ALS Prague Thermal Desorption

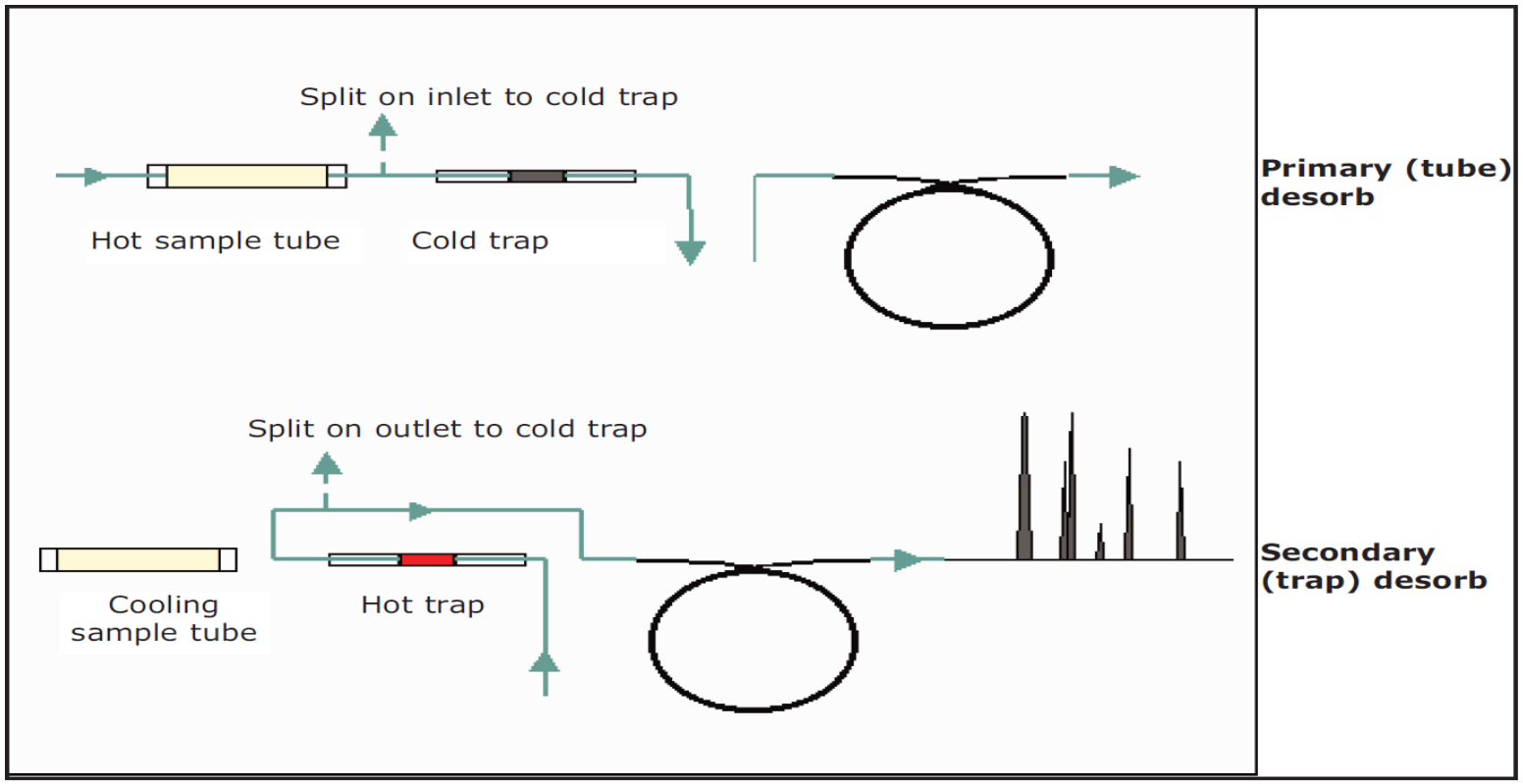
The purpose is to give an idea on how the thermal desorption process works, to pinpoint the key issues involving sample handling and the sampling process and to show method validation progress in the ALS Prague Laboratory

