



Comparative Analytical Methods of VOC Sampling from Individual Books

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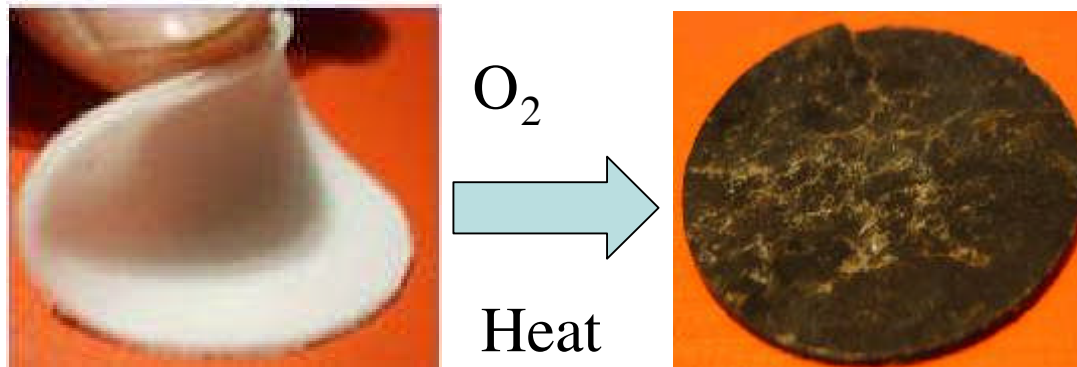
March 2009

The Strathclyde Polymer Degradation Group - Remit

‘A polymer physical chemistry group dedicated to researching all forms of degradation in polymeric materials (both natural and synthetic)’.

- *Collaboration with our exceedingly accurate and precise Analytical Chemistry Colleagues has led to a crossover into the field of conservation science*

Studying Degradation in Synthetic Polymers



The Polymer Degradation Groups
traditional area: High temperatures,
extreme environments....



CL592

CL594

Polymer Degradation in Relation to Conservation Science



Physical – loss of plasticizer from a cellulose acetate artefact causes severe warping



Chemical – breakdown of cellulose nitrate polymer leading to embrittlement and loss of mechanical strength

Volatiles Evolution & Conservation Science – Applications



The study of the evolution of volatile materials from historical & conservation artefacts is of importance for our academic understanding and the preservation of artefacts.

Many classes conservation artefacts both natural and synthetic, evolve volatile materials which are indicative of both the ‘[history](#)’ and the ‘[health](#)’ of that artefact.

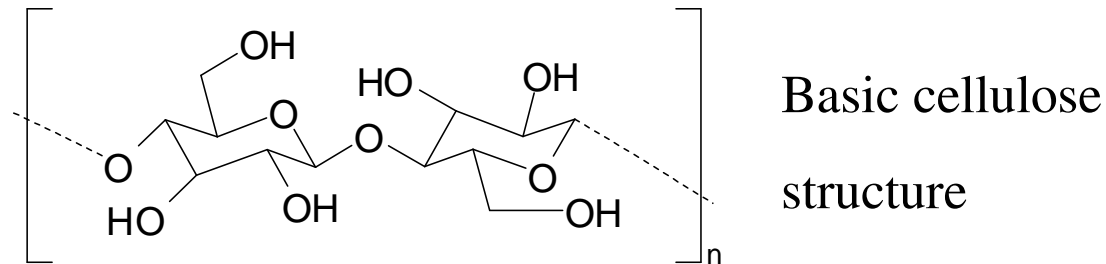


Characterisation of VOC Evolution in Paper Based Books and Manuscripts

*Long Term, Low Temperature Degradation
of Processed Cellulose/Lignin*

Paper and The Problem...

- The vast majority of books and historical manuscripts in library collections across the world are based on paper - a complex product of plant derived cellulose/lignin fibres:



- paper also contains lower molecular weight polysaccharides, known as hemicelluloses
- The most common monosaccharides found in hemicelluloses are D-glucose, D-mannose, D-galactose, D-xylose and L-arabinose.
- The final key component of paper is lignin, a structurally complex aromatic polymer with which the polysaccharides within the plant cells are impregnated

Paper and Degradation

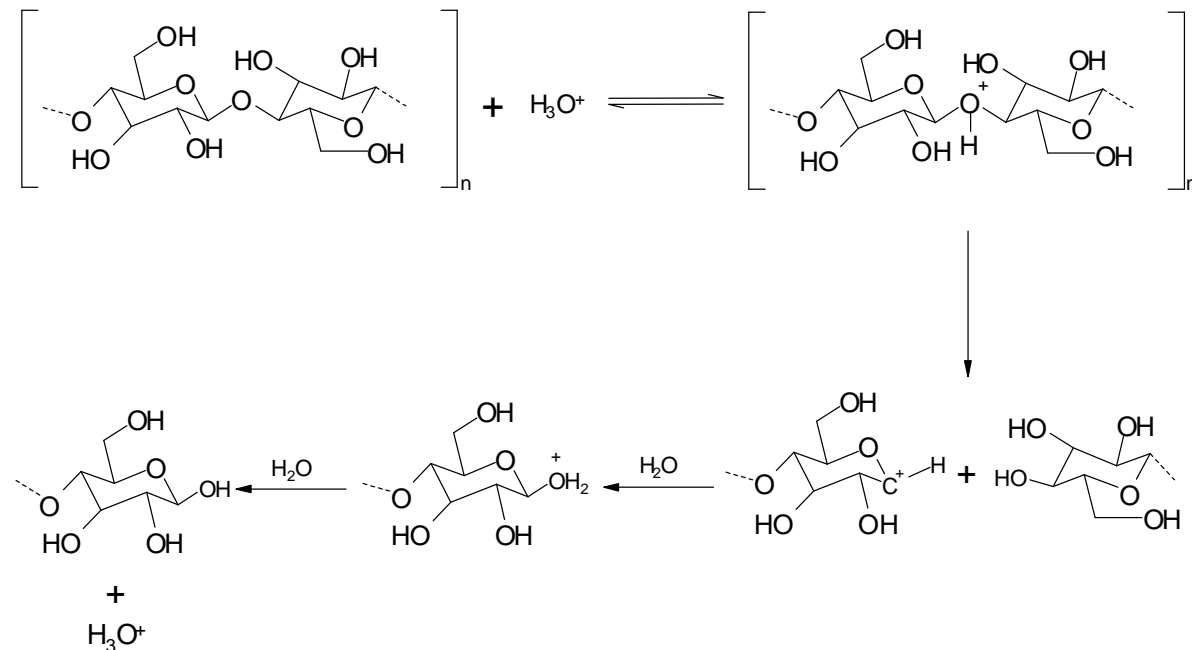
- This naturally derived material is both structurally, morphologically complex and is *eminently* 'degradable'.
- The paper that makes up the lions share of books or other forms of written media is susceptible to a wide variety of degradation processes:
- **Thermo-oxidative degradation**
- **Acid/base accelerated hydrolysis**
- **Microbial attack**
- **Secondary substrate / environmental / misguided remediation effects**

