The resolving power of the field (23.28) will not, generally speaking, be that of the apparatus. The spectrometer here receives the useful part of the beam in the slit S' of width s' of the collector; this slit must be at least as wide as the emergent beam, and we may even choose an appreciably wider value, $s' > s_1'$ for reasons which we shall see later. The resolution criterion for the whole spectrograph therefore requires that masses m and $m + \Delta m$ should not fall on S' simultaneously, so that the resolution of the spectrometer itself is less than that of the field alone (23.28). The former is defined by

$$K_m \left| \frac{\Delta m}{m} \right| = s'$$

if $s \ll s'$, but if this condition is not fulfilled, we can easily take account of s; in the usual cases, then,

$$\left| \frac{m}{\Delta m} \right| = \frac{R}{s'}.$$

If, for example, $R = 15$ cm and $s' = 0{\cdot}5$ mm, the resolving power is about 300. This value is for the most part sufficient in the everyday problems of mass spectrometry.

CHAPTER 24

THE INDIVIDUAL PARTS OF A MASS SPECTROSCOPE

24.1 THE ION SOURCE

We shall first of all study the ion sources which are designed to transform the substance to be analysed into positive ions; so far as is possible, the representatives of each mass m will move at the same velocity (and thus have the same energy V), and the whole bundle of ions will emerge through a slit S in a narrow beam which is the ion object for the analysing field. Every source, therefore, consists of two more or less distinct parts:

(i) The source itself, at which the ionization process is initiated, and which is as nearly equipotential as possible so that the ions are closely homogeneous.

(ii) A mechanism for collimating and accelerating the particles through a potential V, with which an ion beam of the required energy is produced.

Various designs have been proposed, suitably adapted for solids, gases and vapours. We shall only consider ion sources for mass spectroscopy, however.

24.1.1 Sources Produced by Discharge in a Gas

(i) *The ordinary luminous discharge (for gases)*

The earliest of the sources of positive ions is the ordinary luminous discharge in a gas at a pressure p of the order of 10^{-2} mm Hg (the dimensions of the envelope being considerably larger than the mean free path). The cathode is usually perforated by a narrow canal (less than a millimetre in diameter) through which a beam of positive ions which comes from the anode can pass; these are Goldstein's "canal" rays (see Fig. 293a).

This type of source possesses several defects which limit its usefulness. First, the ions are not created in an equipotential region, as their production takes place in the same region as their acceleration; this has the fatal result of producing an ion beam which is extremely heterogeneous in velocity. The energy spread v is an appreciable fraction of the mean energy V which is obtained at the exit; if V is of the order of a few thousand volts, v is about 1000 V. We cannot use a source of this kind in spectroscopy therefore, without either inserting a velocity filter which eliminates the majority of the rays, or using double focusing which has the advantage of retaining a wider band of energies. Further, the ions which are obtained are widely assorted, as the phenomena which occur at the discharge are extremely diverse; single or multiple ionization may occur, with or without

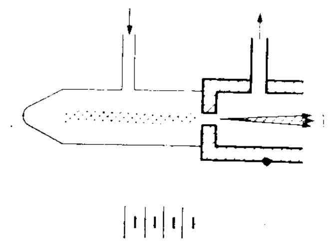

FIG. 293a. A discharge source: the canal rays.

rupture of the molecules, and charge exchange, condensation, and chemical reactions between ions and molecules are all possible. A discharge in oxygen, for example, produces many ions for each isotope: O^+, O^{++}, O_2^+, O_2^{++}, O_3^+ . . . If nitrogen too is present, combinations such as NO^+ will also occur. The spectra, therefore, are rich in bands, which can be used as reference positions and for the measurement of masses m, m', . . . by the doublet method in spectrography.

On the other hand, such a source is not suitable for quantitative analyses, for spectrometry; the spectra become too complex, and—a more important objection, this—the superposition rule is no longer valid. The spectrum of a mixture is not obtained by superimposing the spectra of its constituents.