List of topics

- Principle of thermal desorption
- Initial key steps of TO-17 method
- Sorbent selection process
- Importance of laboratory and field blanks
- Tube preparation and tube handling
- Summary of ALS method validation progress
- Sampling volume

Principle of 2 stage thermal desorption process

Method TO-17 5.2 Two-stage Thermal Desorption - the process of thermally desorbing analytes from a solid or liquid matrix, reconcentrating them on a focusing tube and then rapidly heating the tube to „inject" the concentrated compounds into the GC system in a narrow band of vapor compatible with high resolution capillary gas chromatography.



TO-17 2.3 Initial key steps of method

2.3.1 Selection of a sorbent or sorbent mix tailored for a target compound list, data quality objectives and sampling environment.

2.3.2 Screening the sampling location for VOCs by taking single tube samples to allow estimates of the nature and amount of sample gases.

2.3.3 Initial sampling sequences with two tubes at nominally 1 and 4 liter total sample volumes (or appropriate proportional scaling of these volumes to fit the target list and monitoring objectives).

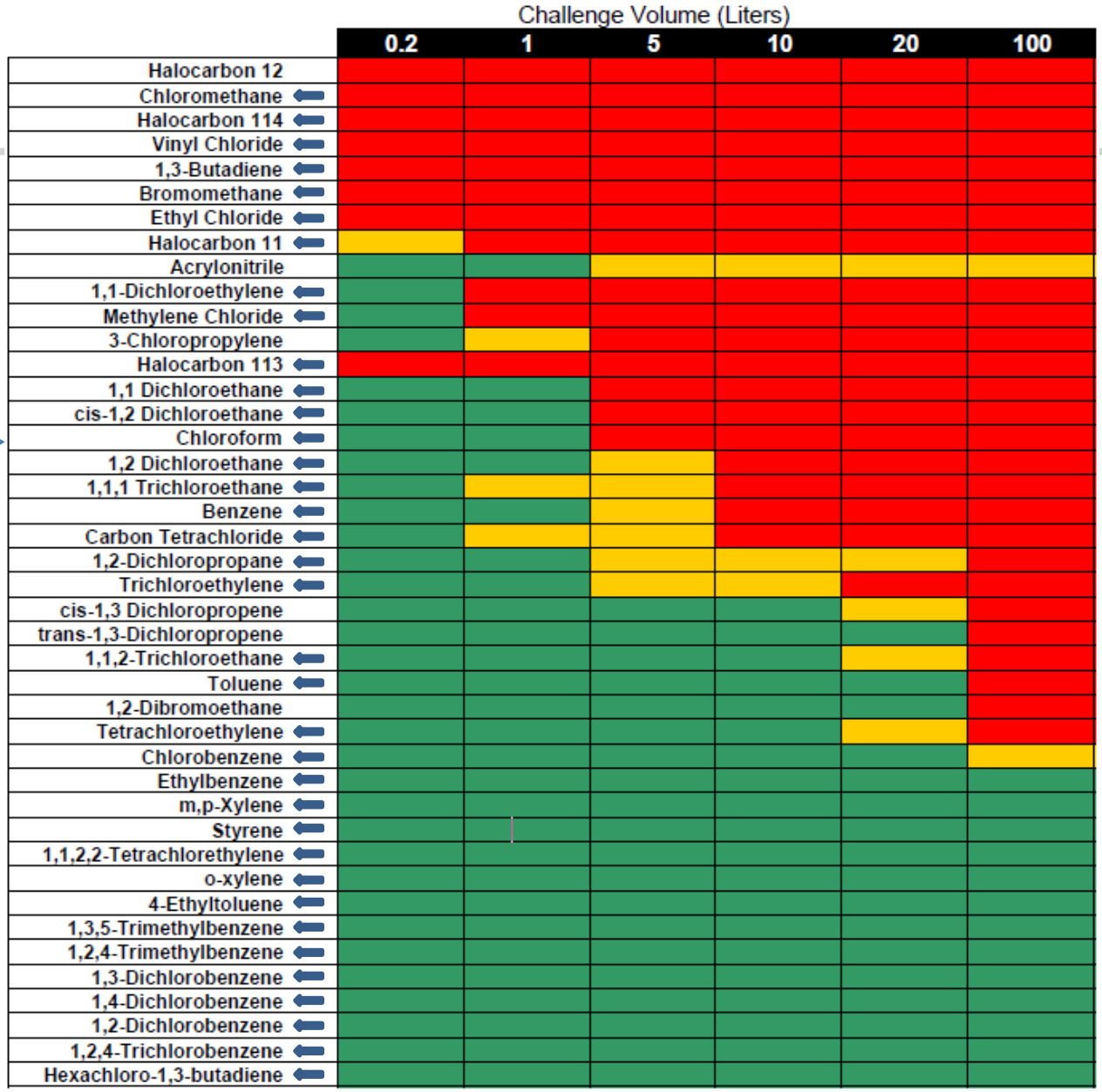
[Note: EPA requires the use of distributed volume pairs for monitoring to insure high quality data. However, in situations where acceptable data have been routinely obtained through use of distributed volume pairs and the ambient air is considered well characterized, cost considerations may warrant single tube sampling. Any attendant risk to data quality objectives is the responsibility of the project's decision maker.]

