

International Comparison CCQM-P51 – Emission level of CF₄ and SF₆

Final Report

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Field

Amount of substance

Subject

Comparison of measurement of carbon tetrafluoride and sulfur hexafluoride in nitrogen

Participants

IMGC(IT), KRISS(KR), NRCCRM(CN)

Organizing body

CCQM

Rationale

CF₄ and SF₆ are the global warming chemicals that are used in semiconductor companies. In Kyoto protocol on climate change in 1997, those chemicals were included in the items to achieve its quantified emission limitation and reduction commitments. Accordingly for the measuring of these gases, it is necessary that measurement results are accurate and traceable, in particular because of the fact that emission level CF₄ and SF₆ are the global warming source gases.

This part of project focuses a comparison to measurement capability for measuring CF₄ and SF₆ at emission level.

At the CCQM gas analysis working group meeting in April 2003, it was agreed that CCQM organize this pilot study (CCQM-P51) for institutes that are participated as study level on CCQM-K15. Therefore, CCQM-P51 was run in parallel to CCQM-K15. The CCQM-K15 was reported as a separated report.

Process of the comparison

The individual cylinders for this comparison were prepared by means of primary methods (gravimetry) at the coordinating laboratory KRISS. The pressure in the cylinders was approximately 10 MPa when distributed. Because of individual preparation of gas mixture, there are some differences in the actual property values of these mixtures, which make working with a single reference value undesirable. However, all property values of these mixtures are within the nominal values as proposed in protocol. The nominal amounts of substance ratios of CF₄ and SF₆ in nitrogen, as used in this key comparison, are summarized in table 1.

Table 1: **Nominal** amount of substance ratios

Component	x (μmol/mol)
Carbon tetrafluoride	100
Sulfur hexafluoride	100
Nitrogen	balance

The cylinders were shipped to participants between July and August 2003. Participated laboratories carried out their measurements from September to November 2003. Reports were received until December 31, 2003.

Measurement protocol

The measurement protocol requested each laboratory to perform at least 3 measurements, with independent calibrations. The replicates, leading to a measurement were to be carried out under repeatability conditions. The protocol informed the participants about the nominal concentration ranges, given as 90 – 110 $\mu\text{mol/mol}$ carbon tetrafluoride, 90 – 110 $\mu\text{mol/mol}$ sulfur hexafluoride and nitrogen as balance. The laboratories were also requested to submit a summary of their uncertainty evaluation used for estimating the uncertainty of their result.

Measurement equation

The measurement model has been taken from the CCQM-K3 [1]. The gas mixtures have been prepared by means of primary methods (gravimetry) [2].

Three groups of uncertainty components have been considered for the preparation:

1. gravimetric preparation (weighing process)
2. purity of the parent gases
3. stability of the gas mixtures (short term stability)

There has been no evidence that there would be relevant effect of adsorption, and the component of gas mixtures has been known as very stable compounds, so that only the first two groups of uncertainty components appear in the model for evaluating the uncertainty from gravimetric preparation.

$$u^2(x_{gravp}) = u^2(x_{weighing}) + u^2(\Delta x_{purity}) \quad (1)$$

A second main contributor to the uncertainty of the reference value of gas mixtures is the uncertainty from verification. The verification process is used to confirm the gravimetric composition by high-precision Gas Mass Spectrometer (Instrument Model: Finnigan MAT 271) as checking internal consistency between prepared cylinders.

For a typical mixture of this project, the following results have been obtained, whereby for u_{ver} the standard deviation s is used (Table 2).

Table 2: Uncertainty components for a typical mixture

Component	$u(x_{gravp})$ (% , rel)	u_{ver} (% , rel)
CF ₄	0.045	0.075
SF ₆	0.045	0.075

The results from table 2 have been used to calculate the uncertainty in the assigned (reference) value

$$U_{gravR} = k u_{gravR} \quad (2)$$

Where

$$u_{gravR} = \sqrt{u^2(x_{gravp}) + u_{ver}^2} \quad (3)$$

and $k = 2$. The relative uncertainty u_{gravR} has been used to compute the combined standard uncertainty of reference value for all mixtures.

