

Outgassing from stainless steel and the effects of the gauges

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Abstract

The true outgassing from surfaces is often masked by the production of gases and pumping within the measuring gauge. Quadrupole mass analysers have been used to measure the outgassing from carefully prepared samples of stainless steel. By using an isolation pressure rise technique coupled to non-evaporable getter pumping, the problem of production of methane by the gauge is overcome and it has been possible to measure the outgassing of methane to very low levels. The specific outgassing rate of methane from 316 L stainless steel is found to be $\leq 5 \times 10^{-22} \text{ mbar l s}^{-1} \text{ cm}^{-2}$. The outgassing of the other gases has been measured using several gauges. The specific outgassing of hydrogen is found to be $4.5 \times 10^{-15} \text{ mbar l s}^{-1} \text{ cm}^{-2}$ and the total of all other gasses amounted to no more than 10% of this figure. Although the measurements of the other gases are more ambiguous than those for methane, it is concluded that, in all probability, only hydrogen is outgassed from stainless steel.

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1. Introduction

It is well known that hot filaments and plasmas act as “chemical factories” in vacuum systems to produce certain gases—mainly water, carbon monoxide, carbon dioxide and methane. Thus, most gauges, including quadrupole mass analysers (QMA), produce these gases. It is thought that the production is due to hydrogen and oxygen reacting with the carbon on the surfaces. Summaries of these effects can be found in Refs. [1–3].

Several authors report the outgassing of methane, see for example Refs. [4–11]. However,

investigations [12,13] showed that most, if not all, the methane from stainless steel was produced in the ion source of the measuring equipment. The true specific outgassing rate was measured to be $\leq 2 \times 10^{-17} \text{ mbar l s}^{-1} \text{ cm}^{-2}$. The problem is apparent at low outgassing rates where accurate measurement is most difficult. In certain situations it is important to have very low partial pressures of hydrocarbons and it is vital to know if methane is really outgassing from the surfaces or is being manufactured in the gauges. In the latter case, turning off the gauges will solve the problem but at the cost of not knowing the pressure. This experiment was designed to extend the previous measurement [12,13] of the true outgassing of methane from stainless steel. Hydrocarbons heavier than methane have not been observed in the mass spectra.

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2. The isolation pressure rise technique

The isolation pressure rise technique (IPR) is useful to measure outgassing rates. A vessel of volume V , containing the material to be measured, of surface area A , is pumped down and isolated. The pressure rise of the constituent gases Δp , in a given time t is then measured and the outgassing rate is given by

$$g = \frac{V \Delta p}{At}. \quad (1)$$

To overcome the problem of the manufacture of methane in the measuring gauge, a feature of the non-evaporable getter (NEG) pump was used; the NEG does not pump methane. The IPR chamber was continuously pumped after closure so that the only pressure rise was due to gases not pumped by the NEG (hydrocarbons and noble gases). After a long time the system was opened up and the pressure rise of the residual gases monitored on an external quadrupole mass analyser. Fig. 1 shows the system, which is composed of all metal and ceramic components to uHV standards. The original measurements had been made on a large chamber [12], but to increase the sensitivity in the present experiment the chamber volume is small but the surface area is relatively large. In addition, the IPR is over a longer time, again to increase the sensitivity.

The chamber is built from 3161 stainless steel and has a volume of ~ 121 , excluding the contents but including the NEG and up to valve V1. The volume between V1 and V2 is 0.71. The chamber holds 250 sheets of 0.5 mm thick 3161 stainless-steel sheets which have a total surface area of $1.25 \times 10^5 \text{ cm}^2$.

The empty system (but not the QMAs, the NEG pump or the stainless-steel sheets) was initially baked in air at 200°C for 1 day. The gauges, NEG

and the sheets were added and the system was pumped by the 330 l s^{-1} turbomolecular pump. After reaching a pressure of $\sim 10^{-6} \text{ mbar}$ the system was baked at 150°C for 10 days to remove most of the water. The NEG was also activated during this period. This relatively low-temperature baking scheme [14] was used in studies for a proposed interferometric gravity wave detector [12]. The stainless-steel sheet had undergone the air bake some 10 years previously. One of the interesting measurements was to see if the beneficial effects of the air bake in reducing the outgassing rate (previously measured at $< 1 \times 10^{-14} \text{ mbar l s}^{-1} \text{ cm}^{-2}$ [12]) were still retained after the sheets had been left in atmosphere (wrapped in an aluminium foil) for this length of time.

Four nominally identical quadrupole mass analysers¹ (double filter analysis, mass 1–100 amu, dual Faraday cup/secondary electron multiplier detectors) were attached to the system, as shown in Fig. 1. All had tungsten filaments in the uHV miniaturised ion sources with platinum source cages. The system can read down to pressures of $\sim 5 \times 10^{-14} \text{ Torr}$. The QMAs were attached to a PC for control and monitoring. The system reads in Torr and this report gives all direct measurements in Torr. Conversions into nitrogen equivalent pressures with the appropriate calibration are given in mbar.