The intensity i of the ion beam which emerges from S is much less than 1 mA. Various improvements have been made with a view to increasing i or to working at a lower pressure p (the superposition of an auxiliary magnetic field or use of an HF potential); the sources become more complex, however, and they are not used for spectroscopy. They are used to supply particle accelerators, giving intense beams of atomic ions. Several studies have been devoted to these discharge processes—an analysis of this work is to be found in the book by Ewald and Hintenberger (1953).

(ii) *The gas arc*

An arc is a discharge in which the cathode is rendered incandescent, either spontaneously, or by auxiliary heating which results in a sharp increase in the intensity of the current and reduces the potential across the terminals (1 A, 50 V for example). The current i is larger and the ions

are considerably more homogeneous ($v = 10$ V, for example); acceleration is in this case a separate operation. Arcs are too complex in construction and too brutal in action to be used in spectroscopy; the only instruments in which they are used are those for separating isotopes where an ion current of a few milliamps is used (Koch and Bendt-Nielsen, 1944; Bernas, 1953), and as ion sources for accelerators such as cyclotrons and synchrocyclotrons.

24.1.2 High Frequency Sparking (for Solids)

A general method for producing ionization of solids is furnished by high frequency spark discharge which was first applied to mass spectroscopy by Dempster (1935). The spark flies between two tapered electrodes or between an axial electrode A and a plate in which an opening has been cut (Fig. 293b). A is composed of the material to be ionized, or of a metal

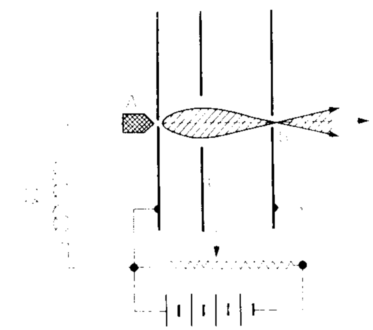

FIG. 293b. A high frequency spark source.

tube in which the material is enclosed in powder form. The pair of electrodes L and S take care of the collimation and the acceleration. The ions which are obtained have a noticeable energy spread v, although less wide than for canal rays—a velocity filter or double focusing is required. Here again, a wide diversity of ions is produced, which gives the method its spectrographic importance, as it complements to a certain extent the luminous discharge—the two phases involved are the solid phase and the gaseous phase respectively.

24.1.3 The Surface Ionization Source (for Solids)

From certain solids, we can instigate evaporation of positive ions by placing the solid over an incandescent anode. This phenomenon occurs for elements which are readily transformed into ions, and which are thus electropositive. We denote the ionization potential by V_i, and the potential barrier at the metal support by V_s; the positive emission varies with $(V_s - V_i)$: the following formula, known as the Langmuir formula (1925), expresses this more precisely:

$$\frac{n'}{n} = \exp\left[\frac{F(V_s - V_i)}{RT}\right] \tag{24.1}$$

(n and n' are the numbers of neutral atoms and positive ions which are evaporated, respectively; $F \simeq 96{,}500$ coulombs = 1 faraday).

A tungsten filament, for example ($V_s = 4{\cdot}55$ V), is perfect for obtaining a beam of Cs^+ ions ($V_i = 3{\cdot}86$ for Cs); for alkali metals, alkaline earths and rare earth metals, oxidized tungsten ($V_s = 8$ V) must be used. These sources were first explored by Dempster (1918) and Moon and Oliphant (1932). Alternatively, we can heat not the element which is to be ionized but one of its compounds—the halides (Koch, 1936) or the alumino-silicates (Blewett and Jones, 1936); this technique has been developed extensively by Couchet (1954). Intense sources (1 mA cm^{-2}) have been studied by Kunsmann (1927), and employed in particular by Smythe, Rumbaugh and West (1934) in their wide beam instrument designed to separate isotopes (Fig. 291). The theory of the emission from compounds is still virtually unknown, but the practical operation is quite satisfactory.

These surface ionizers have a very distinct character. It is clear, first of all, that they are very selective, and do not give parasitic ions since the ionization phenomenon is strictly localized at the anode. Further, as the latter is to all intents and purposes equipotential, the velocity spread v is very small, as it is equal to the spread of the initial thermal energies, about 0·2 V. The ion beam can be formed in the same way as before (Fig. 293b, electrodes L and S).

