

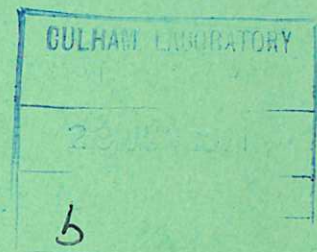
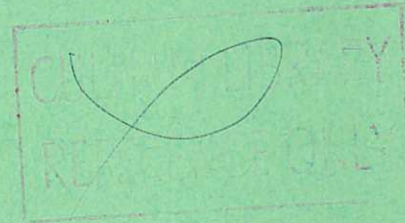
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THE EFFECT OF CLEANING TECHNIQUE ON THE OUTGASSING RATE OF 18/9/1 STAINLESS STEEL

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1969

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by

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(Submitted for Publication to Vacuum)

A B S T R A C T

This paper describes a series of experiments designed to assist in determining the extent to which the room temperature outgassing rate of stainless steel can be reduced by cleaning processes only without recourse to vacuum bakeout. The effect of contact with clean hands on the outgassing of a stainless steel vacuum surface is also discussed.

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1. INTRODUCTION

The technique of reducing the outgassing rate of stainless steel vacuum equipment by baking in vacuo at from 200–450⁰C has been widely used in the attainment of ultra high vacuum. Applied to large plant of complex geometry, however, the method present various engineering design problems which are difficult to overcome. Therefore, when the process concerned does not involve elevated temperatures, it would be a great advantage if the outgassing rate at room temperature could be reduced to below 10^{-12} torr litres sec^{-1} cm^{-2} to obtain ultra high vacuum without recourse to bakeout.

To determine the extent to which this could be achieved by cleaning technique, a study of the outgassing of stainless steel subsequent to various forms of cleaning was undertaken and the apparatus, experimental technique and results are here described.

2. APPARATUS

A cylindrical stainless steel specimen, diameter 16 cm, length 75 cm (and surface area 3750 cm^2) was mounted on a base plate, A (Fig.1), to which three ultra high vacuum isolation valves were attached, each leading to a separate vacuum system. The first of these, (1), led via a known conductance to a turbomolecular pump, B, of 150 litres sec^{-1} pumping speed backed by a rotary pump. The second, (2), led via a chamber containing a nude mass spectrometer ion source to a duct of known conductance terminated by a liquid nitrogen trapped mercury diffusion pump, C. A subsection of this system, consisting of the mass spectrometer analyser tube, was differentially pumped to minimize the effect of the tube's outgassing on the sample outgassing measurements. This section was also pumped

by a liquid nitrogen trapped mercury diffusion pump, D. Diffusion pumps C and D ejected their gas into a common manifold pumped by a 4-stage mercury diffusion pump, E, with a critical backing pressure of 30 torr, which compressed the gas into a storage tank having a facility for periodic pump-out by a liquid nitrogen trapped rotary pump. The third system, (3), was a gas handling device separated from the remainder of the apparatus by a sintered leak of known conductance, F, and was used to make pumping speed measurements. This was also pumped by a liquid nitrogen trapped diffusion pump, G, backed by a rotary pump.

The high vacuum section of system 1 was bakeable to 200°C and that of system 2 to 450°C. The demountable seals used throughout both systems had metal gaskets. These were either gold wire or flat copper rings (conflat type seals).

The mass spectrometer was of the 60° sector type with a radius of curvature of 15 cm and a resolving power of $\frac{M}{\Delta M} = 130$, for a 1% valley. Mass scanning over the range 1-300 a.m.u. in a time of 1 minute was obtained using a variable magnetic field. A partial pressure of 10^{-12} torr was observable using an electron multiplier as detector.

3. EXPERIMENTAL TECHNIQUE

A specimen cleaned to a prescribed technique, was attached to the connecting port, A, and pumped via system 1, during which time a record was made at frequent intervals of total and partial pressures. When the pressure had fallen to about 10^{-7} torr (~ 4 hours) the gas was diverted through the high resolution mass spectrometer (system 2). Pumping then continued accompanied by periodic observations of gas

composition and total outgassing rate for a period of up to 100 hours, depending on the individual requirement.

