CCT/17-30

# FINAL DETERMINATION OF THE BOLTZMANN CONSTANT *k* BY DIELECTRIC-CONSTANT GAS THERMOMETRY (DCGT)

C. Gaiser, B. Fellmuth *et al.*

# Outline

- History & Motivation
- Dielectric-Constant Gas Thermometry
- First Results & Difficulties
- Improvements & Final Result
- Uncertainty estimates & correlations

# Motivation and History

## Situation in 2003:

Fact: Only **one** measurement of the Boltzmann constant on the level of 2 ppm (NIST acoustic gas thermometry).

Demand: A sound new definition of the kelvin should not **only** be based on speed of sound measurements.

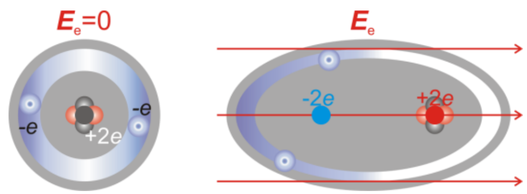
Reaction: First internal study at PTB in 2003 for a determination of k with DCGT based on the **experience** gained at low temperatures (T < 30 K)

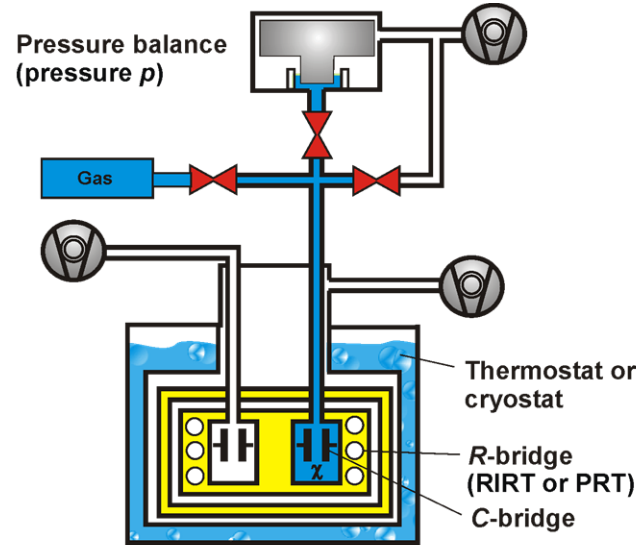
| Component | State of the art (2003) | Goal |
|---|---|---|
| $\chi(p = 0)$ determination | 3 ppm | 1 ppm |
| pressure measurement | 4 ppm | 1 ppm |
| Compressibility $\kappa_{eff}$ | 13 ppm | 0.5 ppm |
| Polarizability $\alpha_0$ | 2 ppm | 0.5 ppm |
| Impurities | 5 ppm | 0.5 ppm |
| Adsorption | 0.5 ppm | 0.2 ppm |
| $T$ measurement | 2 ppm | 1 ppm |
| | | |
| **Type B combined** | **15 ppm** | **2 ppm** |

# Dielectric-Constant Gas Thermometry (DCGT)

## Clausius-Mossotti equation combined with the ideal-gas law:

$$\frac{\varepsilon_\mathrm{r}-1}{\varepsilon_\mathrm{r}+2}=\frac{p}{kT}\,\frac{\alpha_0}{3\varepsilon_0}$$



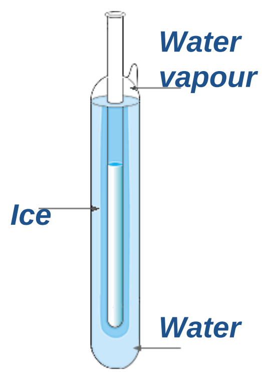




## Measuring quantity :

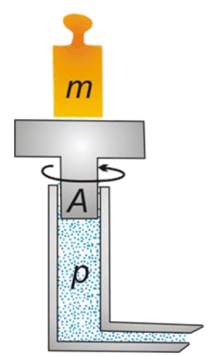
$$\frac{C(p)-C(0)}{C(0)}=\underbrace{\varepsilon_\mathrm{r}-1}_{\chi}+\varepsilon_\mathrm{r}\kappa_\mathrm{eff}\,p$$

| | |
|---|---|
| $\varepsilon_\mathrm{r}$ | dielectric constant |
| $\varepsilon_0$ | electric constant |
| $\alpha_0$ | atomic polarizability |
| $\kappa_\mathrm{eff}$ | effective compressibility |
| $\chi$ | electric susceptibility |
| $p$ | pressure |
| $T$ | temperature |

