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MARKES international

Analisi dell'aria con Thermal Desorber

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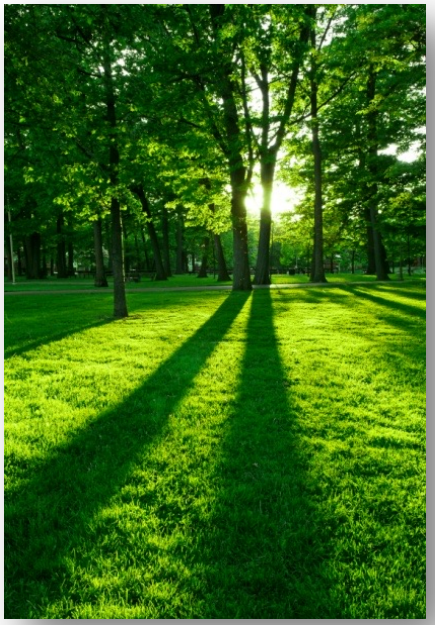
Thermal Desorption, cos'è…

Sistema di campionamento ed analisi dell'aria, sia in campo aperto (zone industriali, residenziali, discariche) sia in campo chiuso (luoghi di lavoro, abitati, ecc.)



Thermal Desorption, cos'è…

Il Sistema di campionamento consiste di un tubo metallic o di vetro contenente un sorbente, in cui viene fatta passare l'aria da analizzare in maniera forzata o passiva.

In tal modo, il sorbente estrae la parte organica volatile dell'aria.

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Thermal Desorption, cos'è…

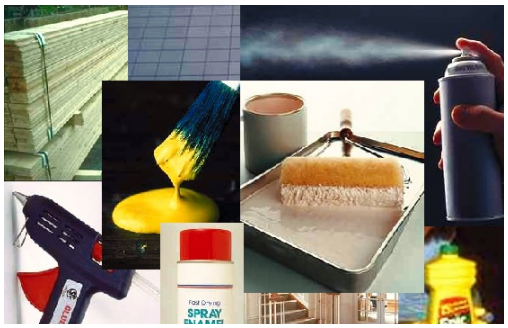
Successivamente il tubo viene portato al TD che mediante riscaldamento e sotto il flusso di un gas inerte, libera i principi attivi direttamente nel GC-MS

Campi di applicazione…

For sample matrices that cannot be directly introduced to the analyser (GC) or require pre-concentration

