SUPELCO
Solutions within.

Trap Selection, Fast GC, and Troubleshooting Strategy for Purge & Trap GC Volatiles

Updated: 18-Jun-2014

Agenda

Overview

Basic P&T Operation

Adsorbents

Trap Selection

Fast GC for Volatiles

Troubleshooting Strategy

Summary / Resources

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sigma-aldrich.com/environmental

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Overview

Why this Topic?

- Purge & trap (P&T) in combination with gas chromatography (GC) is a widely used analytic technique for the analyses of volatiles, particularly in the environmental laboratory industry
- Many analysts performing this work may not fully understand, nor appreciate, the underlying physical/chemical aspects

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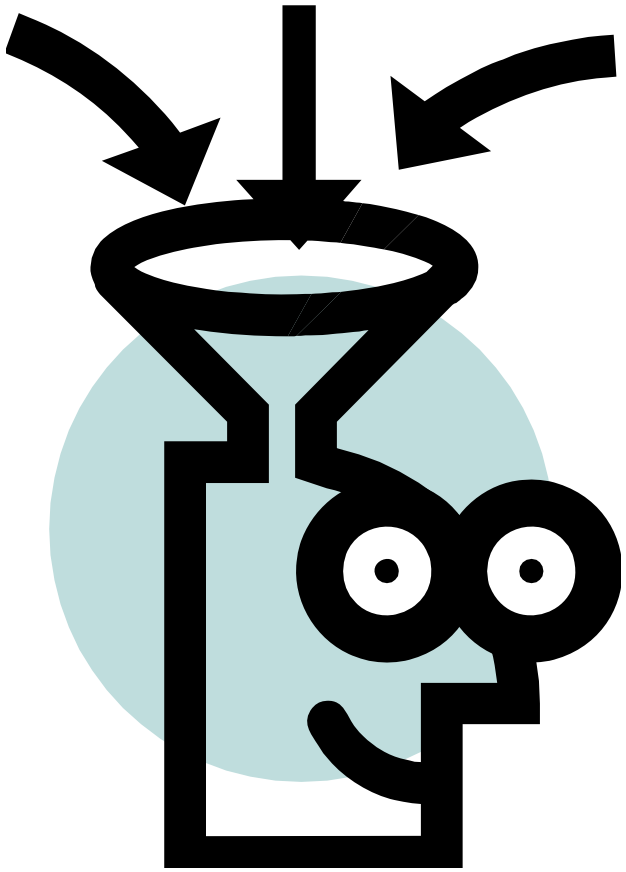
Overview

Goals

- Gain a basic understanding of what adsorbents and traps do
- Learn how to select the proper trap for their applications
- Learn the Principles of Fast GC for volatiles
- Learn how to employ a sound troubleshooting strategy for use when things go wrong



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Basic P&T Operation

Steps Prior to the Start of GC Analysis

- Purge: helium is bubbled through the sample, carrying volatile analytes to the trap
- Dry-purge (optional): dry helium (by-passing the sample) is passed across the trap, removing any residual moisture from the system
- Desorb pre-heat: the trap is heated with no helium flow, causing analytes to be thermally desorbed from the adsorbent(s)

The purge parameters are typically method-specified.

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Basic P&T Operation

Steps During GC Analysis

- Desorb: helium flow is added to the trap in the opposite direction as the purge mode, resulting in analytes being swept onto the head of the GC column
- Bake: the combination of helium flow, heat, and time are used to remove any non-desorbed compounds from the trap, venting them away from the GC, leaving the trap ready for the next sample

The desorb parameters are typically method-specified.

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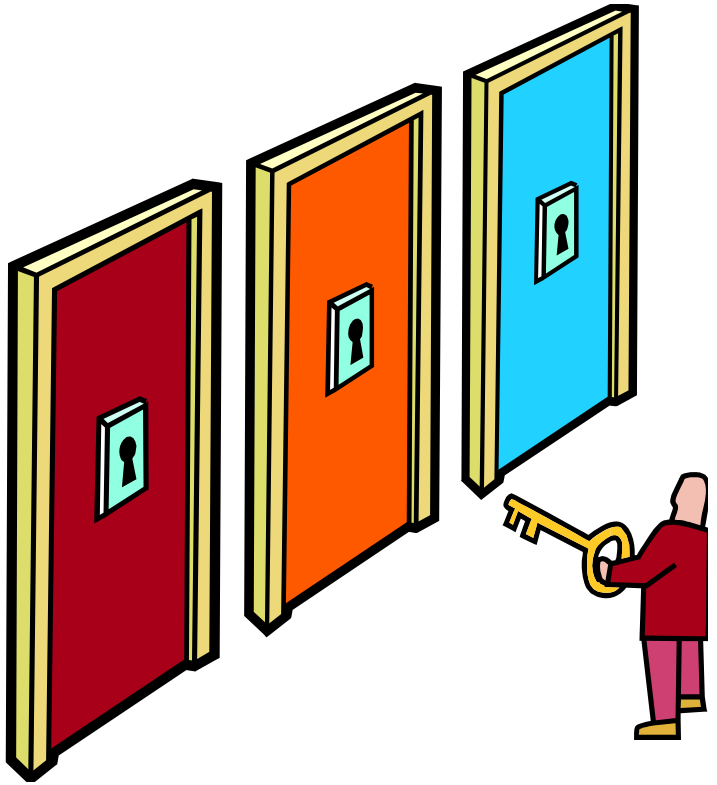
Adsorbents

Commonly Used in Purge Traps

- Carbon adsorbents (Carbopack, Carbotrap, Carboxen, Carbosieve, activated charcoal) trap analytes based on analyte size/shape
- Tenax (a porous polymer) traps analytes predominantly based on analyte size/shape
- Silica gel traps analytes predominantly based on analyte polarity



Each adsorbent has specific advantages and drawbacks.

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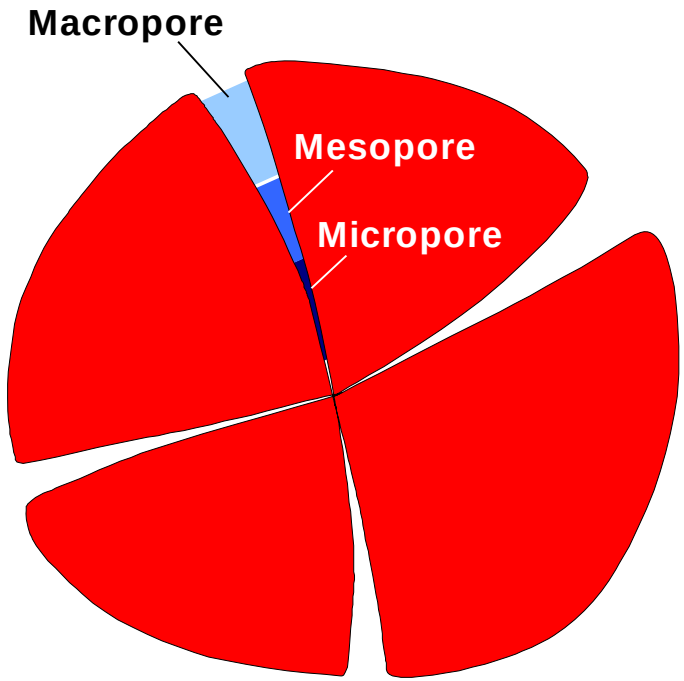
Adsorbents

Particles and Pores

- Pore composition determines adsorption and desorption characteristics
- Specialty carbons can be engineered with:
  - More or less of any pore type to serve a specific purpose
  - Through pores or closed pores, which influences microporous strength
  - Tapered pores (from macro- to meso- to micro-) which increases thermodynamic efficiency



Pore: any cavity present on a solid surface with a depth:width ratio of ~10:1.