The chamber was isolated by closing valve V1; the valve V_{NEG} remained open to pump the test chamber of all but the hydrocarbons and noble gases. Quadrupoles QMA1 and QMA2 were off but QMA3 and QMA4 remained on and were pumped by the turbomolecular pump. After $3.8 \times 10^7 \text{ s}$ (440 days), V2 was closed and V1 immediately opened. The pressures of various residual gas species were recorded on QMA3 and are shown in Fig. 2.

3. Measurements

Fig. 2 shows the peaks of a few selected masses as the valve V2 is closed and V1 is opened. The

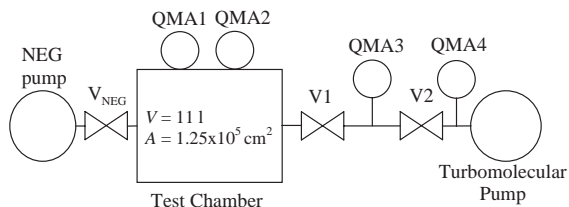


Fig. 1. Schematic diagram of the vacuum system.

¹ Spectra Windows Satellite 100, from Leda-Mass Ltd, now MKS Spectra, Crewe, UK.

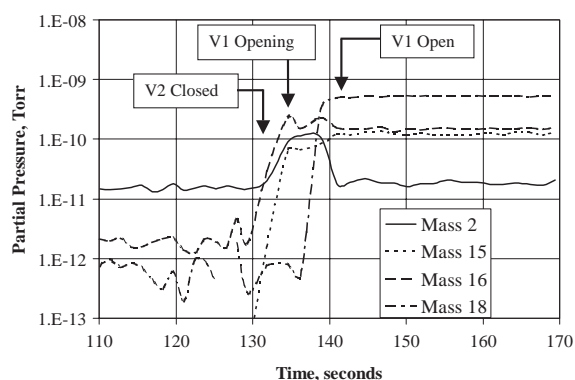


Fig. 2. QMA3 readings at the end of the long IPR. The plots of the different masses are slightly offset (up to ~ 1 s) in time. Only masses 2, 15, 16 and 18 are shown for clarity.

plot covers only 60 s. The closure of V2 is marked by a rise in the pressures, since the gauge is not pumped now. The opening of V1 is marked by a further discontinuity in the pressure, in many cases a lowering of the pressure.

To measure the methane, mass 15 rather than the major peak at 16 is used to avoid any confusion with oxygen, at mass 16, mainly from water. It can be seen that the mass 15 peak increases from below 10^{-13} Torr and rises to $\sim 8 \times 10^{-11}$ Torr as V2 is closed. When V1 starts to open, the pressure rises more slowly due to the fall in the hydrogen pressure in the gauge (due to the NEG pumping) and sharing the methane between the much larger volume of the test chamber and the small volume between V1 and V2. With V1 fully open the 15 peak rises more slowly with time.

The change in the methane pressure, as recorded by mass 15, from closing V2 and fully opening V1 is 4×10^{-11} Torr (before corrections and calibration have been added). It can be argued that during the ~ 2 s required to fully open V1, the mass 15 peak would have risen to $\sim 10^{-7}$ Torr if it had carried on rising at the same rate on closing V2. This quantity of gas in the volume between V1 and V2 when shared with the test volume could easily account for the pressure at the point where V1 is fully open. Hence the methane accumulated in the test volume during the IPR is probably close to zero or certainly less than 10^{-11} Torr. At worst

ignoring all the evidence, the mass 15 peak could not have risen to more than 1.4×10^{-10} Torr, which is the final pressure on fully opening V1.

An IPR of the NEG pumped test chamber was also conducted with QMA1 on (V1 closed). In this case the methane peaks appear to rise up exponentially with time and then flatten out. A steady production rate would not produce this type of curve. Previous experiments [12] had found that the methane pressure was linked to the hydrogen pressure. Assuming a rate of production rate proportional to the hydrogen partial pressure and a break-up rate proportional to the methane partial pressure, a formula can be found for the formation of methane which fits the measured data very well.

4. Calibration

A quadrupole mass spectrometer is not ideal to measure pressures. The gauge reads peak heights and not the partial pressures. The peaks can be shaped in width and amplitude by adjusting the resolution and mass offset voltage setting on the analyser and the amplitude altered by the voltage on the multiplier. The system was calibrated with a small helium leak of 2×10^{-7} mbar ls^{-1} . All the QMAs were set up to give approximately the same reading of the corresponding masses. Corrections were made for gauge sensitivity at the different masses using the manufacturer's data.