Certain negative ions can be evaporated from a hot cathode—in this case, it is with electronegative elements that we are concerned (halogens); these have been studied by Hintenberger (1951) in particular.

24.1.4 Sources Produced by Electron Bombardment (for Gases and Vapours)

The ions emitted by this type of source are produced by electron bombardment and the range of applications is very extensive; sources of this kind were first used by Dempster (1916) and later developed, principally by Bleakney (1932), Tate and Smith (1934) and Nier (1937 and 1947).

(i) *Description and properties of an ordinary source*

The standard model is due to Nier; diagrams of the horizontal xOz projection and the vertical yOz projection are shown in Fig. 294. The substance to be studied is a gas which arrives through the tube G or a

vapour which is produced by heating the appropriate solid in a small adjacent compartment (Bernas and Nier, 1948; Louw and de Villiers, 1954; and Cameron, 1954). The gas penetrates at very low pressure p (10^{-4} to 10^{-5} mm Hg) into a small ionization chamber C, where it is ionized by an

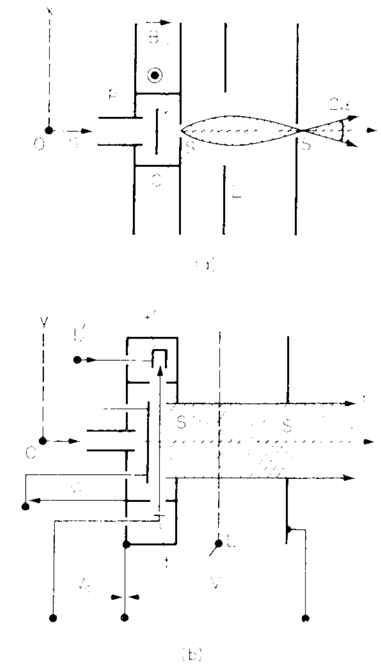

FIG. 294. Nier's source.

electron beam which is emitted by a heated tungsten ribbon t. The accelerating potential V_e of the electrons is applied between t and C—it must, of course, exceed the ionization potential of the gas being analysed, and is usually set between 50 and 100 V. The current I_e of the beam is a few hundred microamps. We shall see later that ions which are created in this way have a very low kinetic energy (V_c); a fraction of these ions has then to be extracted from C through the slit S_c, and accelerated and aimed by the field of the collimating and accelerating electrodes L and S. This can be done with the aid of an auxiliary electrode r, for example, which is held at a positive potential V_r of a few volts with respect to the walls of C; r produces a field which has the desired effect upon the ions without sensibly modifying the electron beam. This latter is considerably more perturbed by the divergent lens effect produced by the slit through which the beam enters C. To prevent the beam from spreading, a vertical magnetic field of a few hundred gauss is often employed; the effect of such a field, we recall, is to wind the electron trajectories in helices around the lines of force, and hence to guide them in a direction which is on the average vertical. This operation is controlled with the aid of the current I_s which is incident upon a collector electrode or trap t' which is placed at the exit from C opposite t. Finally, since the chamber C is pierced with several openings, it is important that the areas of these latter should be as small as possible; it must be possible to maintain the internal pressure p without harming the vacuum outside which is at most of the order of 10^{-6} mm of mercury (cf. § 23.4.2).

A source built in this way can be easily and reproducibly adjusted. As the chamber C is almost equipotential, the velocity spread v is only a few volts; this spread is due to V_r and to the initial kinetic energy V_0 of the ions which is always very slight—in general, it is a question of the mean thermal energy of the particles (about 4×10^{-2} V at normal temperatures). On the other hand, the pressure p is low enough here for each ion of the beam to be the result of a single process; unlike the case of a luminous discharge there are no "reactions" in C. The spectra obtained obey the superposition law and are susceptible to quantitative analysis, and therefore to spectrometry. We shall see that the ion currents i which are obtained are of the order of 10^{-3} A at most, which is normally perfectly adequate.