Macropore diameter >500 Å; Mesopore diameter 20 – 500 Å; Micropore diameter <20 Å

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Adsorbents

Carbon

Advantages

- High desorption temperature (250 ºC)
  - Rapid transfer to the GC, less band broadening and improved chromatography, especially the gases
  - Better removal of large compounds stuck in pores during the bake step
- Hydrophobic nature: less water trapped and pushed over to the GC
- Can be dry-purged: to remove residual moisture from the system
- Engineered pore composition: application specific

Drawbacks

- The stronger carbon adsorbents (Carboxens and Carbosieves) have a great affinity for methanol
  - Fills pores, leaving none available for gases (blow off back of trap)
  - May displace gases (get adsorbed, get displaced, blow off back of trap)
- Adsorbed methanol will be desorbed during the desorption step, leaving the trap ready for the next run (however, the gases will be biased low for that run)
- Solution is to keep total amount of methanol in samples, standards and blanks <50 µL (<20 µL is desirable)

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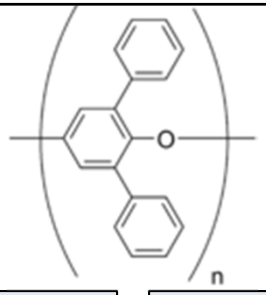
Adsorbents

Tenax



Advantages

- High desorption temperature (250 ºC)
- The ability to trap analytes with a wide range of sizes/shapes (as small as pentane; larger than trichlorobenzene)
- Well-studied (breakthrough volume data for numerous analytes)
- Referenced in many methods and numerous literature and easily obtainable

Drawbacks

- Not suitable for the gases and other small molecules
- Oxidation of the polymer framework can produce high background levels as residual monomers left in the adsorbent are released
  - Detected as aromatic ring compounds
  - Voids can be created, leading to channeling

Tenax is a porous polymer based on 2,6-diphenylene-oxide.

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Adsorbents

Silica Gel

Advantages

- Great affinity for polar analytes (ketones) that are very water-soluble and may not trap well on other adsorbents
- Referenced in many methods and numerous literature
- Easily obtainable

Drawbacks

- Lower recommended desorption temperature (180 ºC)
- Its great affinity for moisture: more water is trapped and subsequently pushed over to the GC
- Cannot be dry-purged without also removing polar analytes

Unlike carbon and Tenax, silica gel traps analytes predominantly based on analyte polarity instead of analyte size/shape.

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Trap Selection

Adsorbent Bed Order (regardless of adsorbents)

- Sample comes into contact with the weakest adsorbent first and the strongest adsorbent last
  - Larger compounds trap on the first bed while the smaller compounds pass through the first bed(s) and are trapped on later bed(s)
  - If a large compound gets onto a strong adsorbent, it may become irreversibly retained
- Traps works similar to a sieve system

Traps can also be designed without a strong adsorbent bed (small compounds blow off the back of the trap during the purge mode).

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Trap Selection

Which Trap is 'Best'?

- No absolute 'best' trap for all situations
- It really depends on
  - The method being followed (the list of analytes)
  - Whether it is desirable to trap small analytes (the gases)
  - The hardware being used
    - Is moisture management available?
    - Is it being used or by-passed?
    - If being used, is it functioning properly?

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Trap Selection

Handling Moisture

- Water is a problem for volatile analyses
  - Chromatographically interferes with the gases
  - Damages quads in GC-MS systems
- Dry-Purge
  - 1-2 minute will remove water to an acceptable level (without loss of adsorbed analytes)
  - 4-5 minute dry-purge will remove virtually all water (with some loss of adsorbed analytes)
- Moisture Management
  - Tubing section which grabs moisture as it passes
  - Must be maintained for proper operation

Note: Traps that contain a silica gel bed cannot be dry-purged.

Note: Do not use a dry-purge with a properly operating moisture management.

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Trap Selection

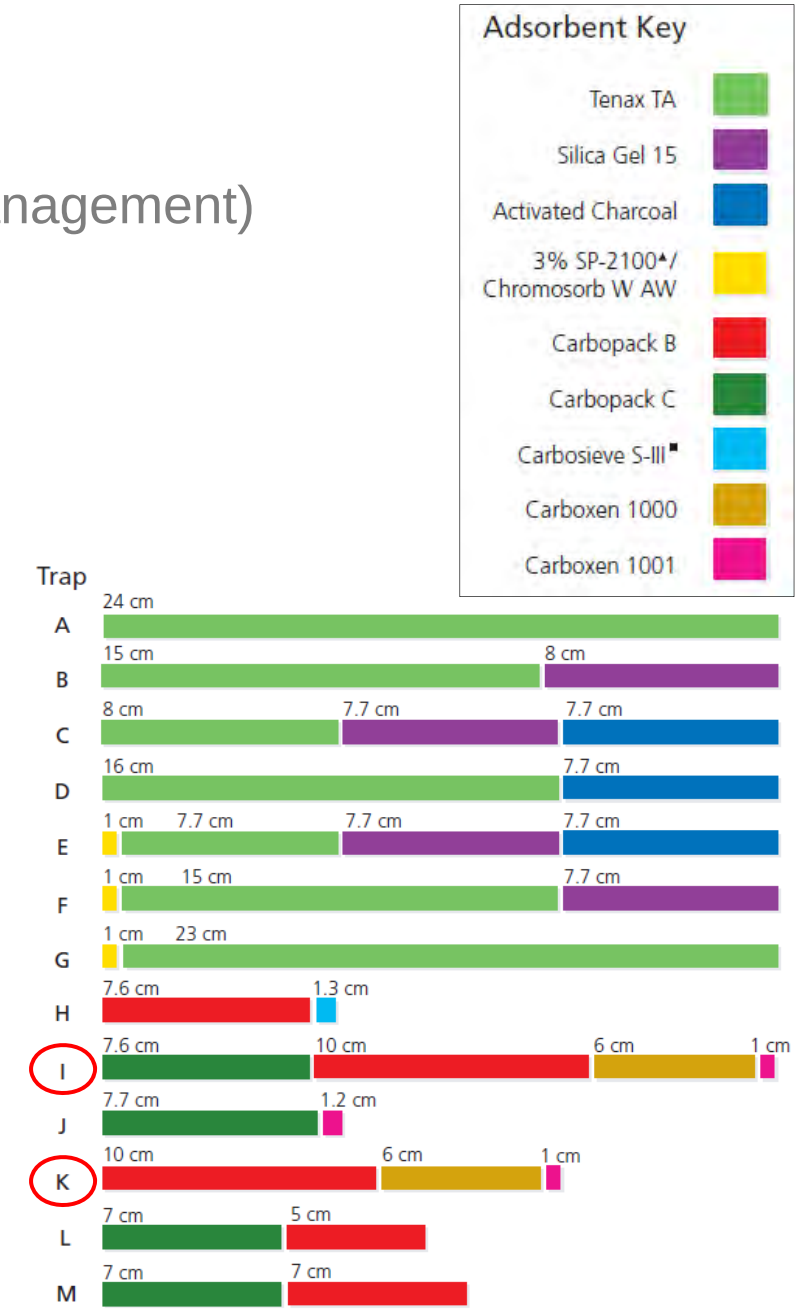
Most Methods (dry-purge; no moisture management)

"K" Trap

- Supelco's most popular trap
- Able to adsorb/desorb small analytes (gases) to less volatile analytes (1,3,5-trichlorobenzene)

"I" Trap

- Has a fourth bed in addition to the three beds in the "K" trap
- The fourth bed is Carbopack C in front
  - Weaker material than any bed in a "K" trap
  - For more efficient adsorption/desorption of larger analytes