Basic Degradation Mechanisms

- The majority of degradation processes involve the decomposition of cellulose.
- The degradation of cellulose occurs due to reactions at the glycosidic linkages and hydroxyl groups:
- There are two main mechanisms through which cellulose degrades; **hydrolysis** and **oxidation**
- The most predominant reaction thought to occur under ambient conditions is acid catalysed hydrolysis, whereas oxidation tends to occur at higher temperatures

Acid Hydrolysis of Cellulose

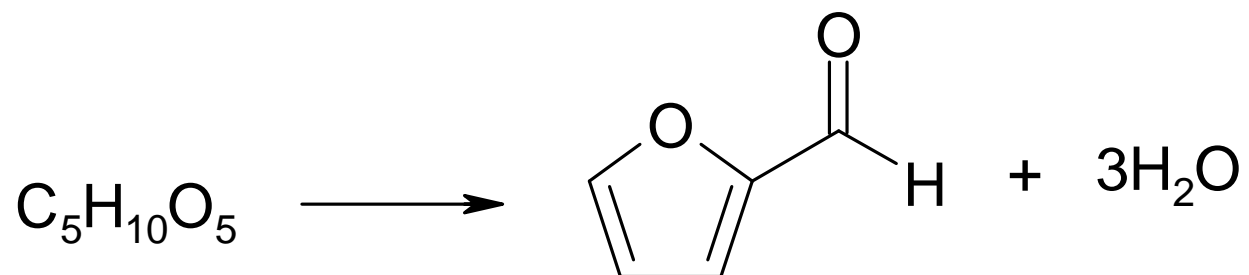
- In acid catalysed hydrolysis, scission of the glycosidic linkages, results in production of D-glucose
- Acid catalysed hydrolysis is comprised of three stages:



- 1) Protonation of the glycosidic oxygen
- 2) Charge transfer onto C-1 to form a carbonium ion (RDS)
- 3) Cleavage of the glycosidic bond followed by attack on the carbonium ion by water to generate the free sugar

Acid Hydrolysis of Cellulose

- Acid hydrolysis results in the formation of glucose and pentose sugars (e.g. xylose), These sugars can then undergo dehydration to form furfural and related cyclic ethers:



- *Recent studies have suggested that acid hydrolysis generates carbohydrate fragments which oxidise forming carboxylic acids. These acids enhance the acidity of the paper and thus initiate an auto-catalytic degradation cycle*

Oxidation of Cellulose

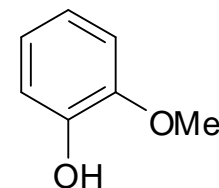
- Cellulose is also sensitive to oxidation:
- In common with synthetic polymers, oxidation induces the formation of carbonyl groups within the polymer
- further oxidisation leads to the formation of carboxylic acids such as formic, acetic, oxalic and lactic acids.
- **A Vicious Circle....** *Acid hydrolysis generates carbohydrate fragments which oxidise forming carboxylic acids - These acids enhance the acidity of the paper, promoting further hydrolysis and thus initiate an auto-catalytic degradation cycle.*

Other Important Factors

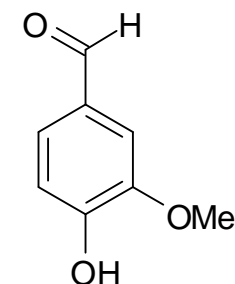
- **Sizing** – Introduces strong acids. e.g. Rosin, a mixture of diterpene acids and aluminium sulphate
- **Inks** – Iron Gall (*need I say more....*)
- **Pollutants** – SO₂, nitrous and nitric oxides all form mineral acids when absorbed into paper.
- **High temperatures** - Accelerate the oxidation and acidic hydrolysis of cellulose, Cellulose has been shown to degrade twice as fast for every increase in temperature of 10°C
- **Humidity** – *too much*: Mould or accelerated hydrolysis, *too little*: Dehydration and loss of mechanical properties
- **Light** – Photo degradation of cellulose and lignin.

A Surfeit of Degradation Products

- The complex material that is paper, and the broad range degradation processes that it can undergo, inevitably results in the production of a wide range of degradation products:
- There are eight main classes of volatile degradation products formed from the long term degradation of paper:
 - Carboxylic acids
 - Alcohols
 - Aldehydes
 - Benzenic derivatives
 - Alkylbenzenes,
 - Aliphatic hydrocarbons
 - Esters and polycyclic aromatic hydrocarbons



Guaiacol



Vanillin

Conservation of Collections

- The degradation processes occurring in paper, typically occur over extended timescales (~20 to >200 years)
- In many cases direct remediation strategies have been unintentionally destructive.
- The processes of paper degradation are interlinked and exceedingly complex.
- In order to understand the problem we first need to know what exactly is occurring.
- ***Can we identify degradation, by its fingerprints??***

The purpose of this Research

- *Characterisation of volatiles evolution in books and manuscripts*



Characterisation of the complex mixture of volatiles evolved from library collections and their significance wrt. the degradation processes occurring in books may yield an effective method of monitoring the 'health' of a library collection

Aims and Strategy

- To develop a full understanding of the 'suite of degradation products' evolved from a range of books undergoing natural degradation
- ✓ To achieve this – Three analytical sampling methods (**SPME**, **silicone strip surface adsorption** and **TVA**) have been trialled on a series of test books.
- Armed with the 'full spectrum' of volatiles evolved, link key fingerprint compounds to ongoing degradation processes
- Application of this knowledge may lead to an effective monitoring strategy.