The outgassing rate was measured by two methods to allow cross-check of results. The methods used were as follows -

1. The sample was isolated from the mass spectrometer which was then valved off from its pump for approximately one minute. During this time the pressure rise in the mass spectrometer ion source chamber was observed using an ionization gauge in conjunction with a continuous line pen recorder. After repumping the mass spectrometer for a few minutes to regain pressure equilibrium, the combined mass spectrometer and sample was isolated from the pump and the procedure repeated. The outgassing of the sample was then calculated using the following formula -

$$Q = \frac{\frac{\delta P_2 V_2}{\delta t_2} - \frac{\delta P_1 V_1}{\delta t_1}}{A_S}$$

where

Q = Outgassing rate per unit area of sample,

δP_1 = Pressure rise in sample during a time δt_1

δP_2 = Pressure rise in combined mass spectrometer and sample during a time δt_2

V_1 = Volume of mass spectrometer

V_2 = Volume of mass spectrometer and sample combined

A_S = Surface area of sample

2. The method was identical with the previous method except that the outgassing of the combined mass spectrometer and sample was measured at the ion source chamber under pumping conditions. The outgassing of the sample was therefore calculated as follows -

$$Q = \frac{P_3 S - \frac{\delta P_1 V_1}{\delta t_1}}{A_S}$$

where

P_3 = Pressure measured at mass spectrometer ion source region during pumping.

S = Pumping speed at mass spectrometer ion source region.

An example of a curve showing the rate of total pressure rise in the isolated mass spectrometer and sample is shown in Fig.2. This shows a change in slope after the first few seconds of isolation and is characteristic of the curves obtained during measurements made under isolation. A partial pressure analysis showed this to be due to a high initial rate of rise in H_2 , CO_2 and CO (Fig.3). The partial pressure of H_2O remained almost constant.

The first part of the curve was therefore chosen as being most representative of the outgassing under pumping conditions. The results obtained using this method agreed to within 50% with those obtained using Method 2, in which the combined outgassing of the sample and mass spectrometer is measured by the dynamic flow method.

Groups of interdependent experiments were carried out on the same specimen whenever possible to avoid errors due to inherent differences of structure.

The base plate, Fig.1 (A), and cover plate used in mounting the sample represented a surface area equal to about 10% of the sample. These were exposed to the specimen during outgassing observations and although they are baked periodically in vacuo along with the remainder of the apparatus they would nevertheless impose a lower limit on the measureable outgassing rate of about

$$5 \times 10^{-13} - 10^{-12} \text{ torr litres sec}^{-1} \text{ cm}^{-2}$$

(i.e. about 10% of the outgassing rate of the plates).

4. EXPERIMENTS AND PROCEDURE

Outgassing Criterion

A newly manufactured sample with a honed surface was vapour degreased in a trichloroethylene vapour degreaser and baked in vacuo at 450^oC in order to remove the initial contamination and hence give it a known outgassing history. It was then exposed to air for 24 hours and without further treatment repumped for 48 hours during which its outgassing characteristics were studied for use as a criterion against which to compare subsequent treatments. The resultant outgassing curve is presented in Fig.4(a).

Effect of Vapour Degreasing

In order to establish the effect of the trichloroethylene vapour degreasing process on the outgassing of a clean sample, the specimen was removed from the apparatus, vapour degreased in a trichloroethylene vapour bath and again evacuated. The outgassing occurring during this pumpdown, Fig.4(b), was almost identical with the previous case. Traces of trichloroethylene were, however, visible in the mass spectrum and represented about 1% of the total gas* after 48 hours pumping, Fig.5.

Removal of Cutting Oil from a Specimen by Trichloroethylene Vapour Degreasing

Having established the quantity and composition of outgassing to be expected from the cleaning medium, its ability to remove cutting oil was tested by exposing the sample to air and smearing it with the cutting oil currently in use for machining[✓]. It was then vapour

* Based on the sensitivity of the mass spectrometer to N₂

✓ Duckham's Aquacut No.40.

degreased and repumped, during which the outgassing rate, Fig.4(c), was almost identical with that previously observed. Comparison of the series of curves (a)-(c) shows the steady improvement which might be expected by frequent and prolonged pumping of a specimen.

Comparison of Gas Evolution from Honed and Machined Surfaces

The following two experiments were made using a fresh specimen. Its cleaning following honing was confined to vapour degreasing and it was not vacuum baked before use. The outgassing rate between 7 and 50 hours during the first pumpdown is shown in Fig.6(d). After pumpdown and re-exposure to air, the honed surface was removed by lathe turning. It was then pumped following vapour degreasing by the method previously used. The resultant outgassing, Fig.6(e) shows a marginal improvement over the honed finish.

