Cleaning Stainless Steel for use in Accelerators – Phase 1

K. J. Middleman, *J. D. Herbert and R. J. Reid*

ASTeC, CCLRC Daresbury Laboratory, UK

* corresponding author, e-mail address: k.j.middleman@dl.ac.uk

Abstract

Particle accelerators such as the SRS at Daresbury Laboratory generally require pressures lower than 10^{-9} mbar for satisfactory stored electron beam lifetimes. To achieve this requires that particular attention be given to the cleanliness of the stainless steel vacuum vessels and other components of the vacuum system. Pre-installation cleaning is an important step in the process.

Currently, trichloroethylene is employed at Daresbury Laboratory as the primary cleaning solvent of choice, having been chosen as the outcome of earlier studies of the effects of various cleaning techniques on outgassing and electron stimulated desorption from stainless steel [1], [2].

However, in light of the re-classification of trichloroethylene by the European Union as a class two carcinogen, with consequent stringent and expensive safety precautions required in order to continue using it, a suitable, more economical, replacement is sought after.

This paper, details the assessment of different cleaning agents against the two criteria important to particle accelerator vacuum systems. The criteria being room temperature thermal outgassing rates and electron stimulated desorption yields. A variety of different cleaning agents, ranging from halogenated solvents to aqueous based

cleaning agents have been tested. A comparison of the performance of a selection of such cleaning agents is presented and a satisfactory alternative to trichloroethylene is proposed.

Introduction

Whether the level of vacuum required for any given application can be attained is limited by many factors, including the materials that are used and the way in which they are prepared. In general, some form of cleaning of vacuum components is necessary to achieve even a modest level of vacuum due to the numerous contaminants such components will have come into contact with during manufacture, e.g. machine oils, greases and human handling. Such contaminants can remain on a surface and can have high outgassing rates in vacuum which ultimately limits the lowest pressure achievable. The base pressure required in a vacuum system therefore determines how rigorously components have to be cleaned. For UHV applications this is particularly important, and meticulous attention to detail is required to achieve outgassing rates of less than 10^{-11} mbar $ls^{-1}cm^{-2}$, typical for such applications.

Synchrotron Light Source Considerations

The two main sources of gas in a synchrotron light source under normal operating conditions are thermal outgassing and photon stimulated desorption (PSD). The subject of thermal outgassing and photon stimulated desorption and their consequences in synchrotron light sources are discussed elsewhere [1-7].

For most UHV applications it is possible to achieve sufficiently clean surfaces with careful handling of vacuum components, wiping with alcohol or a mild detergent, and bakeout. However, for large vacuum systems, such as the Daresbury Synchrotron

Radiation Source (SRS), bakeout can give rise to a number of problems. There is a significant increase in the cost of the machine if an *in-situ* bakeout is required. Also leaks on the vacuum system are often opened up due to the temperature differentials that can exist across components and from the natural expansion and contraction of materials as they are heated and cooled. As a result of such problems, a number of synchrotron light sources now operate without the use of an *in-situ* bakeout. Therefore it is essential that meticulous attention to detail is applied to the preparation of vacuum materials in advance of installation or assembly.

At Daresbury Laboratory, great care is taken over cleaning and preparing components to ensure satisfactory vacuum performance once installed on the SRS. The detail of this cleaning procedure is outlined in table 1 (Note: not all steps are required every time). For the past decade, the solvent Trichloroethylene (Trike^{TM}) has been employed as the primary cleaning agent at Daresbury Laboratory and this has resulted in suitably clean vacuum components for use on the SRS. Consequently, operating pressures in the 10^{-10} mbar range have been obtained with beam lifetimes in excess of 20 hours with stored currents greater than 200mA.

The Need for Change

Trichloroethylene was reclassified by the European Union in June 2001 as a category 2 carcinogen (Risk Phrase R45 – may cause cancer) and related restrictions arose from the Solvent Emissions Directive (SED). As a result, more stringent requirements under both COSHH (Regulations on Control of Substances Hazardous to Health) and SED are to be observed from 2007. Only two practical options remain possible for continued use of trichloroethylene: substitution (i.e. using an alternative solvent) or

enclosing the cleaning process as far as is practicable. For Daresbury Laboratory the most practical option is to replace the solvent with a suitable alternative by 2007.

A program of research was undertaken to assess the efficacy of various cleaning solvents and aqueous detergents in cleaning stainless steel for use in electron storage rings.

