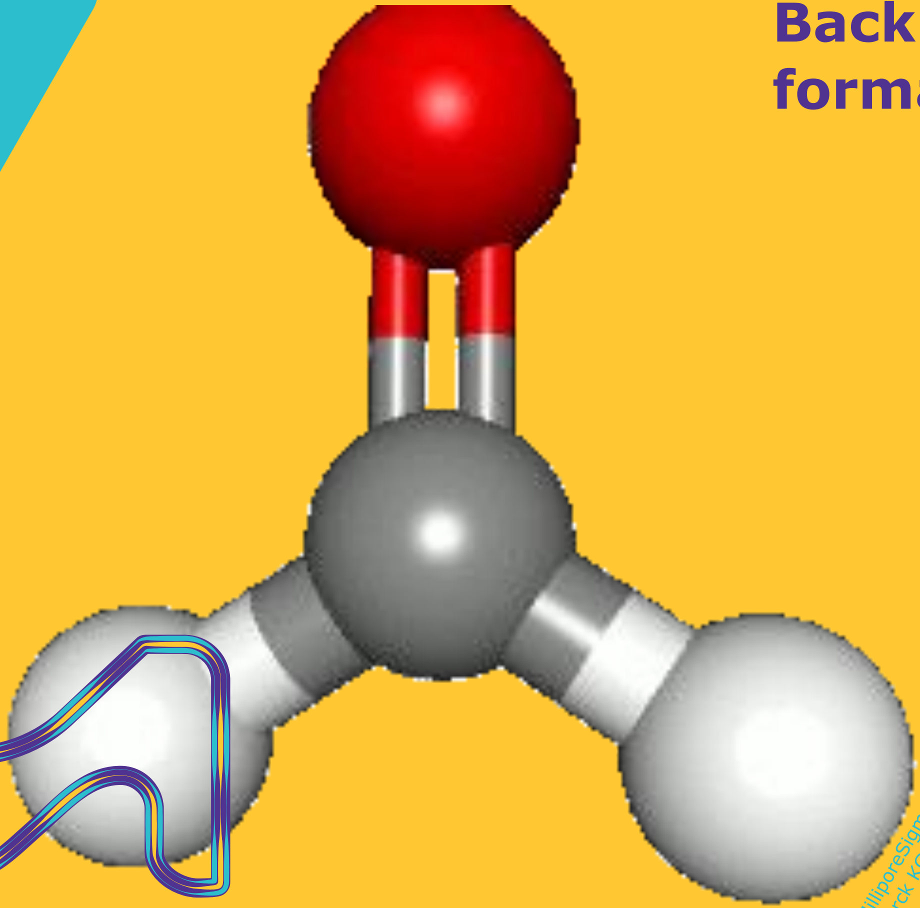
Sample Collection & Analysis of Carbonyls in Air

Back to Basics – the sampling workflow for formaldhyde and other carbonyls in air



Gary Oishi – R & D Scientist
October 17, 2018

Topics

- Chemistry of Carbonyls
- Why we sample carbonyls in air
- Choosing the Sampling Device
  - -Active
  - -Passive
- Making Connections
- Calibration basics
- Sample Prep
- Sample Analysis

Carbonyls

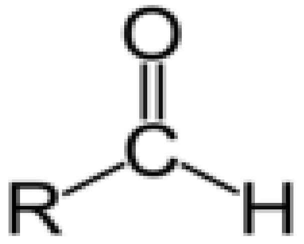
Chemistry of Carbonyls

What are they?

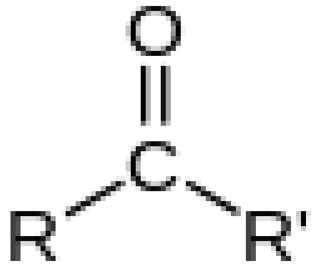
Organic compounds that possess a carbon with a double bonded oxygen. Aldehydes and ketones are the simplest compounds in this group

Formaldehyde where the R groups are hydrogen where R = H

Ketone carbonyl group (CO) is bonded to two carbons



Aldehyde



Ketone

Because of their similar chemical structures, aldehydes and ketones can often be sampled and analyzed with the same sample collection devices.

Why we sample for carbonyls in air
Health Hazards

- Formaldehyde is a suspected carcinogen, it is used in many industry manufacturing processes, but it is also present in residential environments and in the outdoors from auto emissions and other industrial sources.
- Formaldehyde also is an irritant of the eyes, nose and throat as well as other health effects from prolonged exposure – sleep disorders, kidney injury, reproductive disorders and endocrine disorders in men and women
- There are other aldehydes that workers are exposed to but there is limited information on their adverse health effects compared to formaldehyde.

OSHA Formaldehyde Standard (29 CFR 1910.1048)

- Employees must be trained, repeated annually (Hazardous Communication Plan)
- Provide engineering controls and PPE w/fit testing data
- Medical Surveillance for formaldehyde exposure
- Formaldehyde monitoring records with data, and if not monitoring the reasons why
- Must keep associated records for 30 years

Why we sample for carbonyls in air
Safety Data Sheets (SDS)

- Hazard Communication Standard (HCS) (29 CFR 1910.1200(g)), revised in 2012, requires that the chemical manufacturer, distributor, or importer provide Safety Data Sheets (SDSs) (formerly MSDSs or Material Safety Data Sheets) for each hazardous chemical to downstream users to communicate information on these hazards.

- The information contained in the SDS is largely the same as the MSDS, except now the SDSs are required to be presented in a consistent user-friendly, 16-section format

- SDS must also contain Sections 12 through 15, to be consistent with the UN Globally Harmonized System of Classification and Labeling of Chemicals (GHS), but OSHA will not enforce the content of these sections because they concern matters handled by other agencies

2.2 GHS Label elements, including precautionary statements

Pictogram

Signal word	Danger
Hazard statement(s)	
H226	Flammable liquid and vapour.
H301 + H311 + H331	Toxic if swallowed, in contact with skin or if inhaled.
H314	Causes severe skin burns and eye damage.
H317	May cause an allergic skin reaction.
H341	Suspected of causing genetic defects.
H350	May cause cancer.
H370	Causes damage to organs (Eyes).

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Control parameters

Components with workplace control parameters

Component	CAS-No.	Value	Control parameters	Basis
Formaldehyde	50-00-0	TWA	0.1 ppm	USA. ACGIH Threshold Limit Values (TLV)
	Remarks	Dermal Sensitization Respiratory sensitization Upper Respiratory Tract irritation Eye irritation Upper Respiratory Tract cancer 2017 Adoption Confirmed human carcinogen		
		STEL	0.3 ppm	USA. ACGIH Threshold Limit Values (TLV)
		Dermal Sensitization Respiratory sensitization Upper Respiratory Tract irritation Eye irritation Upper Respiratory Tract cancer 2017 Adoption Confirmed human carcinogen		
		TWA	0.016 ppm	USA. NIOSH Recommended Exposure Limits
		Potential Occupational Carcinogen See Appendix A		
		C	0.1 ppm	USA. NIOSH Recommended Exposure Limits
		Potential Occupational Carcinogen See Appendix A 15 minute ceiling value		
		PEL	0.75 ppm	OSHA Specifically Regulated Chemicals/Carcinogens
		1910.1048 This standard applies to all occupational exposures to formaldehyde, i.e. from formaldehyde gas, its solutions, and materials that release formaldehyde OSHA specifically regulated carcinogen		

Why we sample for carbonyls in air

Exposure Limits Table for Aldehydes (select) and associated Analytical Methods

Exposure Limits - Aldehydes (select)						Measurement Methods		
	CAS No.	Formula	OSHA PEL	NIOSH REL	ACGIH	HPLC	GC	Other
Formaldehyde	50-0-0	HCHO	TWA 0.016 ppm; STEL 2.0 ppm	TWA 0.75 ppm; C 0.1 ppm (15 min)	C 0.3 ppm	NIOSH 2016; OSHA 1007	NIOSH 2541; OSHA 52	NIOSH 3500 (VIS); NIOSH 3800 (DR); OSHA ID205 (VIS)
Acetaldehyde	75-07-0	CH_3CHO	OSHA REL 200 ppm	Lowest ppm	C 25 ppm	NIOSH 2018; NIOSH 3507	NIOSH 2538; OSHA 68	
Acrolein	107-02-8	CH_2=CHCHO	TWA 0.1 ppm	TWA 0.1 ppm; STEL 0.3 ppm	TWA 0.1 ppm; STEL 0.3 ppm		NIOSH 2501; OSHA 52	
TWA = Time-weighted average; STEL = Short-Term Exposure Limit; C = Ceiling								

- Numerous methods exist from OSHA and NIOSH, which method do I use?
- Two types of sampling media are most commonly used:
  - 2,4-dinitrophenylhydrazine (2,4-DNPH) on silica gel or FLORISIL® (HPLC-UV)
  - 2-(hydroxymethyl) piperdine (2-HMP) on Amberlite® XAD-2 (GC)

Choosing the Sampling Device
Questions to be Considered

- What is the scope for sampling (i.e. exposure to concentrations greater than action levels)?
- Is there an approved method for what I’m trying to do?
- What if there are multiple methods available?

