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THE QUEEN'S AWARDS FOR ENTERPRISE: INTERNATIONAL TRADE 2015

Thermal Desorption:

Solutions for ‘seeing the stars’

Seeing the stars……

New Delhi, December 2018

Shanghai, Good day vs Bad day

The WHO estimates that 7 million people a year die prematurely from exposure to air pollution globally, with the World Bank calculating the cost to the world economy in lost labour as $225bn.

Why carryout air monitoring?

Ref: WHO, 2018

Where should we be monitoring?

Ref: WHO, 2018

What do we need to monitor?

ENVIRONMENTAL POLLUTION CENTERS

Source: https://www.environmentalpollutioncenters.org/air/

Markes focus

SULFUR OXIDES (SOX)

NITROGEN OXIDES (NOX)

CARBON MONOXIDE (CO)

CARBON DIOXIDE (CO2)

VOCS (VOLATILE ORGANIC COMPOUNDS)

PARTICULATE MATTER (PM)

HG IN GASEOUS FORM

RADIOACTIVE POLLUTANTS

AMMONIA (NH3)

ISO

ASTM

25 1994-2019 European Environment Agency

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

cen

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Source: https://www.environmentalpollutioncenters.org/air/

Air Monitoring of VOCs

How?

- Environmental and public health ⇒ regulations ⇒ standard methods

- ASTM D6196 (pumped and passive tube)
- ASTM D5466 (canister)

Key Organisations

- ISO 16017-1 (pumped tube)
- ISO 16017-2 (passive tube)

- CEN 14662-1 (Pumped tube benzene monitoring
- CEN/TS 13649 (Stationary source emissions)

- US EPA Method TO-15 (canister)
- US EPA Method TO-17 (pumped tube)
- US EPA Method 325 (passive tube)
- US EPA Guidance on ozone precursor monitoring (on-line)

Example legislative methods

Key compound lists

- PAMS – (Photochemical Assessment Monitoring Stations)
  - Ozone precursors
  - On-line monitoring for VVOCs
- TO-15
  - Air toxics
  - Canister sampling
  - 65-component list
- TO-17
  - Air toxics
  - Tube sampling
  - Same as TO-15
- OVOC’s
  - Oxygenated VOCs becoming more of an interest
  - Compounds in list fit into both categories

Key monitoring activities and locations

- Environmental air monitoring
  - Ambient Air
  - Industrial Air
  - Fence-line monitoring
  - Odorous emissions

- Emissions from Products and Materials
  - Consumer goods
  - Air Fresheners
  - Toys
  - Construction products effecting indoor air
  - Medical device testing

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Simultaneous analysis of PAMS, TO-15 and OVOCs from humid air:

117 compounds with no liquid nitrogen

The next step for air monitoring?

Simultaneous analysis of PAMS, TO-15 and OVOCs from humid air: *117 compounds with no liquid nitrogen*

- Automated canister analysis using CIA *Advantage*-xr with GC-MS

Method Requirements

- **Target compounds**
  - 109 compounds from PAMS & TO15 compound lists
  - 8 OVOCs not in PAMS or TO15 compound lists
    1. Formaldehyde
    2. Acetaldehyde
    3. Crotonaldehyde
    4. Methacrylaldehyde
    5. Butyraldehyde
    6. Benzaldehyde
    7. Pentanal
    8. m -Tolualdehyde

- **Canister sampling**
  - Manual sampling method requires the analysis of samples collected in canisters.
  - Canisters must be inert coated stainless steel
- **Pre-concentration**
  - To reach low detection limits large sample volumes are required
  - The pre-concentration device must be capable of quantitatively retaining all compounds up to 600 mL, including very volatile C2 hydrocarbons.
- **Analysis**
  - Separation, identification and quantitation of all target compounds by GC or GC - MS

Successful PAMS, TO-15 & OVOC analysis….

This method requires pre-concentration and chromatographic separation of a high number of compounds ranging widely in volatility and polarity which presents significant challenges for many instruments:

- **Quantitative retention of very volatile to volatile organic compounds in a single analysis**
  - Trapping of the full compounds list up to 600 mL for maximum sensitivity
  - Fast desorption of all compounds for shape peaks aiding GC separation
- **Automated unattended analysis**
  - With enough sample capacity to run all night without user intervention
- **Water removal with no loss of polar compounds**
  - Allows larger sample volumes for maximum sensitivity
  - Protects GC columns and detectors from wear due to water
- **Automated internal standard addition**
  - Provides an independent check of system performance with every sample
- **Ability to sample from pressurised or unpressurised sources**
  - No sample dilution saves time, reduces human error / risks of contamination and reduces reporting limits.
  - Allows the same instrumentation to be used for on-line or canister samples
- **Trapping and separation of 117 compounds with < 60 minute cycle times**
  - Ensures sampling is started at the same time every hour.

