Determination of volatiles in Food – sample preparation strategies and techniques

Dr Kathy Ridgway

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Who are Anatune/what do we do?

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www.anatune.co.uk

Established over 20 years

Our Focus: Sell and Support Solutions

- wide number of industries

Agilent Technologies

Value Added Reseller since 1998

GERSTEL

UK/Ireland distributor since 2003

ITSP™ SOLUTIONS, INC.

Automated SPE and Filtration technology 2010

syft™ Technologies

Real-time VOC analysis solutions 2015

UK wide sales and service team
Applications lab based in Cambridge

Member of Royal Society of Chemistry Enterprise Plus scheme

EnterprisePlus
Supporting small companies in the chemical sciences

ROYAL SOCIETY OF CHEMISTRY

Who am I?

University of Surrey
Bsc(Hons), Chemistry
1989 – 1993

Team leader/Analyst - Chemistry
Unilever
1999 – 2008 • 9 yrs

Chemical Contaminants Expert/Trace analyst
Unilever
Aug 2008 – Apr 2010 • 1 yr 9 mos

Loughborough University
PhD, Analytical Chemistry
2004 – 2008

Technical Specialist
Reading Scientific Services Ltd (RSSL)
May 2010 – May 2014 • 4 yrs 1 mo

GC-MS Applications Chemist
Anatune
Jun 2014 – Present • 3 yrs 5 mos
Cambridge, United Kingdom

Outline of my presentation

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Determination of volatiles in Food

- Why?
- What?
- How?

- From Wikipedia;

Volatile organic compounds (VOCs) are organic chemicals that have a high vapor pressure at ordinary room temperature. VOCs are numerous, varied, and ubiquitous. They include both human-made and naturally occurring chemical compounds. Most scents or odours are VOCs

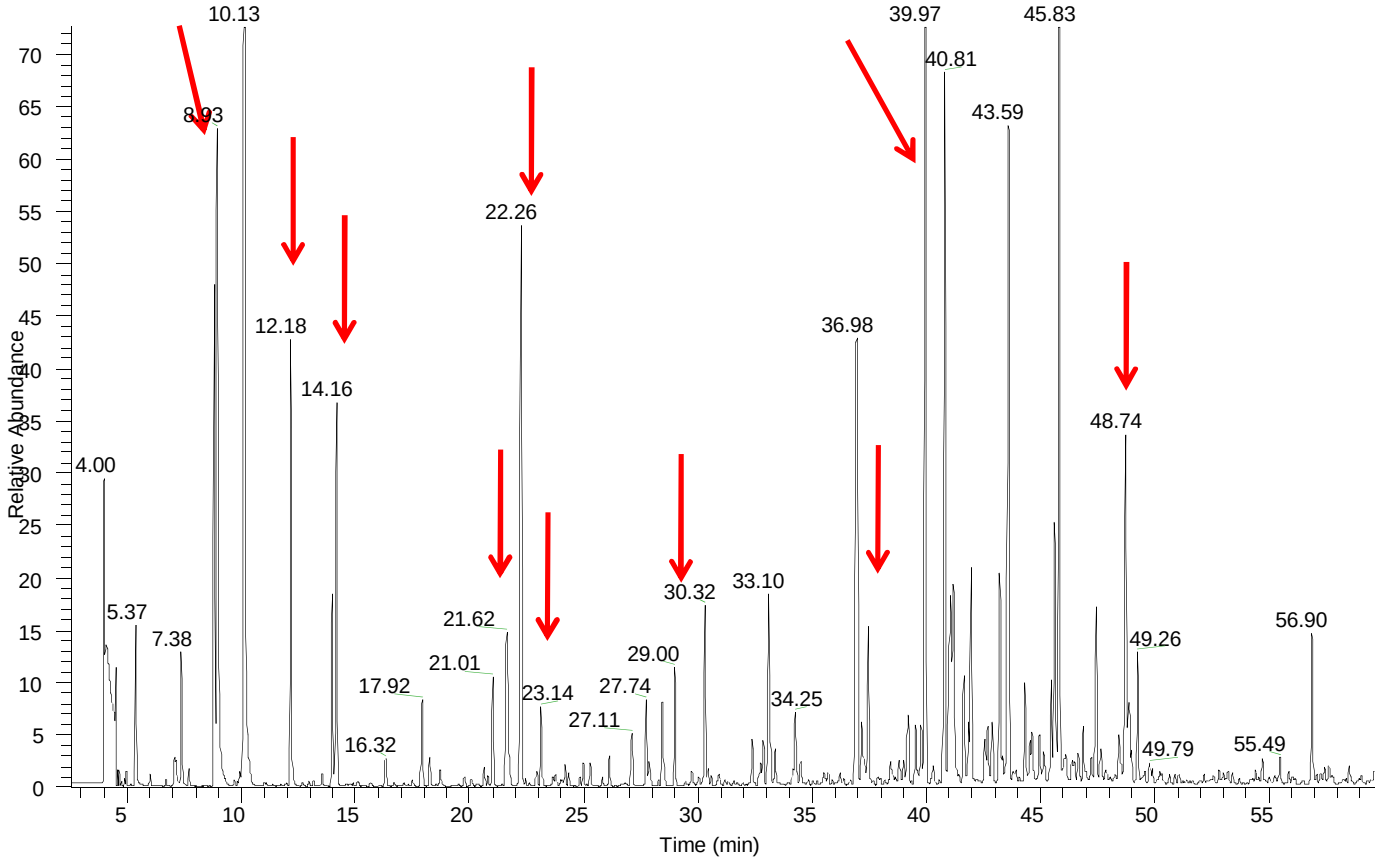
- NOT ALL Volatile compounds are Aroma active..

Why measure volatiles in food?

- Flavour/aroma profile
  - New product development
    - Consumer preference - link to sensory analysis
    - Competitor analysis
    - Effect of processing and formulation on product characteristics
  - Product characterisation
  - Quality control
    - Ingredients, process, product
  - Patent defence/IP claims
- Contaminant
  - Off odour/taint
  - ‘known’/ regulated contaminant
    - Safety evaluation
  - Unknown contaminant/customer complaint
    - Qualitative or quantitative

What to measure?

- Analyse everything? (profile/fingerprint)
- Key volatiles
- Known/Target compounds/ contaminants



How to analyse?

Choice of instrumentation and methods

- The How depends on the why and the what..

Volatile compounds can have a range of chemical and physical properties and it is not always safe to assume that all compounds can be extracted using one analytical approach.

Food - The matrix!

The nature of your sample can have a significant impact on your choice of method.

- Fat content
- Homogeneity
- Amount of sample available

Choice of instrument

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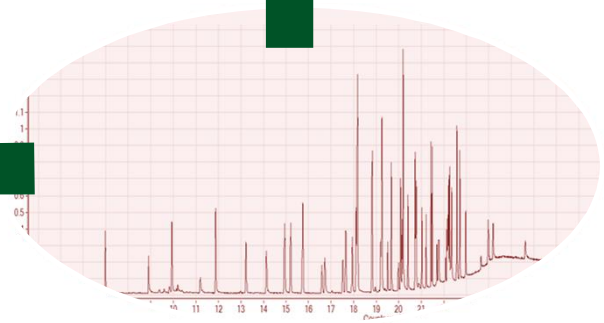
GC-FID,
retention time

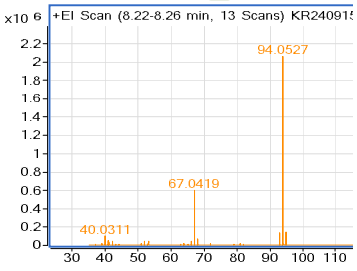
GC-MS,

Retention time and Mass spectra



GC-MS/MS

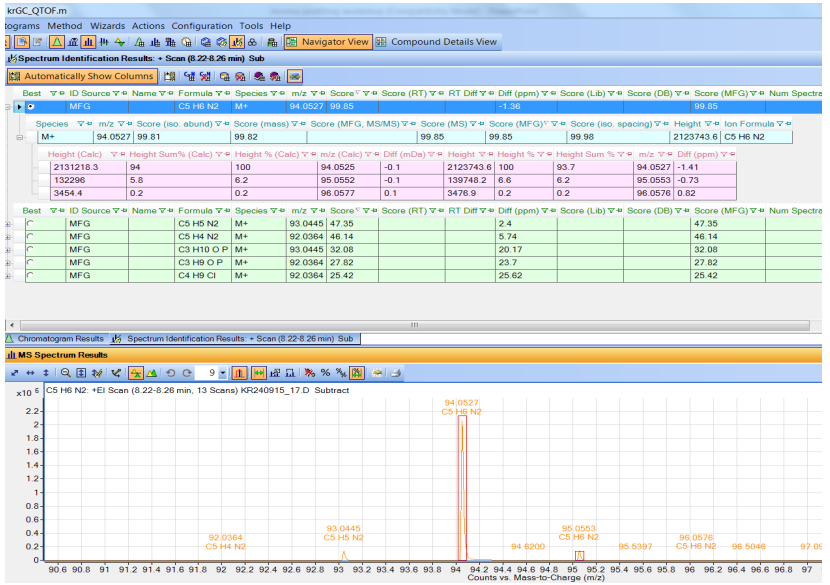
Retention time, MRM transition



GC-QTOF,

Retention time, Mass spectra , accurate mass isotope ratios,

Q to confirm product ion spectra



The ultimate detector

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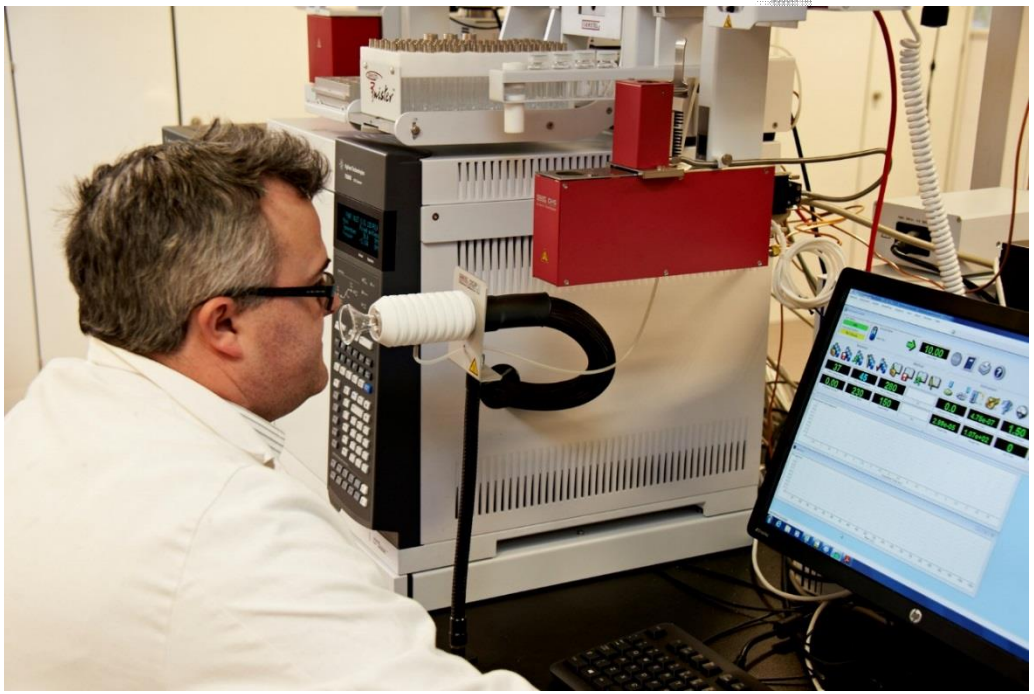

