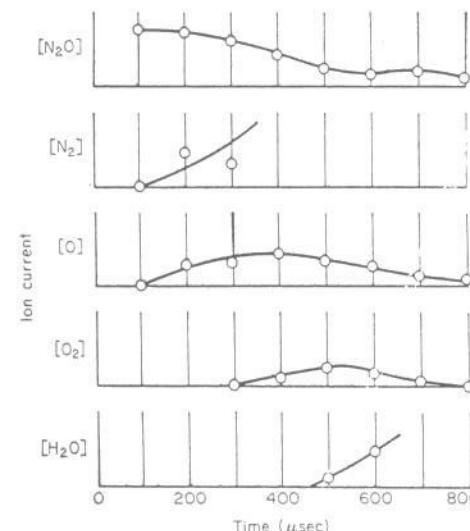


FIG. 4. Results of shock wave studies.⁽⁴⁾

gas flow. The ion currents are recorded by an oscilloscope and a rotating drum high speed camera. Typical results of the shock-wave experiments are plotted in Fig. 4. The curves show the decrease of concentration of the initial compound N_2O and the increase of the concentration of the various decomposition products with time.

III. Bennett-Redhead-type Instruments

In 1950, Bennett⁽⁵⁾ described a r.f. mass spectrometer which is shown in Fig. 5(a). The ions produced by electron bombardment are accelerated through a voltage U and pass the first stage of the spectrometer, which consists of the three grids G_1 , G_2 , G_3 . These grids are distant d from each other and are at the same potential. In addition, a r.f. voltage is applied to the centre grid G_2 . Thus, the ions between grids G_1G_2 and grids G_2G_3 are either accelerated or retarded, depending on their velocity v , on the frequency f of the applied r.f. voltage and on the amplitude of the r.f. voltage in the instant the ions pass through the grids (phase angle). The ions can take up maximum energy when they

meet with an accelerating half-wave of the r.f. voltage between the grids G_1G_2 and the grids G_3G_4 as well. This is the case when the mass-dependent time of flight d/v of the ions between the grids is equal to the duration $1/2f$ of a half-wave of the r.f. oscillation: $d/v \approx 1/2f$. A more exact calculation taking into consideration the optimum phase angle, leads to the condition

$$\frac{d}{v} = 0.74 \frac{1}{2f} \quad (2)$$

The phase angle must be so that the r.f. voltage reverses its polarity at the moments the ions pass the centre grid. Since the ion source delivers

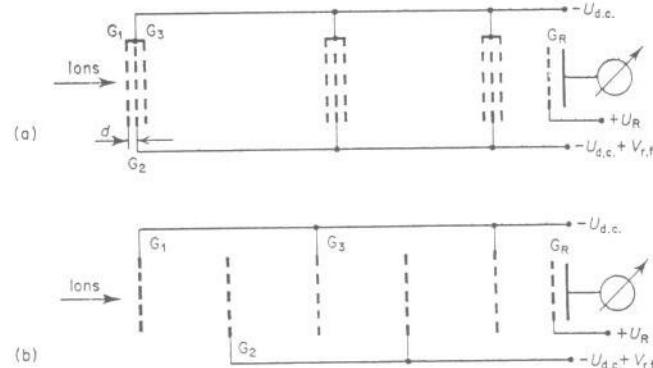


FIG. 5. Radio-frequency mass spectrometer. (a) Bennett-type; (b) Redhead-type.

ions continuously and, consequently, ions possessing the optimum phase angle are always present, the mass selection is determined solely by equation (2). If one eliminates v with equation (1), it follows that

$$m = 0.27 \frac{eU}{f^2 d^2} \quad (3)$$

For improvement of mass selection, one uses, as shown in Fig. 5(a), several r.f. stages, generally three. Their distance from each other must be such that the time of flight of the ions in the field-free drift space amounts to an integral multiple of the oscillation period $1/f$. The ion separation is achieved by a retarding field at the end of the spectrometer tube. This retarding field results from a positive voltage applied to grid G_R . One increases the retarding voltage so far that only those ions, which have taken up a maximum of kinetic energy in the various stages can pass the grid G_R and, consequently, reach the collector. The masses of these ions are given by equation (3). The mass range is scanned by varying the acceleration voltage U or the frequency f .

An instrument similar in construction to the described Bennett

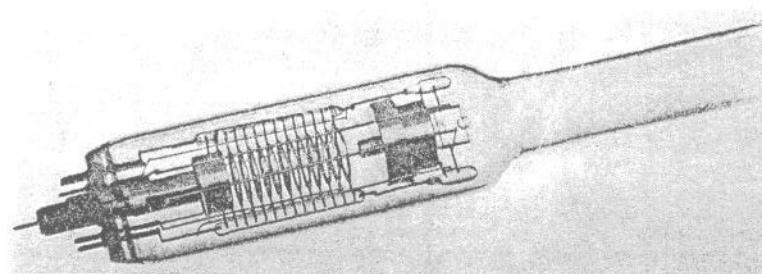


FIG. 6. Tube of the Redhead-type r.f. spectrometer (manufactured by Leybold Company, Köln-Bayenthal, Germany).

spectrometer was designed by Redhead⁽⁶⁾ and Boyd⁽⁷⁾ and is shown in Fig. 5(b). In principle, the separation process is the same as in the Bennett spectrometer, but there is no drift space between the individual r.f. stages. The arrangement of the grids is equidistant. Mathematical analyses of the motion in mass spectrometers of the Bennett-Redhead type have been given by Redhead,⁽⁶⁾ Löcherer⁽⁸⁾ and others.⁽⁹⁾

The r.f. spectrometers according to Bennett and Redhead are simple; they can be built in small dimensions (Fig. 6) and are, therefore, suitable for partial pressure analyses in vacuum systems and for simple gas analyses.⁽¹⁰⁾ Compact constructions of these instruments were suc-

