



MICROMASS
THE MASS SPECTROMETER COMPANY

TECHNICAL INFORMATION

MASS SPECTROMETER PARTIAL PRESSURE GAUGE

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WHY USE A MASS SPECTROMETER?

Fitting a mass spectrometer partial pressure gauge to a vacuum system can be an inexpensive way of obtaining a great deal more information about the vacuum than is available from the customary ion, trigger-discharge or other total pressure gauge. The mass spectrometer tells which are the principle gases or vapours limiting the attainment of lower pressure at any point in the pump down cycle from 10^{-2} to 10^{-11} torr, or less, thus enabling optimisation of the pumping procedure to obtain better results. The mass spectrometer also identifies organic and other contaminants, thus giving information on the cleanliness of the vacuum. Should any leaks be present the mass spectrometer will identify their presence and provide a more rapid and sensitive means for their location than any other device.

The mass spectrometer gauge also enables the true total pressure to be computed from the sum of the individual partial pressures. In contrast the "total pressure" gauges of the ionization type only read "nitrogen equivalent" pressure and can therefore be in error by a factor of more than 4 in either direction depending on the residual gas composition. This is because the sensitivity of such gauges varies by more than a factor of twenty between the most sensitive gases, such as mercury, the high molecular weight hydrocarbons and other large molecule gases, and the least sensitive gases which are hydrogen, helium and neon. Also, these total pressure gauges have serious non-linearity effects at pressures below about 10^{-10} torr whereas mass spectrometers are truly linear down to the lowest detectable pressures.

CHOICE OF INSTRUMENT

The simplest forms of mass spectrometer are of the magnetic deflection type and these are the most suited for general vacuum monitoring on account of price, size, reliability and simplicity of use. However, in some experimental investigations their small stray magnetic field, of the order of several gauss at 6 in (15 cm), can be a limitation. One solution may be to remove the magnet during the actual experimental observations. If this is not practical, due to simultaneous monitoring of the gas composition being required, then it will be necessary either to provide magnetic shielding or to use a non-magnetic type of mass spectrometer, such as the quadrupole.

The least expensive and most compact of all the mass spectrometer gauges is the type based on 180° deflection of the ions in a magnetic field. This type of mass spectrometer is characterised by extremely good reproducibility of performance even under adverse vacuum conditions due to the strong collimation of the electron beam by the magnetic field⁽¹⁾. Furthermore, in more recent designs such as Micromass 1 and 2, all the critical parts of the ion source are very simple to dismantle, clean and re-assemble in case this should eventually become necessary through mis-use or prolonged operation under extremely adverse conditions.

The small radius (1 cm) 180° deflection instruments have the advantage that because their ion path is short (3 cm), they are useable up to higher pressures (10^{-2} torr) than most other types of mass spectrometer.

The only precaution necessary in the use of these mass spectrometers is to ensure that the pressure is below 10^{-2} torr before the filament is switched on and to provide a trip-out means in case the pressure subsequently rises above this value. If ion pumping is being used the pump control unit will provide such pressure indication and protection. Otherwise it will be advisable to fit a simple form of total pressure gauge.

Some mass spectrometers are fitted with electron multiplier detectors and these enable the detection of partial pressures down to 10^{-15} torr using a 1 sec recorder read-out. Alternatively, at some sacrifice in detection limit, a fast response amplifier and oscilloscope may be used to give a standing visual display of the complete spectrum at a repetition rate of 25 scans per second.

Limitations of electron multipliers, apart from additional expense and size, are that their gain changes slowly with age and rapidly, though temporarily if subjected to continuous bombardment by intense ion beams, particularly those of the rare gases. Also the gain is a function of the ion species, depending both on mass and atomic composition. A further limitation is their apparent non-linearity at very low ion currents due to the statistical effects of a relatively small number of individual ions arriving during the scanning of a particular mass peak.

Nevertheless, electron multipliers greatly extend the possibilities of mass spectrometry in studying transient phenomena at low pressures and the fast repetitive scans with oscilloscope display are of very great convenience in everyday vacuum work, where often only semi-quantitative information is required.

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OPERATING PRINCIPLE

Any mass spectrometer does three things:

- (1) It produces ions. This is done in the ion source.
- (2) It separates the ions according to their mass (actually according to their mass to charge ratio so that a double charged ion of mass M is tuned at the $M/2$ position). This is done in the analyser.
- (3) It measures the relative intensity of ions of different mass. This is done in the detector.

Generally the instrument also provides some form of scanning so that the whole, or part, of the mass range can be displayed as a series of peaks of different mass number, each of individual height corresponding to the relative intensity of the ion beam at that mass number. The result is a mass spectrum.

