



# PFC Emissions Monitoring by FT-IR in LCD Manufacturing Processes

MIDAC Corporation



# Overview



- ◆ FT-IR monitoring to reduce PFC emissions in Semiconductor Facilities
- ◆ Applying FT-IR Monitoring to LCD manufacturing process
- ◆ Efforts for reducing PFC emissions in Asian Countries



## FT-IR monitoring to reduce PFC emissions in Semiconductor Facilities



Every semiconductor manufacture in the world is making efforts to monitor and reduce PFC emissions from their facilities based on an agreement of the World Semiconductor Council.

The agreement aims at over-10% reduction of the amount of total PFC emission compare to that of 1995 by 2010.

For PFC emissions monitoring, they already have the established testing methodologies such as “Guidelines for Environmental Characterization for Semiconductor Equipment” presented by International SEMATECH.

## PFC Emission Calculation based on IPCC's Formula (1)

$$[\text{Emission of FC}_i] = (1-h) \sum p(\text{FC}_{i,p}) [(1-C_{i,p}) * (1-A_{i,p} * D_{i,p}) * \text{GWPI} + B_{i,p} (1-A_{i,p} * D_{\text{CF}_4,p}) * \text{GWPCF}_4]$$

Where:

$i$  = FC gas (NF<sub>3</sub>, CF<sub>4</sub>, etc.)

$p$  = Process Type (Etching or CVD chamber cleaning)

$\text{FC}_{i,p}$  = Mass of gas  $i$  fed into process type  $p$  (kg of gas  $i$ )

$A_{i,p}$  = Fraction of gas volume fed into processes with emission control technologies

$C_{i,p}$  = Use rate (fraction destroyed or transformed) for each gas  $i$  and process type  $p$

$D_{i,p}$  = Fraction of gas  $i$  destroyed by emission control technology

$B_{i,p}$  = Fraction of gas  $i$  transformed into CF<sub>4</sub> for each process type

## PFC Emission Calculation based on IPCC's Formula (2)

Method	Process	Emission factor ( $C_i$ , $B_i$ , $d_i$ )
Tier 1	No distinction	Default Value $d_i = 0$
Tier 2a	Small subsets of processes or tools	Company-Specific or Fab –Specific measurement data
Tier 2b	CVD and Etching (only process types)	Default Value or Company (Fab)-Specific measurement data
Tier 2c	No distinction	Default Value



## Introduction of “Guidelines for Environmental Characterization for Semiconductor Equipment” (1)



This document has been designed to provide guidance to equipment and abatement suppliers on how to characterize the environmental performance of their semiconductor processes.

The characterization must include quantification of both air and water emissions.

It also describes tool types and types of emission information required for each tool type.



## Introduction of “Guidelines for Environmental Characterization for Semiconductor Equipment” (2)



For Air Emissions, emissions testing methods must include a volume balance that accounts for >90% of fluorine, chlorine, and bromine.

In order to calculate mass balance of above compounds, specified emission compounds should be quantified for a particular process chemical. There is a list for Target Compounds

*(For details, refer to the section 2.1 of “Guidelines for Environmental Characterization for Semiconductor Equipment”)*

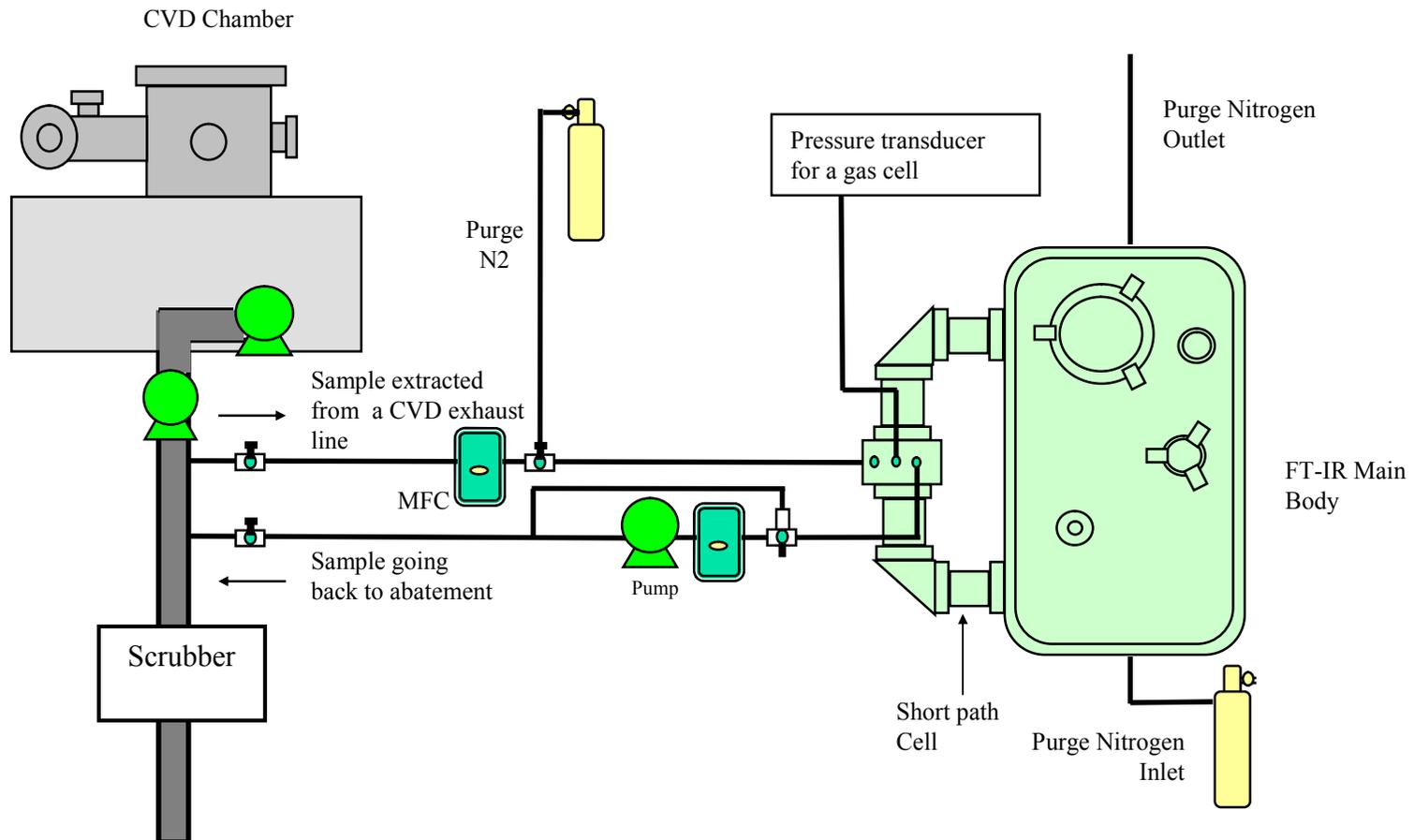
The testing methods must follow an approved method (Fourier transform infrared [FT-IR] or quadruple mass spectroscopy [QMS])