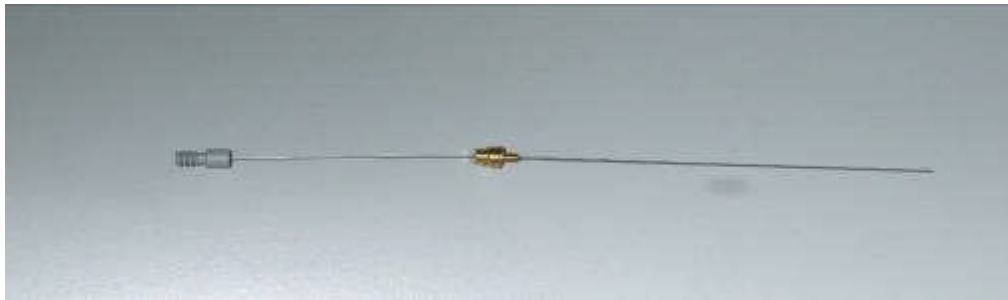
Analytical Methods Employed

- SPME – *Established , High sensitivity, relatively easy to implement, non-destructive, Selective*
- Silicone strip Adsorption – *Relatively novel, yet similar in principle to SPME, potentially cheaper*
- Thermal Volatilisation Analysis – *Complex, time consuming, but entirely non-selective. Highly developmental*



SPME Contact Sampling

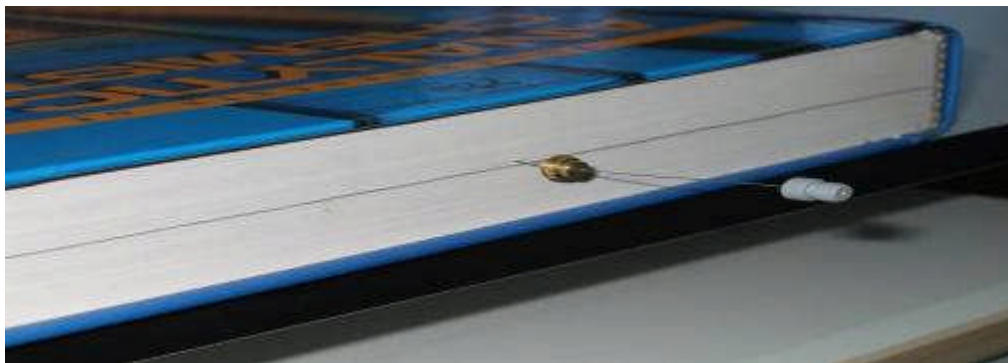
Use of SPME fibre (divinylbenzene/carboxen/PDMS) to trap VOCs:



SPME needle removed from holder



SPME fibre extruded from needle

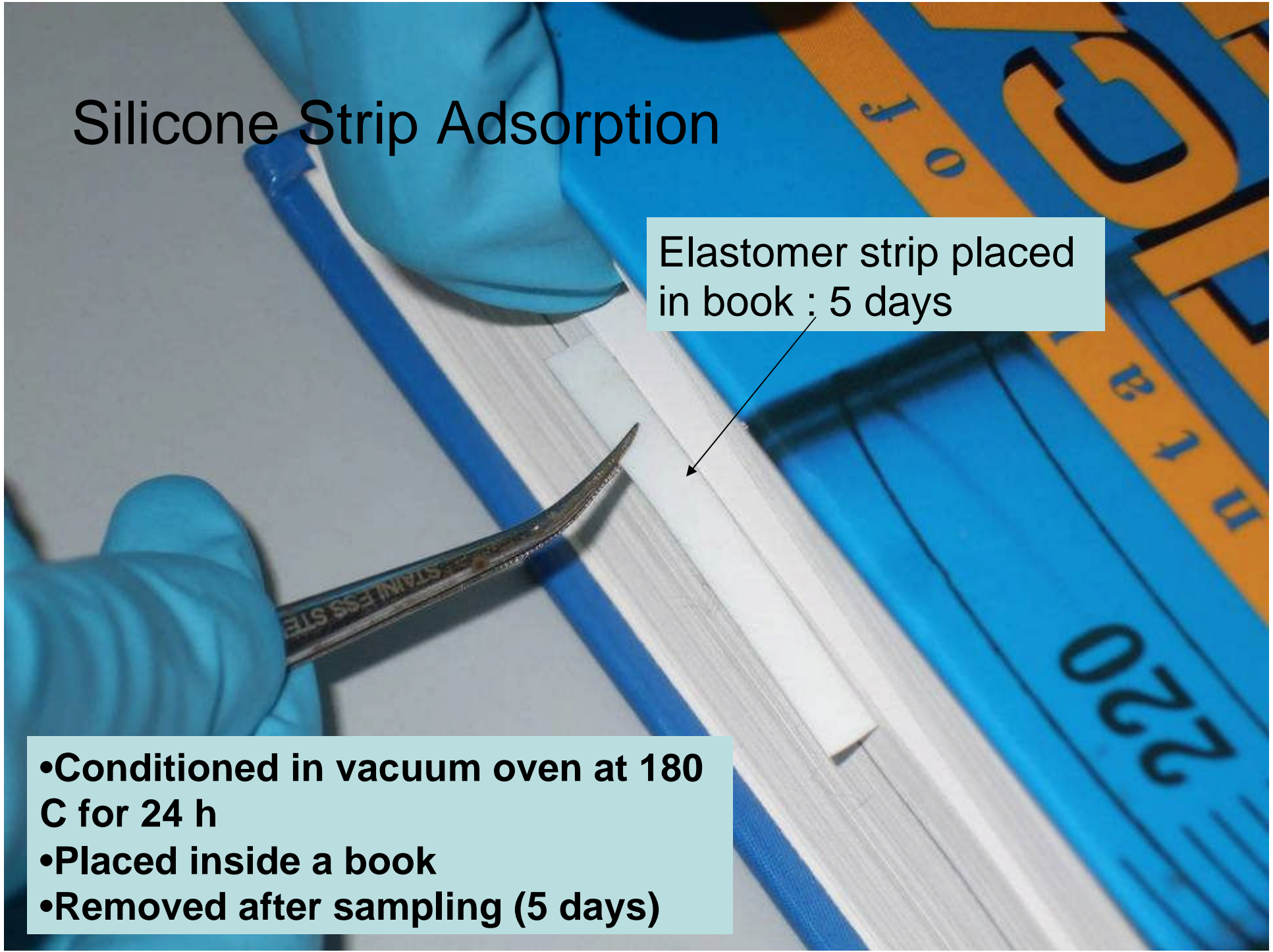


SPME fibre placed inside book and left for 5 days

Silicone Strip Adsorption

Elastomer strip placed
in book : 5 days

- Conditioned in vacuum oven at 180 C for 24 h
- Placed inside a book
- Removed after sampling (5 days)



Silicone Strip Adsorption

Placed inside a Tenax tube for desorption



TDU GC-MS

- Both SPME and Silicone strip sampling rely on the thermal desorption – gas chromatography – mass spectrometry
- TDU GC-MS highly sensitive and can positively identify individual analyte species

