EXTREME HIGH VACUUM

P.A. Redhead
National Research Council
Ottawa, Canada

Abstract

Methods for producing and measuring extreme high vacuum (XHV, which is the pressure range below 10^{-10} Pa) and the limits on measurement and production are examined. Techniques for reducing the outgassing rates of the walls and components of XHV systems, including the gauges or RGAs, are described and some of the lowest measured outgassing rates tabulated. The lowest pressures attained in the XHV range have remained approximately constant for 35 years, explanations for this plateau in ultimate pressure are offered.

1. INTRODUCTION

Ultrahigh vacuum (UHV) is defined as the pressure range between 10^{-6} Pa (in Europe) or 10^{-7} Pa (in the USA) and 10^{-10} Pa; extreme high vacuum (XHV) is defined as the range of pressure below 10^{-10} Pa (7.5×10^{-13} Torr or 10^{-12} mbar). Ultrahigh vacuum is routinely achieved with commercial equipment around the world; XHV is produced and measured with difficulty in a few laboratories with special equipment. The need for UHV is widespread; the need for XHV is limited at this moment to some accelerator and storage ring facilities, to the simulation of interstellar space, in the processing of advanced semiconductor devices, and to a few other specialised applications. Research in the improvement of XHV methods, which is at the limits of vacuum science, will almost certainly improve the techniques used in the higher pressure ranges, as happened in the 1950s and 1960s with the development of UHV. Some of the gas phase parameters of XHV are shown in Table 1.

Table 1

Gas phase parameters at XHV

Pressure (Pa)	Molecular density at 298 K	Molecular flux N_2 at 295 K (molec. cm^{-2} s^{-1})	Molecular mean free path λ* N_2 at 295 K	Monolayer time**
10^{-10}	2.5×10^4 cm^{-3}	2.9×10^8	3.4×10^4 km	44 days
10^{-13}	25 cm^{-3}	2.9×10^5	3.4×10^7 km	120 years
10^{-17} interstellar space	0.25 m^{-3}	29	2.3×10^3 astronomical units	1.2×10^6 years

* Mean free path for electrons is $\lambda_e = 4\sqrt{2}\lambda$, and for ions $\lambda_i = \sqrt{2}\lambda$.
**Assuming 10^{15} sites per cm^2 and a sticking probability of 0.5.

The *production* of XHV in small glass systems by cryogenic methods is not new. In the 1930s P.A. Anderson [1] was measuring the work function of barium and while working in Germany he immersed his sealed-off glass tubes in liquid hydrogen, the pressure must have been in the XHV range but it could not be measured. In the 1950s and for many years thereafter Gomer [2] immersed his sealed-off field emission and field ion macroscopes, about a litre in volume, in liquid hydrogen. These are just two examples of the early production of XHV without measurement capabilities.

In 1950 the invention of the Bayard-Alpert gauge [3] with its reduced X-ray limit made it possible to measure pressures below 10^{-6} Pa for the first time. By the late 1950s pressures approaching the XHV range were being achieved and measured. In 1958 Venema and Bandringa [4] built a glass system pumped by a mercury-diffusion pump which achieved a pressure of about 10^{-10} Pa, as

measured by a Bayard-Alpert gauge with a 25 μm diameter collector wire (to reduce its X-ray limit). Also in 1958 Hobson and Redhead [5] constructed a Pyrex glass system having a Bayard-Alpert gauge and an inverted-magnetron gauge [6] (IMG) which was pumped to about 10^{-8} Pa and then sealed-off. A glass finger extending from the system was immersed in liquid helium and the pressure measured by the inverted-magnetron gauge was about 10^{-10} Pa or less. Hobson has noted [7] that a 1-2 litre volume system pumped to UHV pressures, sealed-off, and then immersed in liquid helium will drop to a pressure of about 10^{-28} Pa if the residual gas is helium, this estimate was based on an extrapolation of the measured helium adsorption isotherm.

In 1962 W.D. Davis [8] used a stainless steel system containing a commercial sputter ion pump (5 l/s), a magnetic sector mass-spectrometer and a B-A gauge. With liquid nitrogen cooling of some of the components a total pressure of 4×10^{-11} Pa was observed. In 1964 Hobson [9] made measurements on an alumino-silicate glass system (used to minimise the permeation of atmospheric helium through the glass envelope) containing a modulated B-A gauge, an inverted-magnetron pump, and a titanium getter. After pumping to 7×10^{-9} Pa the system was sealed-off and the pressure fell to 1×10^{-10} Pa at room temperature, when part of the system was immersed in liquid helium the pressure was 10^{-12} Pa. Pressure measurements were made with the modulated B-A gauge. Thus by 1964 it had been established that XHV could be achieved in small glass systems with the use of cryogenic pumps although the measurement of pressure was still difficult.

In 1977 Thompson and Hanrahan [10] took a complex surface analysis system, made from stainless steel and containing a mass spectrometer, and pumped it to UHV. It was then totally immersed in liquid helium at 4.2 K, the pressure dropped to 10^{-12} Pa at 30 K as the system cooled and then became immeasurable. The metal surface at 4.2 K pumped all gases (including helium) while permeation through the cold envelope was reduced to near zero.

The problem now became how to extend the techniques for producing and measuring XHV, developed for small systems with very small gas loads, to larger systems with sizeable gas loads.

This paper addresses the problems of producing and measuring XHV, it is assumed that the reader is familiar with the science and technology of the production and measurement of UHV. Review articles concerned with XHV should be consulted for further details [11-15]. Information on materials and hardware for XHV, which are not treated in this paper can be found in these reviews.

