Existing Standardization Techniques

- Compressed Gas Standards
- Permeation Tubes
- Liquid Standards
- Reagent Purity

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Short-lived Halocarbon Calibration Workshop
London, 2008

Compressed Gas Standards

Basic Idea: Static dilution of a pure compound (or a known mixture) to working concentration levels

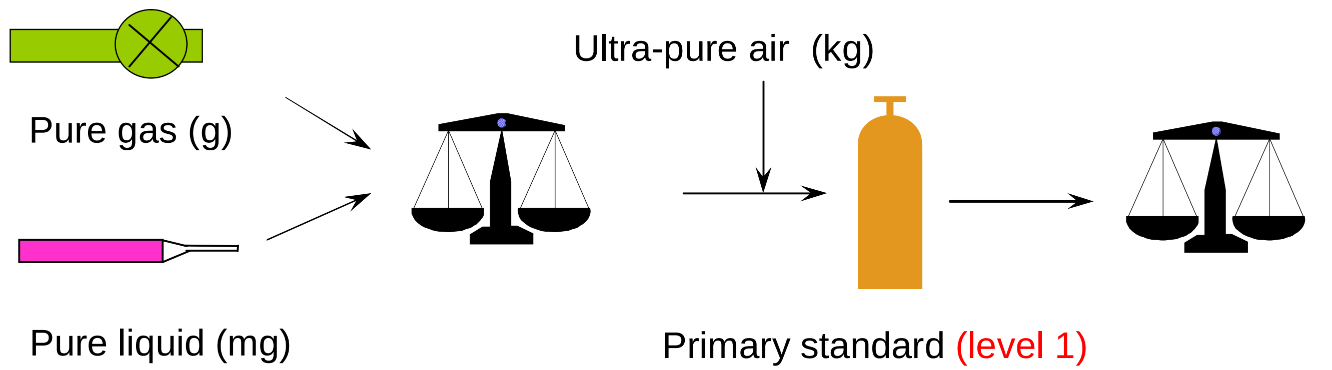
Pros: portability, longevity, multiple species, traceable
Cons: stability, transport issues, multiple steps

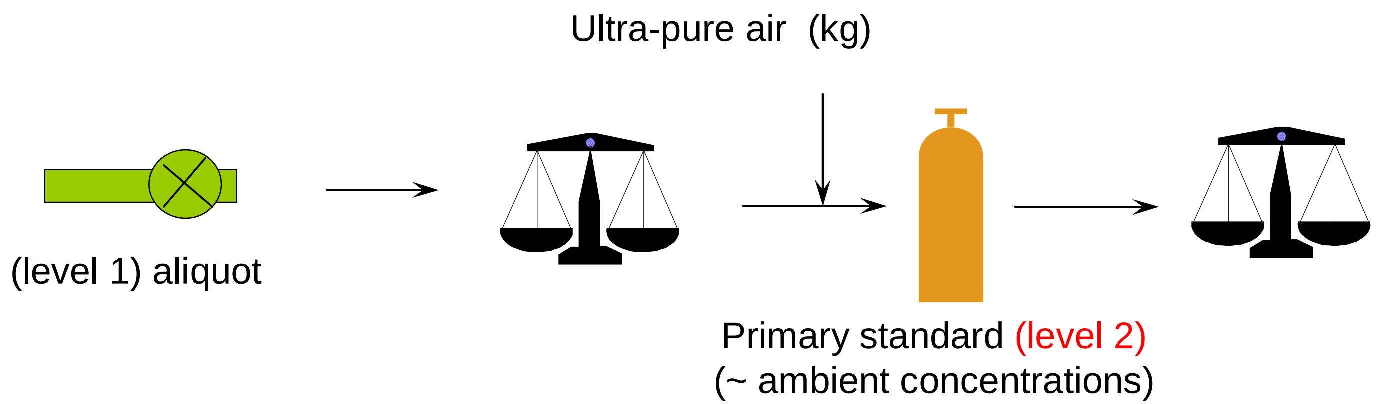
NOAA: Gravimetric method, pure starting material
(all components added gravimetrically)

SIO: Gravimetric/Bootstrapping, pure starting material

NIES: Gravimetric dilution of commercial mixtures

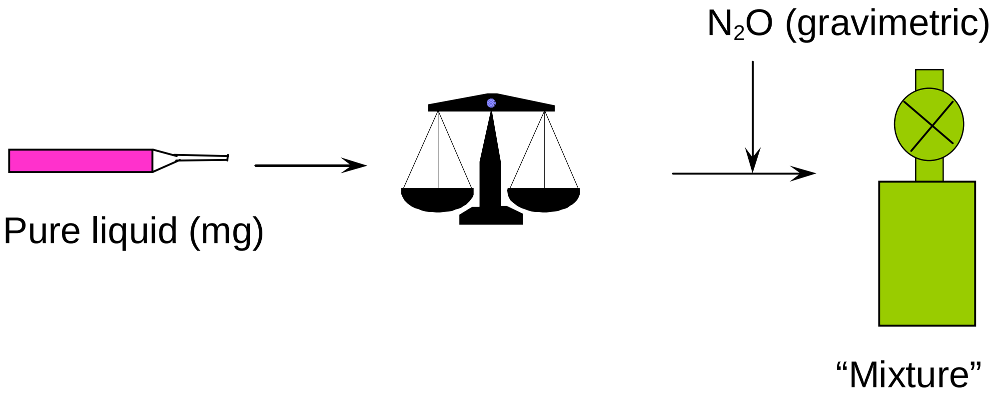
NOAA method

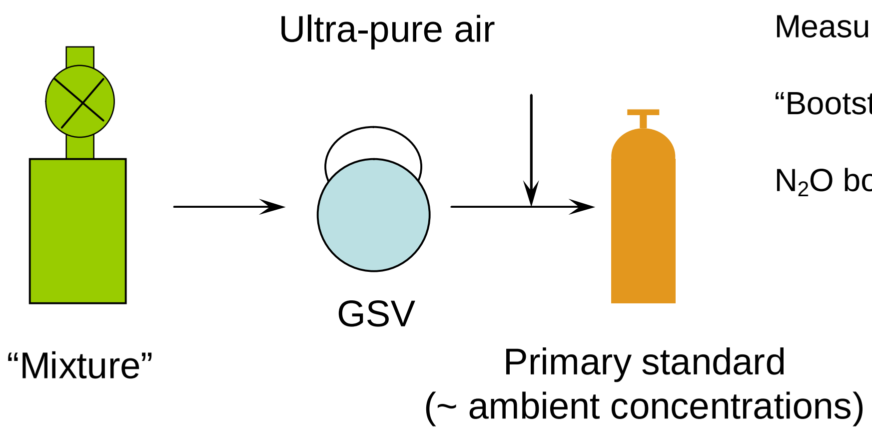

Pure gas (g)
Pure liquid (mg)
Ultra-pure air (kg)
Primary standard (level 1)


