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Determination and Monitoring of Potentially Corrosive Volatile Compounds from Museum Storage Materials - Alternative Analytical Approach to the Oddy Test

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Introduction

Conservators charged with the care and preservation of museum collections are additionally challenged by the potential risk to their specimens from materials associated with storage or display. The system designed to provide protection from external damage contains the potential to do the most harm. Volatile Organic Compounds (VOCs) emitted from various materials – timber, fabric, sealants, paints, plastic - if contained with little ventilation, are known to build up to concentrations where significant chemical damage can occur to the specimen(s) which in itself of course is inherently diverse.

The Natural History Museum (NHM), London, currently employ a simple and user friendly accelerated corrosion screening method called the Oddy Test that was developed in the early 70's to help determine which materials emit harmful compounds likely to be of detriment to a specimen. In short, this involves suspending coupons of reactive metals - copper, silver and lead - in a test tube containing the test material and a source of moisture (i.e. wetted cotton wool). The tube is sealed, heated and held to a set temperature of 60°C for 28 days. After this, the result of any corrosion on the coupon can be assessed against a control by the Conservator and judgement made on a material's qualification for permanent storage, temporary display or indeed none.

Oddy has served as a good and simple indicator for many years and dramatically improved stability choices made when selecting storage display materials.

The test does have several inadequacies that are well acknowledged. For instance: –

- Timescale: - the 28 day incubation time is a long wait for results. A resulting material fail and repeat of the test until a pass is obtained is not always afforded.
- Apparatus variables: - the test is open to potential inconsistencies.
- Interpretation of Results: - conclusions are subjective, determined organoleptically by visual assessment. The compounds causing corrosion are unidentified and unquantifiable.

Instrumental Analytical techniques that can potentially eradicate these inadequacies are available and the application of some have become well established tools within museum conservation departments.

For example:

The use of Headspace Gas Chromatographic Mass Spectrometry (HS-GCMS) can provide qualitative and quantitative data for known and unknown VOCs. Further to, VOC sampling methods are also non-destructive and non-invasive and a number of methods and options are available to collect VOCs and inject to the GCMS for identification and quantification. The Anatune application test laboratory houses comprehensive and extensive capabilities for this discipline.

Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) - A newer complimentary technique to the GCMS offering high sensitivity, rapid and real-time analysis of VOCs and direct sampling will also be applied.

The NHM supplied the laboratory with a selection of samples from common materials used to display and store and from the Oddy apparatus - some of which were known to fail Oddy, and the alternative equivalent believed safe – for analysis. (Listed in table 1).

The initial purpose of the exercise currently presented serves as an initial and basic proof of concept to draw comparison and consider effectiveness of analytical techniques.

Instrumentation

GERSTEL MultiPurpose Robotic Sampler
GERSTEL Cooled Injection System (CIS) 4 and Agilent split/splitless inlet
Agilent 7890 GC with a 7000 GC/QQQ
GERSTEL Robotic SPME and static headspace tools
(fig.1)

Figure 1: Illustration of MPS Robotic Pro on Agilent GC-MS

SYFT TECHNOLOGIES' *VOICE* 200*ULTRA* SIFT-MS running LabSyft software
GERSTEL MultiPurpose Robotic Sampler with: Large capacity 20mL headspace tray, Agitator, 2.5mL heated headspace syringe
(fig.2)

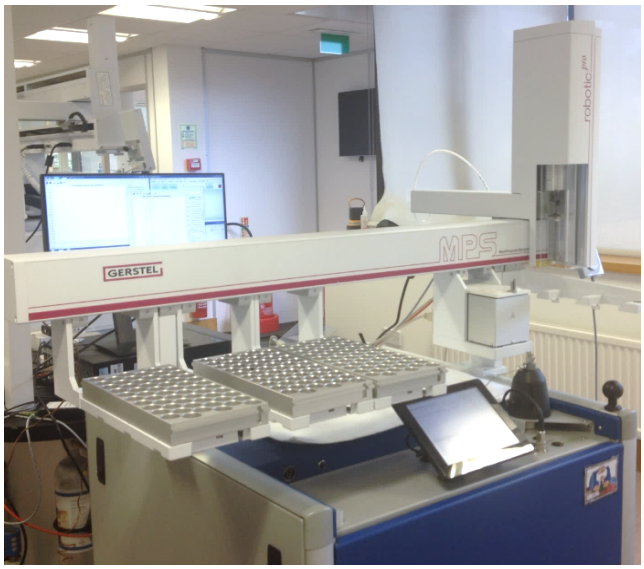

Figure 2 – Automated SIFT-MS system in Anatune Applications Laboratory.