2. GENERAL CONSIDERATIONS

The problems in achieving XHV can be seen in a general way by examining the conservation of mass equation for a vacuum system of volume V, pumped by a pump of speed S with a leak rate of L and a total outgassing rate of Q. Then if L, Q, and S are constant and a single gas predominates

$$V \frac{dp}{dt} = L + Q - Sp \ .$$

The total outgassing rate may be expressed as

$$Q + Q_T + Q_h + Q_d + Q_{st} \tag{2}$$

Q_T is the total thermal outgassing rate from the walls and components of the system ($Q_T = q_T A f$; q_T is the outgassing rate per unit area and f the surface roughness factor),

Q_h is the outgassing rate from heated components,

Q_d is the diffusion rate through envelope ($Q_d = q_d A f$),

Q_{st} is the desorption rate caused by electron, ion, or photon stimulation.

When the ultimate pressure p_∞ is reached then $dp/dt = 0$ and assuming that $L = 0$ (which is essential for XHV)

$$p_\infty = \frac{Q}{S} = \frac{(q_T + q_d)Af + Q_h + Q_{st}}{S} \ . \tag{3}$$

In general the maximum pumping speed that can be applied to a vacuum system of arbitrary size is approximately proportional to the surface area ($S_{max} = kA$), this is true for all types of pump. Thus the ultimate pressure with maximum pumping speed is approximately

$$p_\infty = \text{const.}\left\{(q_T + q_d)f + \frac{Q_h + Q_{st}}{A}\right\} \quad . \tag{4}$$

Although Eq. (4) is approximate it indicates the parameters that must be minimised to obtain ultimate pressures in the XHV range. If $Q_T + Q_d >> Q_h + Q_{st}$ then the ultimate pressure with maximum pumping speed is independent of the system volume and surface area

$$p_\infty = \text{const.}(q_T = q_d)f \quad . \tag{5}$$

The above equations are a considerable simplification since they are only strictly correct if the gas density is uniform throughout the vacuum chamber; at very low pressures in the presence of adsorbing surfaces or localised pumps (e.g. gauges acting as pumps with limiting conductance to the chamber) this is not necessarily the case. In practice, most extended XHV systems tend to exhibit non-uniform pressure distributions, particularly of the chemically active gases that are readily adsorbed in a system at room temperature. The problems of pressure non-uniformity at low pressures have been considered to some extent by Da [16], Grigorev [17], and Haefer [18].

3. PUMPS FOR XHV

We next consider the types of pumps suitable for XHV and their limitations. These pumps fall into two categories, kinetic pumps that impart momentum to the gas molecules and remove them from the vacuum system, and capture pumps that trap gas molecules by ionic entrapment, condensation, adsorption, or chemical reaction at a surface within the vacuum system.

3.1 Kinetic pumps

Two types of kinetic pump are candidates for XHV, they are the diffusion pump and the turbomolecular pump (TMP). The advantage of kinetic pumps is that they can maintain a low pressure indefinitely and remove large quantities of gas permanently from the system, whereas most capture pumps require some form of regeneration after they have pumped a specific quantity of gas and do not remove the gas from the system.

Some of the early experiments to achieve XHV in the 1950s used mercury or oil diffusion pumps with liquid nitrogen traps to prevent the back-streaming of pump fluid into the UHV chamber. Diffusion pumps retain their pumping speed indefinitely as pressure is reduced and they are available with H_2 pumping speeds from 0.1 to over 3.5 m^3 s^{-1}, but the forepressure must be maintained as low as possible because hydrogen in the forevacuum can back-diffuse to some extent through the vapour jets thus reducing the effective hydrogen pumping speed. Uncontaminated pressure in the XHV range cannot be reached with a diffusion pump without extremely careful trapping to prevent any back-streaming of the diffusion pump fluid or the rotary pump oil. It has been claimed that with properly trapped oil diffusion pumps and a getter pump it is possible to achieve 10^{-12} Pa [19]. Diffusion pumps are not now widely used for XHV, partly as a result of difficulties in ensuring dependable, long-term trapping.

Turbomolecular pumps have considerable advantages for XHV since they can provide a completely oil-free system and, unlike diffusion pumps, most designs can be operated in any position. This is possible because the TMP can be designed to operate against a high backing pressure that can be provided by an oil-free diaphragm pump, and the rotor can be magnetically suspended to avoid lubricated bearings. The predominant gas at XHV is hydrogen, thus special steps must be taken to increase the low compression ratio for hydrogen (about 10^4) in the TMP, the conventional TMP is only capable of achieving about 10^8 Pa. In 1990 a tandem TMP structure (with magnetic suspension) consisting of two TMPs on the same shaft was developed [20], the upper section designed for a high

compression ratio and the lower portion for high throughput. This type of pump had a H_2 compression ratio of 5×10^8 and a maximum backing pressure of 0.5 Torr, it achieved a pressure of 10^{-9} Pa. It was shown [21] in 1994 that the eddy-current losses in the magnetic suspension can cause a temperature increase in the rotor of 60°C resulting in outgassing. By coating the lower half of rotor and stator with a high emissivity layer (SiO_2 with emissivity of 0.9) the rotor temperature was reduced to 25°C allowing a pressure of $< 10^{-10}$ Pa to be obtained. Cho et al. [22] used a TMP with magnetic suspension backed by a small molecular drag pump followed by a dry diaphragm pump, after careful baking the final pressure was in the low 10^{-10} Pa range.

3.2   Capture pumps

Capture pumps include ion, getter, and cryopumps (and combinations thereof), and have been reviewed in some detail by Welch [23].