# Epson method datasheet

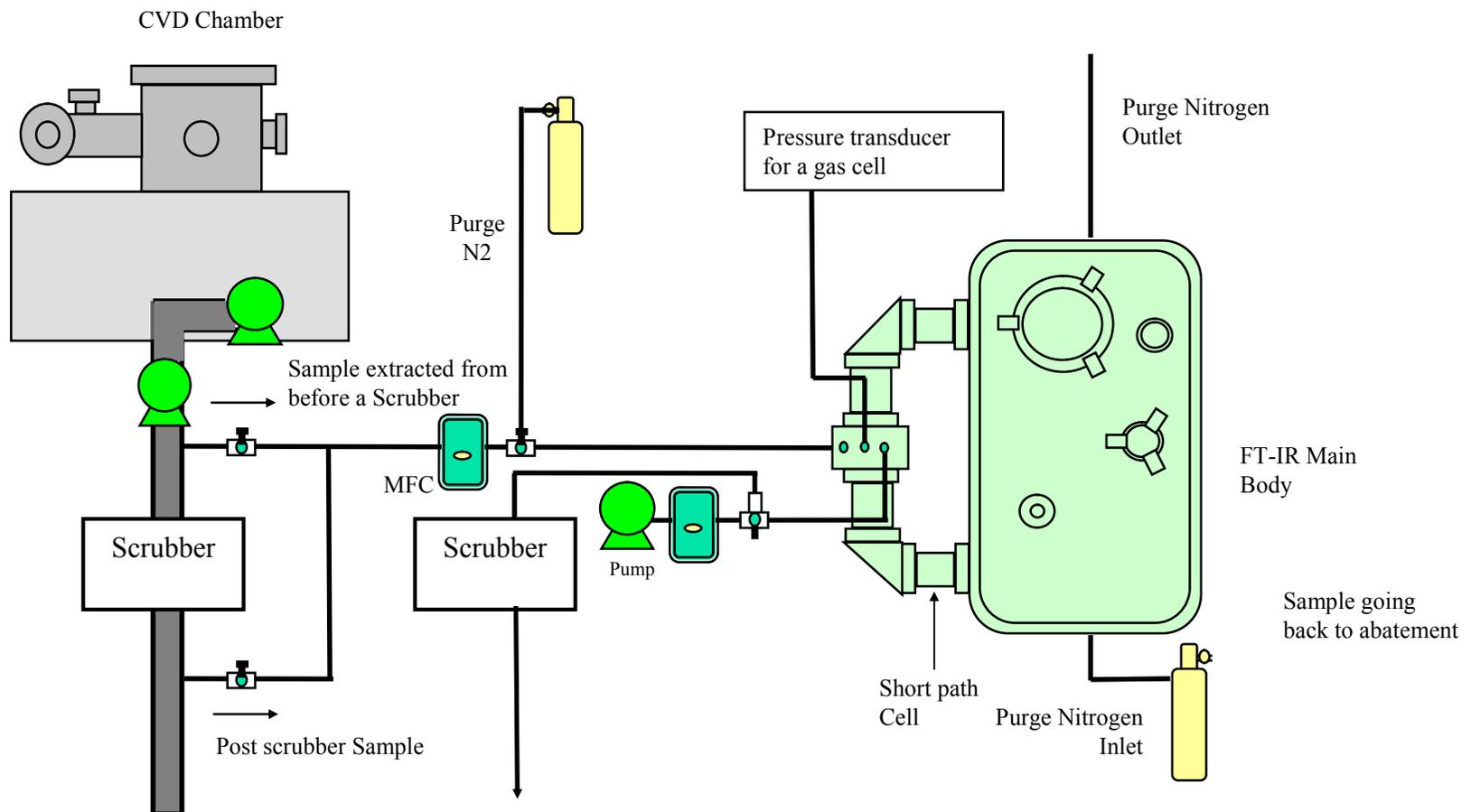
Designed to facilitate FT-IR measurement complying with “Guidelines for Environmental Characterization for Semiconductor Equipment” It was originally created using MIDAC reference libraries, “Standards”.

a molecular formula		Target Compound	measure range	libraries and wave number ranges( $\text{cm}^{-1}$ )
CF4	■	Process Chemical	~60ppm-m	CF4_Z3A, _15A, 2CF429, 59(1230-1305)
CHF3	■	Target Emission	~60ppm-m	TFM_7A(1111-1215)、_15A(1316-1437)
C2F4			~46ppm-m	2C2F4_4, _2(1161-1212)
C2F6	■	Target Emission	~150ppm-m	C2F6_7A(1218-1290), _Z11A, _23A(1082-1136)
C3F8	■		~525ppm-m	C3F8Z3A, 19A, 11A(956-1061)
C4F8	■		~180ppm-m	2C4F8_5, _1(920-1020)
SF6	■		~40ppm-m	SF6_3A, _15A, _Z19A(910-1009)
NF3	■		~105ppm-m	2NF3_31, _30(832-960)
CO		Target Emission	20~300ppm-m	CO_31A(2143-2246)
CO2		Target Emission	~66ppm-m	CO2_51A, _48, _45, _42(2280-2390)
COF2		Target Emission	~106ppm-m	COF2_55A, _43A(1790-2015)
OF2		Target Emission	20~446ppm-m	OF2_17S(755-1012)
HF		Target Emission	~720ppm-m	2HF_30, _28, _26, _24(4032-4080)
SiF4		Target Emission	~57ppm-m	SIF4_38A(1000-1058)
SOF2			~90ppm-m	SOF2_17S(712-860)
SO2F2			~130ppm-m	2SO2F212(1445-1545)
SO2			~126ppm-m	SO2_3A(1290-1415)
NO			50~500ppm-m	NO_27A(1757-1990)
NO2			~140ppm-m	NO2_19A(1525-1791)
N2O			~150ppm-m	2N2O_10, _8(1216-1338)