ION SOURCE. Mass spectrometers for analysing gases and vapours, as in vacuum applications, generally have an electron bombardment type of ion source. In some the electron beam is constrained to a sharply defined ribbon by means of a magnetic field as shown in Fig. 1.

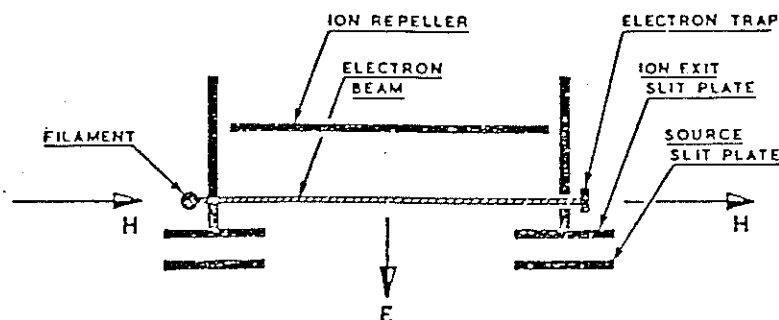


FIG. 1. ELECTRON BOMBARDMENT ION SOURCE WITH MAGNETIC COLLIMATION AS USED IN 180° MASS SPECTROMETERS

With such an arrangement it is possible to stabilise the ionizing electron current rather than the total filament emission. This is done by allowing the electron beam to pass through a large exit aperture in the ionization box and collecting it on the trap electrode. The filament power is then electronically regulated to maintain a constant trap current. Instruments incorporating such a trap current regulator, as distinct from total emission regulator, are to be preferred as the sensitivity is less liable to variation with filament age, alignment or leakage across insulators.

ANALYSER There are many arrangements for separating ions according to their mass but only two basic principles are involved, namely:

- (1) Ions of different mass accelerated through the same potential follow paths of different radii on passing through a magnetic field. This is the basis of the magnetic deflection type of instruments of which the commonest are the 180° instruments (both source and collector immersed in the magnetic field) and the sector instruments (either, or both, source and collector external to field).
- (2) Ions of different mass accelerated through the same potential travel with different velocities. The commonest and most important example today is the radio frequency quadrupole mass filter. Other examples, receiving varying popularity in the past, have been the time-of-flight, linear R. F. and omegatron instruments.

A diagram of a typical 1 cm radius, 180° magnetic deflection instrument is shown in Fig. 2.

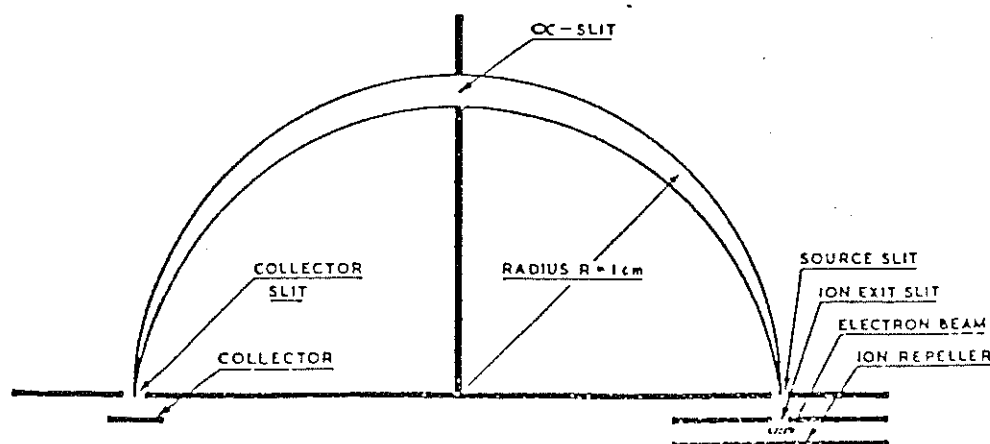


FIG. 2. DIAGRAM OF 1 cm RADIUS, 180° MAGNETIC DEFLECTION MASS SPECTROMETER
(MAGNETIC FIELD DIRECTED INTO PLANE OF THE PAPER)

DETECTOR. Two types of detector are commonly used, namely:

- (1) The Faraday plate. This is a simple plate electrode on to which the ion beam impinges after passing through the collector slit. Generally some means of suppressing secondary electrons from the collector should be provided though this is unnecessary in cases, such as the 180° geometry, where the collector is immersed in the magnetic field.
- (2) The electron multiplier. The ion beam here impinges on the first dynode of an electron multiplier which may have between 9 and 20 stages giving an overall gain of about 10^6 . With this gain it is possible to detect and count the arrival of individual ions though this is rarely done in vacuum applications. The dynodes are commonly of either Be-Cu or Ag-Mg and both have been used successfully for vacuum investigation.