The main problem with a **sputter-ion pump** (SIP) at XHV is that the pumping speed decreases with pressure [24] as the discharge intensity (current per unit pressure) decreases. Re-emission of previously pumped rare gases is also a problem with SIPs. The main purpose of an ion pump in the XHV range is to provide some pumping speed for the gases that are not pumped by getter pumps (methane and the rare gases).

It was shown in the early 1960s that some speed was retained by an SIP at very low pressures, Davis [8] in 1962 achieved pressures in the 10^{-11} Pa range with a commercial 5 l s^{-1} SIP. The rate of decrease of the pumping speed of an SIP at pressures in the UHV and XHV ranges is critically dependent on magnetic field, anode voltage, and dimensions of the pumping cell. Pumping speed is proportional to discharge intensity (i_+/p); i_+/p increases with anode diameter and increasing the magnetic field tends to raise i_+/p at low pressures.

Getter pumps, both evaporable and non-evaporable, are widely used in XHV, however they do not pump the rare gases and their speeds for hydrocarbons are negligible. Evaporated titanium films at room or liquid nitrogen temperatures have been used, in combination with other pumps needed to remove the rare gases and methane, down to pressures of 10^{-11} Pa and below. For chemically active gases (e.g. H_2, H_2O, CO, CO_2, O_2, and N_2) a sticking probability of about 0.5 is achieved on freshly evaporated metal films, thus pumping speeds of about 5 ls^{-1}cm^{-2} can be achieved. Renewal of the film is necessary after about a monolayer of gas has been adsorbed. For titanium a capacity of about one pumped molecule to one evaporated titanium atom is possible. Freshly evaporated titanium films tend to outgas methane unless very pure titanium is used or the film is baked at 100°C for a few hours. Non-evaporable getters (NEG) are very effective in the XHV range because of their high pumping speed to hydrogen. NEGs are particularly useful in accelerators and storage rings since they can be placed very close to beam lines. Benvenuti [25] has achieved pressures as low as 5×10^{-12} Pa in a 3 m long section of an accelerator ring using a 43.5-m long Zr-V-Fe NEG strip, a sputter ion pump (400 l s^{-1}), and a titanium sublimation pump.

Benvenuti has developed a method of coating the interior of a stainless steel system with a thin film (~1μm) of getter material deposited by sputtering [26]. Ti, Zr, V and their binary alloys have been used. The coating is transformed from a gas source to a pump by an in situ bakeout at temperatures of 250-300°C. Pressures as low as 10^{-11} Pa have been produced by this method.

Cryopumps used in the XHV range fall into two categories, a) **cryo-condensation pumps** which physisorb more than 2-3 monolayers of gas on a smooth surface of relatively small area, and b) **cryo-sorption pumps** having a porous surface of very large effective area with less than 2-3 monolayer of physisorbed gas.

For the **cryo-condensation pump** the limiting pressure is the vapour pressure of the adsorbed gas at the temperature of the surface, and the capacity of the cryo-condensation pump is essentially infinite, at least until the thickness of the adsorbed layer causes problems. Condensation coefficients of about 0.5 are typical and hence maximum pumping speeds of about 5 l s^{-1} cm^{-2} are possible; however, such speeds cannot be obtained in most situations because the cryosurface must be protected from room temperature radiation by suitable baffles at an intermediate temperature, the exceptions are when the complete wall of the vacuum system is a cryosurface (e.g. in the cold bore of

an accelerator or storage ring with superconducting magnets). The low-pressure limit can in principle be made infinitely low since desorption can be reduced to near zero by lowering the temperature. Table 2 shows the temperatures at which the vapour pressure of some common gases is equal to 1.3×10^{-8} and 1.3×10^{-11} Pa respectively[15] it can be seen that only hydrogen, neon and helium may limit the pressure in a cryo-condensation pump at 10 K to more than 10^{-11} Pa.

Table 2
Temperatures (K) for two selected vapour pressures of common gases

Gas	Vapour Pressure 1.3×10^{-8} Pa	Vapour Pressure 1.3×10^{-11} Pa
H_2	3.21	2.67
He	0.303	0.250
CH_4	28.2	24.0
H_2O	130.0	113.0
Ne	6.47	5.5
CO	23.7	20.5
N_2	21.1	18.1
O_2	25.2	21.8
Ar	23.7	20.3
CO_2	68.4	59.5
Kr	32.7	27.9
Xe	45.1	38.5

Data mainly from R.E. Honig and H.O. Hook, RCA Review, **21**, 360 (1960).

For the **cryo-sorption pump** the limiting pressure is established by an appropriate isotherm relating the equilibrium pressure to the surface coverage, for the XHV region the Dubinin-Radushkevich isotherm has been found appropriate for most gases [27]. A cryo-surface with less than monolayer coverage at 4.2 K will pump all gases to extremely low pressures.

