Creation of a Cryogenic, Inert Atmosphere Sample Curation Facility: Update

MacEwan Physical Sciences

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Introduction

In our oral presentation at the 2012 MetSoc meeting in Cairns, Australia [1] we described some of the challenges associated with the development and ultimate commissioning of a subzero astromaterials handling facility at the University of Alberta. The facility is unique in that it employs an Ar-filled glove box (most glove boxes used for the handling of planetary materials are filled with purified nitrogen gas) housed within a larger chamber kept at -20°C.The combination of subzero temperatures and a completely inert Ar environment retards the loss of volatile organics while dramatically slowing down the rates of oxidation and hydrolysis of the indigenous compounds within the astromaterials kept within the box. Nonetheless, even within this environment, there is a real danger of contamination from the box components and any accessories coupled to the box, including most importantly, the gloves. We worked hard to minimize surface and airborne contaminants within the box and on the surfaces of the gloves by employing a cleaning regimen that involved the use of both ultrapure water and HPLC grade dichloromethane, but even these procedures could not eliminate contamination from the volatile organics that were released from the interior components through outgassing.

Here we provide an update on efforts to characterize baseline contaminants and test the effects of low temperatures on the glove box system,

The Effect of Temperature on the levels of Volatile Organics in the Box Atmosphere

Much like the vapours arising from the resins, paints and plastics that are used in the construction of new homes, the rate of outgassing of organics within the box was expected to fall over time, and this, we believed would be accelerated by the evacuate-backfill cycles that replace the atmosphere in the box with "fresh" purified Ar gas during the regular use of the box. Moreover, we felt that at the box's nominal operating temperature of -20oC, the rate of outgassing should be greatly curtailed, leading to lower concentrations of the outgassed organics in the atmosphere. During the initial testing of the box to establish baseline contamination levels, a PEG (polyethylene glycol) SPME(solid phase microeextraction) fiber was exposed to the atmosphere in the box for 28 days at room temperature. A photograph of an SPME fiber holder is shown in Figure 1.

Figure 1. SPME Fiber holder assembly (pencil shown for scale)

A subsequent GC-MS analysis performed on our Agilent 5975C GC-MS machine (See Figure 2) revealed that the atmosphere contained the common volatile organic compounds aniline and styrene [1], both of which are used in the assembly of the box, as components of glues and lacquers.

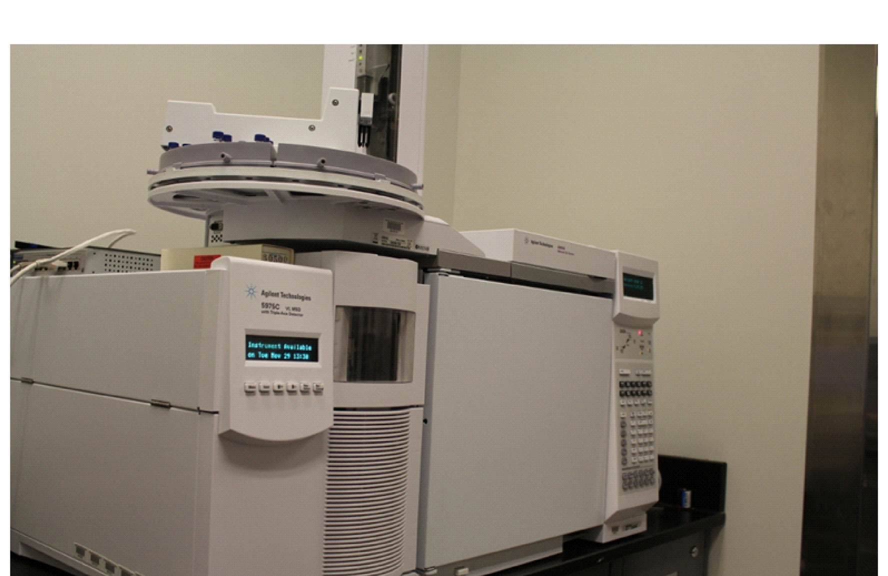

Figure 2. Our Agilent 5975C GC-MS MSD instrument.

To test our hypothesis that lower temperature should result in lower levels of volatile organics, we exposed a new PEG SPME fiber to the box atmosphere for 54 days at the standard operating temperature of -20°C. As expected, a GC-MS analysis of the fiber found that styrene (and aniline*) were essentially now absent from the atmosphere. The GC-MS traces for the room temperature and the low temperature analyses of the box atmosphere are combined in Figure 3. It is noteworthy that most of the peaks in both the room temperature and the low temperature traces are column material (i.e. polyols) and not common organics.