# Configuration for Monitoring CVDs



# Configuration for Monitoring Scrubbers



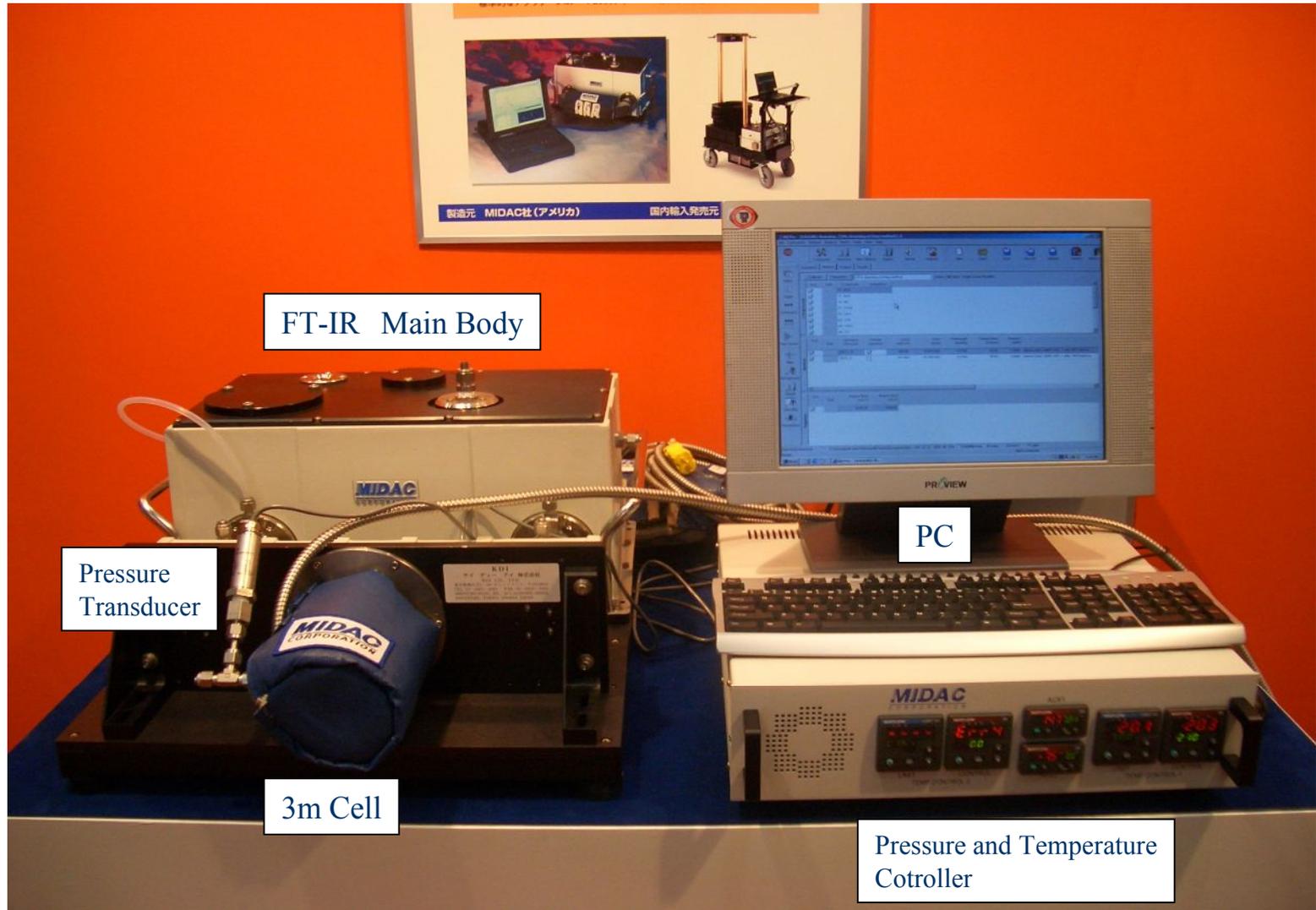
# Measurable concentration ranges of major PFC compounds for each cell path length

MDL: Minimum Detection Limit UDL: Upper Detection Limit

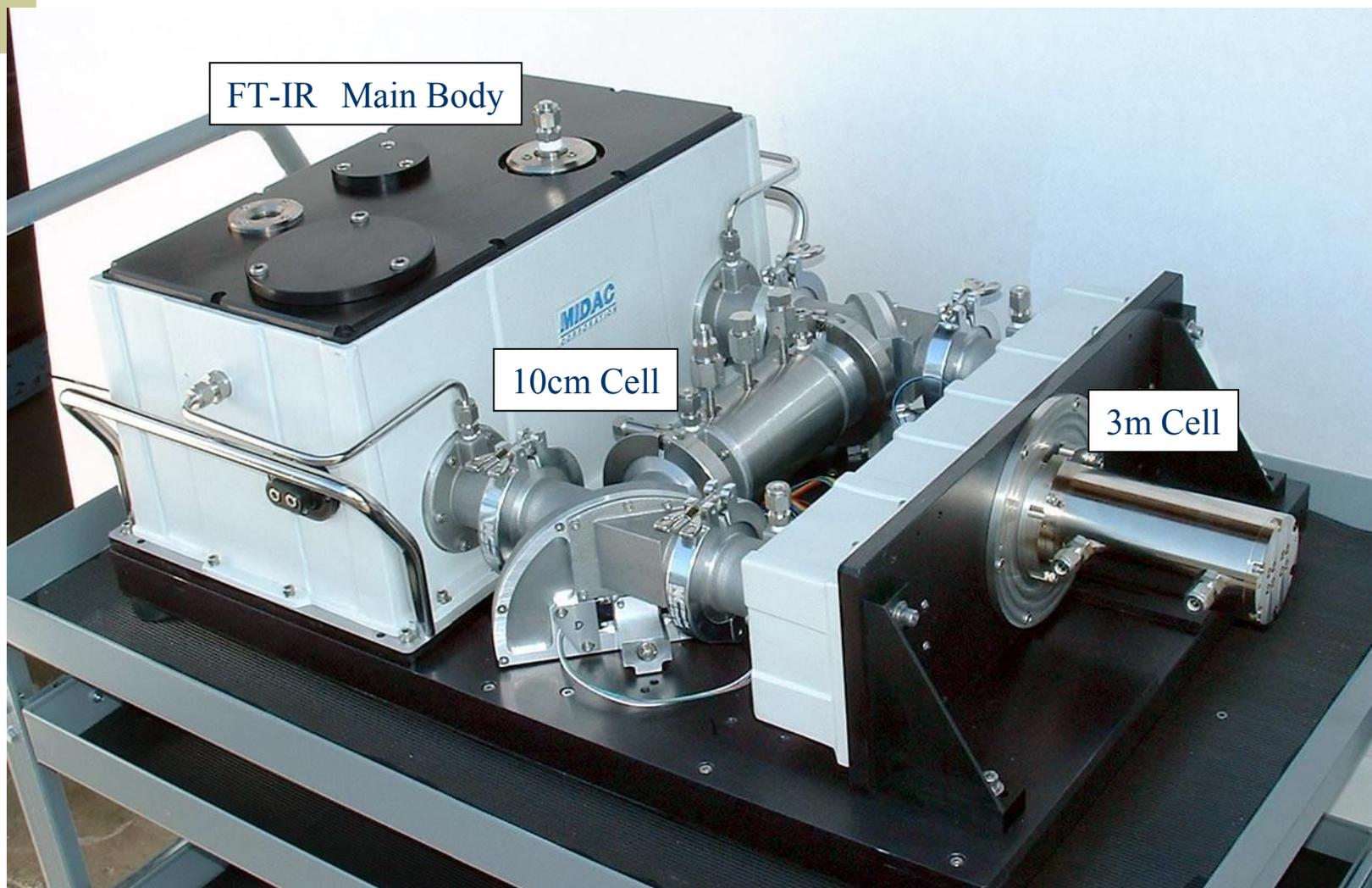
	1cm Cell		10cm Cell		3m Cell		20m Cell	
	MDL PPM	UDL PPM	MDL PPM	UDL PPM	MDL PPM	UDL PPM	MDL PPM	UDL PPM
<b>CF4</b>	3	40000	0.3	4000	0.010	133	0.002	20
<b>CHF3</b>	14	40000	1.4	4000	0.047	133	0.007	20
<b>C2F6</b>	10	40000	1	4000	0.033	133	0.005	20
<b>C3F8</b>	5	50000	0.5	5000	0.017	167	0.003	25
<b>C4F8</b>	25	18000	2.5	1800	0.083	60	0.013	9
<b>SF6</b>	4	3400	0.4	340	0.013	11	0.002	1.7
<b>NF3</b>	27	30000	2.7	3000	0.090	100	0.014	15
<b>CO</b>	500	30000	50	3000	1.667	100	0.250	15
<b>CO2</b>	10	13500	1	1350	0.033	45	0.005	6.75
<b>COF2</b>	100	10000	10	1000	0.333	33	0.050	5
<b>HF</b>	125	72000	12.5	7200	0.417	240	0.063	36
<b>SiF4</b>	45	5700	4.5	570	0.150	19	0.023	2.85
<b>SO2</b>	15	12600	1.5	1260	0.050	42	0.008	6.3
<b>NO</b>	1100	50000	110	5000	3.667	167	0.550	25
<b>NO2</b>	140	14000	14	1400	0.467	47	0.070	7
<b>N2O</b>	360	15000	36	1500	1.200	50	0.180	7.5