Answering these questions can help in pointing you to making an appropriate decision

Choosing the Sampling Device

Types of Sampling Media in Agency Methods

Active Sampling (with a pump)

One of the most common types of sampling media is 2,4-dinitrophenylhydrazine (DNPH) coated silica gel which converts the carbonyl to a hydrazine derivative. It is analyzed in the laboratory by HPLC-UV

Alternative methods for sampling formaldehyde specify sampling devices containing 2-(hydroxymethyl) piperdine (2-HMP) reagent on Amberlite® XAD-2. It is analyzed in the laboratory by GC.

Note: You can source similar devices from your analytical services laboratory partner or directly from a global supplier of industrial hygiene products.

Choosing the Sampling Device
Types of Sampling Media in Agency Methods

Overview of 2,4-DNPH Type Samplers

- NIOSH 2016 specifies plastic holder containing 350 mg of 150-250 µm (60-100 mesh) silica gel coated with 1.0 mg of acidified 2,4-dinitrophenylhydrazine. Pressure drop across sampler should be less than 28 inches of water (7 kPa) at 1.5 L/min. Samplers are commercially available
  - Appendix B specifies use of a glass sealed tube containing two beds of adsorbent 300 mg (front) and 150 mg (back) for breakthrough

All devices in this range contain 350 mg 2,4-DNPH

Multiple device choices
NIOSH 2016 Also specified in EPA TO-11A, EPA IP-6A, ASTM D5197, EPA 100

NIOSH 2016 Appendix B
available in 6 mm I.D and 8 mm ID

Choosing the Sampling Device

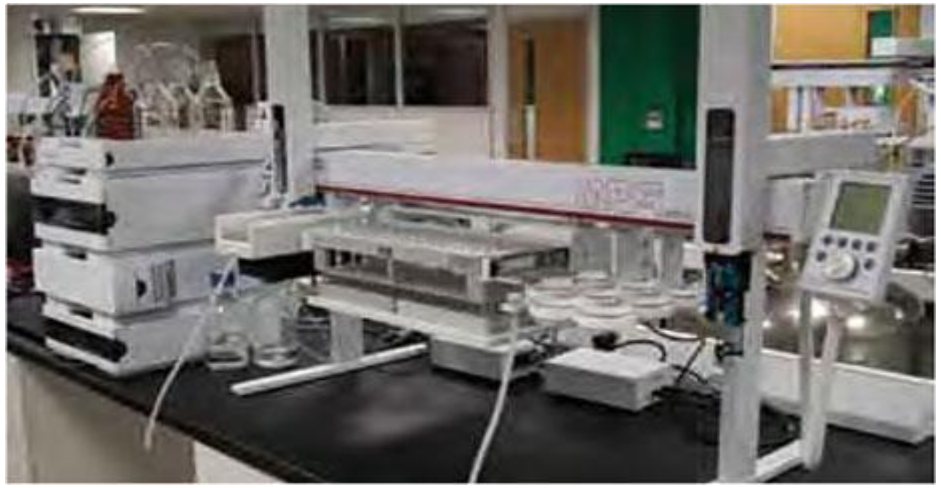
A Closer Look at 2,4-DNPH Sampling Devices

Why so many choices if 350-mg of 2,4-DNPH is the same in each sampling device?
Collection capacity: 75 µg carbonyls

- Users have different end-fitting preferences – connecting to an air sampling pump piggy-back sampling and for extraction and analysis
- Plastic syringe barrels act as *reservoir* for the elution solvent, which saves the laboratory time extracting the aldehydes and ketones from the device.
- Plastic syringe barrel types are amenable to *automated sample preparation* and analysis, whereas glass cartridges sealed at both ends require each adsorbent bed to removed, extracted and analyzed separately

Slip Luer Tip

Luer Lock Tip



Automated Sample Prep and Analysis (HPLC)

Sampling carbonyls in high concentration environments

Choosing the Sampling Device

Sampling in High Concentration Environments – up to 6400 µg carbonyls

- Higher DNPH loading (up to 3X greater)
- 2,4-DNPH coated on silica gel
- 3, 6, and 20 mL syringe barrels
- 350 mg, 1 g, and 10 g bed weights

These devices are necessary when you know you have a high concentration environment and need to access the concentration. *Suitable for aldehydes and ketones.*

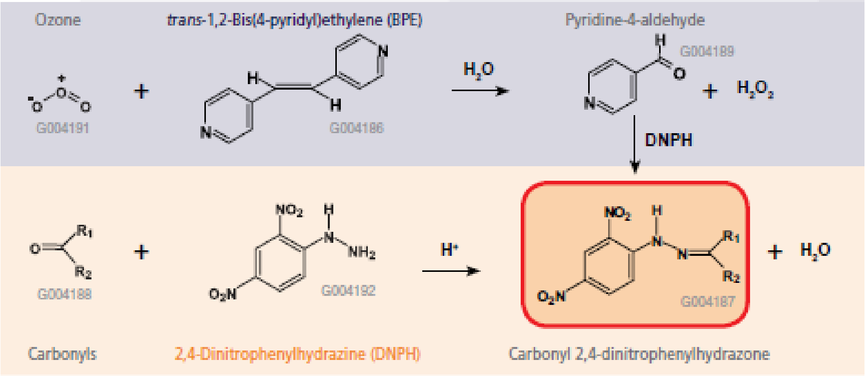
Sampling Interference – Ozone

Sampling Interference - Ozone
Scrubbing Device - Reversible & Rezorian

- Eliminate negative interference
- 1.5 g of Potassium Iodide
- Easy attachment
- 100,000 ppb/hr capacity

Sampling Interference - Ozone
Scrubbing Device - Rezorian BPE-DNPH Cartridge

- Dual-layer design - 130 mg BPE bed weight (for scrubbing ozone), 270 mg 2,4-DNPH for carbonyls
- Luer lock syringe end-fittings
- Not susceptible to humidity, no need for separate ozone scrubber in the sampling train



Proprietary design, not available from other manufacturers

Passive sampling

Passive Sampling

Why Choose Passive vs Active Sampling Devices

- Passive samplers have many advantages over active samplers because they are small, lightweight and do not require complex training to collect samples.
- They are also less expensive than active samplers because they require no sampling pumps and flow meters calibration, and can be used without interrupting workers' ordinary tasks.
- Passive sampling devices can be used for personal sampling from 15 minutes to 8 hours but also can be used for risk assessment 24-hr to long term exposures, up to 3 weeks
- There are certain situations where active sampling is preferred. Air flow across passive samplers has to be sufficient to exchange the analyte concentration in the boundary layer. Active sampling is more forgiving since it continually replaces the air at the face of the sampler. In addition, OSHA recommends using active sampling when monitoring exposures to formaldehyde resulting from the use of formalin solutions. This issue is discussed in detail in OSHA method 1007.

Disadvantages: The contaminant of interest uptake (sampling rate) cannot be *modified because it pre-determined by the device design

The Uptake rate can be modified for radiello type samplers for lesser or greater sampling rates by changing the diffusive body and applying a calculation provided by the manufacturer.

Passive Sampling
Passive Sampling Overview

- Fick's Law

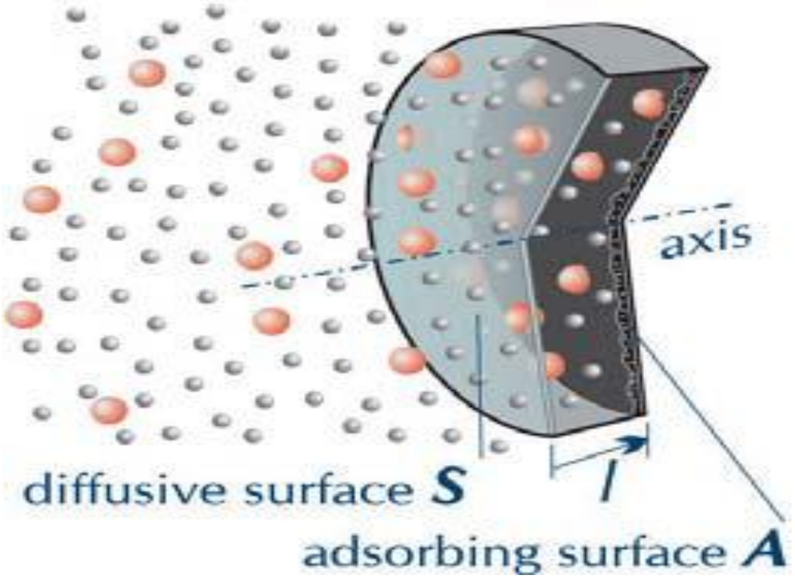
$$\frac{dm}{dt} = D \bullet S \bullet \frac{dc}{dl}$$

