Gas Metrology for Technology Innovation & Sustainable Development

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Chair of Gas Analysis WG

- Introduction of Gas Metrology
- Example of Gas Metrology Application to High Technology for GHG Reduction
- KRISS Capability on Gas Metrology

National Metrology Institutes (NMI)

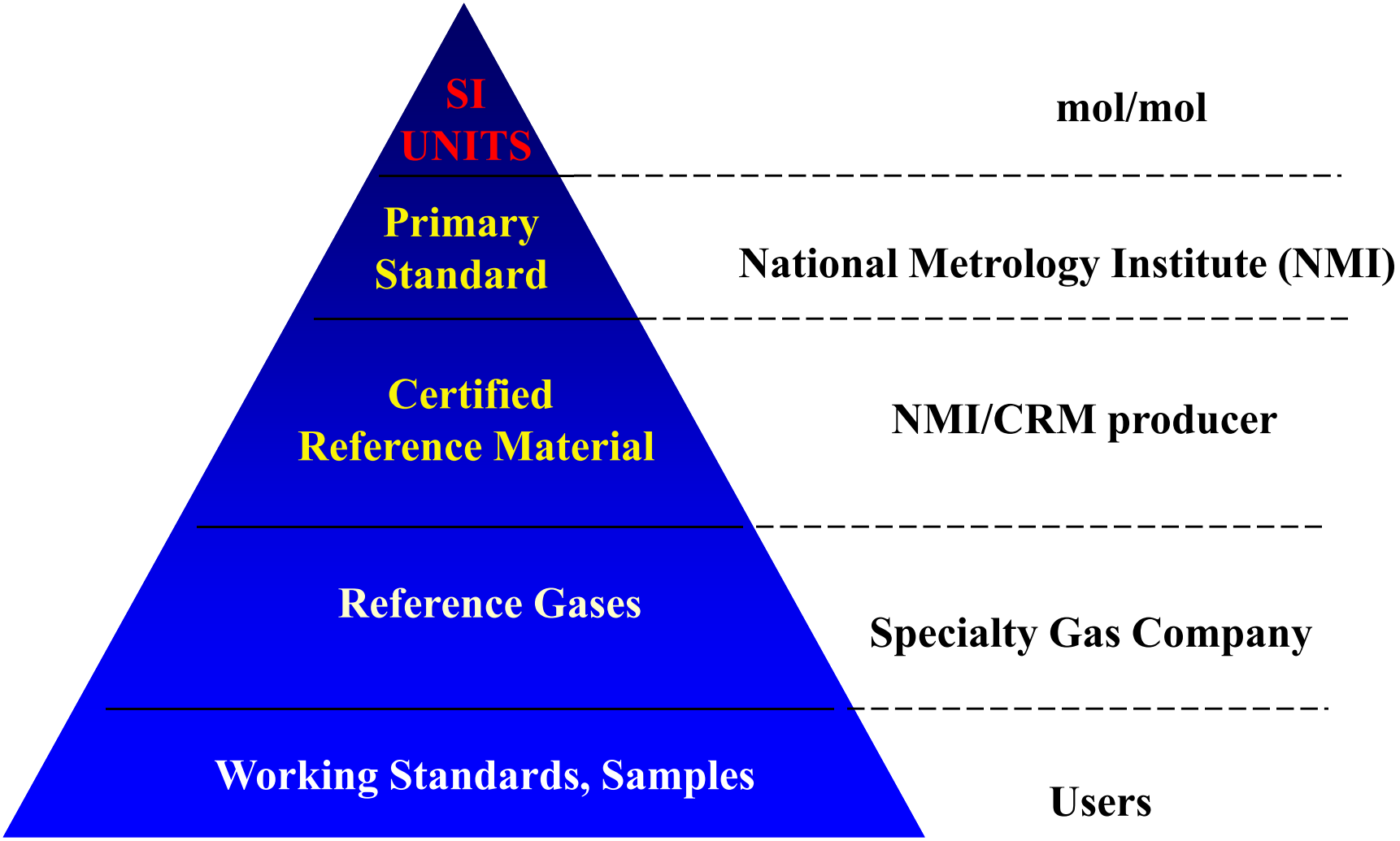
- **Highest authority in metrology**
- **Maintain the national measurement standards**
  - Directly traceable to primary standards when NMI realize the SI units of measurement standards
  - Should insure that the measurements are traceable to a primary standards when NMI does not realize the SI units.
- **Responsible for disseminating the national measurement standard**
- **Mission: Increase Competitiveness of National Economy and Quality of Life through Metrology (Technology Innovation & Sustainable Development)**

ROLE OF METROLOGY

Over the last decade, there has been a significant increase in the recognition of metrology and the important role it plays in improving

- ❑ **Productivity**
- ❑ **Product Quality**
- ❑ **Product Defect Reduction**
- ❑ **Impacts on Global Trade Issue**
- ❑ **Increase Reliability on Legal Procedure**