Measurement methods

The following methods of measurement and calibration methods have been employed (Table 3 and 4) by

participants. Laboratory B participated only on SF₆.

Table 3: Measurement and calibration methods for CF₄

Laboratory	Measurement method	Calibration method	Traceability
NRCCRM	GC-TCD	One point	own gravimetric standard
KRISS	GC-AED	One point	own gravimetric standard

Table 4: Measurement and calibration methods for SF₆

Laboratory	Measurement method	Calibration method	Traceability
NRCCRM	GC-TCD	One point	own gravimetric standard
IMGC	Laser absorption spectroscopy	One point, 2 mixtures	KRISS
KRISS	GC-AED	One point	own gravimetric standard

Results

In the current comparison on gas mixtures, measurements were performed on individually prepared gas mixtures with (slightly) different concentrations. Since the coordinating laboratory prepared these mixtures using the same methods and materials, the individual gravimetric values can be adopted as reference values. The difference between the gravimetric and analyzed values has been taken as degree of equivalence, defined as

$$D_i = x_{lab,i} - x_{ref,i} \quad (4)$$

which is treated as same way as previously adopted methods [1]. The combined standard uncertainty of the degree of equivalence can be expressed as

$$u(D_i) = \sqrt{u_{lab,i}^2 + u_{ref,i}^2} \quad (5)$$

and the expanded uncertainty, at a 95% confidence level

$$U(D_i) = k \sqrt{u_{lab,i}^2 + u_{ref,i}^2} \quad (6)$$

where k denotes the coverage factor. For all degrees of equivalence, $k = 2$ (normal distribution, approximately 95% level of confidence).

In tables 5 and 6, the results of this comparison are presented. The table contains the following information.

- x_{grav} Assigned amount of substance fraction of a component
- u_{grav} Standard uncertainty of the assigned value x_{grav}
- x_{lab} Result as reported by the participant
- k_{lab} Coverage factor as reported by participant
- U_{lab} Expanded uncertainty as reported by participant
- D_i Degree of equivalence, difference between laboratory value and the gravimetric value
- $U(D_i)$ Expanded uncertainty of the degree of equivalence

The differences between gravimetric and reported value are given as degree of equivalence, that is the difference between the value measured by the laboratory and the gravimetric value.

The uncertainties in the degrees of equivalence are given with $k = 2$ for all laboratories, taking into consideration both the uncertainty reported from the laboratory as well as the uncertainty from gravimetry (and validation). The combined standard uncertainty of a laboratory has been computed from U_{lab} and k_{lab} . This implies that if a laboratory used a k value deviating from $k = 2$, this information has been appreciated to obtain an estimate for the combined standard uncertainty of the result.

Table 5: Results for CF₄

Lab	Cylinder	x_{grav} ($\mu\text{mol/mol}$)	u_{grav} ($\mu\text{mol/mol}$)	x_{lab} ($\mu\text{mol/mol}$)	U_{lab} ($\mu\text{mol/mol}$)	k_{lab}	D_i ($\mu\text{mol/mol}$)	$U(D_i)$ ($\mu\text{mol/mol}$)
NRCCRM	ME2236	102.456	0.179	102.2	2.04	2	-0.256	2.075
KRISS	ME2233	100.398	0.171	100.35	0.15	$\frac{2.0}{1}$	-0.044	0.371

