

# MASS SPECTROMETRY

## *Survey*

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The problem faced by mass spectrometry is threefold:

1. Determination of isotopic constitution where chemical identity is known.
2. Identification and abundance measurements of chemical elements or their compounds.
3. Preparation of isotopically pure and of chemically extremely pure samples by means of electromagnetic mass separation (Calutron-technique).

As the Conference is primarily interested in the first two items, only these will be dealt with.

The mass spectrometer works with ionized matter in its gaseous state, and a spectrometer must therefore include: (a) an ion source with an attached sample introduction system; (b) an analyzer which sorts the ions according to their  $e/m$  value, which generally means according to their mass (e.g. mass number 16 for  $^{16}\text{O}^+$ ); and (c) a detector or collector of ions, with attached amplifiers, recorders or data-handling equipment to represent the results.

Ion sources, analyzers, detectors and representation facilities can be built in several ways based upon many different physical principles, and the finished mass spectrometer, therefore, represents a judicious choice of components, which are suitable for solving only a special problem or group of problems. Such groups of problems are the analysis of gases to various ends, or the analysis of solids.

Fig. 1 shows six mass spectra of gases as an example of obtainable results. The three upper spectra all refer to krypton, and the three lower ones to xenon. Further, the two on the left represent atmospheric gases, the two in the middle are from gas released in the fuel of an atomic reactor, whereas the two at the right are due to spontaneous fission in very old uranium minerals. Similarly, if an organic compound is put into a mass spectrometer, it will usually dissociate and develop a characteristic mass spectrum, which is typical for an isomer too. Thus, a way of identifying compounds is provided. Further, the signal at peak height may in a good precision instrument be significant within 1:1000 or 1:10,000 of its value, and thus be used for quantitative measurement.

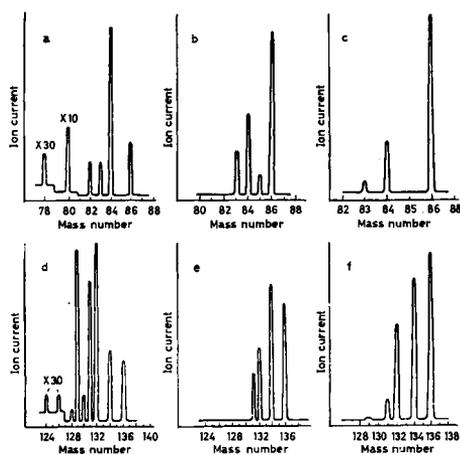


Fig. 1.—Mass spectra of samples of krypton and xenon, demonstrating usefulness of mass spectrometric method (H. G. Thode).

## ION SOURCES

Any electrical discharge between cold electrodes would provide ions, but it is rarely used in such a crude form. The modern source is generally based on a design by Nier, where a narrow and well-controlled electron beam is used to ionize a gas or vapour from the substance to be analyzed. The ions are accelerated and enter the analyzer as a mono-energetic beam (Fig. 2).

The source may also incorporate gas inlet systems or vaporizers for samples when needed. A further refinement is the use of molecular beams, instead of just having the gas molecules entering the source at a random distribution. Such designs may be effective in removing non-ionized molecules from the source region, which would induce memory effects due to adsorption ( $UF_6$ ). It may also help to solve another problem described by Bentley [2].

Although the Nier source is known to have a high efficiency and is easy to handle, it has the drawback of producing complicated dissociation patterns of organic compounds. This complicates the analysis of mixtures and work has therefore been devoted to achieve ionization by means of field emission and photo-ionization. In this case, the energy transferred to the molecule is on an average much smaller and only the so-called parent line of the molecule may appear (at mass number identical with molecular weight). On the other hand, the ordinary pattern of dissociation is extremely useful for structural analysis, as shown in the Scientific Exhibition from Karolinska Institutet, Chemical Department, Stockholm, Sweden.

Another way of producing ions is by thermo-ionization. This method is based on the fact that a lot of elements, such as alkaline and earth alkaline metals, rare earths, uranium and aktinides or their compounds, are ionized

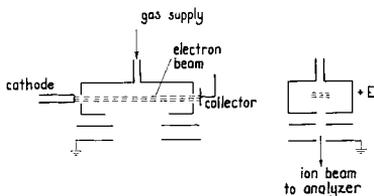


Fig. 2.

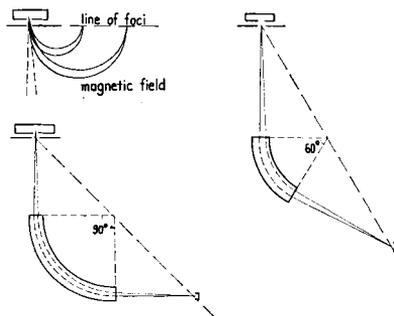


Fig. 3.