Measurement Hierarchy in Gas Metrology

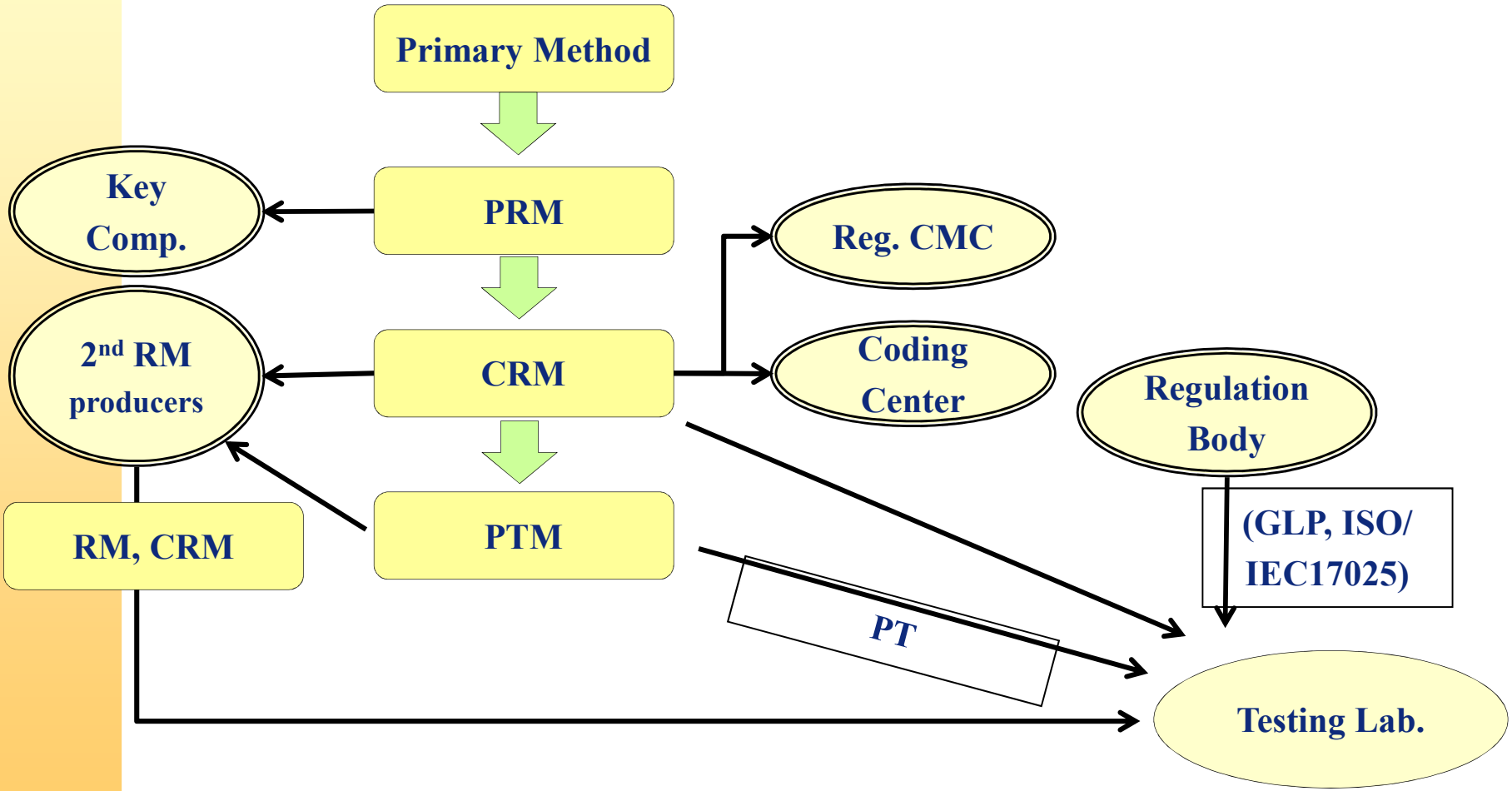


Gas Metrology

- **Gas metrology for Industry and Quality of Life**
  - **Produce Certified Reference Materials**
  - **Improve Process Control, Quality Control**
  - **Precise measurement of Emission,**
    Global warming, and Indoor air quality

- **Gas Metrology for Science (as expert in measurement)**
  - **Ar mole fraction in air: Air density**
  - **Ne, Ar, He, C, N atomic weight (~ppm level accuracy)**
  - **Triple point of gases, Boltzmann constant, Gas constant**

Reference Material / National System



Roles of Gas Metrologist for Industry

- CRM development
  - Environmental Effect : Global warming
  - Working Environmental Condition
  - Process Control for Quality
- Testing services
- Providing PT program
- Education on Gas Analysis
- Development of Analytical system :
  - simple & fast for quantification

Application Areas and Needs of CRM

Object	Application Fields	Needs of CRM
Service to industries	High Quality Products: Quality control of manufacturing process	O
	Regulation for trade: RoHS, WEEE, Safety Regulation	O O O
	New technology: R&D	O
Regulations	Determine the limit for regulation: Toxic chemical producers, Govnt Agency	△
	Standards: Procedure, ISO/TC activity, Validation	O
	Testing report: QC, Traceability, Quantification	O O O
	Ability of Testing Lab: Participate in PT program	O O

Target Gas Chemicals for Analysis

- CFCs, PFCs : CF_4, C_2F_6, SF_6, NF_3, Freon, Renewable refrigerants
- Metal Hydrides : SiH_4, PH_3, AsH_3, B_2H_6
- Acids : F_2, Cl_2, HF, HCl, BF_3, HBr, WF_6
- Odors : NH_3, H_2S etc.
- VOCs : BTX, Acetone, Alcohol, HCOH
- Environment: NO, CO, SO2, O3, Particles, GHG
- Pure Gases : He, N_2, H_2, Ar, N_2O, O_2, Air
- Gases in Liquid, Solid & Biomaterials
- Gases in Products (Lamps, Package, Vacuum, Detectors, Display Pane ……)

Procedure of Gas Analysis

- Validated procedure
- Calibration of Instrument & Apparatus
- Confirm of Environmental Condition
- Get Gas CRMs
- Comparison of Samples and Gas CRMs
- Evaluation of results
- Report Concentration & its Uncertainty

