HALOCARBON MEASUREMENTS AT CAPE GRIM, TASMANIA

P. Fraser (CSIRO)

INSTRUMENT : BRAZZOS (LOVELOCK) GC

CONSTANT FREQUENCY (COULOMETRIC) ECD

SILICONE OV101 COLUMN, N_2 CARRIER GAS

ISOTHERMAL

SPECIES :	CCl_3F (CFC-11)	1-2 %
	CH_3CCl_3 (METHYL CHLOROFORM)	8 %
PRECISION	CCl_4 (CCl_4)	1-2 %

MEASUREMENT FREQUENCY : 4 samples / day

CALIBRATION : CCl_3F, CCl_4 ... Coulometry / ambient air tank

CH_3CCl_3 .... none

PERIOD : 1976 – 1982

PROBLEMS : POOR PRECISION

LINEARITY

CALIBRATION STABILITY

HALOCARBON MEASUREMENTS AT CAPE GRIM, TASMANIA

ALE (ATMOSPHERIC LIFETIME EXPERIMENT)

INSTRUMENT : HEWLETT PACKARD 5840 GC
CONSTANT CURRENT ECDs
2 COLUMNS - SILICONE & PORASIL (D)
CARRIER GAS - Ar / CH_4
ISOTHERMAL

SPECIES & PRECISION :	SILICONE	PORASIL (D)
	CCl_3F 0.6 %	CCl_3F 1.0 %
	CH_3CCl_3 1.6 %	CCl_2F_2 0.5 %
	CCl_4 0.9 %	N_2O 0.3 %

MEASUREMENT FREQUENCY : 4 Samples / day

CALIBRATION : CCl_3F, CCl_2F_2 } STATIC DILUTION (RASMUSSEN) & COULOMETRY (LOVELOCK)

CH_3CCl_3, N_2O } STATIC DILUTION (RASMUSSEN)

CCl_4 COULOMETRY (LOVELOCK)

PERIOD : 1978 – 1985

PROBLEMS : CALIBRATION STABILITY
LINEARITY
SHARED INTEGRATION

HALOCARBON MEASUREMENTS AT CAPE GRIM, TASMANIA

GAGE (GLOBAL ATMOSPHERIC GASES EXPERIMENT)

INSTRUMENT : HEWLETT PACKARD 5880 GC

3 COLUMNS - SILICONE, PORASIL (D), MOL. SIEVE

3 DETECTORS - 2 CONSTANT CURRENT ECDS

1 FID

CARRIER GAS Ar/CH_4 & N_2

ISOTHERMAL

SPECIES & PECISION :	SILICONE	PORASIL (D)	MOLECULAR SIEVE
	CCl_3F 0.4%	CCl_3F 0.3%	CH_4 0.1%
	CCl_2FCCl_2F 1.5%	CCl_2F_2 0.3%	
	CH_3CCl_3 0.4%	N_2O 0.1%	
	CCl_4 0.2%		
	$CHCl_3$ 5%		

MEASUREMENT FREQUENCY : 12 Samples / day

CALIBRATION : CCl_3F, CCl_2F_2, CH_3CCl_3, CCl_4, N_2O
- Same as ALE

CCl_2FCCl_2F — MAKIDE (STATIC DILUTION)

$CHCl_3$ — NIST (DYNAMIC DILUTION)

CH_4 — RASMUSSEN / NIST

PERIOD : 1981 — 1992

PROBLEMS : CALIBRATION STABILITY
LINEARITY

HALOCARBON MEASUREMENTS AT CAPE GRIM, TASMANIA

AGAGE (ADVANCED GLOBAL ATMOSPHERIC GASES EXPERIMENT)

INSTRUMENT : HEWLETT PACKARD 5890 GC II

2 COLUMNS — SILICONE, PORASIL (C)
2 ECDs
CARLE GC (CH_4)
1 COLUMN — MOLECULAR SIEVE
1 FID

installed at Cape Grim late 1992.

IMPROVEMENTS

(1) HIGHER PRECISION CH_4 measurements.

(2) HIGHER PRECISION N_2O measurements.

(3) REDUCED CALIBRATION GAS CONSUMPTION.

(4) HIGHER FREQ. OF MEASUREMENT.

(5) DAILY LINEARITY CHECKS.

(6) NEW, REPRODUCIBLE ABSOLUTE STANDARDS.

" CALIBRATION STANDARDS FOR MEASUREMENT OF ATMOSPHERIC HALOCARBONS "

Yoshihiro MAKIDE, Prof.