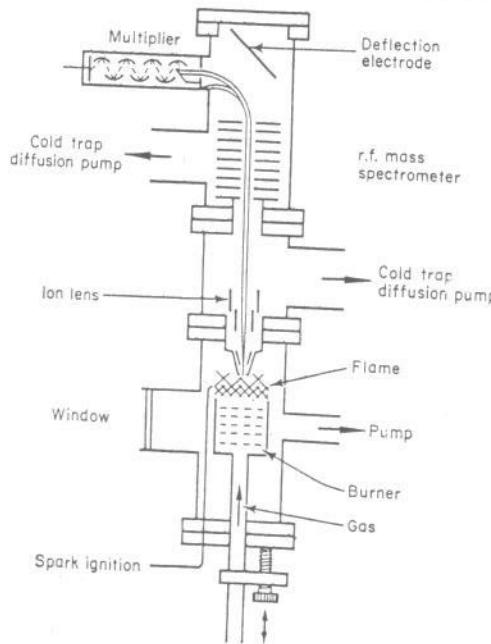


FIG. 7. Mass analysis of ions from flames.⁽¹²⁾

cessfully used in rockets for upper atmosphere research.⁽¹¹⁾ The resolution is not very high, and decreases with increasing mass. With tubes of 20 cm length, the resolution $M/\Delta M$ is about 50. Despite the large cross-section of the ion beam, the partial pressure sensitivity is limited because only a small percentage of the ions possess the optimum phase angle for gaining maximum energy. The smallest partial pressure detectable is in the 10^{-9} torr region. Figure 7 shows an instrument of the Redhead type as part of an arrangement used by Calcote and Reuter⁽¹²⁾ for the analysis of ions from flames. This special version⁽¹³⁾ of the instrument has a deflexion plate for ion selection instead of a retarding grid.

IV. Mass Synchrometer

There are two r.f. mass spectrometers requiring a magnet: The mass synchrometer and the omegatron. In both instruments, the ions travel on circular orbits. The flight time per orbit in a magnetic field is dependent on the mass of the ion. With an orbital radius r and a velocity v , the flight time per orbit is given by

$$t = \frac{2\pi r}{v} \quad (4)$$

Since the radius r is related to the velocity v and mass m of the ions and to the magnetic field density B by the equation

$$r = \frac{mv}{eB} \quad (5)$$

(e = elementary charge), it follows that

$$t = \frac{2\pi m}{eB} \quad (6)$$

As can be seen from equation (6), with the magnetic field density B held constant, the flight time per orbit is dependent only on the ion mass and not on the radius and the velocity. In the case of the mass synchrometer, about which Smith⁽¹⁴⁾ reported in 1951, the separation by time of flight differences in the magnetic field is fairly simple to understand. A short ion pulse is emitted from the ion source and enters a slit system after half a circulation on orbit 1 (Fig. 8). When a negative square pulse of short duration and suitable magnitude is applied to the centre plate of this system, then part of the ions are re-

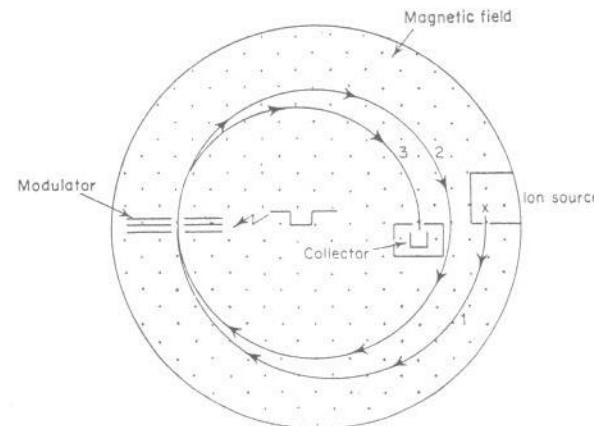


FIG. 8. Mass synchrometer.

tarded and forced to travel on the circular orbit 2 without hitting the ion source. When a second short retarding pulse is applied to the slit system after an integral number of circulations performed by ions of a certain mass, these ions reach the detector on orbit 3. The masses can be determined by measuring the circulation periods of the ions.

The accuracy in mass determination obtained with the mass synchrometer is extremely high. Hence, instruments of this type are primarily used in the field of nuclear physics for precise mass determination of the atoms. They are less suitable for analytical work. The reasons are the complexity of instrumentation, the fairly large magnetic field required, and the fact that the ion source and collector are within this field. Sample introduction and ion detection by multiplier are more difficult than with instruments having ion source and collector outside the magnetic field.

Similar to the mass synchrometer are two other r.f. mass spectrometers with circular orbits, described by Goudsmit *et al.*⁽¹⁵⁾ and Mamyrin *et al.*⁽¹⁶⁾

V. Omegatron

The omegatron, which was first described by Hipple, Sommer and Thomas⁽¹⁷⁾ in 1949, is based on the same principle as the mass synchrometer. Mass separation is effected by differences in flight time on a circular orbit. As shown in Fig. 9, a fine electron beam, which is directed

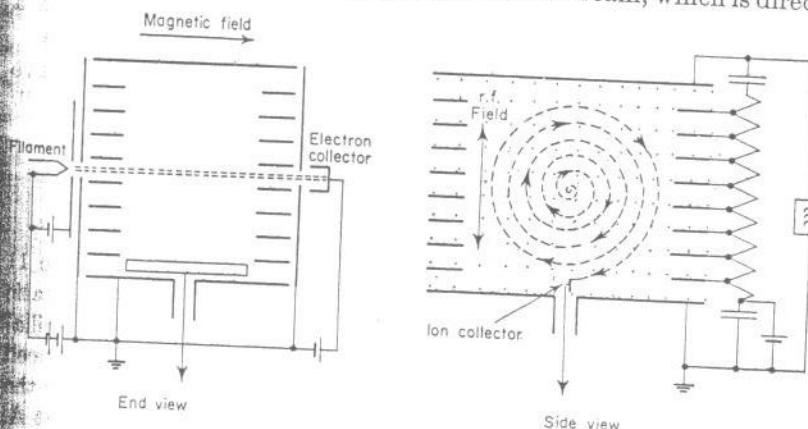


FIG. 9. Schematic view of the omegatron.

parallel to the magnetic field, ionizes the gas. An electrical r.f. field perpendicular to the magnetic flux extracts the ions. Since the velocity of these ions is still very low in the beginning, the ion path has a small radius in the plane perpendicular to the lines of the magnetic flux. The ions follow circular orbits approximately; the flight time per orbit

is given by equation (6). When the frequency of the applied r.f. field coincides to the circulation frequency for a certain mass, then ions having this mass are accelerated. Similar to the conditions in the cyclotron, the ions gain energy with each circulation so that they move outward in spirals until they hit the ion collector. The mass spectrum is scanned by varying either the r.f. frequency or the magnetic field. Ions with a different mass can also be present in the accelerating phase of the r.f. field for a limited number of circulations. However, because these ions move either too quickly or too slowly, they will soon enter a field where they are retarded on each circulation. The radius of the orbit decreases again, and the ions move inward in spirals. After several circulations the radius of the orbit will increase again, and so on. These ions do not reach the collector; by means of a small draw-out voltage on the r.f. electrodes they are slowly forced out of the centre and caught by the electrodes.