Table 6: Results for SF₆

Lab	Cylinder	x_{grav} ($\mu\text{mol/mol}$)	u_{grav} ($\mu\text{mol/mol}$)	x_{lab} ($\mu\text{mol/mol}$)	U_{lab} ($\mu\text{mol/mol}$)	k_{lab}	D_i ($\mu\text{mol/mol}$)	$U(D_i)$ ($\mu\text{mol/mol}$)
NRCCRM	ME2236	100.192	0.170	101.6	1.52	2	1.408	1.562
IMGC	ME2244	98.969	0.173	93.8	1.31	2	-5.169	1.355
KRISS	ME2233	99.837	0.170	99.9	0.26	2.06	0.063	0.421

Degrees of equivalence

The degrees of equivalence for carbon tetrafluoride and sulfur hexafluoride are shown in figure 1 and 2. The error bars represent the expanded uncertainty at a 95 % level of confidence.

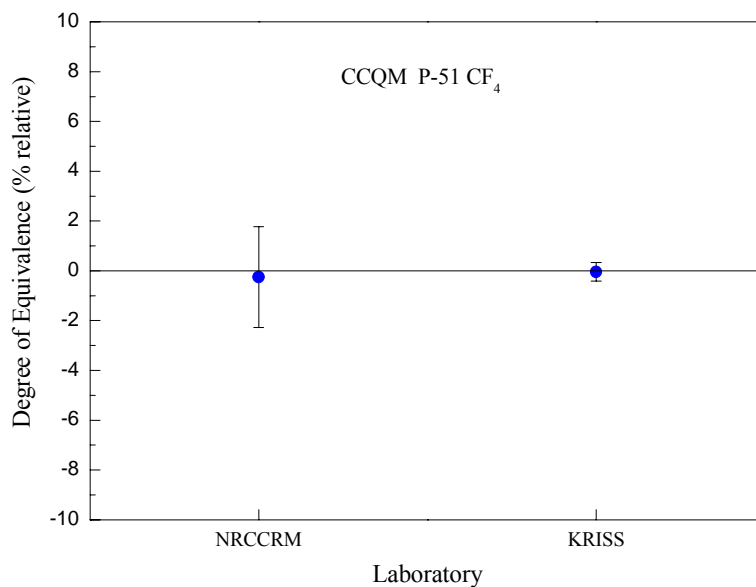


Fig. 1. Degree of equivalence for CF₄

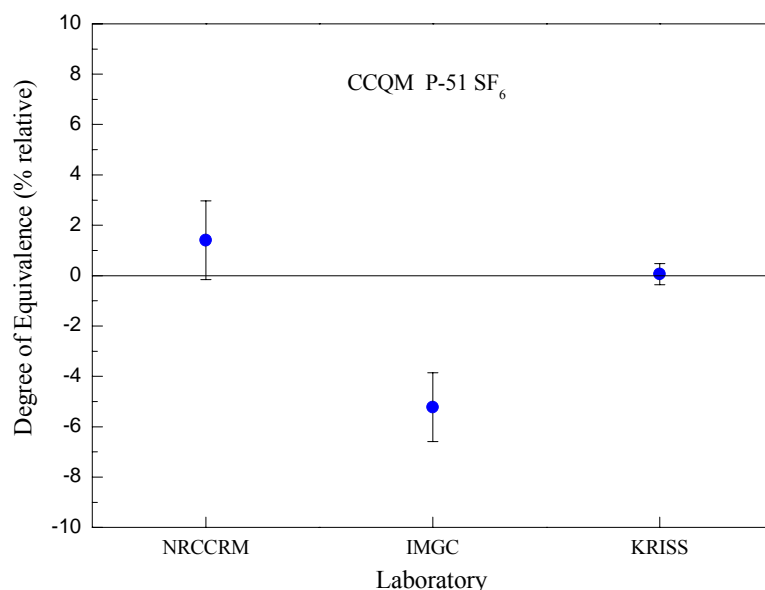


Fig. 2. Degree of equivalence for SF₆

Conclusions

The results of NRCCRM and KRISS agree with the reference value within 2 % relative, for both CF₄ and SF₆. IMG C participated in SF₆ only with the analytical technique of laser absorption spectroscopy. However, the result from IMG C does not agree with reference value. At the CCQM gas analysis working group meeting in April 2004, IMG C mentioned that they found a leakage of a valve in their analytical system, which may explain their discrepancy with the reference value.