Phenomenological Tests

The two main criteria adopted were achieving sufficiently low room temperature thermal outgassing rates and electron stimulated desorption yields. In each case, both total and partial pressure information is of importance. Standard test pieces (Figure 2) were deliberately contaminated in a standardised way with the following contaminants:

Fomblin vacuum pump oil, rotary pump oil, new workshop machine cutting oil, used workshop machine cutting oil, workshop machine grease, silicone vacuum grease, marking dyes, hand soap and by human handling. After contamination, the samples were then cleaned in the various solvents before mounting in the measurement system.

(a) Thermal Outgassing

Outgassing rates were measured using the throughput method [8,9] in the apparatus shown schematically in figure 1. During all measurements, clean oil-free pumping is provided solely by the turbomolecular pump set to ensure that there are no spurious pumping speed effects dependent on the molecular species being pumped. The conductance, C, shown is an all-metal vacuum valve with a small hole drilled in the valve plate. In the open position, good pumping speed is available at the sample, for example during pump down. When closed, it provides a well-defined conductance

(calculated as 2.34 l/s) for the thermal outgassing measurements. The ion pump shown provides pumping during bakeout cycles and is valved off during measurements.

The total pressure gauges (Bayard-Alpert gauges) and Residual Gas Analyser (RGA) used were not calibrated in the absolute sense. However, performance cross checks were made frequently at pressures between 10^{-5} and 10^{-10} mbar to ensure that there were no spurious effects. As a result, there is a high degree of confidence in the *comparability* of results, although values are not absolute. Since all measurements for the different cleaning solvents were compared against a well-defined standard process (see table 1) this approach is not unreasonable.

The RGA provides information on the outgassing species and the resultant spectra are compared to assess the efficacy of the various solvents in reducing high-mass species, which is of particular importance in this work.

All measurements were taken under well-defined conditions at a fixed time following closure of the conductance valve. Frequent blank runs without a test sample were carried out to ensure that no cross contamination from sample to sample occurred and to give confidence in the overall stability of the measurement system.

(b) Electron Stimulated Desorption (ESD)

The best way to assess the effectiveness of various cleaning solvents in reducing PSD would be to measure directly the photon yield, η molecules per photon. However, this in practice requires the use of a dedicated beamline on a synchrotron radiation source. Such a facility is not available in our laboratory but they are available elsewhere [10,11]. η has been measured typically to be between $10^{-2} - 10^{-3}$ molecules per photon for baked stainless steel when first introduced into a synchrotron light source [5,6].

With continued exposure to photons, this figure decreases to approximately 10^{-6} molecules per photon or lower.

An alternative method is to use electron stimulated desorption (ESD) as an analogue of PSD. It is necessary to make the assumption that a surface that exhibits low ESD will also exhibit low PSD. Since PSD is believed to be mediated by secondary electron emission [12,13], this is not unreasonable. ESD coefficients are defined as the number of gas molecules released into the vacuum system per incident electron impinging on the surface of that system. This was the method adopted in this work.

The cylindrical sample shown in figure 2 surrounds the filament and is electrically isolated from the vacuum system by ceramic spacers. The filament is heated and a bias voltage is applied to the sample, and the sample is bombarded with thermionically emitted electrons of well-defined kinetic energy. Further details of the ESD experiment can be found elsewhere [1,2].

Results

Thermal Outgassing

Table 2 shows the thermal outgassing results for all the solvents and aqueous cleaners tested and it is clear that the thermal outgassing results were inconclusive. This is because the measured values are close to the sensitivity limit of the system, estimated at about 2×10^{-12} mbar l s^{-1} cm^{-2}.

Although the total thermal outgassing measurements proved inconclusive, table 2 also shows the hydrocarbon contamination for each solvent and aqueous cleaner calculated as a percentage of the total pressure in the system. Hydrocarbon contamination is defined at Daresbury Laboratory as all species above mass 38, excluding masses 40

and 44. The sum total of such partial pressures should be less than 1% of the total pressure of the system if the vacuum component is to be accepted for UHV use. Table 2 shows that the aqueous cleaners used were not adequate for removing high mass species, with all three tested showing hydrocarbon contamination levels well above the 1% limit. Both n-propyl bromides also failed. The only solvents deemed satisfactory were trichloroethylene, isopropyl alcohol and the hydrofluoroether. Table 2 also shows the measured partial pressure at mass 69 (characteristic of Fomblin oil) normalised against the measured partial pressure at mass 28. Hydrofluoroether is clearly as good as trichloroethylene as far as outgassing is concerned.