Preconcentration: Introducing the CIA *Advantage*-xr

UNITY-xr; Efficient cryogen-free trapping
Electrically-cooled focusing trap eliminates the cost of liquid nitrogen and ensures fast sample throughput.
- *Trap all 117 compounds*

Outstanding productivity
Up to 27 samples at high and low concentrations can be analysed in one unattended sequence
- *Automated, unattended analysis*

Platform-neutral
Compatible with all major makes of GC and GC–MS.

Accurate MFC controlled sampling
- *Sample from pressurised or unpressurised samples*

Unparalleled analyte range
Inert, optimised flow paths allow quantitative recovery of C_2 to C_{44}, including reactive and thermally labile species .

Dry-Focus3™: Trouble-free sampling of humid air
- *Remove water with no loss of polar compounds*
- *Utilising Kori-xr*

Precise quantitative analysis
- *Automated Internal standard* capability is compliant with international methods

Overlap mode
Prepare one sample while the previous analysis is running
- Fast sample – to sample cycle times

Whole system configuration

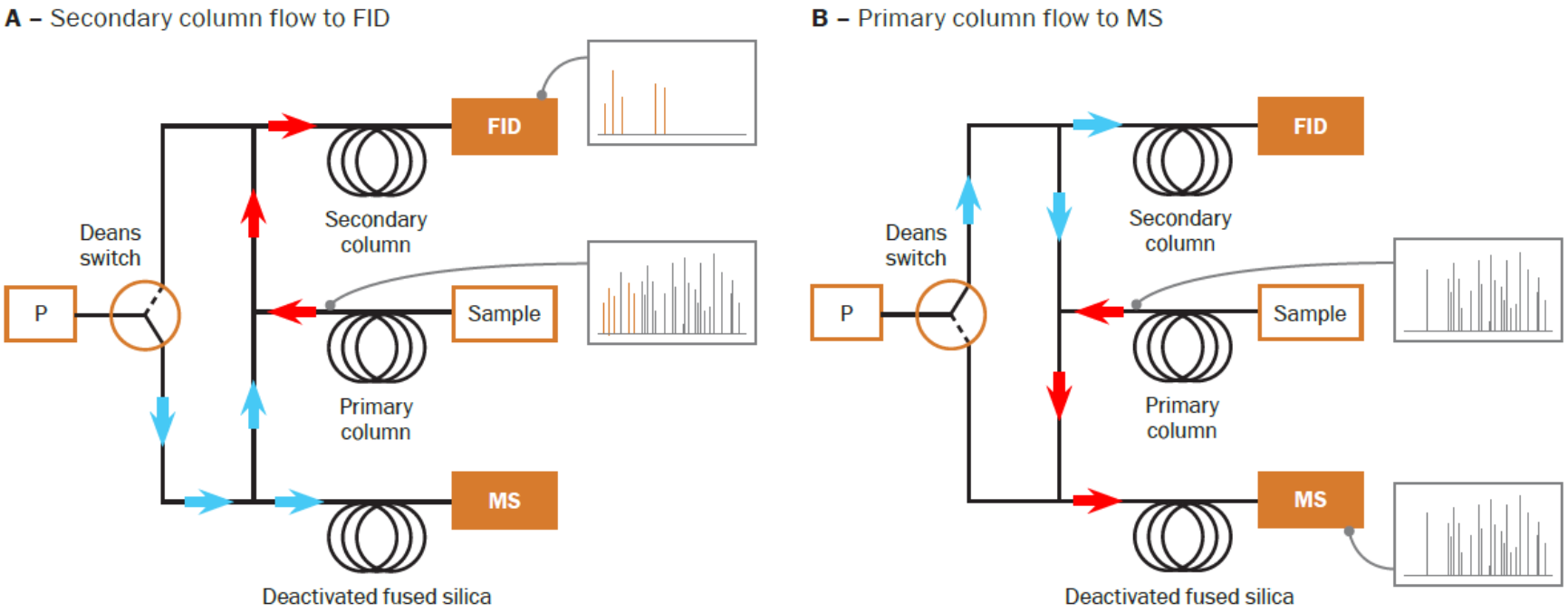
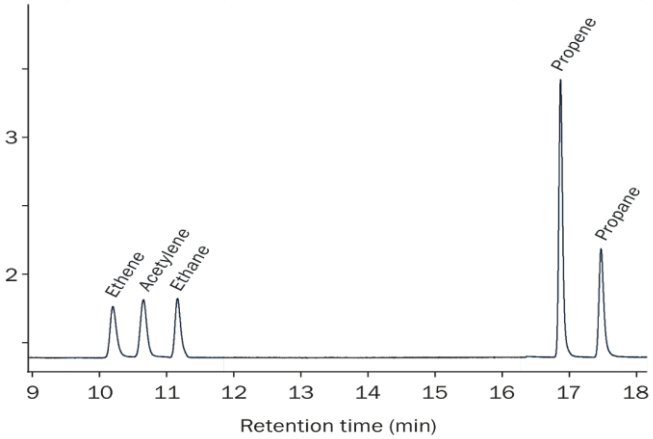