(ii) *High intensity sources*

More intense sources have been produced. The procedure known as *oscillating electrons* represents a large advance, by extending the length of the path of the ionizing beam considerably (Finkelstein, 1940). An application of this procedure is to be found in the source due to Heil (1943), which we can describe by supposing that in Fig. 294, the trap t' is replaced by a second emissive ribbon at the same potential as the first ribbon, t. The reflecting electrodes are distributed on one side and the other in such a way that each ionizing electron traverses the chamber C a large number of times. The increase in intensity can also be obtained by arranging that a higher proportion of ions emerges from the ionization chamber; this can be done by directing the electron beam along the axis and concentrating the resulting ions by means of suitable electrodes at the exit slit (Cassignol, Geller and Moreau, 1953).

Finally, other types of intense source can be obtained by intensifying the ionizing beam I_e and increasing the pressure p; the behaviour then tends towards that of arcs, however, and the spectra no longer obey the superposition law. We might mention as examples the sources of Walcher (1944) and Bernas and Nier (1948) which can be used for isotope separation—the currents i can reach a milliampère.

(iii) *Various ionization processes*

It is useful to introduce the reader at this point to the various ionization phenomena which are produced at the source by the electron bombardment; for further details, the article by Hagstrum and Tate (1941) or the book by Robertson (1954) should be consulted. For the present, we shall examine a simple example, namely, carbon monoxide. This diatomic gas produces the following ions (e = electron):

$$CO + e \rightarrow \begin{cases} CO^+ + 2e & \text{(i)} \\ CO^{++} + 3e & \text{(ii)} \\ C^+ + O + e & \text{(iii)} \\ C^+ + O + 2e & \text{(iv)} \\ C + O^+ + 2e & \text{(v)} \\ C + O & \text{(vi)} \end{cases} \quad (24.2)$$

(the reaction $CO + e \rightarrow C + O + e$ can obviously not be detected here). The frequency of each of these reactions, that is, the probability with which each occurs, can be calculated; this probability is often defined by the number of times n that the reaction in question is produced by an electron over a distance of 1 cm of its trajectory at a pressure of 1 mm of mercury. At the pressure p of the ionization chamber C, the order of magnitude of n is at most 10; only a small fraction of the electrons is useful, therefore—we shall restate this conclusion more precisely a little later when we are examining the yield of a source.

The determination of n is one of the most important applications of the mass spectrometer; in particular, we study the variation of n as a function of the energy V_e of the ionizing electrons. For the reaction mentioned above, the following results are obtained: (i) and (ii) are ionizations in the proper sense of the word, while (iii) (iv) and (v) are ionizations with simultaneous destruction of the molecule; these five reactions can occur beyond a threshold potential V_i, which is the *ionization potential* or more generally, the potential at which the corresponding ions first appear. For (i) and (ii) the values of this potential are 14 and 41 V respectively. The variation of probability as a function of V_e is of the form labelled a in Fig. 295. Reaction (vi) is a capture accompanied by destruction of the molecule, and its probability curve is different in form; the function has a maximum (or "resonance") for $V_e = 9{\cdot}5$ V (see Fig. 295, curve b). CO thus gives the positive ions which have the following integral masses when V_e is of the order of 100 V, and the various isotopes have been extracted: 12 (C^+), 16 (O^+), 14 (CO^{++}) and 28 (CO^+). If we were to analyse the negative ions in the spectroscope (and for this, we should have simply to change the sign of the potential V), we should obtain only 16 (O^-) which is a considerably less characteristic result. Here we have the first justification for the preference which is accorded to positive ions; another reason is that the reactions which result in negative ions have markedly smaller probabilities than the others.

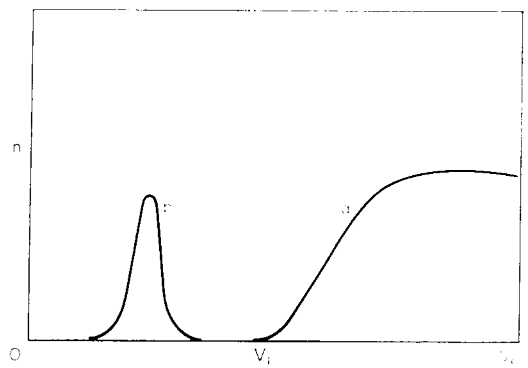

FIG. 295. The two types of ionization curve.