$\frac{dm}{dt}$ = rate of diffusion

$\frac{dc}{dl}$ = concentration gradient

D = diffusion coefficient

S = diffusive surface



Passive Sampling

Passive Sampling Overview

$$\frac{dm}{dt} = D \bullet S \bullet \frac{dc}{dl}$$

Integrating the equation

$$\frac{m}{t} = D \bullet \frac{S}{l}(C - C_0)$$

With negligible concentration at the adsorbing surface

$$\frac{m}{tC} = D \bullet \frac{S}{l}$$

$\frac{m}{tC}$ = Q = sampling rate (L/min)

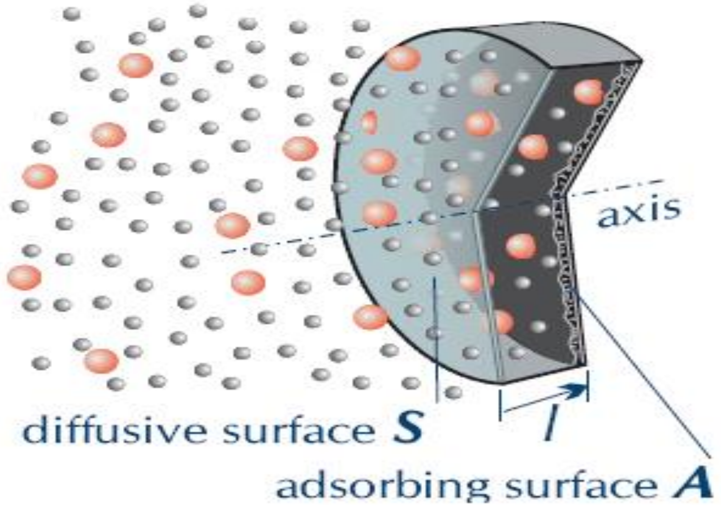
Simplified now becomes

$$\boldsymbol{sampling\ rate = diffusion\ coefficient \bullet \frac{diffusive\ surface}{diffusive\ path}}$$

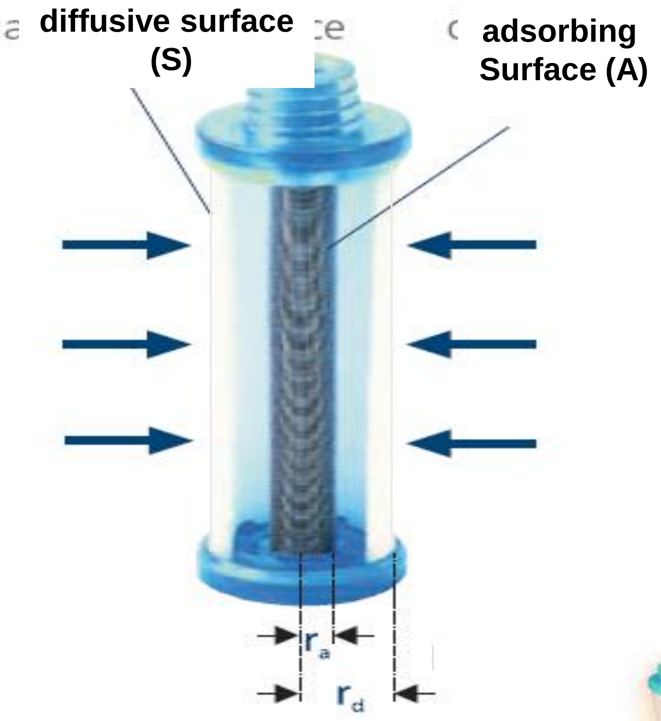
Passive Sampling

Axial vs. Radial Device Designs

Axial Passive Sampler



Radial Passive Sampler



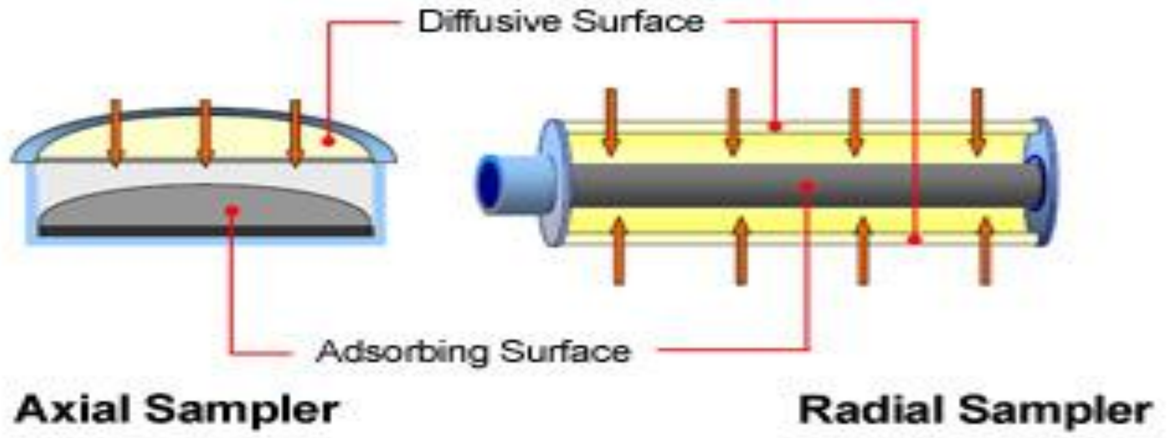
Axial and radial passive sampling devices are available from multiple sources

Passive Sampling
Axial vs. Radial Device Designs

$$sampling\ rate = diffusion\ coefficient \bullet \frac{diffusive\ surface}{diffusive\ path}$$

Radial design vs flat axial design

- Improves analytical sensitivity
- Increases sampling rate
- Increases sampling capacity



Passive Sampling

A Comparison of Passive Sampling Devices

Sampling rates: OSHA vs Manufacturer Published Data

Sampler Type Sampling Rates	OSHA Method 1007[1] Formaldehyde (760 mm Hg, 25 ºC)	Manufacturer Published Formaldehyde
Axial		
Chemdisk-AL[2]	13.56 mL/min	16.2 mL/min
UMEx 100[3]	29.77 mL/min	20.4 – 28.6 mL/min
Radial		
DSD-DNPH[4]	70.45 mL/min	71.9 mL/min
Radiello 165[5]	Not tested	99.0 mL/min

Measurement of sampling rates is achieved by generating a test atmosphere from a known concentration of formaldehyde gas into an exposure chamber loaded with passive samplers; active samplers are tested at the same atmospheres. Typically three different concentrations and time periods are tested to determine the sampling rate. *For more information, please refer to OSHA method 1007. References below:*

1. OSHA Method 1007 2. Assay Technology Technical Insert, 9159-571, 06/2014 3. SKC Publication 1529 Rev 1702 4. DSD-DNPH Application Manual – T708004, MilliporeSigma 5. Radiello Manual – IYP, MilliporeSigma

Sampler Capacity

Sampler Type Capacity	Manufacturer Published Formaldehyde
Axial	
Chemdisk-AL[2]	12.5 ppm (8 hr)
UMEx 100[3]	29 µg/sample
Radial	
DSD-DNPH[4]	150 µg/sample
Radiello 165	400 µg/sample

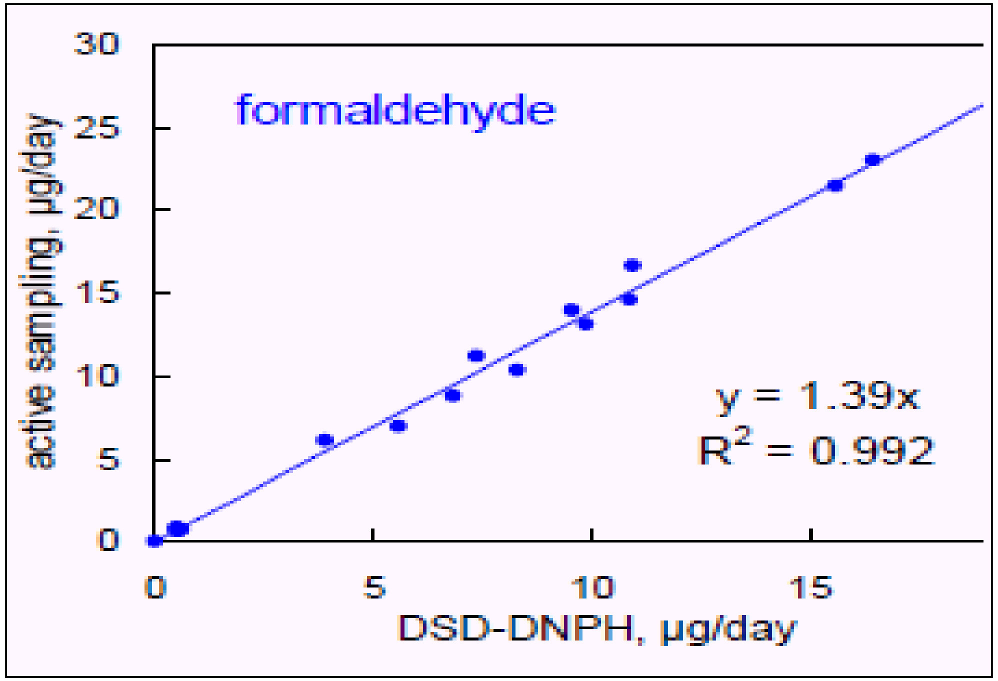
Analyte capacity is an important specification for passive samplers and should be considered particularly when:

- When there is a need for long-term sampling (greater than seven days). When the sampler capacity is reached, the analyte of interest back-diffuses off of the adsorbent and back into the environment, resulting in an underestimation of exposure.