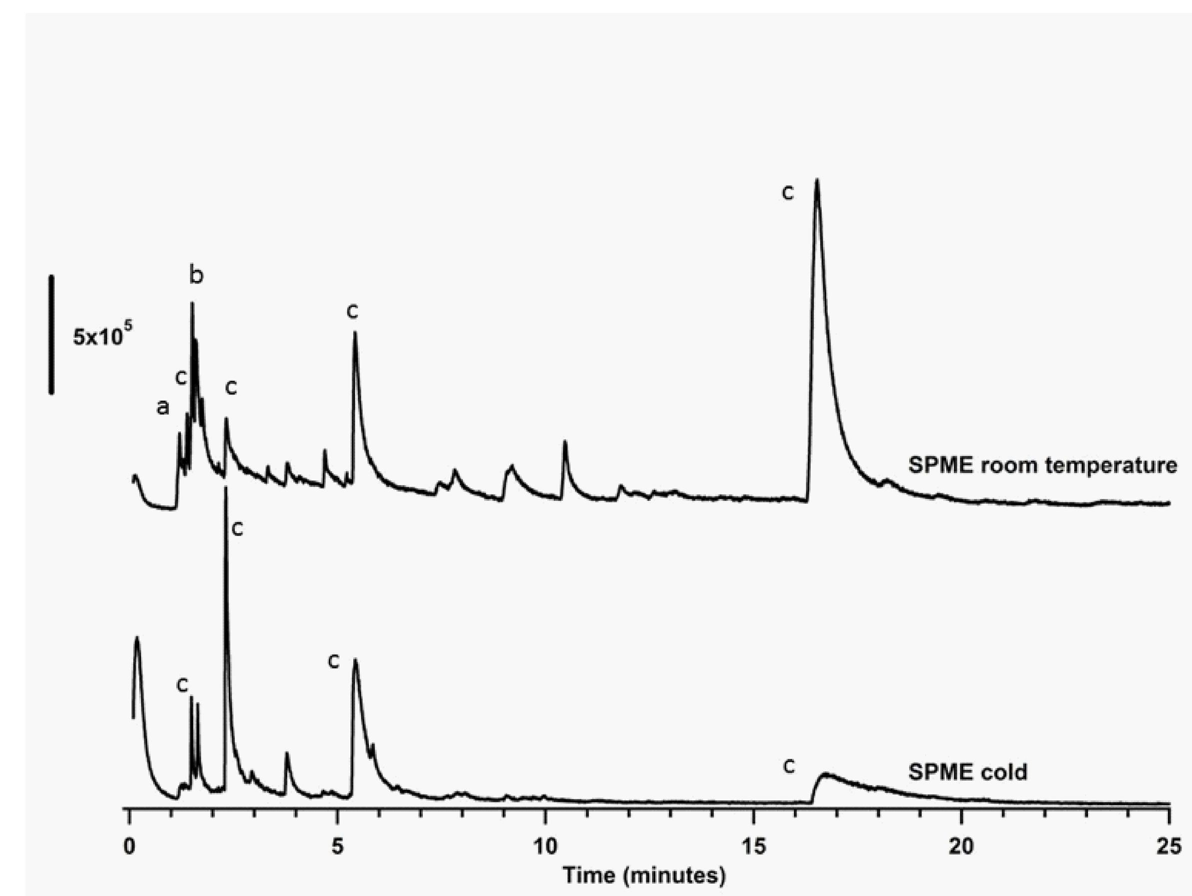

Figure 3. SPME GC-MS traces for the room temperature and the low temperature analyses. Key: a = styrene, b =aniline, c = column material

Apparently, the combination of decreasing rates of outgassing over time and repeated flushing of Ar via pump down-refill cycles, has resulted in there being virtually no volatile organics left in the box atmosphere at its -20°C operating temperature. (*n.b. in any case, we would not expect to find any aniline remaining in the atmosphere as it freezes at -6.3°C, which is well above the -20°C standard operating temperature for the box).

We will continue to monitor the atmosphere within the box over the next 10-12 months by the SPME-GC-MS methodology to see if it has truly stabilized and also to look for any adventitious organics accidentally brought into the box during regular operations.

The Saga of the Gloves: The Switch from Hypalon to Polyurethane

The Hypalon™ gloves that were supplied with the MBraun box proved to be unusable as the polymer that makes up these gloves becomes extremely rigid at subzero temperatures. Fortuitously, we were able to find a replacement polymer, viz. polyurethane, that retains its elasticity down to -20°C. A photograph of the new polyurethane gloves attached to the box at -20°C is shown in Figure 4. Prior to their installation, the polyurethane gloves were cleaned with clean room wipes soaked with 1) ultrapure water and then 2) HPLC-grade dichloromethane (see Figure 5).

Figure 4. Glove box at -20°C equipped with the new polyurethane gloves.

Figure 5. Cleaning of the outer and inner surfaces of the polyurethane gloves with dichloromethane prior to their attachment to the box.