Dilute Environmental Vapour Samples

Material Emissions – construction, automotive

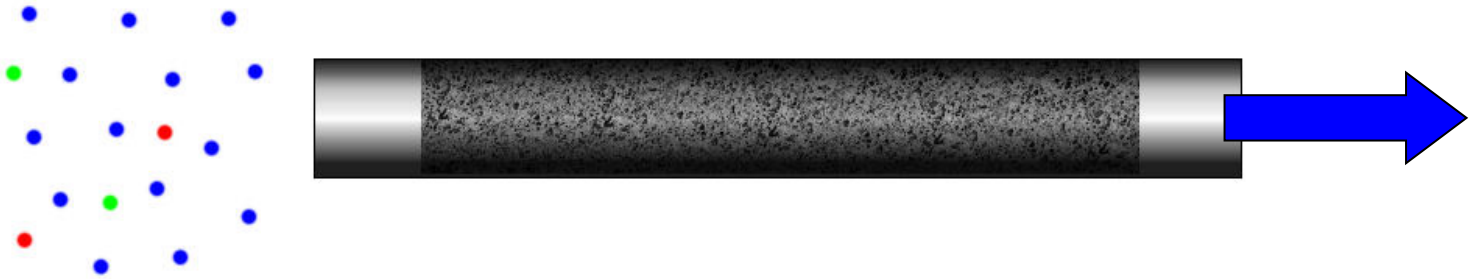


Food, Flavour and Fragrance

Defence and Forensic

Thermal Desorption, cos'è…

Sorbent Material

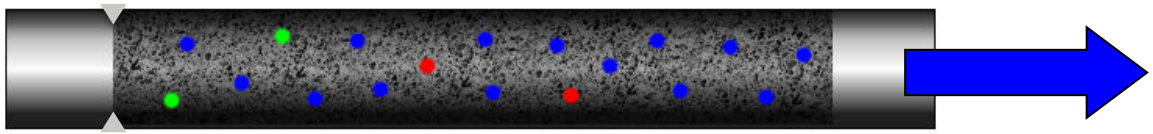


Sample Matrix

e.g. Air

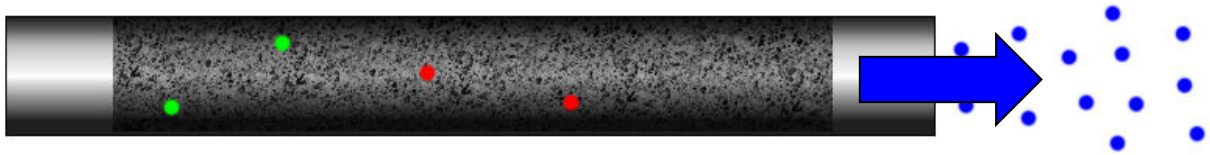
Thermal Desorption, cos'è…

Sample passes onto the sorbent



Compounds of interest are adsorbed
on the sorbent surface

Thermal Desorption, cos'è…



Lighter gases such as nitrogen, argon and carbon dioxide pass through the sorbent

Thermal Desorption, cos'è…

The sorbent tube is now heated in a reversed flow of clean carrier gas (back flushed)

Thermal Desorption, cos'è…

Compounds are released from the sorbent into the flow of carrier gas

It combines preconcentration, desorption/extraction and GC injection into one sensitive and fully automated operation

It is a simple extension of the technique of Gas Chromatography and is a **sample introduction technology** for difficult or real-world samples. Analytes undergo **pre-concentration** from litre samples to µl vapour band on the GC

Thermal Desorption, cos'è…

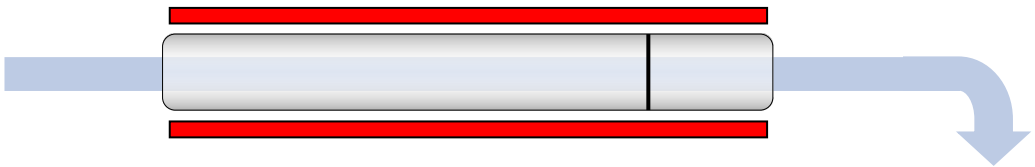
PROBLEM: Compounds are released SLOWLY from the sorbent tube

Would lead to **very wide** chromatographic peaks and low sensitivity

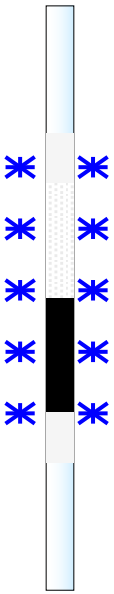
Thermal Desorption, cos'è…

ANSWER: All modern thermal desorption instruments incorporate a two-stage desorption procedure.

Sorbent Tube



Electrically cooled, narrow bore cold trap



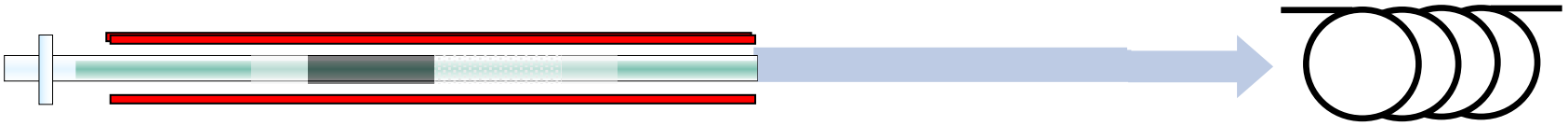
STAGE 1

Transfer compounds from tube to secondary focussing trap

Thermal Desorption, cos'è…

STAGE 2

Rapid transfer of compounds from cold trap to GC



- Cold trap heated rapidly (100°C/sec) for sharp chromatographic peaks
- Transfer of analytes through narrow bore transfer line of cold trap for greater volatility range