Passive Sampling
Axial vs. Radial Device Designs

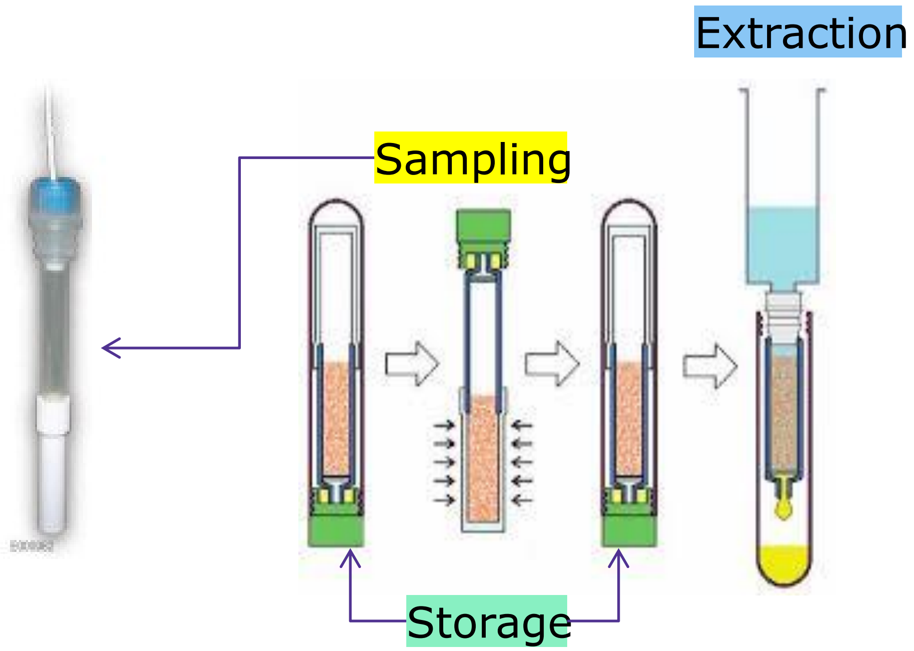
- Sampling rate obtained by direct comparison to active sampling

Type	Sampling Rate (mL/min)
Axial	13 – 30
Radial	70 - 99



Passive Sampling – Radial Sampling Devices

DSD-DNPH



- OSHA Method 1007 for Formaldehyde
- Formaldehyde Sampling Rate: 71.9 mL/min
- Easy to use, extraction is simple for the laboratory
- No pump required

Passive Sampling – Radial Sampling Devices
Radiello for Aldehydes

Sampling Rates

Sampling rates values Q at 298 K (25 °C) and 1013 hPa are listed below:

	Q_{298} rate $ml\cdot min^{-1}$	linearity range $\mu g\cdot m^{-3}\cdot min$	limit of quantitation[1] $\mu g\cdot m^{-3}$	uncertainty at 2σ %
acetaldehyde	84	1,000÷12,000,000	0.1	15.9
acrolein	33	3,000÷3,000,000	0.3	16.5
benzaldehyde	92	1,000÷8,000,000	0.1	17.2
butanal	11	9,000÷10,000,000	0.9	23.5
hexanal	18	5,000÷15,000,000	0.6	20.2
formaldehyde	99	1,000÷4,000,000	0.1	13.8
glutaric aldehyde	90	1,000÷3,000,000	0.1	14.5
isopentanal	61	1,500÷12,000,000	0.2	17
pentanal	27	4,000÷12,000,000	0.4	22.9
propanal	39	3,000÷8,000,000	0.3	17.1