In the preparation of highly porous surfaces for cryo-sorption pumps at XHV it is necessary to obtain good thermal contact between the porous material and the underlying cooled surface to achieve rapid thermal equilibrium. Figure 1 shows adsorption isotherms for hydrogen on several different surfaces [28] at 4.3 K, the sudden drops at pressures in the 10^{-13} Torr range are probably due to the X-ray limit of the extractor gauge used to measure pressure. It can be seen that the porous aluminium oxide surface (anodised aluminium with an oxide layer having small pores and a thickness of about 40 μm) has a hydrogen adsorption capacity more than 10^3 times as great as a smooth stainless steel surface.
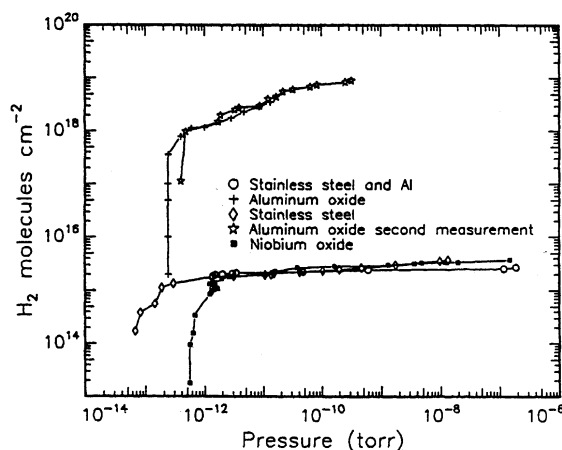

Fig. 1 Hydrogen adsorption isotherms at 4.3 K on various surfaces [28].

The choice of pump(s) for XHV depends on the application and the resources available. For relatively small systems a good choice is the magnetically suspended turbomolecular pump backed with a diaphragm pump combined with a getter pump. The use of liquid helium cryopumps, including the possibility of complete immersion, is economical where liquid helium is readily available.

For large systems the choice of pumps is dominated by costs and frequently by the difficulty of access to the vacuum chamber (as in accelerators and storage rings). Non-evaporable getters combined with sputter-ion or cryopumps are a frequent choice. Where superconducting magnets are used it is possible to use the cold bore of the beam line as a cryo-pump, this has been done in some storage rings and accelerators.

4. PRESSURE MEASUREMENT AT XHV

4.1 Ionisation gauges

The requirements for an XHV gauge is that the X-ray limit be sufficiently low and that the gauge design permits the separation of ESD ions from gas-phase ions. Table 3 lists six hot-cathode gauge designs with X-ray limits in the XHV range and which are able to separate ESD ions from gas phase ions. Only the extractor gauge is commercially available at present.

Table 3
Characteristics of gauges suitable for XHV

Gauge	Electron Emission (A)	P_x** (Pa)	P_{min}*** (Pa)	Sensitivity (A Pa^{-1})	References
Hot-cathode magnetron (Lafferty gauge)	1×10^{-6}	6×10^{-13}	10^{-14}	7×10^{-4} [N_2]	[36]
Extractor (Leybold IE511)	1.3×10^{-3}	2×10^{-10}	10^{-11}	1×10^{-4} [N_2]	[34]
90• Bent-beam (Helmer gauge)	3×10^{-3}	$< 2 \times 10^{-12}$	10^{-12}	1×10^{-3} [N_2]	[29]
180° Bent-beam* (Ion spectroscopy gauge)	5×10^{-3}	$< 2.5 \times 10^{-13}$	$< 10^{-12}$	4×10^{-4} [N_2]	[30]
256.4° Bent-beam*	1×10^{-4}	$< 6 \times 10^{-12}$	4×10^{-13}	1.8×10^{-6} [H_2]	[31]
Bessel box* (A-T gauge)	3×10^{-5}	3.5×10^{-11}	10^{-12}	1.8×10^{-7} [N_2]	[37]

* These gauges have electron multipliers.
** Pressure at which the ion current equals the residual current (the X-ray limit).
*** Approximate lowest measurable pressure.

Separation of ESD ions from gas phase ions is possible because of their differing energies. Electron space charge, in the grid of an ionisation gauge or the ion source of an RGA, causes a reduction of potential. Thus ESD ions released from the surface of the grid have a higher energy than gas phase ions generated within the grid.

Three of these gauges have electrostatic energy filters that separate the ESD and gas-phase ions on the basis of their initial kinetic energy, and reduce the X-ray limit by shielding the ion collector from the direct X-ray flux. These are the 90°, 180°, and 256.4° bent-beam gauges which are shown schematically in Fig. 2, the first two are also known as the Helmer gauge [29] and the ion spectroscopy gauge [30] respectively. All three gauges use electron multipliers (SEMs) and the 90° and 256.4° gauges have cylindrical deflection electrodes while the 180° gauge has hemispherical deflectors. The 256.4° gauge [31] has been tested with a cold emitter [32] (a field emission array) and its operation as a T-O-F mass spectrometer [33] will be discussed later.

Figure 3 shows the other three gauges schematically. The extractor gauge [34] can measure to less than 10^{-11} Pa with subtraction of the X-ray limit that can be easily measured on the operating gauge [35] this gauge does not have an SEM. It has been shown that the extractor gauge is relatively insensitive to ESD ions. The hot-cathode magnetron gauge is potentially capable of measuring to a lower pressure than any other if provided with an SEM. There is no separation of ESD and gas phase ions in this gauge but the electron current at the anode surface is so low that ESD effects are small. Its X-ray limit has been further reduced by the addition of a suppresser electrode in front of the collector [36]. Like all long-electron-path gauges it is subject to instabilities which are minimised by operation at very low electron currents. The Bessel box gauge [37] (A-T gauge) is an attractively simple design providing separation of ESD and gas phase ions.