The simple example of CO gives some indication of the complexity of the spectra which will be produced by polyatomic molecules, the hydrocarbons for example. This complexity is sometimes still further increased by the fact that some ions are *metastable*, by which we mean that they are not extant throughout the whole passage through the spectroscope; it is the ions which result from their dissociation which are responsible for the appearance of lines which seem to correspond to non-integral masses in the spectra (Hipple, Fox and Condon, 1946; and Hipple, 1947).

The initial kinetic energy (V_c) of the ions which are produced is necessarily equal to the thermal value for straightforward ionizations, such as (i) and (ii), by virtue of the elementary laws of collision in mechanics. This is no longer true when the ionizations are accompanied by breakdown of the molecules, as the ions which are produced in certain reactions may possess a supplementary kinetic energy; this is at most of the order of one or two volts, however, and hence only slightly disturbs the homogeneity of the complete ion beam.

24.1.5 Focusing and Accelerating the Ions in a Source

As an example, we consider a source due to Nier (Fig. 294), which behaves very much like every other source of fairly homogeneous ions. The problem is, we recall, to produce an ion beam of energy V and small aperture 2α, which emerges through an exit slit S. The latter is earthed, as this helps the insulation of the ionization chamber C which is held at the

positive potential V. With the aid of an electrode with a slit L which is supplied by a potentiometer, the concentration onto S of the ions which are produced in C can be improved; simple ion optics shows how this can be done.

(i) *The existence of lenses*

All the slits are vertical; we shall always be working in conditions where the optical system possesses a "horizontal" symmetry plane, that of the analysing field. The optics is here further simplified (Fig. 296): on the one

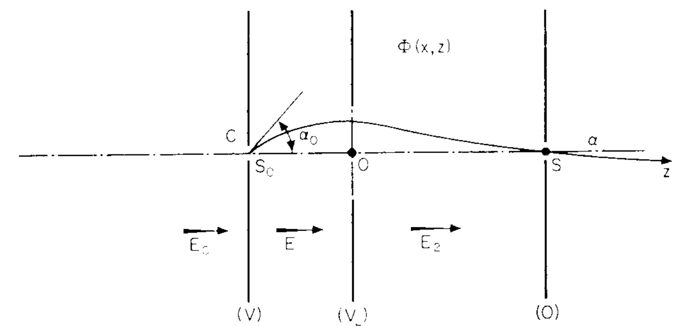

FIG. 296. Focusing within an ion source.

hand, the focusing is only horizontal since the fields depend only upon x and z so long as the slits are narrow enough; otherwise we should expect to find vertical focusing (Bertein, 1950). On the other hand, the source possesses a vertical symmetry plane also, so that the optic axis Oz is rectilinear; the coordinate system $Oxyz$ reverts to the Cartesian form. If we use the same notation as in the preceding chapter, the focusing equation (23.12)—in the Gaussian approximation—is reduced to:

$$2\varphi x'' + \varphi' x' + \varphi'' x = 0. \tag{24.3}$$

This could be demonstrated directly very simply by modelling the analysis on that of the optics of axially symmetric systems; the Laplace equation gives•

$$\varphi_2 = -\frac{\varphi''}{2}.$$

The slits play the role of a lens, a role which has been analysed to various approximations (Bertein, 1950, 1951; and Vauthier, 1950, 1954). A particularly simple approximation to the potential distribution on the axis, $\varphi(z)$, is the distribution created by the juxtaposition of the uniform fields, E_0, E_1, E_2, . . . which would be produced by diaphragms without openings; this in fact is Gans' method (§ 4.5.2). In such conditions, the rays are composed of parabolic arcs, joined at known angles of refraction (Davisson and Calbick, 1932) at each diaphragm. We can, however, put less confidence in this kind of analysis for the trajectories within the chamber C; here, we shall simply remark that C forms a kind of immersion objective (§ 8.3 and Chapter 13) with the extractor field E_0, which creates an ionic object at S_0. L has then to image S_0 on S, a requirement which we can analyse by establishing a general conjugacy relation:

$$\frac{E_1}{1 - V_1'} - \frac{E_2}{1 - V_2'} + E_1 - E_2 = 0, \qquad (24.4)$$

in which E_1 and E_2 are the fields on one side and the other, V_1' and V_2' are the potentials at the object and the image due to these fields; the unit of potential is the potential of L, and the origin is the zero of these energies. In the present application,