Multiple detectors

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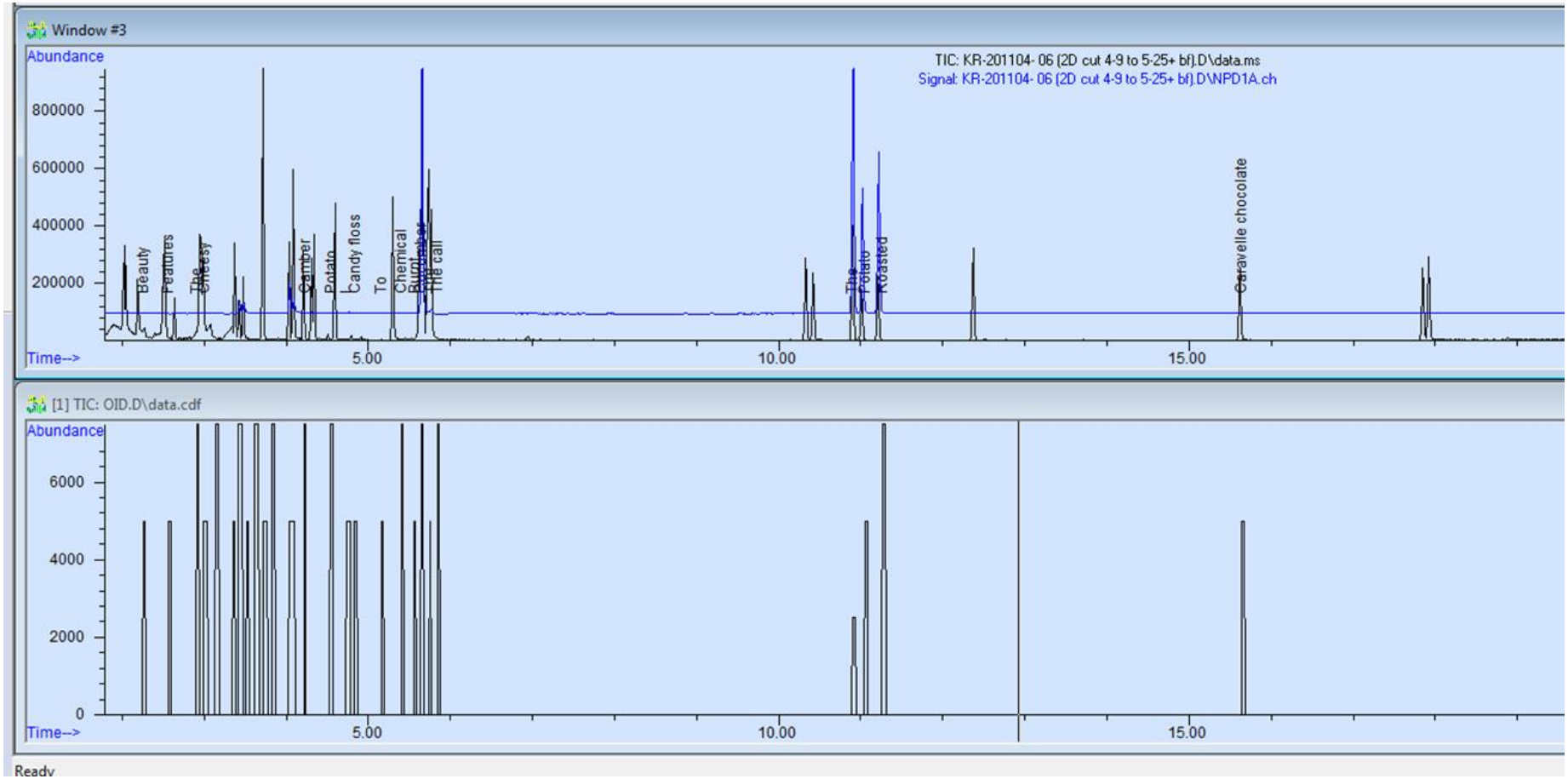
Signals overlaid (MS, NPD, ODP) with annotation



Sensory Descriptors and Thresholds

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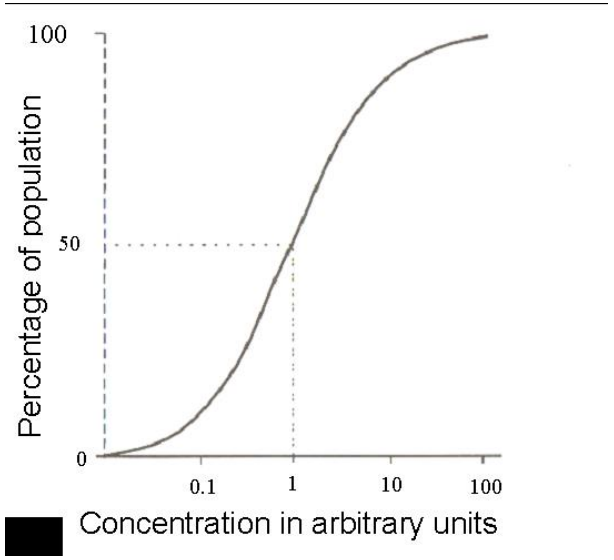
Compound	Descriptor (Taste)	Threshold (ppb)
2,4-Dichloroanisole	Sweet, fruity, scented	0.4
2,6-Dichloroanisole	Musty, medicinal, phenolic	0.04
2-Chlorophenol	Disinfectant, medicinal	0.1
2,6-Dibromophenol	Iodoform	$5x10^{-4}$
Styrene	Hydrocarbon, plastic	37
2,4,6-Tribromoanisole	Musty	8×10^{-6}
Geosmin	Earthy, musty	0.05
Guaiacol	Smoky, phenolic, medicinal	50
6-Chloro-*o*-cresol	Disinfectant, medicinal	0.08
p-Cresol	Phenolic, horse manure	2



Analytical Challenges

- Extremely low levels can be relevant
- Complex and variety of matrices
  - Understand what is ‘normal’
  - Selectivity vs sensitivity
  - Trace contaminant vs matrix components
- Homogeneity
  - Consider sampling
- Potential for sample contamination (lab environment)
- Sensory descriptors (consumer vs. experts)
- Sample not changed during extraction
- Screening or targeted analysis?
- Does everything need to be identified?

The ideal sample prep

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- Why do sample Prep?
  - Removal of matrix interferences
    - Increased selectivity
    - Improved chromatography
  - Analyte enrichment
    - Increase sensitivity – achieve lower limits of detection
  - Reduce instrument maintenance

- The ideal sample prep

  Selective(?) sensitive, minimum number of steps,
  environmentally friendly, robust,
  Automated?

Automation modules available

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MultiPurpose Sampler MPS for GC/MS


Cooled Injection System CIS


Automated Liner EXchange ALEX


easy Liner Exchange eLEX


Opiate Solution


Headspace


Thermal Desorption System TDS


Thermal Desorption Unit TDU


Automated TDU Liner Exchange ATEX


Solid Phase Microextraction SPME


Twister


Dynamic Headspace DHS

TDU PYRO


µFlowManager


Barcode Reader


Selectable 1D/2D GC/MS


Olfactory Detection Port OPD


Preparative Fraction Collector PFC


MultiPurpose Sampler MPS for LC/MS


Filtration


LC/MS Effluent Optimizer LEO


MPS Workstation


Solid Phase Extraction SPE


Disposable Pipette Extraction DPX


MultiPurpose Sampler MPS for LC/MS


MultiPosition Evaporation Station mVAP


MAESTRO PrepAhead


MAESTRO Software


MultiPosition Vortex Station mVorx


Agitation


Centrifuge CF200


Microwave

Filtration and SPE

And more …

Sample preparation options

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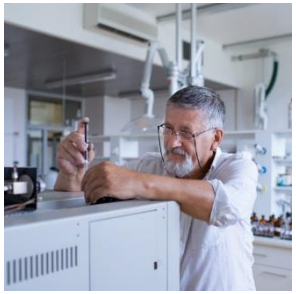
Liquid injection



Static headspace

SBSE

SPME

Dynamic headspace (DHS)
(and MVM)

Stir Bar Sorptive Extraction (SBSE)

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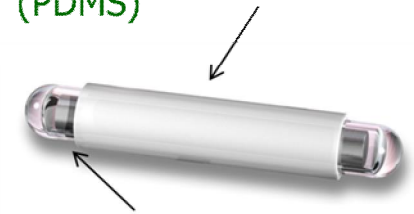
GERSTEL Twister™

Phase Polydimethylsiloxane (PDMS)



Sample preparation

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Twister- direct immersion (aq) (SBSE)

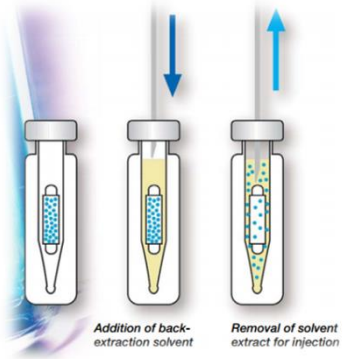
Twister- Headspace (HSSE)