Sorbent selection

- A successful analysis depends on the correct sorbent selection for the desired compound range.
- One of the illustrative criterions for sorbent selection is the challenging volume (the volume pulled through the tube needed to release an analyte)
- The following 3 slides demonstrate proposed composition of sorbents contained in a sampling tube which is able to capture all required analytes. Combination of multiple sorbents has several advantages over single sorbent tubes.

Tenax TA challenging volumes

Comment: Tenax TA is not suitable for all compounds from Chloroform and above



Performance Key

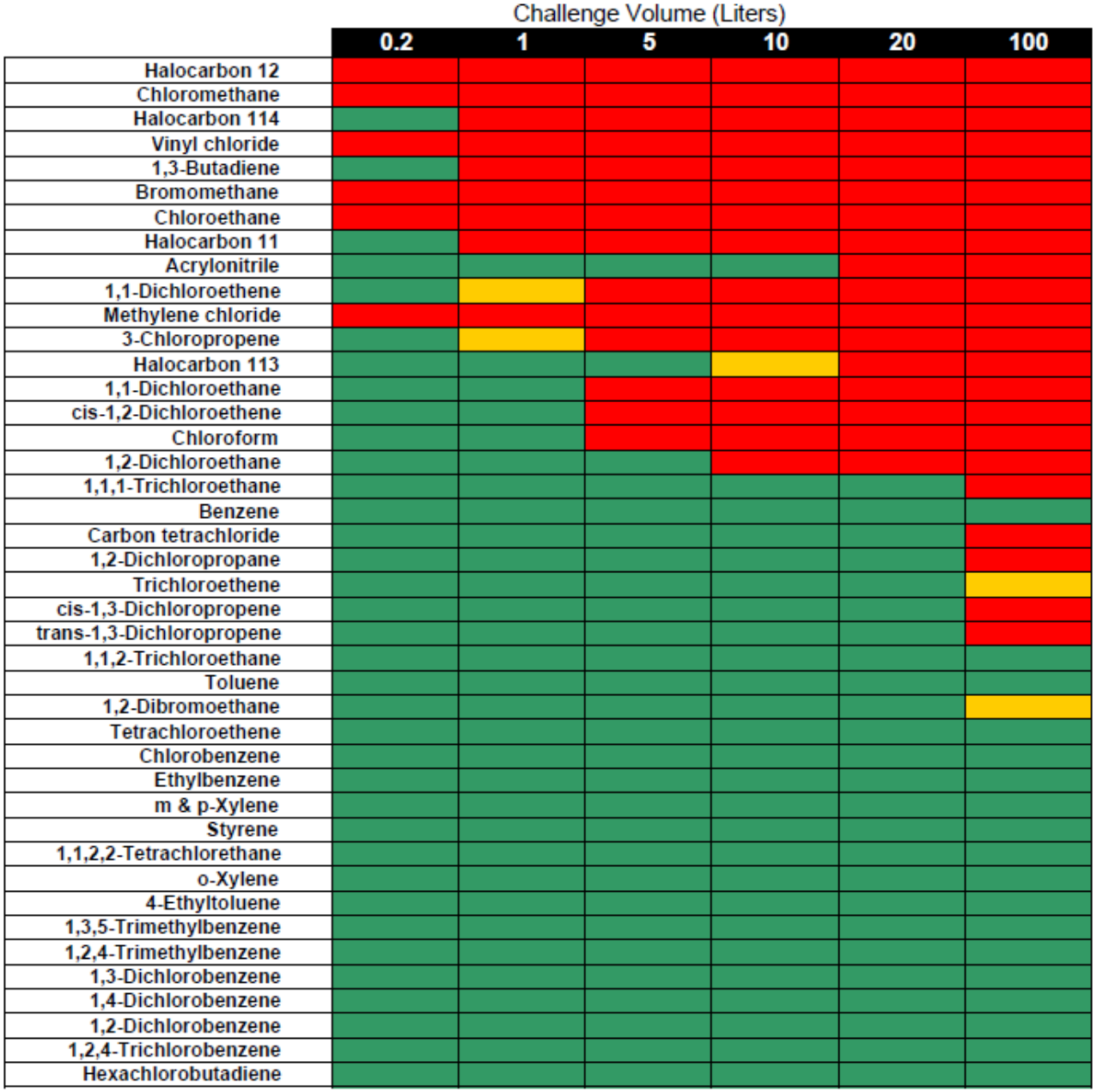
Safe to use: Recovery is greater than 80%