Effect of Electropolishing on Gas Evolution

A new cylinder with a turned surface was vapour degreased and electropolished in the following solution -

N. butyl alcohol	- 90 parts by volume
Orthophosphoric acid	- S = 1.75, 350 parts by volume
Current used	- Approx 0.075 A cm ⁻² (Total 180 A)
Time	- 50 minutes
Recommended temperature	- 70 ⁰ C (probably rose to 90 ⁰ C)

After electropolishing, the specimen was washed in tap water followed by washing in demineralised water. Outgassing during the pumpdown which followed is shown by the curve, Fig.7(f). Mass spectra indicated a higher general hydrocarbon background than expected. The specimen was therefore removed from the system and vapour degreased.

During the pumpdown which followed, Fig.7(g), a normal hydrocarbon background was observed. In order to determine whether the contamination had come from the polishing bath or demineralised water the sample was rewashed in demineralised water, dried in air and again repumped, Fig.7(h). The increased outgassing shown at the earlier stages of this pumping cycle was due to a higher partial pressure of water vapour not hydrocarbons. It was therefore concluded that the excess hydrocarbon, shown previously, resulted from the polishing process, possibly from polymerization of the butyl alcohol due to the temperature of the bath rising, at the latter stage to between 80° and 90°C.

Specimen Baked in Air

A method of reducing the outgassing rate of stainless steel by the production of an oxide layer obtained by baking in air at between 430° and 500°C following electropolishing has been described by L. Petermann⁽¹⁾. This is said to make possible the production of residual pressures of the order 10^{-10} torr within large containers by means of relatively small pumping speeds without bakeout in vacuo. Further improvement can be obtained if bakeout at from 200-300°C in vacuo is applied for a few hours.

To test the advantages of this technique, (without use of the bakeout in vacuo) over the normal electropolished surface, the sample was removed from the apparatus and baked in air at 500°C for 1 hour and repumped. The outgassing curve for this experiment, Fig.7(i), showed an improvement over (h) by a factor of 2, which was almost entirely due to a reduction in water vapour.

Specimen Treated by Diversey Chemical Polishing Process

A newly-machined (lathe-turned) specimen was vapour degreased and chemically polished using the DS-9 chemical cleaning process marketed by Diversey Company and reported by Milleron⁽²⁾ to show promise as a cleaning technique for ultra high vacuum equipment. The resultant outgassing curve is reproduced in Fig.7(j) and shows an evolution rate approximately 5 times worse than for the air-baked specimen (i). Mass spectra indicate this to be primarily due to water.

Plasma Torch Cleaning

A newly manufactured specimen with a turned finish, degreased for the purpose of leak proving, was re-contaminated by wiping the inner face with a cloth moistened with lard oil, (the cutting oil used during turning). It was then cleaned by application of a plasma jet*.

After treatment the specimen was returned to the outgassing apparatus protected in polythene bags. On pumpdown the outgassing curve, Fig.7(k), was obtained.

A further specimen produced under identical conditions, contaminated as before but not cleaned, was studied for comparison with the variously cleaned samples. Following pumping on the turbo-pumped system for 24 hours, the outgassing rate remained still too high for permanent transfer to the mass spectrometer system. A short exposure, however, gave the point, Fig.7(l), and a mass spectrum primarily composed of hydrocarbons.

* The process was carried out by Tetronics Research & Development Co. Ltd. of Faringdon, Berks, using argon gas and a constricted arc between a non-consumable electrode and specially designed nozzle. The equipment used was of their own design.

Effect of Vapour-Blasting on the Outgassing of a Specimen

This cleaning technique consists of bombarding a contaminated area with a high pressure jet of very small glass balls suspended in water containing a degreasing agent and is a useful means of removing very tenacious material from the surface of stainless steel.

To determine the effect of this technique on the outgassing properties, a new lathe-turned sample was degreased in a trichloro-ethylene vapour bath and its outgassing characteristics observed during pumpdown, Fig.8(m). Its surface was then vapour blasted using glass balls of 100-150 μm diameter (Vaquashene 10/15 medium*) suspended in water containing degreasing agent (Vaqua 'D'*). This was applied at a nozzle pressure of $5.6 \times 10^4 \text{ kG m}^{-2}$ (80 p.s.i.) and gave a fine satin finish. After air drying the sample was repumped and the outgassing curve, Fig.8(n), compared with that obtained before treatment.

Effect on Surface Outgassing Produced by Contact with Clean Hands

Finally an experiment was made to establish the effect on outgassing caused by touching the surface of a dynamically pumped ultra high vacuum vessel with thoroughly clean hands.