[1]after 7 days exposure

- Easy to use
- No pump required
- Formaldehyde Sampling Rate: 99 mL/min

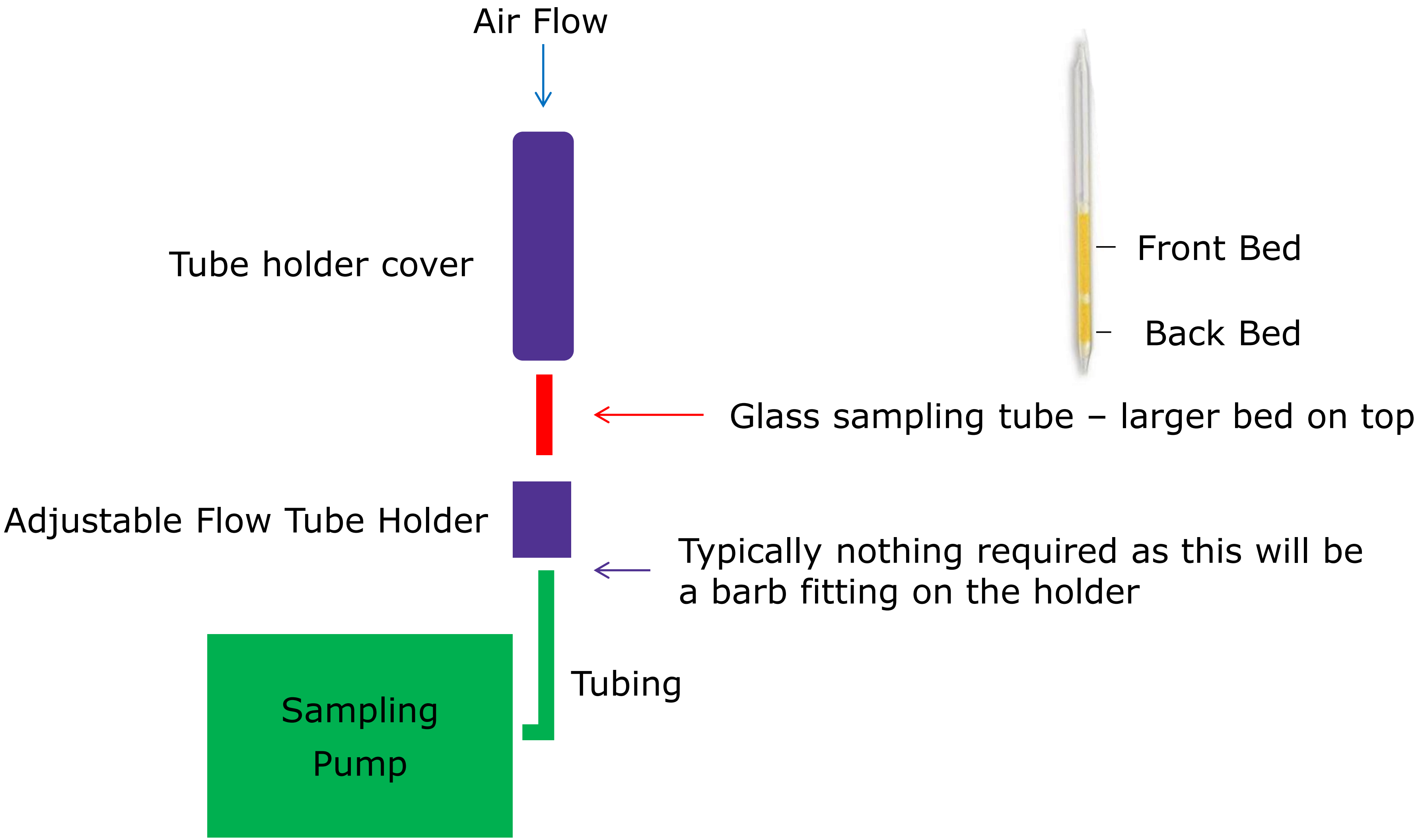
Other Sampling Devices

Other Devices for Sampling Carbonyls
2-HMP Coated XAD-2 Sorbent Tubes

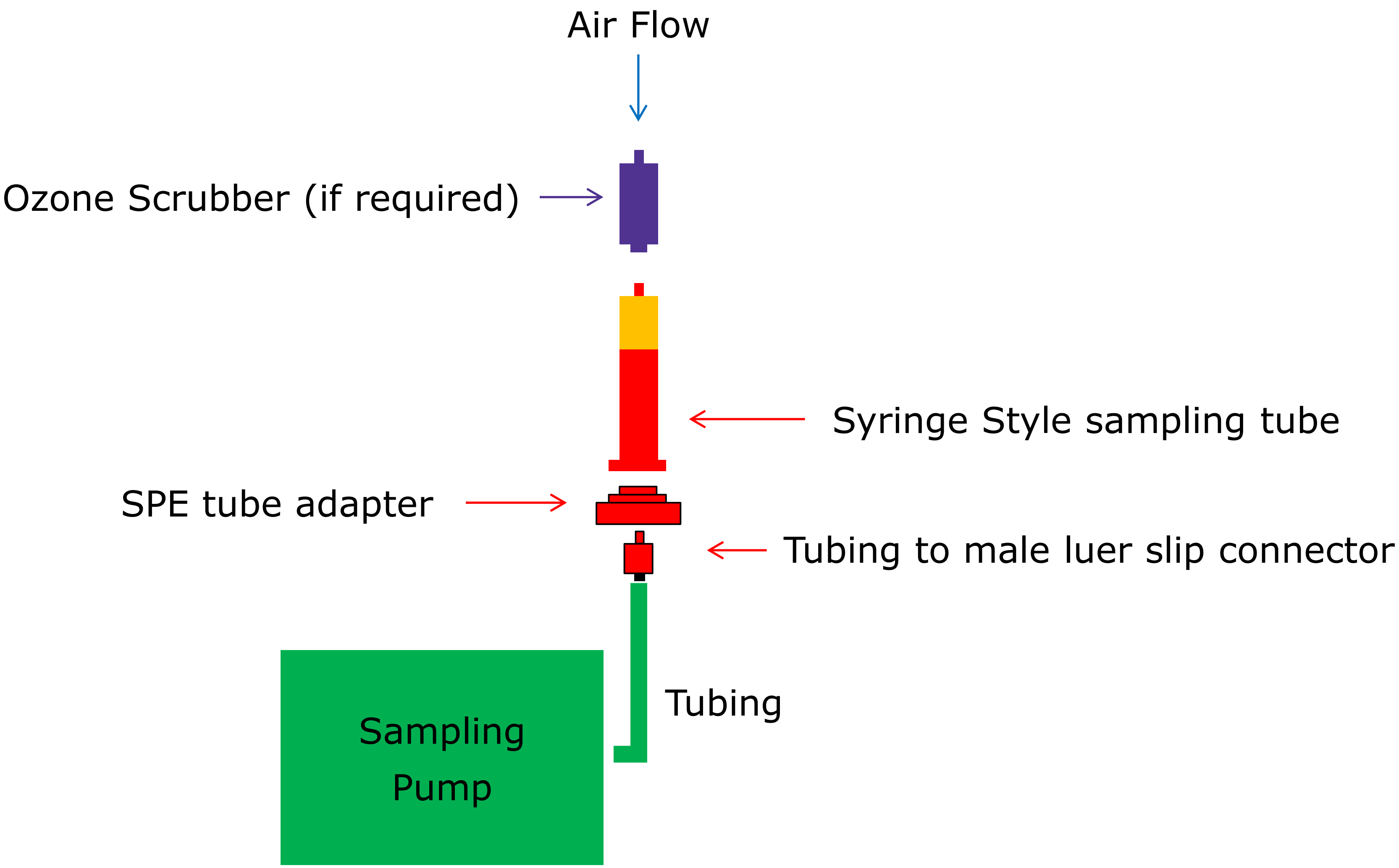
- Preferred method for simultaneous determination of formaldehyde and acrolein in industrial environments
- 2-HMP coated 20/40 Amberlite® XAD®-2, available in multiple sizes
- Collected samples are stable for up to 3 weeks at room temperature
- GC method w/good analytical sensitivity (working range of 0.24 – 16 ppm for 10L air sample.

Active Sampler connection

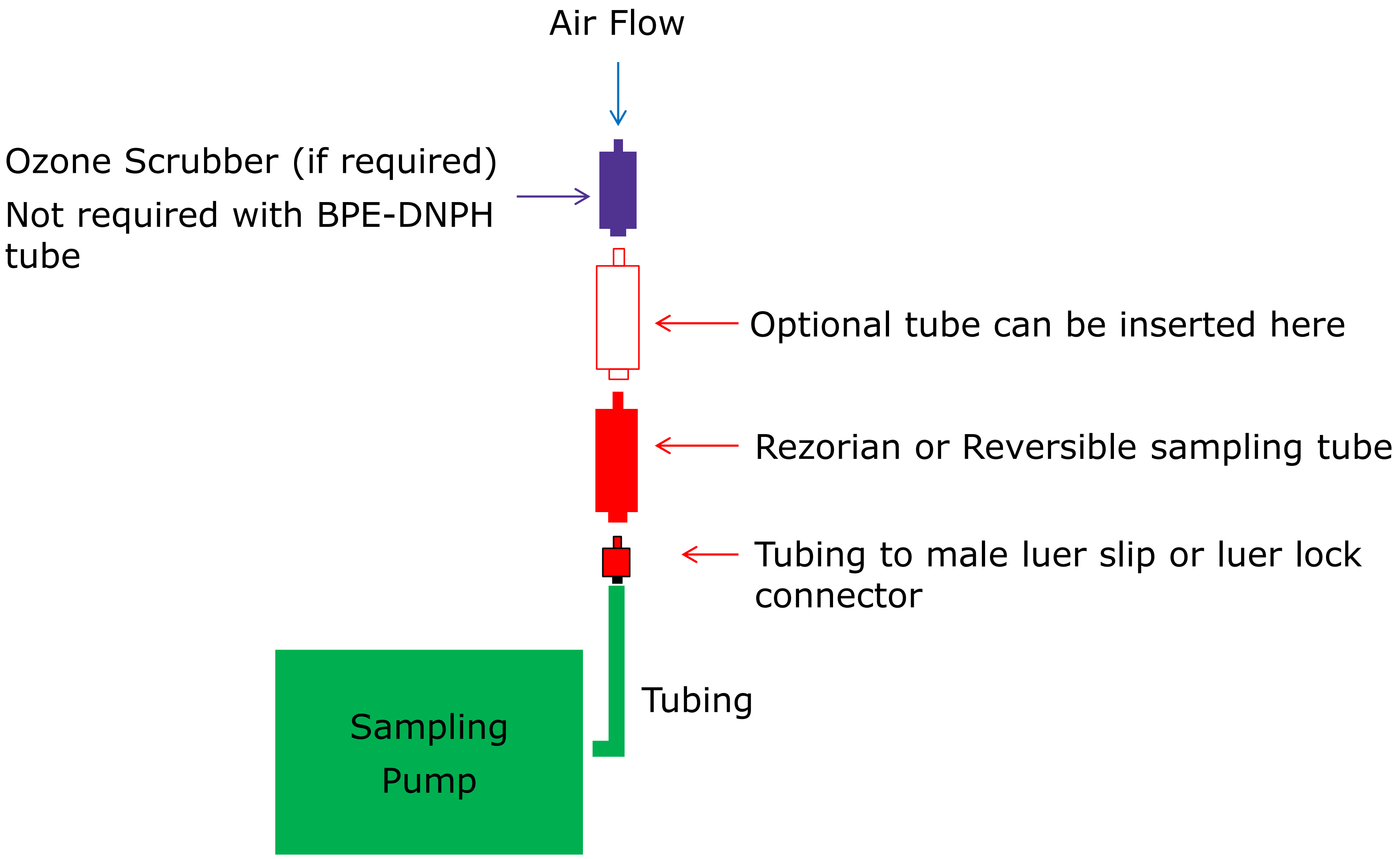
Sampler Connections-Glass Sampling Tubes (ORBO)



Sampler Connections-Syringe Style Sampling Tubes (SPE)



Sampler Connections-Rezorian or Reversible Style Sampling Tubes



Calibration

Calibration - basics

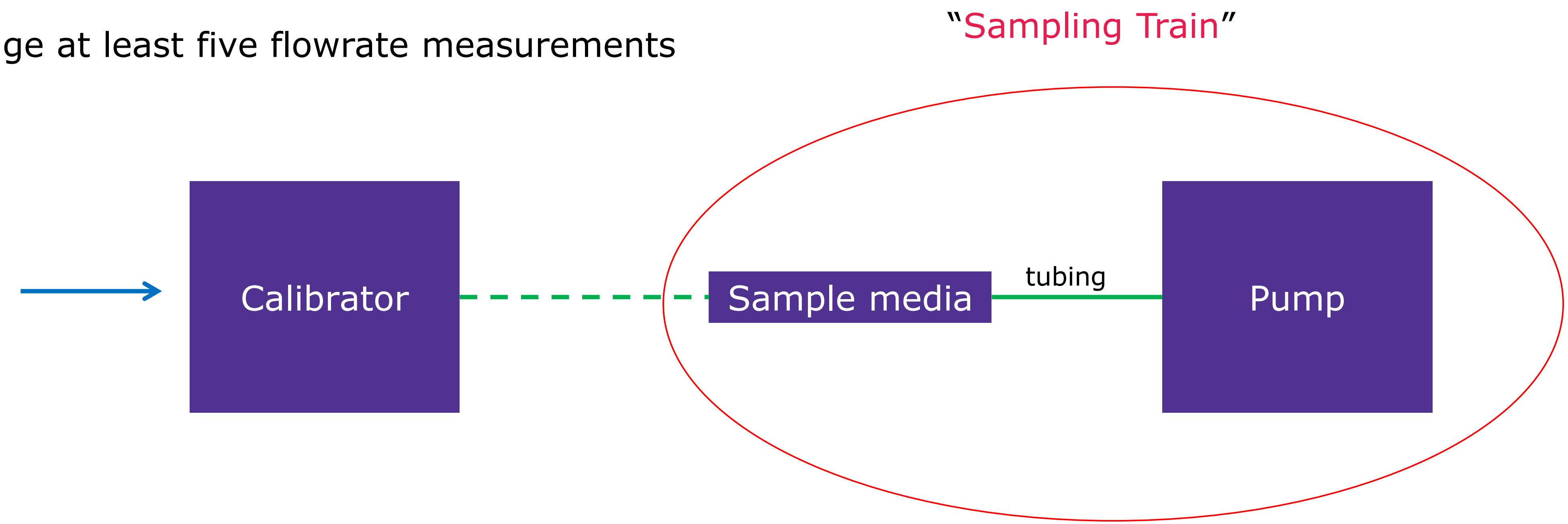
- Active samplers only!
- How lucky for passive sampling
- We’ll try to keep things simple as possible