Instruments for Gas Analysis

GC-TCD : inorganic gas
GC-FID : organic gas
GC-SCD : S containing gas mixture
GC-FID-Methanator : CO, CO_2
GC-MSD : unknown gas identification
GC-ECD : F, Cl chemicals
GC-DID : ppb – ppm
GC-AED : Metallic gas, similar PRM
FTIR, NDIR, CRDS: impurities, CO_2, CO, CH_4, N_2O
Dedicated analyzer: NO_x, SO_2, O_3, H_2O etc.
Gas MS : isolated samples, limited amount
IRMS : isotopic ratio

Procedure of Comparison Measurement

- Making calibration line:
  - One point calibration: linear line through origin
  - Two points Calib.: linear line
  - Multi points Calib.: non-linear lines
- Use CRMs with most similar concentration
- If matrix is different, correct that effect
- Check repeatability & reproducibility
- Correct drift effect
- Keep good baseline (purity of carrier gas)

Economy of Republic of Korea : 50 year Ago

Main Export Products during 1960s and 1970s

[1960s: Raw Materials]

1960

	Products	%
1	Iron Ore	13.0
2	Tungsten	12.6
3	Raw Silk Thread	6.7
4	Coal	5.8
5	Squid	5.5
6	Live Fish	4.5
7	Graphite	4.2
8	Wood Board	3.3
9	Rice	3.3
10	Bristle (hair)	3.0

[1970s: Light industry goods]

1970

	Products	%
1	Textiles	40.8
2	Wood Board	11.0
3	Wig (false hair)	10.8
4	Iron Ore	5.9
5	Electronics	3.5
6	Vegitables	2.3
7	Shoes	2.1
8	Lead & Lead Product	1.6
9	Steel Products	1.5
10	Metal Goods	1.5

Economy of Republic of Korea : Recent

Main Export Products in Present

[2000s: High Tech & Heavy Chemicals]

	2000		2006	
	Products	%	Products	%
1	Semiconductor	15.1	Semiconductor	10.2
2	Computer	8.4	Car	10.1
3	Car	7.7	Wireless Goods	8.3
4	Petroleum Chemicals	5.5	Shipbuilding	6.8
5	Shipbuilding	4.8	Petroleum Chemicals	6.3
6	Wireless Goods	4.7	Computer	3.9
7	Steel Plates	2.8	Plat Panel Display	3.8
8	Clothes	2.7	Synthetic Resins	3.4
9	Synthetic Textiles	2.1	Steel Plates	3.4
10	Electronics	2.1	Automobile Parts	3.1

Economic Growth of Korea

- Light Industries *1960-70*
- Heavy & Chemical Industries *1970-80*
- Electronics *1980-95*
- Information & Communication *1995-Present*

World Products from Korea

- **DRAM:** World market share **1st (45%)**

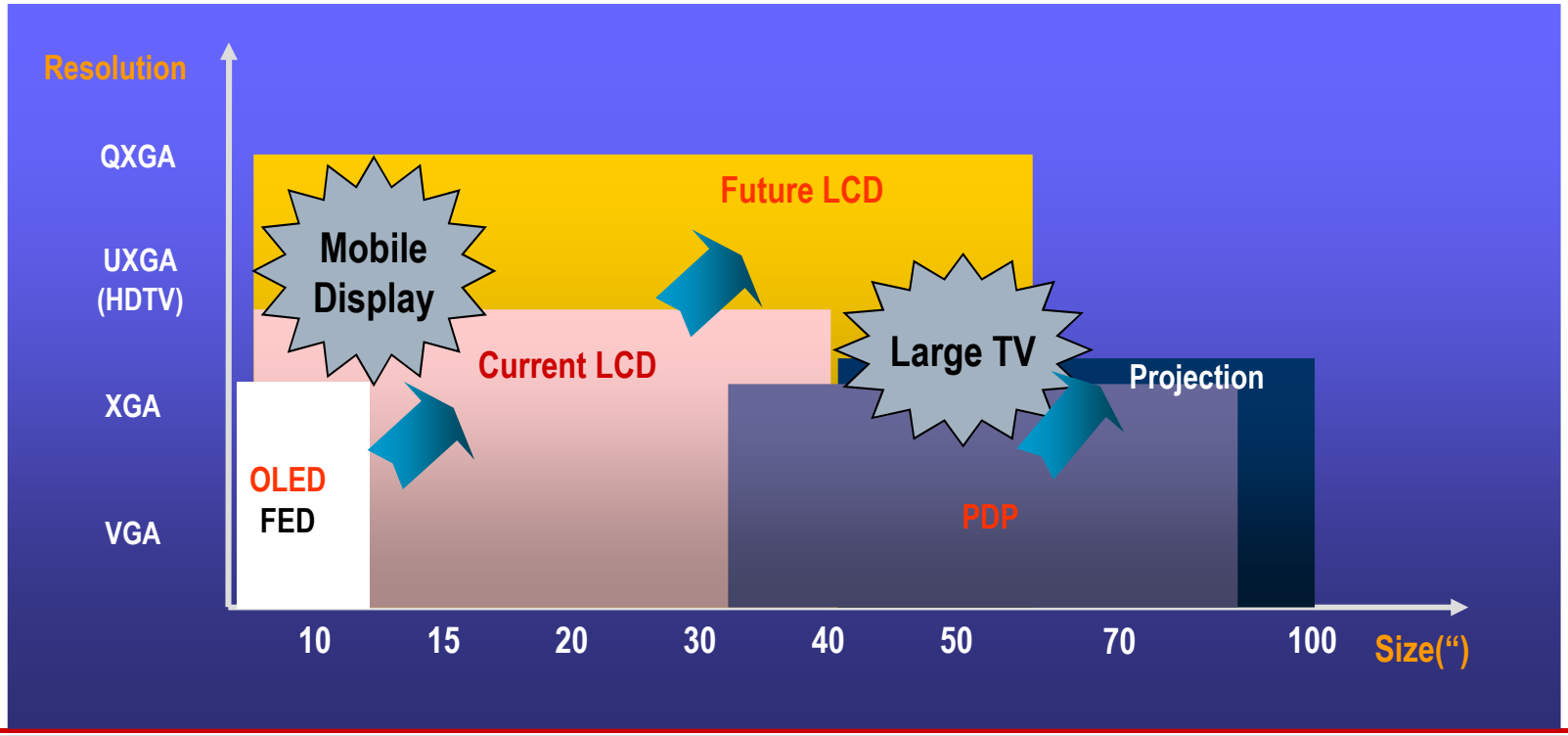
- **Display Panel:** World market share **1st (35%)**
- **Shipbuilding:** World market share **1st (40%)**