Sampling concerns

- Selectivity (introduction of bias)
- Low mass cut-off



Selective Substrate Adsorption

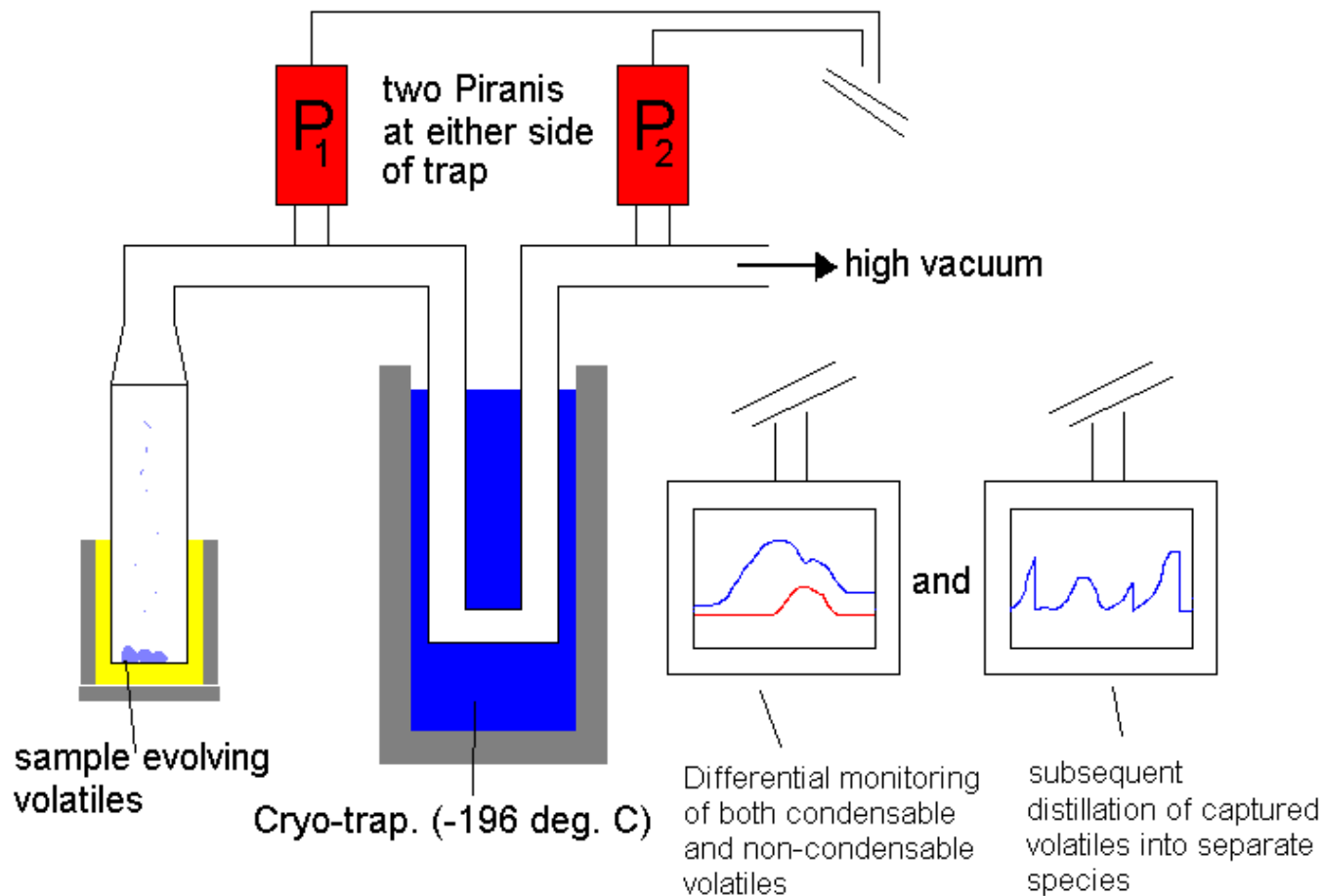
- Both SPME and the silicone uptake sampling methods rely on pre-concentration of VOC's onto an adsorbing substrate (either a SPME fibre or the surface of a silicone strip).
- Each of these methods subsequently involve thermal desorption of adsorbed VOC species directly into a GC-MS system where the collected VOC's are identified and the relative quantities of each VOC compared.
- Highly sensitive, yet inherently selective.
- Possibility of missing key species and artificially amplifying others



Thermal Volatilisation Analysis

Non-selective, cryo-trapping technique

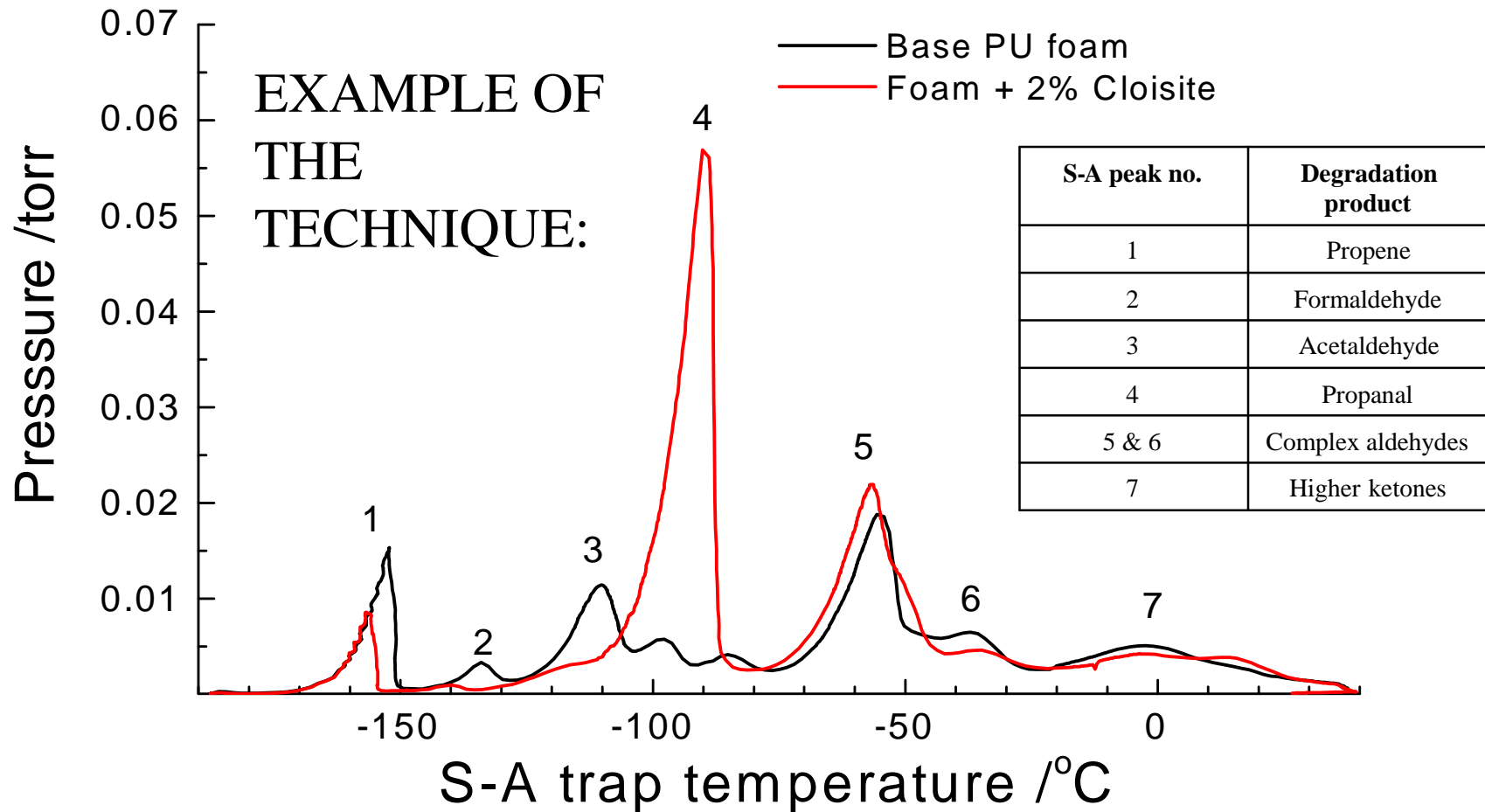
TVA is based upon the principle of monitoring the pressure above a sample as it is heated under a continuously pumped vacuum