Ultra-pure air (kg)
(level 1) aliquot
Primary standard (level 2)
(~ ambient concentrations)

Scale: Dry air mole fraction (not pptv)

SIO method



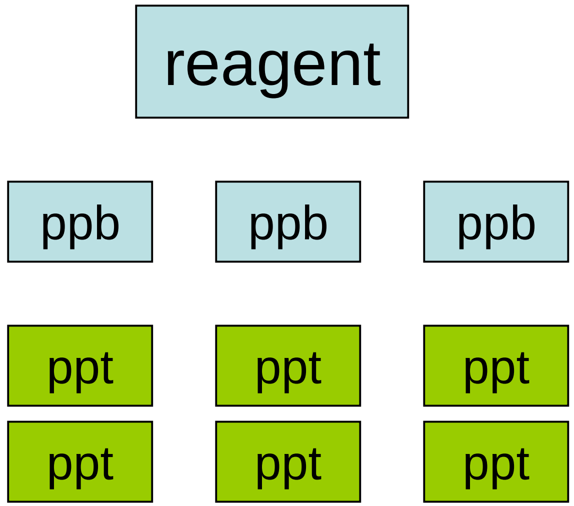


Measure N_2O to determine dilution factor.

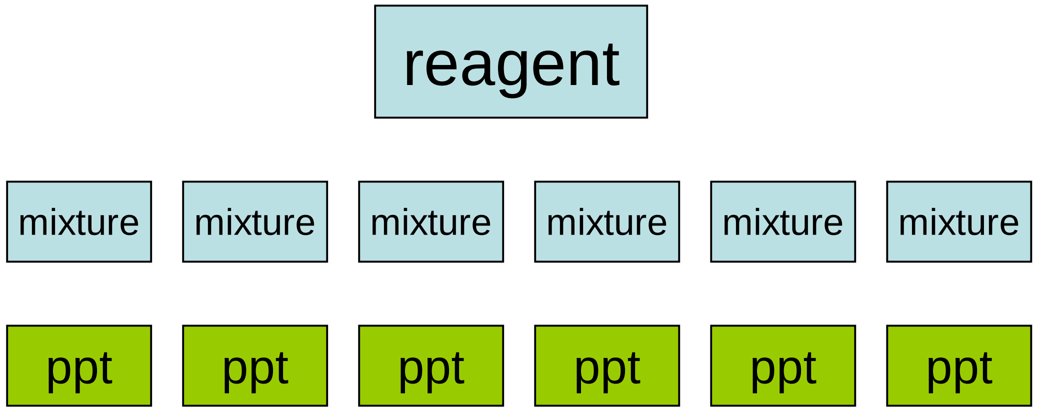
"Bootstrap to N_2O"

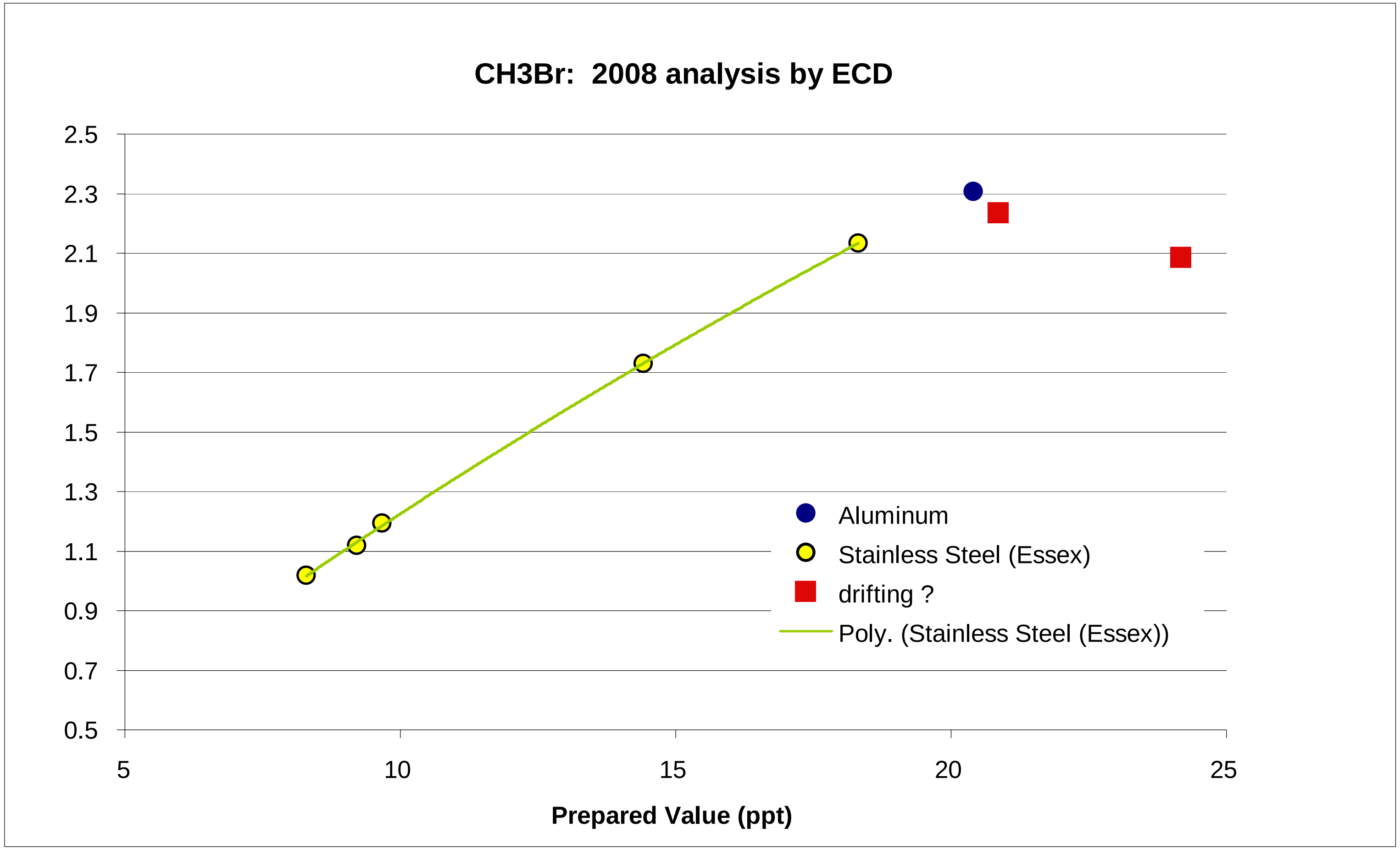
N_2O bootstrapped to CO_2 (Keeling)