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Trap Selection

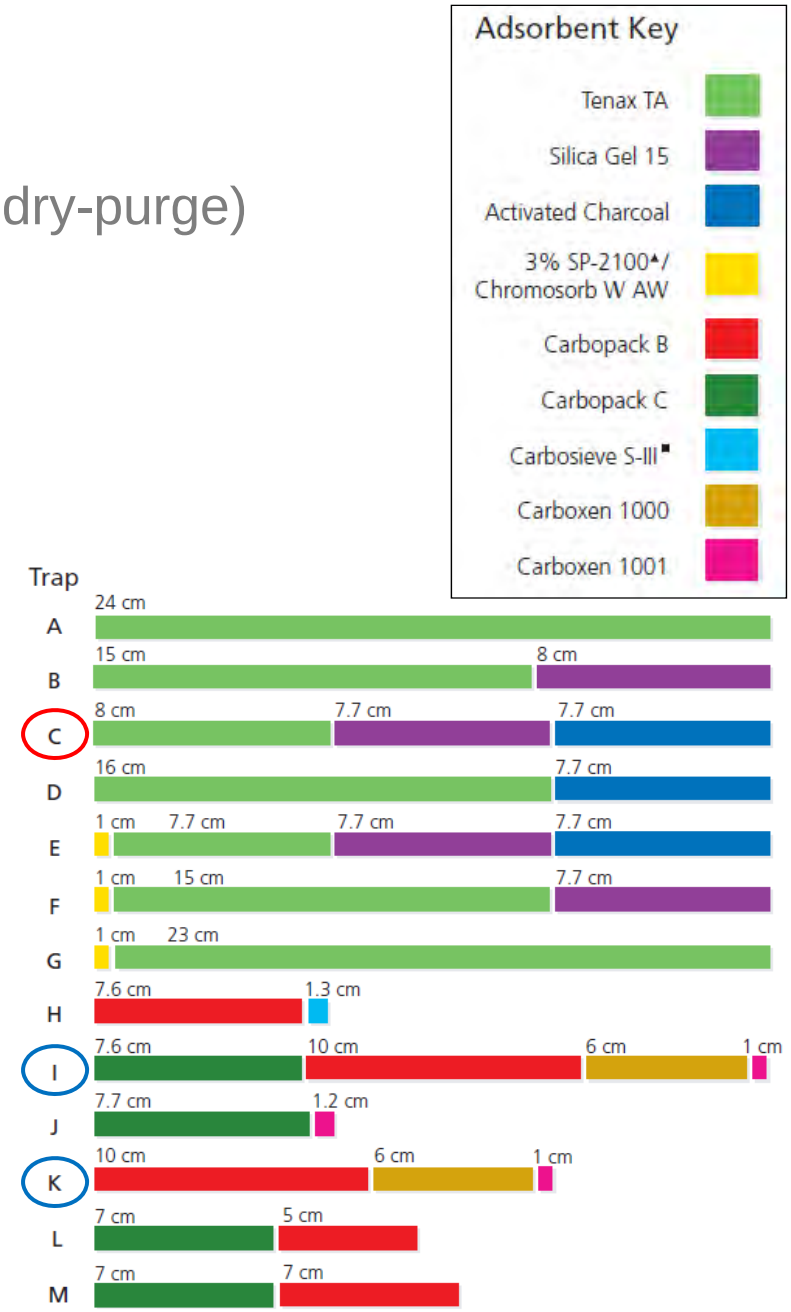
Most Methods (moisture management; no dry-purge)

"C" Trap or "#10" Trap

- Great traps as long as moisture is being managed by the concentrator
- Both traps have similarly arranged beds using a combination of different materials
  - Tenax polymer bed for analytes larger in size than pentane (BTEX and halocarbons)
  - Silica gel bed for polar analytes (ketones)
  - Carbon bed for small analytes (gases)
    - "C" trap has activated charcoal
    - "#10" trap has a stronger carbon

"K" Trap or "I" Trap

- Will also work



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Trap Selection

Medium-Level Soil Methods

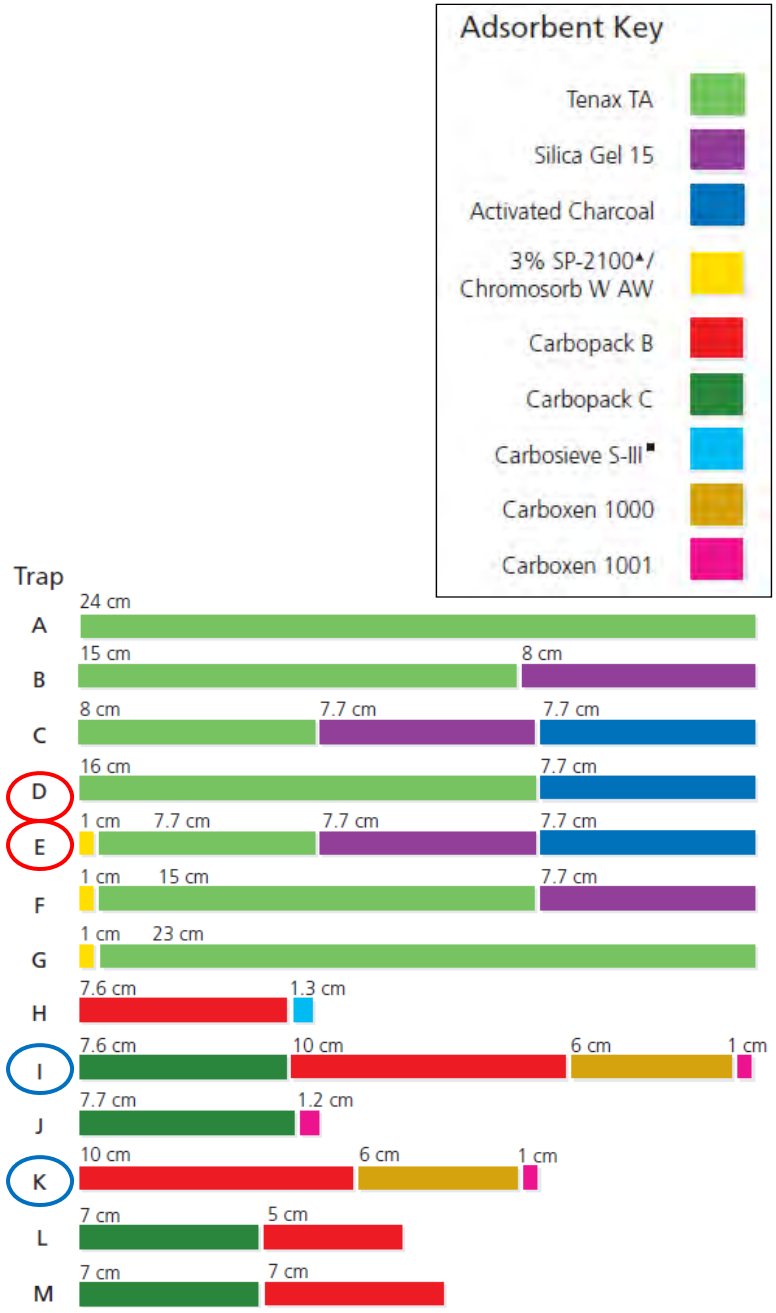
100 µL methanol extract added to 5 mL water

"E" Trap or "D" Trap

- This amount of methanol is not a problem
- Drawbacks are lower (180 ºC) desorption temperature (peaks not as sharp) and increased moisture transferred to the GC
- Try "D" trap if increased moisture is an issue (no silica gel bed)