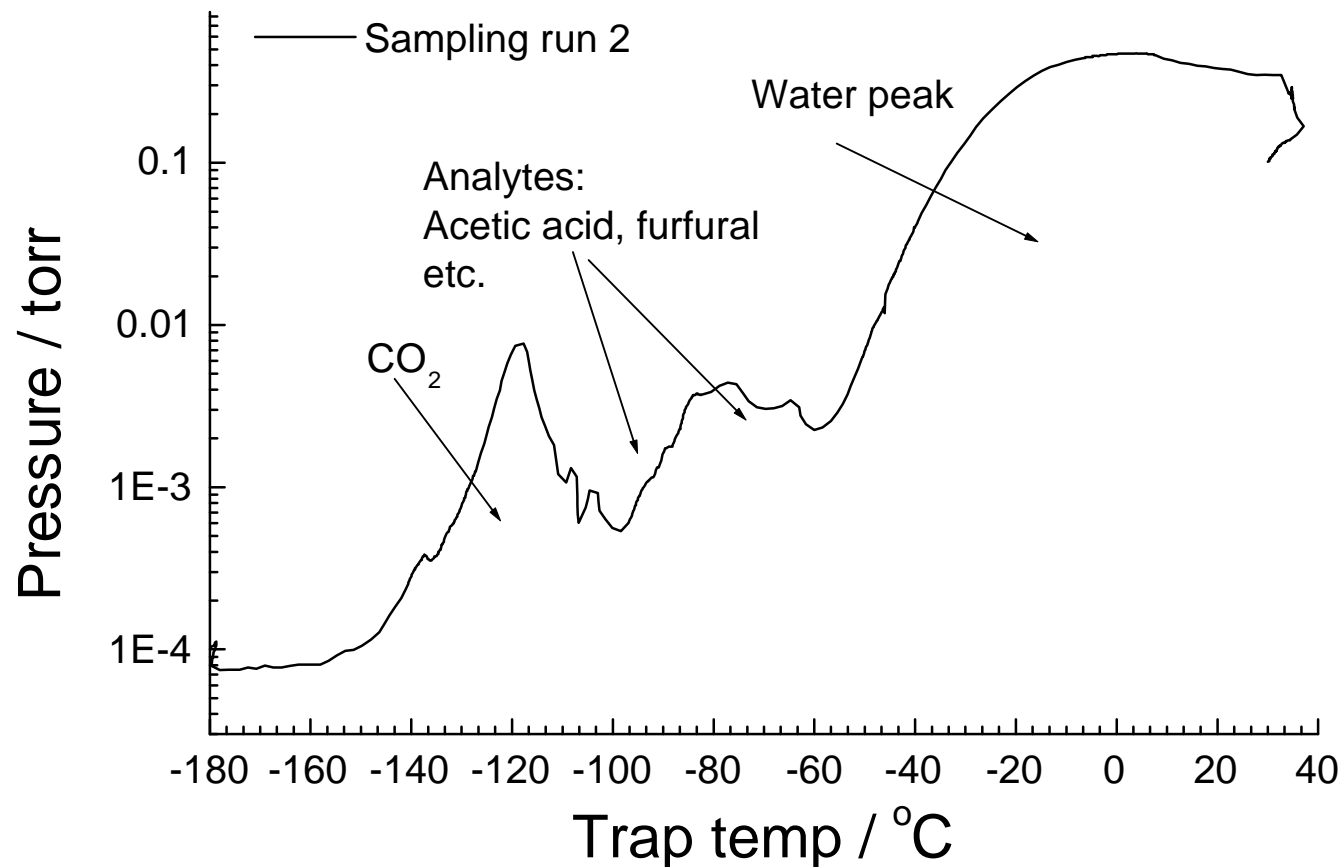
- Simple principle, yet sensitive technique
- Evolution of volatiles recorded as the rate of pressure change vs. temperature
- cryo-trapping allows capture and characterisation of condensable volatiles