Electron Stimulated Desorption

Figure 3 shows the RGA spectra taken during the ESD experiments relevant to each solvent or aqueous cleaner, and table 2 lists the measured ESD yields. All the RGA spectra shown are on the same scale, the x-axis between 1-200 amu and the y-axis between 4×10^{-8} – 4×10^{-12} mbar.

Initial ESD yields for baked stainless steel have been measured previously and are typically in the range of 10^{-2} – 10^{-3} molecules per photon [5,6]. Table 2 clearly shows only two of the cleaners tested resulted in yields of about 10^{-2} molecules per electron, namely trichloroethylene and the hydrofluoroether. Yields for isopropyl alcohol and n-propyl bromide 1 were in the range of 10^{-1} molecules per electron, whereas those for n-propyl bromide 2 and the aqueous cleaners were in the range of 2-5 molecules per electron. The spectra shown in figure 3 confirm the results shown in table 2, where clearly the amount of contamination desorbed as a result of electron bombardment is substantial for the aqueous cleaners and for n-propyl bromide 2. Such gas loads would be unacceptable for successful operation of a synchrotron machine.

These results, combined with the thermal outgassing results, suggest the aqueous cleaners tested are not suitable for cleaning vacuum components for UHV operation. This is in contrast to the results reported by Benvenuti *et al* [7] where aqueous cleaners performed better than solvents for UHV applications based on ESD and Auger Electron Spectroscopy (AES) measurements, the ESD yields for the aqueous cleaners tested being lower than those for solvents. However, it should be noted that the ESD yields for the aqueous cleaners tested were not as low as those measured for their standard cleaning process which involves cleaning with the solvent perchloroethylene. There are some fundamental differences in experimental technique compared to our procedure and this could also have contributed to differing results. However, it is worth noting that in earlier work [1,2] similar results were observed to the ones reported here, suggesting that aqueous cleaners are indeed not adequate for UHV applications.

Conclusions

The work presented here has provided suitable alternatives to trichloroethylene. The aqueous cleaners tested were not adequate in reducing contamination to acceptable levels. Whilst the solvents performed better, not all of those tested were adequate. In particular n-propyl bromide 2 produced a thermal outgassing result approximately an order of magnitude higher than the other solvents and a desorption yield equivalent to the aqueous cleaners. n-propyl bromide 1 and isopropyl alcohol were both adequate to prepare vacuum components for UHV use, however, neither was as effective as trichloroethylene. Overall, the hydrofluoroether performed best in each of the tests carried out and was more effective than our current solvent of choice, trichloroethylene.
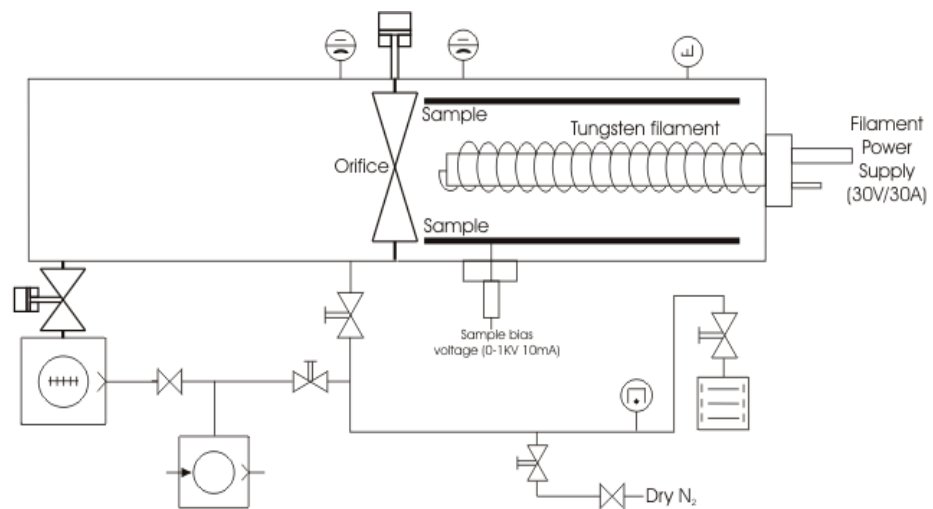
Future work will test the hydrofluoroether over of a period of time to clarify its suitability as a long-term replacement for trichloroethylene. Work to optimise the cleaning process will also be undertaken, including the assessment of co-solvent cleaning processes, which are believed to be more cost effective for cleaning vacuum components. The outcome of this further work, which will be presented in due course combined with the work presented here, will lead to the development of a satisfactory new cleaning process.