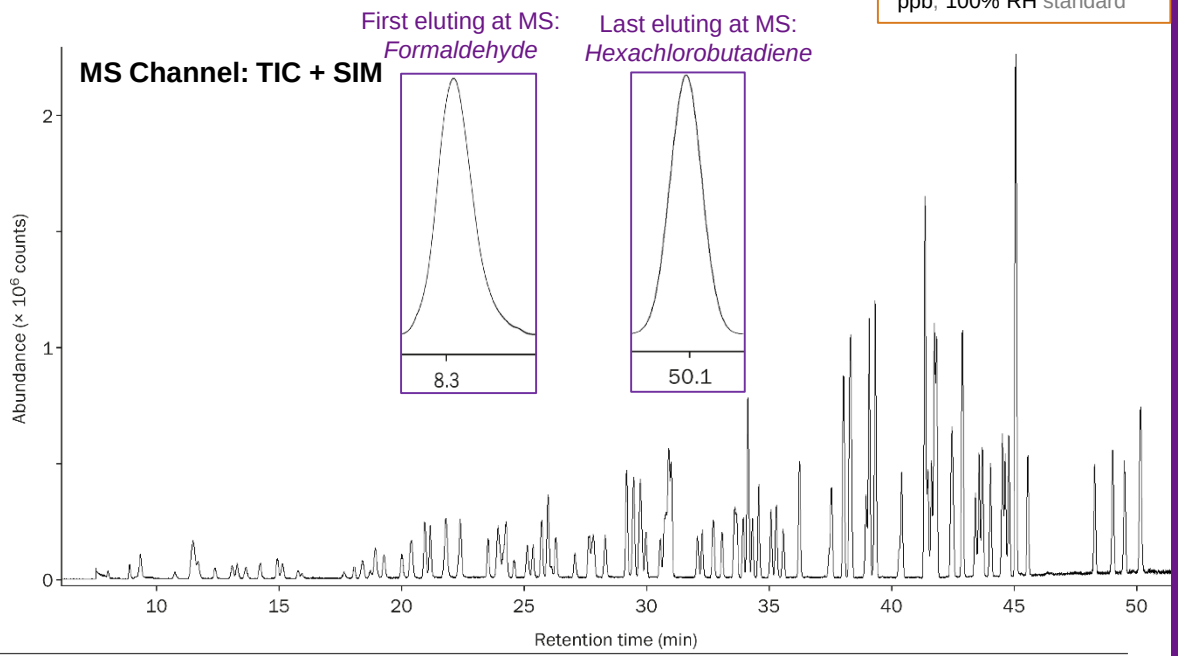
Figure 4: Dual-column GC–MS/FID instrument operation. = Analyte flow. = Gas flow. P = Carrier gas pressure supply.