Sample
Solid/ Liquid

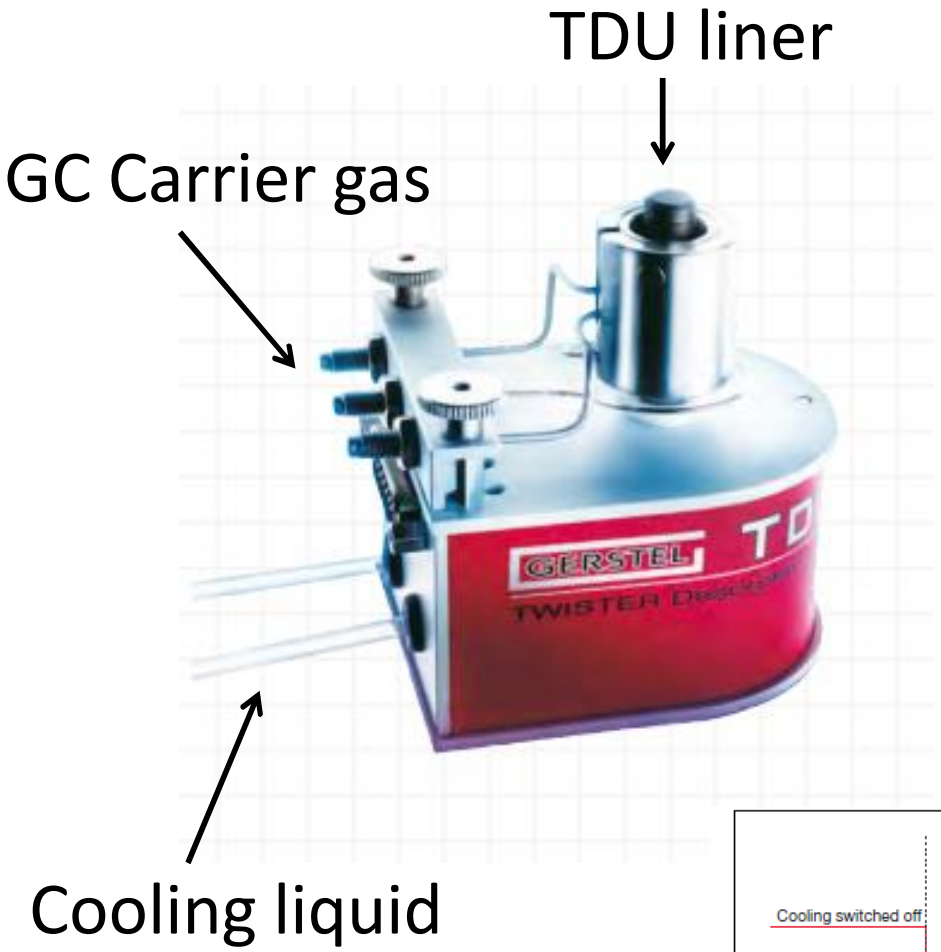
Sample analysis

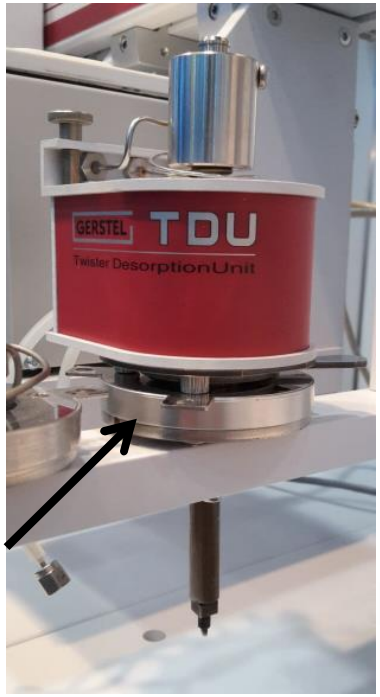
Thermal desorption
(TDU- GC-MS)

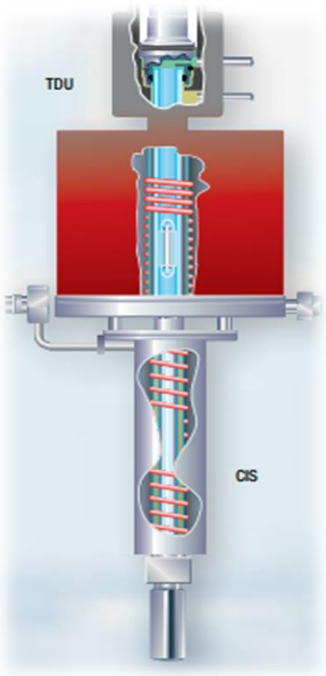
Back extraction
(GC-MS or LC-MS)

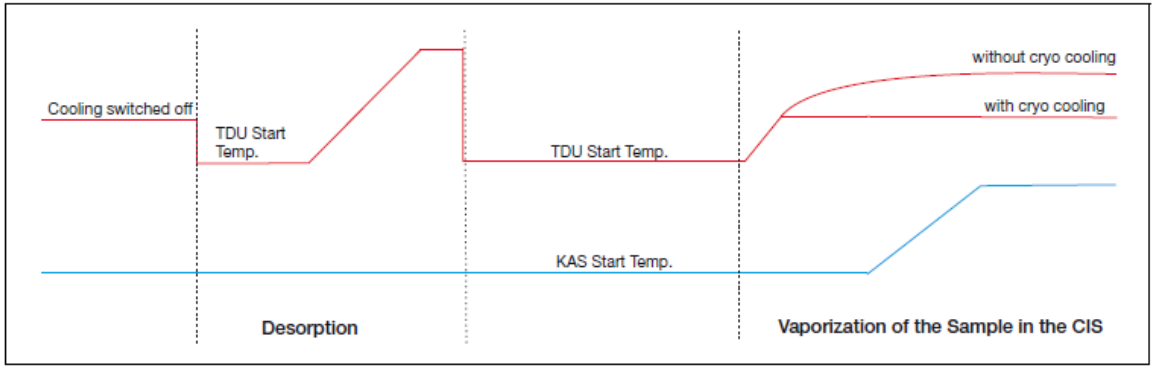


Thermal Desorption Unit (TDU)









TDU

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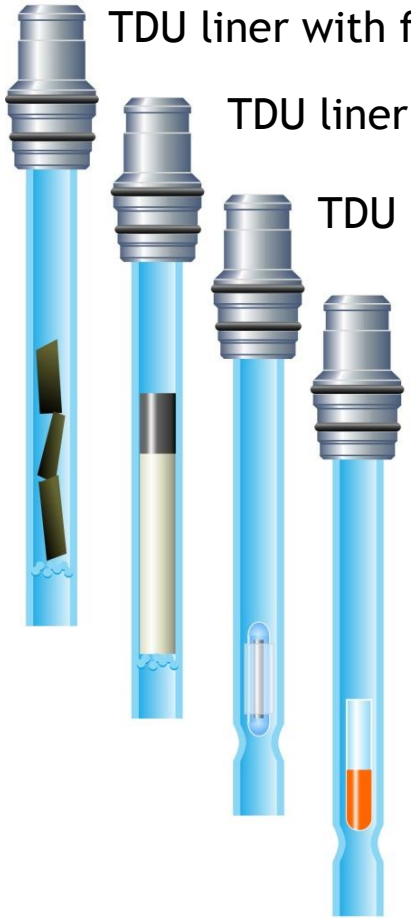
Å Universal Thermal Desorption Unit