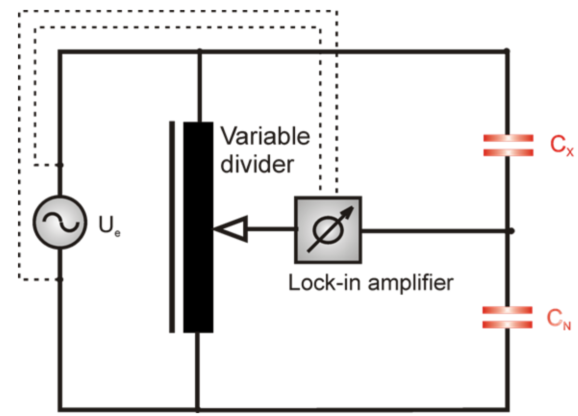
### Temperature




### Pressure

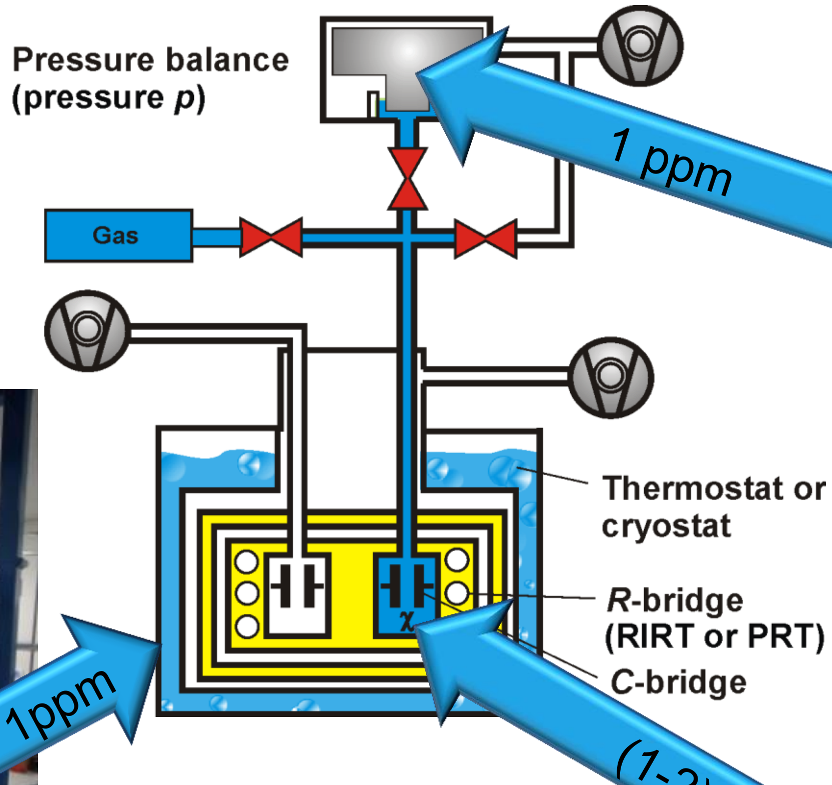



### Capacitance ratio

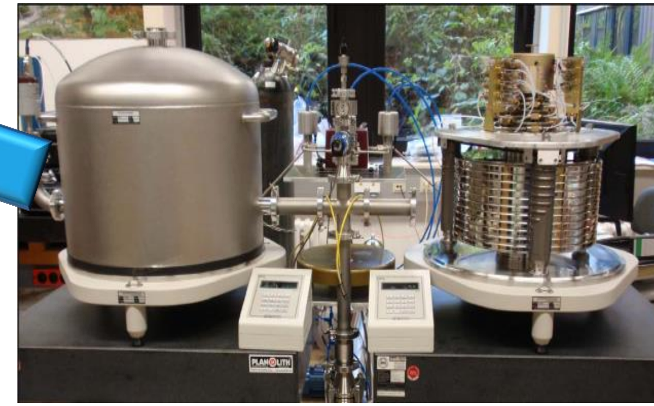