Methods

Headspace GC-MS can be used to identify volatile compounds in a variety of materials and SIFT-MS enables real time monitoring and/or rapid detection of target compounds. Whereas static headspace provides information for those compounds present at relatively high levels in samples, other approaches that provide enrichment can be employed to determine those components at trace levels. Solid phase micro extraction (SPME) is one such technique.

Samples provided were analysed using headspace solid phase micro extraction (HS-SPME) using a mixed (Divinylbenzene (DVB)/Carboxen/ Polydimethylsiloxane (PDMS)) fibre.

The SPME was automated using a GERSTEL MPS Robotic Pro mounted on an Agilent 78990B GC with a 7000 A Tandem mass spectrometer (QQQ), with extractor ion source, using MS1 scan acquisition. Peaks were tentatively identified using NIST mass spectral library search. The System set up is shown in Figure 1.

Subsequently the headspace of selected samples was analysed using SIFT-MS for some of the target compounds identified (shown in figure 2).

Samples

Item	Sample type	Analytical Method Applied
1	Resin Clear –Oddy "pass"	HS-SPME to GCMS
2	Resin White – Oddy "fail"	HS-SPME to GCMS
3	Oddy tube Bung unused (top)	HS-SPME to GCMS
4	Oddy tube Bung unused (bottom)	HS-SPME to GCMS
5	Oddy tube Bung used (top)	HS-SPME to GCMS
6	Oddy tube Bung used (bottom)	HS-SPME to GCMS
7	Heat Shrink Tubing – Oddy "Pass"	HS-SPME to GCMS
8	Heat Shrink Tubing – Oddy "Fail"	HS-SPME to GCMS
9	MDF - Ultralite	HS-SPME to GCMS + SIFT-MS
10	MDF – Classic FSC mix 60%	HS-SPME to GCMS + SIFT-MS

Table 1 – material samples provided by NHM

Sample extraction:

Samples received included 2 types of MDF, heat shrink tubing and resins. The bungs used for the Oddy tests were also analysed (one used and one unused). A sample from both the top and the bottom (contact surface) of each bung was taken. Samples were chopped roughly and aliquots weighed into 20mL headspace vials.

HS-SPME: Aliquots of each sample (1g MDF, 0.5g heat shrink tubing and bungs and 0.2g Resin) were taken and extracted using a Mixed (DVB/Carboxen/PDMS) fibre at 60°C.

GC/MS conditions:

DB-Wax 30m x 0.25mm x 0.25µm, 1.5mL/min flow. Oven ramped from 40°C to 250°C.

SPME fibres were desorbed in splitless mode (injector at 250°C). The system was set up to split to an MSD and FID detector at a ratio of approximately: 1:1

SIFT-MS analysis:

MDF samples were analysed by heating a 1g aliquot sample 60°C for 30 minutes in a 20mL vial and 2.5ml of sample headspace was taken. The SIFT-MS was set to measure Formaldehyde, Acetic acid, Hexanal and Furfural.

Results

Figure 3 shows GCMS spectra resulting from the VOC recovered from the headspace of the resin samples. Clear differences can be clearly observed between the pass and fail. A selection of larger peaks have been numbered and identified as listed in table 2.

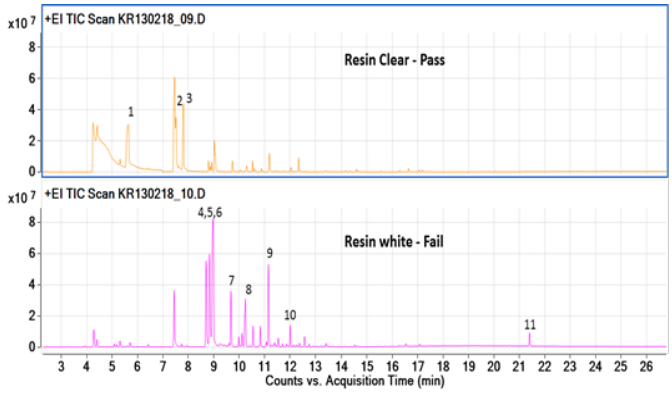

Figure 3 – GC-MS comparison of resin samples

Peak No.	Compound
1	Isopropyl alcohol
2	Tert-butyl glycidylether
3	Butyl acetate
4,5,6	Ethyl benzene and xylenes
7	propyl benzene
8	Ethyl toluene
9,10	Trimethylbenzene
11	2-methyl-3(2H)-isothiazolone