For this experiment a new sample was used. It was firstly vapour degreased and the outgassing characteristics observed, Fig.9(o). This was followed by bake to 400°C for approximately 18 hours to reduce the outgassing to a minimum. On cooling it was exposed to air for 24 hours and repumped, Fig.9(p), to obtain an outgassing curve for comparison with a sweat contaminated surface.

*Supplied by Abrasive Developments Ltd.

At this stage the hands of three members of the laboratory staff were scrubbed, using soap and hot water for five minutes, then in running hot water only for two minutes, followed by rinsing in flowing distilled water and finally dried in hot air. After drying, the hands were enclosed in clean polythene bags fastened round the wrists by elastic bands. Twenty minutes later the bags were removed and the hands wiped over the inner surface of the previously outgassed cylinder. The resultant outgassing curve obtained on pumpdown is shown in Fig.9(q).

5. SUMMARY OF RESULTS AND CONCLUSIONS

Experiment showed that cleaning a new, lathe-turned stainless steel specimen by suspension in a clean trichloroethylene vapour bath resulted in a rate of pumpdown at room temperature equivalent within a few percent to that exhibited by a similar specimen which had been vapour degreased, vacuum baked and then exposed to air. Traces of trichloroethylene amounting to about 1% were observed until the end of the experiment (after 100 hours) when they represented an outgassing rate of about 10^{-13} torr litres sec^{-1} cm^{-2} *. Earlier experiments reported⁽³⁾ show that when the temperature of an unbaked specimen is raised, however, its outgassing rate is much greater than that of a vacuum pre-baked sample.

The results obtained by comparing the outgassing of an unbaked hone surface of about $0.025 \mu\text{m}$ with that of a lathe turned finish of $1.25-1.7 \mu\text{m}$ obtained from the same sample following removal of the honing, Fig.6(d and e), shows a marginally lower outgassing for the lathe-turned finish in spite of the apparently larger surface

*Based on the gauge calibration for nitrogen

available for outgassing. This may be due to trapping of contaminant within the surface during honing. The possibility is supported by comparisons with a pre-baked honed surface of another sample, Fig.4(b) which shows a factor of two lower rate than the machined specimen, Fig.6(e). The differences, however, are marginal and depend on one set of results.

Comparison of the outgassing of a vapour blasted surface and an untreated vapour degreased lathe-turned surface, Fig.8 (m and n), indicate that provided a very small size of glass ball is used, (e.g. 100-150 μm diameter), vapour blasting can be safely used in many cases for the removal of tenacious material adhering to the surface of stainless steel.

The outgassing gassing curve obtained from the electropolished sample, Fig.7(g), lay within the general group of curves obtained from honed and turned surfaces. The process does not, therefore, justify the hazard of long term contamination resulting from trapping of polishing solution within crevices.

Bakeout of the specimen at 500°C in air, Fig.7(i), produced a factor of 2 improvement over the electropolished specimen (g), but only a minor advantage over the best vapour degreased specimen, Fig.9(o). It appears, therefore, that the main advantage of this method is obtained when it is followed by a minor bake at between $200\text{--}300^{\circ}\text{C}$ ⁽¹⁾. This unfortunately places the method outside the scope of this investigation, which is confined to unbakeable systems.

Application of the plasma torch to the surface of a specimen contaminated with cutting oil produced a factor of approximately 2 improvement over the better of the 2 vapour degreased specimens

(m and o), demonstrating the feasibility of using the method for cleaning up local contamination. The conditions during the experiment were, however, carefully controlled and further study would be required to determine the possibility of applying the arc manually over a surface. In addition, the probability of the decontamination having been reduced by high temperatures cannot be overlooked since temperatures up to 700°C were momentarily observed on the outer wall as the arc passed along the inner surface.

Although the foregoing results show that air bake following electropolishing and plasma arc cleaning give marginal improvement over the trichloroethylene vapour bath for the removal of normal manufacturing soil, the difficulties involved in their application do not appear to justify their general use. Of the methods tested, therefore, the trichloroethylene vapour bath shows itself to be the best for general use. In all cases water was the most predominant component of the residual gas composition.

After 70 hours pumping, for example, the vapour degreased specimen showed a mass spectrum of the following composition -

58%	H ₂ O
20%	CO
12%	CO ₂
9%	Hydrocarbons
1%	Trichloroethylene

Previous experience shows that up to about 50% of the CO and CO₂ can result from the ionization gauge used for total pressure measurement, although the percentage due to this varies considerably. It is nevertheless seen that any further worthwhile reductions in outgassing rate would require a process for the removal of water vapour.