"K" Trap or "I" Trap

- Will also work



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Trap Selection

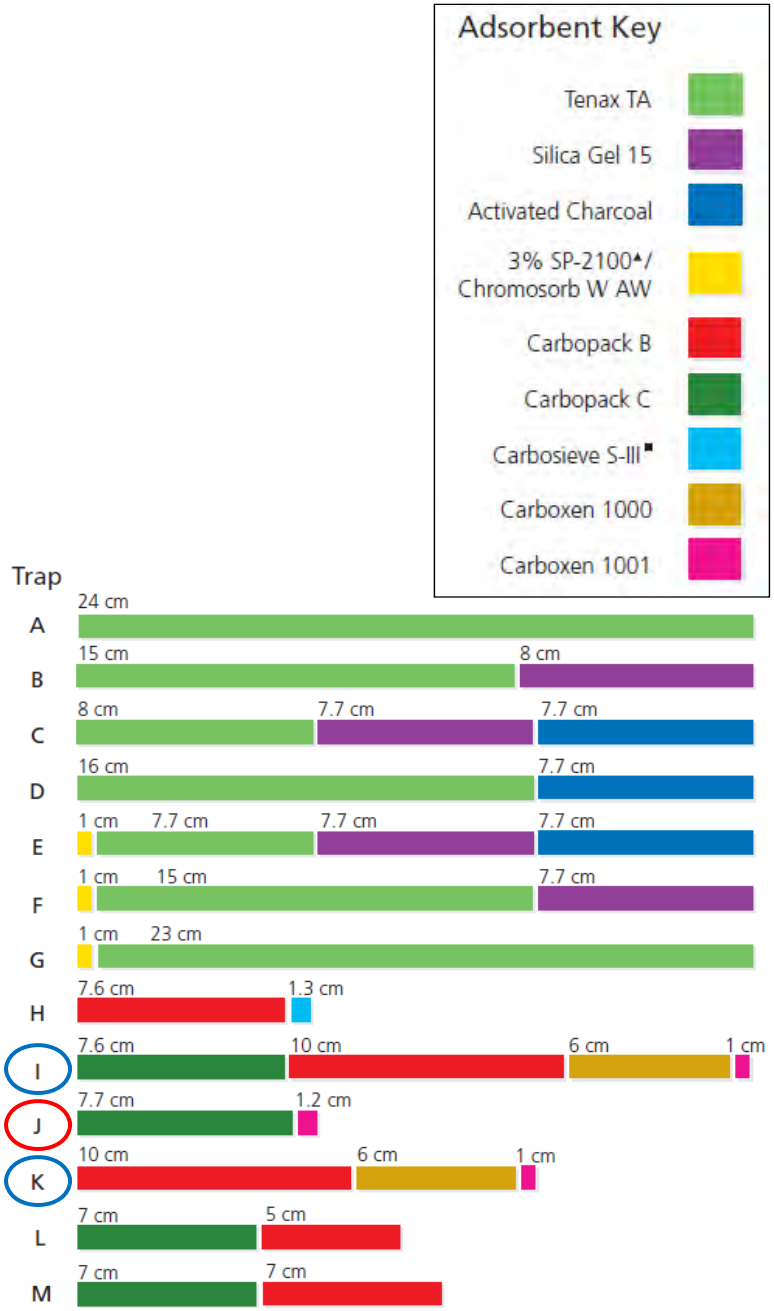
BTEX-Only Methods

“J” Trap

- Designed specifically for BTEX analysis
- Will not adsorb small compounds (methanol, gases, MTBE), which allows for a shorter analytical run

“K” Trap or “I” Trap

- Will also work



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Trap Selection

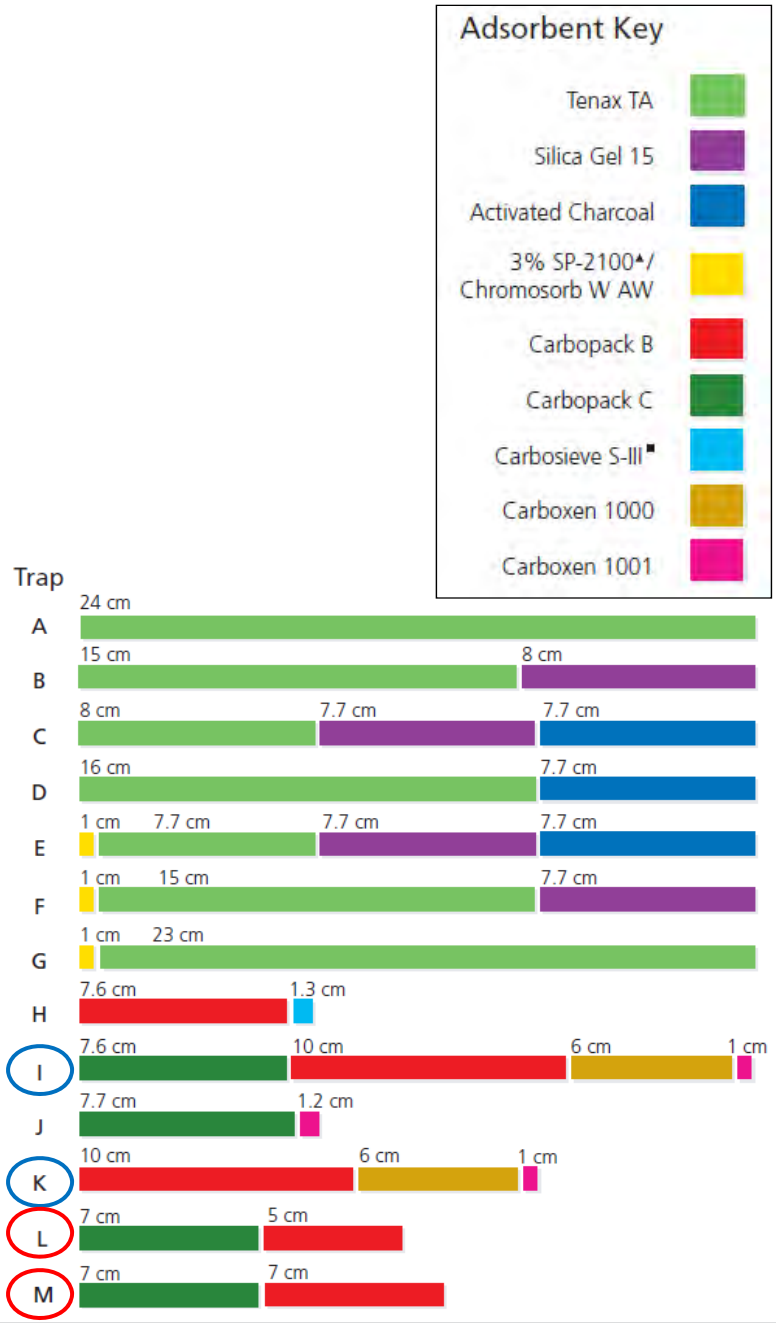
BTEX+MTBE and/or GRO methods

"M" Trap or "L" Trap

- Developed for underground storage tank (UST) and leaking underground fuel tank (LUFT) testing
- Methanol and the gases will not be trapped
  - Use "M" trap for BTEX, MTBE and analytes as small as n-pentane
  - Use "L" trap for BTEX and MTBE

"K" Trap or "I" Trap

- Will also work



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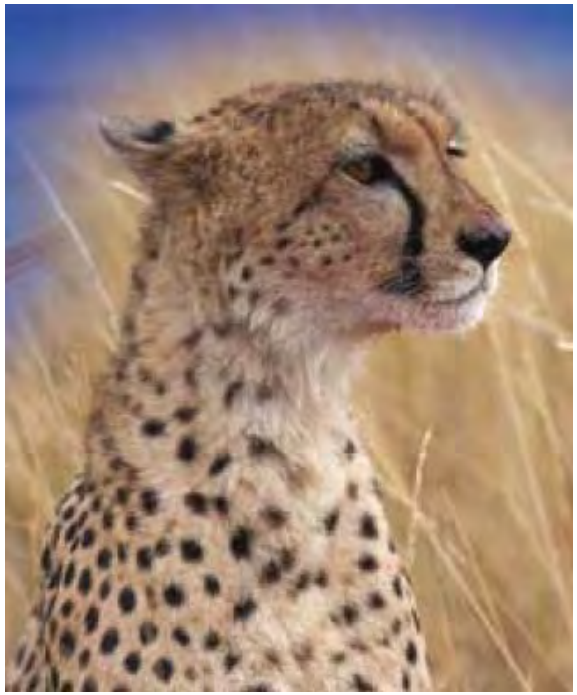
Fast GC for Volatiles

The Principles of Fast GC

- Decrease analysis time by using:
  1. Shorter column
  2. Quicker oven temperature ramp rate
  3. Higher carrier gas linear velocity

But these changes also decrease resolution!

- Offset the decrease in resolution by also using:
  4. Narrow I.D. column
  5. Hydrogen carrier gas
  6. Low film thickness



Fast GC is manipulating a number of column and instrument parameters to provide faster analysis times while maintaining resolution.