Table 2 – Resin headspace sample comparison. Major peaks (Peak IDs from NIST Atomic Spectra Database)

Figure 4 shows GCMS spectra resulting from the VOC recovered from the headspace of the samples taken from the bungs used to seal the Oddy test tubes. Observe reproducible spectra of each sample top and exposed bottom surface, suggest the bung material although used and unused differ (possibly due to age) remain unaffected and inert to the volatiles emitted from the Oddy test sample. For illustration, Table 3 contains a further selection of some major peaks from these spectra

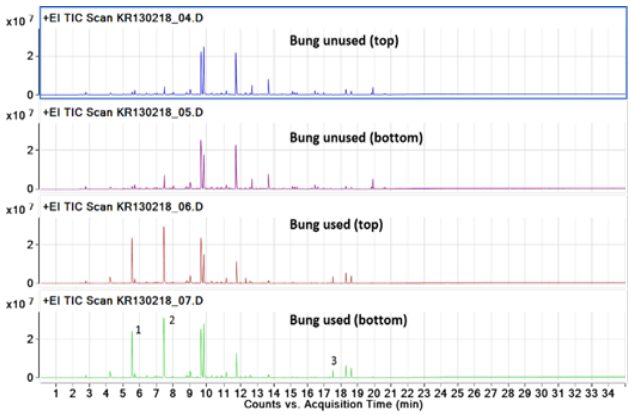

Figure 4: GC-MS comparison of bung sample Head space

Peak No.	Compound
1	Octamethyltetrasiloxane
2	Decamethylcyclopentasiloxane
3	Butoxyethoxyethanol

Table 3 – Bung sample comparison. Major peaks (Peak IDs from NIST Atomic Spectra Database)

Figure 5 shows GCMS spectra resulting from the VOC recovered from the headspace of the samples taken from the Headspace of the Heat Shrink tubing samples. Fail sample Abundant in acids. Table 4 contains a further selection of some major peaks from these spectra

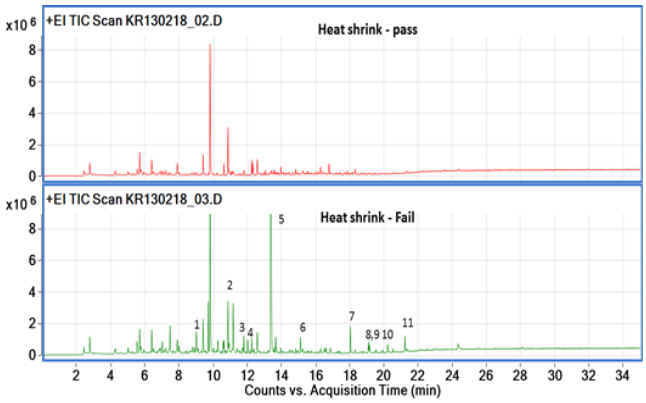

Figure 5: GC-MS Comparison of Heat Shrink tubing sample Head space

Peak No.	Compound
1	Xylene
2,3	Trimethylbenzene
4	Ethyltoulene
5	Acetic acid
6	Propylene Glycol
7	Hexanoic acid
8	Ethylhexanoic acid
9	Hepatnoic acid
10	Octatonic acid
11	Nonanoic acid

Table 4 – Heat Shrink headspace sample comparison. Major peaks (Peak IDs from NIST Atomic Spectra Database)

Figure 6 shows GCMS spectra resulting from the VOC recovered from the headspace of headspace of MDF samples. In the same manner as all other samples, a selection of peaks are identified and listed in table 5.