NOAA

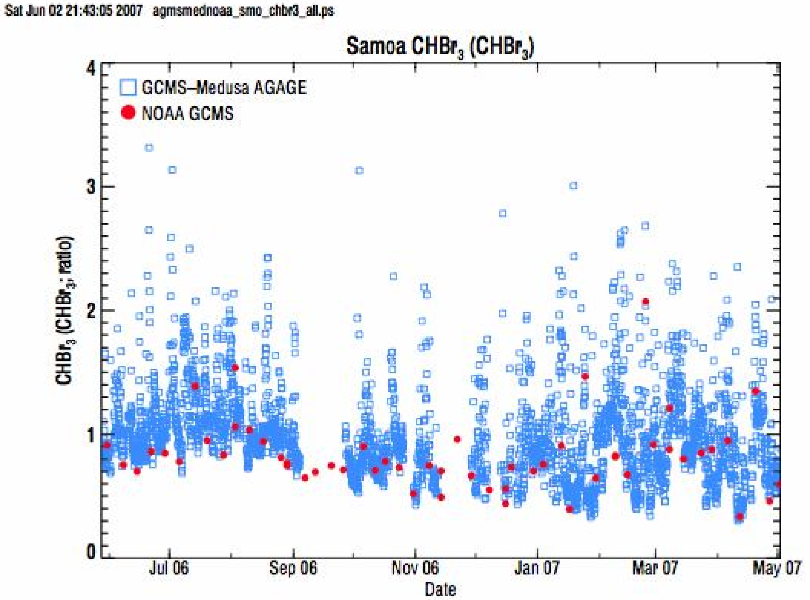


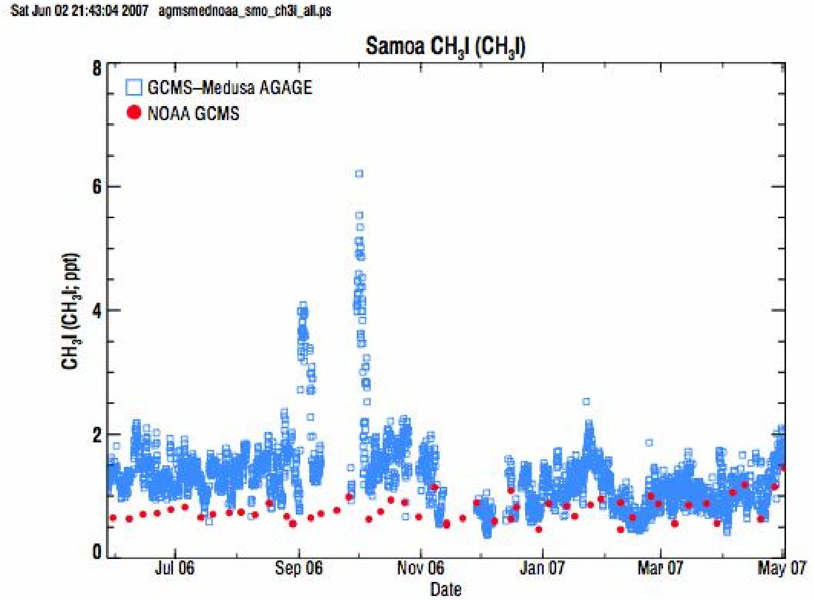
SIO

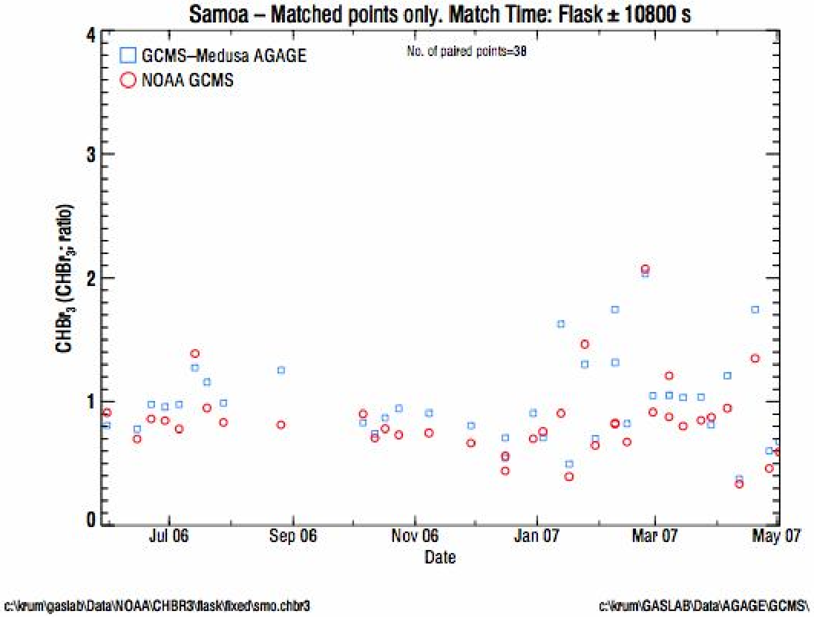

reagent
mixture
mixture
mixture
mixture
mixture
mixture
ppt
ppt
ppt
ppt
ppt
ppt



Uncertainties (NOAA): ~5% for VSL halocarbons


Sat Jun 02 21:43:05 2007 agmsmednoaa_smo_chbr3_all.ps
Samoa CHBr3 (CHBr3)
GCMS–Medusa AGAGE
NOAA GCMS
CHBr3 (CHBr3; ratio)
Jul 06
Sep 06
Nov 06
Jan 07
Mar 07
May 07
Date


Sat Jun 02 21:43:04 2007 agmsmednoaa_smo_ch3i_all.ps
Samoa CH3I (CH3I)
GCMS–Medusa AGAGE
NOAA GCMS
CH3I (CH3I; ppt)
Jul 06
Sep 06
Nov 06
Jan 07
Mar 07
May 07
Date