PAMS, TO-15 & OVOC in a single analysis with no liquid cryogen

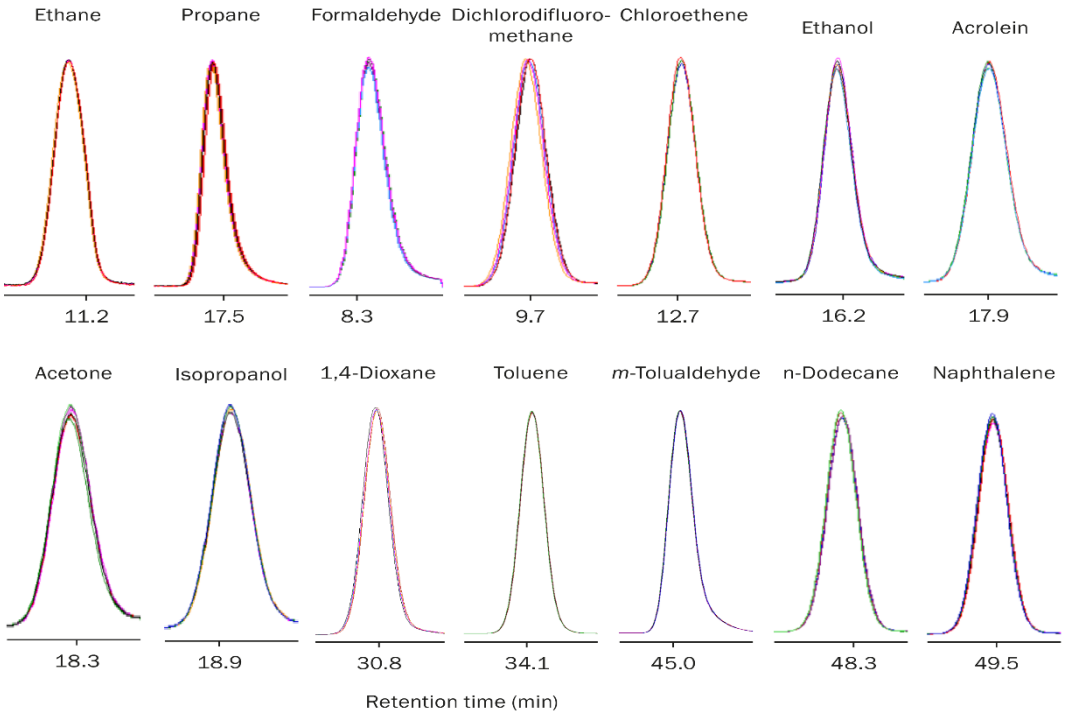
- Dual column system with Deans switch
- Cryogen free pre-concentration AND cryogen free chromatography – oven start temp +35°C
- Excellent peak shape for VVOC at FID, as well as VOC & OVOCs *across the full compound range*
- <60 minute cycle time

Total Ion Chromatogram (TIC) of 400 mL of the 10 ppb, 100% RH standard





PAMS, TO-15 & OVOC in a single analysis with no liquid cryogen



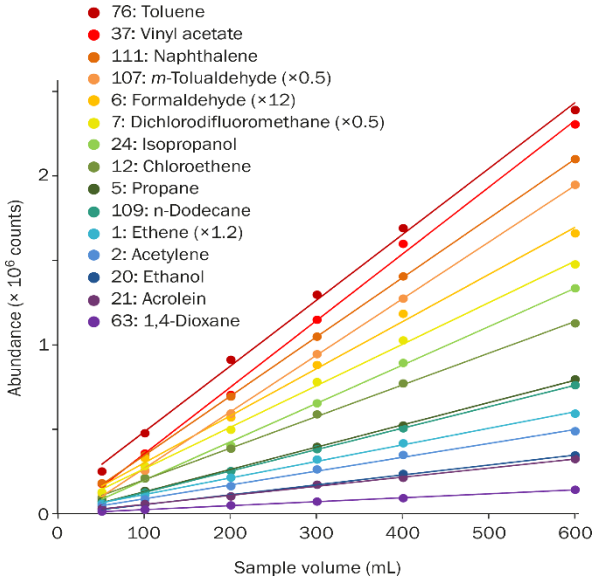
Example compounds covering the polarity and volatility range of the target list:
10 replicate analysis of 10 ppb standard at 100% RH overlay perfectly for all compounds

- **Highly reproducible data**
  - < 7.5% RSD on response across 10 replicates for all compounds
  - < 2.1% RSD for internal standard compounds
- **Very stable retention times**
  - < 0.17% RSD across 16 replicates for all compounds

PAMS, TO-15 & OVOC in a single analysis with no liquid cryogen

Excellent linearity at 100% relative humidity

- 1.25 to 15 ppb equivalent
- All R^2 values > 0.990
- Relative response factors highly reproducible
  - % RSD of RRF ≤ 12 % (method limit 30%)