Caution: Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20%

** indicates this analyte was strongly adsorbed*

Carbograph1TD challenging volumes



Performance Key

Safe to use: Recovery is greater than 80%

Caution: Recovery is between 21 to 79%

Not Recommended: Recovery is less than 20%

** indicates this analyte was strongly adsorbed*

Carboxen 1003 challenging volumes

	Challenge Volume (Liters)					
	0.2	1	5	10	20	100
Halocarbon 12						
Chloromethane						
Halocarbon 114						
Vinyl chloride						
1,3-Butadiene						
Bromomethane						
Chloroethane						
Halocarbon 11						
Acrylonitrile						
1,1-Dichloroethene						
Methylene chloride						
3-Chloropropene						
Halocarbon 113						
1,1-Dichloroethane						
cis-1,2-Dichloroethene						
Chloroform						
1,2-Dichloroethane						
1,1,1-Trichloroethane						
Benzene *						
Carbon tetrachloride						
1,2-Dichloropropane						
Trichloroethene						
cis-1,3-Dichloropropene						
trans-1,3-Dichloropropene						
1,1,2-Trichloroethane						
Toluene *						
1,2-Dibromoethane						
Tetrachloroethene *						
Chlorobenzene *						
Ethylbenzene *						
m & p-Xylene *						
Styrene *						
1,1,2,2-Tetrachlorethane						
o-Xylene *						
4-Ethyltoluene						
1,3,5-Trimethylbenzene						
1,2,4-Trimethylbenzene						
1,3-Dichlorobenzene *						
1,4-Dichlorobenzene *						
1,2-Dichlorobenzene *						
1,2,4-Trichlorobenzene						
Hexachlorobutadiene						

Performance Key

Safe to use: Recovery is greater than 80%
Caution: Recovery is between 21 to 79%
Not Recommended: Recovery is less than 20%

** indicates this analyte was strongly adsorbed*

SUPELCO

ALS Prague: Comparison between Tenax TA and multisorbent tubes – challenge volumes tested: 0.2, 0.5, 1 and 2 Litres