The University of Tokyo

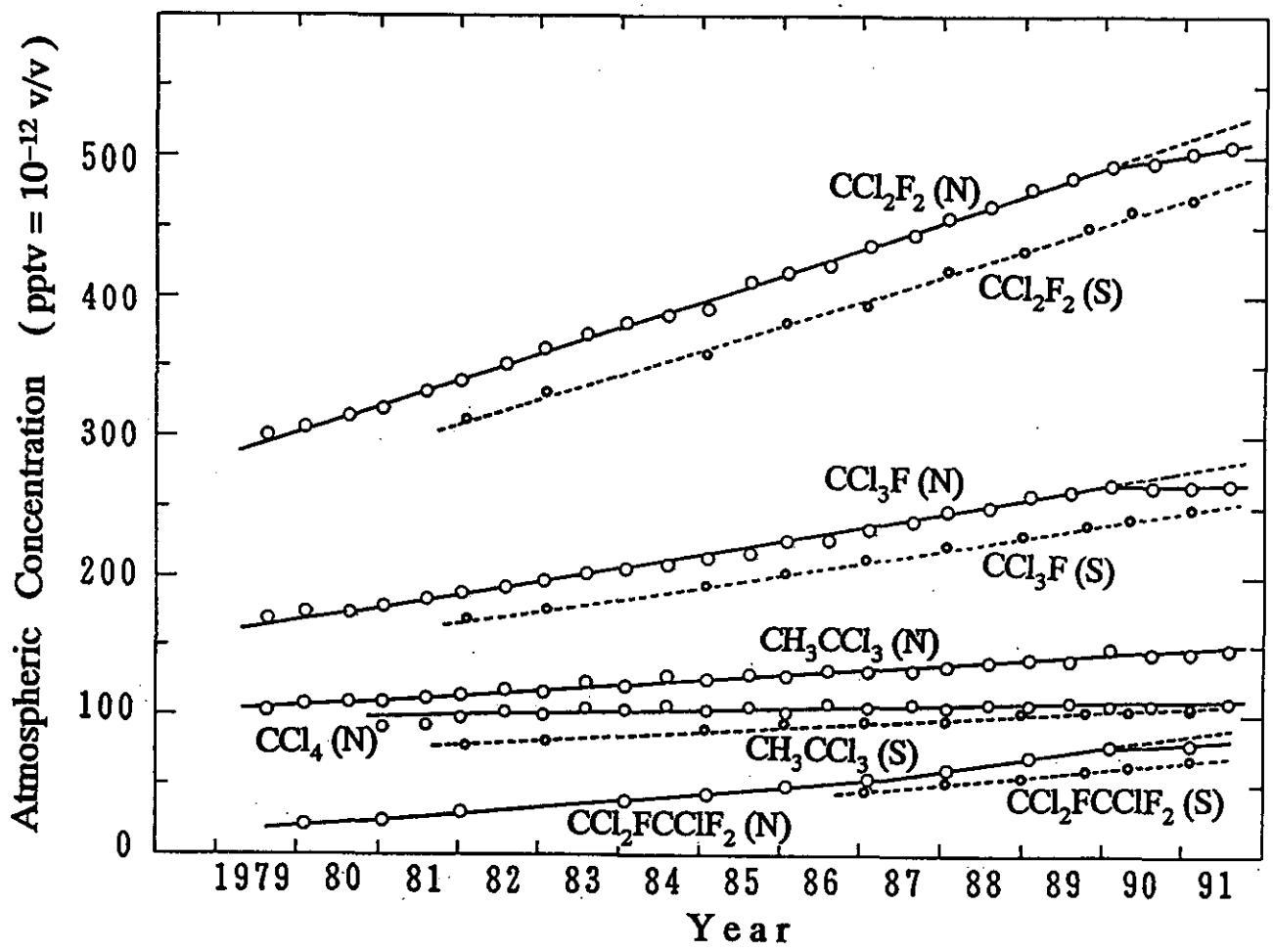


Fig. Observed Atmospheric Concentrations of Halocarbons in the Mid-latitude Northern Hemisphere (N : Hokkaido, Japan, 42–45°N) and Southern Hemisphere (S : Syowa Station, Antarctica, 69°S)

HALOCARBON STANDARDS :

(1) Difficulties in the Preparation of Halocarbon Standards :

1) Extremely Low Concentrations at pptv (10^{-12} v/v) Levels

2) Adsorption and Contamination Problems
e.g. CCl_4, CH_3CCl_3, CFC113

(2) Extremely Large Dilution Ranges :

CO_2 : $3x10^3$, CH_4 : $5x10^5$, N_20 : $3x10^6$

Halocarbons, CFCs & Halons : $2x10^9$ — 10^{12}

(3) Dilution Methods :

1) Dynamic Dilution :
Less precise
Less accurate
Maximum dilution ranges: 10^3 -10^4

2) Static Dilution :
Complicated
Needs a vacuum line equipped with accurately known volumes and reliable pressure gages

(4) First Step Dilution:

1) by Weight (Gravimetric) :
   Accurate
   Costly
   Adsorption problem for sticky halocarbons