5. Results

5.1. Hydrogen

When the system was clean and had pumped for many days on the NEG pump, the measured hydrogen peak (mass 2) was 1.2×10^{-11} Torr on QMA1, QMA2 and QMA3. This corresponds to a partial pressure of hydrogen of 2×10^{-11} mbar, when corrected for the gauge sensitivity, cracking pattern and the helium calibration. The NEG has a speed of $\sim 30 \text{ ls}^{-1}$ for hydrogen from a previous calibration, so the specific outgassing rate of the stainless steel sheets is 4.5×10^{-15} mbar $\text{ls}^{-1} \text{ cm}^{-2}$.

This compares favourably with the previous measurement of $<10^{-14}$ mbar l s⁻¹ cm⁻² [12]. It would appear that the remarkable benefits of the low-temperature air bake are still present after 10 years, and indicate that the process gives stable long-term results.

Since the QMA is able to maintain a partial pressure of $\sim 1.8 \times 10^{-9}$ mbar of hydrogen with no other pumping, the speed of the gauge is calculated to be 1.21 s⁻¹ for hydrogen.

5.2. Methane

The recorded value of the change in pressure of mass 15 on opening the valve V1 is 4×10^{-11} Torr. Correcting this by the calibration factor gives the partial pressure of methane accumulated over the IPR of 14 months as 1.1×10^{-10} mbar. Putting this number into (1) gives the specific outgassing rate of methane as, $g = 2.9 \times 10^{-22}$ mbar l s⁻¹ cm⁻². The outgassing rate is probably an overestimate since there is strong evidence, as explained in Section 3, that there was no, or very little, accumulated methane. The accuracy of the calibrating leak is $\pm 10\%$ and of the measurement is estimated to be $\pm 30\%$. Thus the outgassing rate is $\leq 5 \times 10^{-22}$ mbar l s⁻¹ cm⁻².

5.3. Water

It can be seen from Fig. 2 that on opening the valve V1 at the end of the long IPR the largest partial pressure is of mass 18—water. This is a surprising result and is unlikely to be produced by QMA3, since the mass 18 peak does not alter on closing V2 and the hydrogen barely increases on opening V1 (as the test chamber is pumped by the NEG). Moreover, the water is not increased when more gauges are operated, indicating that water is not produced in the gauges.

There is some evidence from previous experiments [13] that the hydrogen in the system is converted to water, presumably by interaction with the oxygen on the stainless steel surface. This is an interesting, if not worrying effect since it implies that the system may never be in simple equilibrium, with just hydrogen coming off the surface.

However, it is surprising that the water should have risen to this level since it is pumped by the NEG. The NEG pumps the water at a slower rate, ~ 61 s⁻¹, and has a smaller capacity (about 50 times less) than for hydrogen. It may be that the pump had become saturated with water during the IPR. The measured outgassing rate before the IPR was $\sim 3 \times 10^{-17}$ mbar l s⁻¹ cm⁻² for water, so the total quantity evolved during the 14-month IPR should have been 1.4×10^{-4} mbar l. The pump should have had a capacity of a few bar l for water. Thus the pump should not be anywhere near saturation. The result needs to be confirmed by further experiments.

5.4. Carbon monoxide and carbon dioxide

It is not possible to measure unambiguously the real outgassing of these gases in the same way as for methane. The partial pressures of the gases were measured in the test chamber, with V2 closed and the NEG pumping, using a combination of the quadrupole analysers Q1, Q2 and Q3. The partial pressures on one gauge were measured with no other gauge on, with one other gauge on and with two on. This was done for all combinations of the three gauges. The result showed that the hydrogen peaks were unaffected by the other gauges being on or off, but that the partial pressures of CO and CO₂ were proportional to the number of gauges that were on. It was concluded that within the accuracy of the measurements, the gauges produced over 80% of these gases.

The measured partial pressure of CO and CO₂ varied with the hydrogen pressure and indicated that they would be zero if the hydrogen pressure was zero. Fremery [15] has shown these pressures to be proportional to the gauge emission current. Hence it is concluded that $>80\%$ of the gas is produced in the QMAs and in all probability this figure is 100%. Hence under the same conditions as the measurement of the hydrogen in Section 5.1, the measured outgassing rate is $\leq 6 \times 10^{-17}$ mbar l s⁻¹ cm⁻² for carbon monoxide and $\leq 3 \times 10^{-18}$ mbar l s⁻¹ cm⁻² for carbon dioxide.

6. Conclusions

It is very likely that methane is not outgassed from clean stainless steel; the methane is all due to production in the QMA. In addition the outgassing of CO and CO₂ is very small, $<10^{-16}$ mbar l s⁻¹ cm⁻², and probably zero. Within the measuring capabilities of the equipment these gases are also totally produced in the gauges. The water is still problematic and requires further study, but indications are that it is produced by interaction of hydrogen with oxygen on the surface of the stainless steel. Hence it is very likely that only hydrogen is outgassed from clean stainless steel, as conjectured recently by Fremery [15].

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