TDU liner with frit for thermal extraction of solid samples

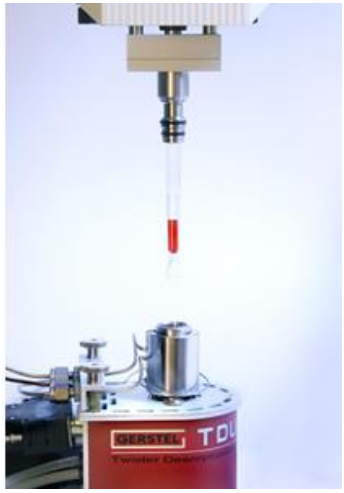
TDU liner packed with adsorbent

TDU liner for Twister desorption

TDU liner for thermal extraction in µ-vials

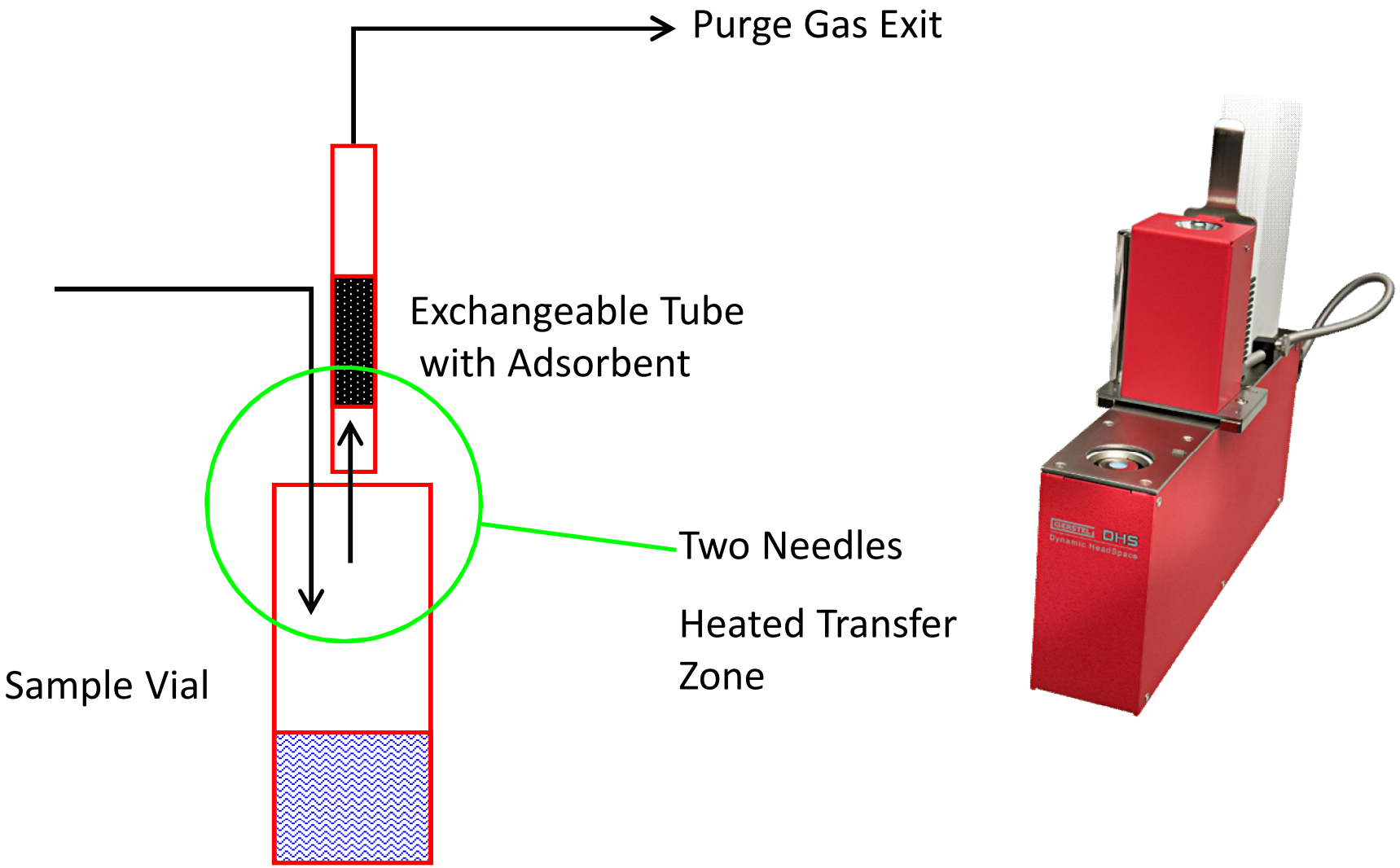
ATEX – Automatic Tube Extraction

-look at volatiles in a non-volatile matrix

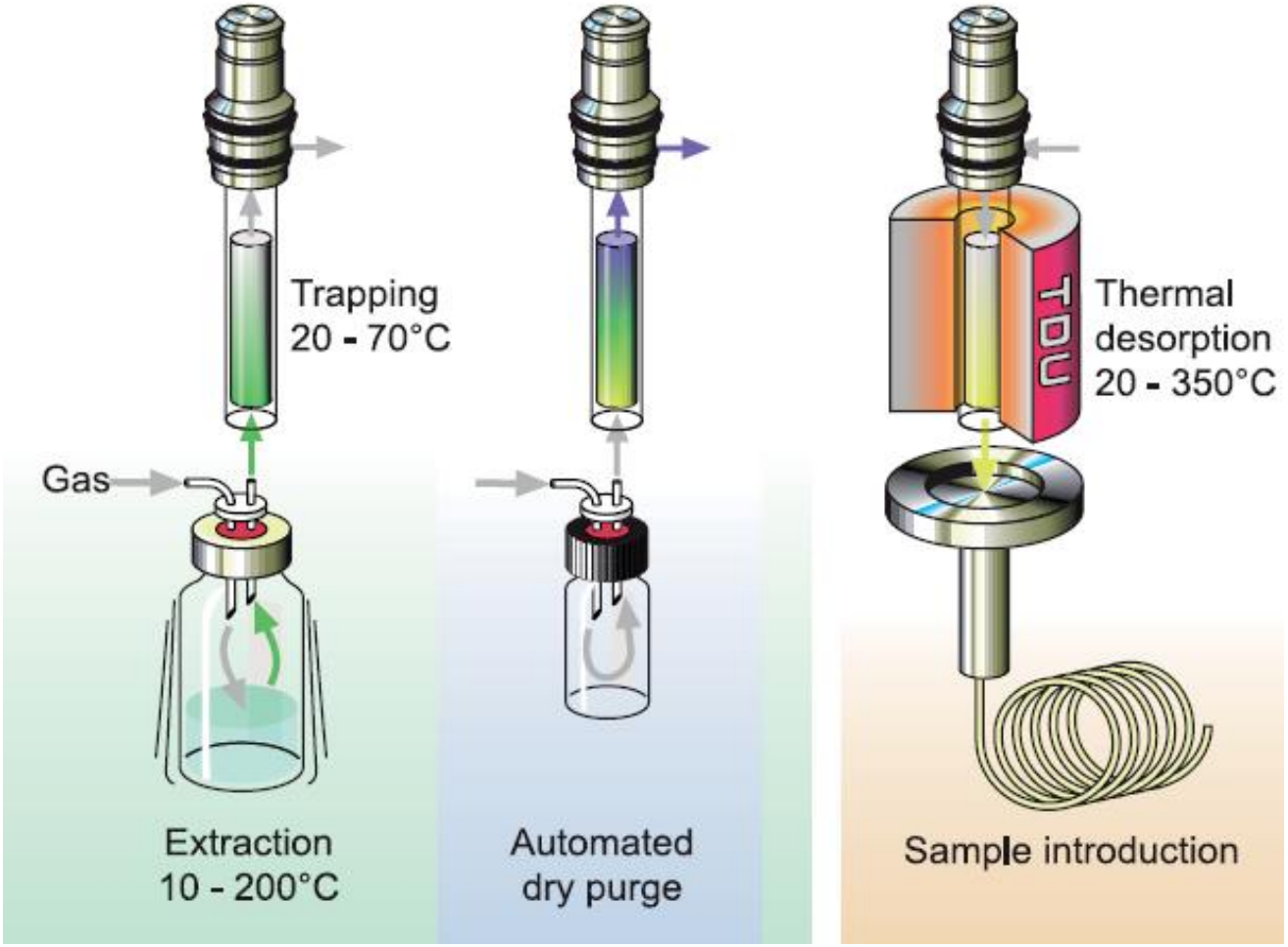


- Complex, dirty matrix, low level target analytes
- Direct (LVI) analysis of extracts
  - Less inlet maintenance

Dynamic Headspace (DHS)



Dynamic Headspace (DHS)



Static *vs* Dynamic headspace

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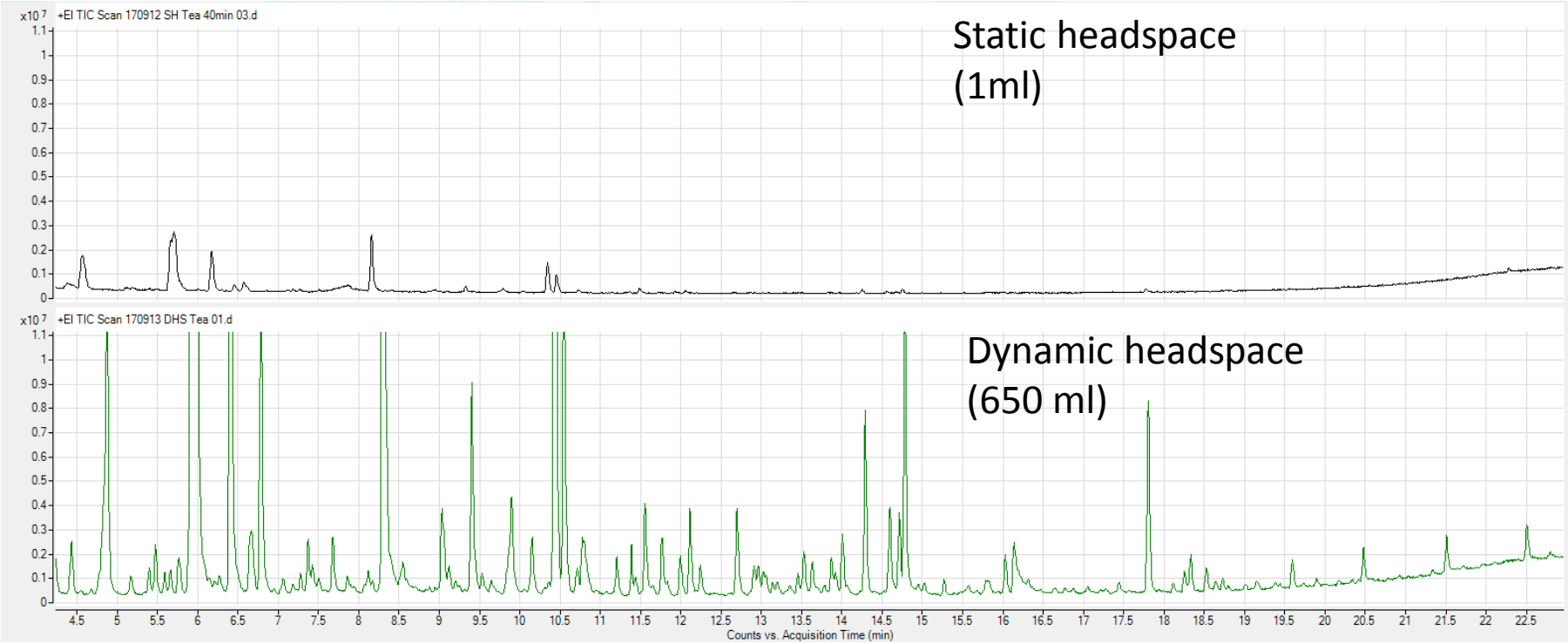
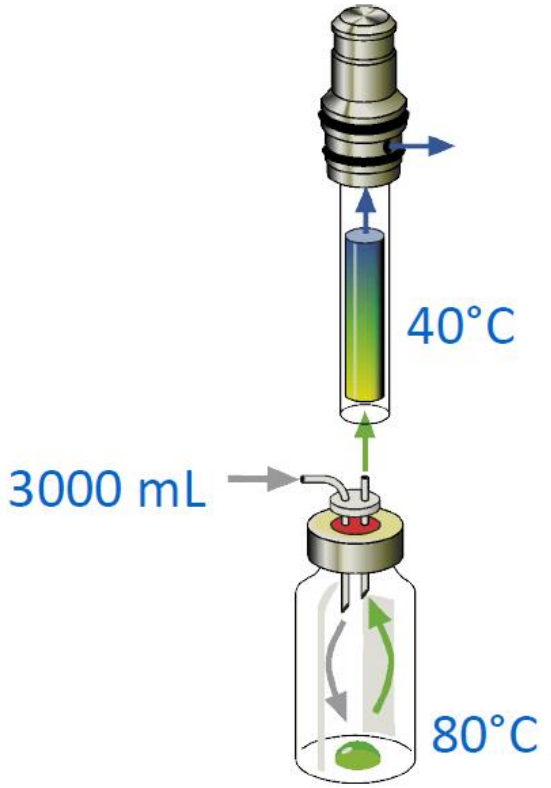
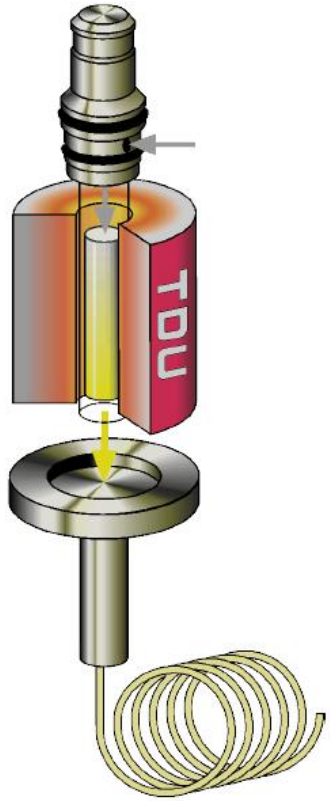
Determination of Volatiles in tea



Fully Evaporative Technique (FET)
Dynamic Headspace (DHS)





Dynamic Headspace (DHS):

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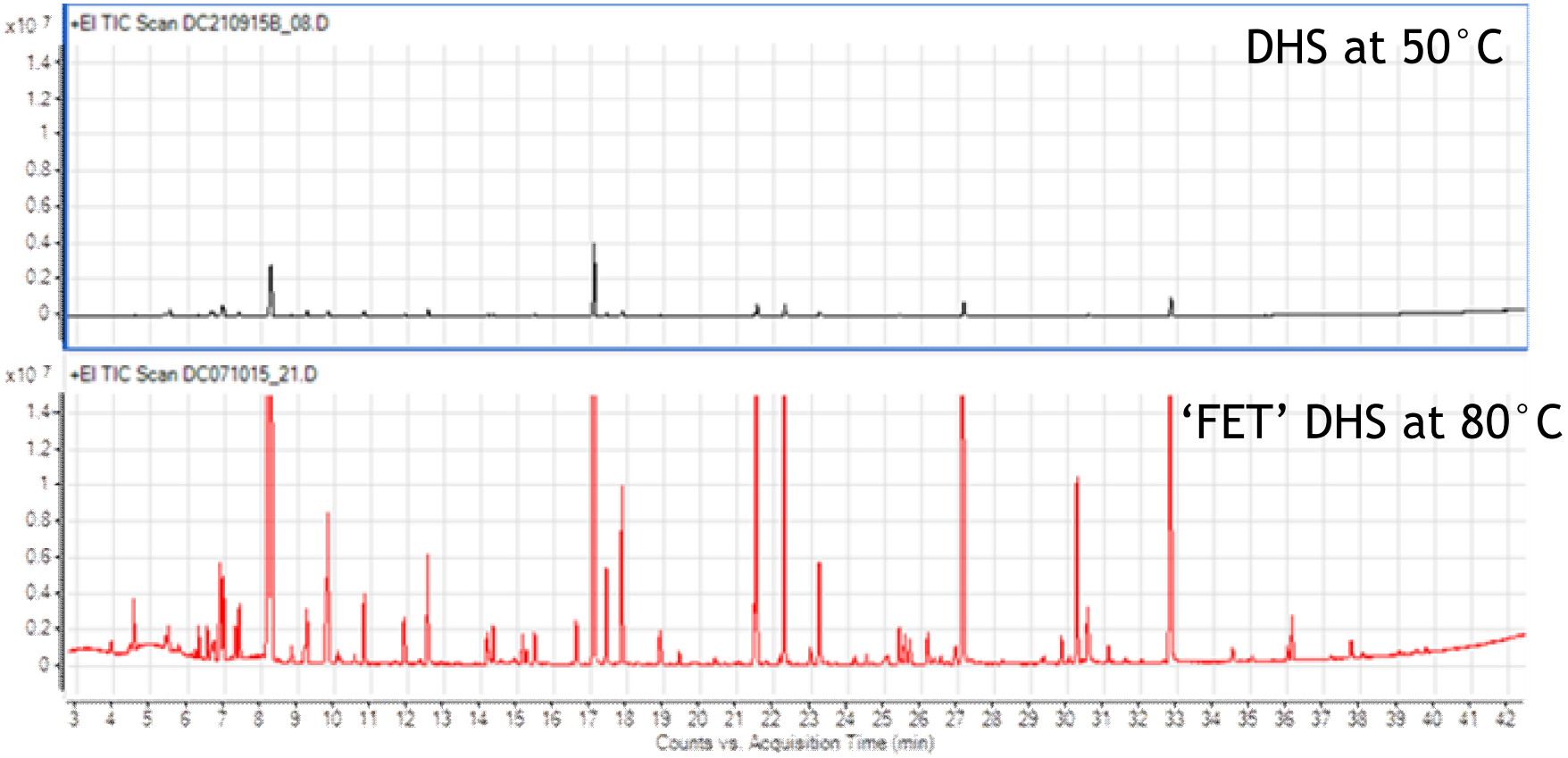
Comparison of methods