A possible future method of measuring XHV pressures is the lifetime of charged particles in a Penning trap.
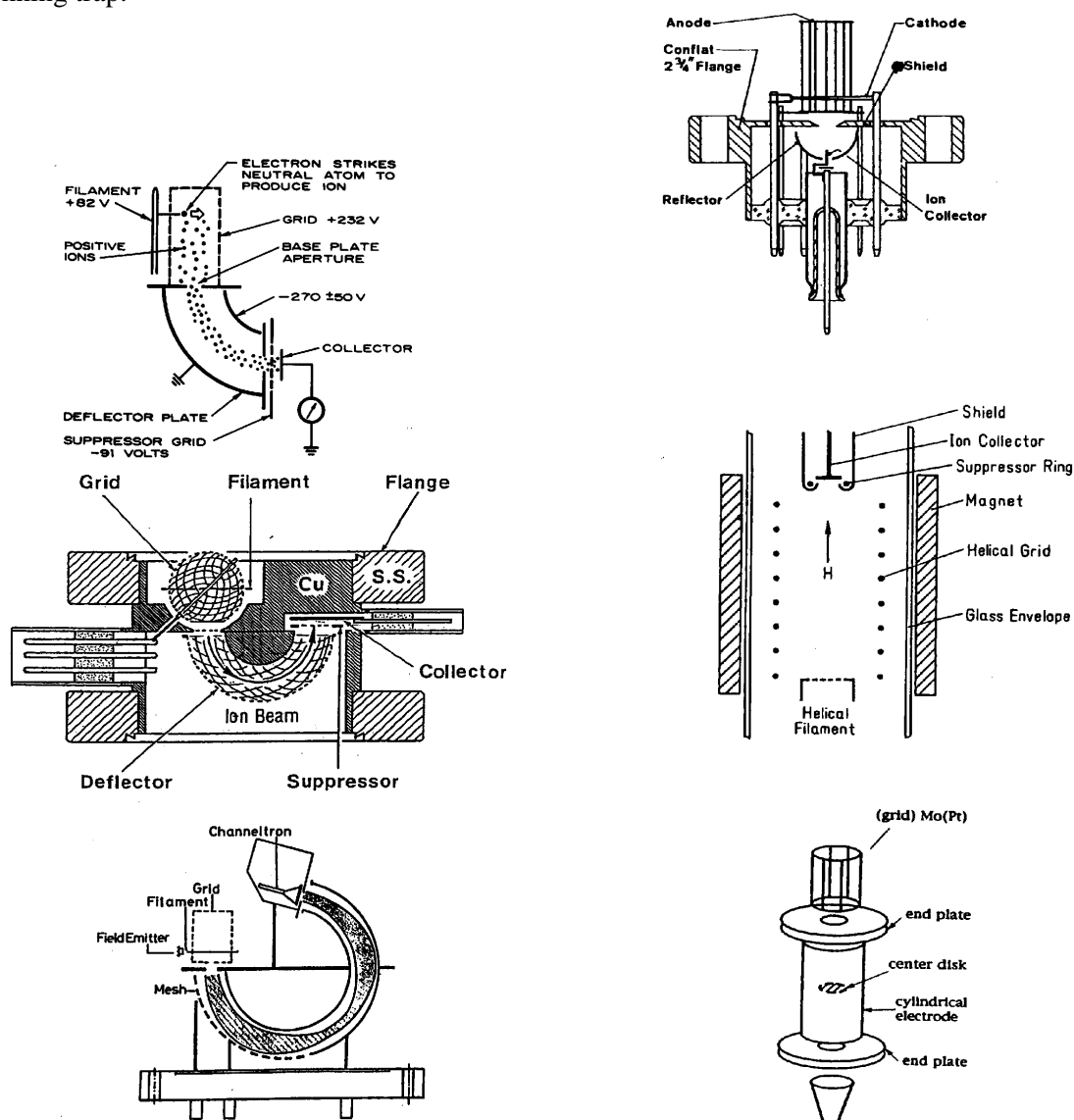

Fig. 2   Diagrams of three bent-beam gauges suitable for XHV. Top, the Helmer gauge [29] (90° bent-beam). Middle, the ion spectroscopy gauge [30] (180° bent-beam). Bottom, 256.4° bent-beam [31].

Fig. 3 Diagrams of three other gauges for XHV. Top, the extractor gauge [34]. Middle, the hot-cathode magnetron gauge with suppresser electrode [36]. Bottom, the A-T gauge [37] (Bessel box filter).

4.2 Processes limiting XHV measurements

The physical and chemical processes limiting the minimum measurable pressure of ionisation gauges and mass-spectrometers (i.e RGAs and leak detectors) in the XHV range include:

1. X-ray limit

2. Electron-stimulated desorption (ESD) of positive and negative ions and neutrals

3. Effects at hot cathodes

a) Increased outgassing resulting from the heating of electrodes and the envelope by radiation from the hot cathode.

b) Evaporation of neutrals and ions from the cathode.

c) Chemical reactions of gas molecules at the hot surface resulting in changes in gas composition.