Fig. 2.—Principle of electron bombardment or Nier type ion source.

Fig. 3.—Focusing of mono-energetic ions by means of homogeneous 180°, 90° and 60° magnetic fields.

when in contact with hot tungsten (and other metals, such as Ta and Re). However, discrimination between elements makes this method unsuitable for quantitative analysis of mixtures by the direct method, and it is only useful for isotopic analysis, or for quantitative analysis of one element at a time by the isotope dilution method.

A high-frequency spark known from optical spectroscopy has been introduced as a means for the chemical analysis of solid substances. The spark erodes the electrodes made from the sample, and after a starting period the composition of the ion beam should be representative of the composition of the electrodes. Ions from this source, however, are no longer mono-energetic, and multiple charged ions are common. This produces problems for the analyzer.

### MAGNETIC ANALYZERS

Suppose an ion source produces a mono-energetic beam of ions, and let the beam enter into a homogeneous magnetic field at right angles to the field lines. The ions begin to run in circles, and after 180° of deflection focal points will appear, which are at the right place to locate a detector, for example, a photographic plate or slit with a collector behind it. This situation is explained in Fig. 3, to the upper left. Suppose only single charged ions are dealt with, the relationship between the magnetic field, the radius of curvature, the acceleration voltage and the mass number will be

$$H_{\text{gauss}} \cdot r_{\text{cm}} = 144 \sqrt{E_{\text{volt}} \cdot M},$$

where  $M = 16$  for  $^{16}\text{O}^+$ . For practical reasons, sector fields of an angle of 90° or 60°, as also shown in Fig. 3, are mostly preferred to the 180° field.

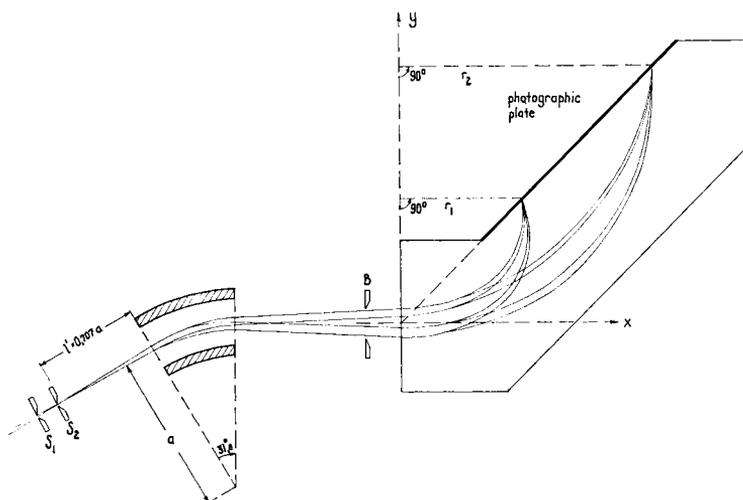


Fig. 4.—Ion optics of the Mattauch-Herzog spectrometer. The sector field is an electrostatic field separating ions with regard to their energy. The magnetic field re-focusses all ions according to mass numbers only on a photographic plate.

It may also be mentioned that by means of special shapes for the entrance and exit boundaries of the fields or by slight distortion of their homogeneity, ion-optical aberrations can be reduced, wider beam angles be used and intensity be increased. Such measures have found their way into commercial instruments as well.

Of particular concern in high-resolution mass spectrometry, and especially in connection with ion sources giving a large energy spread, such as the high-frequency spark source, is the demand that ions of varying energy should always be assigned to their proper mass. As the above equation reveals, the magnetic field by itself cannot do this, and the proper answer is combinations of electrostatic and magnetic fields. Especially important here is the Mattauch-Herzog arrangement explained in Fig. 4, upon which two of the instruments presented at the Conference are based. Fig. 4 shows that the electrostatic cylindrical field spreads the ion beam in accordance with kinetic energy, and this spread is later counteracted in the magnetic field. In the Mattauch-Herzog design all masses can be focussed simultaneously on a single photographic plate (which, due to its integrating property, gives an obvious advantage when using a source giving an unstable ion beam in trace element analysis).

#### NON-MAGNETIC ANALYZERS

With an ion source that produces mono-energetic ions, the ion *velocity* varies in inverse proportion to the square root of the mass. This enables

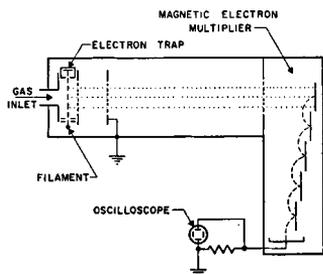


Fig. 5.