Since above values are theoretically calculated based on Minimum and Upper Detection Limits of 1m Cell, Limits can change depending on measurement environments or if gasses are mixed.

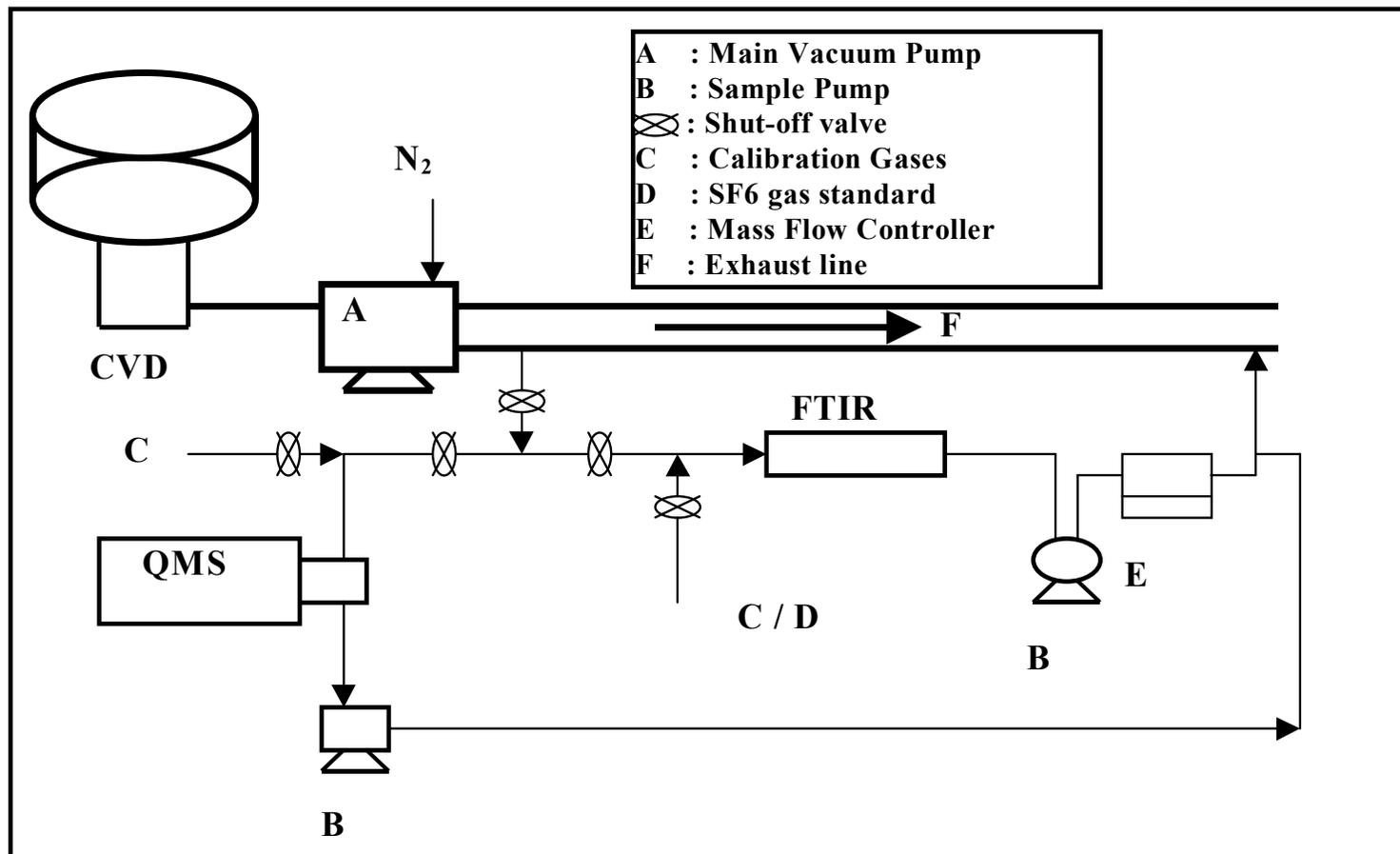
# MIDAC I4000 Series



## MIDAC I4000 Series Dual Cell Model



# QMS & FTIR Setup for Exhaust Monitoring



# QMS and FTIR as Complementary Tools(1)

## FT-IR

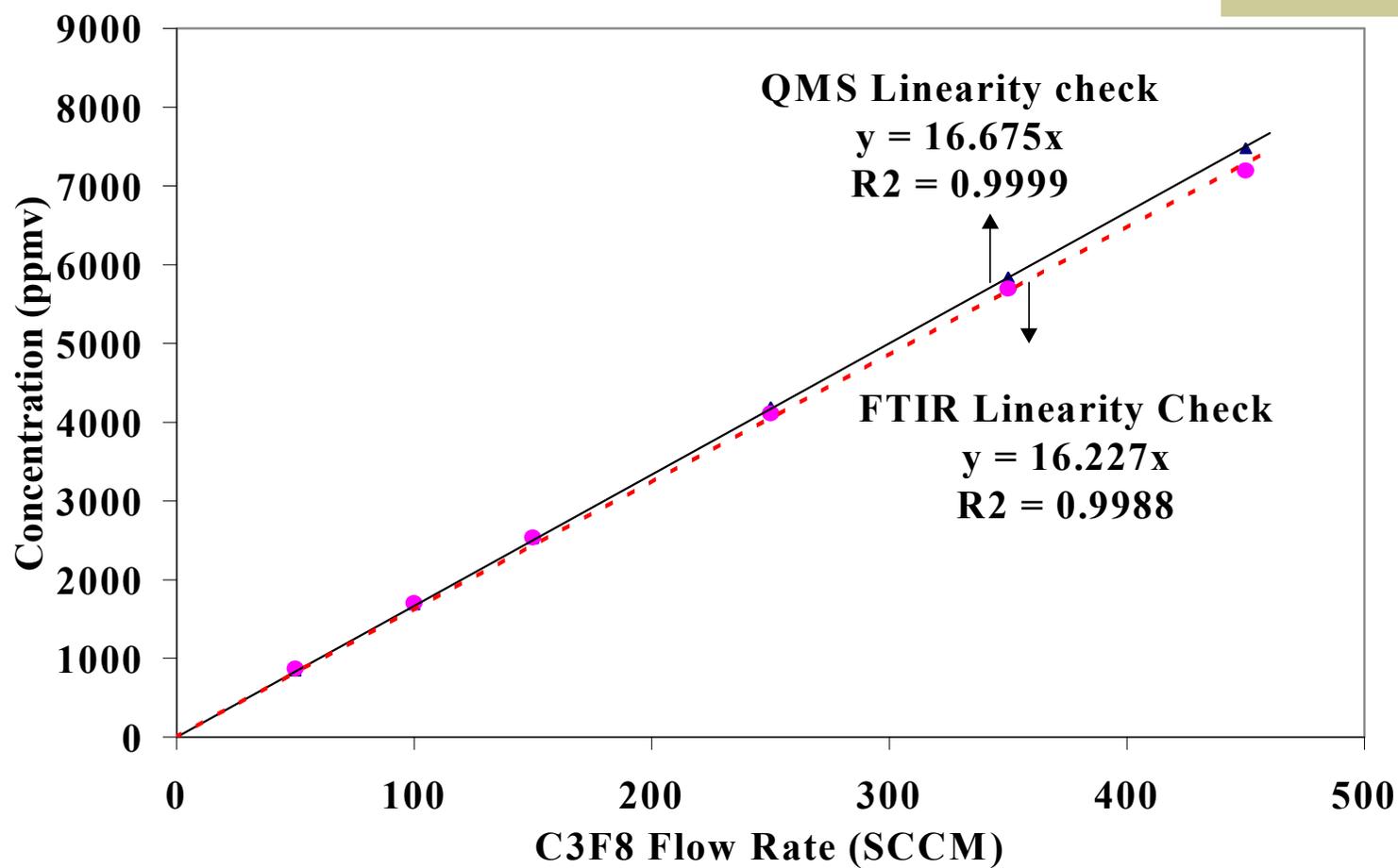
- ◆ Advantages:
  - On Site Quantitative Analysis of all PFCs and most of the HAPs
  - Non destructive and Real-Time Analysis
  - Relatively low cost
  - Off-site calibration and periodic on-site response checks
- ◆ QA(*Quality Assurance*)/QC(*Quality Control*) Check:
  - Cell path length
  - Linearity check
- ◆ Disadvantages:
  - Cannot detect homonuclear diatomic species (Ex: F<sub>2</sub>, Cl<sub>2</sub> etc.)