References

- [1] Van der Veen A.M.H, De Leer E.W.B., Perrochet J.-F., Wang Lin Zhen, Heine H.-J., Knopf D., Richter W., Barbe J., Marschal A., Vargha G., Deák E., Takahashi C., Kim J.S., Kim Y.D., Kim B.M., Kustikov Y.A., Khatskevitch E.A., Pankratov V.V., Popova T.A., Konopelko L., Musil S., Holland P., Milton M.J.T., Miller W.R., Guenther F.R., International Comparison CCQM-K3, Final Report
- [2] International Organization for Standardization, ISO 6142:2001 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods, 2nd edition
- [3] International Comparison CCQM-K15 – Emission level of CF₄ and SF₆

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CCQM-P51

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December 2003

Measurement report of NRCCRM

Method

The analyze methods and the instruments are listed in table 1:

Table 1

Components analyzed	Instruments used	Detector	Calibration method
CF4	HP 6890 (Agilent US)	TCD	Single point and linearity calibration
SF6	HP 6890 (Agilent US)	TCD	Single point and linearity calibration

Calibration

The calibration gas mixtures were prepared by a gravimetric method. The purity of raw gases and impurities interested were determined with a standard normalized method by gas chromatography. The measurement uncertainty of purities is less than 0.1%. The balance we used in preparing the calibration gas mixtures is made in Japan and the type is H2-30K (capacity: 30 kg, readability: 1mg).

Evaluation of uncertainty

Having taken a series of measurements, we can eliminate or decrease most parts of uncertainties (including those related to the balance and poises, gas cylinder, components interest, etc.) to the level that can be ignored. In this work, for the final measurement results, we mainly take two parts of uncertainty into account. One of them is uncertainty of the calibration gas mixtures we prepared, the other is uncertainty of the analytical method we used.

Measurement report of IMG C

Method

Mole fraction measurement have been performed on the mixture prepared –by KRISS only of gas SF₆ | (not of CF₄) as we declared in the GAWG meeting of April 2003.

The analytical method applied is Laser absorption spectroscopy.

The attached scheme describes the method in detail.

The CO₂ laser radiation, frequency locked on the saturated absorption of the SF₆ P(33) A(2,1) line, is simultaneously detected by two MCT detectors, the first detecting the laser power without gas absorption (I₀), the second detecting the laser power after the gas absorption (I_t).

The difference between the two signals is measured with a lock-in amplifier and recorded on the computer every second for about –2000 s. The temperature and the pressure of the gas in the absorption cell are measured respectively with a PT100 sensor and a capacitive MKS Baratron transducer and recorded synchronously with the lock-in signal, every second for about 2000 s.

The SF₆ mole fraction x is obtained by the relation:

$$x = -K \frac{T}{P} \ln \left(\frac{I_t}{I_0} \right) \quad (1)$$
$$K = \frac{R}{N_A \sigma L}$$

K is, for our measurement, the calibration factor.

Calibration

The calibration has been done with two reference gases at the value respectively of (109.94 ± 0.16) mol/mol and (90.30 ± 0.14) mol/mol, gravimetrically prepared by KRISS. The value of the unknown gas mole fraction is obtained by the relation:

$$x_{unk} = \frac{\left(\frac{T_{unk}}{T_{ref}} \right) (1 + S_{unk})}{\left(\frac{P_{unk}}{P_{ref}} \right) (1 + S_{ref})} x_{ref} \quad (2)$$

where T and P are the measured values respectively of temperature and pressure and S is the lock-in signal.

In this formula the ln I_t/I₀ has been linearized.

The gas sample is prepared filling the cell at a defined pressure value. The cell is evacuated and re-filled two or three times before every measurement.