Quali composti…

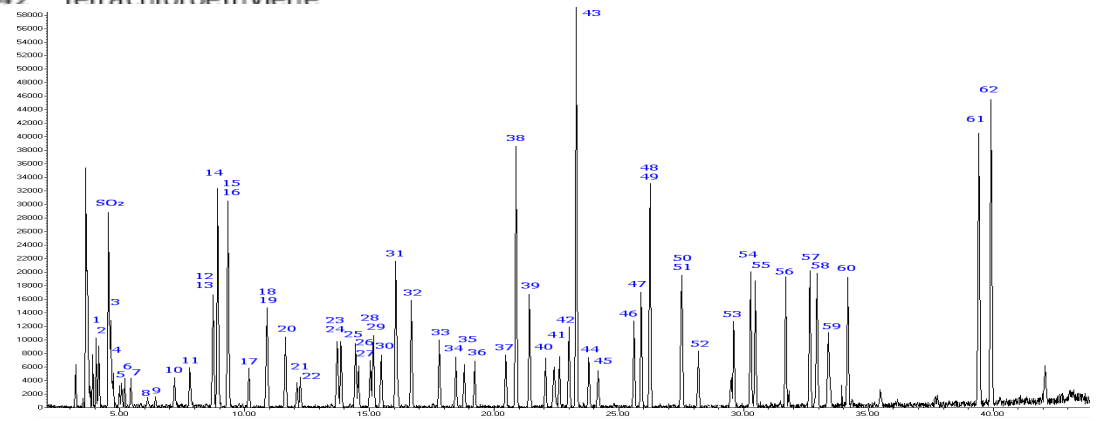
Any volatile or semi-volatile organic compounds which meet the following criteria:

✓ ≤ n-C_{40}, bpt ≤ 525˚C
✓ Compatible with ‘standard’ GC analysis
✓ The sorbent or matrix containing the compounds is compatible with the high temperatures required
x Inorganic compounds
x Most permanent gases (CO_2, Ar, N_2 etc.) and other compounds with very low boiling points (methane, formaldehyde)
x Compounds bigger than n-C_{40}
x Compounds which are not compatible with gas chromatography (or which require on-column injection or derivitisation)

EPA TO-17

1 Propylene
2 Dichlorodifluoromethane
3 1,2-Dichlorotetrafluoroethane
4 Methyl chloride
5 1,2-Dichloroethane
6 1,3–Butadiene
7 Vinyl chloride
8 Methyl bromide (bromomethane)
9 Chloroethane
10 Trichlorotrifluoroethane (Freon® 113)
11 Ethanol
12 1,2,-Dichloroethylene
13 1,1,2-Trichlorotrifluoroethane
14 Acetone
15 Carbon disulfide
16 Isopropyl alcohol
17 Methylene chloride
18 Tert-butyl methyl ether
19 *n*-Hexane
20 1,1-Dichloroethane
21 Vinyl acetate
22 Cis-1,2-Dichloroethylene
23 Methyl ethyl ketone
24 Ethyl acetate
25 Tetrahydrofuran
26 Chloroform
27 1,1,1-Trichloroethane
28 Cyclohexane
29 Carbon tetrachloride
30 Benzene
31 *n*-Heptane
32 Trichloroethylene
33 1,2-Dichloropropane
34 1,4-Dioxane
35 Bromodichloromethane
36 Trans-1,3-dichloropropene
37 Methyl isobutyl ketone
38 Toluene
39 Cis-1,3-Dichloropropene
40 Trans-1,2-Dichloroethylene
41 1,1,2-Trichloroethane
42 Tetrachloroethylene
43 Methyl *n*-butyl ketone
44 Dibromochloromethane
45 1,2–Dibromoethane
46 Chlorobenzene
47 Xylene
48 Xylene
49 Xylene
50 Styrene
51 Tribromomethane
52 1,1,2,2-Tetrachloroethane
53 1,2,4-Trimethylbenzene
54 1,3,5-Trimethylbenzene
55 1-Ethyl-4-methyl benzene
56 Ethylbenzene
57 1,2-Dichlorobenzene
58 1,3-Dichlorobenzene
59 Chloromethylbenzene (alpha)
60 1,4–Dichlorobenzene
61 1,2,4–Trichlorobenzene
62 Hexachloro-1,3-butadiene