The omegatron can be built in very small dimensions, e.g. with a largest orbital radius of only about 1 cm (Fig. 10). Due to the small volume and owing to the fact that the ion current is not limited by any slits, the omegatron is a sensitive analysis instrument for the smallest quantities of gases. Therefore, it is widely used for the analysis of residual gases in vacuum systems. The detection limit is of the order of 10^{-11} torr. The resolution is moderate and decreases with increasing mass. A usable resolution $M/\Delta M$ up to 60 can be achieved with tubes of about 3 cm diameter. A disadvantage of the omegatron is that a magnet is required and ion detection with multiplier is not possible.

Theoretical and experimental studies of the mode of function have been carried out by Berry,⁽¹⁸⁾ Brubaker,⁽¹⁹⁾ Klopfer,⁽²⁰⁾ Schuchardt⁽²¹⁾ and others.⁽²²⁾

VI. Farvitron

The farvitron tube was designed by Tretner⁽²³⁾ in 1959. Figure 11 shows the principle: the ions perform oscillations in an electrostatic potential well between points A and B. The frequency of these oscillations is dependent on the mass. Ions of the same mass can be induced to oscillate in phase, if new ions are added in point A at exactly the moment when the already oscillating ion bunch reverses motion at A. When ions of a different mass are produced at A, then these ions, too, begin to oscillate; however, no oscillating bunch is formed from ions of this other mass, because their oscillation frequency is different, and consequently the addition of new ions is not in phase with the reversal of motion. The pulse frequency of the electron beam, that means the repetition rate of the ion production at point A, is controlled by an r.f.

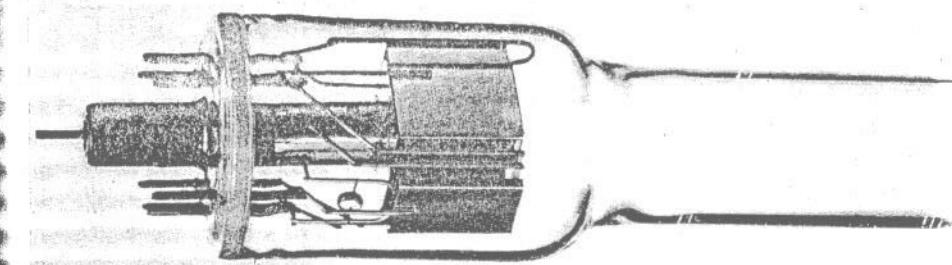


FIG. 10. Omegatron tube (manufactured by Leybold Company, Köln-Bayenthal, Germany).

voltage applied to the Wehnelt cylinder. The mass range can be scanned by varying this pulse frequency. One can modulate the frequency periodically over the entire frequency range and mass range respectively, e.g. with 50 c/s so that oscillating ion bunches from the various ions can be produced shortly after one another. These ion bunches are formed quickly and, when the r.f. frequency is no longer in phase with the frequency of the ion oscillation, will just as quickly disperse. The oscillating ion bunches influence on the signal electrode a high frequency voltage, the amplitude of which is proportional to the charge

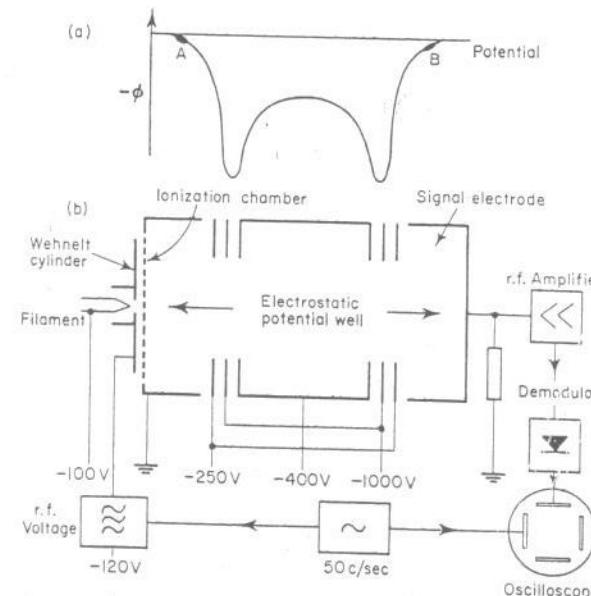


FIG. 11. Farvitron. (a) Potential, (b) schematic view.

and thus to the number of ions. This high frequency signal is amplified, demodulated and fed to an oscilloscope, showing the whole mass spectrum. Thus, quick changes of the composition of the gas in the farvitron tube can be observed.

The farvitron was developed especially for the analysis of residual gases in high and ultra-high vacuum systems. However, the height of the mass peaks is no exact quantitative measure for the composition of the gas, since the more heavy and more abundant components are indicated primarily. This means the farvitron is a partial pressure indicator only. The mass range is from 1 to 100 u. The resolution $M/\Delta M$ is dependent on masses and rather low. As a maximum, two peaks with unit mass difference can be differentiated at mass number 20, but cannot

be separated completely. However, to compensate for this limited performance data, the instrument is simple, easy to build (Fig. 12) and consequently not expensive.

VII. Quadrupole Mass Spectrometer

The quadrupole mass spectrometer or mass filter was invented by Paul and co-workers⁽²⁴⁾ in 1953. The principle is shown in Fig. 13. The ions formed by electron bombardment are focused by an electrical lens and injected into the quadrupole field as a beam with circular cross-section. This field is produced by four parallel cylindrical rods to

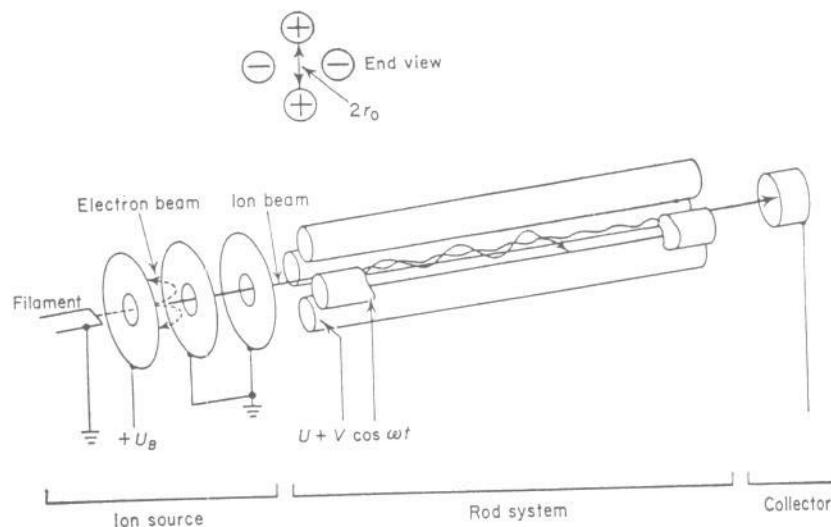


FIG. 13. Schematic view of the quadrupole mass spectrometer or mass filter.