The gas is transferred from the cylinder to the measurement cell with stainless steel tubes and valves for high purity gases after evacuation of some day with turbo molecular pump heated at 100 °C.

The calibration measurement has been repeated two times giving the following results:

x_{ref} μmol/mol	x_{unk} μmol/mol
109.94 ± 0.16	93.90 ± 1.31
90.30 ± 0.14	93.69 ± 1.31

Evaluation of uncertainty

The values uncertainty is calculated in accordance to the GUM from the equation (2):

Standard uncertainty component	Source of uncertainty y_i	Value of standard uncertainty $u(y_i)$	Sensitivity coefficient β_i	Uncertainty contribution $u_i(x) \equiv \beta_i u(y_i)$ (μmol/mol)
$u(P_{ref})$	Pressure	3.6 Pa	x/P_{ref}	$1.2 \cdot 10^{-4} x$
	certificate fluctuations	2 Pa 3 Pa		
$u(P_{unk})$	Pressure	3.6 Pa	x/P_{unk}	$1.2 \cdot 10^{-4} x$
	certificate fluctuations	2 Pa 3 Pa		
$u(T_{ref})$	Temperature	0.03 K	x/T_{ref}	$1.0 \cdot 10^{-4} x$
	certificate fluctuations	0.003 K 0.03 K		
$u(T_{unk})$	Temperature	0.03 K	x/T_{unk}	$1.0 \cdot 10^{-4} x$
	certificate fluctuations	0.003 K 0.03 K		
$u[(1 + S_{unk})/(1 + S_{ref})]$	Lock-in signal	2.06 mV	$x/[(1 + S_{unk})/(1 + S_{ref})]$	$0.7 \cdot 10^{-2} x$
	fluctuations zero drift	2 mV 0.5 mV		
x_{ref}	Reference mixture		x/x_{ref}	$1.5 \cdot 10^{-3} x$ $1.4 \cdot 10^{-3} x$
	90.30 μmol/mol 109.94 μmol/mol	0.14 μmol/mol 0.16 μmol/mol		
Combined standard uncertainty			$u_c(x)$ ($x_{ref} = 90.30 \mu\text{mol/mol}$) ($x_{ref} = 109.94 \mu\text{mol/mol}$)	$0.0072 x \mu\text{mol/mol}$ $0.0071 x \mu\text{mol/mol}$
Expanded uncertainty			$U_{k=2} = k u_c(x)$	$0.014 x \mu\text{mol/mol}$

Measurement report of KRISS

Method

The instrument used for CF₄ and SF₆ determination is HP6890 GC/ AED(2350G)
Configuration of analysis system: gas cylinder -> regulator -> MFC -> sample injection valve -> column -> detector -> integrator -> area comparison -> results

Gas Chromatograph with AED, Carrier gas : Helium
Cavity & Transfer Line Temp. : 250°C, Oven Temp. : 30°C
Column: Polaplot Alumina, 50m, 0.53mm, 0.025mm film thickness
Measurement Wavelength : C(193nm), S(181nm)
Carrier Flow : 4mL/min, Split Ratio : 5:1
Sample loop: 0.5cc, Sample Flow Rate: 100 mL/min

Calibration

Calibration Standards

The calibration standards for CCQM K-15 were prepared by gravimetric method in KRISS. All source gases were analyzed impurities for purity analysis. The primary standards with 0.05% ~0.15% overall uncertainty are used.

Instrument Calibration

One-point calibration method used to determine the composition of a sample gas mixture by comparing with a primary reference gas mixture with similar concentration prepared by gravimetric method.

Sample Handling

The sample cylinders were stood for more than one week at room temperature before measurements. We used mass-flow controllers to transfer sample gases.

Evaluation of uncertainty

They estimated the uncertainty in the gravimetric methods and measurements. Their uncertainties are given in Tables.