How do we calibrate our sampling flowrate for the sampling train that we about to use?

The sampling train that will be used needs to be flow calibrated against either a bubble flowmeter (primary standard) or mass flowmeter (secondary standard).

Calibration - basics
Work Flow

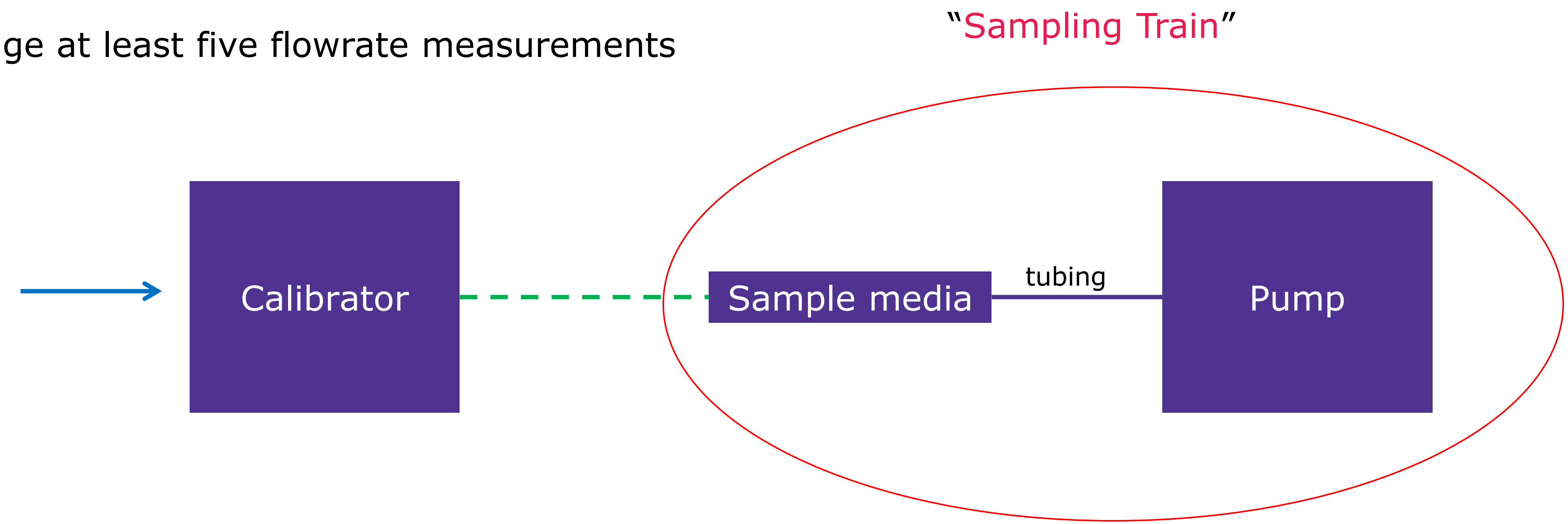
Average at least five flowrate measurements



Start pump at the selected flowrate

Calibration - basics
Work Flow

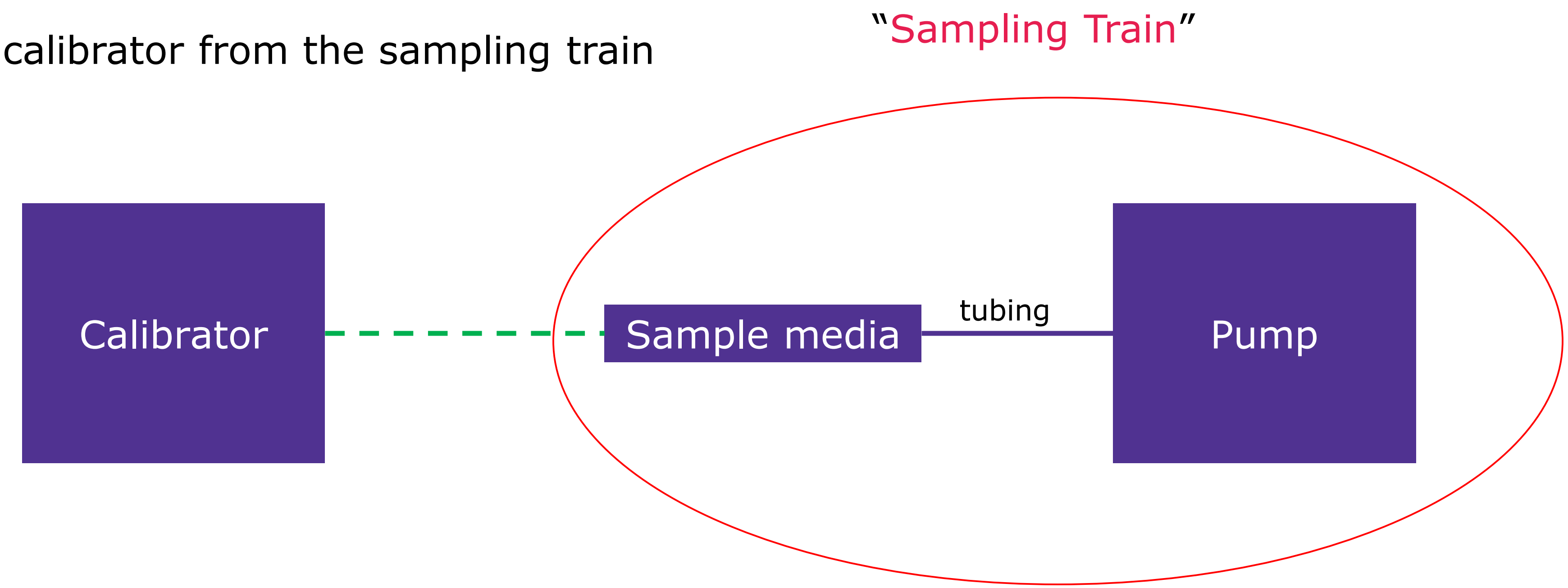
Average at least five flowrate measurements



Be sure to adjust the flow rate on the pump to match the reading on the calibrator

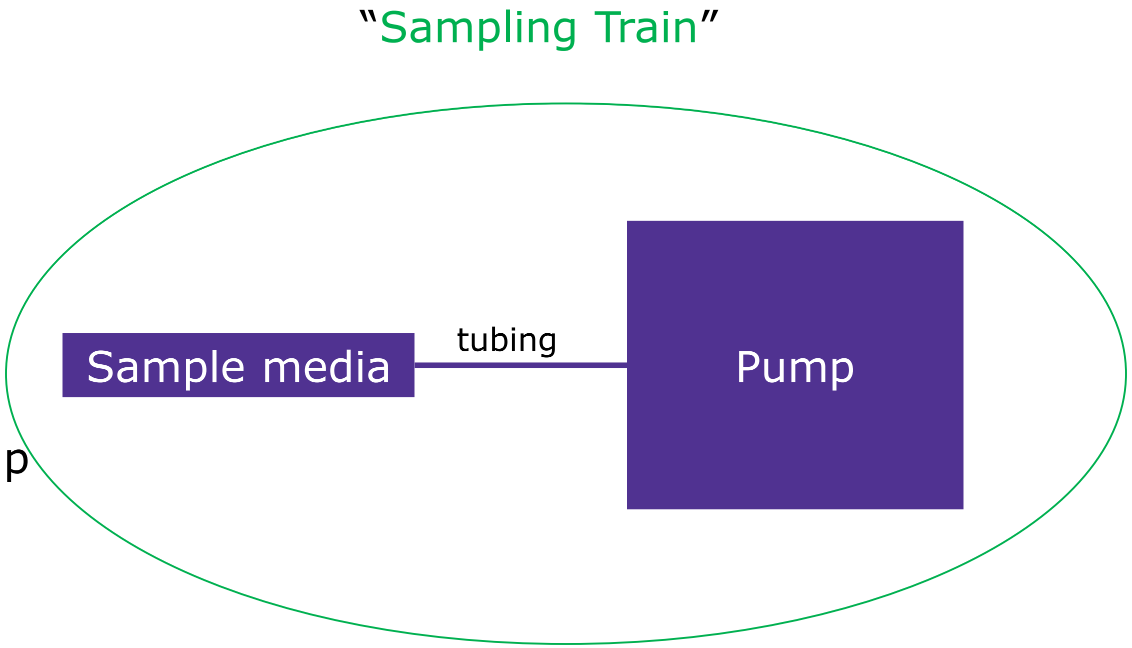
Calibration - basics
Work Flow

Disconnect the calibrator from the sampling train



Calibration - basics
Work Flow

- Calibrated “Sampling Train”
- Ready to begin sample acquistion
- Record all pertinent start information
- When sampling period is completed stop the pump
- Record all pertinent end information
- Attach calibrator once more to the sampling train for flowrate verification