- **Car:** World market share **6th**
- **Iron Plates:** World market share **4 %**

Evolution of Display Screen

- Monitor : From CRT to LCD/LED
- Large Screen TV : competition of LCD & PDP (> 50")
- Mobile : LCD & OLED (< 10")

(VGA: 640 x 480, XGA: 1024 x 788, UXGA: 1600 x 1200, QXGA: 2048 x 1536)

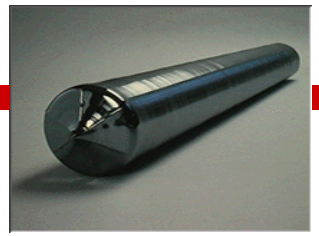


Development of OLED Display

- Large Screen OLED Display
- Thin ~ 30 mm
  - amorphous-Si TFT– Large screen
  - poly-Si TFT– Long lifetime

Semiconductor Manufacturing Process


Si Growth


Ingot


Si Wafer


Oxidation

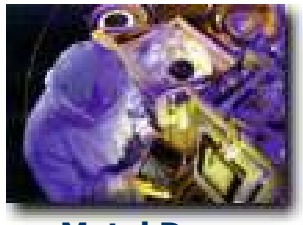

PR Coating


Photo Stepper


Etch


Ashing

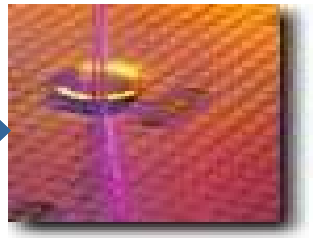

Wet

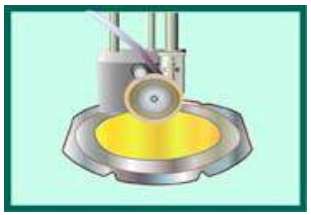

Metal Depo

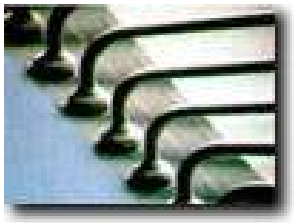

CVD

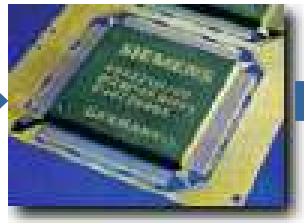

Implant


CMP


Coating

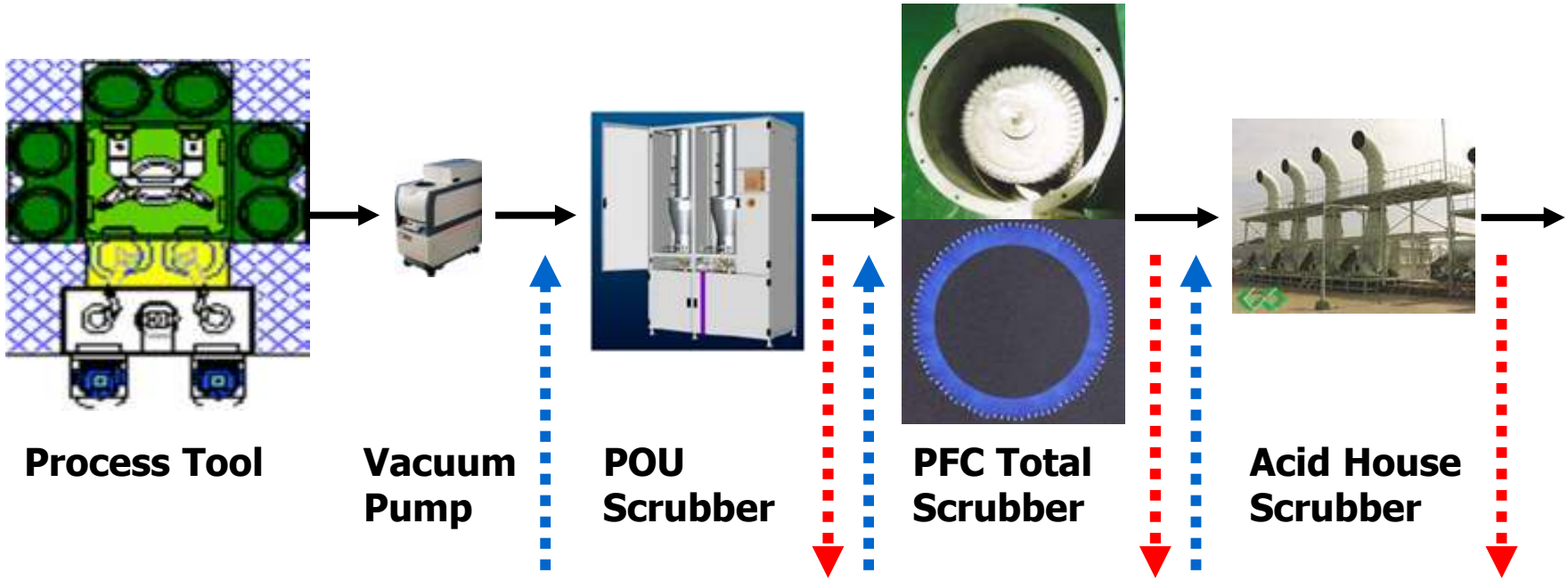

Sawing


Wire Bond


PKG

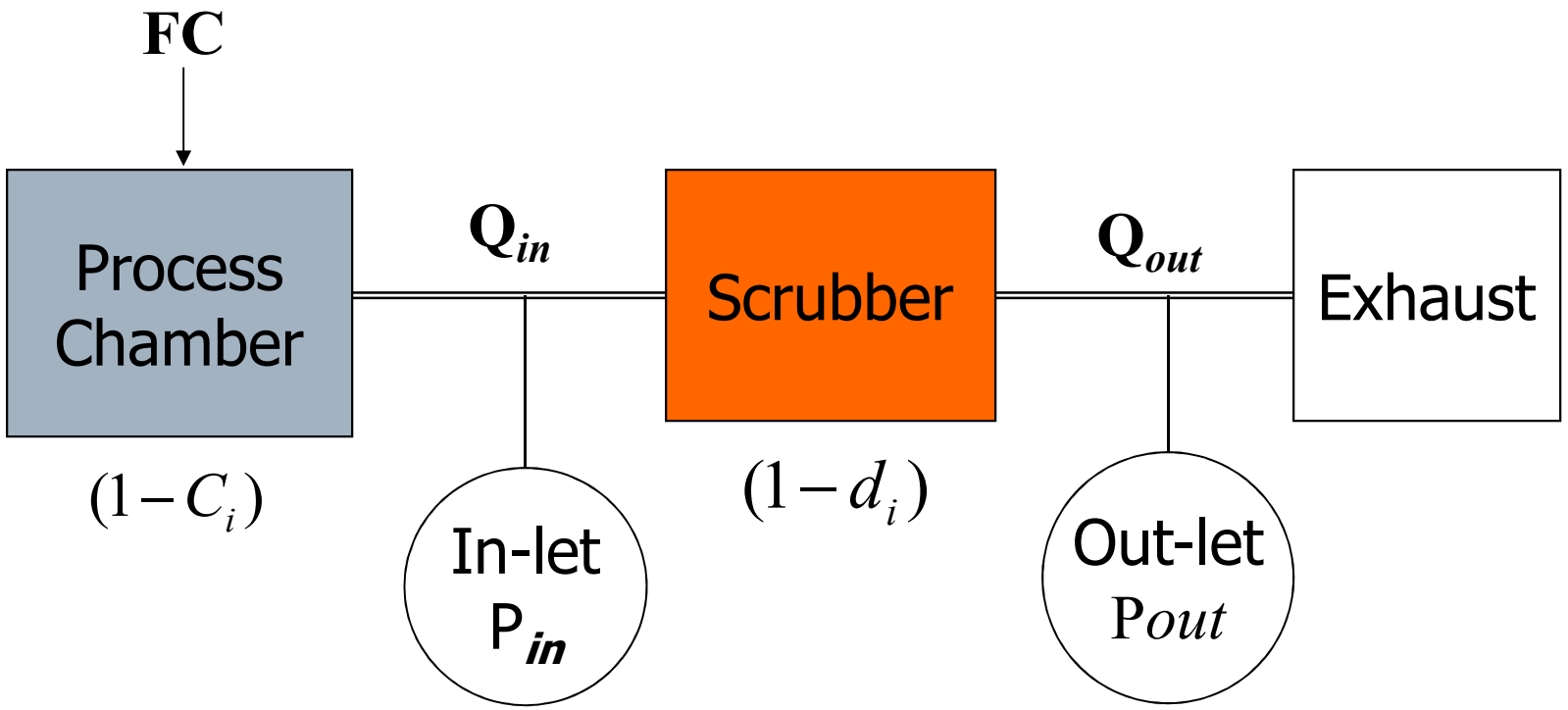

IC Chip

Exhaust Gas Analysis for the Sustainable Development



Abatement System Efficiency Analysis

Efficiency of PFC Scrubber



$$Emissio\ of\ FC_i = (1-h) \bullet FC_i \bullet (1-C_i) \bullet (1-d_i)$$

$$C_i = Q_{in} \cdot P_{in} / FC_{in} \qquad d_i = Q_{out} \cdot P_{out} / Q_{in} \cdot P_{in}$$