Fig. 5.—Principle of the Bendix time-of-flight mass spectrometer.

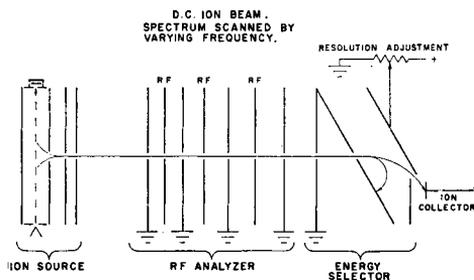


Fig. 6.

Fig. 6.—Schematic diagram of Beckman radio-frequency mass spectrometer.

two principles of separation to be used, and has led to mass spectrometers which are cheaper and more easily adaptable to some problems than the magnetic spectrometers. Although such spectrometers are not represented at this Conference, they should be mentioned here, for the benefit of prospective users.

The time-of-flight principle works by means of a pulsed ion source. Let the sweep of a cathode-ray oscillograph be time-synchronized with the source and let the signal from the ion collector be fed into the vertical deflectors, and a mass spectrum will appear on the screen (Fig. 5).

Another and somewhat similar instrument is the radio-frequency spectrometer. The ion beam passes through a series of grids alternately at some fixed or at r.f. potentials. The arrangement works as a velocity sieve, and by modulating the frequency, a mass spectrum can be scanned (Fig. 6). Such instruments are lightweight and are mechanically and electrically simpler, as well as being cheaper and faster. However, resolution cannot be driven as far as in the magnetic instruments and the usually acute peaks in the mass spectra make quantitative measurements more difficult (Fig. 7). Their right use is rapid identification and semi-quantitative estimation of the gases present, e.g. when following out-gassing processes in vacuum technology. For identification of compounds only, such instruments may be as good as any, and they can be attached to a gas chromatograph, for example,

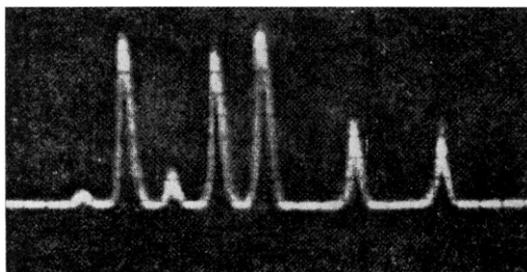


Fig. 7.—Xenon mass spectrum as given by a Bendix TOF mass spectrometer.

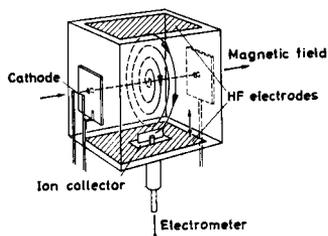


Fig. 8.

Fig. 8.—The omegatron.

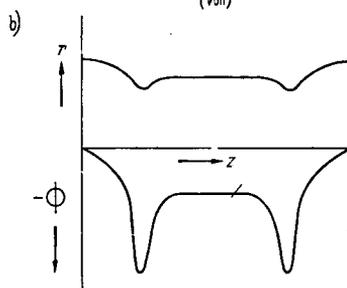
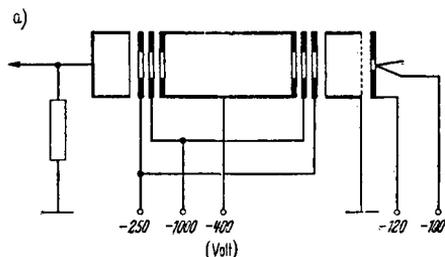


Fig. 9.

Fig. 9.—Cross section through a Farvitron, its potential curve and ion path (W. Tretnner).

for such identification [1]. The quantity of sample can be determined by the gas chromatographic method anyway. A quadrupole mass filter, invented by Prof. Paul and collaborators, is described in greater detail in the paper delivered by Dr. Brubaker [3], and is therefore omitted here.

#### *Resonance principles*

In the omegatron, a high frequency field is maintained within a magnetic field at right angles to it. Ions generated in the centre may become accelerated and spiral outwards, where they eventually hit an electrode (Fig. 8). However, they have to fulfil a resonance condition into which mass and high frequency enter. Choosing the latter suitably, resonance can be established consecutively for all the ions of the components of the gas content of the chamber, which thus is examined for its composition. The outstanding feature of this device is the simplicity of construction and extremely high sensitivity in the ultra-high vacuum range. For example, it has been used in this range to identify helium diffusing through glass at room temperature.