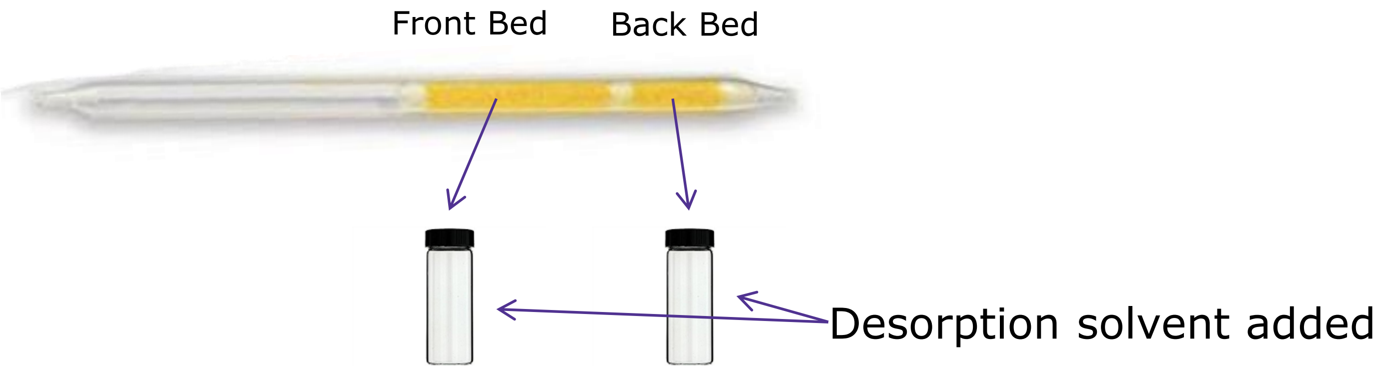


Sample Preparation

Sample Preparation

Steps involved (Glass sampling tube - ORBO)

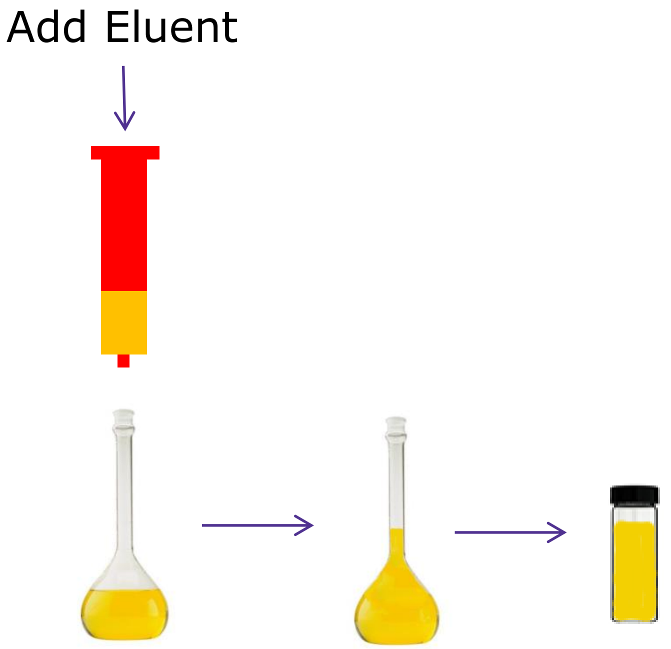
- Remove sampling media to appropriate sized sample vial (front bed and back bed into separate vials)
- Check method if the bed separator is also to included in the preparation
- Add desorbing solution to each vial
- Desorb for the specified time



Sample Preparation

Steps involved (Syringe Style - SPE)

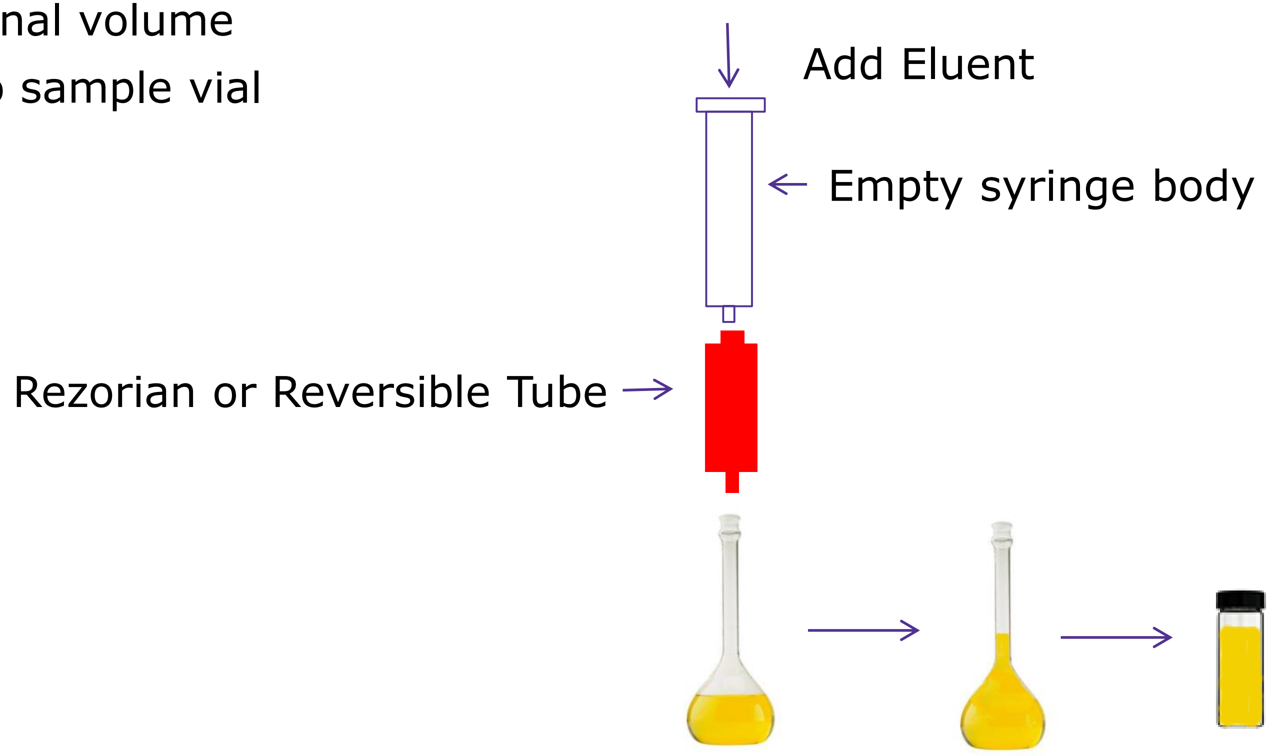
- Add the specified volume (divided into aliquots) of eluent to the syringe body – eluting into a volumetric flask
- Elution can be done using gravity or vacuum can be used if necessary (elution flow about 1drop/sec)
- Dilute to final volume
- Transfer to sample vial



Sample Preparation

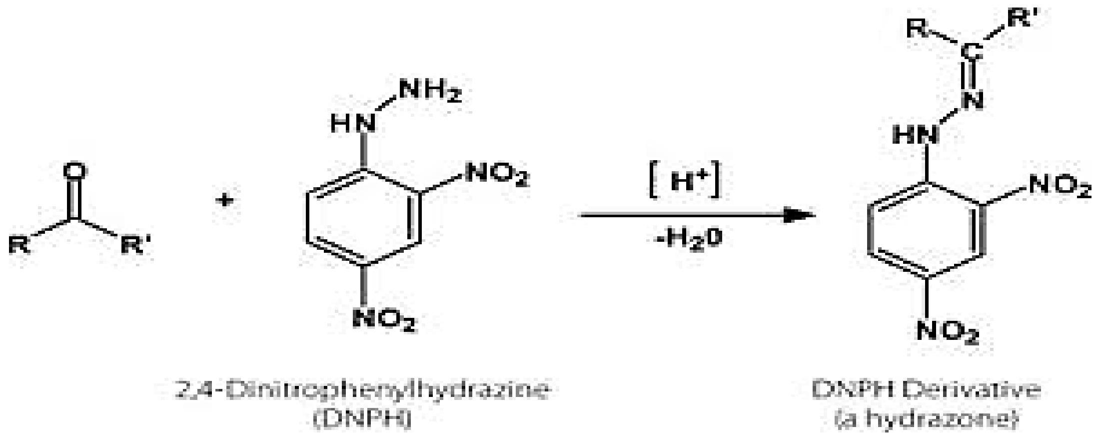
Steps involved (Rezorian or Reversible Style)