Low method detection limits

- All MDLs < 200 ppt
- Average MDL ~ 50 ppt

Compounds	MDL (ppt)
Toluene	8
Vinyl acetate	72
Naphthalene	26
m-Tolualdehdye	70
Formaldehyde	105
Dichlorodifluoromethane	22
Isopropanol	114
Chloroethene	47
Propane	22
N-Dodecane	73
Ethene	92
Acetylene	99
Ethanol	43
1,4-Dioxane	120

Summary

Markes cryogen-free CIA *Advantage*-xr solution provides:

- Analysis of VVOCs, OVOCs and VOCs simultaneously with no liquid nitrogen
- Excellent peak shape and retention of VVOCs, OVOCs and VOCs
- Low method detection limits
- Automated sequencing of up to 27 canister/on-line samples, standards and blanks
- Superior water removal: no loss of polar compounds
- Maximum productivity with sample overlap function
- Linearity from 1.25 to 15ppb and beyond
- High precision (low %RSD)
- Negligible carryover from high concentration samples
- Long-term retention time and response stability for high confidence data.

From outdoor to indoor…

- Potential health risks that arise from poor indoor air quality have prompted regulation of a wide range of materials
- The average American spends 93% of their time indoors…
- 86% in houses, offices, etc…
- … and 7% in automobiles.
- The majority of items which can effect the air quality in these locations are now regulated

Standard methods

The evolution of materials testing

- VIAQ – **Whole cabin testing**
  - (ISO12219-1, HJ 400, New UN specification - ECE/TRANS/WP.29/GRPE/2017/1, VDA)

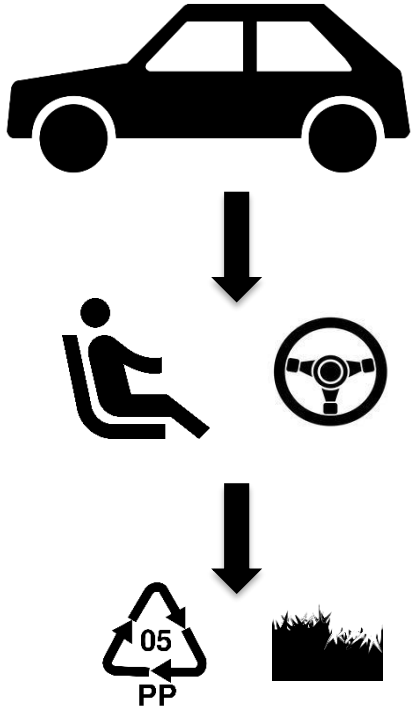
- Material emission testing typically carried out using:

Assembly testing

  - Small chambers (ISO12219-4 & 6) and Tedlar bags ~2000L for sampling assemblies (ISO 12219-9).

Screening

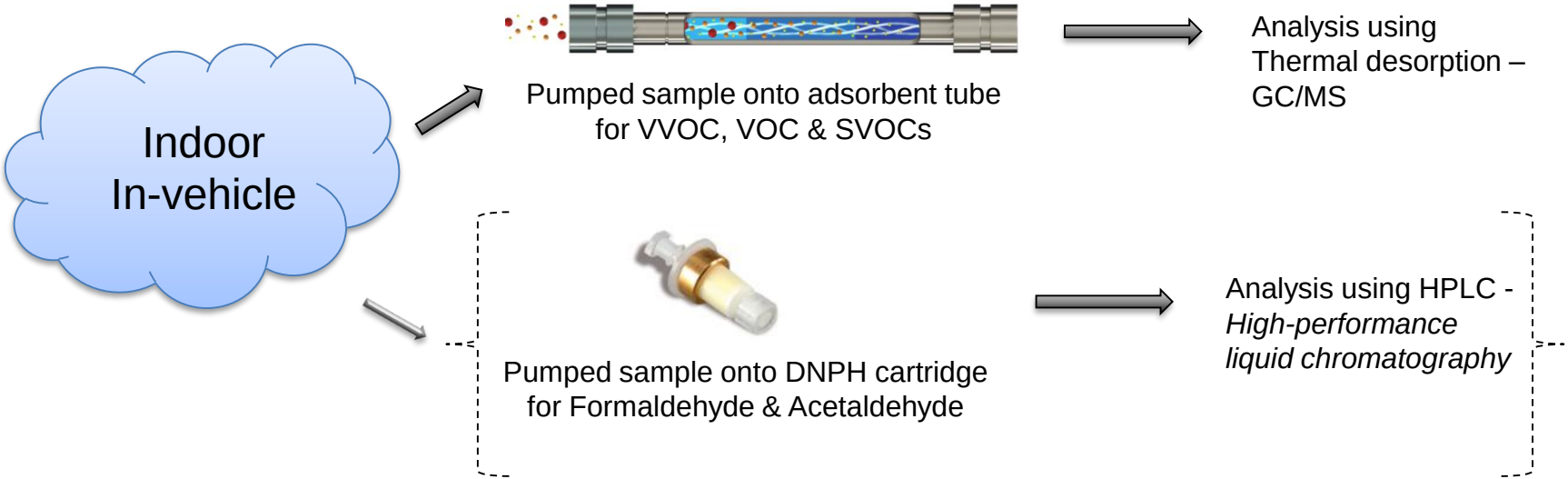
  - Direct desorption (VDA278)
  - Micro-Scale Chambers (ISO12219-3)
  - ~20L Tedlar Bag Sampling (ISO12219-2)