$$V_1' \simeq 0, \qquad V_2' = \frac{V}{V - V_2}.$$

An examination of the linear magnification γ shows that it is possible to select the position of L in such a way that the passage of the rays through S is assured, when the width of the two slits S_0 and S are comparable and of the usual order of magnitude, namely, a few tenths of a millimetre. With the aid of the Helmholtz–Lagrange relation, however,

$$\gamma \frac{\alpha}{\alpha_0} \sim \sqrt{\frac{v}{V}} \sim \frac{1}{30}, \quad \text{for example.} \qquad (24.5)$$

We can foresee that when the concentration is strong ($\gamma < 1$) there is a risk of the angle α being too large for the analysing field to produce good focusing. The sources of Nier (1947)—see Fig. 300—include stops which are placed behind S precisely to limit the aperture of the beam.

(ii) *The influence of the magnetic field of the source (of induction B_0)*

The vertical field exerts a transverse force on the ions, parallel to the axis Ox; the result is simply a slight horizontal displacement of the trajectories and hence of the focusing. Since the slit S is narrow, the ions could miss it; they can, however, always be brought back to S by applying a small potential difference between the two half-plates of which L is composed. We should notice that this phenomenon depends upon the mass m of the ions, so that we shall find discrimination.

24.1.6 The Yield from a Source and Its Perturbations

(i) *Calculation of the ion current, i, at the exit, S*

We shall always talk in terms of a source of the standard form. We suppose that a given gas enters the ionization chamber at a pressure p. If the electron beam is of intensity I_e and the mean length is l, while n is measured with respect to the total ionization, the ion current created in C is

$$I = n\, I_e\, l\, p. \qquad (24.6)$$

For everyday orders of magnitude: $l = 1$ cm, $p = 10^{-4}$ mm Hg, $n = 5$ and $I_e = 100\ \mu$A, we find $I = 5 \times 10^{-8}$ A.

It is, however, clear that the majority of the ions does not reach the slit S_0, so that the current i which emerges through S is only

$$i = K I \quad \text{where} \quad K \ll 1. \qquad (24.7)$$

K is difficult to calculate, as the process of extraction of the ions from C is complex. It seems reasonable to take K of the order of $\frac{1}{100}$ at most, which would give $i \simeq 5 \times 10^{-10}$ A.

(ii) *Discrimination*

The formulae (24.6) and (24.7) above can be applied equally well to the total ion current and to the current of any one particular type of ion.

If ions of one mass are emitted by the source more easily than those of another mass—if the ratio $K = i/I$ depends upon the nature of the ions, that is—we say that there is discrimination within the source. This discrimination may have several origins, as K is an overall measure of a complex type of transmission.

In spectrometry where the potential V is scanned, the value of V which corresponds to reception is higher for light ions than for heavy ions; the same is true, therefore, of the values of the field E_0 by which the extraction is for the most part produced. The discrimination, in consequence, favours light ions (Coggeshall, 1944; Washburn and Berry, 1946). We can estimate the importance of this phenomenon by comparing the results of an analysis of CCl_4 obtained by the two methods of scanning (Blears and Mettrick, 1947). The units are arbitrary (see the table on page 826).

When the scanning is magnetic, the magnetic field B_0 of the source is a cause of discrimination, at least in the normal situation where it is held constant; the mass m for which the half-plates have been corrected tends to be favoured with respect to the others. This defect can be overcome by using only relatively low values of B_0, of about 100 or 200 gauss.

THE IONIC INTENSITY OF IONS OF MASS m AS OBTAINED AT THE RECEIVER

m	B scanning	V scanning
35	100	100
47	133	97
82	118	52
35/37 (abundant chlorine isotopes)	3·10	3·17

Another type of discrimination affects ions which are formed with an initial kinetic energy, as this energy clearly modifies the trajectories within C, and hence the extraction phenomenon.

In fact, however, we shall see later on that if it is important to reduce discrimination in the measurements of the relative isotope abundance as far as possible, this is no longer true in actual chemical analyses. In the latter case, the important thing is that we should work in constant conditions, and hence we must struggle to overcome the parasitic processes which are more harmful than simple discrimination.