References

1. J.D. Herbert, R.J. Reid, A.E. Groome, J. Vac. Sci. Technol. A**12**(4), p1767, (1994)

2. J.D. Herbert and R.J. Reid, Vacuum, Vol. **47**, 6-8, p693 (1996)

3. O. Grobner and A.G. Matthewson, J. Vac. Sci. Technol. A**12**(3), p846, (1994)

4. C.L. Foerster, H.J. Halama and G. Korn, J. Vac. Sci. Technol. A**10**(4), p2077, (1992)

5. C. Herbeaux and P. Marin, J. Vac. Sci. Technol. A**17**(2), p635, (1999)

6. J. Gomez-Goni, O. Grobner and A.G. Matthewson, J. Vac. Sci. A**12**(4), p1714, (1994)

7. C. Benvenuti, P. Chiggiato et al, Vacuum, Vol. **53**, p317-320 (1999)

8. R.M. Zabel, Rev. Sci. Instrum. **4**, 233, (1933)

9. S.H. Cross, Vacuum, Vol. **10**, 86 (1960)

10. E. Miyauchi, S. Okamura, T. Taguchi, S. Goto and T. Hisatsugu, Jap. J. App. Phy. **30(2B)**, 313, (1991)

11. O. Grobner, A.G. Matthewson, H. Stori and P. Strubin, Vacuum, Vol. **33**, 397, (1983)

12. G.E. Fischer and R.A. Mack, J. Vac. Sci. Technol. **2**, p123, (1965)

13. M. Bernardini and L. Malter, J. Vac. Sci. Technol. **2**, p130, (1965)

1	Wash in a high-pressure hot water (~ 80°C) jet, using a simple mild alkaline detergent. Rinse component thoroughly with water until all visible traces of the detergent have been removed.
2	Remove any scaling or deposited surface films by stripping with alumina or glass beads in a water jet in a slurry blaster.
3	Wash down with a high-pressure hot water (~ 80°C) jet ensuring residual beads are washed away. Pay attention to trapped areas or crevices.
4	Dry using an air blower with clean dry air, hot if possible.
5	Immerse completely in an ultrasonically agitated bath of clean hot stabilised trichloroethylene for at least 15 minutes.
6	Vapour wash in trichloroethylene vapour for at least 15 minutes.
7	Ensure all solvent residues have been drained off, paying attention to blind areas.
8	Wash down with a high-pressure hot water (~ 80°C) jet using clean demineralised water.
9	Immerse in a bath of hot (60°C) alkaline degreaser (P3 Almeco^{TM} P36 or T5161) with ultrasonic agitation for 5 minutes. After removal from the bath carry out next step of the procedure immediately
10	Wash down with a high-pressure hot water (~ 80°C) jet using clean demineralised water.
11	Dry in an air oven at ~ 100°C with an air blower using clean, dry, hot air.
12	Allow to cool in a dry, dust free area. Inspect item for sign of contamination, faulty cleaning or damage.
13	Seal in aluminium foil and protect flange faces.

Table 1: Daresbury Laboratory cleaning procedure

Sample

Tungsten filament

Sample

Orifice

Filament
Power
Supply
(30V/30A)

Sample bias
voltage (0-1KV 10mA)

Dry N₂

Key:

Turbomolecular pump	Thermal conductivity gauge	Gas Ballast Pump
Ion Pump	Residual Gas Analyser (RGA)	Valve (usually a screw down type)
Inverted Magnetron Gauge (IMG)	Hot Cathode Ionisation Gauge	
Membrane Gauge	Fine Leak Valve	
Manual Valve	Pneumatically operated gate valve	