- Attach an empty syringe body to the female luer slip or luer lock depending on style
- Add the specified volume (divided into aliquots) of eluent to the syringe body – eluting into a volumetric flask
- Elution can be done using gravity or vacuum can be used if necessary (elution flow about 1drop/sec)
- Dilute to final volume
- Transfer to sample vial



Analysis

Analysis



- Stable chromophoric derivatization product
- Allows speciation
- Simple reverse phase method

Sample Analysis

Analytical Technique: HPLC

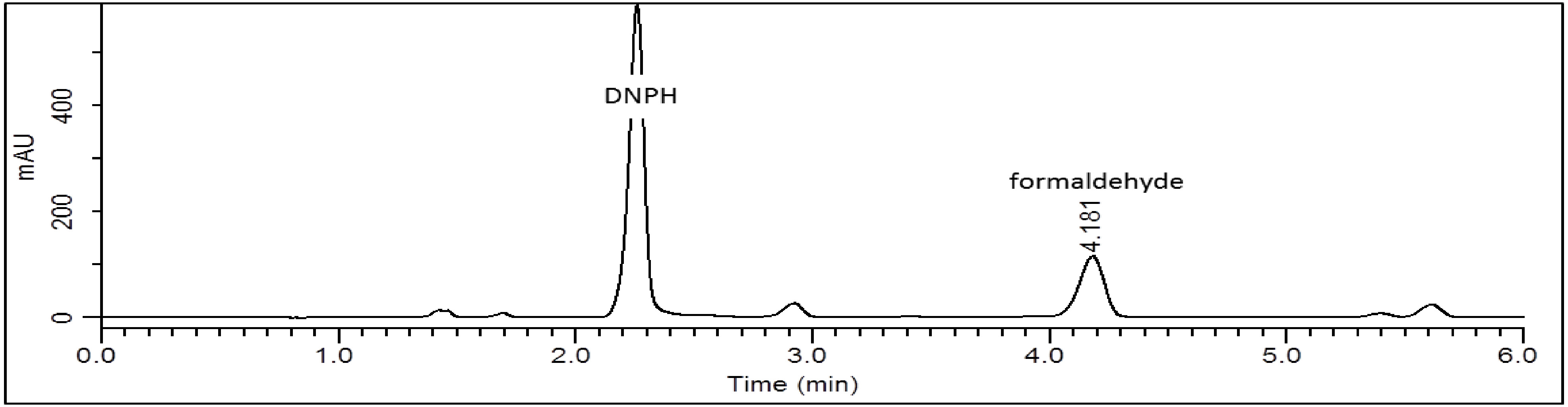
Liquid chromatograph conditions:

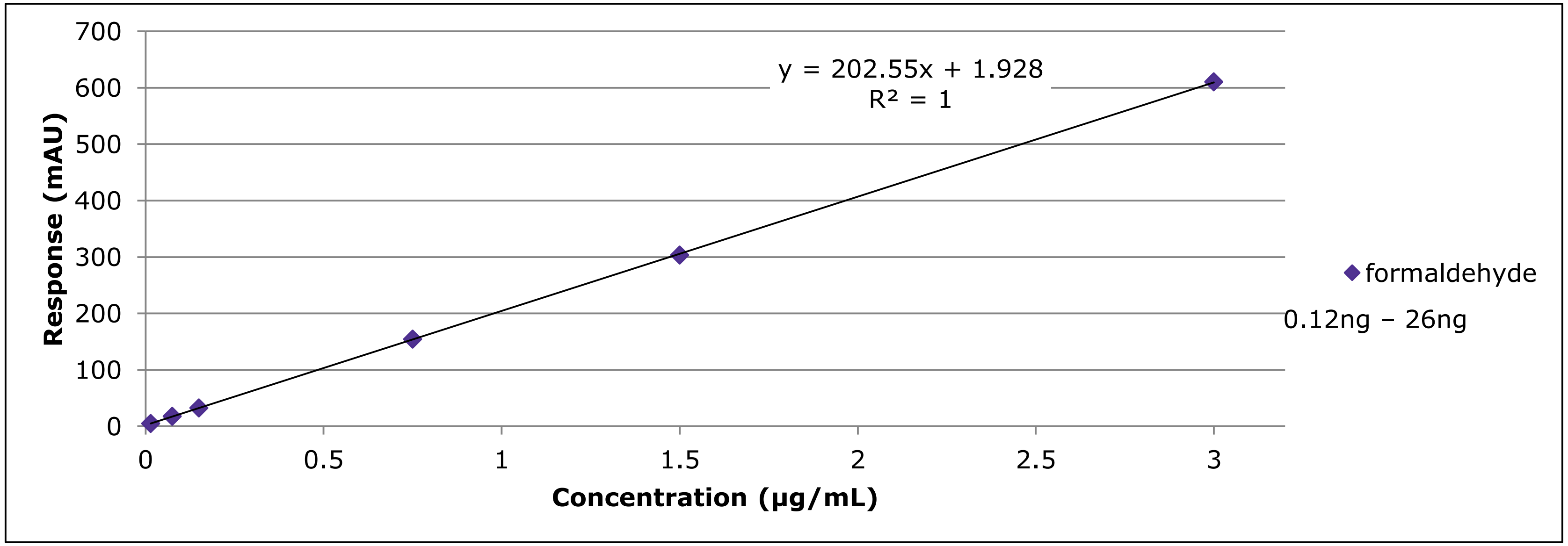
Mobile Phase:	(A) acetonitrile; (B) water
Gradient:	40% A held for 2.75 min; to 60% A in 5.25 min; held for 4.7 min
Flow rate:	1.4 mL/min
Column temp.:	40^{o}C
Detector:	UV @ 360 nm
Injection:	8 µL
Instrument:	HPLC Instrument with UV Detector
Column:	RP-Amide HPLC Column or C18 Column 15cm x4.6mm, 2.7um

Standard:	TO-11A/IP-6A Aldehyde/Ketone-DNPH Mix (Certified Reference Material)

Note: Analytical techniques may vary by laboratory.

Sample Analysis





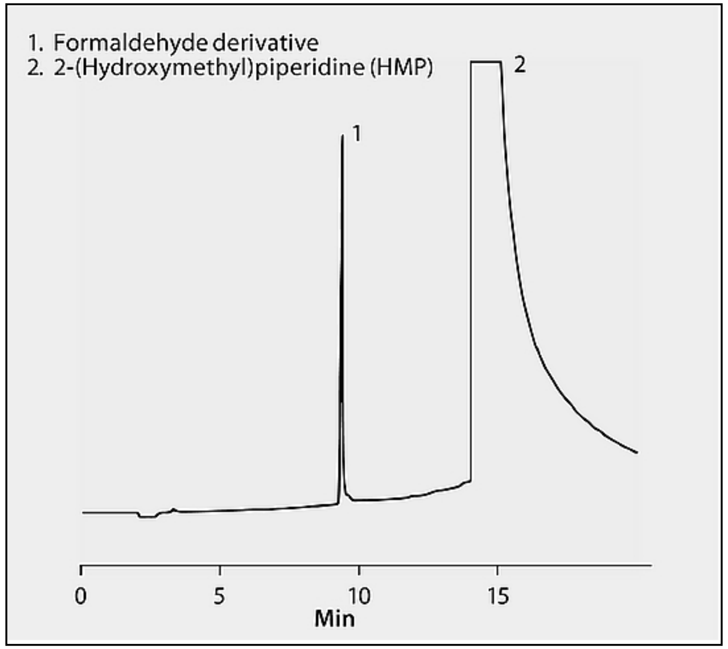
Sample Analysis

Analytical Technique: GC

GC chromatograph conditions:

Column:	Wax Capillary Column, 30m x 0.53 mm I.D., 0.5 µm
Oven:	50 °C (2 min) to 200 °C at 10 °C/min
Carrier gas:	Helium, 7 mL/min
Injection:	1 µL splitless, 220 °C
Detector:	NPD, 220 °C

Chromatogram: 10 µg formaldehyde



Note: Analytical techniques may vary by laboratory.

Summary

- Differences in samplers
- Making connections is all about having the right connector
- Flowrate responsibility
- Sample Prep routine workflow
- Sample analysis basic chromatography

Thank You

Questions?

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