Samoa – Matched points only. Match Time: Flask ± 10800 s
GCMS–Medusa AGAGE
NOAA GCMS
No. of paired points=38
CHBr3 (CHBr3; ratio)
Jul 06
Sep 06
Nov 06
Jan 07
Mar 07
May 07
Date
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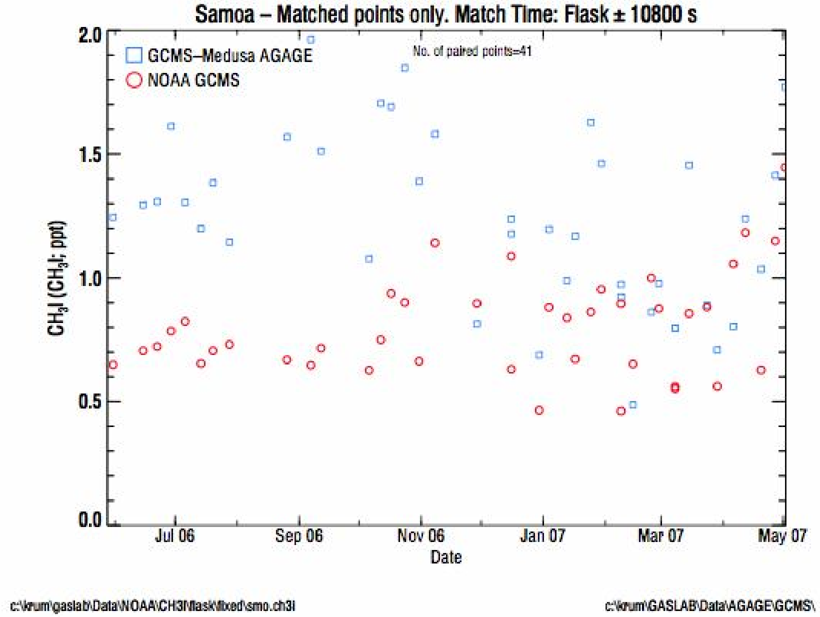
c:\krum\GASLAB\Data\AGAGE\GCMS\


Samoa – Matched points only. Match Time: Flask ± 10800 s
GCMS–Medusa AGAGE
NOAA GCMS
No. of paired points=41
CH3I (CH3I; ppt)
Jul 06
Sep 06
Nov 06
Jan 07
Mar 07
May 07
Date
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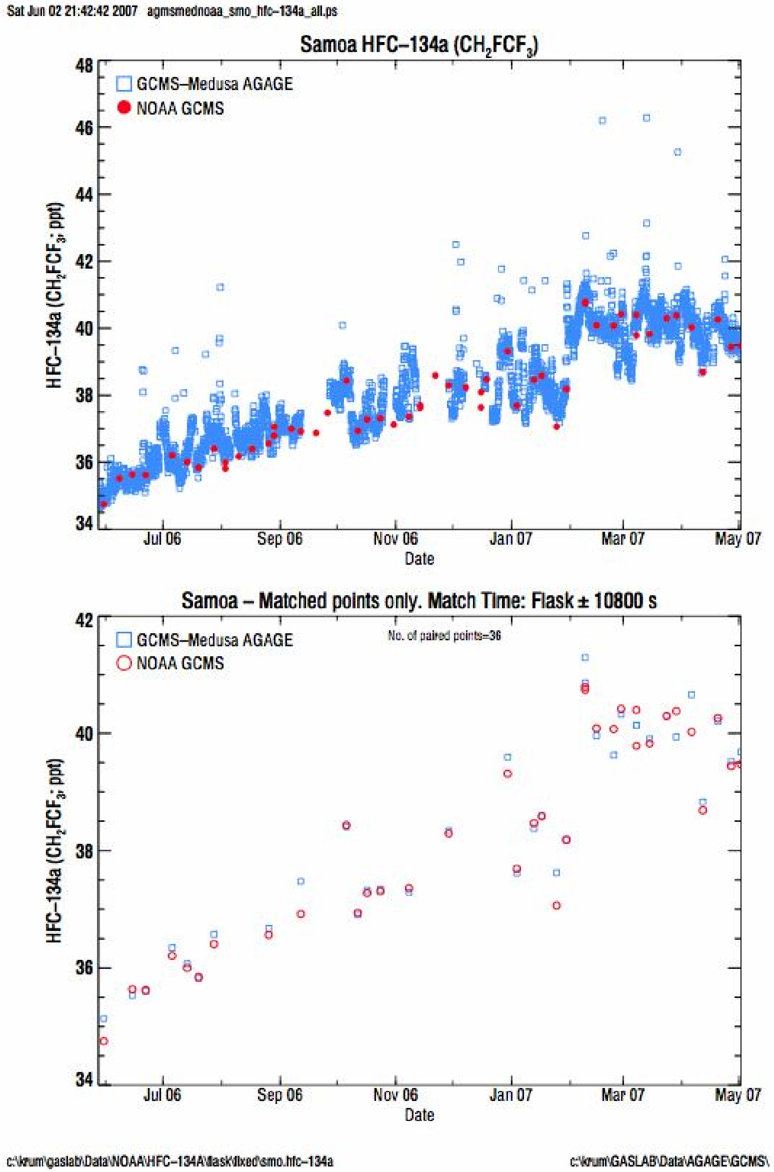
c:\krum\GASLAB\Data\AGAGE\GCMS\