Splitless desorption of ‘Air toxics’ tube loaded with 1 L of 1 ppb std GC/MS



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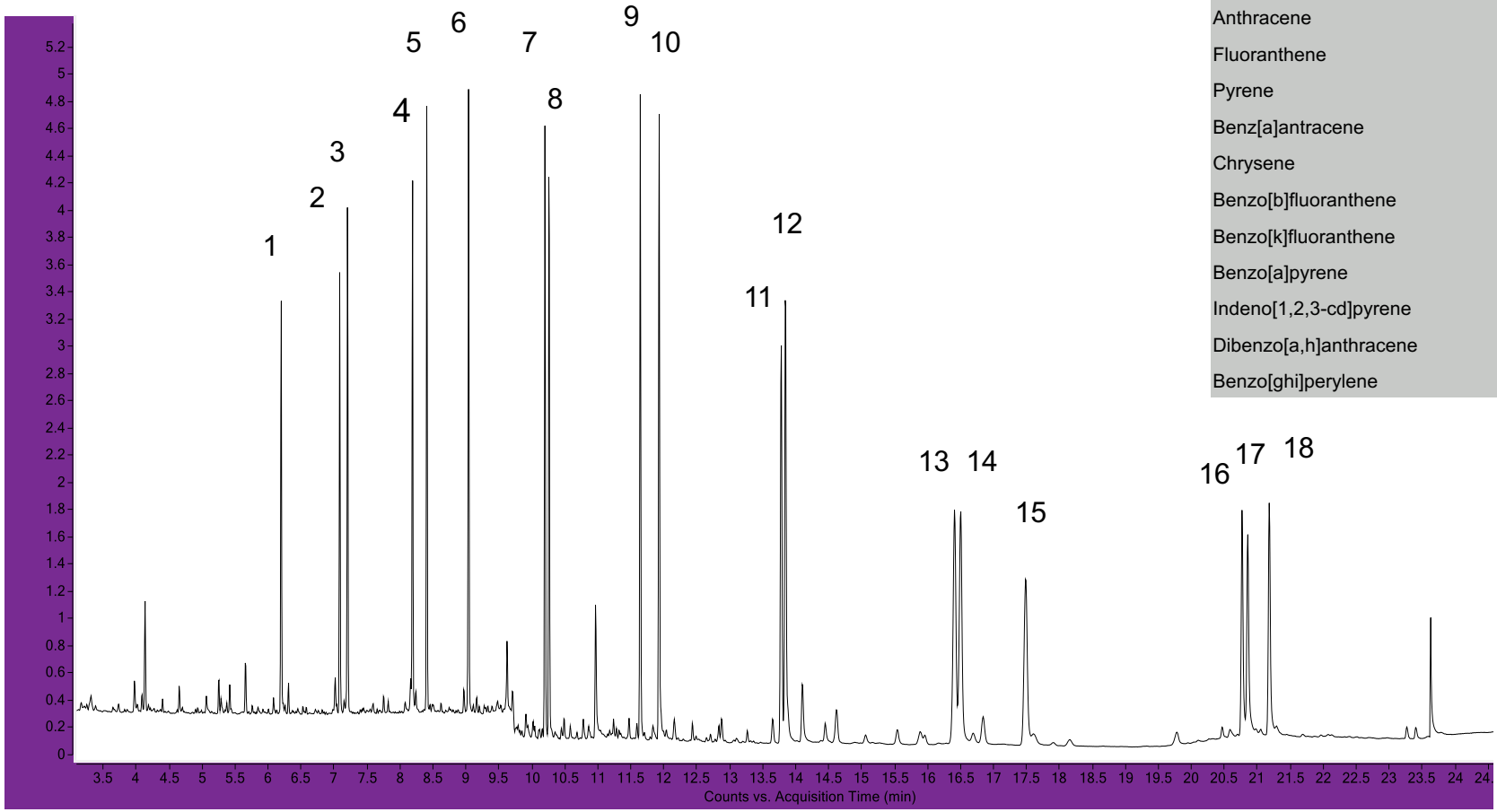
IPA in aria ambientale

Compounds	
Naphthalene	1
1-methyl naphthalene	2
2-methyl naphthalene	3
Acenaphthylene	4
Acenaphthene	5
Fluorene	6
Phenanthrene	7
Anthracene	8
Fluoranthene	9
Pyrene	10
Benz[a]antracene	11
Chrysene	12
Benzo[b]fluoranthene	13
Benzo[k]fluoranthene	14
Benzo[a]pyrene	15
Indeno[1,2,3-cd]pyrene	16
Dibenzo[a,h]anthracene	17
Benzo[ghi]perylene	18