(iii) *The various parasitic effects*

It is the fluctuating nature of these effects which is dangerous. We classify them as hysteresis, "memory" effects, and ageing; we shall mention only the most important.

The substances of which the source is composed tend to be outgassed in the course of operation, because of the relatively high temperature at the ribbon t (which can reach 150°) and the electron bombardment of the surfaces. Parasitic lines appear in the spectra.

The gas to be analysed may be thermally modified (dissociation) in the vicinity of t. This phenomenon varies in time with the ageing of t or its possible replacement.

The gas may affect the emissive power of the ribbon itself (by modifying the work function); the hydrocarbons may increase it by one-third, while oxygenized substances have an even clearer reducing effect. Adjustment of the source electrically considerably attenuates these perturbations.

There is a risk of the metal surfaces becoming charged, by being covered with films of impurity; the trajectories are modified, especially in C.

If we are to operate in the constant conditions which are necessary for analyses, these defects must be reduced as much as possible if fluctuations which clearly exceed 1 per cent are to be avoided. The metal parts should be made of tantalum, stainless steel, or nichrome and the insulators of pyrex or melted silica. The source and the analysing tube must be dehydrated (250 to 300°), especially after exposure to air.

It is recommended that the emissive ribbon should be conditioned and for further details, the reader should consult the book by Barnard.

24.2 COLLECTION OF THE IONS

24.2.1 The Photographic Plate (Spectrographs)

The ion beams which emerge from the analysing field can be made visible with the aid of a fluorescent screen composed of willemite or zinc sulphide, provided their energy (V) is at least of the order of 5 kV. For recording the spectra in the spectrograph, the photographic plate has been in regular use since its introduction by Thomson (1911) in his parabola method. As a result of the very low penetration by the ions, useful emulsions contain very little gelatine, and are of very fine grain (for example, Schumann or Ilford plates). The potentials V should be relatively high, for example 20 kV or more. The exposures last at least a few minutes.

Once the law which describes the blackening of the plate had been determined experimentally, we could in principle measure the intensities i and hence arrive at spectrometry proper—this would be less straightforward than making electrical measurements at the collector, however. We might mention that the darkening is not strictly proportional to the product it, which measures the number of ions received (Lichtblau and Mattauch, 1941).

24.2.2 The Collector (Spectrometers)

By scanning either the magnetic induction B or the potential V, the various beams are brought successively into a small Faraday cage C which is placed behind a slit S'. C thus captures the current i which corresponds to each mass in turn (Fig. 297). The width s' of S' must be chosen to be at least equal to the width of the line s_1' and in fact, we use a decidedly higher value, so that the beam i is wholly received not only for a particular value of B (or of V) but for a small range of neighbouring values; in these conditions, each peak which is recorded has a flat top, which simplifies the interpretation.

The resolving power of the instrument is affected by s'. The slit S' is earthed, and the same is effectively true of C (see below).

The addition of an intermediate stop D' which is held at a negative potential of the order of 20 V prevents the secondary electrons which are produced at C by ion bombardment from leaving, as their departure would falsify the measurements of the current i. Another diaphragm D'', held at an appreciable positive potential (smaller than V, however), improves the spectrum by eliminating the continuous background which is produced by ions which have been scattered by the residual gas. Since the energy of

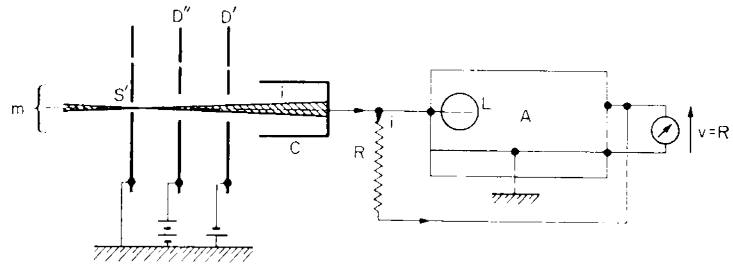

FIG. 297. Reception of the ion current.

these scattered ions is less than V. D'' creates a potential barrier which prevents them from reaching the collector, without disturbing the useful ions at all (Nier, Stevens *et al.*, 1947).