# QMS and FTIR as Complementary Tools(2)

## QMS

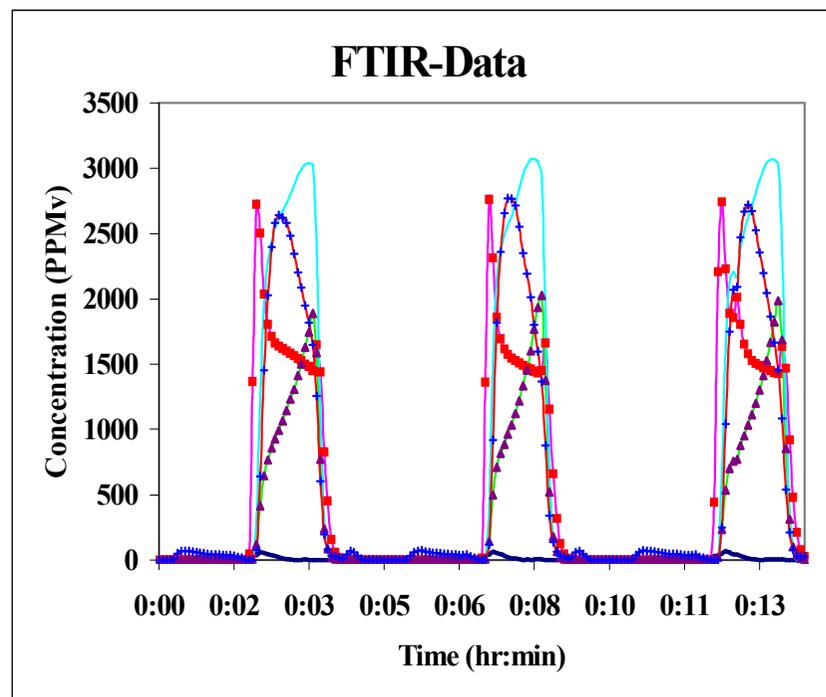
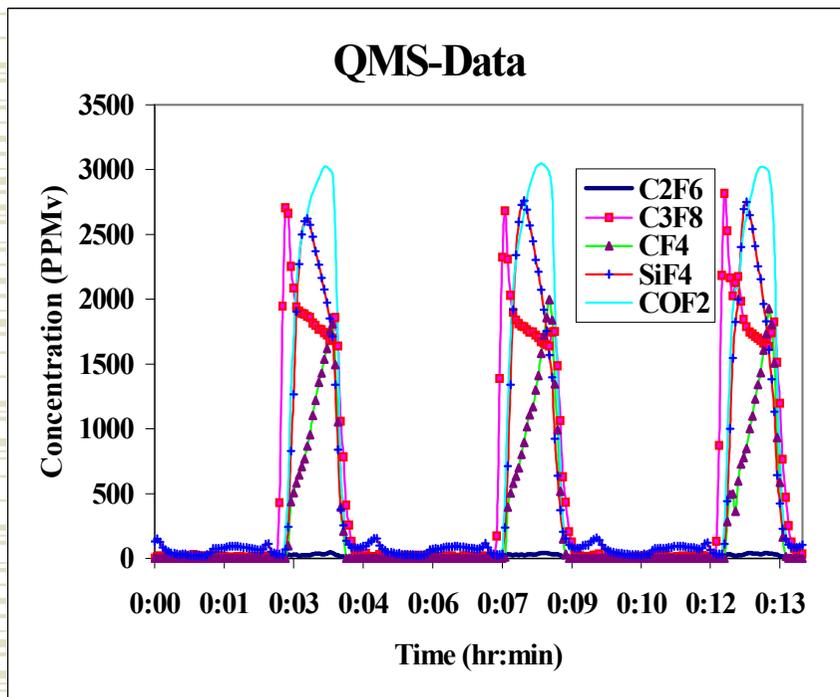
- ◆ Advantages:
  - On-Site Quantitative Analysis of all PFCs and HAPs
  - Non destructive and Real-Time Analysis
  - Wide Dynamic Range
- ◆ QA (*Quality Assurance*)/QC(*Quality Control*) Check:
  - Calibration drift (depends on nature of exhaust stream)
  - Periodic on-site calibration checks
- ◆ Disadvantages:
  - Can monitor only pre selected target species
  - Needs to be calibrated on-site for all target gases
  - Any silicon based sources should be avoided to transport exhaust gases into QMS

# Linearity Check for QMS & FTIR

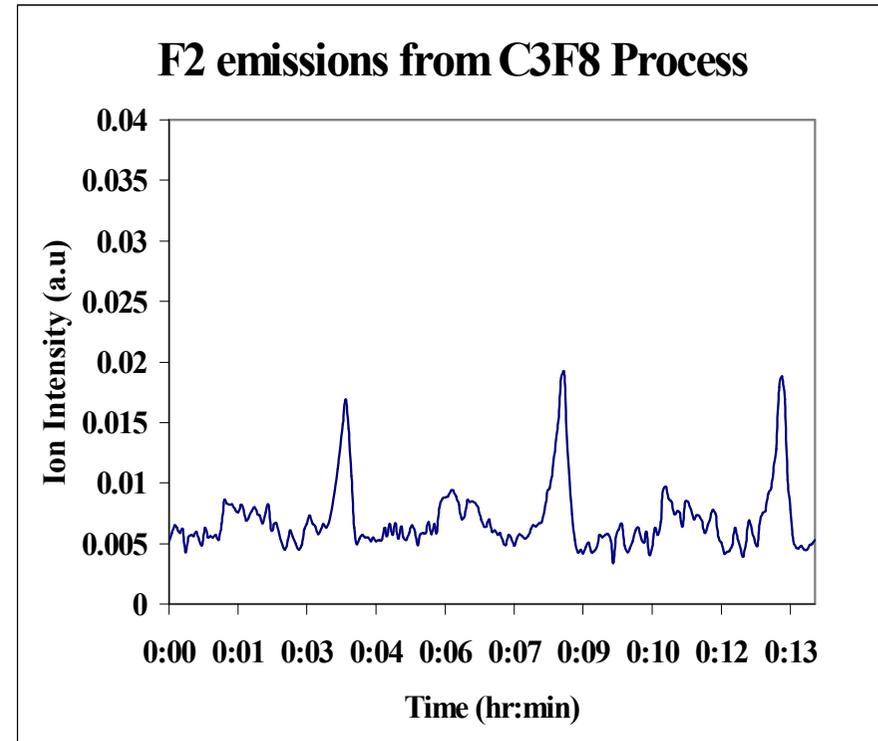
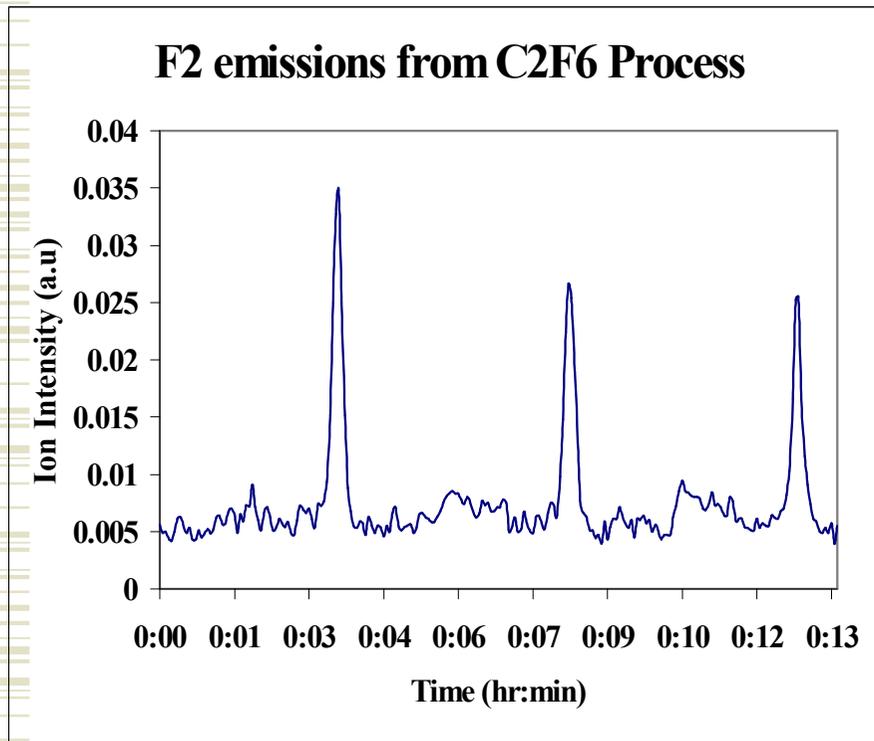


Note: ppmv means ppm by volume

# QMS and FTIR Emission Analysis for C<sub>3</sub>F<sub>8</sub> Chamber Clean Recipe



# QMS analysis of F<sub>2</sub> from C<sub>2</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> chamber cleans



*Note: a.u. means arbitrary unit*



Applying FT-IR Monitoring  
to LCD manufacturing process



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# Trend of PFC Emission Reduction Activities in LCD Industry

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## Position Paper Regarding PFC Emission Reduction Goal

Emission reduction for PFCs proposed by the World LCD Industry Cooperation Committee (WLICC) Working Group 1 (WG1) has been approved by members of the WLICC (the LCD Industries Research Committee in Japan, or LIREC/JEITA, the Environment Association of LCD in Korea, or EALCD/EDIRAK, and the Taiwan TFT-LCD Association, or TTLA) at the second WLICC main committee meeting held in Taiwan on January 20th, 2002.