SCAN AND READ-OUT. Scanning on magnetic deflection instruments is by varying either the ion accelerating voltage ($M \propto 1/V$) or the magnetic field ($M \propto H^2$) and on quadrupole instruments by varying either the voltages ($M \propto V$) or frequency ($M \propto 1/f^2$) applied to the quadrupole rods. On some magnetic instruments the voltage is varied by a motor driven potentiometer with calibrated linear mass scale and the circuit is chosen so that the mass scan against time is linear, thus giving a linear mass scale on the recorded spectrum. Such a feature greatly simplifies the identification of unknown spectra.

Read-out can be on any recording system with appropriate input characteristics and response time. Those most commonly used for vacuum applications are the 1 sec. potentiometric pen recorder for the simpler type of mass spectrometer and the cathode ray oscilloscope for those fitted with an electron multiplier. However the U.V. type of multi-channel galvanometer, strip chart, recorder offers advantages where high speed and precise quantitative measurements over a wide range of signals are required. Typically such a recorder would be used with 3-channels set for sensitivities of $\times 1$, $\times 10$ and $\times 100$.

RESOLVING POWER DEFINITIONS

There are many definitions of resolving power but the one most commonly accepted by mass spectroscopists in comparing instrument performances is known as the "10% valley definition". According to this definition if the resolving power is specified as X , the valley between two peaks of equal height, h , at masses $X-1$ and X will approach to within 10% h of the base line see Fig. 3a).

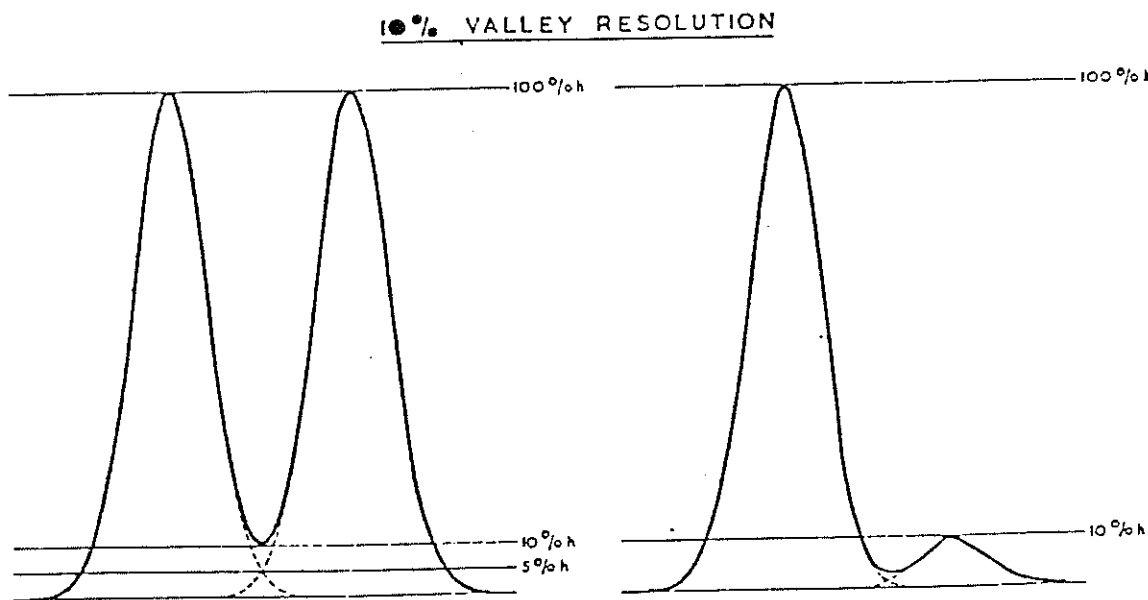


FIG. 3a.

PLOT OF TYPICAL PEAKS AT MASSES $X-1$ AND X , WHERE ' X ' IS THE RESOLVING POWER ON '10% VALLEY' DEFINITION

Such a definition also means that the resolving power can be measured from a single peak, occurring anywhere in the spectrum by measuring the width, ΔM at 5% peak amplitude, that is $RP = M/\Delta M$ where M = mass number of peak and ΔM is the peak width measured in atomic mass units and for a magnetic deflection instrument $M/\Delta M$ is determined as the ratio of the ion acceleration voltage, V , required to tune in mass M to the voltage, ΔV , required to move from one 5% height point on the peak to the opposite one, that is:

$$RP = M/\Delta M = V/\Delta V$$

The "10% valley" resolution number is the highest mass at which accurate quantitative measurements can be made for two peaks at adjacent mass numbers and not differing in intensity by more than 10 : 1.