# Main Challenges

**Goal:**
**$u_r(k) \approx 2$ ppm**




## Pressure



## Temperature

## Change of capacitance ratio

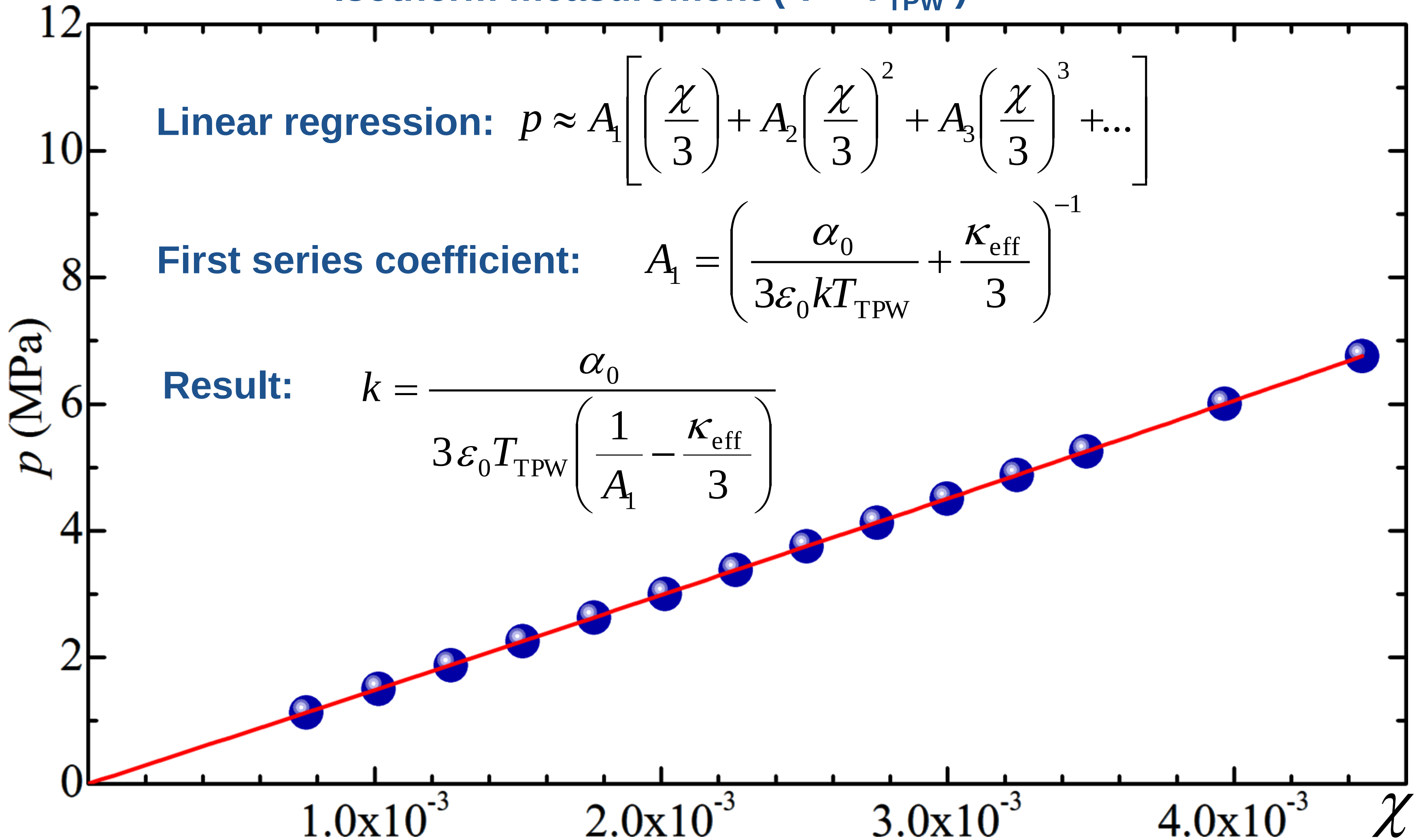
# Determination of the Boltzmann constant with DCGT