How to comply with standard methods

Emission testing methods based on the same principles/instrumentation

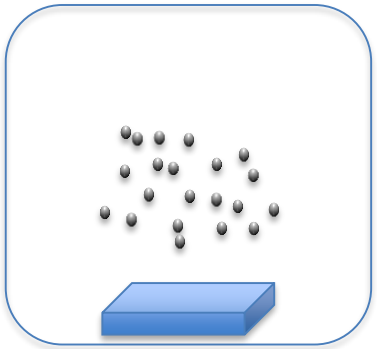
Whole Air testing (ISO 16000-6, EN16516, HJ400, ISO12219-1, UN (ECE/TRANS/WP.29/GRPE/2017/))



How to comply with standard methods

Emission testing methods based on the same principles/instrumentation

Materials testing (ISO16000-9, ISO 12219- 2,3,4,6, EN16516, ASTM D7706-11, ASTM D7859)



Chamber/Bag testing

Pumped sample onto adsorbent tube for VVOC, VOC & SVOCs

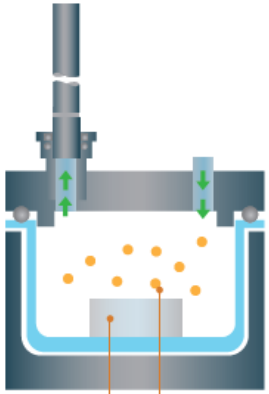
Analysis using Thermal desorption – GC/MS

Pumped sample onto DNPH cartridge for Formaldehyde & Acetaldehyde

Analysis using HPLC - *High-performance liquid chromatography*

Product screening for manufacturers

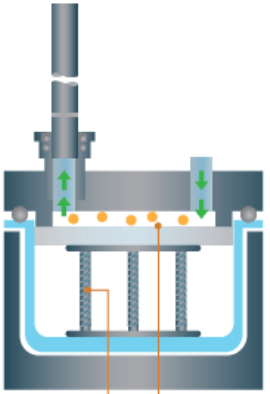
Bulk emissions testing is valuable for profiling odours and emissions, and for testing of raw materials and foods.



Samples are placed straight into the chambers.

Vapours swept from the entire sample are collected.

Surface emissions testing: This approach is suitable for determining area-specific emission rates from flat samples.



Sprung spacers raise planar samples to the top of the chamber.

A seal forms when the lid is closed, so only vapours released from the sample's surface are collected.

Why screen materials?

- Predict results of longer, more expensive tests
- To show uniformity across a range
- Trouble shoot customers complaints
- Compare products with competitors
- Determine new formulations for lower emitting products
- Odour profiling