Compound name	TENAX				Multisorbent			
	0.2 L	0.5 L	1 L	2 L	0.2 L	0.5 L	1 L	2 L
1.2-Dichloro-1.1.2.2-tetrafluoroethane (CFC-114)								
Chloromethane								
Vinyl Chloride								
1.3-Butadiene								
Bromomethane								
Chloroethane								
Trichlorofluoromethane								
Ethanol								
1.1-Dichloroethene								
1.1.2-Trichloro-1.2.2-trifluoroethane (CFC-113)								
Acetone								
Carbon Disulfide								
2-Propanol (Isopropyl Alcohol)								
Dichloromethane (Methylene Chloride)								
trans-1,2-Dichloroethene								
n-Hexane								
1.1-Dichloroethane								
2-Butanone (MEK)								
cis-1,2-Dichloroethene								
Tetrahydrofuran (THF)								
Chloroform								
1.1.1-Trichloroethane								
Cyclohexane								
Tetrachloromethane (Carbon Tetrachloride)								
Benzene								
1.2-Dichloroethane								
2.2.4-Trimethylpentane (Isooctane)								
n-Heptane								
Trichloroethene								
Methylcyclohexane								
1.2-Dichloropropane								
1.4-Dioxane								
Methyl iso-Butyl Ketone (4-Methyl-2-pentanone)								
Toluene								
1.1.2-Trichloroethane								
Tetrachloroethene								
2-Hexanone								
Chlorobenzene								
Ethylbenzene								
meta-Xylene a para-Xylene								
o-Xylene								
Styrene								
Isopropylbenzene (Cumene)								
1.1.2.2-Tetrachloroethane								
n-Propylbenzene								
4-Ethyltoluene								
1.3.5-Trimethylbenzene								
1.2.4-Trimethylbenzene								
1.3-Dichlorobenzene								
1.4-Dichlorobenzene								
1.2-Dichlorobenzene								
1.3.5-Trichlorobenzene								
1.2.4-Trichlorobenzene								
Hexachlorobutadiene								
1.2.3-Trichlorobenzene								

Less than 20% resovery

Between 20% and 80% recovery

Better than 80% recovery

Comment:
The first 5 analytes had the recovery less than 1% on Tenax TA

Laboratory blanks (TO-17/Markes)

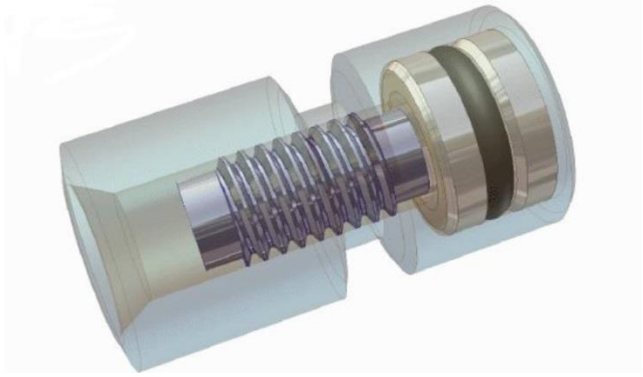
- Laboratory blanks are prepared in the same way and at the same time as tubes to be used for a monitoring exercise, but are never removed from the laboratory. They are simply kept inside a suitable storage container throughout the sample collection process and analysed with the sampled tubes. Laboratory blanks are used to check tube conditioning procedures and inherent sorbent stability.