4. Desorption from the gauge electrodes and walls by soft X-rays produced by the ionising electrons.

These limitations are the same as in the UHV range and have been described in detail elsewhere (see Ref. [14] and references contained therein). Here we shall only consider those effects that are particularly troublesome at XHV. The separation of ESD ions from gas phase ions in XHV gauges has been discussed above and Fig. 4 shows an example of the separation achieved in two types of bent-beam gauges, the ion spectroscopy and the Bessel box gauges. However, the ESD of neutrals from the grid of a gauge or RGA dominate the ESD problem at XHV [38]. Watanabe [39] has demonstrated that this effect can be reduced by heating the grid to about 550°C to minimise the surface coverage of adsorbed gas, see Fig. 5.
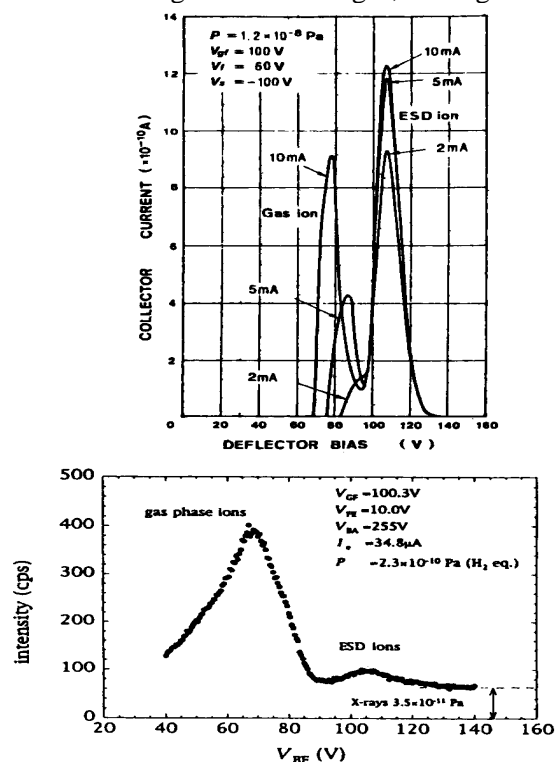

Fig. 4 Demonstration of the separation of ESD and gas phase ions in two bent-beam gauges. Top, the ion spectroscopy gauge [30]. Bottom, the Bessel box gauge [39].
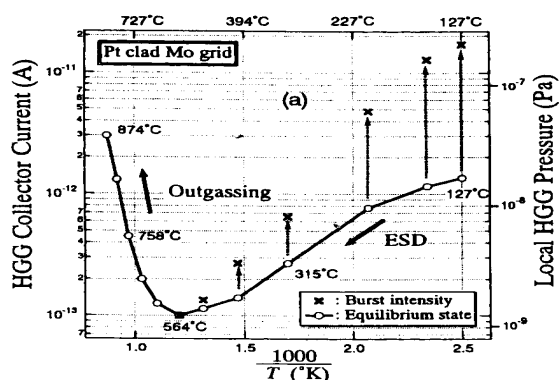
Fig. 5 Pressure, or extractor gauge ion current, vs. the reciprocal of grid temperature. The crosses indicate the pressure bursts after 30 minutes interruption of electron emission [39].

The outgassing resulting from a hot cathode, which is a particular problem at XHV, can be minimised by three methods: a) Using a low work function cathode to reduce the heating power required; thoria or yttria coatings on a refractory metal or a dispenser cathode [40] have been used successfully. b) Using a cold emitter such as an FEA, though the reliability and outgassing of these cathodes for use in vacuum gauges and RGAs is not yet assured. c) The metal envelope of the gauge or RGA can be replaced with a material of low emissivity and high conductivity to reduce the power required to heat the cathode. OFHC copper is a suitable material, a gauge envelope made of this material rather than stainless steel reduced the outgassing rate by a factor of 10 for an ionisation gauge [41] and a factor of 100 for an RGA [42].

In spite of improvements in reducing the ESD of neutrals and the outgassing due to cathode heating the outgassing from the gauge or RGA appears to be the limiting factor in attaining lower pressures in the XHV range. Desorption caused by soft X-rays may also be a limiting factor but this effect has not yet been carefully studied.

4.3   Residual gas analysers

In an RGA there is no practical X-ray limit since any X-ray induced photocurrent only adds to the mass independent background current. However, ESD ions are produced by electron bombardment of material adsorbed on the electron collector of the ion source, the ESD ions most frequently seen are; 1 (H^+), 10 and 11 (B^+ when LaB_6 cathodes are used), 16 (O^+), 19 (F^+), 23 (Na^+), 28 (CO^+), 35 and 37 (Cl^-), and 39 (K^+).

The mass-filter action of a quadrupole MS is very sensitive to the kinetic energy with which the ions are injected into the quadrupole structure. A complete separation of the two types of ions is possible either by modulating the ion accelerating voltage (typically at 125 Hz) and adjusting the mean value of the ion accelerating voltage while detecting the ion current with a lock-in amplifier [43], or by placing an electrostatic energy analyser between the ion source and the quadrupole structure [44], or between the quadrupole and the electron multiplier [45]. A time-of-flight technique has been applied to a quadrupole MS to separate ESD and gas phase ions [46]. By coupling the output of an ion-spectroscopy gauge to a quadrupole F. Watanabe has been able to completely separate the spectra of ESD ions and has demonstrated that neutral species dominate ESD at low pressures. It may be necessary to heat the grid (electron collector) of the ion source of an RGA to minimise the outgassing of neutrals by ESD.

The 256.4° bent-beam gauge has been operated as a TOF mass spectrometer [33] giving complete separation of ESD and gas phase ions, Fig. 6 shows the mass spectra obtained at a pressure of 23×10^{-10} Pa. Only a large H_2 peak is seen in the gas phase spectrum, the ESD spectrum shows H^+, H_2^+, O^+ and other ions.

The problems of thermal outgassing from an RGA are the same as for ionisation gauges and the same methods for reduction can be used. Methods to reduce the outgassing from quadrupole RGAs have been examined by several experimenters [41, 47, 48]. Cold emitters (FEAs), to reduce heating of the ion source, have been tested in quadrupoles successfully [46] but the problem of noise and long term stability are not yet resolved.

5.   LEAK DETECTION

It is necessary to reduce the leak rate into an XHV system to as near zero as possible, this raises the problem of the measurement of very small leak rates. The sensitivity of conventional helium leak detectors is about 10^{-12} Pa $m^3 s^{-1}$, a higher sensitivity is desirable to test XHV systems. To achieve this increased sensitivity it is necessary to accumulate the helium, that enters the system through the leak, either in the gas or adsorbed phase.