There is also a linear system which makes use of D.C. potentials and high frequency so that the ions oscillate along the axis of a tube, thus giving rise to an r.f. signal on an electrode. The instrument is commercially known as the Farvitron and is described in detail by Dr Nöller [4]. (Figs. 9 and 10.)

These resonance spectrometers exhibit similar advantages and disadvantages as the non-magnetic spectrometers previously mentioned. Further, as

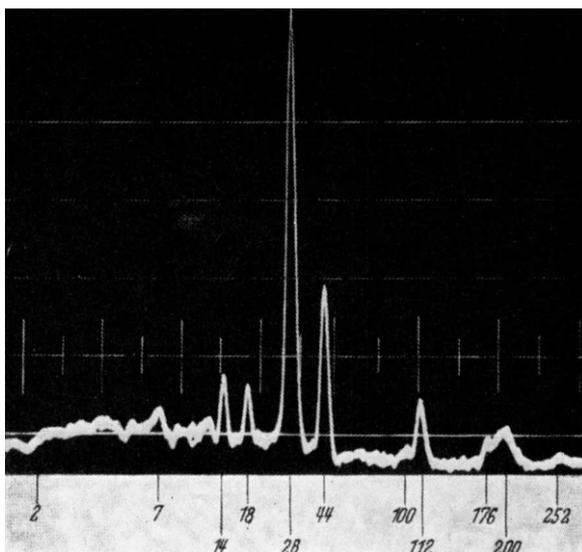


Fig. 10.—Mass spectrum as obtained by a Farvitron. Harmonics to mass number 28 can be observed on mass numbers 14 and 7 (W. Tretnner).

a resonance principle being involved and owing to disturbance by non-resonant ions, they will favour the most abundant species present and suppress others.

The omegatron and Farvitron have been designed more expressly than other spectrometers for direct connection to some other vacuum equipment in order to carry out gas analysis there. The tubes are relatively cheap and may simply be regarded as a more elaborate kind of vacuum gauge. Several tubes can be served by the same supply, with one at a time being kept in operation.

### ION DETECTION AND RECORDING

Ion currents to be detected are mostly low in intensity. They may range from as much as  $10^{-9}$  A in extreme cases down to virtually single ions. Basically different systems are in use.

One system is the photographic plate, which once appeared quite obsolete, but was later re-established as an essential item of the Mattauch mass spectrometer applied to trace element analysis. It should be pointed out that on *nuclear* plates the tracks of individual ions are also observable.

Another system is the electrical one, which is basically just an ion collector or Faraday cage with a lead connecting it to an amplifier. For special applications, parallel collectors and amplifiers can be arranged in the spectrometer, working on different mass numbers simultaneously. By interconnection of the output, isotopic abundancies, for example, can be measured direct as ratios of electric currents.

The Faraday cage can be replaced by an electron multiplier, giving rise to a large burst of electrons for each ion impinging on the first diode (cf. Fig. 5). This, of course, increases sensitivity and speed, and single ions may thus be counted.

Systems for visualizing impinging ions on fluorescent screens or of secondary electrons have been designed, but they are not in general use.

Evaluation of mass spectra is sometimes tedious and time-consuming. There is a tendency to equip mass spectrometers with direct data-handling equipment, and new developments appear to be on the way.

### VERY WEAK INTENSITIES AND BACKGROUND

This is a special problem which appears in very many connections. One may look for a very rare constituent produced by cosmic rays in a meteorite, for an impurity in an extremely pure sample, or for a reaction product in nuclear research. After what has been said previously about counting single ions, one should in principle always be able to detect the compound if it is there at all. However, imperfections in the technique may preclude identification.

A common difficulty is impurities in the spectrometer itself, which just mingle with or mask the ions looked for. Modern designs of spectrometers try to employ ultra-high vacuum techniques wherever possible, thus providing cleaner systems. A very high resolution may help, too, because it makes it possible to discriminate between a component looked for and a hydrocarbon impurity, for example, of the same mass number, but differing in weight by the very small packing fraction.

In the analyzer still another effect takes place. Residual gases give rise to stray ions giving a background everywhere in the spectrum, though mostly at the heavier mass side of stronger lines. A better vacuum in the analyser too will help indeed, but two or three analyzers in series do better by a factor of several powers of 10. Hitherto, such unwieldy instruments have come into use only in certain specialized nuclear research.

Another approach to the detection of very weak components is presented by Dr. Bentley. Its principle is modulating the admission of the sample [2].

### REFERENCES

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2. BENTLEY, P. G., *Proc. 5th Intern. Instruments and Measurements Conf.*, Stockholm, September 13-16, 1960.
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