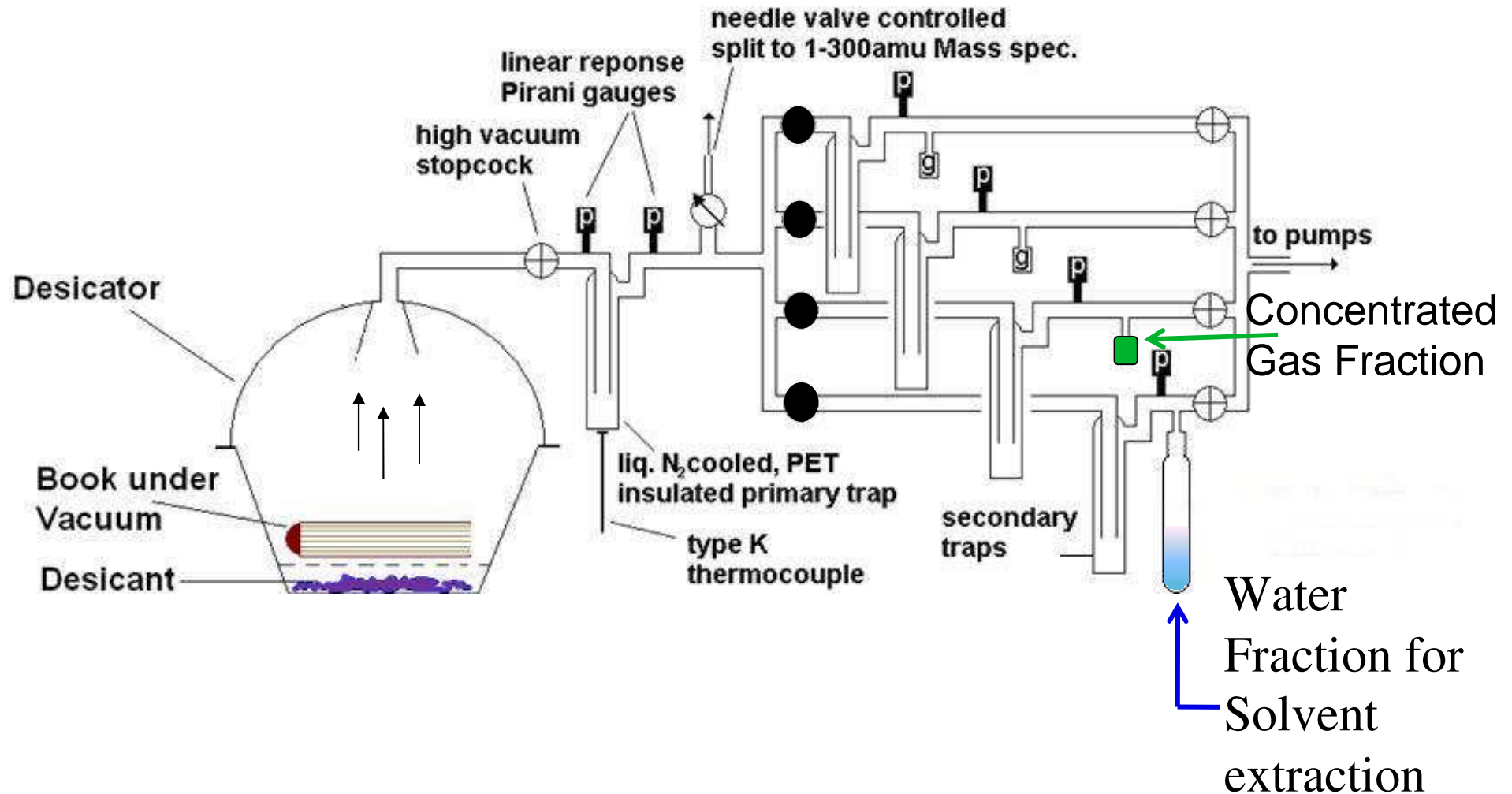
TVA Characterisation of PU foams



Initial attempts at sampling and directly characterising VOC's from books proved problematic....Water swamps the analytes:

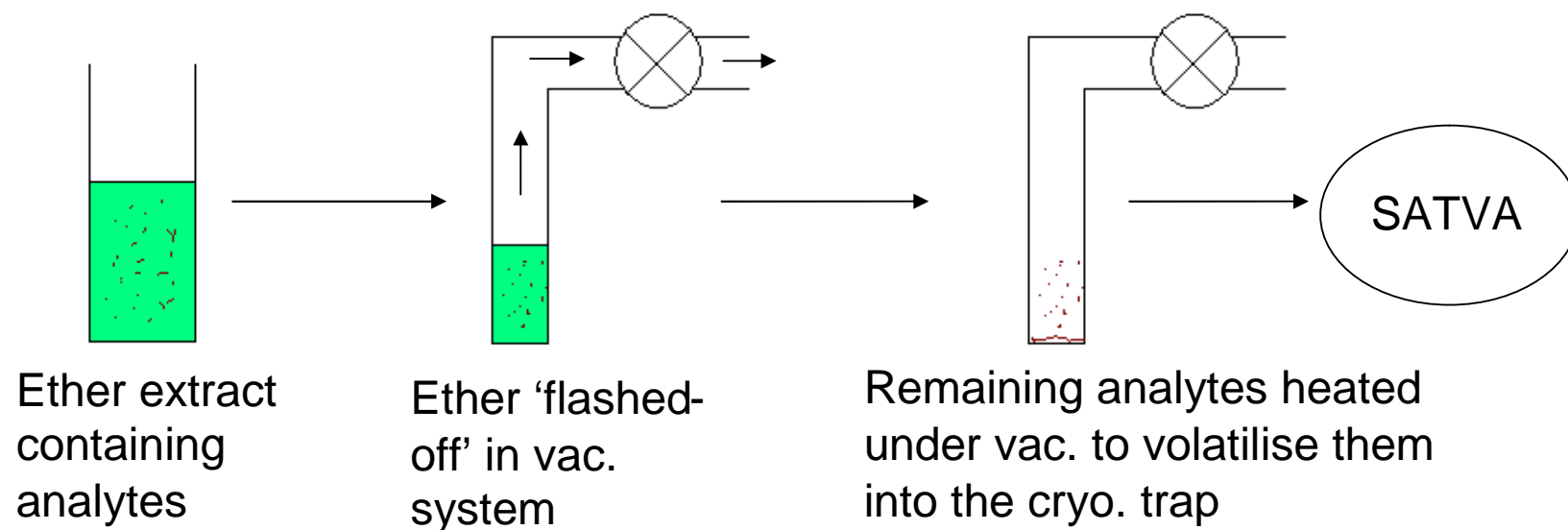


Modified TVA – Experimental Details



Flash Ether Distillation of the Water Fraction

- Flash ether distillation involves switching the solvent from water (high boiling) to a low boiling solvent that will 'flash-off' rapidly as a front at low temperatures under vacuum ($\sim -90^{\circ}\text{C}$), leaving the majority of the analytes behind for analysis