cross-section. This field is produced by four parallel cylindrical rods to which there is applied a d.c. voltage U with superimposed r.f. voltage V . The potential Φ of the field is given by:

$$\Phi = (U + V \cos \omega t) \cdot (x^2 - y^2)/r_0^2 \quad (7)$$

Hence the trajectory of ions having the mass m is described by the following equations of motion:

$$\begin{aligned} m\ddot{x} + 2e(U + V \cos \omega t) \cdot x/r_0^2 &= 0 \\ m\ddot{y} - 2e(U + V \cos \omega t) \cdot y/r_0^2 &= 0 \\ m\ddot{z} &= 0 \end{aligned} \quad (8)$$

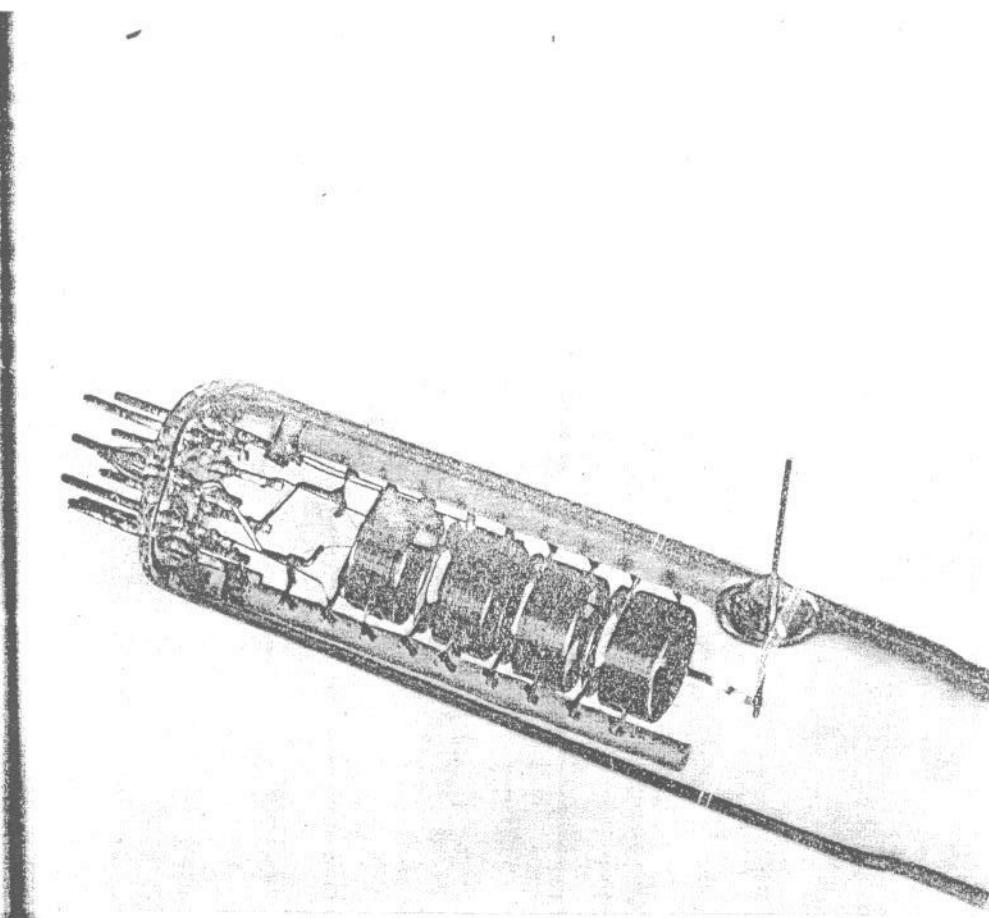


FIG. 12. Farvitron tube (manufactured by Leybold Company, Köln-Bayenthal, Germany).

$$m = \frac{4eV}{q^2 r_0^2 \omega^2} = \frac{V}{U} \frac{m}{q} \frac{a}{2}$$

$$\frac{4e}{r_0^2 \omega^2} = \frac{a}{2} \frac{m}{U}$$

$$a = \frac{2U}{V}$$

By using the transform ion parameters

$$\begin{aligned}\omega t &= 2\xi \\ a &= \frac{8eU}{mr_0^2\omega^2} \\ q &= \frac{4eV}{mr_0^2\omega^2}\end{aligned}\quad (9)$$

one finds Mathieu's differential equations

$$\begin{aligned}\ddot{y} + (a + 2q \cdot \cos 2\xi) \cdot x &= 0 \\ \ddot{x} - (a + 2q \cdot \cos 2\xi) \cdot y &= 0\end{aligned}\quad (10)$$

The solutions of these equations show that the injected ions perform oscillations perpendicular to the longitudinal axis z . These oscillations remain below a maximum amplitude only for certain values of the parameters a and q (stable solutions of equation (10)), i.e. with U , field radius r_0 and frequency ω held constant, for a certain mass or mass range of ions. Only these ions can pass through the quadrupole field. Ions of other masses perform unstable oscillations with rapidly rising amplitudes so that they hit the rod electrodes.