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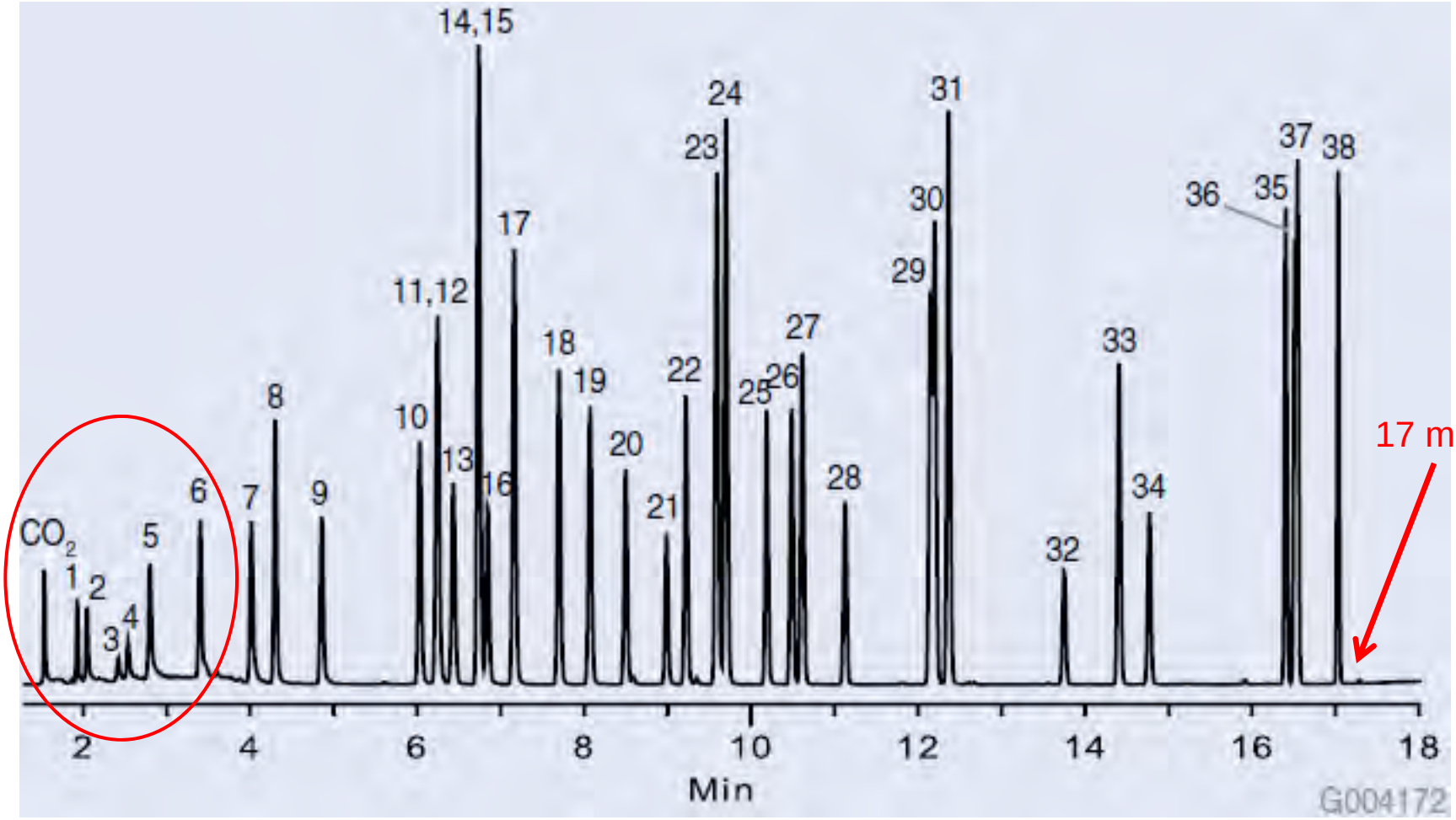
Fast GC for Volatiles

Conventional GC (30 m x 0.25 mm I.D., 1.4 µm), 30:1 Split



17 minute run; poor responses for the gases.

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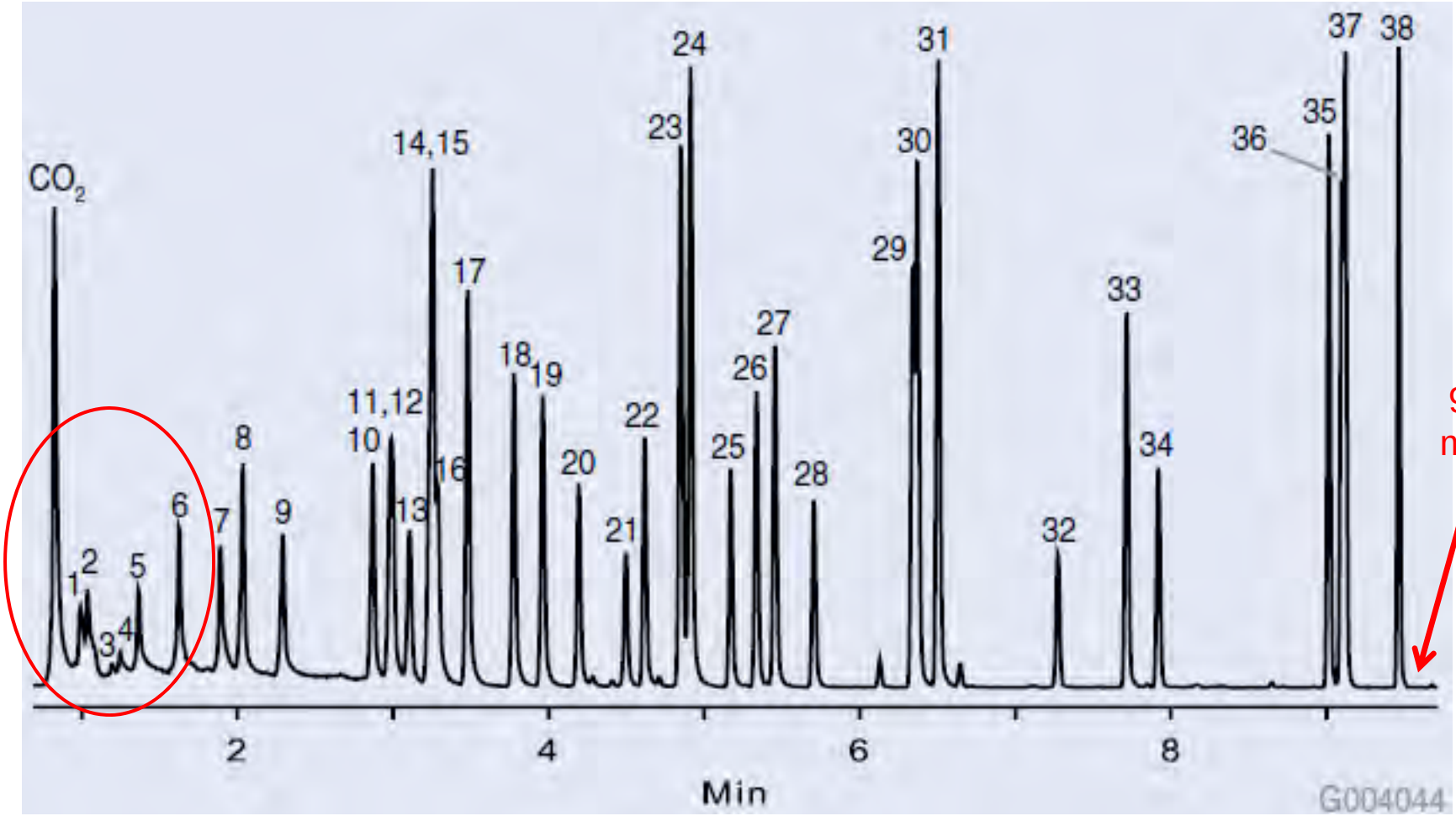
Fast GC for Volatiles

Fast GC (20 m x 0.18 mm I.D., 1.0 µm), 30:1 Split



9.5 minute run; still poor responses for the gases.