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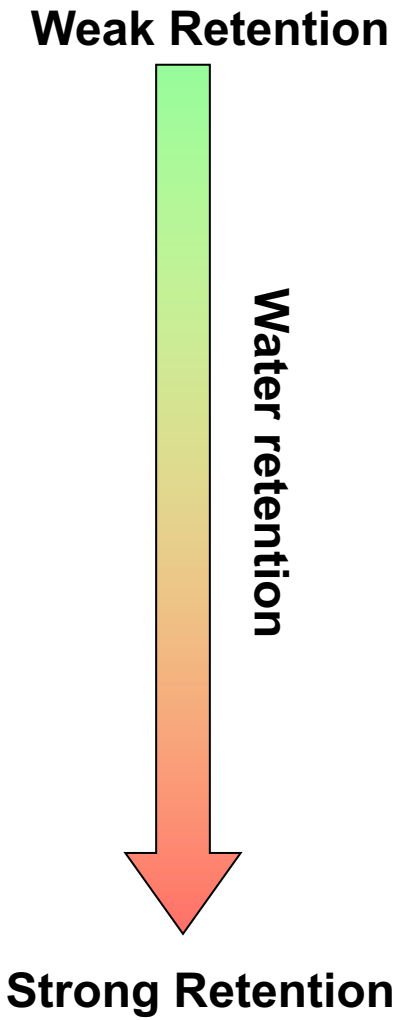
Thermal Desorption, cos'è…

Sorbent name	Volatility range
Tenax TA	C_7 – C_{30}
Carbograph 2TD	C_8 – C_{20}
Carbograph 1TD	$C_{5/6}$ – C_{14}
Carbograph 5TD	$C_{3/4}$ – $C_{6/7}$
SulfiCarb	C_3 – C_8
Carboxen 1003	C_2 – C_5
Carbosieve SIII	C_2 – C_5



Campionamento…

Three sampling methods

a. Passive (diffusive) sampling

b. Direct sampling

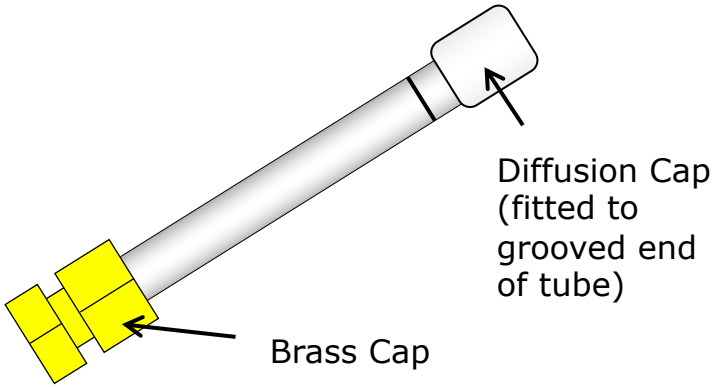
c. Active (pumped) sampling

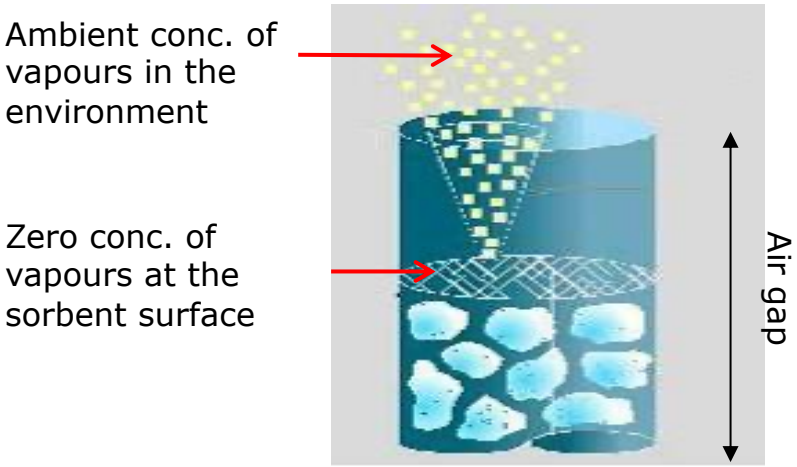
Campionamento Passivo (diffusivo)

- Diffusive sampling = a simple and cost effective method of collecting the large number of samples required in many air monitoring programmes. See Markes Application note #8 for an overview

- Vapours migrate across the air gap at a constant “uptake rate” as tube dimensions are consistent (Fick’s law)

- Diffusive sampling is a slow process, typically sample for days





Campionamento Passivo (diffusivo)

Only compatible with single bed sorbent tubes - only one end of the tube is exposed

$$\text{Conc (ppm)} = \frac{\text{Mass on tube(ng)}}{\text{Uptake Rate x Sample Time (mins)}}$$