A general illustration for the existence of stable or unstable solutions is given in Fig. 14. The transformation parameters a and q are the

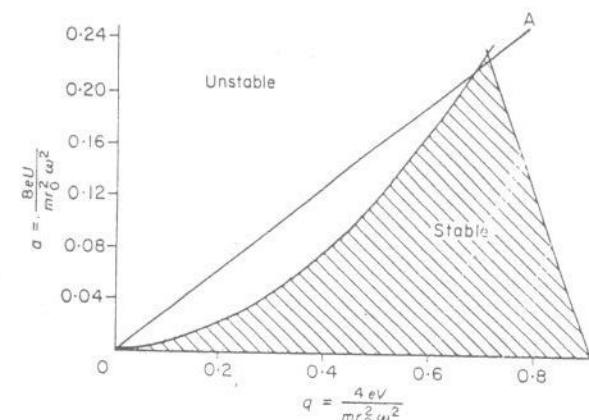


FIG. 14. Stability diagram.

ordinate and abscissa respectively. The parameters a and q which correspond to the stable solutions are within the shaded area, the so-called stability area. In the remaining areas, the parameters a and q correspond to unstable solutions. For a given constant ratio a/q and therefore U/V —the ratio of d.c. voltage U and superimposed r.f. voltage V —all mass numbers lie on the straight line A which intersects the

zero point of the coordinates. The slope of line A, given by the U/V ratio. According to the chosen U/V ratio a larger or smaller mass range ΔM will fall within the stable area. This means that all ions having a mass within this range ΔM can pass the mass filter. The resolution will increase when the mass range ΔM falling in the stable area gets smaller. In order to make ΔM smaller one has to increase the slope of the line A which means one has to increase the U/V ratio. Hence, the higher the U/V ratio the higher the resolution and consequently the lower the transmission (number of ions of one mass passing the quadrupole system to number of ions entering the system) will be. The scanning of the mass range can be effected by varying the voltages of both U and V with ratio U/V remaining constant. If one increases the voltages U and V the masses will move along the line A through the stable area beginning with the lower masses (see equation (9)). This means that one mass after the other will be recorded. The mass scale is linear with respect to U and V , i.e. mass indication is very simple, a voltmeter can be directly calibrated in mass numbers. Mass scanning can be performed too by altering the frequency. But in this case with increasing frequency the masses move in the opposite direction through the stable area and the mass scale is not linear with respect to the frequency (see equation (9)).

Various instruments of this type have been built by Paul and his group. These instruments were used, e.g. for the detection of molecular beams, for the separation of isotopes and for the precision determination of masses.⁽²⁵⁾ Günther and Hänlein⁽²⁶⁾ developed a mass filter for the partial pressure analysis in vacuum systems. Brubaker⁽²⁷⁾ and Schaefer⁽²⁸⁾ described mass filters for upper atmosphere studies. A simplified version of the mass filter, the "monopole mass spectrometer" was described by v. Zahn.⁽²⁹⁾

Figure 15 shows a mass filter tube,⁽³⁰⁾ which was designed for those applications where a small and versatile mass spectrometer can be used with advantage: e.g. partial pressure analyses in high and ultra-high vacuum systems, gas analytical work, molecular beam studies, mass analysis of ions and free radicals from gas discharges and flames. The performance of this mass filter will be discussed in some detail in the following sections.

A. DIMENSIONING OF THE TUBE

Considering one of the main applications of a small mass spectrometer, the residual gas analysis, the following requirements should be met: (a) the highest possible partial pressure sensitivity, (b) a mass range which comprises the usual components of the residual gas, (c) a resolu-

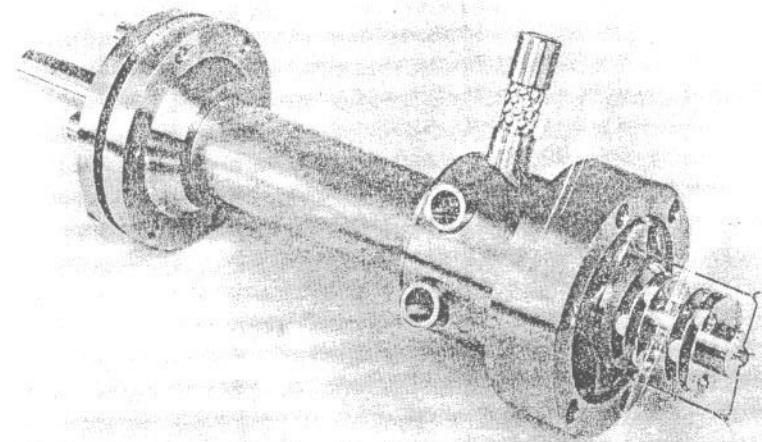


FIG. 15. Tube of mass filter (model AMP 3, manufactured by Atlas MAT GmbH, Bremen, Germany).

tion to separate these components, (d) a possibly small volume of the tube to minimize measuring errors resulting from the tube itself, (e) ease of operation by a control unit of small dimensions, and not too expensive and complicated electronics.

As these requirements are partly contradictory one has to find a favourable compromise. If one restricts the mass range to 1-100 u which, in general, is the most important mass range in partial pressure

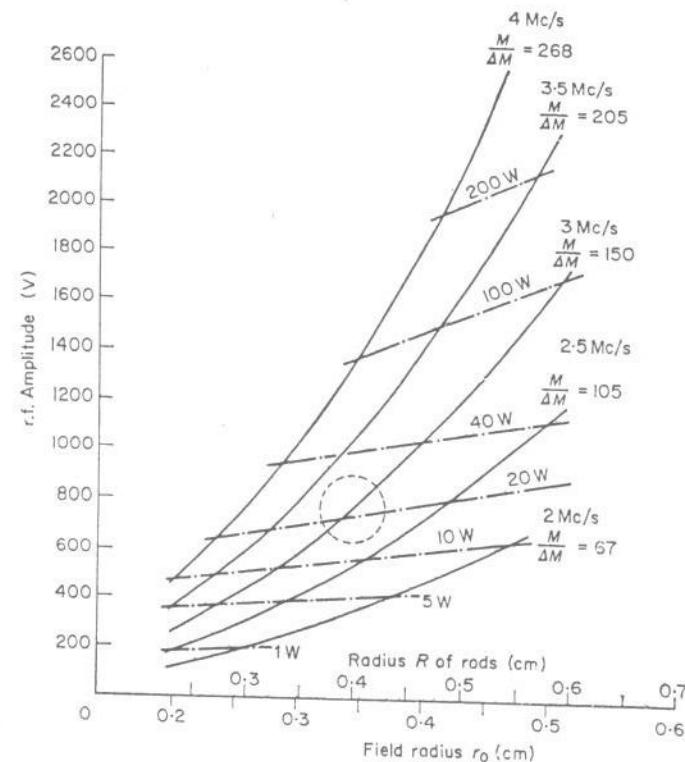


FIG. 16. Relation between field radius r_0 and r.f. amplitude V .

analyses, and if one limits the rod length to 20 cm then for ions of mass number 100 and energy 100 eV the theoretical relationship between the field radius r_0 and both high frequency voltage V and output power W of the generator is given in Fig. 16. The parameter is the frequency or, in turn, the max. resolution. The resolution depends to a large extent on the chosen frequency. This dependency can be explained by the fact that for a certain resolution it is necessary for the ions to perform a certain number of oscillations in the quadrupole field in order to be separated. If one selects for instance the line which belongs to the

resolution $M/\Delta M = 150$ and moves up along the line, then one can obtain a high sensitivity since the field radius and in turn the ion beam cross-section become large. This, however, calls for an undesired increase of the r.f. amplitude and in turn output power. If one moves too far down the line the radius of the field becomes smaller, therefore, sensitivity is reduced. A reasonable compromise lies in the area which is marked by a dotted circle. The selected design data for the tube in Fig. 15 are given in Table I.