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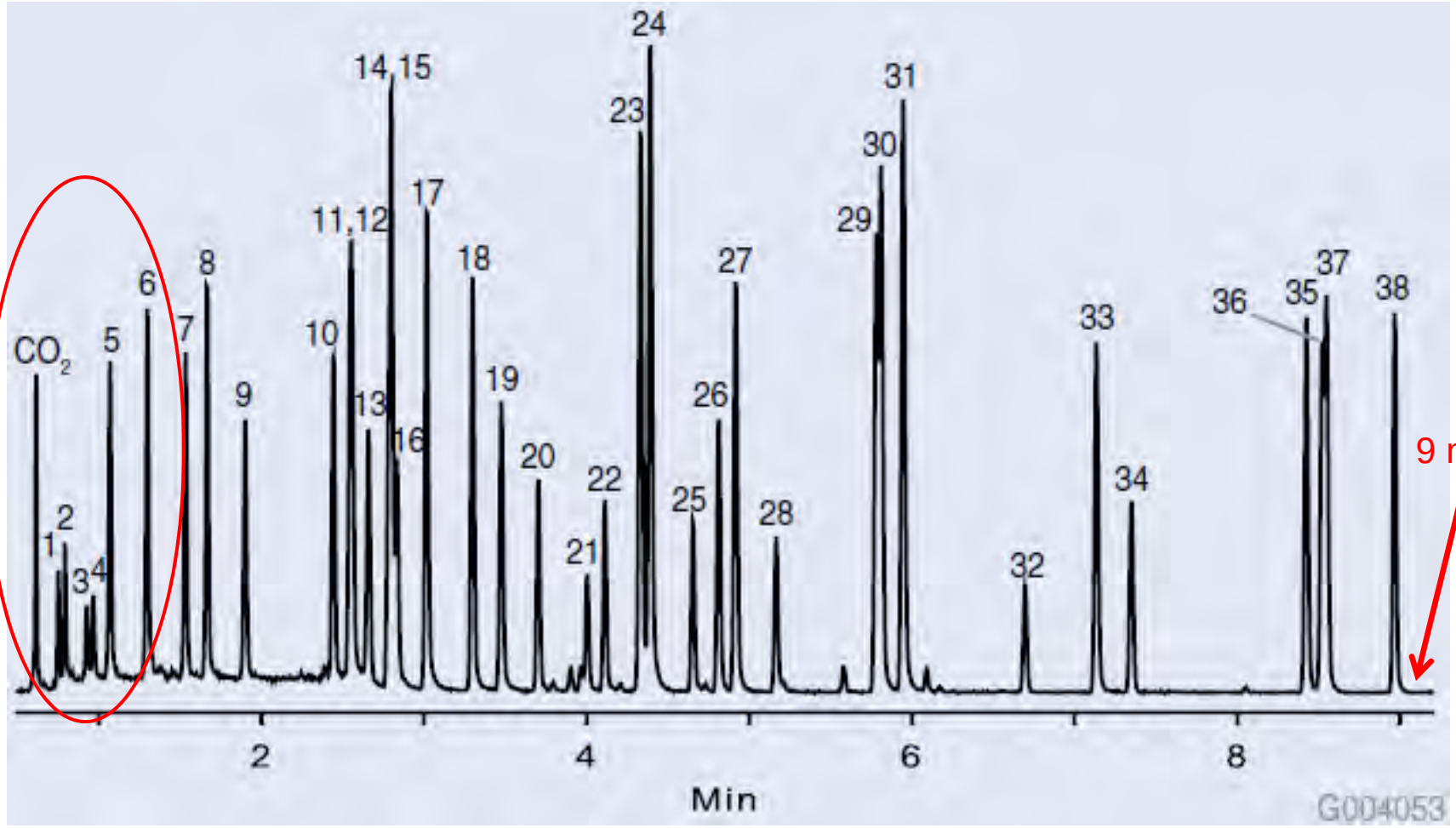
Fast GC for Volatiles

Fast GC (20 m x 0.18 mm I.D., 1.0 µm), 100:1 Split



9 minute run; much improved responses and peak shapes for the gases.

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Fast GC for Volatiles

Modified Column Parameters and Instrument Conditions

	Conventional GC	Fast GC (30:1 split)	Fast GC (100:1 split)
desorption process	40 mL/min at 210 ºC for 2 min	40 mL/min at 210 ºC for 2 min	150 mL/min at 210 ºC for 2 min
column	SPB-624, 30 m x 0.25 mm I.D., 1.4 µm (24255)	SPB-624, 20 m x 0.18 mm I.D., 1.0 µm (28662-U)	SPB-624, 20 m x 0.18 mm I.D., 1.0 µm (28662-U)
oven	40 ºC (2 min), 7 ºC/min to 135 ºC, 30 ºC/min to 230 ºC (3 min)	40 ºC (1 min), 11 ºC/min to 125 ºC, 35 ºC/min to 230 ºC (2 min)	40 ºC (1 min), 11 ºC/min to 125 ºC, 35 ºC/min to 230 ºC (2 min)
carrier gas	helium, 1.1 mL/min	helium, 1.2 mL/min	helium, 1.5 mL/min
injection	30:1 split	30:1 split	100:1 split

Common mistake is not increasing the split when switching to a narrow I.D. column.

Sensitivity maintained because very sharp/narrow peaks are produced (greater signal-to-noise).

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Fast GC for Volatiles

Identical Column Parameters and Instrument Conditions

- sample/matrix: each analyte at 50 ppb in 5 mL water
- purge trap: VOCARB 3000 “K” (24940-U)
- purge: 40 mL/min at 25 ºC for 11 min
- dry purge: 2 min
- desorption pre-heat: 205 ºC
- bake.: 260 ºC for 10 min
- transfer line/valve temp.: 110 ºC
- inj. temp.: 150 ºC
- detector: MS (interface at 200 ºC), 35-400 m/z
- liner: 0.75 mm I.D., direct (SPME) type, straight design

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Fast GC for Volatiles

Peak IDs

1. Chloromethane
2. Vinyl Chloride
3. Bromomethane
4. Chloroethane
5. Trichlorofluoromethane
6. 1,1-Dichloroethene
7. Methylene chloride
8. trans-1,2-Dichloroethene
9. 1,1-Dichloroethane
10. Chloroform
11. Dibromofluoromethane (surr.)
12. 1,1,1-Trichloroethane
13. Carbon tetrachloride
14. 1,2-Dichloroethane-d4 (surr.)
15. Benzene
16. 1,2-Dichloroethane
17. Fluorobenzene (I.S.)
18. Trichloroethene
19. 1,2-Dichloropropane
20. Bromodichloromethane
21. 2-Chloroethyl vinyl ether
22. cis-1,3-Dichloropropene
23. Toluene-d8 (surr.)
24. Toluene
25. trans-1,3-Dichloropropene
26. 1,1,2-Trichloroethane
27. Tetrachloroethene
28. Dibromochloromethane
29. Chlorobenzene-d5 (I.S.)
30. Chlorobenzene
31. Ethylbenzene
32. Bromoform
33. 4-Bromofluorobenzene (surr.)
34. 1,1,2,2-Tetrachloroethane
35. 1,3-Dichlorobenzene
36. 1,4-Dichlorobenzene-d4 (I.S.)
37. 1,4-Dichlorobenzene
38. 1,2-Dichlorobenzene

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Fast GC for Volatiles

Taking Advantage of a <10 Minute GC Run

- Ballistic Dry-Purge and Bake
  - EST: Encon Evolution
  - Tekmar: Stratum PTC
  - Tekmar: Velocity XPT

- Two Concentrators per GC
  - EST: Centurion WS
  - EST: PT^2
  - OI: PT Express

Example equipment that allows P&T to catch up with improvements in GC speed.