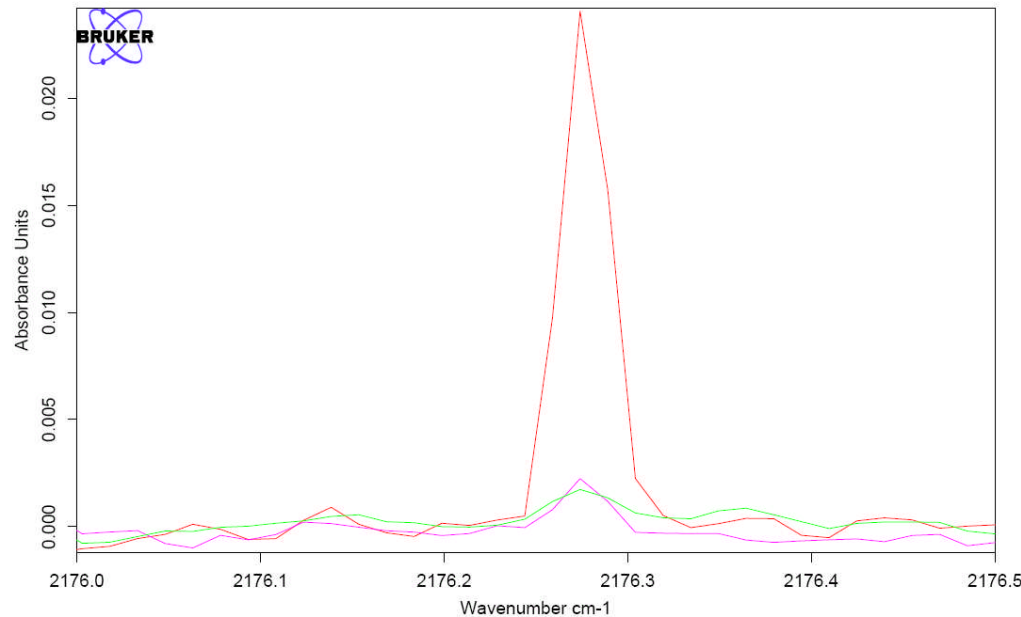


TVA in Summary

- Adaptation of the TVA system has allowed the problem of the excessive water to analyte ratio to be overcome.
- Successful detection of both low and high mol. wt. analytes is now possible
- Further development of the technique is likely to lead to improvements in resolution – yielding a non-selective method of assaying volatiles evolution from books

A comparison with Commercial EGA

- This data was obtained in collaboration with RAL by placing the books in Tedlar bags then flushing, filling with N₂ and accumulating over the books for 7 days. The gas was sampled by transferring a long path FTIR cell



- Water (not shown) and CO at ppm levels were observed

Comparative Sampling in Summary:

- Commonalties have been observed between differing sampling methods. SPME has detected a wide range of analytes, whilst silicone strip adsorption appears selective for Furfural.
- TVA has been hindered by water, however it has allowed the detection of analytes not usually observed using other sampling methods -
- At the high end of volatility, acetone and methanol
- At the low volatility range – Phthalate acid esters



Experts seek cure for books

PRINT: PRESERVATION

Scottish scientists develop a nose for revealing really healthy reads



Researcher Jim Levicki with his machine designed to analyse books

Photograph: Kirsty Anderson

By Jasper Hamill

DESPITE fears the internet could kill off the printed word, death by natural causes may be a greater threat to our literary heritage and Scottish scientists are searching for the cure.

A researcher from Strathclyde University has teamed up with the British Library to design a method of "smelling" the chemicals given off by decaying paper, hoping the technique will lead to an easy way to test the "health" of valuable or ancient books and ensure their survival.

Helped along by a team of scientists who are bottling the atmosphere of the British Library in small test tubes, Jim Levicki, a postdoctorate researcher at the university's department of pure and applied chemistry, is working to isolate these chemical markers of degradation – the smell of which will be familiar to anyone who has inhaled the musty air of old bookshops.

He said: "The problem is that libraries have massive collections of old books, historical documents or newspapers, and very little is known about how they break down over time. People want to preserve

them but there is very little known about the science of how they decay.

"We're starting from the bottom up to find out exactly what happens to books when they age. We lose part of our history and cultural heritage through the decay of these things. Look at what happened when the library of Alexandria burned down. This is the same process, but slower."

Levicki has designed a unique machine – bearing a gold panel dedicating it to his engineer grandfather, James Stuart – in which a book is left for 48 hours, to give off its odours. The chemicals that

make up the smells are then distilled, isolated and examined using a mass spectrometer.

When the results are finalised, it is hoped a portable chemical "nose" will be designed that could, for example, sit on the end of the robot arms that fetch books from the British Library's archive or be placed along the shelves to warn of the signs of degradation.

Some previous methods of maintaining books have been almost comical in their ineptitude. Librarians last century tried to dip books in baths of chemicals or even laminate them, failing to realise the plastic only lasts around 20 years before it starts to resemble yellowed sticky tape.

Compounding the problem is that many of the industrial processes devised to satisfy the enormous demand for books from the 19th to 20th-century were flawed. Many modern tomes are printed on acidic paper, hastening their own demise.

Magazines and newspapers are even more flammable, with some newspaper archives in such disrepair that their odour of acetic acid – used as vinegar – is as "overpowering as a chip shop". As a written record, these can be as important as books.

NEED TO KNOW

THE FACTS A Scottish scientist has invented a method of "sniffing" the odours given off by books to detect the tell-tale signs of degradation.

BACKGROUND The British Library and Strathclyde University are collaborating on the project aimed at finding a way of preserving books and printed material.

NEED TO KNOW MORE?

www.bl.uk/conservation
More information on the British Library's conservation efforts.