A more drastic means of clarifying the spectra consists in holding the whole collector at the same potential as the source; the most convenient arrangement is to connect both to earth, and the analysing tube will then have to be connected to the high tension ($-V$). This arrangement has been used to study the ions which are produced by the dissociation of metastable ions which have been formed in the source (§24.1.4. See Hipple, Fox and Condon, 1946; and Hipple, 1947). It transpires that all such ions have an energy smaller than V, just as do the scattered ions.

Rather than try to prevent the emission of secondary electrons, we can, on the contrary, take advantage of it as a means of amplifying the value, i, of the current received considerably; it is possible to achieve this by placing a multiplier in front of the Faraday cage (Allen, 1939, 1950; Nier, Roberts and Franklin, 1949; and Barnett, Evans and Stier, 1954). The incident current will, of course, still have to be amplified by a valve circuit, but the value of electron multiplication resides in the fact that the importance of the background noise is reduced, to such an extent that the limiting value of i which can be detected is reduced from 10^{-15} to 10^{-17} A. This is a well-known phenomenon, which was first put to use in television where the particles to be detected are photons. In the present case where ions replace the photons, the theory is the same (Zworykin and Morton, 1955) but to obtain long-term stability seems to be difficult as the flow of ions damages the first plate of the photomultiplier.

24.3 THE ELECTRICAL CIRCUITRY OF A SPECTROSCOPE

The circuits are fed from an alternating supply, in commercial instruments at least. Arrangements for rectifying and smoothing the potential must be provided therefore, to avoid fluctuations prejudicial both to the resolution and to the sensitivity. These arrangements are not markedly different from the ones we have described in connexion with the microscope (Chapter 18).

24.3.1 Measurement of the Ion Currents *i* (Spectrometers)

The ion current which falls on the collector is at most of the order of 10^{-10} A, and it is usually measured with the aid of an electrometer, with which currents down to 10^{-15} A can be detected. The current i flows through a very high resistance R, $10^{11}\,\Omega$ say, which is connected to the collector C (Fig. 297); we have simply to measure the potential across the terminals $v = Ri$. For this, R is placed at the input of an electrometer valve L, which is a vacuum tube in which the control grid g is highly insulated by means of various special features of the construction and operation: the presence of a supplementary grid, an under-heated filament, low potentials to avoid ionization of the residual gas (10 V at most), and a special structure to avoid both the emission of very soft X-rays by the plate and photo-electric emission by the grid in the presence of this weak radiation.

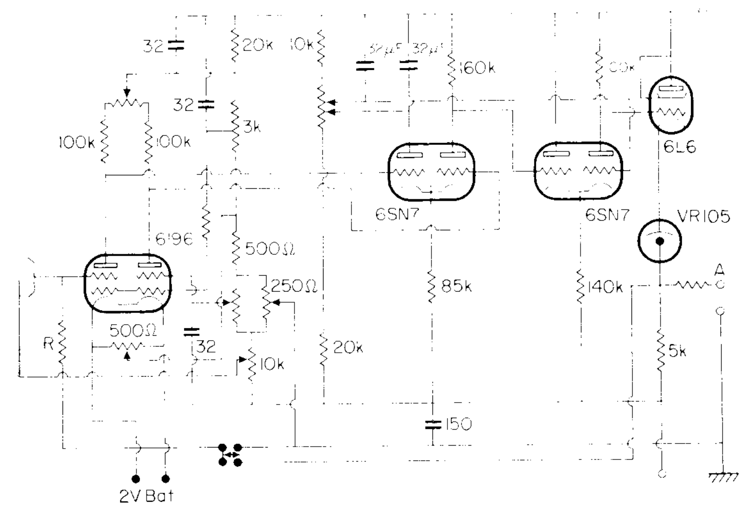

FIG. 298. Amplifier for measuring ion currents (after Bertein, Vastel and Beaussier).

These are serious inconveniences in making a direct reading with a galvanometer, for example, of the measurement obtained at the exit of L. Furthermore, the characteristics of L are very curved, and hence there is a complete lack of proportionality. Finally, parasitic capacities and the capacities