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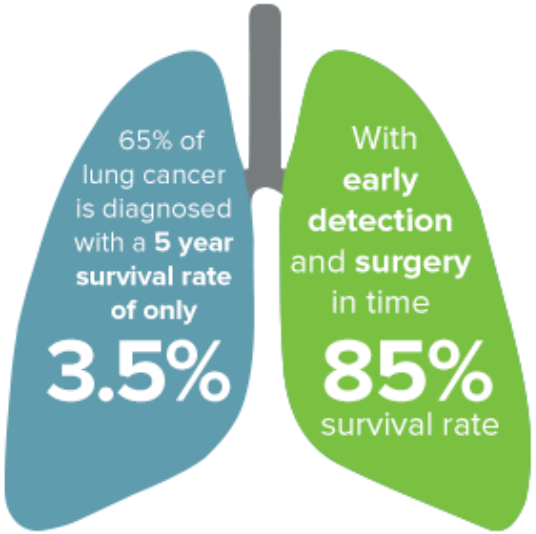
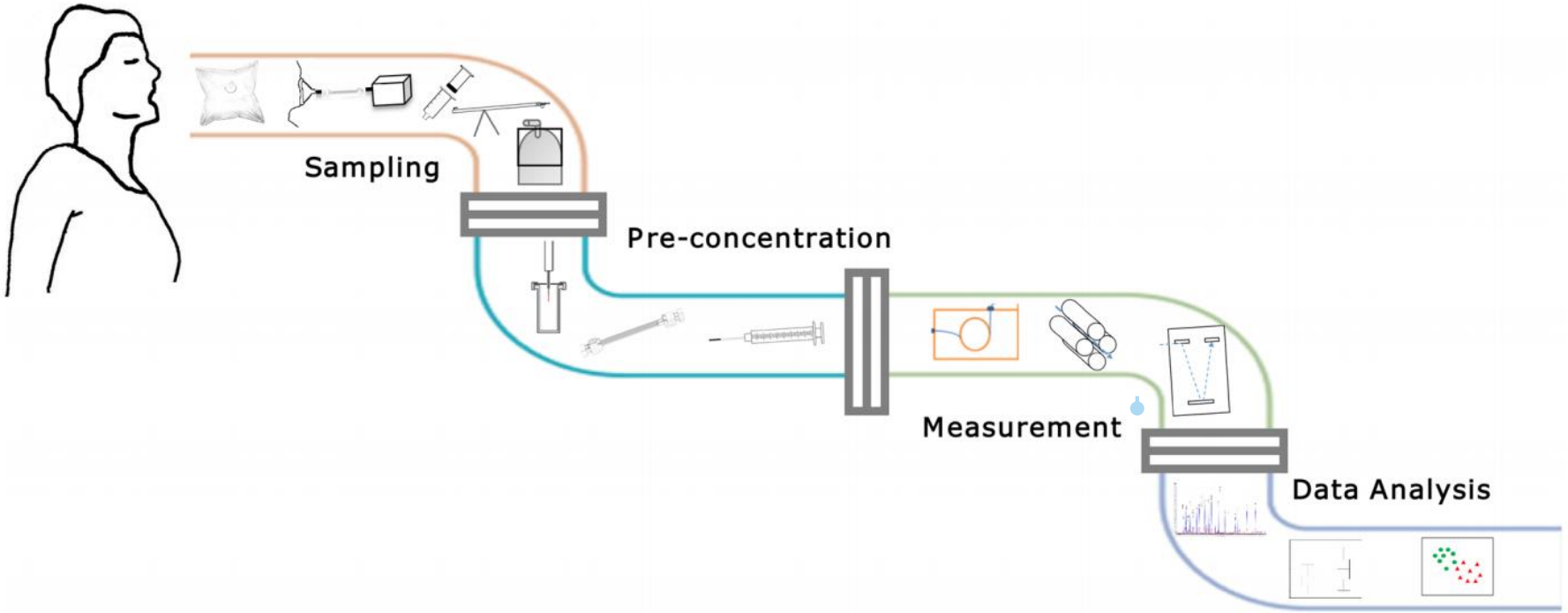
Breath Analysis