Experiments, Fig.9(o-q) indicate that the increase in outgassing rate of a surface due to contact with very clean hands is negligible in a dynamic system of the type undergoing study, although it is recommended that the use of bare hands should be reserved for cases of emergency due to the danger of absentmindedly handling contaminated surfaces (e.g. local objects used for support, hair cream, etc).

In cases where it is possible to make comparison between the data obtained in the present experiments and that of other investigators, the results show satisfactory agreement with those of the more recent workers (e.g. references 4,5,6) who use ultra high vacuum equipment. Earlier investigators (e.g. references 7,8) working under less clean conditions with higher ultimate pressures show somewhat higher rates of gas evolution, Table 1. The foregoing conclusions, therefore, strictly apply only to the conditions under which the measurements were made, since it is known that outgassing rate can be influenced by the pressure of the system in which it is measured. (Lewis⁽⁹⁾). Thus care must be taken in extrapolating to other systems which have an appreciably different ratio of surface area to pumping speed.

TABLE I

Reference	Total outgassing rate in torr litres sec ⁻¹ cm ⁻² after 'h' hours pumping.			Notes
	10 hrs	24 hrs	40 hrs	
Blears et al Ref.7	2.1×10^{-8}			After pre-bake in vacuo for 45 hrs at 350°C and exposed to air for 3 hrs.
Geller Ref.8	2×10^{-8}			
Power Ref.4		2×10^{-10}		
Calder and Lewin Ref.5			1.4×10^{-11}	
Strausser Ref.6	2×10^{-10}			
Barton and Govier	1.2×10^{-10} (A)	5×10^{-11} (B)	1.7×10^{-11} (C)	(A) Fig.8(m) (B) Fig.8(m) (C) Fig.9(p)

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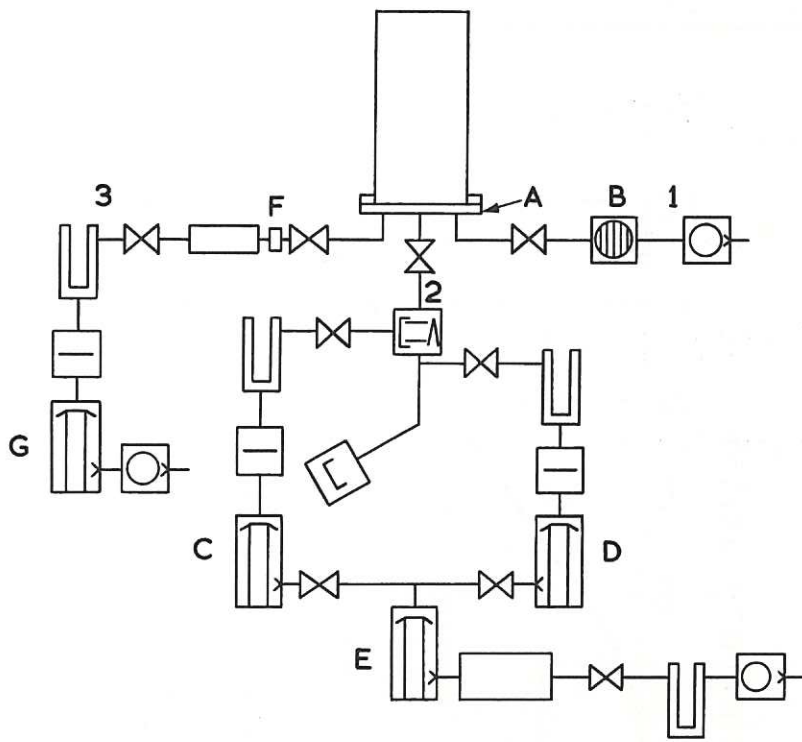


Fig.1 Schematic diagram of apparatus (CLM-P 210)