Drippings from the used DCM-soaked wipes were analyzed by GC-MS. The trace for one run is shown in Figure 6. Not surprisingly, the two dominant species in the rinse were the monomeric species methylene diphenyl diisocyanate and 2,2'-(1,4-butanediyl)bis-oxirane, from which the polyurethane polymer, the primary component of the gloves, is derived. This important result shows that the gloves, like the internal components of the box itself, must be scrupulously cleaned before they are installed. Indeed, not just the gloves, but any accessory linked to the box must be thoroughly cleaned before being linked to the box, to minimize the transfer of contaminants to the critical working areas within the box.

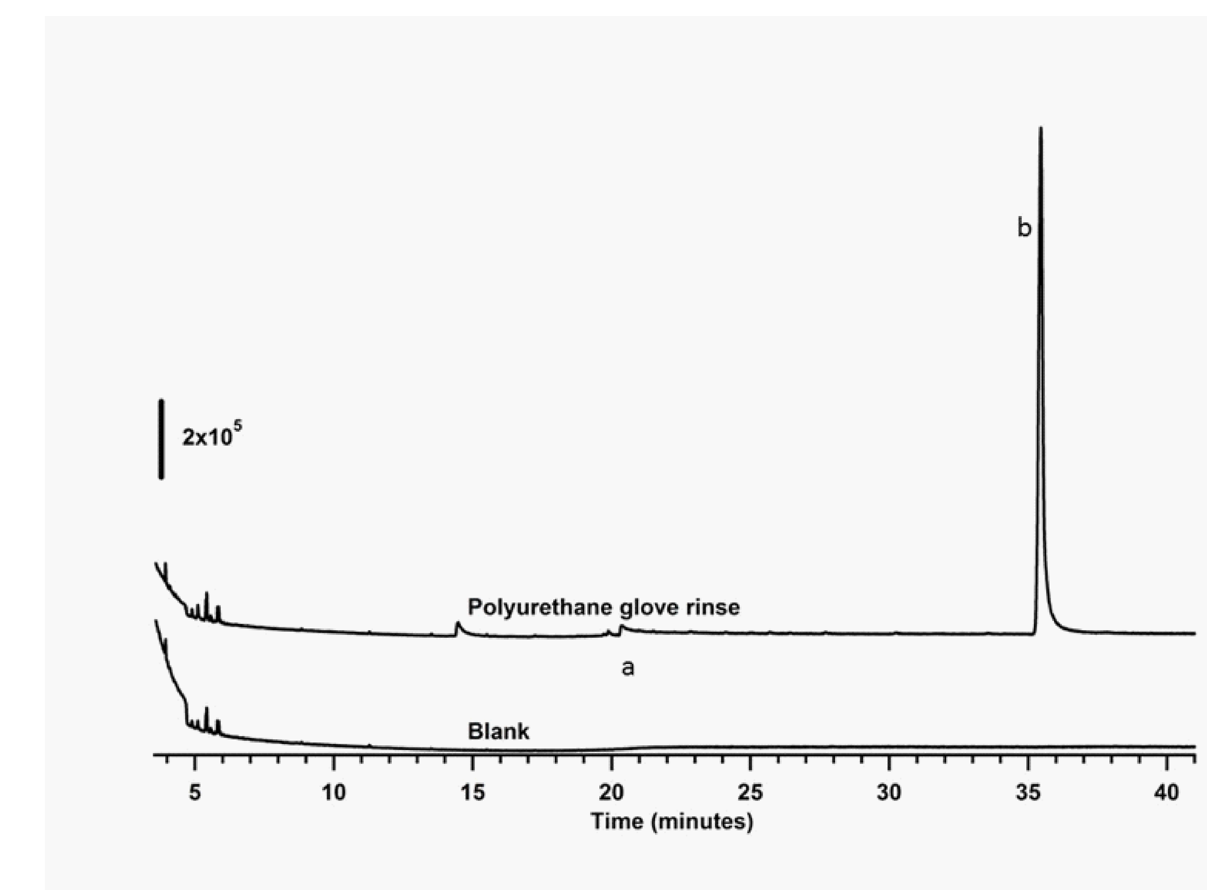

Figure 6. GC-MS trace of the organics removed from the polyurethane gloves by the dichloromethane wash. Key: a = methylene diphenyl diisocyanate, b = 2,2'-(1,4-butanediyl)bis-oxirane.

Conclusions and Recommendations

Unlike hypalon gloves, polyurethane gloves retain their flexibility down to -20°C, but they come comtaminated with surface organic residues that must be removed before the gloves are installed.

The atmosphere within new glove boxes tends to become contaminated with outgassed organics that are released by the glues, resins and plastics used in the construction of the box. Over time, through the regular use of the box, which involves evacuation and backfill cycles that bring purified Ar gas into the box, the concentrations of the outgassed organic vapours fall to sub ppm levels. Moreover, at low temperatures, less volatile outgassed compounds such as aniline, which has a freezing point above -20°C, are removed from the box atmosphere through condensation.

Acknowledgements

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References

[1] Hilts, R.W. et al 2012. "Creation of a Cryogenic, Inert Atmosphere Curation Facility", *Meteoritics and Planetary Science* 47:A186.