Sat Jun 02 21:42:42 2007 agmsmednoaa_smo_hfc-134a_all.ps
Samoa HFC-134a (CH_2FCF_3)
GCMS-Medusa AGAGE
NOAA GCMS
HFC-134a (CH_2FCF_3; ppt)
Date
Jul 06
Sep 06
Nov 06
Jan 07
Mar 07
May 07
Samoa – Matched points only. Match Time: Flask ± 10800 s
No. of paired points=36
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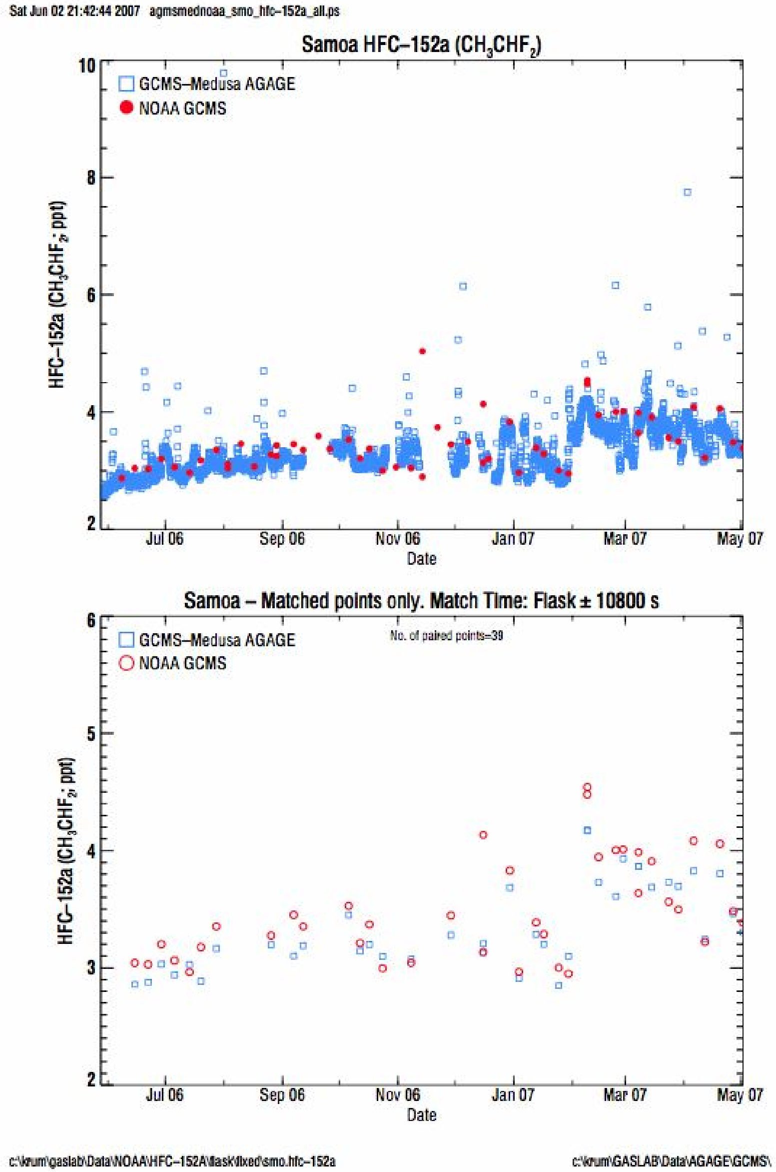
c:\krum\GASLAB\Data\AGAGE\GCMS\



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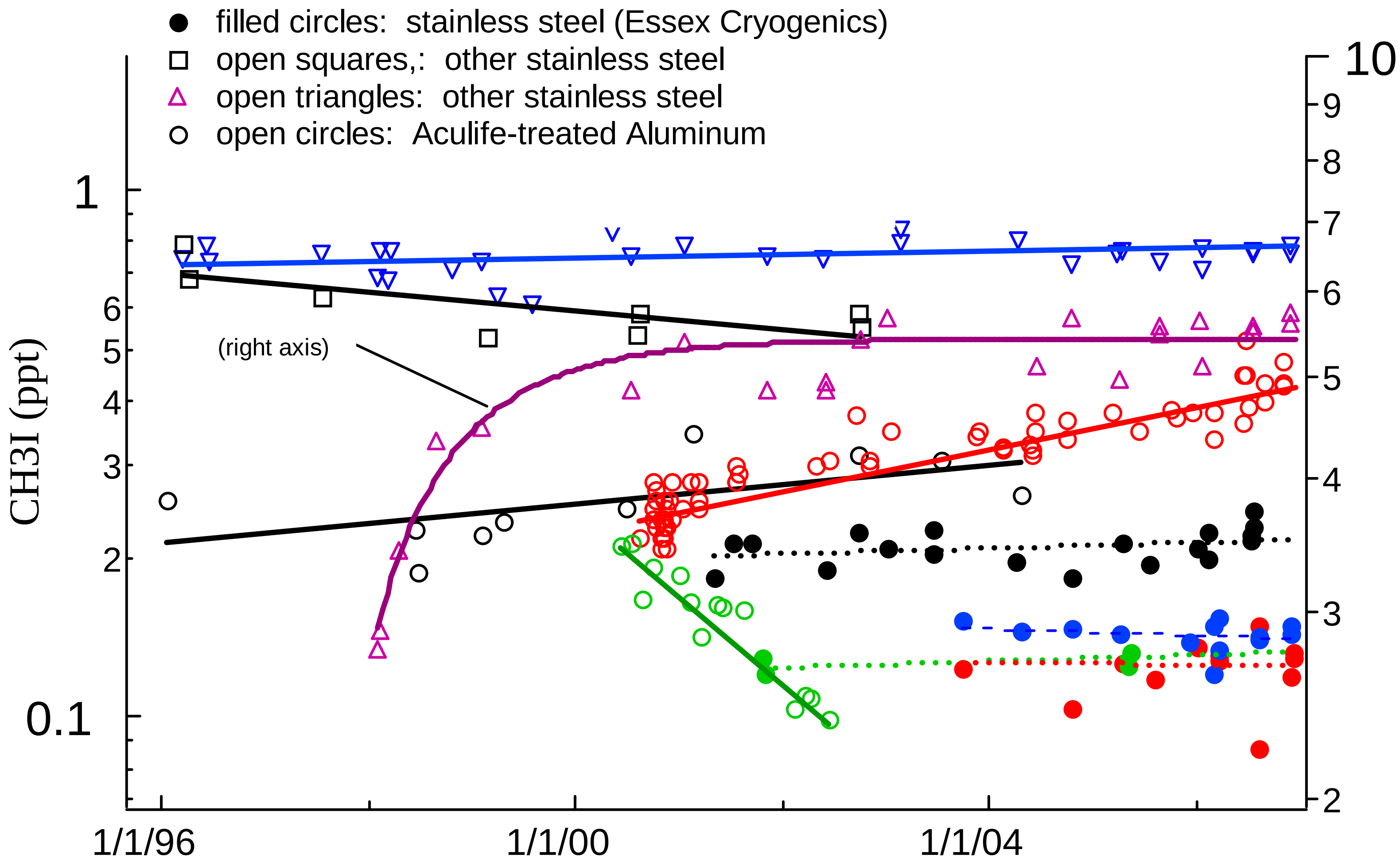
Samoa HFC-152a (CH_3CHF_2)
GCMS-Medusa AGAGE
NOAA GCMS
HFC-152a (CH_3CHF_2; ppt)
Date
Jul 06
Sep 06
Nov 06
Jan 07
Mar 07
May 07
Samoa – Matched points only. Match Time: Flask ± 10800 s
No. of paired points=39
c:\krum\gaslab\Data\NOAA\HFC-152A\flask\fixed\smo.hfc-152a
c:\krum\GASLAB\Data\AGAGE\GCMS\

Limitations: Stability



Permeation Systems

Basic Idea: Dynamic dilution of a pure compound (or a known mixture) to working concentration levels