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# Trend of PFC Emission Reduction Activities in LCD Industry

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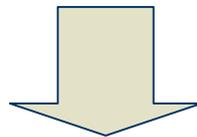


## Consensus on the PFC emission reduction goal

LIREC, EALCD and TTLA have reached a consensus to reduce the aggregate absolute emissions of PFCs from the TFT-LCD fabrication facilities to less than 0.82 MMTCE (million metric tons of carbon equivalent) by the year of 2010.

# Challenge against PFC Emission Reduction Activities in LCD Industry

- ◆ The target emissions correspond to approximately 0.013% of global climate change gas emissions of the world for 1998. Unless countermeasures are taken, the aggregate emissions in 2010 might reach more than ten times of the target emissions and exceed the target emissions of the LCD industry.
- ◆ LCD companies are now using Tier2C (Default Value) of IPCC calculation formula, resulting in wide gap between our estimate and actual data.

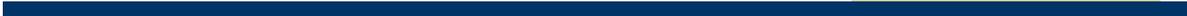


(Big Challenge!)

Considering above situations, shift from Tier 2C to Tier 2A or Tier 2B is expected, which means increase of actual measurement in each company or fab.

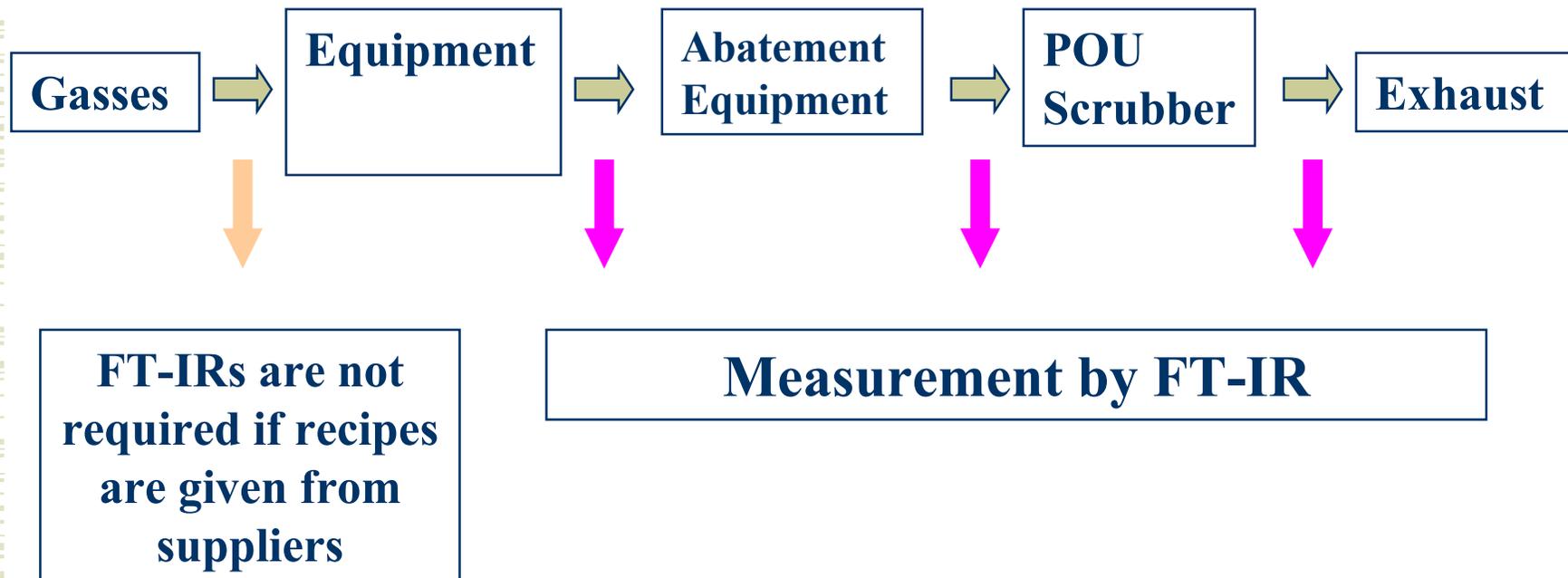


## Problems in applying PFC Emissions Monitoring by FT-IR to LCD Industry



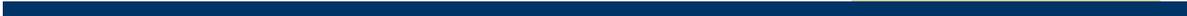
- ◆ Lower FT-IR placement in LCD companies than Semiconductor
- ◆ Inexperienced FT-IR operators, or even worse, lack of operators.

# Where should we monitor by FT-IR in a fab?





## How many units FT-IR are required for a single fab?



[Example]

For an intermediate level FT-IR operator, a single point measurement will take two hours with single (roaming) FT-IR spectrometer ...