Dynamic Headspace (DHS):
Multi-Volatile Method

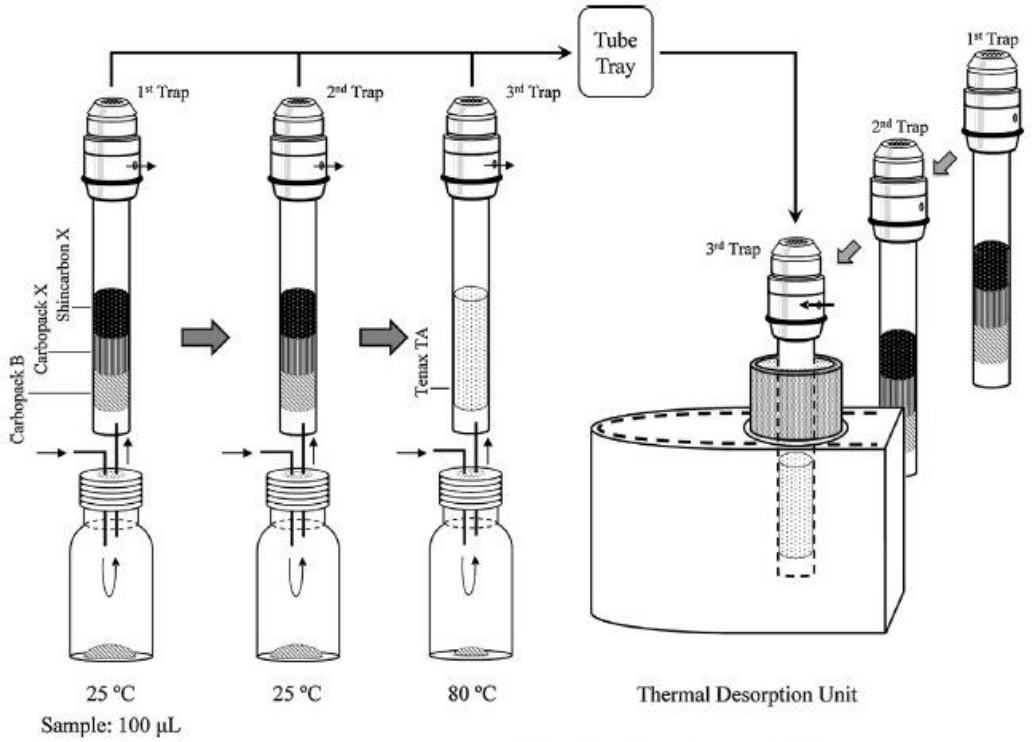


Fig. 1. Schematic procedure for multi-volatile method (MVM) analysis with sequential DHS sampling.

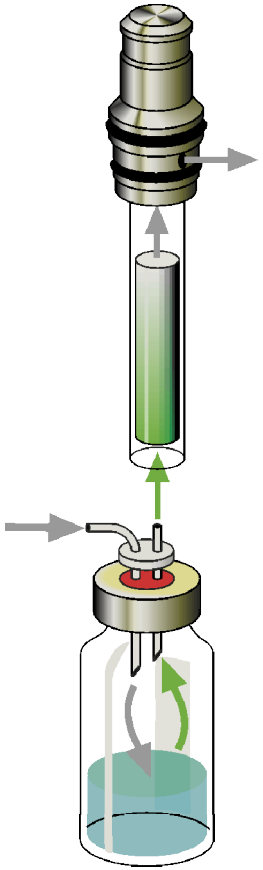
Journal of Chromatography A

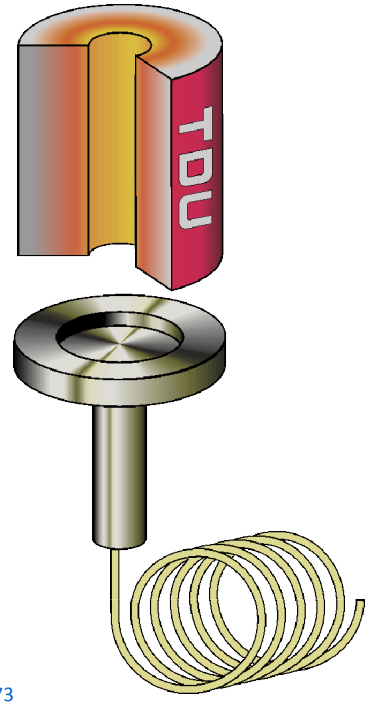
Multi-volatile method for aroma analysis using sequential dynamic headspace sampling with an application to brewed coffee

Nobuo Ochiaia,∗, Jun Tsunokawaa, Kikuo Sasamotoa, Andreas Hoffmann

Dynamic Headspace

Method 1: Very Volatile Analytes





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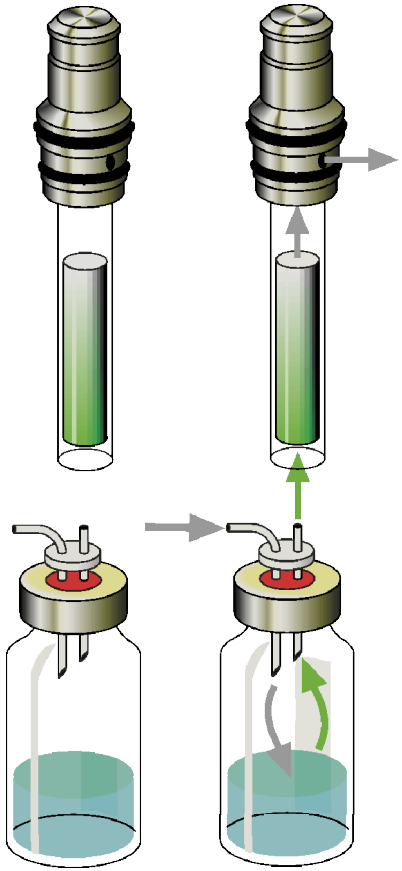
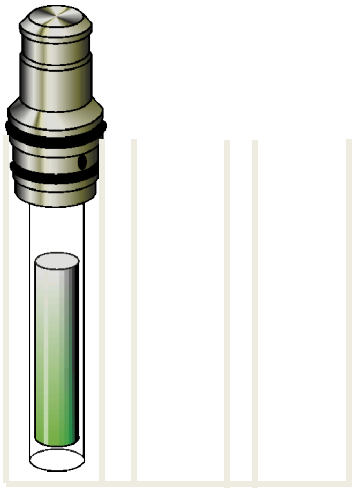
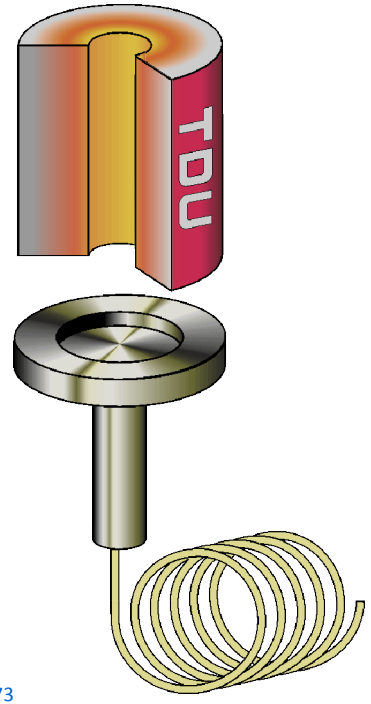
Dynamic Headspace

Method 2: Volatile or Semi Volatile Analytes







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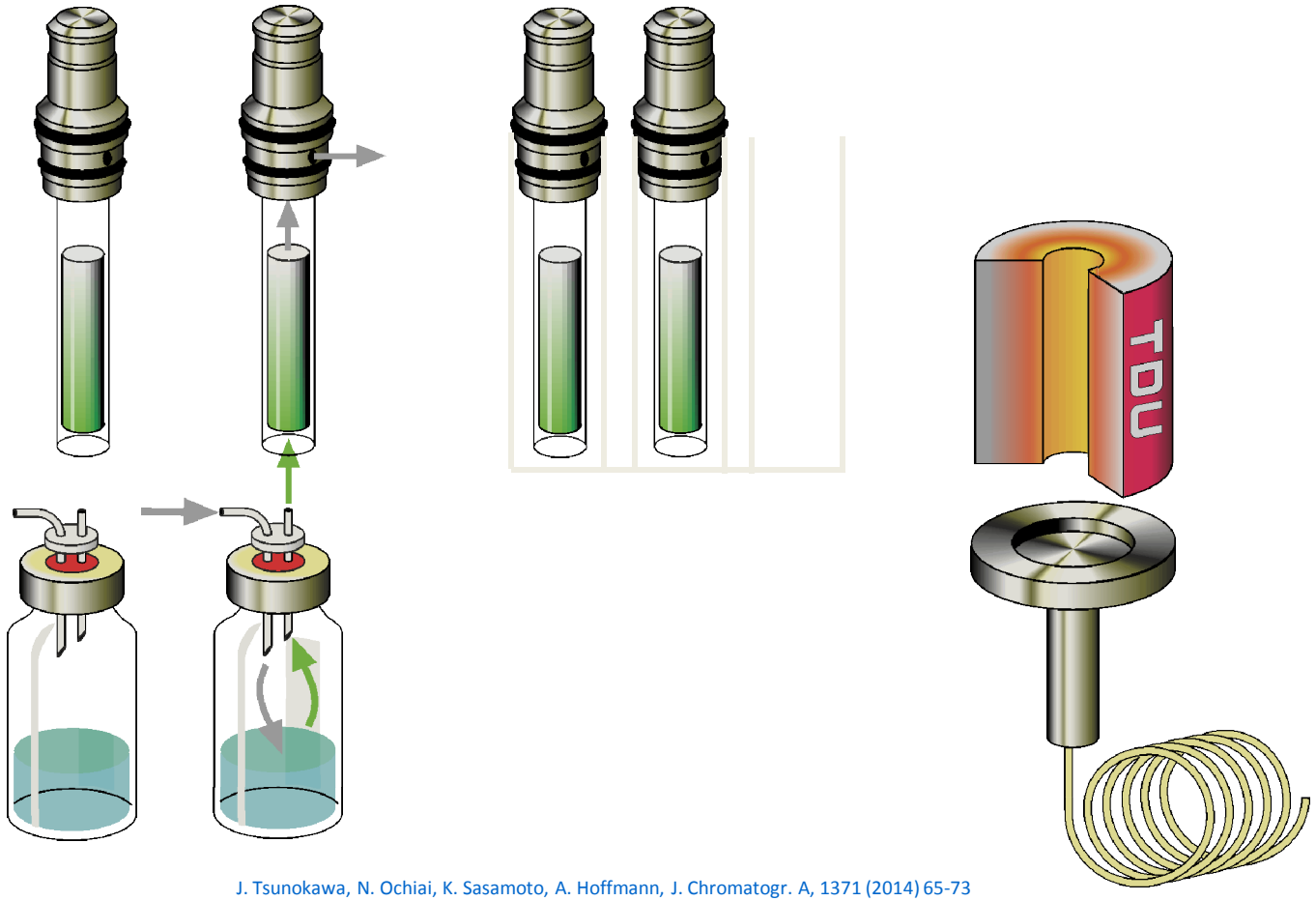
Dynamic Headspace