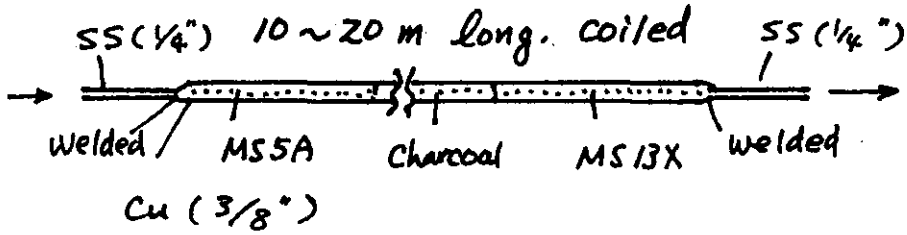
2) by Volume / Pressure :
   Temperature: ±0.3°C change →0.1% error
   Pressure: 0.05% error →0.05% error
   Ideal gas condition: at low pressure

(5) Dilution Gases / Carrier Gases :

1) High Purity Nitrogen As a Carrier Gas and As an Early Stage Dilution Gas of Standard

2) High Purity Air for Final Dilution of Standard

3) Further Purification of the High Purity Gases for the Halocarbon Measurements :
   Purification Column:
   MS 5A → Charcoal → MS 13X
   (MS13X is effective for large size halocarbons)
   activated at 350°C, and used at room temperature



4) Contamination from the System :

Pressure controller, mass flow controller, and valves contain rubber diaphragm or often have been Washed by halocarbons (e.g. Nupro SS Bellows valves by CFC 113)

5) Further Purification after the Flow Control :

Short purification column packed with MS 13X works well for the halocarbon measurements.

(6) Static Dilution Procedure :

Volume : 1 – 10 ml ----→ 1 – 5 – 10 l

10^2 – 10^3 – 10^4 times dilution

Pressure : 10 – 100 Torr ----→ 10000 Torr

10^2 --- 10^3 times dilution

(1 gage) (2 gages)

In order to avoid systematic error and contamination,

- 2 to 3 step dilution using volume – pressure combination is convenient and accurate enough.

→ each dilution must be done using different systems.

PREPARATION OF CCl_4, CH_3CCl_3, AND OTHER HEAVY (STICKY) HALOCARBON STANDARDS BY INTRODUCING WATER VAPOR:

(1) Observed Phenomena :

1) Natural air with high humidity can be stored for long time without change.

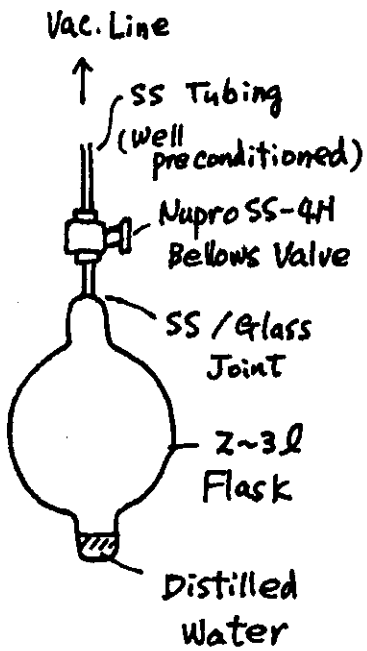
2) CCl_4 and other heavy halocarbons in extremely dry samples (or stratospheric samples) decrease (or disappear) rapidly.

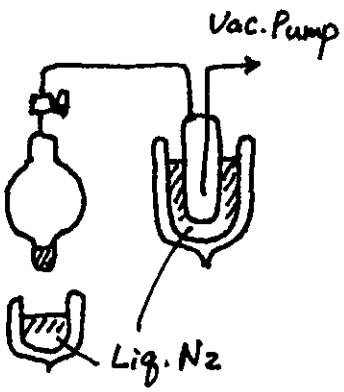
3) CCl_4 standard (in extremely pure, extremely dry nitrogen or air) can not be prepared without change.

(2) Resolution :

Introduction of water (diluted by nitrogen or air) into the system / canister can prevent the adsorption of CCl_4, etc., on the active metal surface inside and column packings.

(3) Preparation of Halocarbon Free Purified Water and Water Saturated Gas Reservoir :





1) Introduce ion-exchanged and distilled water into a clean glass flask equipped with a stainless steel connection.

2) Attach a well treated (conditioned) all stainless steel bellows valve (e.g. Nupro SS-4H).

3) Roughly evacuate the flask.

4) Freeze the water inside from the bottom of the flask very slowly leaving the water surface unfrozen.

5) Before the water surface freeze, evacuate the flask for short time ; water vapor works as diffusion pump oil and removes the impurities in the gas phase.

6) Close the valve and thaw the ice inside.

7) Repeat the process 4)- 6) more than 10 times.

8) Introduce the purified nitrogen or air into the flask.