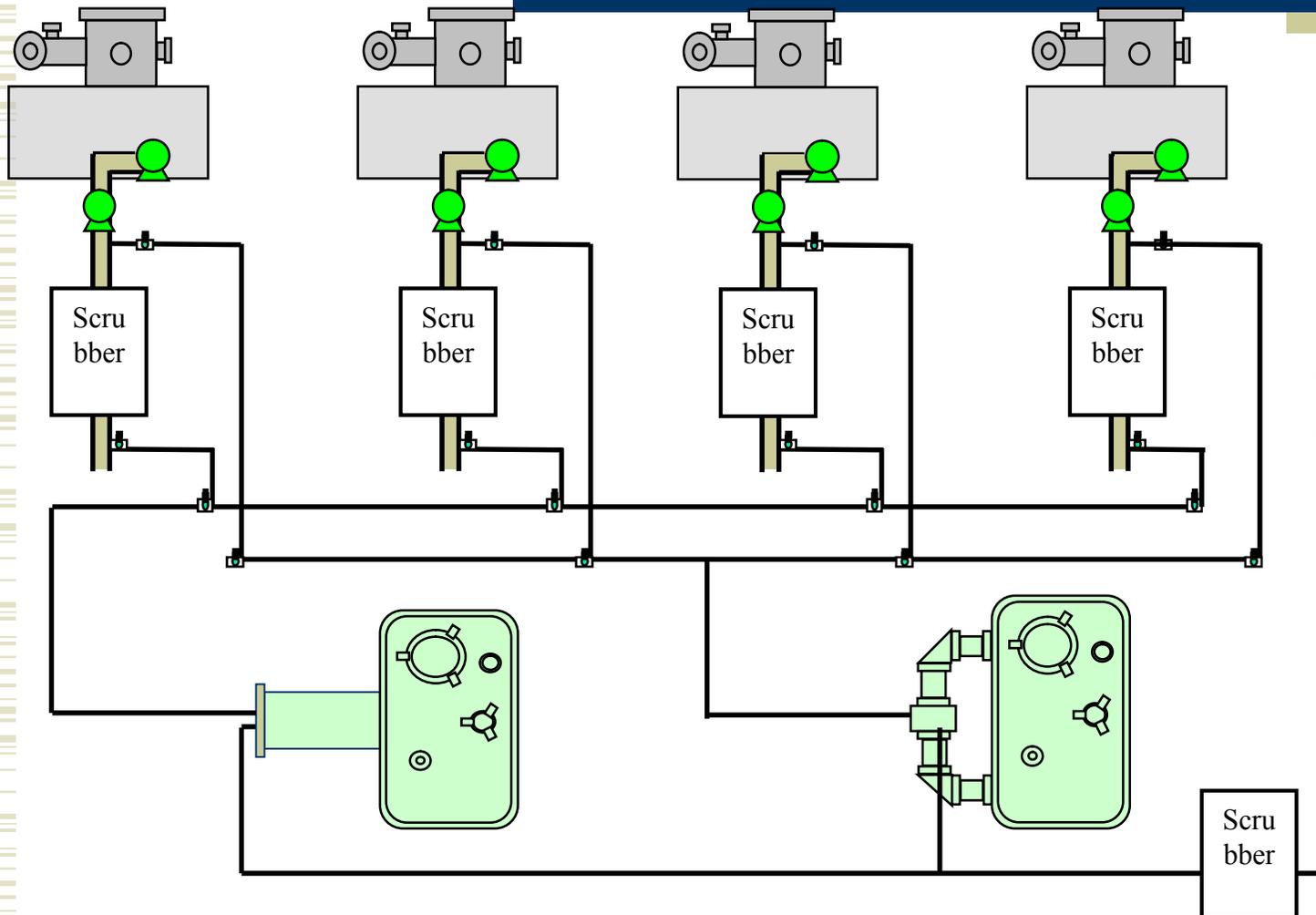
Of course, he can not fully engage himself for monitoring, so maybe 2 or 4 hours a day.(1points or 2 points per day)

Assuming that the fab has 300 monitoring points and he should monitor turn by turn, it will take 300 or 150 days to complete monitoring one cycle of total 300 points...

*What if your fab had more monitoring points, or new regulation requires you to monitor your points more frequently?*

# Proposal for usage of sampling manifold FT-IR

*1 CVD line takes 10 minutes\*12 = 120 minutes for monitoring a dozen CVDs with just two FT-IR with one person! Combination of these sets enables to finish monitoring over 300 points in a fab for a month or even a week!*



Up to twelve measuring points  
for one sampling manifold

## Cost for purchasing FT-IR and piping

Cost for 12 points...

(1) One FT-IR (For higher or lower concentration)	\$100,000~\$120,000
+	
(2) One twelve line manifold	\$5000
+	
(3) One Quad Head Pump (to draw sample to FT-IR)	\$3000
+	
(4) Cost for piping 12 lines	depends on fab
(5) Flexibly using roaming dual cell FT-IR! <i>(Use where pipe length are too long)</i>	\$160,000

Ex. Measure 96 points (Long, Short each 48 points) with manifolds and other 24 points with dual cell

$$\text{Cost} = 8 * [(1) + (2) + (3) + (4)] + (5) = \underline{\$1,104,000 + \text{Piping costs}}$$

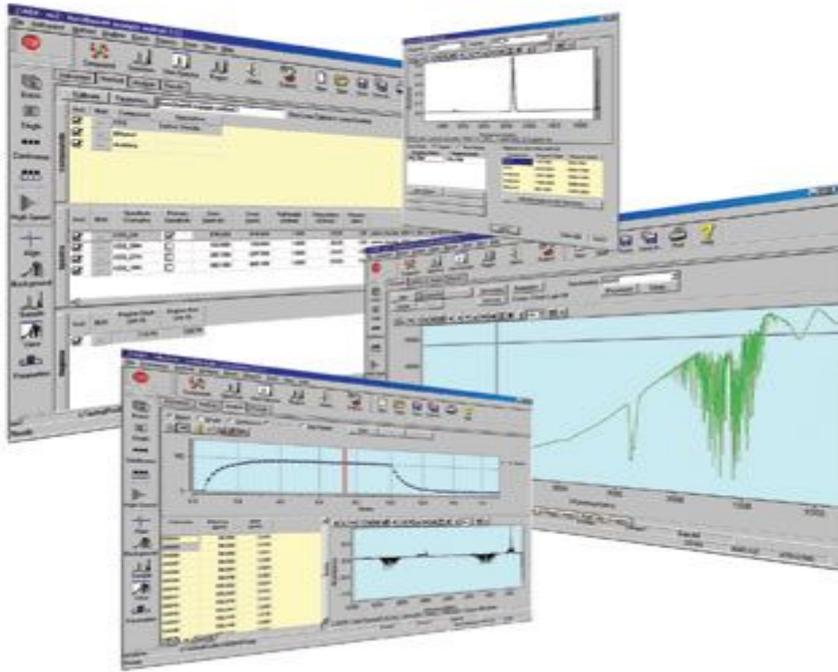


↓ Example of manifold usage for monitoring low level concentration gasses

↑ Explosion Proof Enclosure



# Easy software for entry operator



User Friendly

MIDAC experts will give you powerful support.

Reliable Results

*AutoQuant Pro*<sup>TM</sup>

SOFTWARE FOR GAS PHASE INFRARED SPECTRAL ANALYSIS



# References



- 1) QMS & FTIR for On-line Semiconductor Exhaust Characterization  
by *M. Kataoka\**, *S. Kesari\*\** *Sumitomo-3M*, *\*\*3M Company*
- 2) Position Paper Regarding PFC Emission Reduction Goal  
by *World LCD Industry Cooperation Committee*
- 3) Guidelines for Environmental Characterization  
for Semiconductor Equipment  
by *International SEMATECH*