TABLE I
Mechanical and electrical data of typical mass spectrometer tube

| | | | |
|-------------------|--------|------------------------|-------------|
| Diameter of rods | 8 mm | Max. r.f. amplitude | $V = 800$ V |
| Diameter of field | 6.9 mm | Max. d.c. voltage | $U = 120$ V |
| Length of rods | 200 mm | Frequency | 3 Mc/s |
| | | Max. r.f. output power | 30 W |

B. CONSTRUCTION OF THE TUBE

Figure 17 shows the construction of the all-metal tube. Since the ion source is free and accessible from all sides special inlet devices as molecular beam systems can be attached. In the case of partial pressure analyses the source protrudes directly into the evacuated vessel. Thus errors caused in the measurement of partial pressures are greatly minimized. Such errors are noticeable in the case when the ion source and evacuated vessel are interconnected via tubulation. The total length of the quadrupole tube with ion source and collector is 30 cm. The tube can be baked at temperatures up to 400° C. The precise alignment of the rods and the ion source is not affected by this temperature since all critical parts are spring-retained to maintain their exact positions. The tube can easily be demounted, all parts are self aligning.

Figure 18 shows a sectional view of the ion source which is mounted on alumina-balls. For molecular beam studies the molecular beam can pass through the ion source in the direction of the electron beam.

In order to obtain the maximum detection sensitivity, the Faraday collector can be replaced by a multiplier. The multiplier is flange-mounted at an angle with respect to the longitudinal axis of the mass filter (Fig. 19). When the multiplier's control unit is switched on, the positive ions are forced by the high negative voltage at the first dynode on to a bent path and thus strike the surface of this dynode. Without high voltage at the first dynode the ions hit the Faraday collector and the ion current is amplified by the d.c. amplifier only. The change

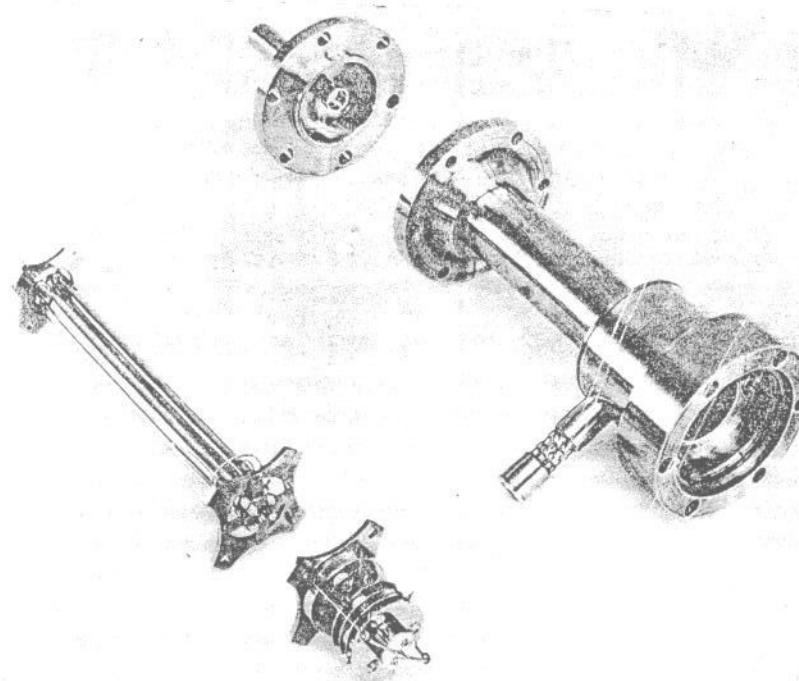


FIG. 17. Tube of the mass filter model AMP 3 demounted.

from one mode of ion current measurement to the other one is simple in this way. Such a rapid change-over is required, e.g. when the pressure in the vacuum system increases rapidly and the high ion currents

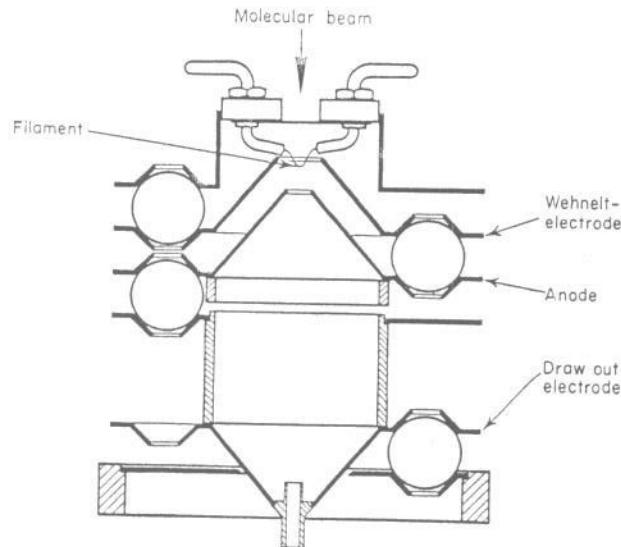


FIG. 18. Sectional view of the ion source.

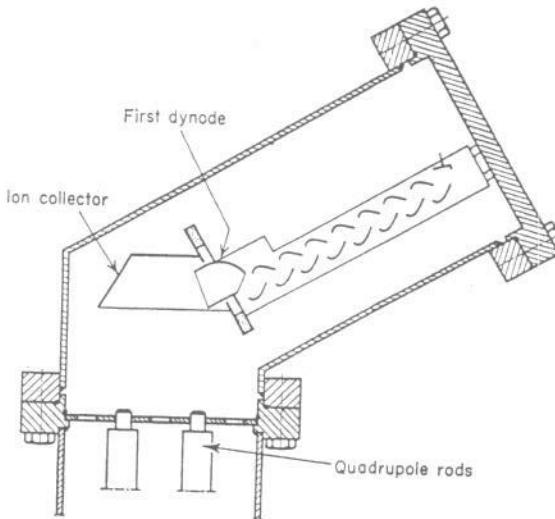


FIG. 19. Secondary electron multiplier.

would exceed the permissible maximum current of the multiplier, or, when besides high partial pressures small pressures are to be measured. The mounting of the multiplier at an angle to the longitudinal axis has

another advantage. The soft X-rays produced by the electron beam in the ion source are prevented from hitting the surface of the first dynode since this lies—optically speaking—in shade. The X-rays would otherwise increase the dark current of the multiplier considerably.