Method 3: Volatile, low volatile and hydrophillic analytes



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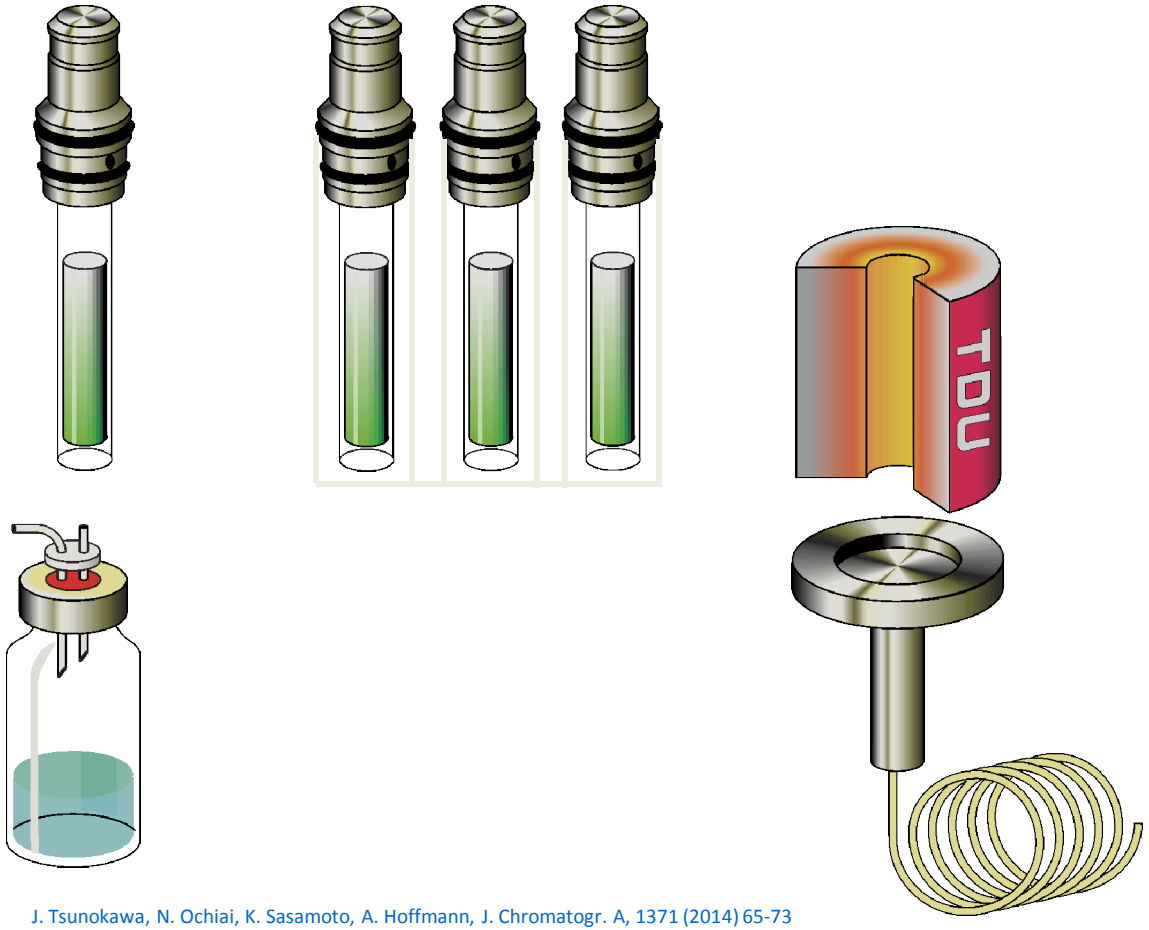
Dynamic Headspace

Method 3: Volatile, low volatile and hydrophillic analytes



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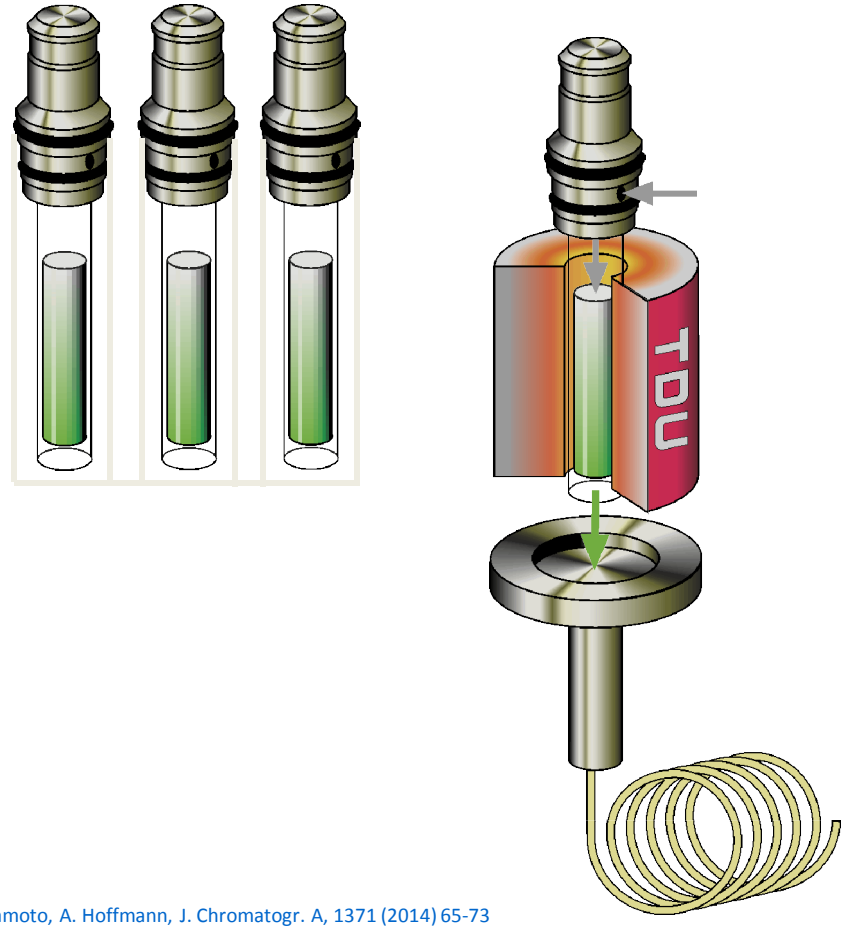
Dynamic Headspace

Method 4: TDU Multi Desorption



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Dynamic Headspace

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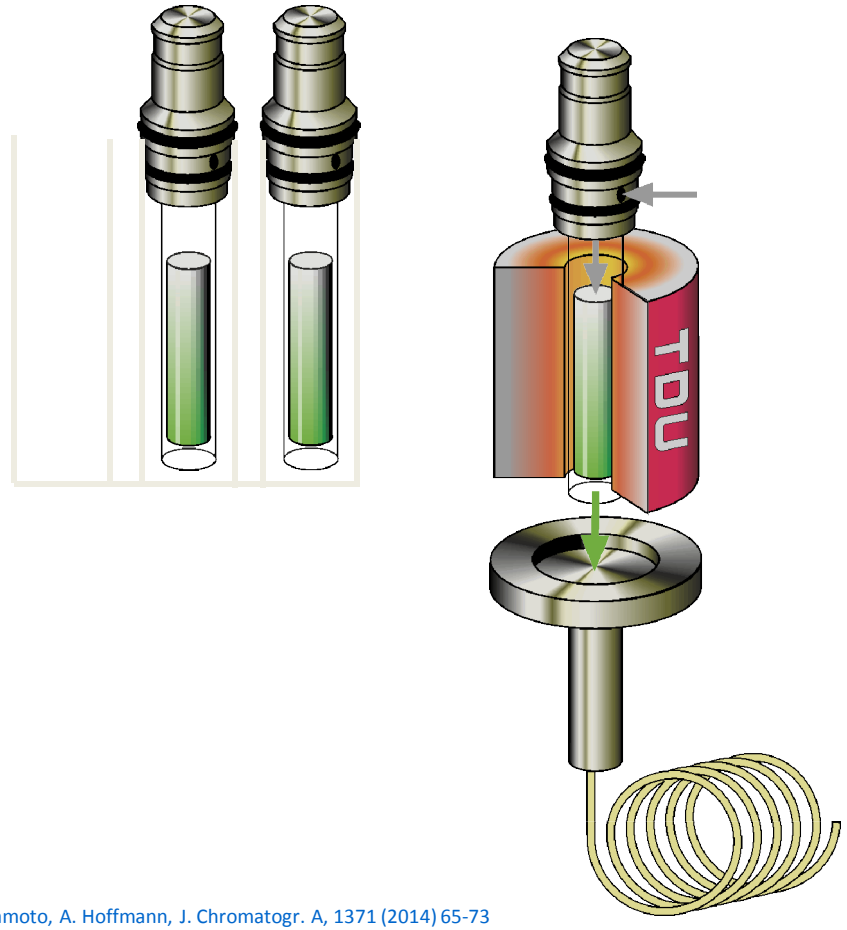