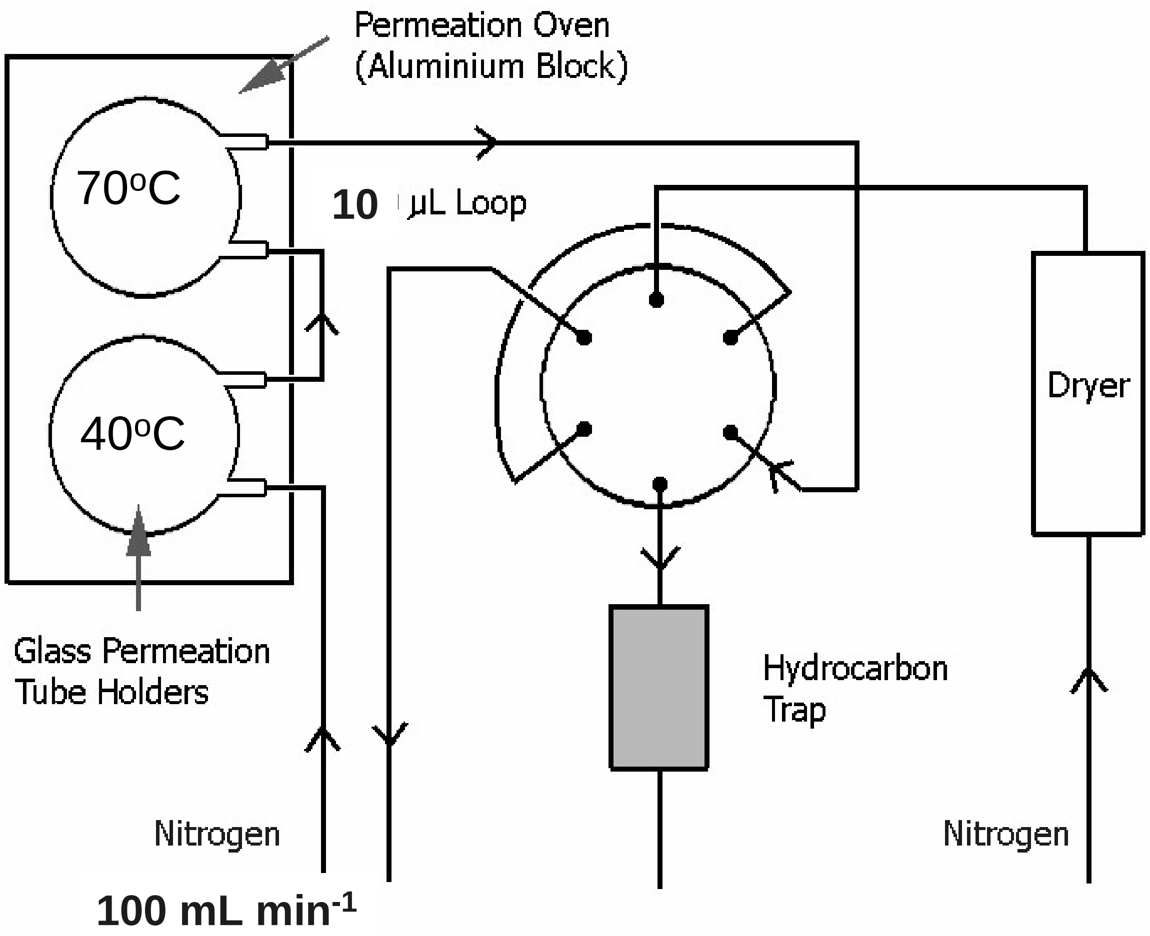
Pros: multiple species, simple linearity check

Cons: ?

Permeation system used at University of York

CH_3I, C_2H_5I, CH_2ICl, $CHCl_3$, CH_2Br_2, $CHBr_2Cl$

1-and 2- C_3H_7I, CH_2IBr, $CHBr_3$, CH_2I_2



See Wevill and Carpenter, 2004

- Commercial (Ecoscientific) permeation tubes filled in-house

- Loop system introduces ppt level halocarbons into gas stream

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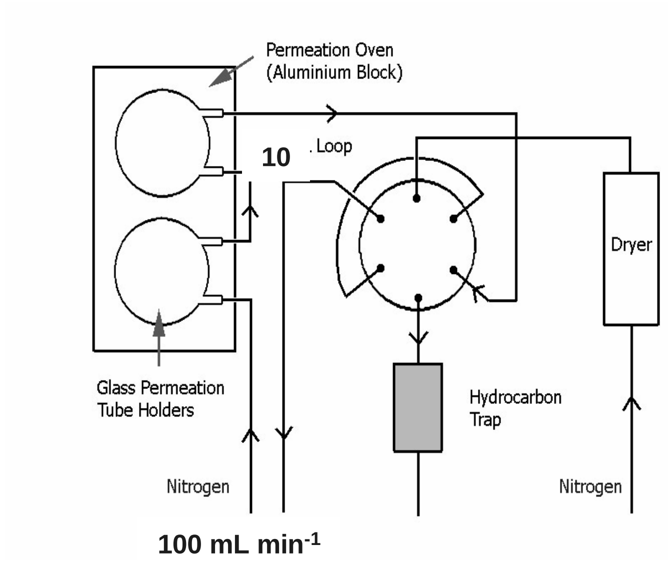
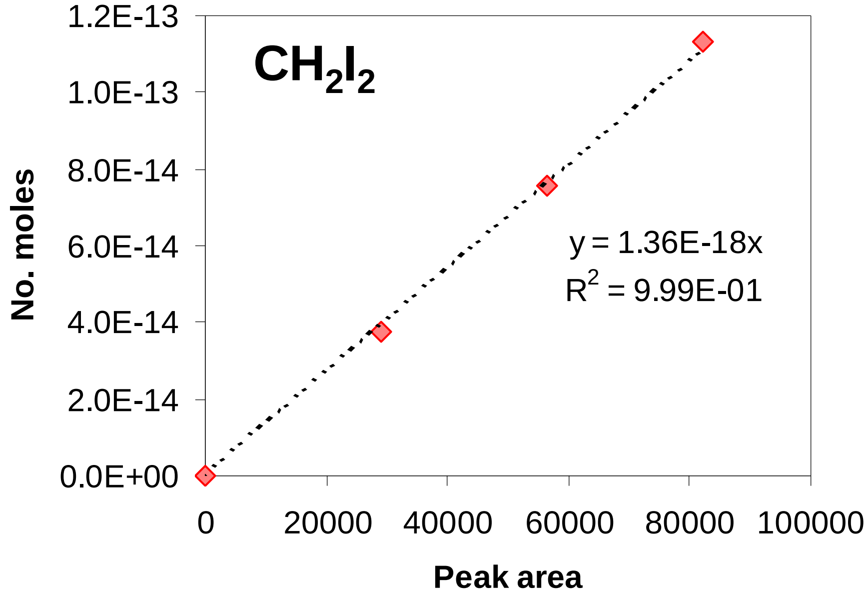
- Calculate no. of moles in 1 loop:

$$= \frac{\text{permeation rate (g/min}^{-1}) \times \text{loop vol (mL)}}{\text{RMM (g mol}^{-1}) \times \text{flow rate (mL/min}^{-1})}$$