The sensitivity of a helium leak detector can be increased by reducing the helium pumping speed to zero in a closed system and allowing the helium to accumulate in the gas phase, the pumping speed to active gases can be kept high by the use of non-evaporable getters or a cryopump operating at about 18K, neither of which will pump helium. The leak rate is determined, after calibration, by the

rate of rise of the helium ion current in the mass spectrometer (usually a quadrupole). A helium leak detector system using non-evaporable getters and the rate of rise method [49] is claimed to routinely detect leaks as small as 10^{-16} Pa m^{3}s^{-1}.
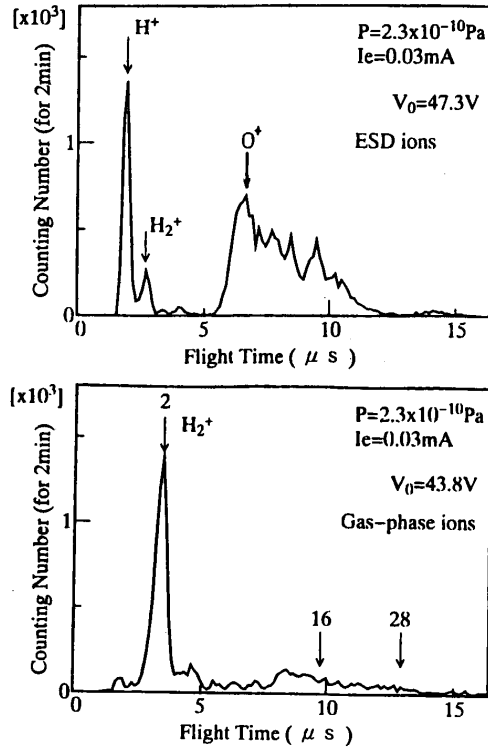

Fig. 6 The T-O-F spectra obtained with the 256.4° bent-beam gauge [33] at 2.3x10^{-10} Pa. Top, gas phase ions. Bottom, ESD ions.
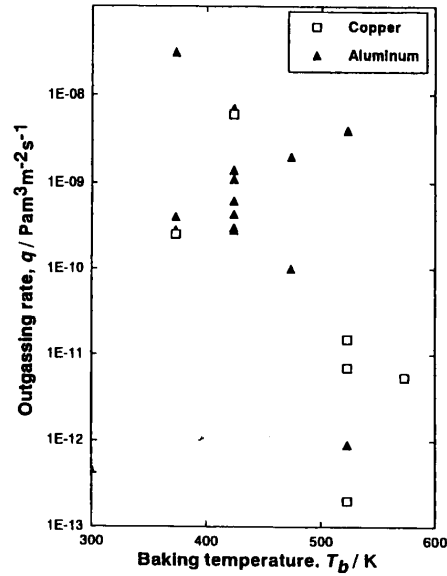
Fig. 7 Outgassing rate of copper and aluminium as a function of bakeout temperature [58].

Another method has been developed [50] in which the helium is adsorbed on a metal plate at 9 K or less in a closed system, the active gases are adsorbed on surfaces at about 20 K which may have porous carbon or non-evaporable getter material on them. The temperature of the helium adsorbing plate is raised to 10 to 20 K by an internal heater and the pressure of the desorbed helium is monitored with an RGA. This cycle is repeated with the plate cooled to 9 K or less for one minute and then heated to 10-20 K for one minute. With a one minute accumulation time at < 9 K a sensitivity of 10^{-16} Pa m^{3}s^{-1} is claimed, with longer accumulation times a sensitivity of 10^{-19} Pa m^{3}s^{-1} is claimed.

A special problem arises in leak detection of long pipes maintained at temperatures near 4.2 K as in cryogenic beam lines of accelerators and storage rings. Hobson and Welch have developed a theory to explain the delay in a pulse of helium gas moving down a cold pipe to a helium leak detector [51] and the predictions of the theory have been confirmed experimentally [52]. The time for a He pressure front from a 7.6×10^{-6} Pa m^3 s^{-1} leak to propagate down a 75.3 m long stainless steel tube was 20 hours at 1.9 K , with a 9.3×10^{-6} Pa m^3 s^{-1} leak at 4.25 K the time was 5 hours.

6. REDUCTION OF OUTGASSING

Reduction of the outgassing rates of the materials used in the construction of vacuum systems is essential if the XHV is to be achieved. In a metal system the residual gas is almost entirely hydrogen at XHV. Outgassing rates can be reduced by:

   a) Lowering the temperature of all or part of the system.

   b) High temperature vacuum firing to reduce the amount of dissolved hydrogen.

c) Baking of the vacuum system to remove water (150 to 450°C). It is important to achieve as uniform a temperature distribution as possible while baking.

d) Surface treatment to reduce surface roughness and remove porous oxides. This includes electropolishing, surface machining under special conditions, and glow-discharge cleaning.

e) Surface treatments to create oxide or other films on the surface that act as a barrier to diffusion of hydrogen from the bulk.

f) Deposition of films of low hydrogen permeability on a metal substrate, e.g. titanium nitride or boron nitride.

g) Choice of material with a low solubility for hydrogen (e.g. copper).