The detrimental health effects of Air Pollution - early detection saves lives



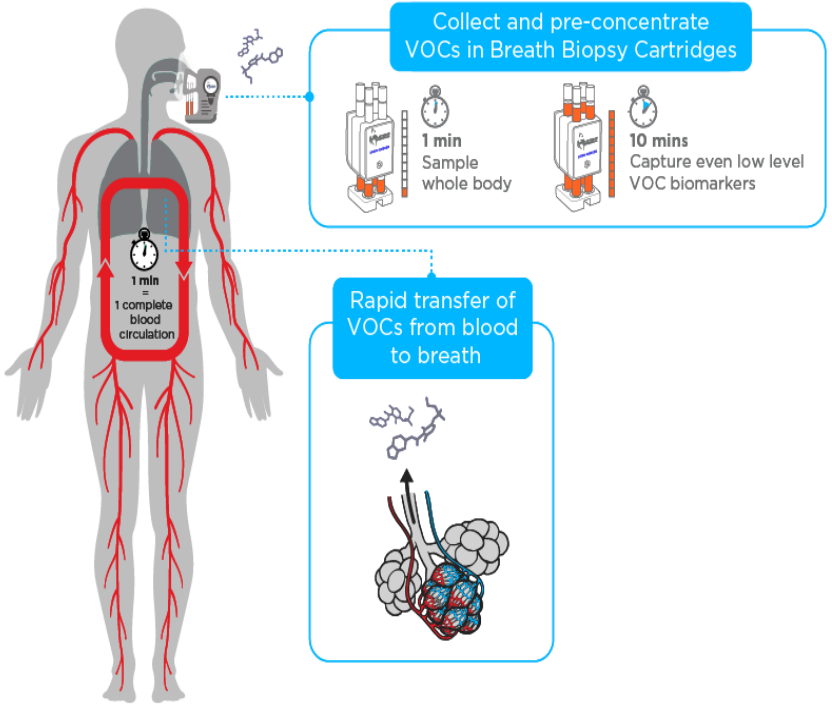
Source: http://www.who.int/airpollution/infographics/who-lunggraphic.jpg?ua=1

Analytical challenges in breath analysis



Source: Lawal et al., *Exhaled breath analysis: a review of 'breath-taking' methods for off-line analysis* (2017) Metabolomics, 13:110

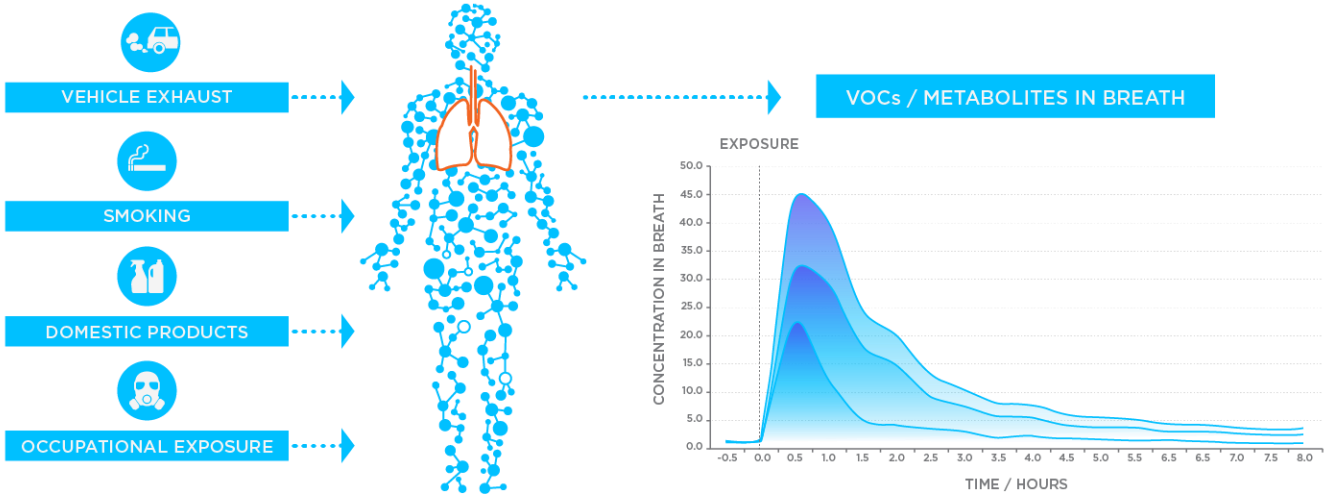
What is breath analysis?



- VOC biomarkers in breath are relevant for a wide range of diseases
- Breath VOCs can also be used to monitor exposure to harmful VOCs
- Breath enables whole body blood sampling
- Non-invasive sampling
- No specialist medical training required
- Samples can easily be stored and transported

Monitoring chemical exposure

- VOCs can be absorbed through the lungs and skin and are often metabolised by the liver.
- These VOCs and their metabolites can be measured on exhaled breath, providing an opportunity for non-invasive biomonitoring.



Breath sampling

How it works

- Alveolar (‘end-tidal’) breath collected and transferred onto sorbent tube
  - Provides information on VOC levels in blood (Pollutants and metabolites)

➢ **Markes’ Bio-VOC**

➢ **ReCIVA breath sampler** (Owlstone Medical)

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