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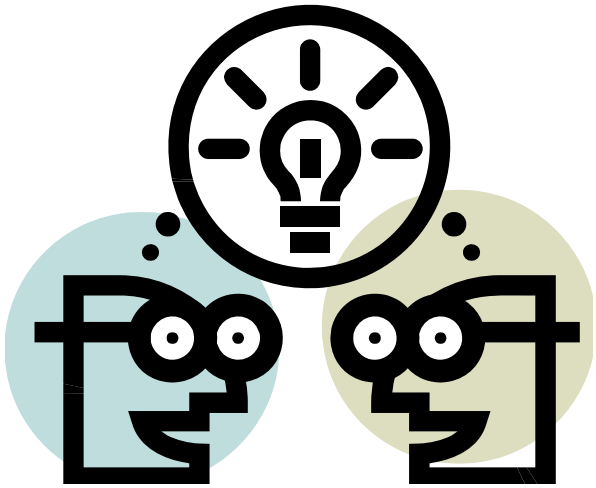
Troubleshooting Strategy

Best Practices

Documentation

- Use maintenance log books
- May save weeks of troubleshooting



Make one change at a time

- To uncover root cause
- Multiple changes may offset each other

Keep a ‘good’ trap

- Remove and store the trap as a reference for when issues occur at a later time
- Replace the caps, place in original shipping container, label properly, and protect from vibration

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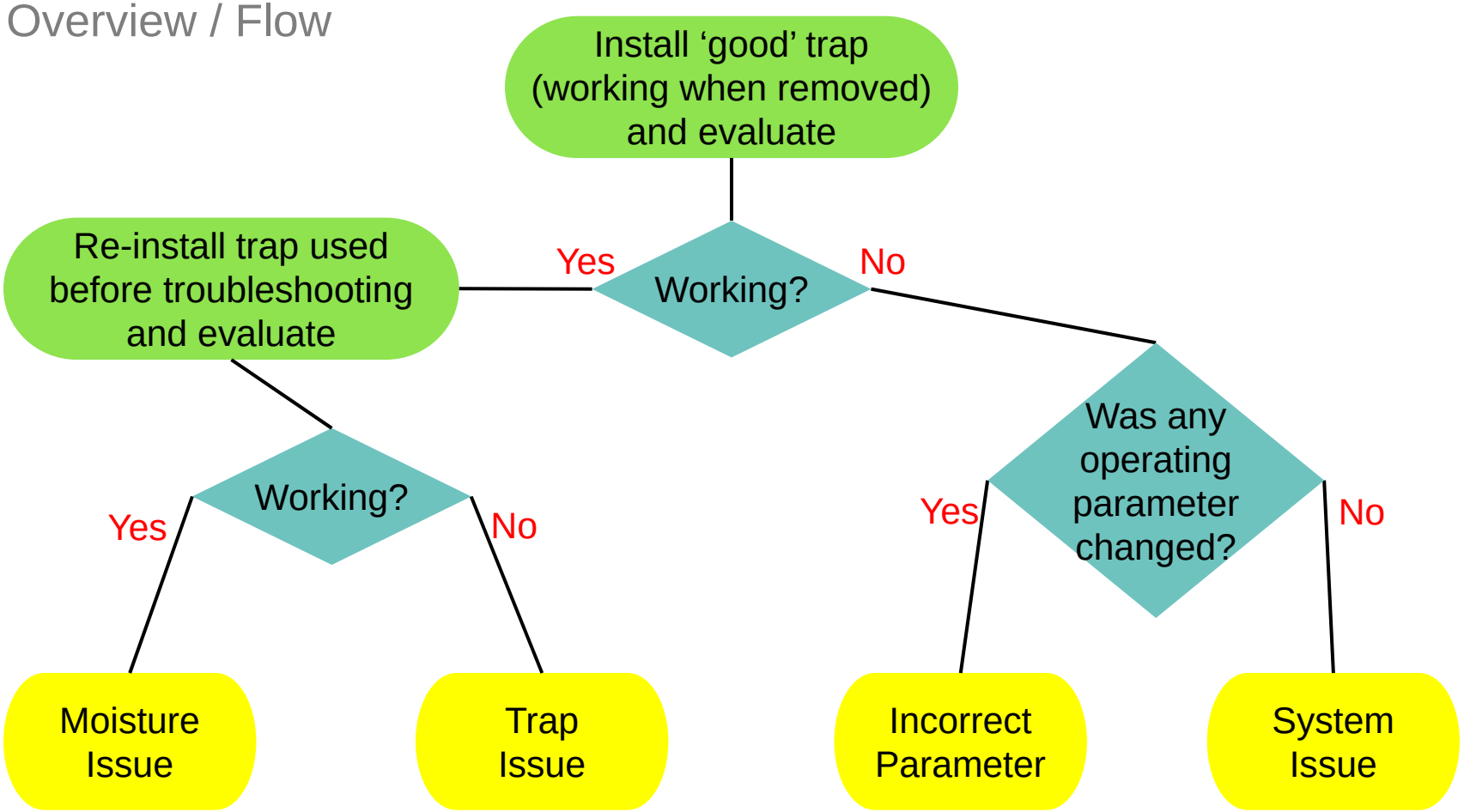
Troubleshooting Strategy

Overview / Flow



Supelco Technical Service strategy successfully used to help many customers over many years.

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Troubleshooting Strategy

Potential Cause: Moisture Issue

- As samples are purged, moisture is carried into the concentrator
- If active sites or cold spots develop, moisture will accumulate, causing
  - Low/no response of the more water-soluble analytes
  - Decreased I.S. response throughout the tune window
- Opening the system allowed the moisture to escape
  - When the non-working trap was removed
  - Also why the non-working trap now seems to work

Perform preventative maintenance on moisture management or find/eliminate active site and/or cold spot.

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Troubleshooting Strategy

Potential Cause: Trap Issue

Try an elevated bake-out

- Make sure that a PTFE ferrule is NOT installed on the trap (use a VESPEL or graphite ferrule able to withstand 400 ºC or higher)
- Bake trap with 40 mL/min helium at 375 ºC for 4 hours
- Cool the trap down and discard the ferrule
- Replace with a new ferrule (whatever normally used)
- Evaluate performance (if it works, great; if not, it is a 'bad' trap)

Note: This procedure is only for use with a Supelco carbon trap (H, I, J, K, L, or M). These traps can easily handle this temperature. The reason that Supelco does not list this on the data sheet is that many customers use PTFE ferrules (maximum temperature is 300 ºC) and we do not want to be responsible for melted PTFE stuck in instruments. Customers must verify that their instrument can handle this temperature.

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Troubleshooting Strategy

Potential Cause: Incorrect Parameter

- Autosampler, concentrator, GC inlet, column dimension, and detector combinations are quite large
- Impossible to write up what each individual parameter should be (depends on hardware being used)
- Recommend contacting a Technical Service (have complete list of all operating parameters handy)
  - Concentrator manufacturers (CDS, EST, O.I., Tekmar)
  - Trap manufacturers (CDS, EST, O.I., Supelco, Tekmar)
  - System manufacturers (Agilent, PerkinElmer, Shimadzu, Thermo, Varian)
  - Third-party (MDL [www.ecsmdl.com])

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Troubleshooting Strategy

Potential Cause: System Issue

Make 50 and 200 ng/µL standards (with I.S./surr.) in methanol and perform the following five runs

1. Inject 0.5 µL (200 ng/µL) into the GC (if accessible)
2. Inject 2 µL (50 ng/µL) into the top of the trap; step to desorb pre-heat
3. Inject 2 µL (50 ng/µL) into the top of the trap; dry-purge 5 minutes then step to desorb pre-heat
4. Inject 2 µL (50 ng/µL) into 5 mL water; set-up manually on concentrator (do not use autosampler)
5. Inject 2 µL (50 ng/µL) into 5 mL water; set-up manually on the autosampler

A drastic loss of response indicates where the issue resides.

Focus further troubleshooting in this area.