Figure 1: Schematic drawing of vacuum system used for this research

Figure 2: Stainless steel samples used for thermal outgassing and ESD tests

Cleaning Agent	Net outgassing rate due to residual contaminants (mbar l s^{-1} cm^{-2})	Hydrocarbon contamination (%)	Ratio of Mass 69 to Mass 28	Pressure rise from ESD (mbar)	Desorption Yield (molecules/electron)
Blank Run (No sample)	$8.2 \times 10^{-13} \pm 5.8 \times 10^{-13}$	0.46	1.8×10^{-4}	-	-
Trichloroethylene (No contamination)	$<2 \times 10^{-12}$	0.58	3.2×10^{-4}	-	-
Trichloroethylene (No contamination)	$<2 \times 10^{-12}$	0.53	8.3×10^{-4}	-	-
Trichloroethylene (Full contamination)	$<2 \times 10^{-12}$	0.90	8.5×10^{-4}	6.3×10^{-6}	0.055
Trichloroethylene (Full contamination)	$<2 \times 10^{-12}$	0.92	5.8×10^{-4}	-	-
n-propyl bromide 1 – Manufacturer 1	$<2 \times 10^{-12}$	1.34	6.1×10^{-4}	3.6×10^{-6}	0.29
n-propyl bromide 2 – Manufacturer 2	$6 \times 10^{-12} \pm 2 \times 10^{-12}$	2.52	1.9×10^{-2}	2.7×10^{-5}	2.19
Hydrofluoroether – Experiment 1	$<2 \times 10^{-12}$	0.52	4.3×10^{-4}	2.1×10^{-7}	0.017
Hydrofluoroether – Experiment 2	$<2 \times 10^{-12}$	0.86	2.7×10^{-4}	-	-
Isopropyl alcohol	$<2 \times 10^{-12}$	0.93	1.0×10^{-3}	4.3×10^{-6}	0.35
Aqueous cleaner 1	$<2 \times 10^{-12}$	2.86	1.6×10^{-3}	5.5×10^{-5}	4.46
Aqueous cleaner 2	$1.2 \times 10^{-11} \pm 2 \times 10^{-12}$	2.03	1.93×10^{-3}	3.7×10^{-5}	2.99
Aqueous cleaner 3	$<2 \times 10^{-12}$	2.70	2.2×10^{-3}	2.6×10^{-5}	2.12