The general problems of reducing outgassing have been described in several texts (e.g. see Ref. [14] and references therein), here we shall only comment on a few methods that have proven useful for the extremely low rates necessary for XHV. A rough indication of the outgassing rates per unit area necessary for XHV can be obtained by assuming that the maximum applied pumping speed is proportional to the surface area of the vacuum chamber. Then if the effective entrance area of the pump(s) is A_p (i.e. the area of a perfect pump where all impinging molecules are pumped) Eq. 3 becomes

$$q = k p_\infty \frac{A_p}{A} \qquad (6)$$

where $k = 4.4 \times 10^2 \ \mathrm{m^3 \ s^{-1} \ m^2}$ for hydrogen at 295 K, and A is the surface area of the vacuum chamber. Table 5 shows the outgassing rates needed to achieve 10^{-10} and 10^{-14} Pa with $A_p/A = 0.1$ and 1, the latter value being approachable when all surfaces are covered with getter material or at cryo-pumping temperatures. The outgassing rates of all the components of the system, including gauges RGAs and other active devices must be commensurate to achieve these pressures.

Table 4
Outgassing rates required to reach XHV

A_p/A	p_∞ (Pa)	q (Pa m s^{-1})
0.1	10^{-10}	4.4×10^{-9}
0.1	10^{-14}	4.4×10^{-13}
1	10^{-10}	4.4×10^{-10}
1	10^{-14}	4.4×10^{-12}

The oxidation of stainless steel, believed to form an oxide barrier to hydrogen diffusion from the bulk, has been shown by many experimenters to reduce the outgassing rate to the 10^{-11} Pa m s^{-1} range. Recent measurements by Bernadini [53] et al. have shown that firing stainless steel in air at about 400°C drives out most of the hydrogen in the bulk but the presence of the oxide layer does not reduce outgassing.

An alternate method of reducing the amount of hydrogen in stainless steel is to vacuum fire at 960°C. This method is more expensive than air firing and is liable to cause stress corrosion cracking if the sample is kept in the range 450 to 850°C for too long. The outgassing rates after vacuum firing observed by different experimenters are in some disagreement. Marin [54] et al. found that the outgassing rate after vacuum firing was 3×10^{-11} Pa m s^{-1} whereas the rate after air firing the same type of sample was 1×10^{-12} Pa m s^{-1}. Fremery on the other hand has measured an outgassing rate of 1×10^{-12} Pa m s^{-1} after vacuum firing at 960°C.

Titanium nitride has been deposited on electrolytically polished stainless steel using a hollow cathode discharge [55] after vacuum firing twice at 430°C for 100 h and 500°C for 100 h. The outgassing rate at room temperature was lowered by a factor 10 by the TiN layer to 1×10^{-13} Pa m s^{-1}

Ishimaru [56] has described an aluminium alloy system where the chamber was machined in an atmosphere of dry oxygen and argon (the EX process) after bakeout at 150°C for 24 hours the outgassing rate was about 10^{-10} Pa m s^{-1}, an ultimate pressure of 4×10^{-11} Pa was claimed.

Koyatsu [57] has measured an outgassing rate of 10^{-12} Pa m s^{-1} from OFHC copper after baking at 250°C (softening temperature 200°C), the same rate was obtained from chromium-copper (0.5% Cr, 99.5%Cu) after baking at 100°C (softening temperature 500°C).

Figure 7 shows the outgassing rates of copper and aluminium as a function of the bakeout temperature [58] demonstrating that higher bakeout temperatures are effective in lowering outgassing rates. Table 5 lists some of the lowest measured outgassing rates at room temperature.

Table 5
Some measured outgassing rates at room temperature suitable for XHV

Material	Surface treatment	Outgassing rate (Pa m s^{-1})	Reference
Stainless steel	Glass bead blasted + vacuum fired at 550°C /3 days + baked at 250°C/24 h.	1.6×10^{-13} [H_2]	[59]
Stainless steel (304L)	Air fired at 400°C/38h + baked at 150°C/7 days. Air fired 390°C/100 h + baked at 150°C.	1×10^{-12} [H_2] 5×10^{-12} [H_2]	[54] [53]
Stainless steel	Vacuum fired at 960°C/25 h +baked at 180°C /6 h.	1×10^{-12} [H_2]	[60]
Aluminium	Vacuum fired at 960°C/25 h +baked at 180°C /6 .	9×10^{-13} [N_2]	[58]
Copper (OFHC)	Vacuum fired at 550°C/3 days + baked 250°C/24 h	6×10^{-14} [H_2]	[59]
Copper (OFHC)	Baked at 525°C	2×10^{-13} [N_2]	[58]
TiN on stainless steel.	Vacuum fired at 430°C/100 h and 500°C/ 100 h.	1×10^{-13} [H_2]	[61]
Aluminosilicate glass	Baked at 500°C/18 h + 600°C/2 h + 700°C/2 h/500°C/10 h.	2.5×10^{-13} [N_2]	[62]

7.   CONCLUSIONS

Methods for producing and measuring XHV in both small and large systems are well advanced although much of the necessary equipment is still not commercially available. The physical processes limiting the lowest achievable pressures are relatively well understood and methods to lower the limits are at least predictable. Two exceptions are a) the outgassing from gauges and RGAs due to the ESD of neutrals, and b) desorption in ion gauges and RGAs due to soft X-rays, where some recent work has outlined the problems but more needs to be done.

In 1964 Hobson measured a pressure of 10^{-12} Pa in an aluminosilicate glass system, in the last 35 years there has been no significant improvement in the lowest measured pressure. This is similar to the pressure plateau from 1916 to 1950 at 10^{-6} Pa as a result of the X-ray effect in hot-cathode gauges. It is probable that the present plateau also results from effects in gauges, namely the outgassing produced by the ESD of neutrals and by soft X-rays.

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