Uncertainty evaluation of weighing

1	Uncertainty related to the balance & the weights	Value (mg)	Distribution	Standard uncertainty (mg)
1.	Resolution of balance	1	Rectangular	0.289
2.	Accuracy of balance including linearity	1	Rectangular	0.577
3.	Incorrect zero point	1	Rectangular	0.289
4.	Drift(thermal and time effects)	1	Rectangular	0.289
5.	Instability due to draught	Negligible		
6.	Location of cylinder on the balance pan	Negligible		
7.	Uncertainties in the weights used	0.05	Rectangular	0.025
8.	Buoyancy effects on the weights used	1.68	Rectangular	0.97
	Total (mg)			1.235

2 Uncertainty related to the gas cylinder	Value (mg)	Distribution	Standard uncertainty (mg)
1. Loss of metal, paints or labels from surface of cylinder	0.1	Rectangular	0.058
2. Loss of metal from threads of valve/fitting	0.5	Rectangular	0.289
3. Dirt on cylinder, valves or associated fitting	0.1	Rectangular	0.058
4. Adsorption/desorption effects on the external cylinder surface	0.1	Rectangular	0.058
5. Buoyancy effects on the cylinder itself			
5.1 Cylinder temperature differs from surrounding air due to e.g. filling with gas	0.6	Rectangular	0.346
5.2 Change of cylinder volume during filling	1.1	Rectangular	0.635
5.3 Change of density of surrounding air due to change in temperature, air, pressure, humidity and CO ₂ content	Negligible		
6. Uncertainty in determination of external cylinder volume	Negligible		
Total (mg)			0.783

3 Uncertainties related to the component gases	Value(mg)	Distribution	Standard uncertainty(mg)
1. Residual gases in cylinder	0.057	Rectangular	0.033
2. Uncertainties of leakage of gas			
2.1 Leakage of air into the cylinder after evacuation	1	Rectangular	0.289
2.2 Leakage of gas from the cylinder valve during filling	1	Rectangular	0.289
2.3 Escape of gas from cylinder into transport lines	Negligible		
3. Gas remaining in transfer system when weight loss method is used	Negligible		
4. Absorption/reaction of components on internal cylinder surface	Negligible		
5. Reaction between components	Negligible		
6. Insufficient homogenization	Negligible		
Total (mg)			0.410

Total uncertainties in weighing (1.519 mg: standard uncertainty)

Model used for evaluating measurement uncertainty for CF₄ & SF₆:

Model equation

$$C_{\text{sample}} = A_{\text{sample}} \times C_{\text{std}} / A_{\text{std}}$$

$$C_{\text{final}} = C_{\text{sample}} \times f_{\text{rep}}$$

Typical evaluation of the measurement uncertainty for CF₄:

Quantity X_i	Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$
A _{sample}	1892.33	A		0.8343	0.053	0.0442
C _{std}	100.207	B	normal	0.041	1.0015	0.0411
f _{rep}	0.999933	B	normal	0.00021	100.3608	0.021
A _{std}	1889.43	A		0.6436	-0.0531	0.0342

A_{sample} : the peak area of sample

C_{std} : the concentration of standard gas (1×10⁻⁶ mol/mol)

A_{std} : the peak area of standard

f_{rep} : the factor of reproducibility in analysis.

Typical evaluation of the measurement uncertainty for SF₆:

Quantity X_i	Estimate x_i	Evaluation type (A or B)	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$
A _{sample}	1163.98	A		0.9684	0.086	0.0833
C _{std}	100.075	B	normal	0.041	0.9982	0.0409
f _{rep}	1.00024	B	normal	0.00073	99.8716	0.073
A _{std}	1166.35	A		0.4637	-0.0856	0.0397

A_{sample} : the peak area of sample

C_{std} : the concentration of standard gas (1×10⁻⁶ mol/mol)

A_{std} : the peak area of standard

f_{rep} : the factor of reproducibility in analysis.