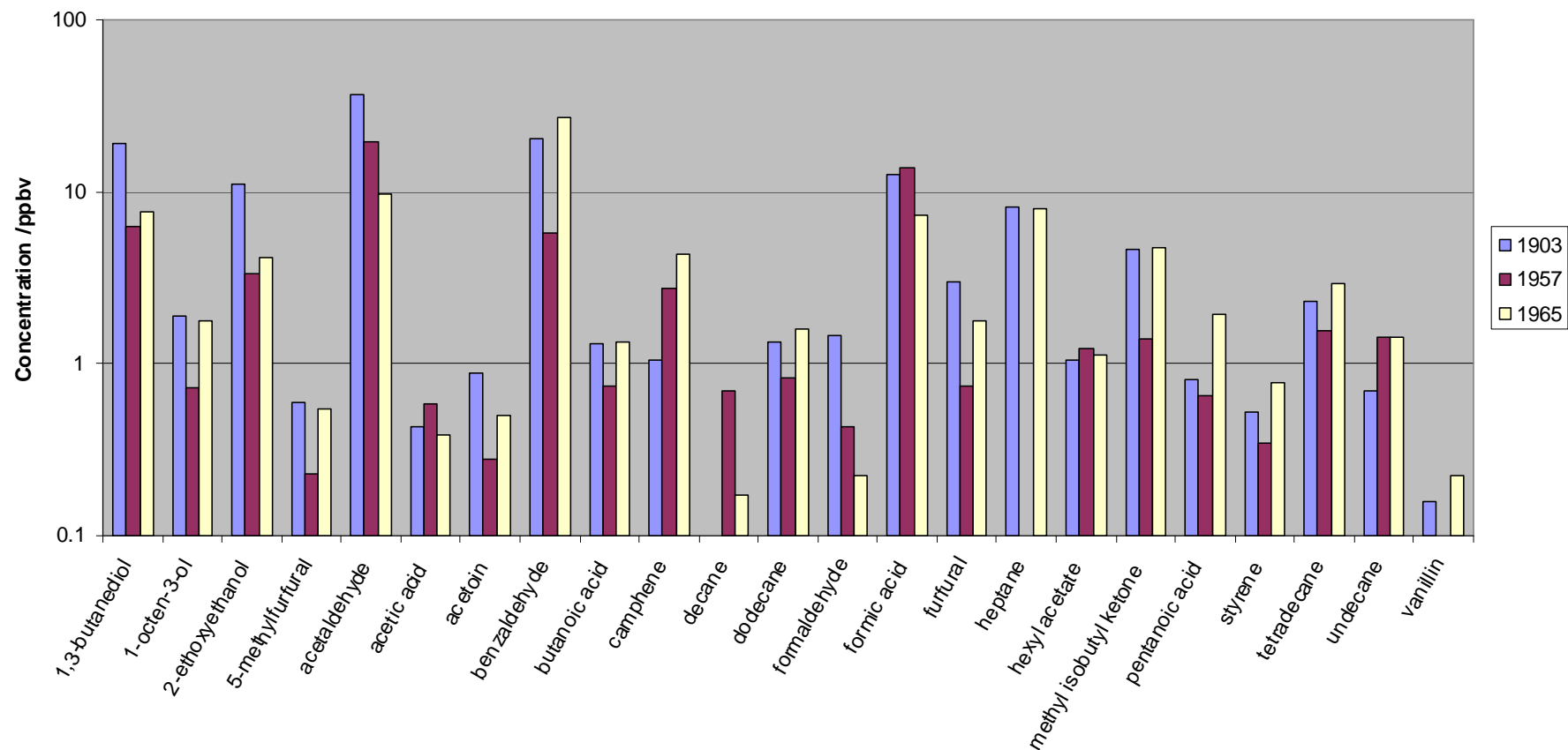
Positive Publicity

Further developments & *promising new techniques*

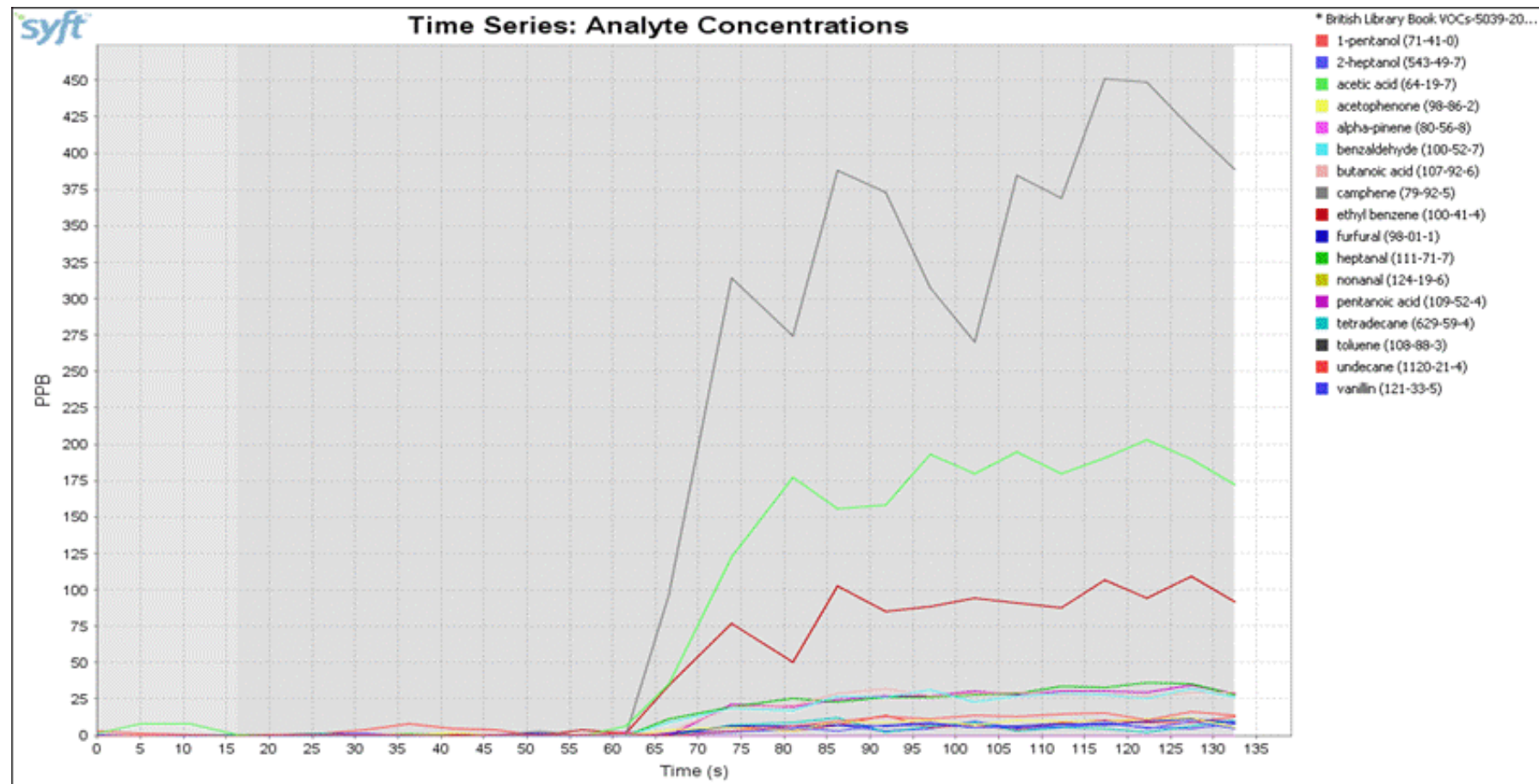
- We continue to see further potential in our existing suite of techniques, however the field is continually advancing and there are now a number of exciting and potentially useful new techniques available:
- **FAIMS** and **SYFT** - both direct 'sniffing' MS methods
 - Developmental, yet highly promising.....

Direct SYFT MS measurements of Whitakers Almanacs – No calibration of the technique as yet, however the potential is clear.

Whitakers Almanac - SYFT 11/3/09
Volatiles Significantly Above Background



This SYFT trace was obtained by holding the MS probe to the edge of the book, then opening the book at 60s – see increased analyte profiles



In Conclusion

- We are beginning gain something of an understanding of the complexities of linking VOC emissions with degradation in paper
- There are a number of promising techniques that may prove highly useful in increasing or 'global understanding' of VOC emission in relation of paper degradation
- There is a lot of work to be done.

Thanks

- All the Library and Archive Partners involved in the Project
- The Andrew W. Mellon Foundation for their funding of this research