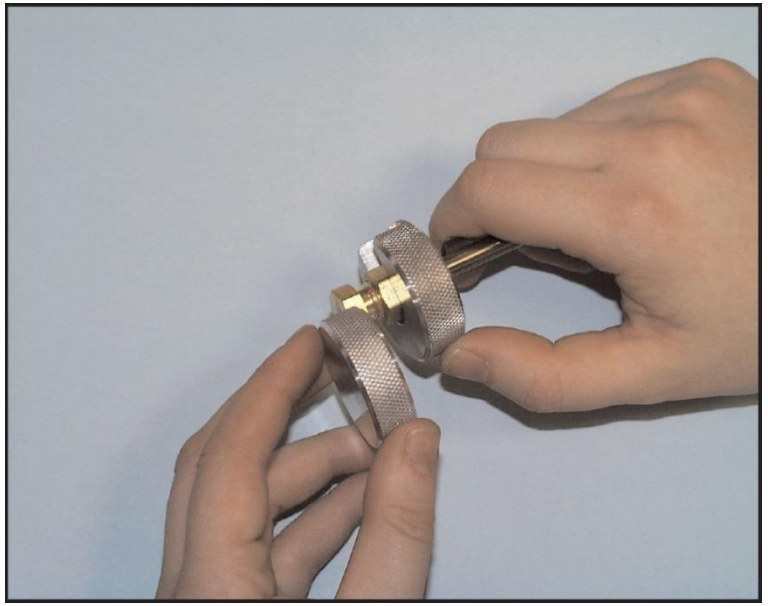
Field blanks (TO-17/Markes)

- Field blanks are prepared as laboratory blanks above, but are transported with the tubes to be used for sample collection. Once at the monitoring location, all the processes carried out on the sampling tubes (e.g. unwrapping, uncapping, recapping, rewrapping, etc.), except sample collection itself, should also be carried out on the field blanks. They provide important controls for all tube handling, storage and transport procedures.

Tube preparation, handling and storage

- Tube preparation begins with an adequate conditioning process
- 10% of conditioned tubes within a conditioned batch are tested
- Tubes are capped with brass/PTFE storage caps using Cap Lok tools
- Tubes are stored in an air tight container





Tube preparation, handling and storage

- If the multi-sorbent tubes are to be stored for longer than one week, or will be exposed to low temperatures (an aircraft hold, by rail / road overnight during cold weather) then the following procedure must be undertaken:
- take the samples in the normal way and cap with ¼-inch brass storage caps in the field as usual
- place the tubes in an air tight container and place in a clean refrigerator
- when the tubes have reached the 'cold' temperature, briefly remove them from the refrigerator and check and re-tighten the caps (due to the difference in the thermal properties of brass and stainless steel the caps may have become slightly loose).
- return the samples, in their container, to the clean refrigerator

Calibration Range ALS Prague

- Calibration is done on multi-sorbent tube (TENAX TA, Carbograph 1TD, Carboxen 1003)
- Calibration range is 2 ng/tube - 1000 ng/tube
  - exception: Bromomethane, CFC-114 (upper limit 100ng/tube)
  - Exception: Chloromethan (upper limit 400ng/tube)

ALS Prague method limits of quantification – fortified blanks at 2ng/tube

Compound name	LOQ [ng/tube]	Compound name	LOQ [ng/tube]
1.2-Dichloro-1.1.2.2-tetrafluoroethane (CFC-114)	4.0	Trichloroethene	4.0
Chloromethane	14.0	Methylcyclohexane	4.0
Vinyl Chloride	2.0	1.2-Dichloropropane	4.0
1.3-Butadiene	2.0	1.4-Dioxane	10.0
Bromomethane	4.0	Methyl iso-Butyl Ketone	4.0
Chloroethane	4.0	Toluene	4.0
Trichlorofluoromethane	4.0	1.1.2-Trichloroethane	4.0
Ethanol	10.0	Tetrachloroethene	4.0
1.1-Dichloroethene	4.0	2-Hexanone	4.0
1.1.2-Trichloro-1.2.2-trifluoroethane (CFC-113)	4.0	Chlorobenzene	4.0
Acetone	20.0	Ethylbenzene	4.0
Carbon Disulfide	20.0	meta-Xylene a para-Xylene	4.0
2-Propanol (Isopropyl Alcohol)	4.0	o-Xylene	4.0
Dichloromethane (Methylene Chloride)	10.0	Styrene	4.0
trans-1,2-Dichloroethene	4.0	Isopropylbenzene (Cumene)	4.0
n-Hexane	4.0	1.1.2.2-Tetrachloroethane	4.0
1.1-Dichloroethane	4.0	n-Propylbenzene	4.0
2-Butanone (MEK)	20.0	4-Ethyltoluene	4.0
cis-1,2-Dichloroethene	4.0	1.3.5-Trimethylbenzene	4.0
Tetrahydrofuran (THF)	4.0	1.2.4-Trimethylbenzene	4.0
Chloroform	4.0	1.3-Dichlorobenzene	4.0
1.1.1-Trichloroethane	4.0	1.4-Dichlorobenzene	4.0
Cyclohexane	2.0	1.2-Dichlorobenzene	4.0
Tetrachloromethane (Carbon Tetrachloride)	4.0	1.3.5-Trichlorobenzene	10.0
Benzene	4.0	1.2.4-Trichlorobenzene	10.0
1.2-Dichloroethane	4.0	Hexachlorobutadiene	10.0
2.2.4-Trimethylpentane (Isooctane)	4.0	1.2.3-Trichlorobenzene	10.0
n-Heptane	4.0		