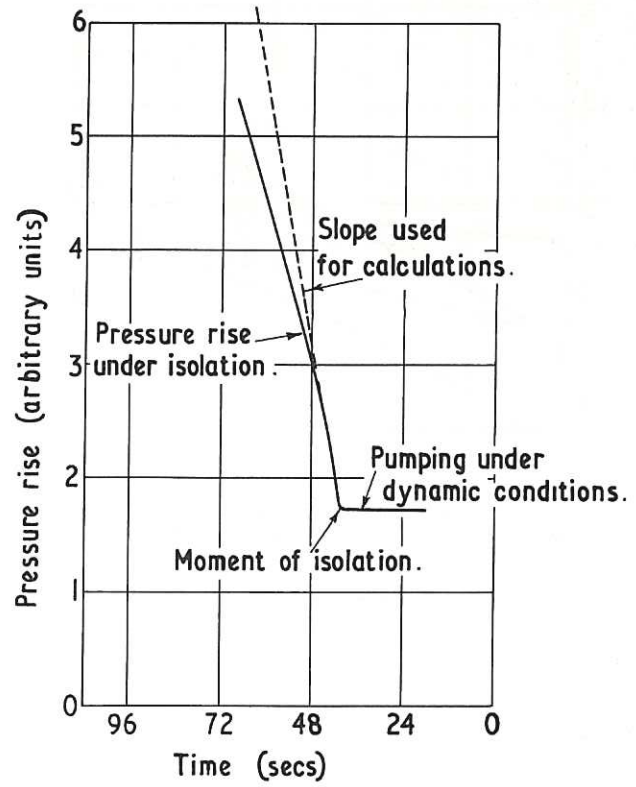


Fig.2 Pressure rise in isolated vessel vs time (CLM-P 210)

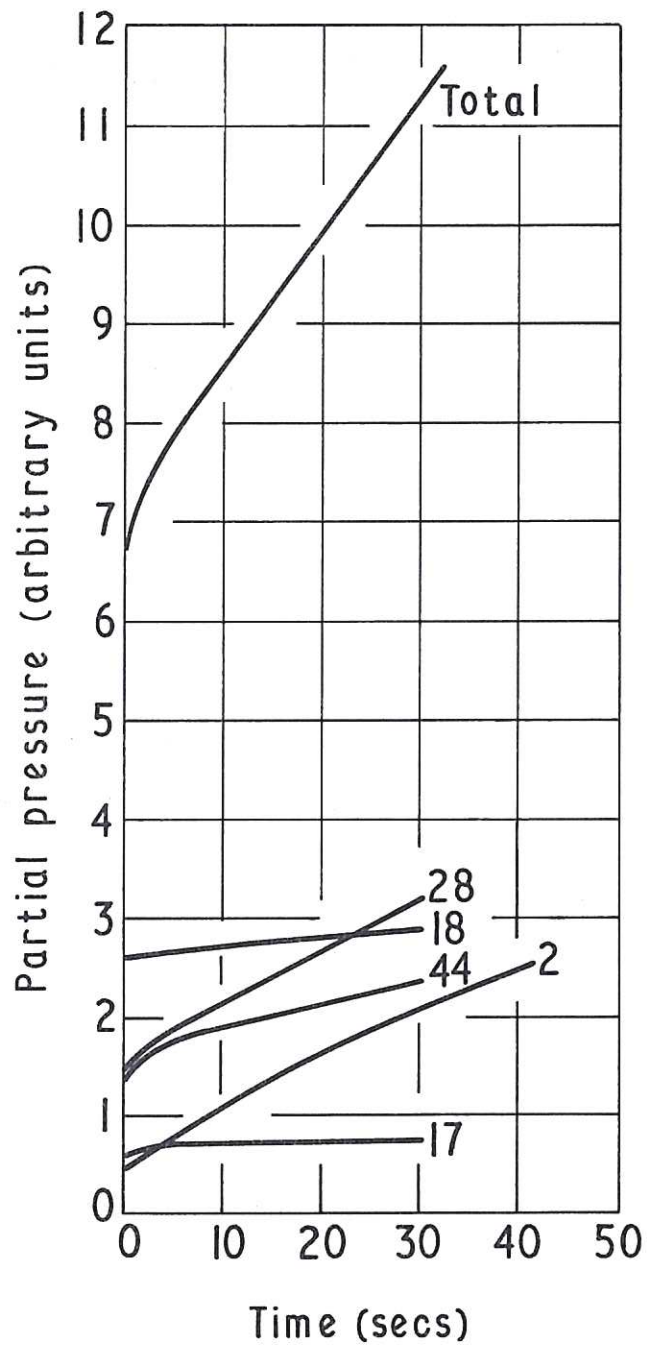
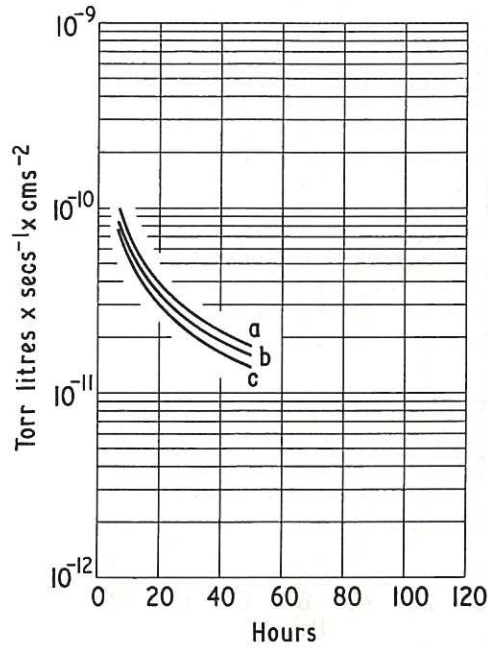