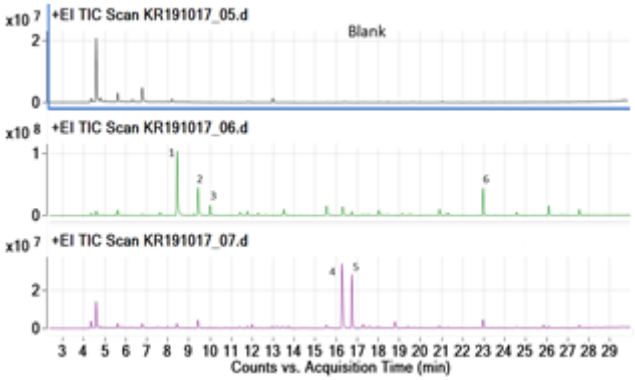

Figure 6: GC-MS comparison of MDF sample Head space

Peak No.	Compound
1	α-pinene
2	Hexanal
3	β -Pinene
4	Acetic acid
5	Furfural
6	Hexanoic acid

Table 5 – MDF headspace sample comparison. Major peaks (Peak IDs from NIST Atomic Spectra Database).

Following on from the MDF GCMS results, the identified peaks from table 5 were then set as targets and the MDF were sampled on SIFT-MS. Illustration of the resulting analyses (figs. 7-10)

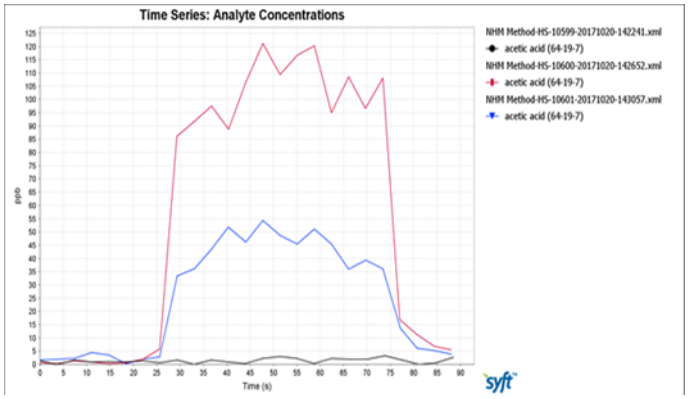

Figure 7: Acetic acid by SIFT-MS (Blank, Ultralite MDF, FSC mix 60% classic MDF, fire retardant)

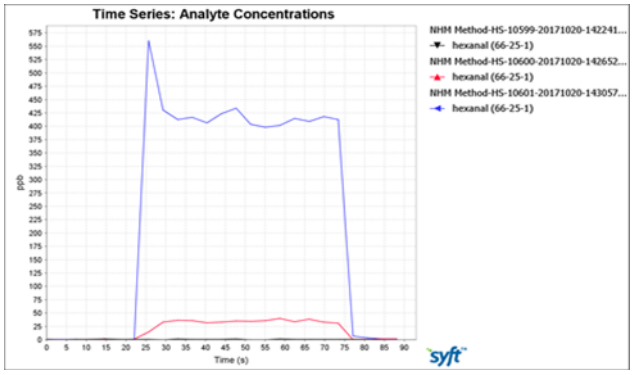

Figure 8: Hexanal by SIFT-MS (Blank, Ultralite MDF, FSC mix 60% classic MDF, fire retardant)

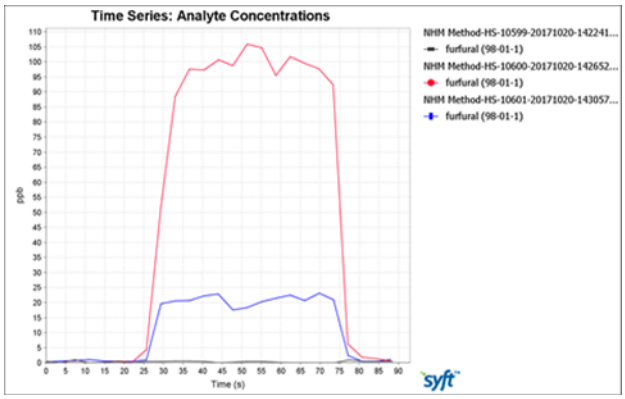

Figure 9 : Furfural by SIFT-MS (Blank, Ultralite MDF, FSC mix 60% classic MDF, fire retardant)