9) Use the flask as a water saturated nitrogen / air reservoir.

TREATMENT OF SAMPLING CANISTERS FOR CCl_4 (and OTHER HALOCARBON) MEASUREMENT :

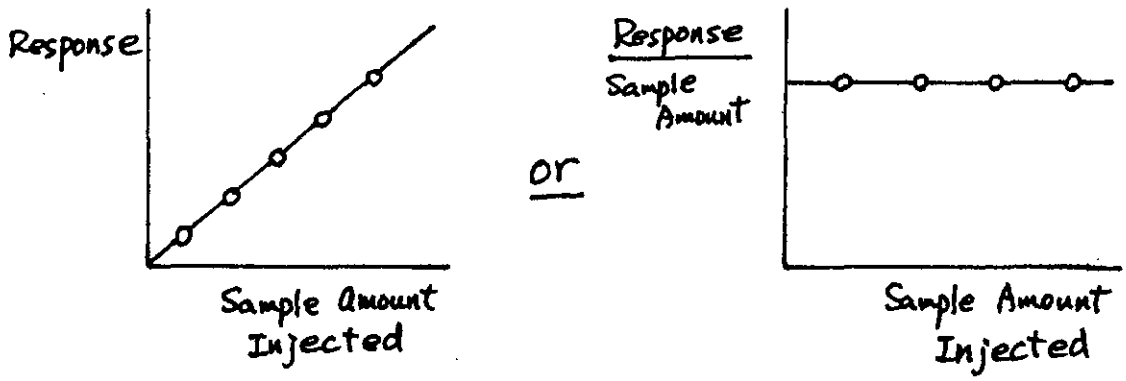
!! After the cleaning by using water, the canisters are evacuated and heated to below 110°C.

At this temperature (110°C), most impurities are evacuated leaving the water on the metal surface.

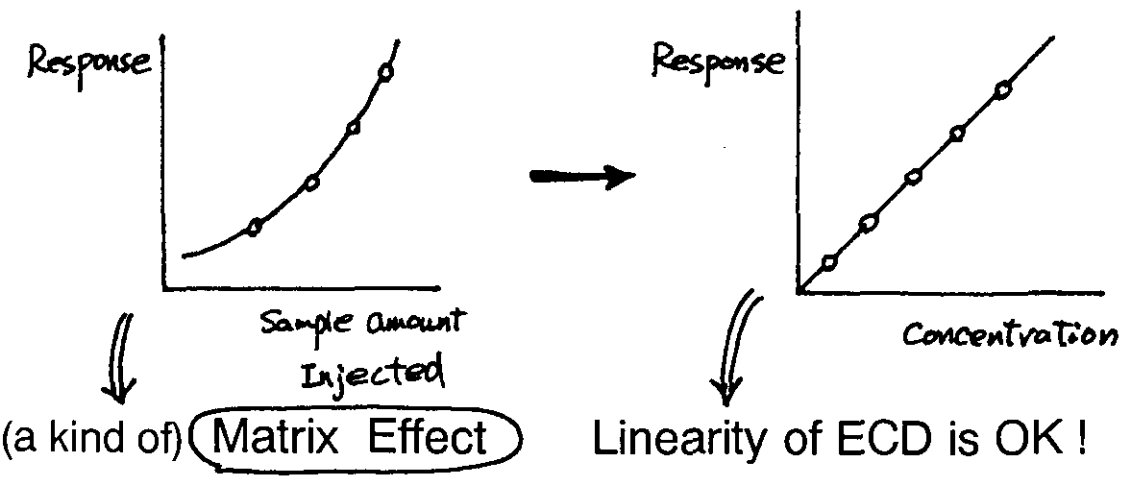
CALIBRATION OF THE EC DETECTOR RESPONSE :

LINEARITY OF THE DETECTOR AND MATRIX GAS EFFECT :

▸ If natural air samples (or standards) show a constant sensitivity by changing sample size introduced
→ Everything is working perfectly.



▸▸ If not → The linearity of the detector response has to be checked by changing the concentration itself ; not by changing the introduced sample amount.



(a kind of) Matrix Effect

Linearity of ECD is OK !

Linearity of the ECD Detector :

Since atmospheric measurement (of the background concentration samples) uses the lower part of the linear range of the detector response, there is no problem of the linearity in most cases.

Matrix Gas Effect on ECD Response :

Example : O_2 effect on N_2O signal
Air effect on CFC-12 signal

Oxygen in the air peak especially affect on the small retention time compounds (or small molecules)

This is the " Matrix Effect " Which Dr. R. Weiss and Dr. J. Elkins have claimed as the " Non-linearity of the EC Detector "

RESOLUTION !!

1) By pass the air peak by using a valve before the detector.
or
2) Separate the air peak by using a precolumn.
or
3) Preconcentrate the minor constituents at low temperature trap.