$$Q_{out} = 1 / P_{He}$$

Emission Reduction Methodology for PFC & SF_6

- Validated Procedures

  Approved CDM Methodology by UNFCCC

  - **UNFCCC: UN Framework Convention on Climate Change**

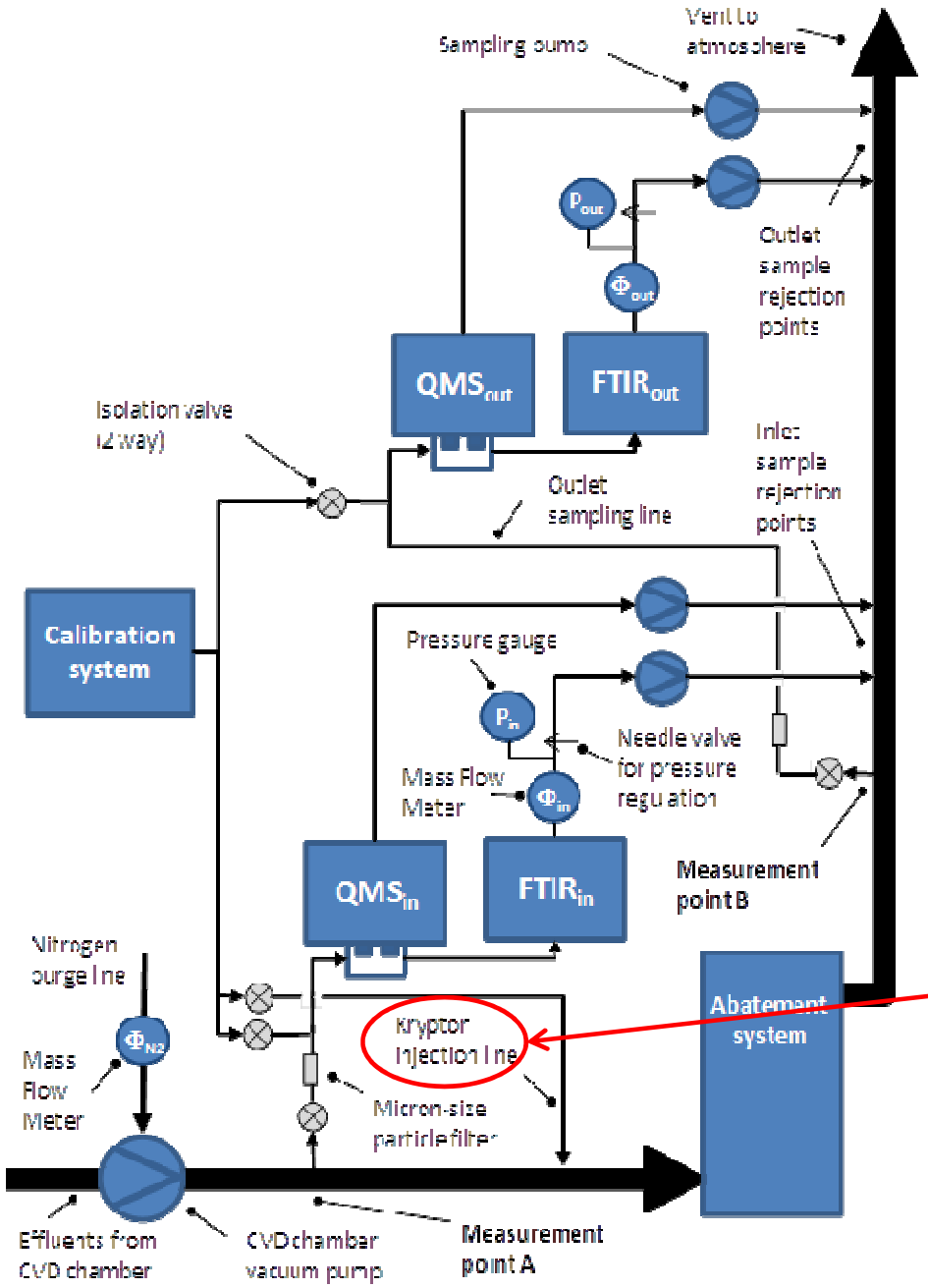
  Korean EPA modified UNFCCC methodology

- Reference Gas Mixtures (CRMs)

  for calibration & validation

Approved Methodology by UNFCCC

Methodology	Applying Company	Reduction Mechanism	Monitoring Instrument
AM0078	Display Process in LG & Samsung	SF6 Abatement by fuel combustion	QMS, FTIR Annubar Water Analysis
AM0092	Semiconductor in Chartered Semi & Hynix	Substitution of C2F6 with c-C4F8	FTIR QMS(Kr)
AM0096	Semiconductor in Samsung	CF4 Abatement by electrical heater	QMS(He)



AM0092 Schematic: Baseline & project emission

QMS

FTIR

MFC

Kr

Cal. System

Strategy of Quantification

Quantification by QMS with Reference Standard Gas:

N_2, O_2, CO_2, Ar, SF_6, He, Kr, Xe

Quantification by FTIR with Reference Standard Gas:

CO_2, CO, SF_6, NO, SO_2

Quantification by FTIR with Library Information:

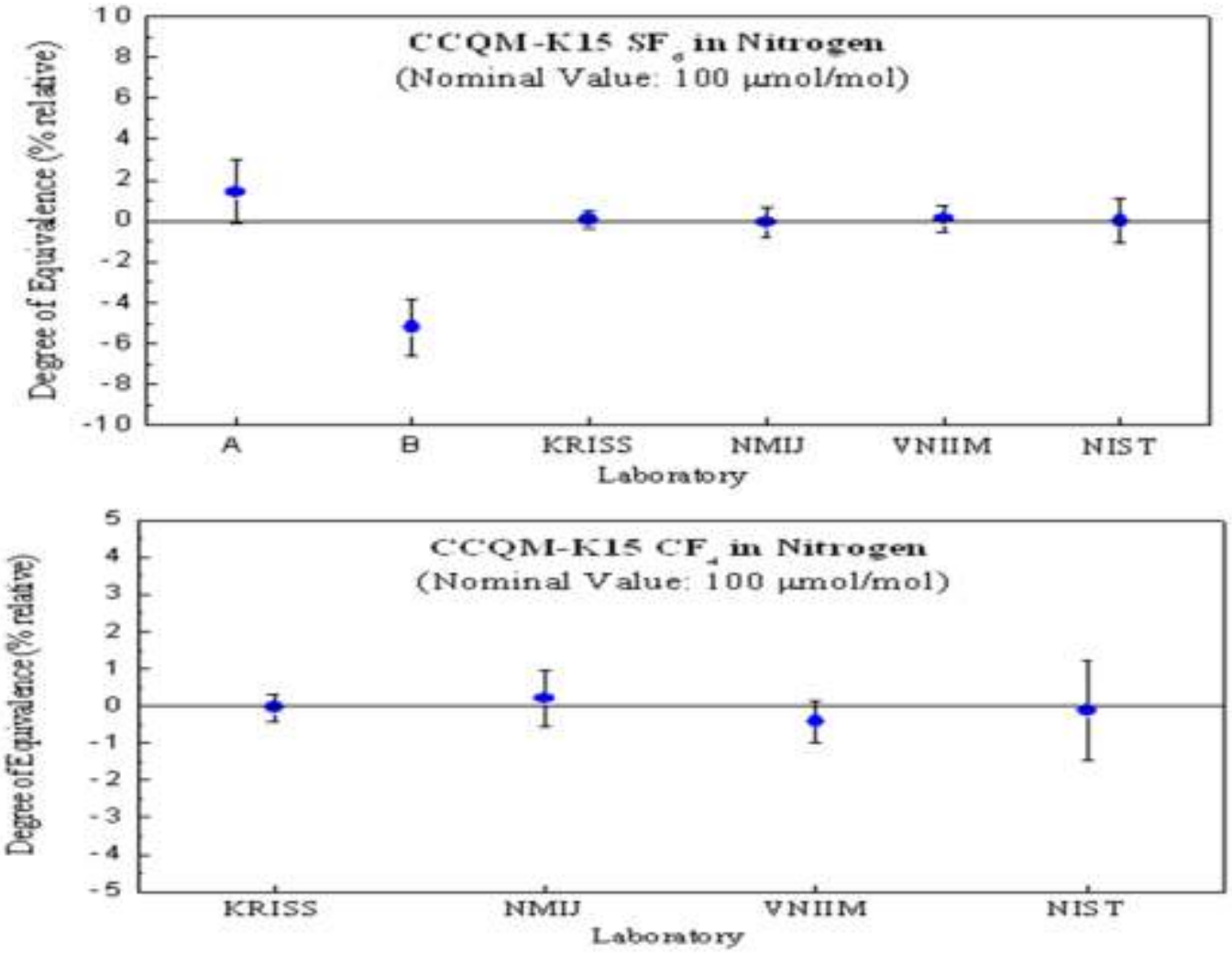
HF, SiF_4, SOF_2, SO_2F_2, …

Difficult components: F_2, Cl_2 (memory effect in QMS)

To support industry on PFC emission

CCQM-K15 (2003)

- Coordinating Lab: KRISS
- Subatance: SF_6 & CF_4 hundred μmol/mol level



Primary Reference Material

- Purity assessment
  - Molecular weights of source gases (isotopic ratio)
  - Impurity analysis based on final concentration
- Accurate mixing (Gravimetry)
- Internal consistency by comparison (4 cyl. at a time)
- Stability test (2 cyl. after 6 months)
- Verification through KC (including uncertainty)
- Register to BIPM CMC (as NMI)
- Validation of life time by periodical reproduction
- Economically not good (managing by national body)

Fully Automated Weighing System (2006)

"Maximum capacity 15 kg / Readability 1 mg

- Much easier, much faster, highly precise: round type
- Pressure, temperature, relative humidity recorded automatically
- Two or three cylinders measured serially (e.g., A-B-A-B, A-B-C-A-B-C, or A-C-A-C cylinders)
- Date, time, pressure, temperature, relative humidity are all automatically recorded by a customized program developed at KRISS

NIST, NPL
NMISA,
ASTAR/NMC
NIM, LIPI
ITRI/NMC

A Recent Change in the Comparator Balance (2007)

Mettler Toledo AG (Model XP26003L)
Maximum capacity 26.1 kg / Readability 1 mg
※ Therefore, now we can measure the weights of cylinders having a volumetric capacity of up to 10 L.

KRISS 한국표준과학연구원

Developed CRMs in KRISS

- CFC & PFC Gases : For semiconductor companies

  $CFCl_3$, CF_2Cl_2, CF_3Cl, $C_2F_3Cl_3$ ---- 1×10^{-2} mol/mol, 1-100 μmol/mol

  NF_3, C_3F_6, SF_6, CF_4, CHF_4, C_3F_8 ---- 1×10^{-2} mol/mol, 1-100 μmol/mol

- Green House Gases :

  CO_2 ---- 1×10^{-2} mol/mol, 380 μmol/mol

  CH_4 ---- 1×10^{-2} mol/mol, 1.8 μmol/mol

  CO_2+CH_4+N_2O ---- mixture at ambient level

  CFCs, PFC, NF_3, SF_6--- ambient level

- Air Pollution Monitoring Gases :

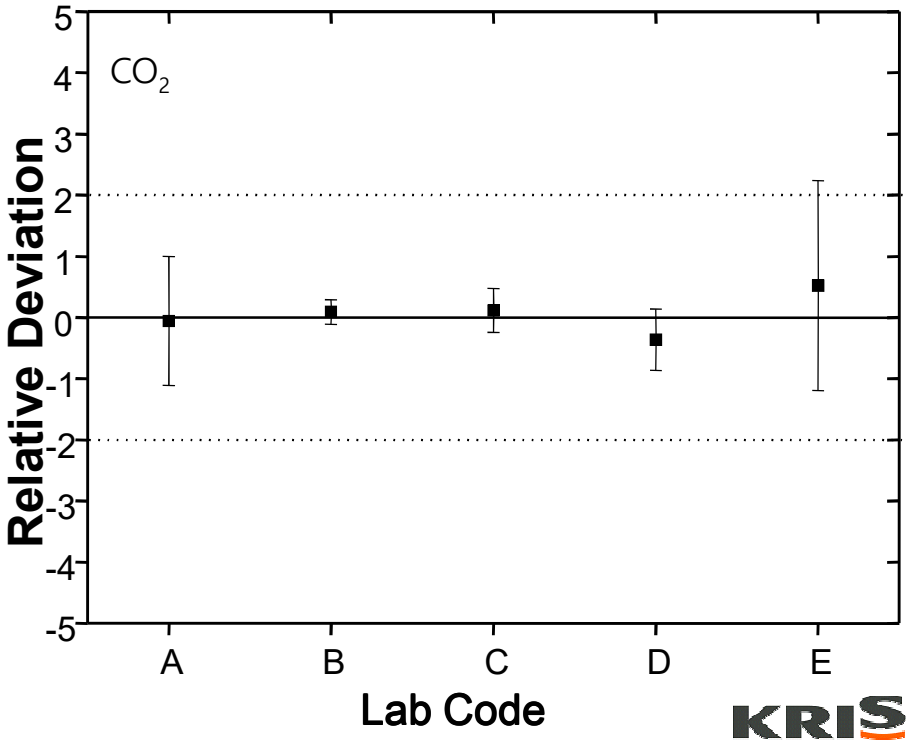
  CO, NO, SO_2, VOCs, Aldehydes, (O_3 Primary calibration system)