Fig. 3 (CLM-P 210)
 Partial pressure rise in vessel under isolation vs time



- a. Honed sample following bake in vacuo at 450°C & exposed to air. (Sample I Exp 2)
- b. Sample exposed to air & vapour degreased. (Sample I Exp 3)
- c. Sample following smearing with cutting oil & vapour degreasing. (Sample I Exp 4)

Fig. 4 (CLM- P 210)
Total outgassing per cm² of sample as a function of pumping time.

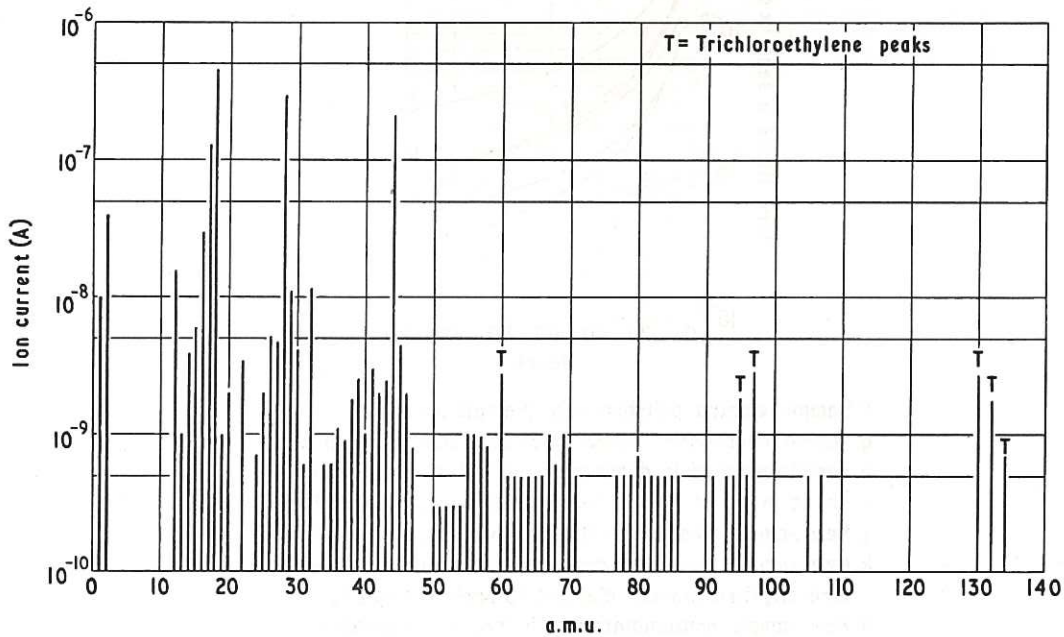
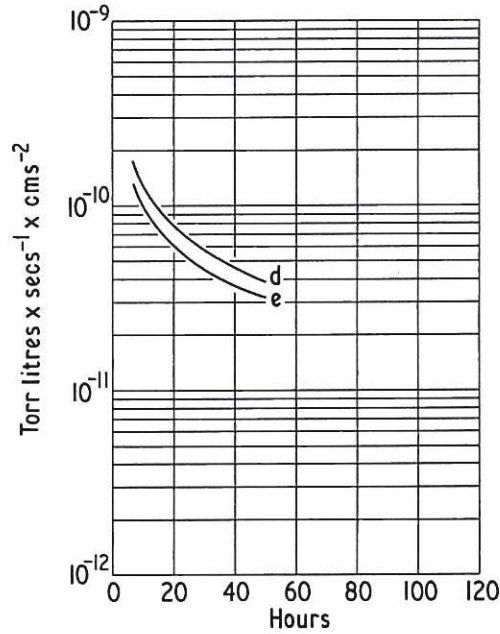
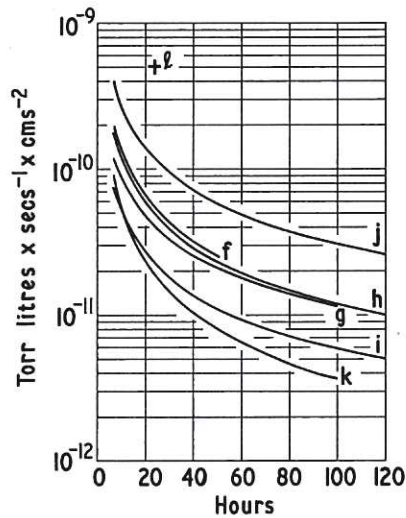