C. ELECTRONIC CONTROL UNIT

The 19-inch control unit of the analyser tube (Fig. 20) comprises the r.f. generator, a power supply for the ion source, a d.c. amplifier, a high voltage generator for the multiplier and a power supply for an additional Penning gauge that switches off the ion source and quadrupole voltages when the total pressure exceeds 5×10^{-4} torr. The control unit makes it possible to scan the mass spectrum automatically with a speed ranging from one scan in eleven minutes to three scans per second.

D. PERFORMANCE DATA

The performance data of the instrument are listed in Table II. The

TABLE II
Performance data of typical mass spectrometer

| | | | |
|----------------------------------------|---------------------------|--------------------------------------|-------------------------|
| Mass range | 1-120 u | Max. pressure | 2×10^{-4} mmHg |
| Max. scanning rate | 3 spectra/sec | Smallest detectable partial pressure | |
| Resolution (10%, valley definition) | $M/\Delta M = 100$ | | |
| Sensitivity (Argon) | | | |
| 10% Transmission, $M/\Delta M = 100$ | 1×10^{-5} A/mmHg | with d.c. amplifier | 10^{-10} mmHg |
| 100% Transmission, $M/\Delta M = 35$ | 1×10^{-4} A/mmHg | with multiplier | 10^{-12} mmHg |

transmission and resolution can be varied by varying the ratio U/V of the d.c. and r.f. voltages. The resolution can be increased at the expense of transmission and vice versa. For 100% transmission the sensitivity is approx. 1×10^{-4} A/torr; this gives a detection limit of better than 10^{-12} torr. The maximum resolution $M/\Delta M$ is about 100. This efficient performance with respect to resolution and sensitivity makes the mass filter especially useful for residual gas analyses in high and ultra-high vacuum systems, and for detection and identification of molecules in reaction studies.

When discussing the dimensions of the tube it has already been mentioned that to obtain a given resolution, a certain number of oscillations performed by the ions within the quadrupole field are required:

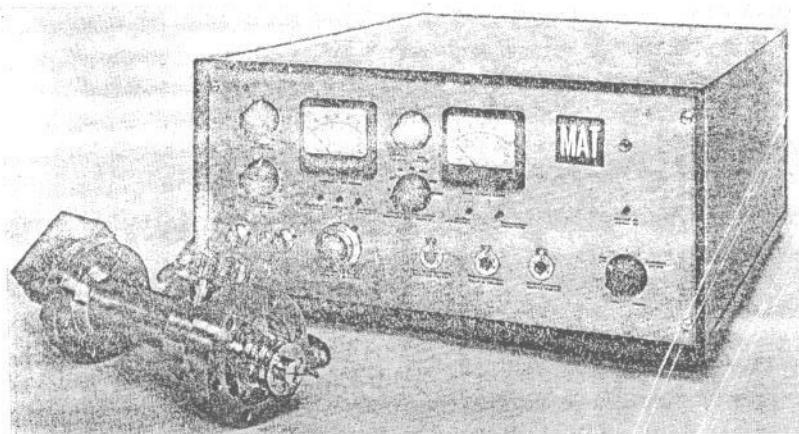


FIG. 20. Tube with control unit.

The longer the ions remain in the quadrupole field, meaning that their injection energy is low, the higher the resolution will be. The dotted line in Fig. 21 represents the theoretical relationship⁽²⁵⁾ between

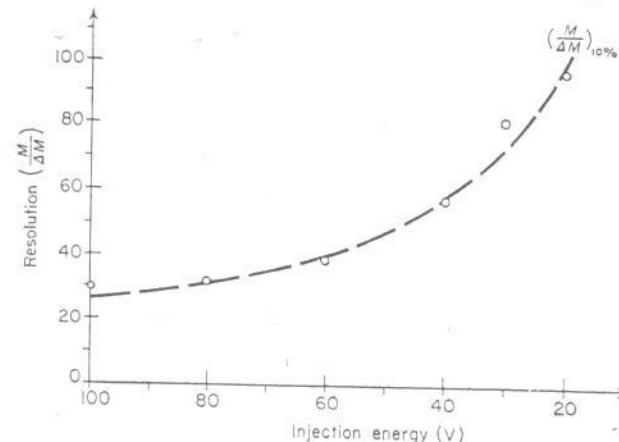


FIG. 21. Relation between resolution and injection energy.

maximum possible resolution and ion energy. The measured values for the H_2O^+ ions are plotted likewise. As indicated by this graph: the lower the injection energy the higher the resolution. Consequently, in order to achieve maximum resolution, the ions are retarded from 120 eV (focusing voltage) to approximately 40 eV at the entrance of the quadrupole field by appropriate setting of the ion source voltages.

The abundance sensitivity can be recognized from the argon spectrum (Fig. 22). The amount of the main peak's tail with respect to the adjacent peak is of the order 10^{-4} .

It is useful to obtain a mass-independent partial pressure sensitivity. When scanning the mass spectrum by varying the r.f. voltage, the ratio U/V of the d.c. and r.f. voltages should remain constant, according to theory. Constant U/V ratio means that the slope of the line A in Fig. 14 remains constant. For an exact constant ratio, however, one measures a decrease in partial pressure sensitivity, that means ion transmission of the quadrupole system, with rising mass (Fig. 23). To obtain an approximately mass-independent ion current one must vary the U/V ratio according to a certain functional relationship during mass scanning. A device for the functional variation of the U/V ratio is incorporated in the electronic control unit.

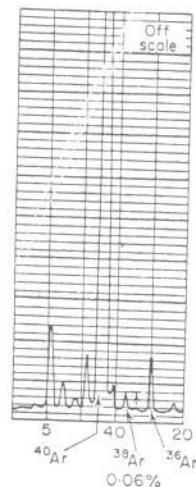


FIG. 22. Abundance sensitivity.