Primary Reference Gas Mixture for Green House Gases

substance	Range of Certified Values	Uncertainty (k=2)	ref
CO_2	above 10 µmol/mol	0.06 at 380 µmol/mol	CCQM-K52, K120
CH_4	above 100 nmol/mol	0.002 at 1.9 µmol/mol	CCQM-K82
N_2O	above 50 nmol/mol	0.24 at 320 nmol/mol	CCQM-K68
SF_6 NF_3	above 6 pmol/mol for SF_6 above 1 nmol/mol for NF_3 (0.5 pmol/mol after 2011)	0.06 at 6 pmol/mol for SF_6 0.01 at 1 nmol/mol for NF_3	CCQM-K15
PFCs	above 10 pmol/mol for CF_4 above 100 µmol/mol for C_2F_6 (50 pmol/mol after 2011)	0.1 at 10 pmol/mol for CF_4	CCQM-K15
HFCs	above 30 pmol/mol for HFC23	0.15 at 50 omol/mol	CCQM-K84
CFCs	µmol/mol~50 pmol/mol for CFC 11,12,113	0.5 at 50 pmol/mol	CCQM-K84

Proficiency Test for Specialty Gas Companies

- PT provided by official body
- Round Robin Test
- 1:1 comparison (bilateral, trilateral)



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Better Standards, Better Life

Gas Analysis in IT industry by KRISS

Developing New product:
Organic Light Emitting Display

QC: Process Control

Reduction of GHGs:

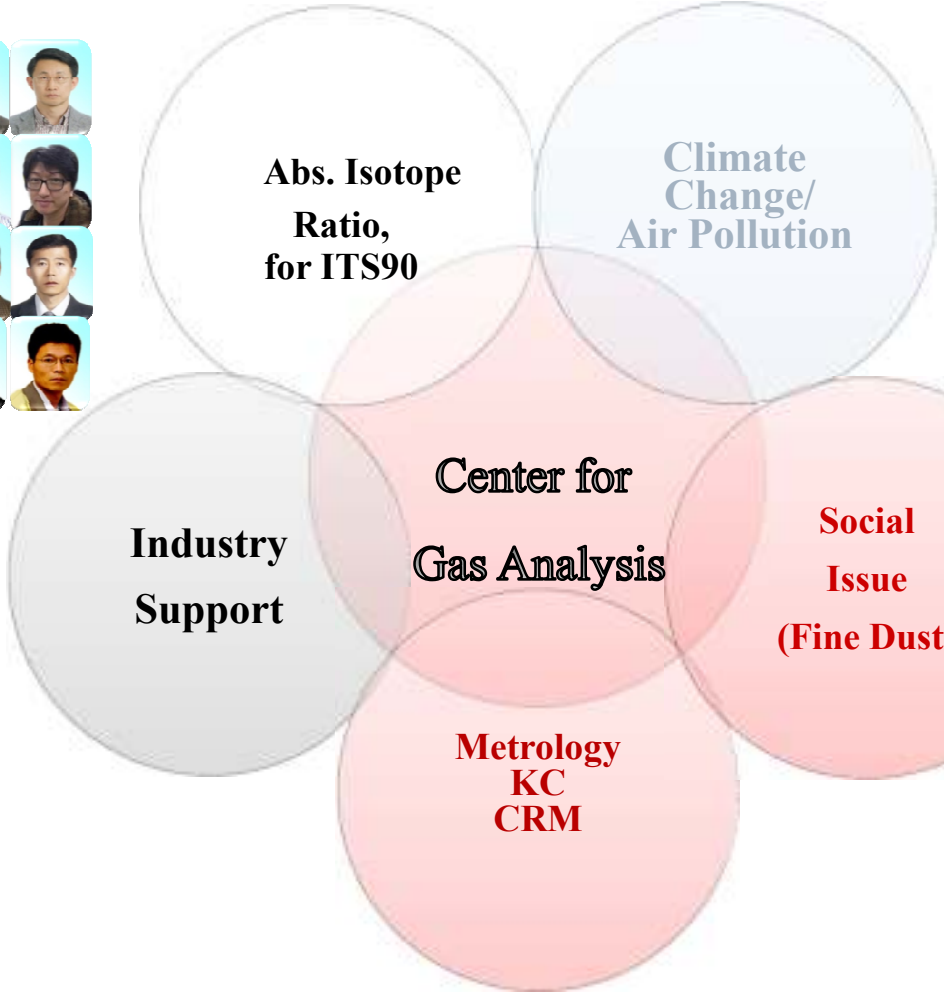
Gas Scrubber

New Technology:
Backlight & PDP

- Gas Analysis : Quality control of products, development of new product & problem solving in process

Human Resources of Center for Gas Analysis

Researcher: 9
Engineer: 8
Technician: 3



Ph.D Std.: 4
Ms D Std: 9
Temp. member: 3

Technology Innovation & Sustainable Development

by Gas Analysis Center