Fig. 5 (CLM-P 210)
Mass spectrum of vapour degreased sample after 48 hours pumping
(Experiment 3, sample 1, 22/11/67)



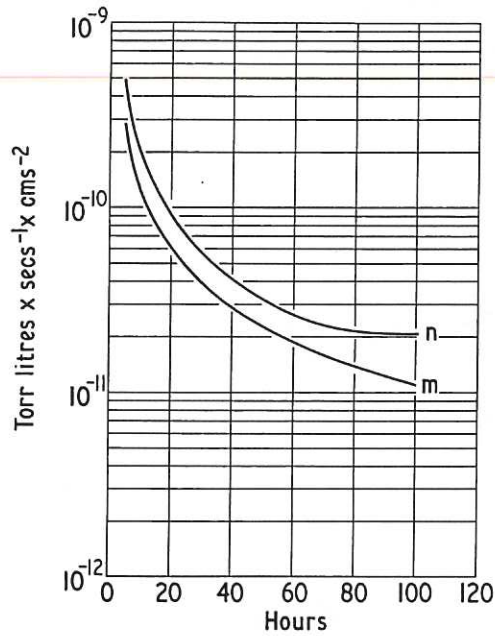
- d. Sample honed & degreased (Sample 2, Exp.5)
- e. Sample machined & degreased (Sample 2, Exp.9)

Fig. 6 (CLM-P 210)
Total outgassing per cm² of sample as a function of pumping time.



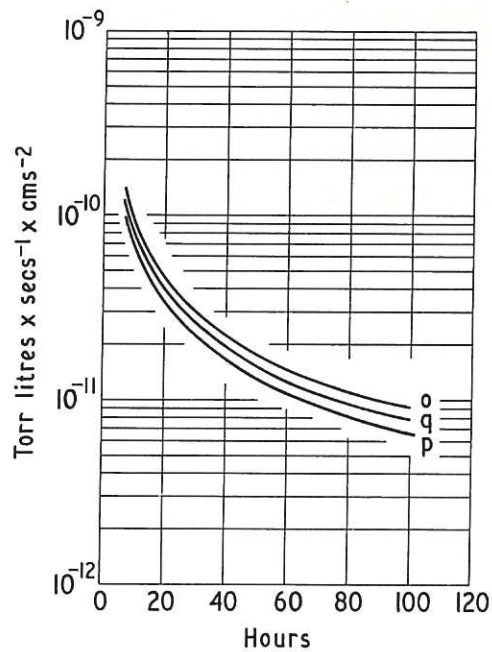
- f. Sample electro polished only. (Sample 5 Exp 12)
- g. Vapour degreased following Exp 12. (Sample 5 Exp 13)
- h. Sample washed in demineralised water. (Sample 5 Exp 14)
- i. Baked in air at 500°C following Exp 14. (Sample 5 Exp 15)
- j. New sample cleaned by Diversy process. (Sample 6 Exp 17)
- k. New sample machined degreased & contaminated with lard oil, then plasma cleaned. (Sample 8 Exp 23)
- l. New sample contaminated with lard oil, no cleaning. (Sample 9 Exp 30)

Fig. 7 (CLM-P 210)
Total outgassing per cm² of sample as a function of pumping time.



- m. New sample machined & degreased. (Sample 10, Exp.31).
- n. Same sample following vapour blasting & degreasing. (Sample 10, Exp.32).

Fig. 8 (CLM-P 210)
Total outgassing per cm² of sample as a function of pumping time .



- o. Sample vapour degreased only. (Sample 7 Exp 18)
- p. Following exposure to air after bake at 400°C in vacuo. (Sample 7 Exp 20)
- q. Sample smeared with sweat. (Sample 7 Exp 21)

Fig. 9 (CLM-P 210)
Total outgassing per cm² of sample as a function of pumping time .