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Dynamic Headspace

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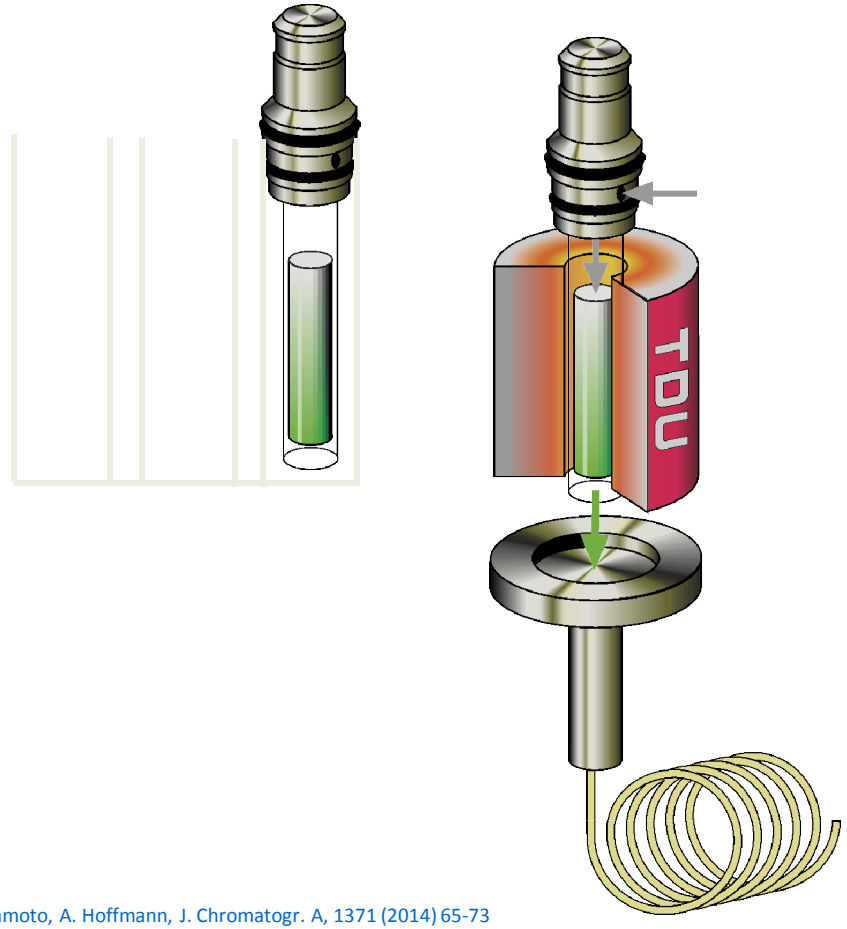

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Dynamic Headspace

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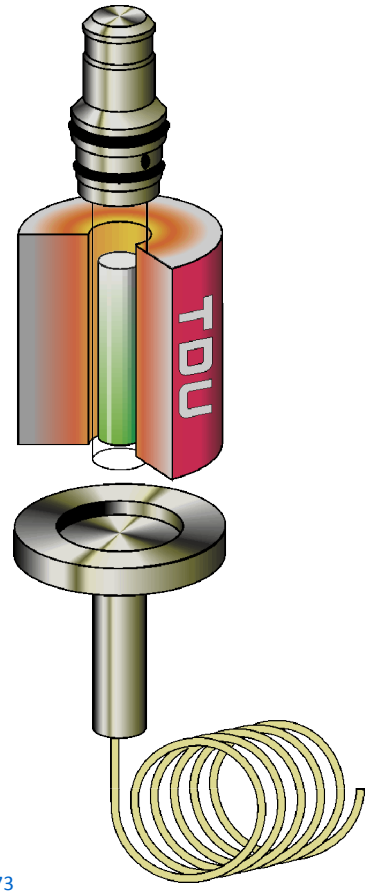

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Multivolatile Method

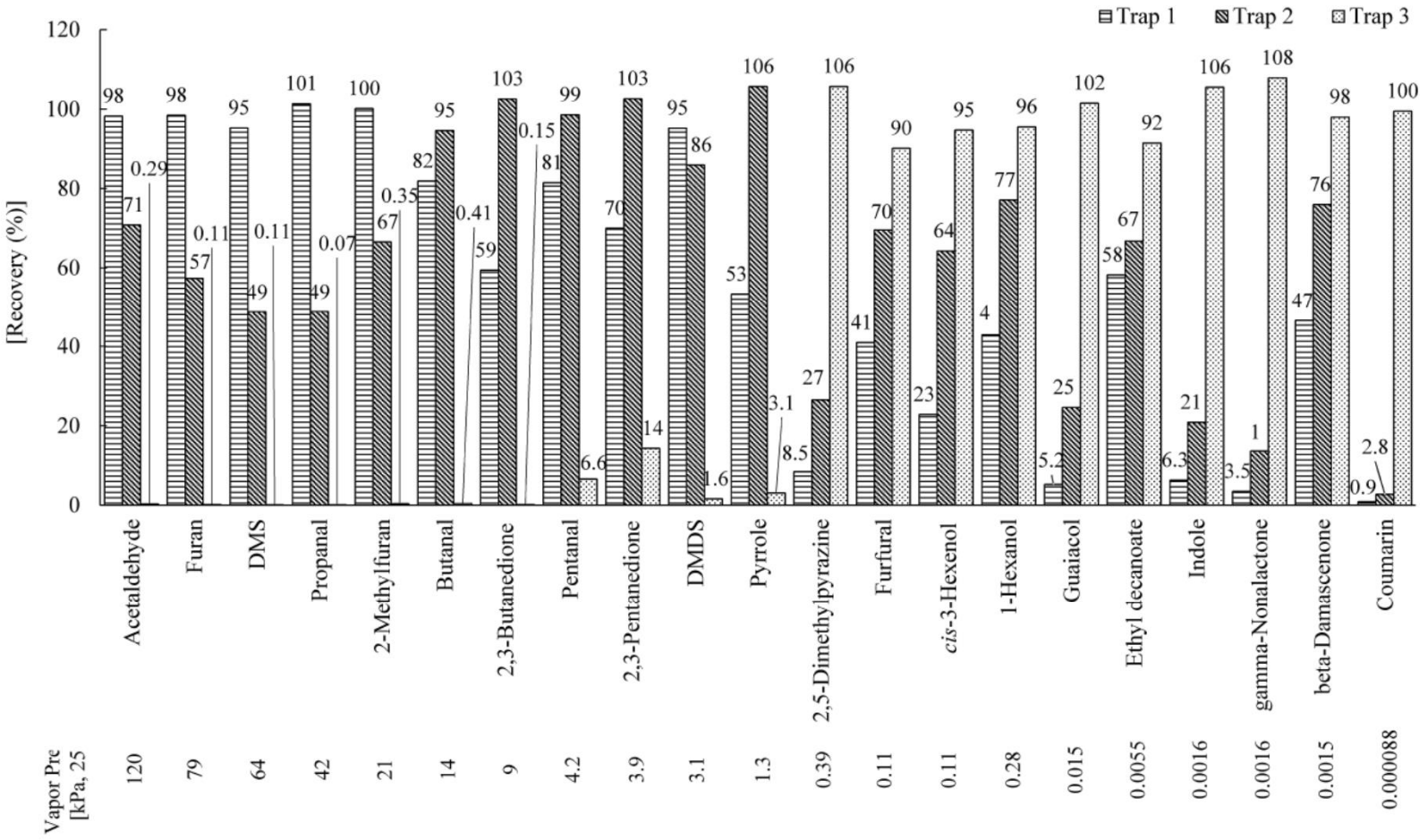

Fig. 3. Comparison of recoveries between three DHS sampling conditions for the test aroma compounds in 100 μL of water spiked at 100 ng mL^{-1}.

Multi-volatile Method

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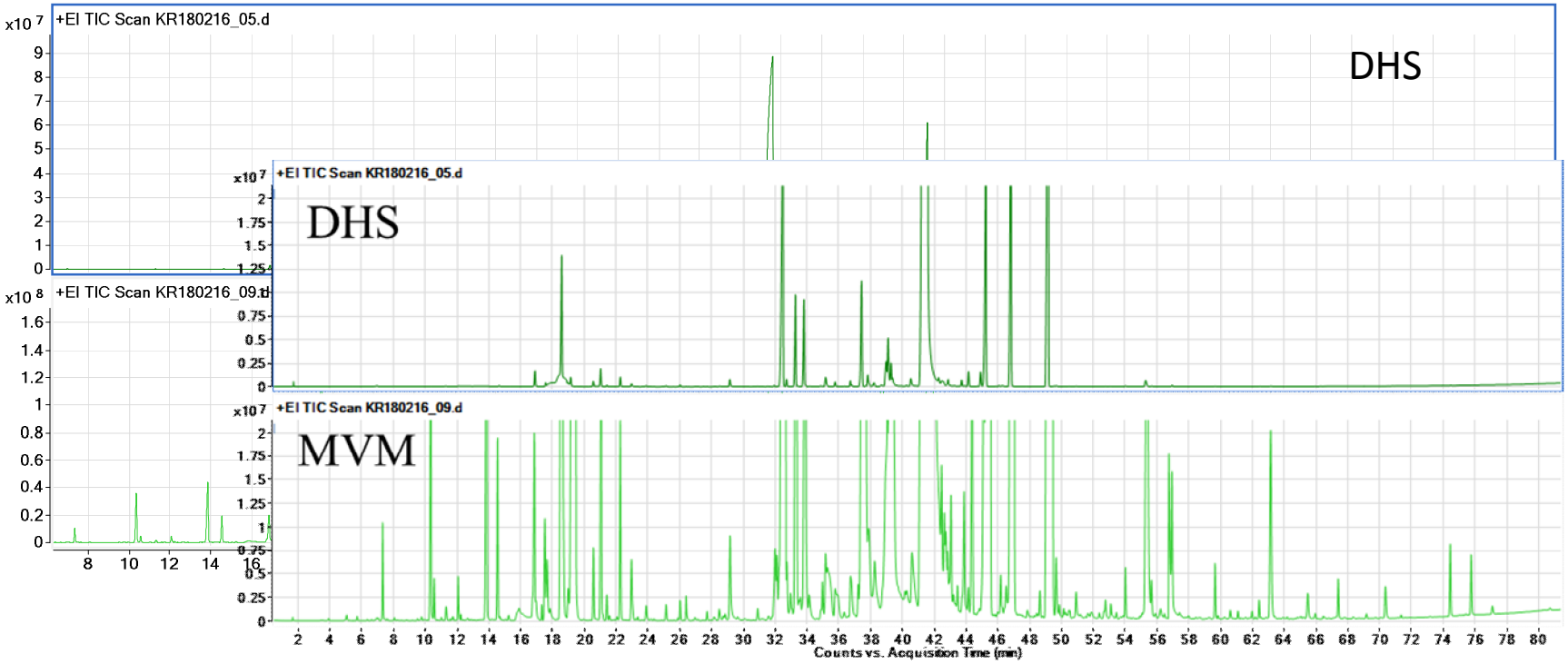
Comparison of single DHS with Tenax and MVM method (flavoured complex matrix)