Table 1: Results of the net thermal outgassing rates measured for each solvent and aqueous cleaner used to clean the contaminated sample, the relative effect of each cleaning agent in removing high-mass species and the ESD yields measured from the total pressure rise in the system.
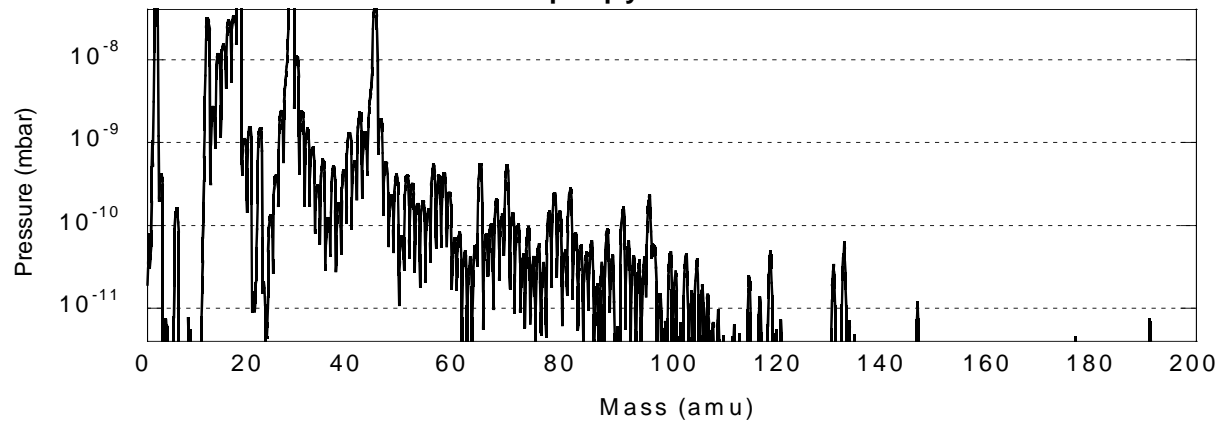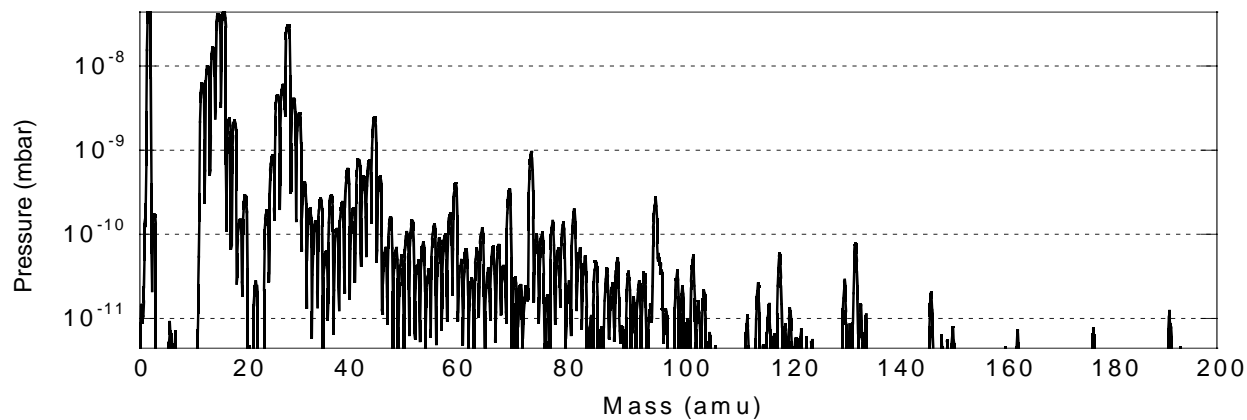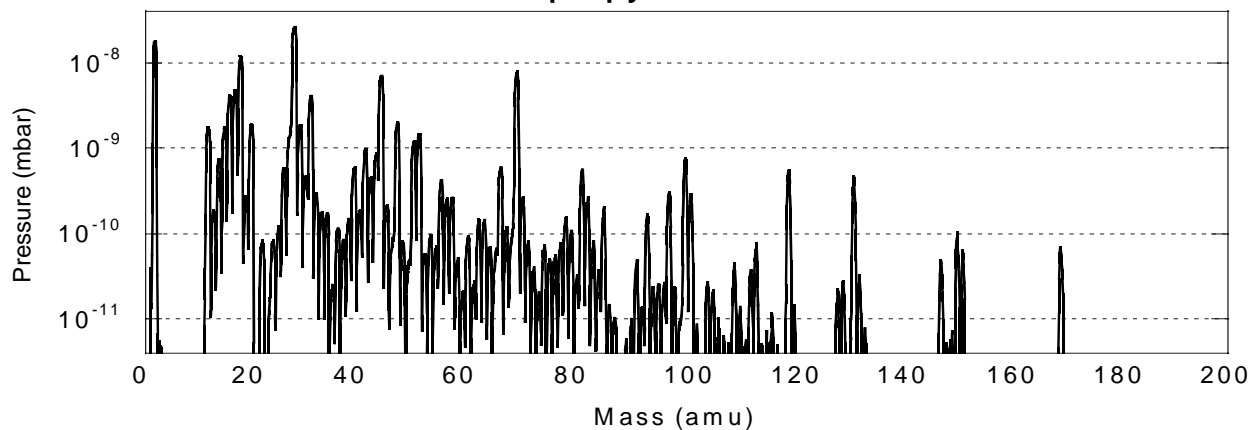
Trichloroethylene
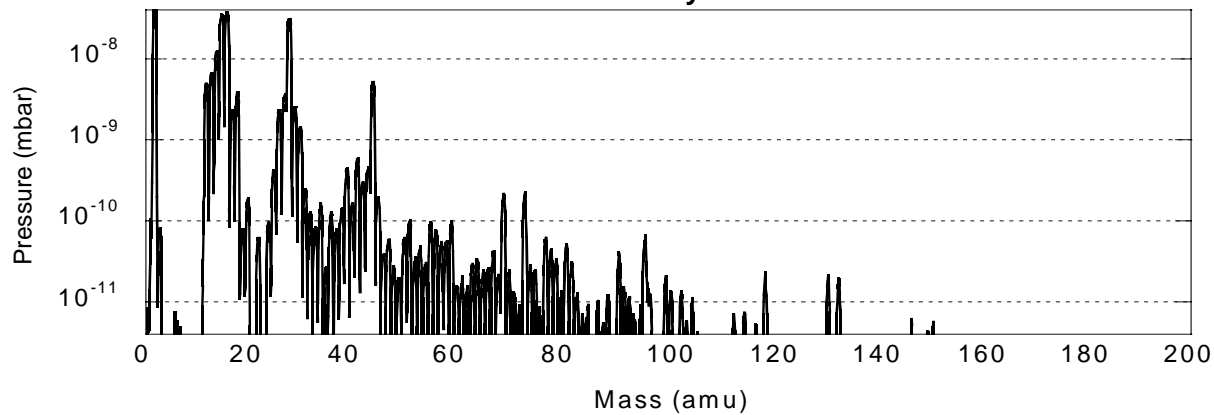
Hydrofluoroether
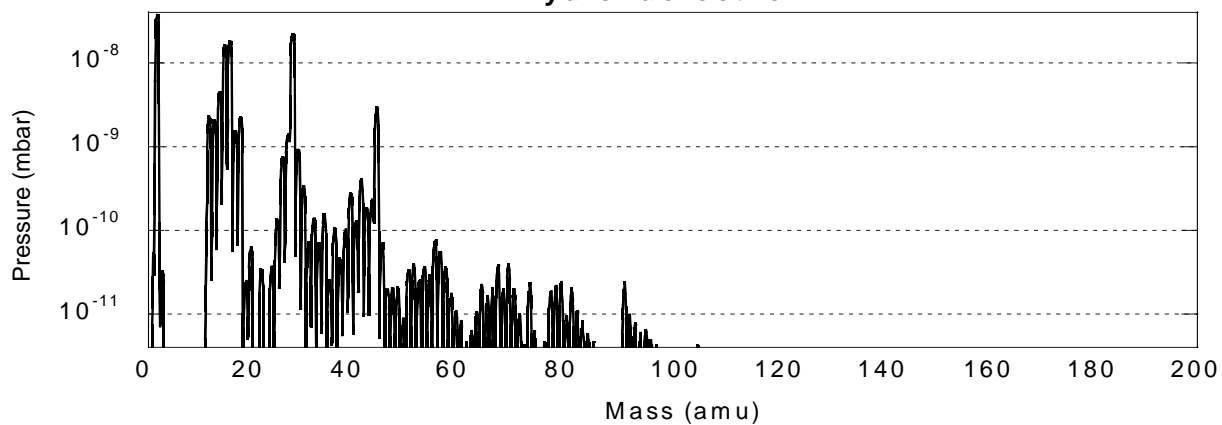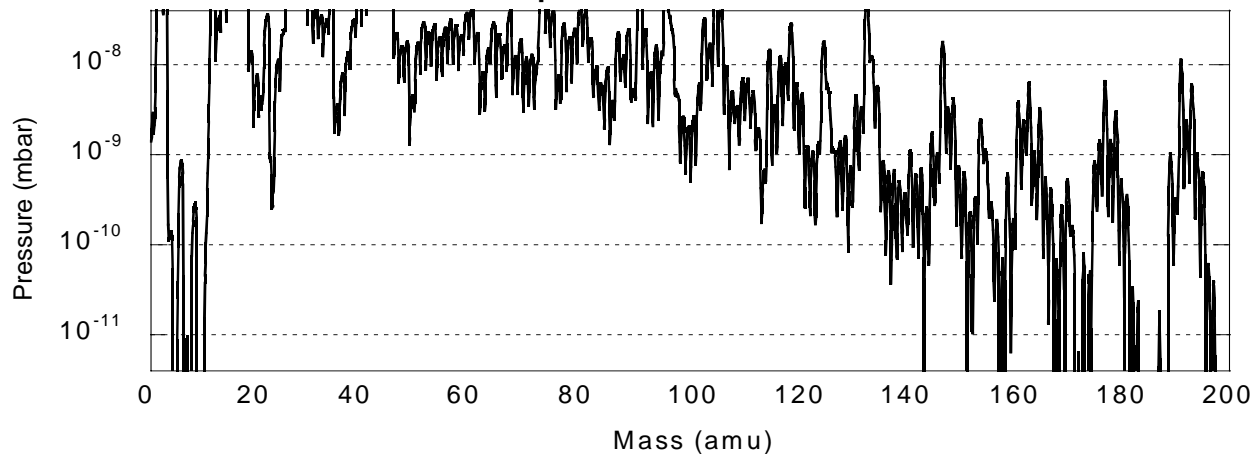