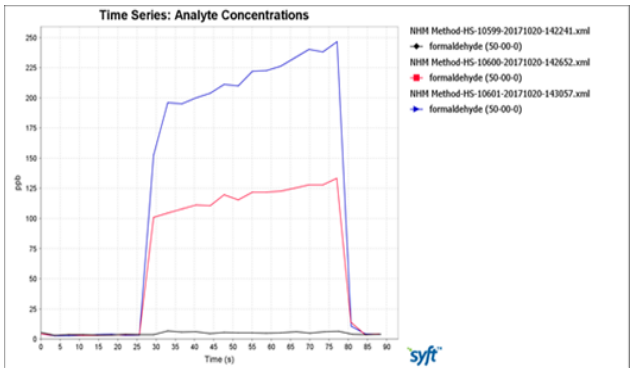

Figure 10 : Formaldehyde by SIFT-MS (Blank, Ultralite MDF, FSC mix 60% classic MDF, fire retardant)

Discussion

This application note illustrates the use of two complimentary techniques, SPME-GC/MS and SIFT-MS which could be used to gain more information than the standard Oddy test and could reduce the testing time for some materials. GC/MS gave a simple way to identify and separate chemicals enabling unknowns to be identified simply. SIFT-MS gave a rapid targeted approach which could be used to screen for standard chemicals linked closely to Oddy test failures.

Using SPME-GC/MS to look at the heat shrink tubing identified a number of differences between the pass and fail samples - the most notable being the acetic acid, and a range of organic acids, along with some aromatic compounds. With regard to the few major peaks that have been selected and identified here, the confirmation of acetic acid is a good example of a prolific commonplace compound which emits from many materials such as silicone sealants, breakdown of polyvinyl acetate films, wood and composite wood products like MDF and block board. It's presence in significant concentrations not only causes damage to metals but most other matter including cellulosic, mineral and rock. The detection of these acids clearly explains the reason the Oddy result was a fail.

The reason for the failure of the resin samples is possibly not so obvious. Differences were largely aromatic BTEX type compounds, and a response for 2-methyl-3(2H)-isothiazolone (CAS 2682-20-4), (which is used as a biocide) in the failed sample. Without knowing detail of the Oddy fail it could be inferred that the benzene type compounds may have shown on the lead coupon, and

indeed more thorough investigation could well disclose other compounds. The detection of the ester/acetate in the “pass” resin could warrant further investigation with such compounds, though not impacting a metal coupon, may affect cellulosic/keratin containing items although there is no direct proof of this. Further work would be required to confirm the compounds and levels responsible for any potential Oddy test failure and potential corrosion.

The SIFT-MS data of the MDF detects the acetic acid clearly as with all other selected compounds but most significantly the SIFT-MS provides capability of detecting Formaldehyde a compound ordinarily tricky to detect. A potentially useful tool.

Wood composites commonly bonded with formaldehyde based adhesives offer variable stability which is added to as the wood itself will also show formaldehyde owing to polysaccharide degradation. This would mean that different batches of the same MDF may pass and fail for this chemical alone and that a pass or fail result may only be valid for the batch used. This would mean that a rapid test of each batch used may be useful when using these materials. Furfural levels measure in the Ultralite MDF could indicate a different bonding material compared to the other MDF sample. Furfural based resins can be substituted for formaldehyde based ones.

Conclusion

Inadequacies of the Oddy test listed earlier are solved by the application of the methods shown here; - time taken to get results from each method is significantly reduced; - reproducible accuracy is much increased with sample preparation and apparatus use reduced; - the ability to identify is gained.

A combination of factors will influence volatile emissions from materials, not just temperature and humidity. Cellulosic and organic matter may be vulnerable where metal is not; old resin coatings and adhesives from old conservation treatments may exist; the constitution of the artefact occasionally undetermined might have hidden vulnerability and remain unknown without potential destructive investigation- inorganic rocks and minerals contain or can form salts – exposure to acidic compounds will encourage growth/formation – structure of the rock will split, and shatter. Conservation is a discipline where there is much to consider.

Instrumental analytical techniques can help with this and will offer a wider and more extensive testing capability – wherein a greater number of materials and avenues of question can be analysed under a variety of measured and tailored test conditions. Application of SIFT-MS introduces instantaneous results and real-time quantification of multiple compounds – (in little over a minute) either taking headspace from a vial of a sample, or in-situ in a display cabinet for example. It offers the prospect of monitoring the airspace of the environment or case, or assessment of material degradation for targeted compounds of interest within realistic ambient conditions in a non-invasive manner.
The subsequent knowledge gained can further build a comprehensive collection of data to further inform preventative conservation decisions.