ALS Prague repeatability – fortified blanks at 2ng/tube

Compound name	RSD	BIAS	Compound name	RSD	BIAS
1.2-Dichloro-1.1.2.2-tetrafluoroethane (CFC-114)	8.4%	10.9%	Trichloroethene	4.0%	2.4%
Chloromethane	31.5%	23.9%	Methylcyclohexane	3.3%	8.4%
Vinyl Chloride	4.3%	0.2%	1.2-Dichloropropane	4.7%	2.8%
1.3-Butadiene	11.6%	27.2%	1.4-Dioxane	6.6%	6.3%
Bromomethane	4.1%	0.3%	Methyl iso-Butyl Ketone (4-Methyl-2-pentanone)	4.6%	1.5%
Chloroethane	5.2%	4.1%	Toluene	5.3%	6.1%
Trichlorofluoromethane	6.4%	4.9%	1.1.2-Trichloroethane	4.8%	14.7%
Ethanol	31.7%	31.5%	Tetrachloroethene	13.7%	20.6%
1.1-Dichloroethene	6.9%	4.2%	2-Hexanone	3.8%	7.6%
1.1.2-Trichloro-1.2.2-trifluoroethane (CFC-113)	5.3%	1.1%	Chlorobenzene	2.7%	12.2%
Acetone	30.2%	42.4%	Ethylbenzene	4.0%	11.1%
Carbon Disulfide	3.0%	6.7%	meta-Xylene a para-Xylene	4.9%	11.5%
2-Propanol (Isopropyl Alcohol)	10.5%	3.6%	o-Xylene	4.7%	24.7%
Dichloromethane (Methylene Chloride)	6.5%	4.2%	Styrene	3.5%	14.9%
trans-1,2-Dichloroethene	5.2%	1.3%	Isopropylbenzene (Cumene)	6.1%	0.8%
n-Hexane	5.5%	7.5%	1.1.2.2-Tetrachloroethane	4.7%	16.7%
1.1-Dichloroethane	6.9%	4.0%	n-Propylbenzene	13.8%	38.7%
2-Butanone (MEK)	5.0%	3.4%	4-Ethyltoluene	4.8%	17.7%
cis-1,2-Dichloroethene	12.6%	14.0%	1.3.5-Trimethylbenzene	7.7%	15.7%
Tetrahydrofuran (THF)	5.3%	1.6%	1.2.4-Trimethylbenzene	4.5%	11.4%
Chloroform	5.7%	7.3%	1.3-Dichlorobenzene	6.5%	22.0%
1.1.1-Trichloroethane	5.6%	5.8%	1.4-Dichlorobenzene	4.2%	4.0%
Cyclohexane	4.8%	1.1%	1.2-Dichlorobenzene	5.8%	28.2%
Tetrachloromethane (Carbon Tetrachloride)	5.4%	3.8%	1.3.5-Trichlorobenzene	5.3%	38.9%
Benzene	7.0%	4.3%	1.2.4-Trichlorobenzene	5.5%	32.9%
1.2-Dichloroethane	7.5%	4.6%	Hexachlorobutadiene	4.1%	38.6%
2.2.4-Trimethylpentane (Isooctane)	4.8%	2.0%	1.2.3-Trichlorobenzene	6.5%	32.5%
n-Heptane	5.9%	7.3%			