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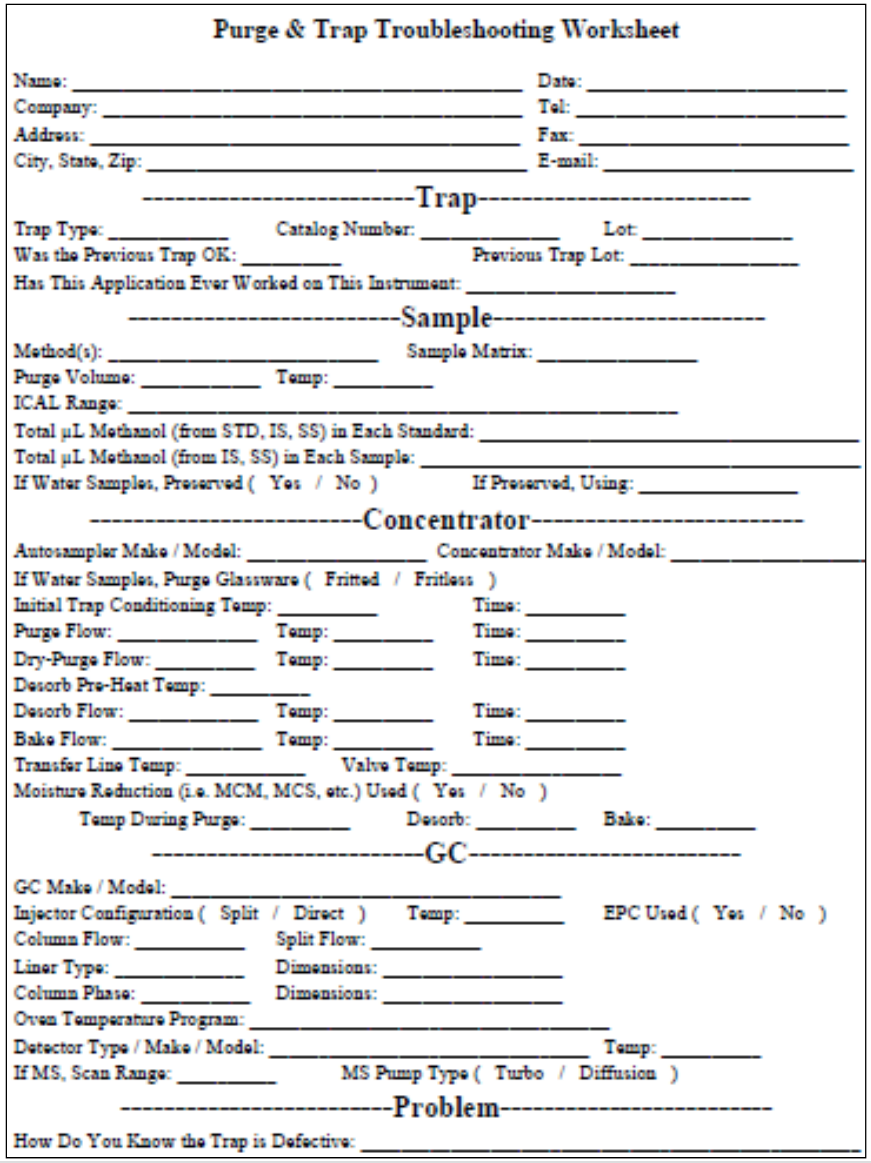
Troubleshooting Strategy

Troubleshooting Worksheet (T596001)

- Should work for any combination of:
  - Trap type
  - Sample matrix
  - Concentrator make/model
  - Moisture reduction strategy
  - GC conditions
- Fill out and use for phone, fax, or email correspondence with any of the Technical Services



Purge & Trap Troubleshooting Worksheet

Name: _____ Date: _____
Company: _____ Tel: _____
Address: _____ Fax: _____
City, State, Zip: _____ E-mail: _____

----------Trap----------

Trap Type: _____ Catalog Number: _____ Lot: _____
Was the Previous Trap OK: _____ Previous Trap Lot: _____
Has This Application Ever Worked on This Instrument: _____

----------Sample----------

Method(s): _____ Sample Matrix: _____
Purge Volume: _____ Temp: _____
ICAL Range: _____
Total µL Methanol (from STD, IS, SS) in Each Standard: _____
Total µL Methanol (from IS, SS) in Each Sample: _____
If Water Samples, Preserved (Yes / No) If Preserved, Using: _____

----------Concentrator----------

Autosampler Make / Model: _____ Concentrator Make / Model: _____
If Water Samples, Purge Glassware (Fritted / Fritless)
Initial Trap Conditioning Temp: _____ Time: _____
Purge Flow: _____ Temp: _____ Time: _____
Dry-Purge Flow: _____ Temp: _____ Time: _____
Desorb Pre-Heat Temp: _____
Desorb Flow: _____ Temp: _____ Time: _____
Bake Flow: _____ Temp: _____ Time: _____
Transfer Line Temp: _____ Valve Temp: _____
Moisture Reduction (i.e. MCM, MCS, etc.) Used (Yes / No)
Temp During Purge: _____ Desorb: _____ Bake: _____

----------GC----------

GC Make / Model: _____
Injector Configuration (Split / Direct) Temp: _____ EPC Used (Yes / No)
Column Flow: _____ Split Flow: _____
Liner Type: _____ Dimensions: _____
Column Phase: _____ Dimensions: _____
Oven Temperature Program: _____
Detector Type / Make / Model: _____ Temp: _____
If MS, Scan Range: _____ MS Pump Type (Turbo / Diffusion)

----------Problem----------

How Do You Know the Trap is Defective: _____

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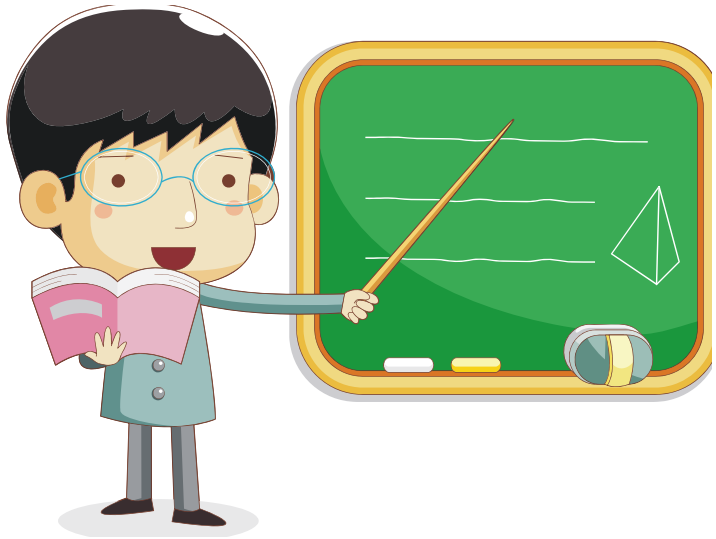
Summary / Resources

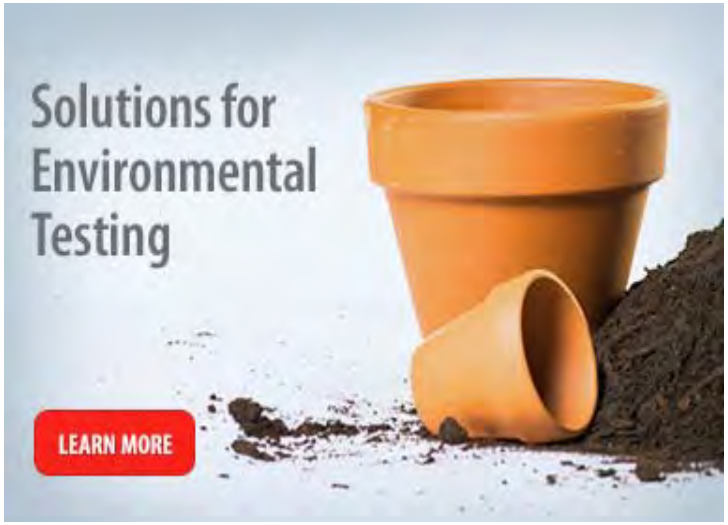
Summary

- Select the proper trap for the application
- “K” trap will work for most applications
- Employ Fast GC to increase throughput
- Use a sound troubleshooting strategy



Web Site (*sigma-aldrich.com/environmental*)

- Sections for organics, metals, wet chemistry, sample collection, chromatograms, and newsletters
- From sample collection through sample preparation to analysis, we have you covered



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Supelco site
Bellefonte, Pennsylvania (USA)


Fluka site
Buchs (Switzerland)

Thank You!