However for much semi-quantitative work, as is often all that is required in vacuum investigations, a lesser resolution capability is adequate. This has led to a second number, "the unit mass resolution" of "50% valley resolution" being quoted. Suppose this number is Y . Then unit mass resolution means that two peaks at $Y-1$ and Y will be detectable as separate masses provided that their intensity ratio is not more than 10 : 1. (see Fig. 3b).

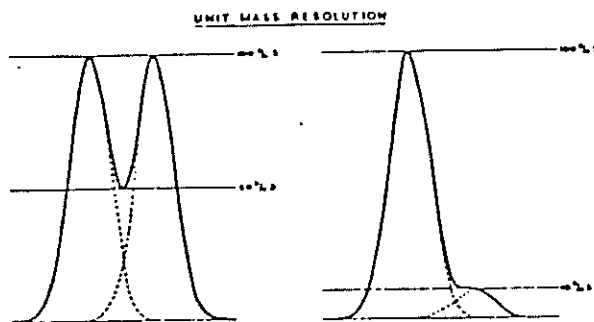


FIG. 3b. UNIT MASS RESOLUTION. TWO TYPICAL PEAKS AT MASSES 1-1 AND 2, WHERE Z IS THE RESOLVING POWER ON THE UNIT MASS DEFINITION.

A third definition, used by some manufacturers but not generally approved of by mass spectroscopists, is the "resolution at half-height", which is given as $RP = M/\Delta M$ where ΔM is the peak width between the 50% h points (see Fig. 3c). This definition gives a high number which is not directly related to a corresponding ability to separate peaks in the corresponding mass region as is shown in the Figure.

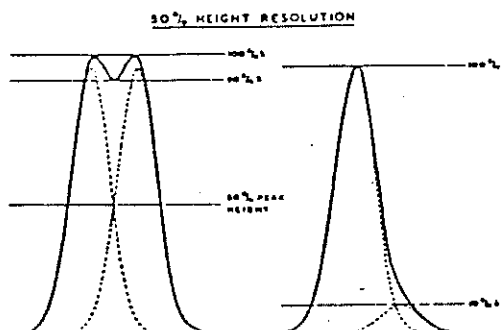


FIG. 3c. 50% HEIGHT RESOLUTION. TWO TYPICAL PEAKS AT MASSES 1-1 AND 2, WHERE Z IS THE RESOLVING POWER ON THE 50% HEIGHT DEFINITION.

The ratios of the three resolving powers $X : Y : Z$, defined above, will depend on the detailed shape of the mass peaks and this can vary with the type of instrument and operating conditions. However, for the typical shapes shown in the figures the ratio $X : Y : Z$ is 100 : 144 : 200.

INTERPRETATION OF MASS SPECTRA

ANALYSIS OF THE COMMON GASES. A mass spectrum is a unique means of identification. Consider, for example, the carbon monoxide spectrum shown in Fig. 4.

When molecules of carbon monoxide are struck by electrons the 'parent' or molecule ion CO^+ , the fragment ions C^+ and O^+ and doubly charged ions CO^{++} are formed in different proportions, giving a characteristic spectrum, as shown, with main peaks at masses 28, 12, 16 and 14. In addition there will be other minor peaks due to the less abundant isotopes, for example at mass 29 a peak due to $^{13}C^{16}O^+$ and $^{12}C^{17}O^+$ and at mass 30 are due to $^{12}C^{18}O^+$.

SCALE ☒ = x 1 RANGE
☐ = x 10 RANGE

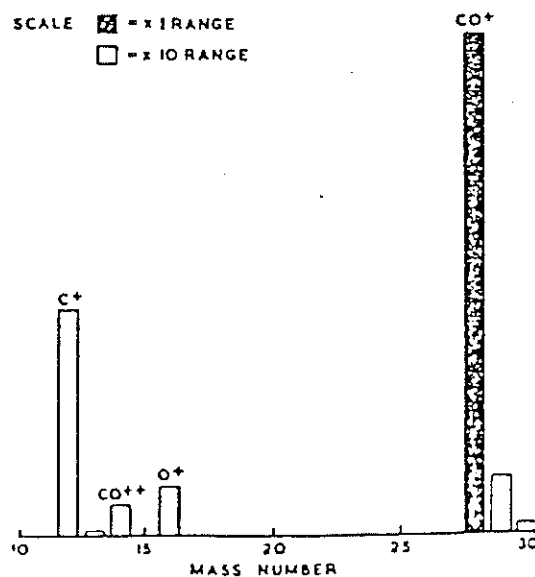


FIG. 4. CARBON MONOXIDE SPECTRUM

For a particular mass spectrometer the fragment peaks should always occur in the same ratio. Thus each gas component may be characterised by its own individual spectrum which is conveniently expressed as a 'cracking' pattern such as given in Table 1.