Isopropyl alcohol

N-propyl bromide 1

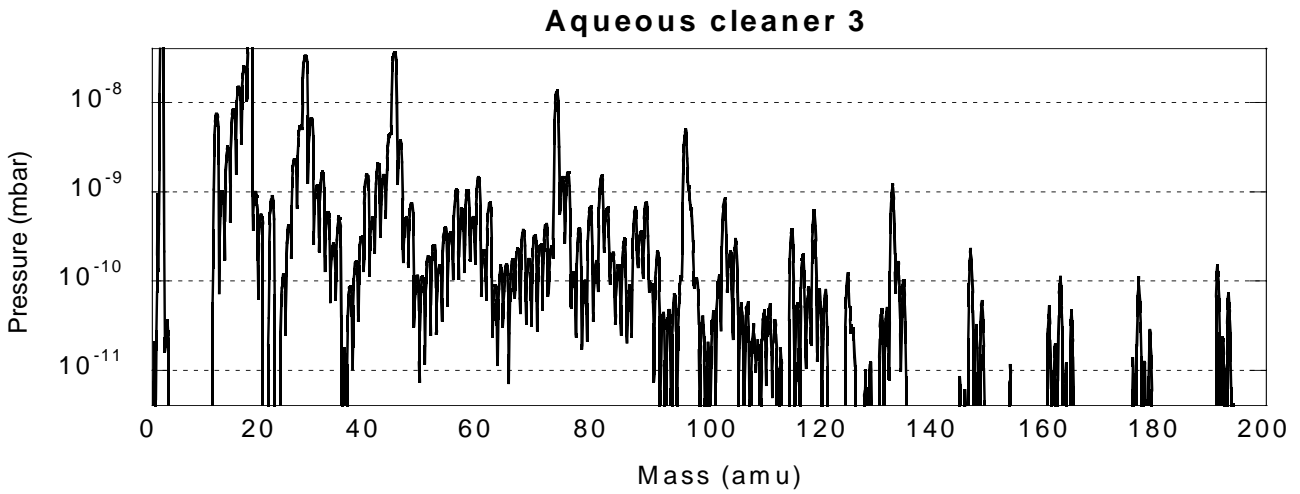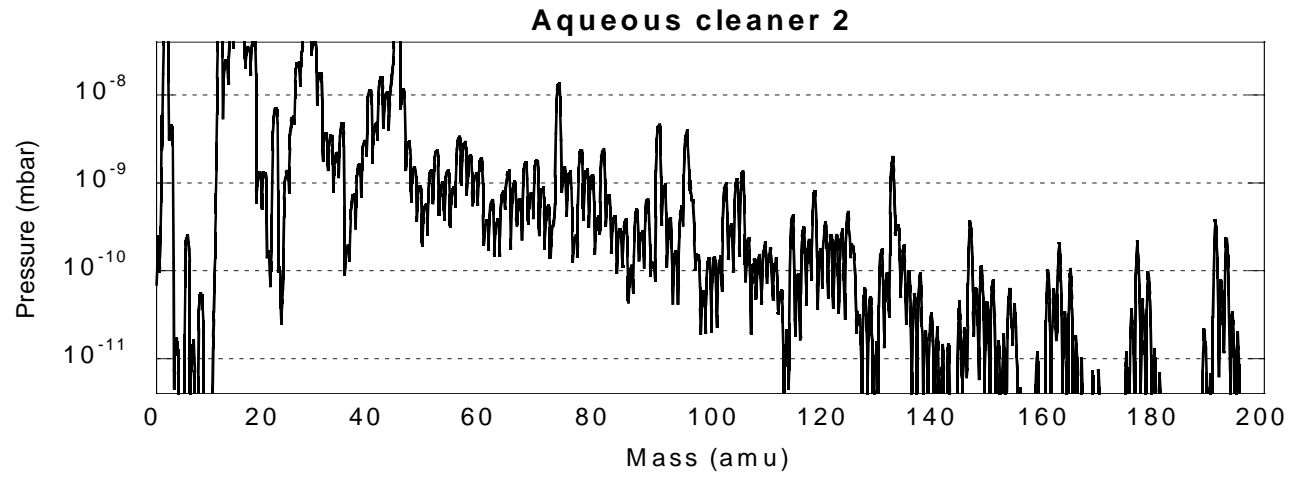# N-propyl bromide 2

Aqueous Cleaner 1

Figure 3: RGA spectra showing the amount of gas generated during ESD tests. Each spectrum corresponds to each of the cleaning agents tested.