- Inject 0- 3 loops into gas stream, determine moles/PA



Assuming normal dist., standard deviation of the slope, s_m:

$$s_m = \sqrt{\frac{SS_{resid}/(N-2)}{\Sigma(x_i - x)^2}} \quad \sim 3\%$$

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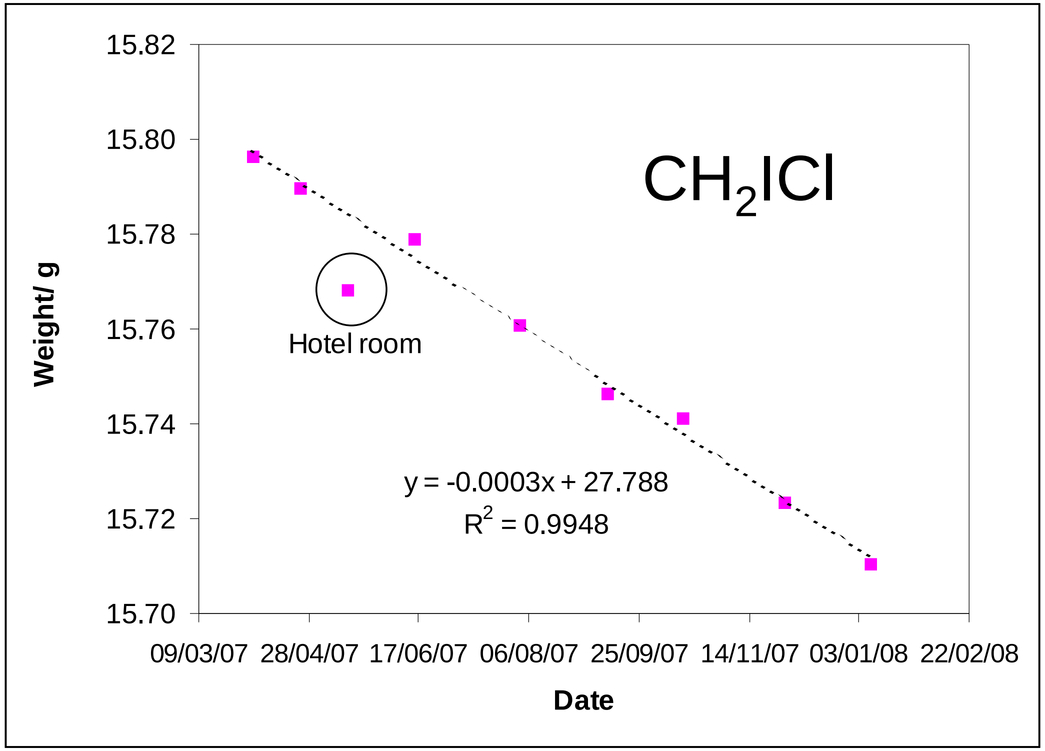
Uncertainty in permeation weighings



Data points are average of 6 weighings and include error bars

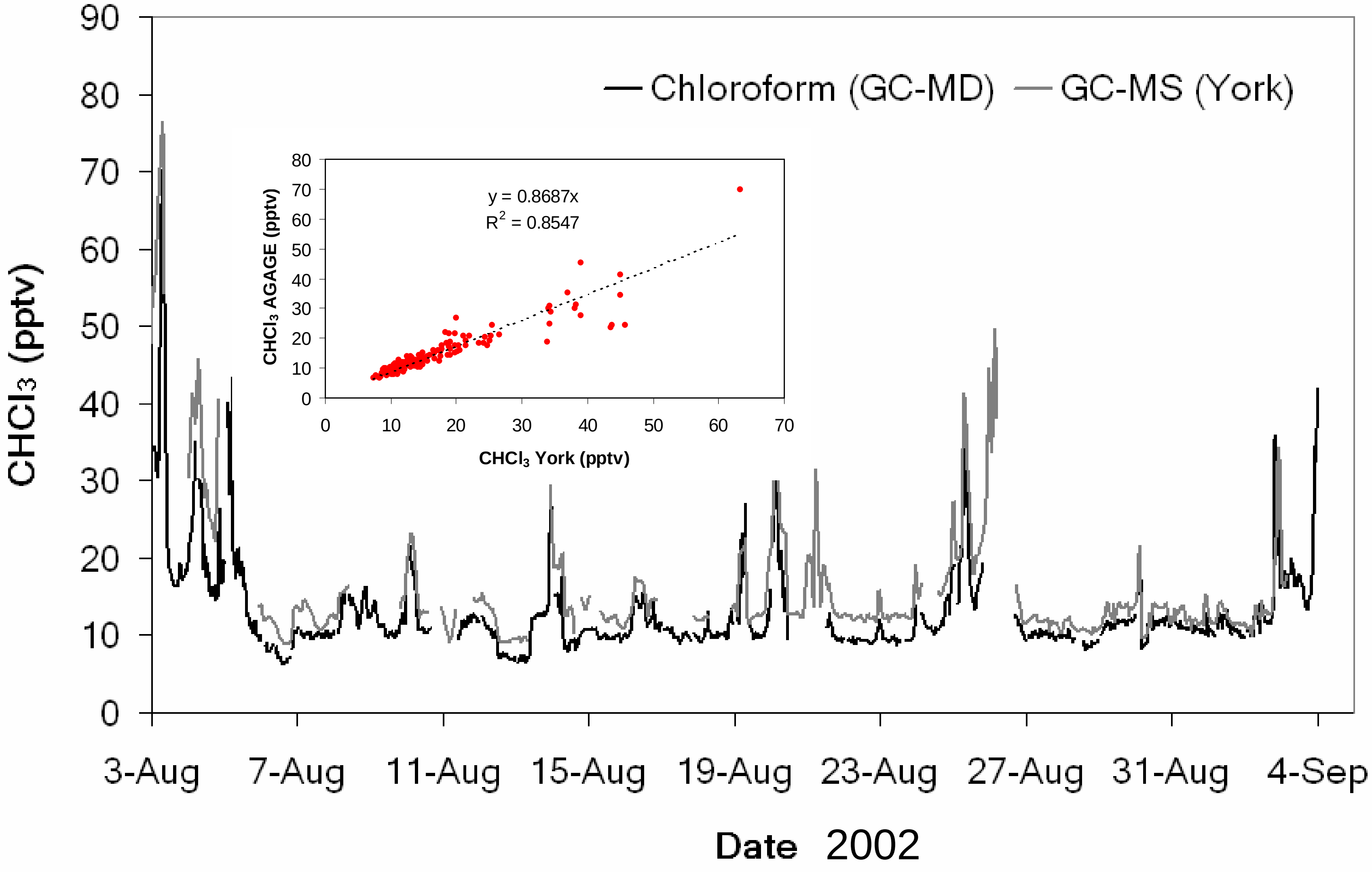
- This can be major uncertainty unless several months of weighings are made.
- Standard deviation of slope, $s_{m,}$ for 9 month period of weighings ~ $\pm$ 5 %