By this means one can reduce the dependency considerably. Figure 24 shows the residual gas spectrum of a vacuum container recorded with the optimum functional relationship between r.f. and d.c. voltage amplitudes.

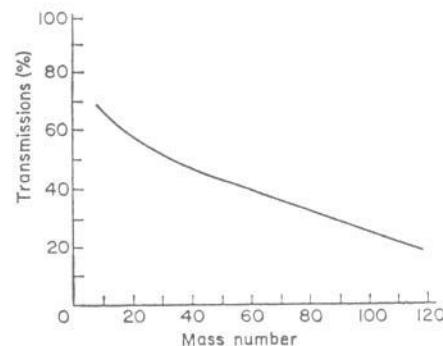


FIG. 23. Relation between transmission and mass number.

The stability of the instrument can be seen from the data given in Table III. Plotted are the mean values of the relative peak heights of a mixture comprising helium, argon and freon. The standard deviation of $\pm 1\%$ of the peak heights has been evaluated from 40 mass spectra

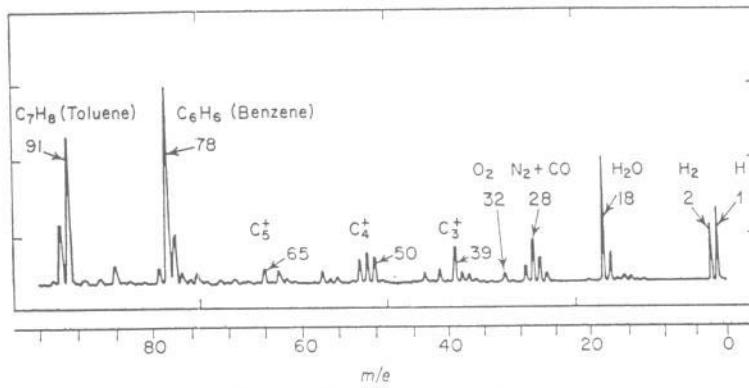


FIG. 24. Residual gas spectrum.

recorded in 8 h. Besides resolution, abundance sensitivity and stability the detection limit is of importance. When the Faraday ion collector is used, the partial pressure sensitivity (collector ion current/partial pressure in the ion source) and the noise of the d.c. amplifier determine for the detection limit. The thermal noise of the input resistor corresponds to a current of about 2×10^{-15} A. The smallest detectable current is 4×10^{-15} A when one considers the double noise width as the measuring limit. With the partial pressure sensitivity of 1×10^{-5}

A/torr valid for a resolution $M/\Delta M$ of about 100 corresponding to 10% transmission (see Table II) one gets a detection limit of 4×10^{-10} torr. At a lower resolution of about 35 which means about 100% transmission the detection limit is in the 4×10^{-11} torr region.

TABLE III

| Ion | He^+ | Ar^{2+} | Ar^+ | CF_2^+ | CF_2Cl^+ | CFCl_2^+ |
|-----------------------------------------------------|---------------|------------------|---------------|-----------------|--------------------------|-------------------|
| m/e | 4 | 20 | 40 | 50 | 87 | 101 |
| Peak heights (% of total current) | 23.5 | 4.1 | 23.2 | 13.9 | 28.0 | 7.3 |
| Standard deviation of peak heights (40 runs in 8 h) | 1.2% | 1.3% | 1.1% | 1.1% | 1.0% | 1.3% |
| Standard deviation of total current | | | | | $\pm 0.8\%$ | |

By using the secondary electron multiplier as a pre-amplifier the detection limit and accuracy respectively are determined by the statistical ion current fluctuations and the dark current of the multiplier system itself rather than by the thermal noise of the resistor. The dark current of the 16 stage multiplier is of the order 10^{-19} A. This means ion currents of 10^{-17} A and below are easily detectable. With the sensitivity of 1×10^{-5} A/torr for resolution 100 a detection limit of better than 10^{-12} torr is obtained.

Besides increasing the detection sensitivity, the multiplier reduces the time constant of the amplifier so that one can raise the scanning speed up to a few mass spectra per second for oscilloscope recording. This allows one to follow rapid changes in the composition of residual gases. Figure 25 shows a part of a mass spectrum scanned in 0.2 sec.

← 0.2 sec →

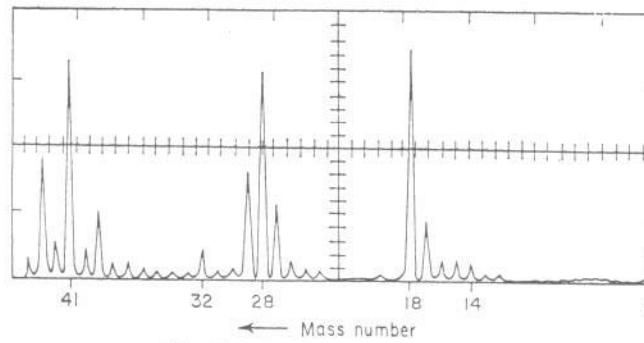


FIG. 25. Oscillographic recording.

The quadrupole system offers the possibility that the separation of masses can be made ineffective by switching off the d.c. voltage U . In this manner a measurement of total ion current and thereby total pressure can be performed. From the stability diagram, Fig. 14, it may be seen that d.c. voltage zero means that the line A coincides with the x -axis. Thus, all masses greater than a certain cut-off mass can pass the rod system. This cut-off mass can be varied by changing the r.f. ampli-

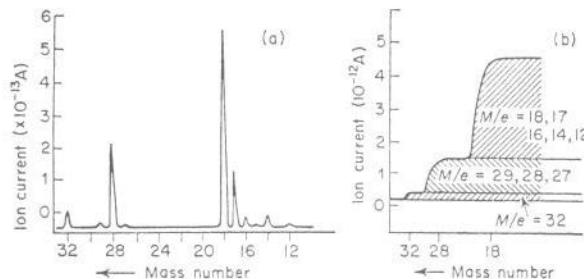


FIG. 26. (a) Section of a residual gas spectrum, (b) Corresponding total current measurement.

tude. At very low r.f. amplitudes all ions are collected. When the r.f. amplitude is increased the ion current drops stepwise (Fig. 26). At the maximum r.f. amplitude—mass setting to approx. mass number 120—only those ions with masses greater than 120 u will be collected. This measuring technique is useful for residual gas analyses because it allows to detect even—as a group—high molecular weight components having masses beyond the nominal mass range of the measuring tube.

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