TABLE 1 Cracking pattern for carbon monoxide

m/e	12	13	14	14.5	15	16	28	29	30
Relative Intensity	4.5	0.046	0.60	0.006	0.001	0.96	100.0	1.13	0.20

Some residual gas atmospheres are so simple that it is not necessary to know the cracking patterns. A common example is when only H_2 , water vapour and N_2 are present. In which case each component has a unique peak which is not interfered with by the cracking pattern spectrum of the other components. (Note: the H_2^+ peak of H_2O is negligible). In such cases it is only necessary to know the relative sensitivity of each component to nitrogen and the absolute sensitivity of the latter. With this information the identification and partial pressure of each component is easily worked out.

In other cases the spectra of the various components may overlap as happens for example when CO_2 , O_2 , CO and N_2 are present (see Fig. 5). To obtain the partial pressures for such an atmosphere requires a knowledge of the cracking patterns of each component gas present, in addition to the relative and absolute sensitivities.

The procedure in the example quoted would be first to subtract the contributions of the two higher mass components from the measured spectrum. This may be done since the 44-peak is uniquely representative of CO_2 , and the 32 peak is uniquely representative of O_2 . Two simultaneous equations based on the 12 and 14 peaks can then be set up and solved to determine the relative contributions of CO and N_2 at mass 28.

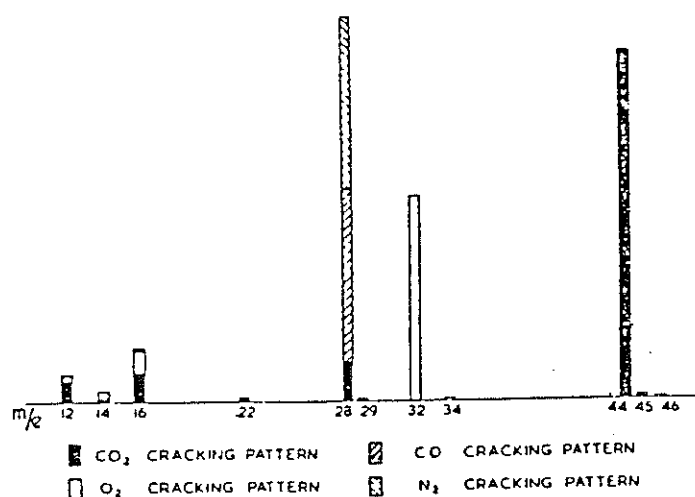


Fig. 5. Spectrum of a simple gas mixture.

Cracking patterns, relative and absolute sensitivities for magnetic deflection instruments are very reproducible and for the accuracies $\sim 10\%$ commonly required in vacuum studies it should be sufficient to use the manufacturers' data such as given in Table 2.

TABLE 2. Relative sensitivities for some common gases on a 1 cm 180° mass spectrometer

Gas:	H_2	He	CH_4	H_2O	Ne	CO	N_2	O_2	A	CO_2	Kr	Xe	Hg
Relative Sensitivity	0.700	.23	1.08	1.17	0.24	1.09	1.00	0.62	1.16	0.90	0.80	1.56	1.30

For greater accuracy than 10% the mass spectrometer should be individually calibrated.

IDENTIFICATION OF ORGANIC VAPOURS. Detailed and comprehensive tables of cracking patterns have been catalogued for many thousands of chemical compounds and if a complete spectrum of an unknown material is available its cracking pattern may be computed and compared with an appropriate catalogue. The work involved may however be tedious and the answer uncertain if the unknown spectrum is not due to single pure compound.

An alternative and simpler approach proposed by Craig et al.⁽²⁾ is to use a low resolving power (20 to 40) and obtain 'fingerprint' spectra such as shown in Fig. 6. Such simplified spectra, once initially identified, are quick to recognise again and are adequate for most vacuum investigations where the main problem is usually to identify the major organic contaminant and establish its approximate partial pressure.