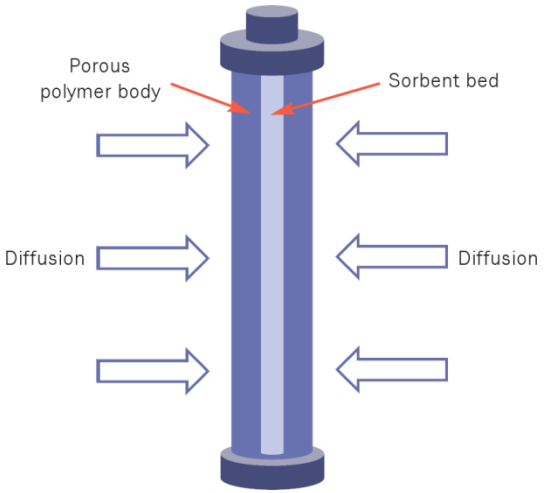
- Uptake rates of many analytes on a range of sorbents have now been published (see Markes Application Note #1 and #42)
- If an uptake rate is not available in the literature it is possible to determine it experimentally but this is difficult
  - Involves collecting several diffusive + pumped samples from the same 'atmosphere'
  - The pumped samples provide you with the known concentration so you can then calculate the uptake rate for the diffusive samplers

Campionamento Passivo (diffusivo)

- Two types of diffusive samplers:
  - Tube-type axial samplers (sorbent tubes)

    - Uptake rates typically 1-3ng ppm^{-1} min^{-1}

  - Radial Diffusive samplers (sorbent cartridges)
    - Use for analysis of low concentrations over shorter periods e.g. workplace monitoring (<1ppb over 8hours)
    - Cylindrical sorbent cartridge placed inside empty sorbent tube and analysed
    - Uptake rates typically 50-100x faster than axial sampling



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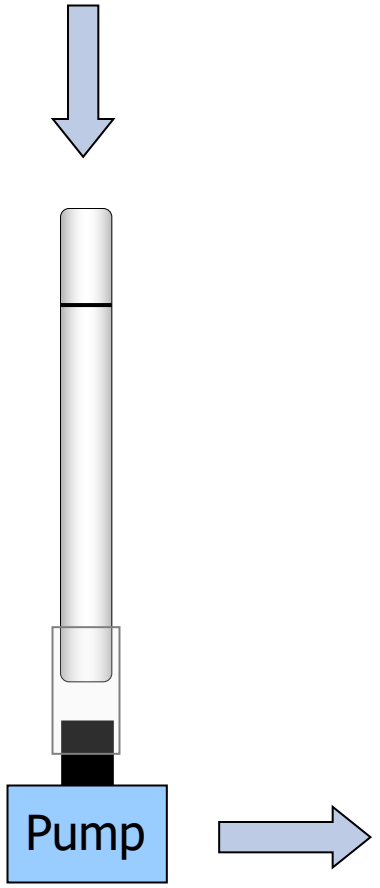
Campionamento Attivo (forzato)

- Pump air through sorbent tube
- Flow Rate = 20 – 200 ml/min
- Much faster technique compared to diffusive sampling
- Fully quantitative – know how much is sampled
- Important do not exceed breakthrough volume for a compound on a given sorbent



Campionamento Attivo

Constant flow pump

- Pump varies its speed to maintain a constant (programmed) flow
- Set a defined sampling flow and time

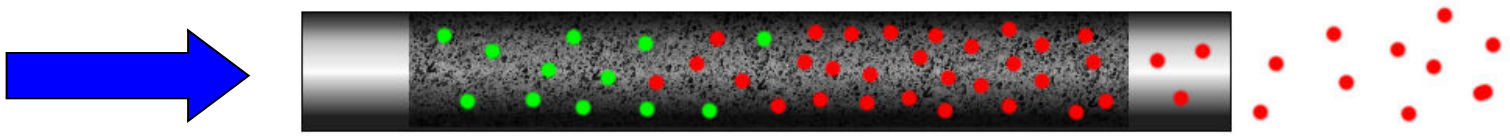
Constant pressure pump

- Flow will vary with differing tube impedance
- Must measure / verify flow when changing tube types as different sorbents have differing impedances

Syringe pump

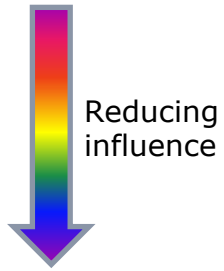
- Simple way to take pumped samples that doesn't require electrical power or re-calibration

Breakthrough



Affected by:

Type of sorbent	stronger sorbent = stronger interaction
Sample volume	lower volume = less risk of breakthrough
Temperature	lower temp. = stronger interaction
Mass or sorbent	more sorbent = more surface area



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Grazie per l'attenzione