ALS Prague repeatability – fortified blanks at 100ng/tube

Compound name	RSD	BIAS	Compound name	RSD	BIAS
1.2-Dichloro-1.1.2.2-tetrafluoroethane (CFC-114)	6.1%	4.3%	Trichloroethene	2.0%	7.2%
Chloromethane	7.4%	14.7%	Methylcyclohexane	2.3%	3.4%
Vinyl Chloride	5.7%	11.9%	1.2-Dichloropropane	2.7%	0.7%
1.3-Butadiene	9.0%	5.8%	1.4-Dioxane	2.3%	6.4%
Bromomethane	7.8%	1.2%	Methyl iso-Butyl Ketone (4-Methyl-2-pentanone)	2.4%	3.2%
Chloroethane	5.9%	8.2%	Toluene	2.0%	9.9%
Trichlorofluoromethane	4.2%	7.5%	1.1.2-Trichloroethane	1.9%	5.0%
Ethanol	3.7%	4.1%	Tetrachloroethene	1.8%	8.5%
1.1-Dichloroethene	4.0%	6.8%	2-Hexanone	5.3%	10.1%
1.1.2-Trichloro-1.2.2-trifluoroethane (CFC-113)	2.8%	1.9%	Chlorobenzene	1.6%	7.1%
Acetone	4.6%	11.0%	Ethylbenzene	2.1%	5.0%
Carbon Disulfide	3.4%	7.3%	meta-Xylene a para-Xylene	2.4%	3.8%
2-Propanol (Isopropyl Alcohol)	4.7%	6.1%	o-Xylene	1.9%	6.6%
Dichloromethane (Methylene Chloride)	3.2%	0.4%	Styrene	2.1%	9.3%
trans-1,2-Dichloroethene	2.6%	2.3%	Isopropylbenzene (Cumene)	2.4%	7.8%
n-Hexane	2.9%	5.7%	1.1.2.2-Tetrachloroethane	2.1%	5.2%
1.1-Dichloroethane	2.7%	1.1%	n-Propylbenzene	2.4%	6.4%
2-Butanone (MEK)	3.6%	6.9%	4-Ethyltoluene	2.4%	10.2%
cis-1,2-Dichloroethene	2.0%	3.8%	1.3.5-Trimethylbenzene	2.3%	9.8%
Tetrahydrofuran (THF)	2.9%	4.9%	1.2.4-Trimethylbenzene	2.5%	6.9%
Chloroform	2.1%	1.4%	1.3-Dichlorobenzene	2.8%	9.2%
1.1.1-Trichloroethane	2.8%	0.6%	1.4-Dichlorobenzene	2.9%	10.6%
Cyclohexane	3.5%	4.0%	1.2-Dichlorobenzene	3.1%	9.0%
Tetrachloromethane (Carbon Tetrachloride)	2.7%	0.2%	1.3.5-Trichlorobenzene	2.3%	12.2%
Benzene	2.1%	2.6%	1.2.4-Trichlorobenzene	3.5%	16.2%
1.2-Dichloroethane	3.0%	4.0%	Hexachlorobutadiene	2.1%	12.1%
2.2.4-Trimethylpentane (Isooctane)	2.5%	0.3%	1.2.3-Trichlorobenzene	3.3%	13.2%
n-Heptane	3.1%	4.9%			

Sampling

- What are the legislation limits for VOC' in Israel?
- How quickly needs to be sample taken?
- How many pumps are available for single sampling?
  - (Is duplicate determination possible?)
- Would it be possible to send out tubes to the sampling site in an air tight containers? Ideally 3 tubes per sampling site.
- Can we distribute Cap Lok tools with every sample?
- How long does it take to receive a sample in ALS Prague from the day the sample is taken?