Dynamic Headspace (DHS):Multi-Volatile Method

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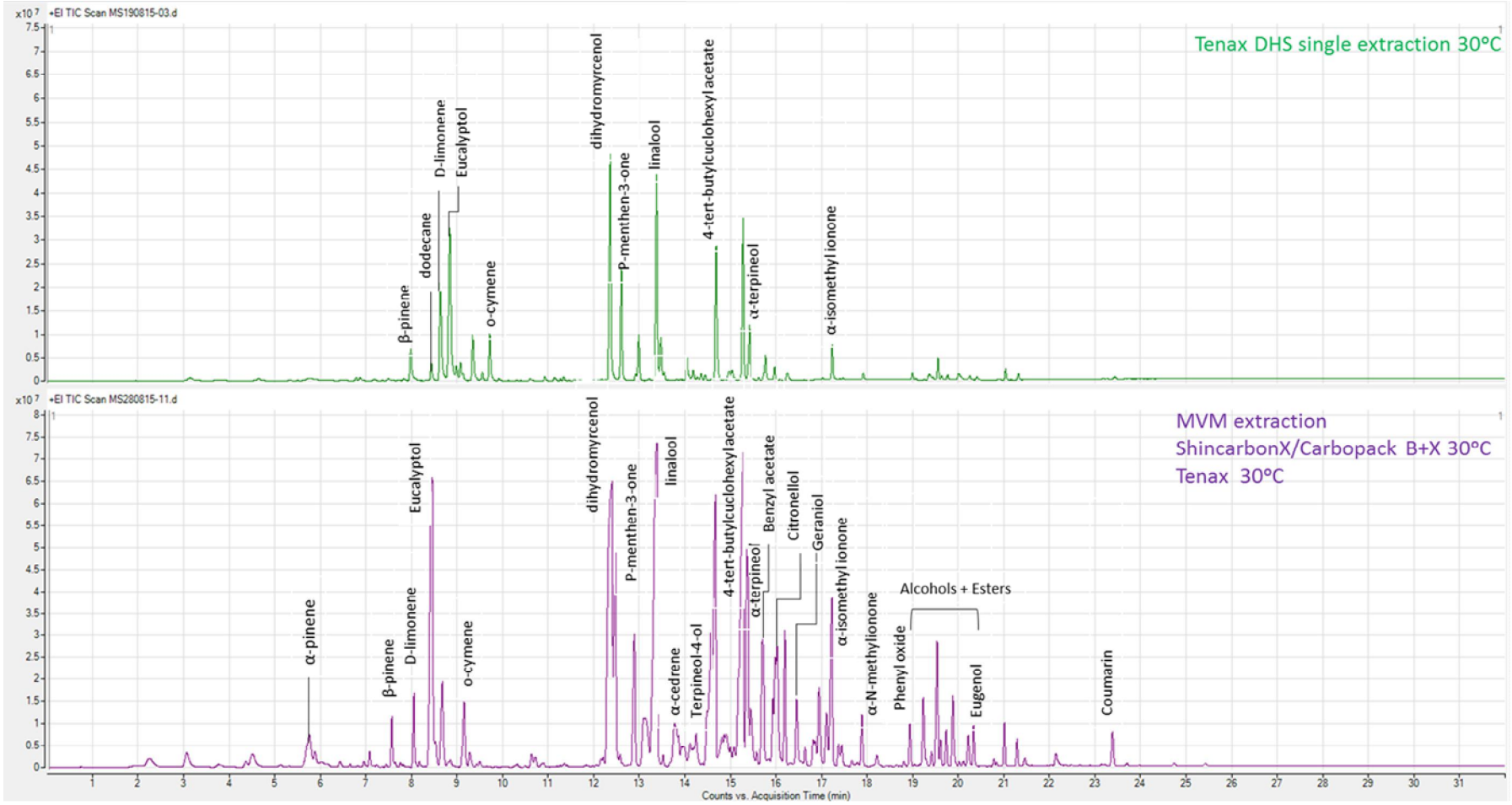
Fragrance in soap



Comparison of techniques

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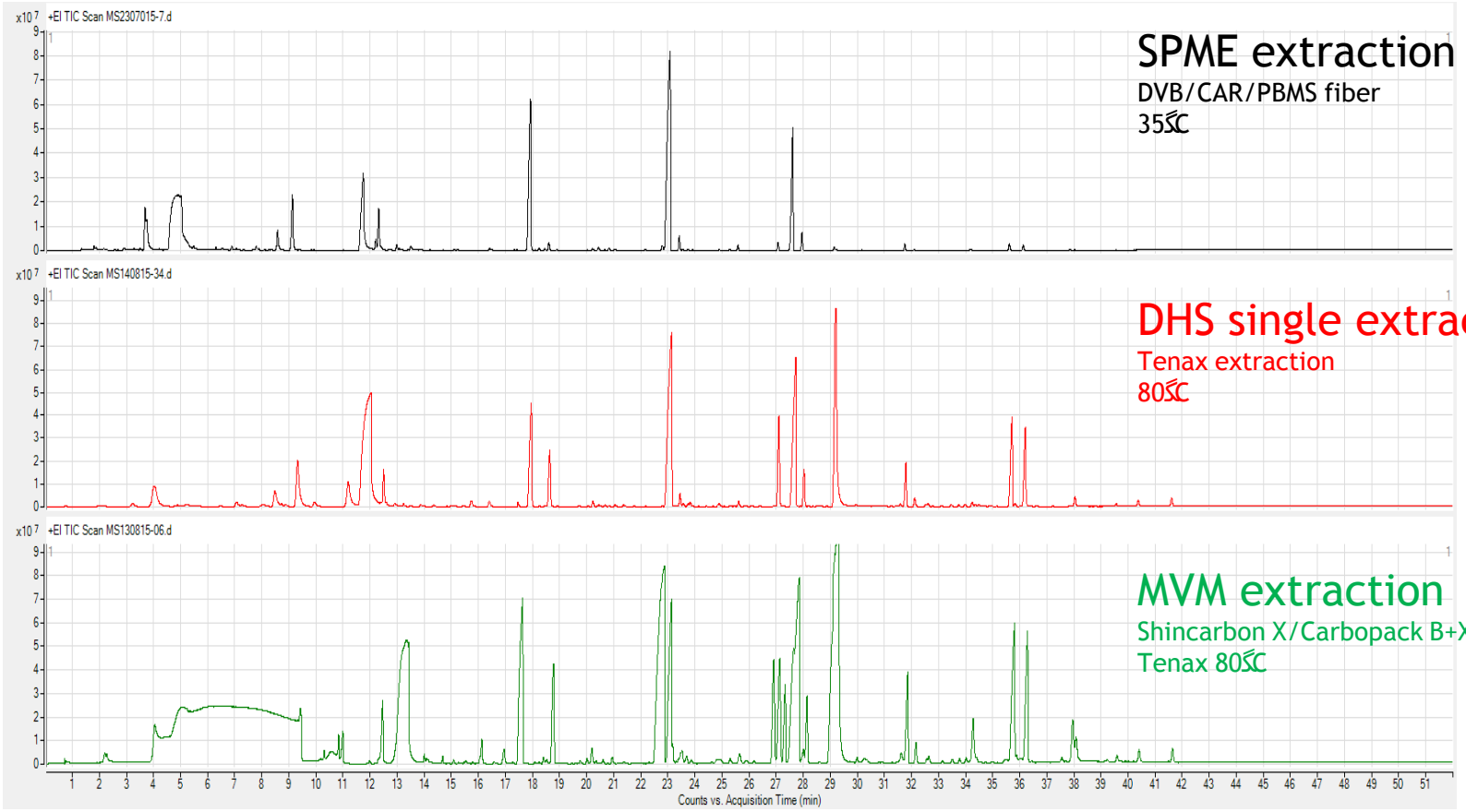
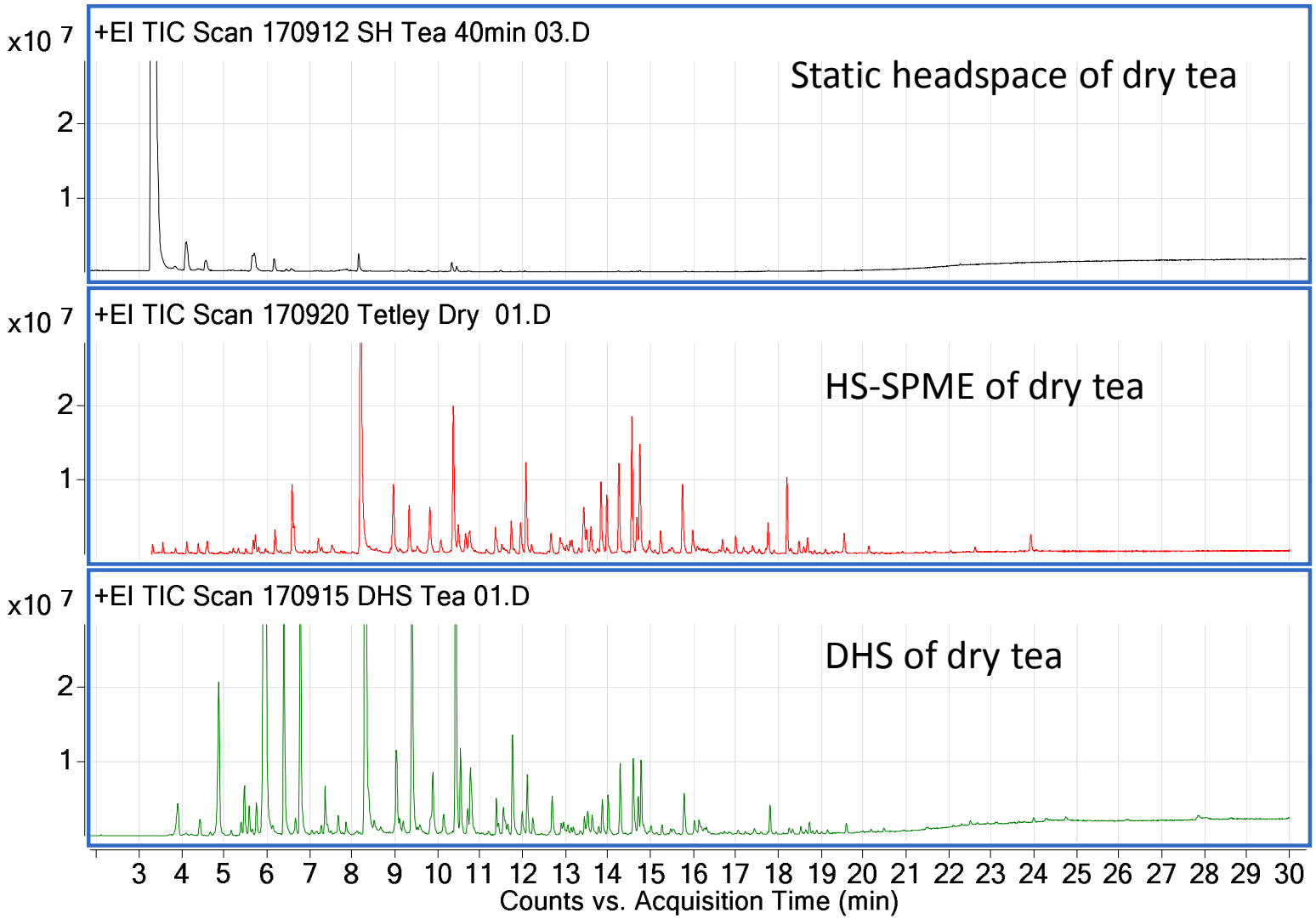
Whisky



Comparison of techniques



Sample preparation options

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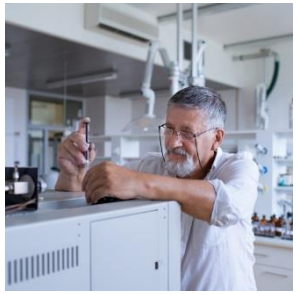
Liquid injection



Static headspace limited sensitivity (no selectivity)

ATEX

Dynamic headspace (DHS) – increased sensitivity, limited selectivity

SBSE

SBSE and SPME increased sensitivity (some selectivity)

MVM for widest range of compounds- trace levels

SIFT-MS

Selected Ion Flow Tube Mass Spectrometer

Gas phase/headspace/breath

Concentrations monitored in real time

Direct analysis – no sample preparation

Ultra sensitive measurements

Wide dynamic range

Wide range of compounds measured –

Including small polar

Determination of volatiles in Food

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