Total uncertainty s_y/y for $y = a \times b/c$ can be estimated as:

$$s_y/y = \sqrt{(s_a/a)^2 + (s_b/b)^2 + (s_c/c)^2}$$

Uncertainty associated with gas-phase sampling		%RSD	
a) bias	sample line loss		0
b) bias	sample flow rate	±	2
c) bias	atmospheric artefacts		0
d) noise	reproducibility of repeat air standards (which takes into account noise on integration of chromatograms)	±	4.4
Uncertainty associated with water sampling			
e) bias	losses in water sample		0
f) bias	sample flow rate (manufacturers uncertainty)	±	2
g) noise	reproducibility of purge efficiency (which takes into account human error on purge volumes + noise on integration of chromatograms)	±	10.3
Uncertainty associated with calibration and detection			
h) noise	perm tube weighings	±	5
i) bias	stated mass balance uncertainty	±	1
j) noise	calibration linear regression	±	3
k) bias	flow rate through permeation tube + dilution flow	±	2
l) bias	loop volume	±	10
total uncertainty air,%			**12.7**
total uncertainty water,%			**15.8**

Comparison with AGAGE $CHCl_3$ measurements at Mace Head:

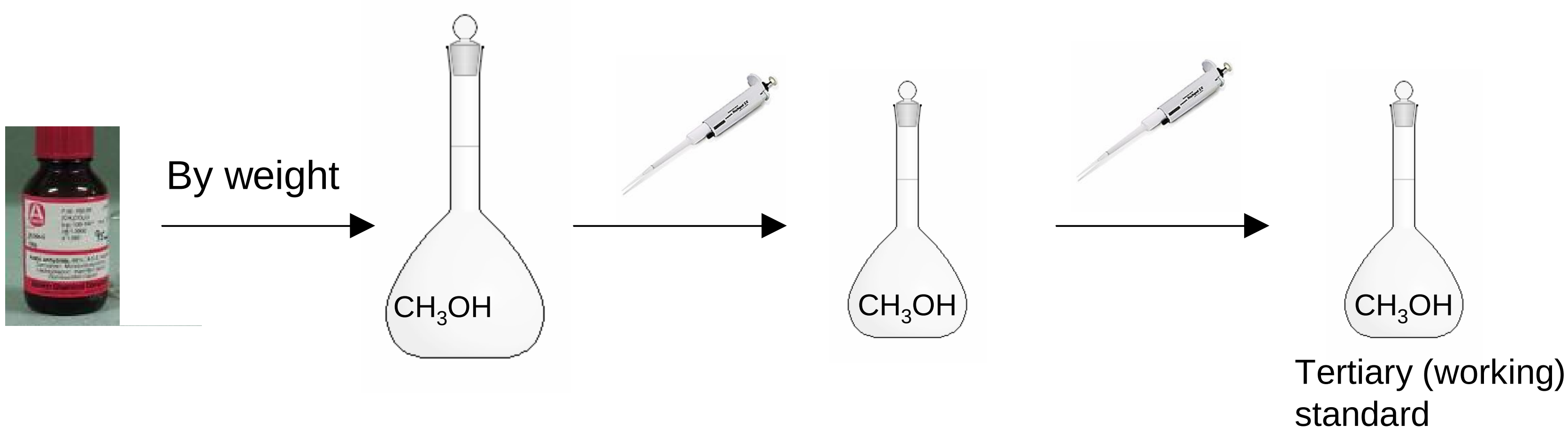


Liquid Standards

Basic Idea: Static dilution of a pure compound in a solvent using volumetric or gravimetric techniques

Pros: simplicity, direct calibration of sea water
Cons: ?

Preparation of liquid halocarbon standards -UEA



1. Preparation of primary standard:
   - A 50 ml volumetric flask containing methanol near to level is weighed (4 decimals)
   - The flask is weighed again after addition of 0.5-2 grams of commercial neat halocarbon and then taken to volume
2. Primary standards are shipped into the field on dry ice and are kept in a freezer until use.
3. Secondary and tertiary (working) standards are prepared by successive dilution before calibrating.
4. For calibrations, variable amounts (µL) of working standard are injected into syringes containing 40 ml of halocarbon-free seawater.
5. The seawater is injected in the purge vessel and treated in the same manner as the samples.

When using class-A glassware and calibrated scales and pipettes, the relative error in the standard concentration is ~ 2%.

Reagent Purity

$CHBr_3$ (Sigma-Aldrich)
98%
1% CH_2Br_2
1% $CHBrCBr_2$

$CHCl_3$ (Sigma-Aldrich)
99+ %

Halon-1211 (Scott Specialty Gases)
99%
1% $CHBrF_2$

CH_3Br (Matheson)
99%
1% CH_3Cl

Reagent Purity

$CHBr_3$ (Sigma-Aldrich)
98%
1% CH_2Br_2
1% $CHBrCBr_2$

$CHCl_3$ (Sigma-Aldrich)
99+ %

Halon-1211 (Scott Specialty Gases)
99%
1% $CHBrF_2$

CH_3Br (Matheson)
99%
1% CH_3Cl

$CHBr_3$ (Spectrum)
94%
1% CH_2Br_2
2% dichloropropanol
3% unknown

CH_2BrCl (Sigma-Aldrich)
96%
3% CH_2Cl_2
1% CH_2Br_2

CH_2Br_2 (Sigma-Aldrich))
90%
9% CH_2BrCl
1% CH_2Cl_2

END