## Isotherm measurement ( $T \approx T_{TPW}$ )

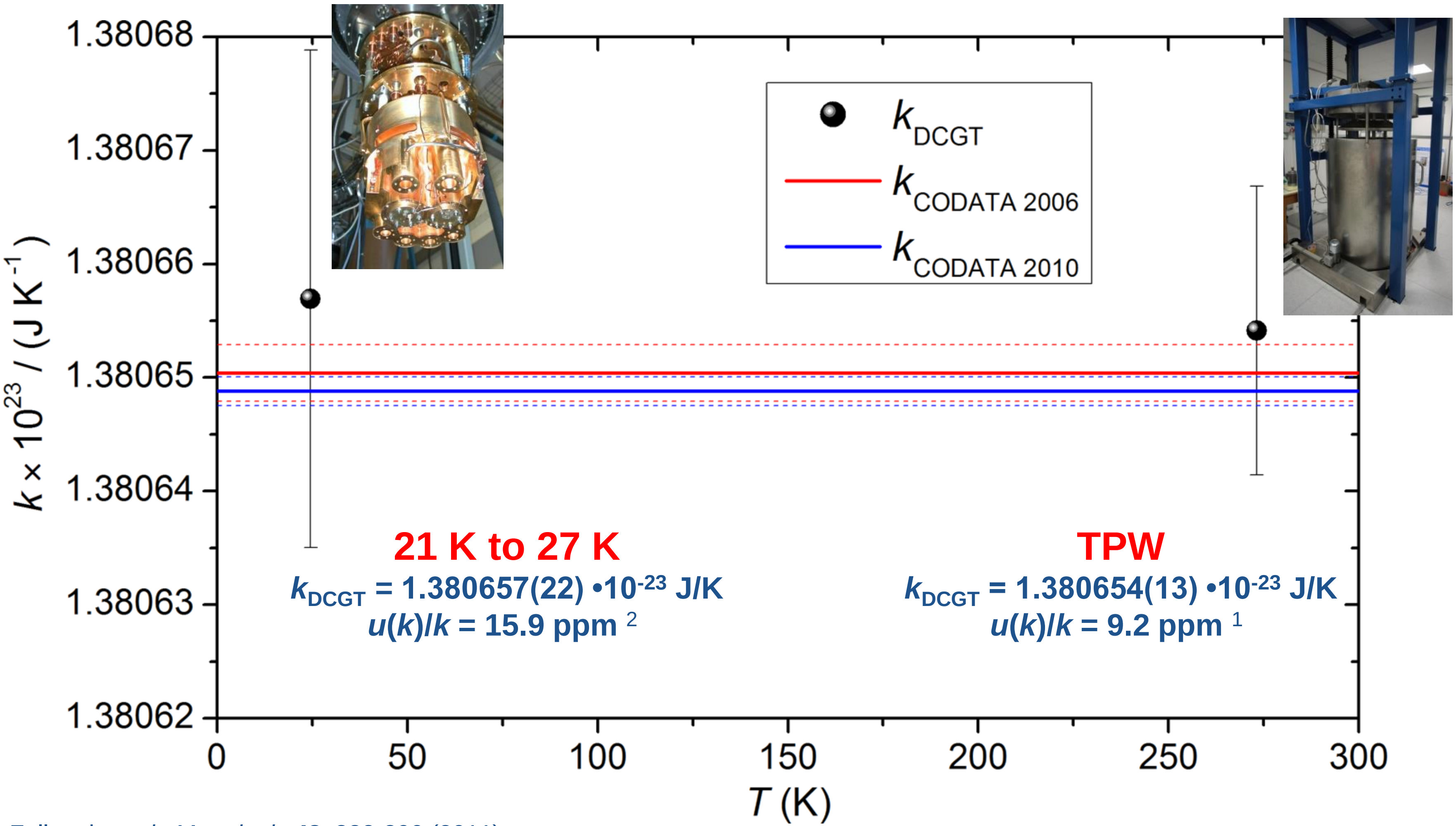
**Linear regression:** $$p \approx A_1\left[\left(\frac{\chi}{3}\right) + A_2\left(\frac{\chi}{3}\right)^2 + A_3\left(\frac{\chi}{3}\right)^3 + \ldots\right]$$

**First series coefficient:** $$A_1 = \left(\frac{\alpha_0}{3\varepsilon_0 k T_{TPW}} + \frac{\kappa_{eff}}{3}\right)^{-1}$$

**Result:** $$k = \frac{\alpha_0}{3\varepsilon_0 T_{TPW}\left(\frac{1}{A_1} - \frac{\kappa_{eff}}{3}\right)}$$



# Determination of the Boltzmann constant with DCGT 2011




[1] B. Fellmuth *et al.*, *Metrologia* **48**, 382-390 (2011)
[2] C. Gaiser and B. Fellmuth, *Metrologia*, **49**, L4-L7 (2012)

# Reducing the uncertainty of the effective compressibility

Improvements in RUS measurements (e.g. temperature-dependent measurements)

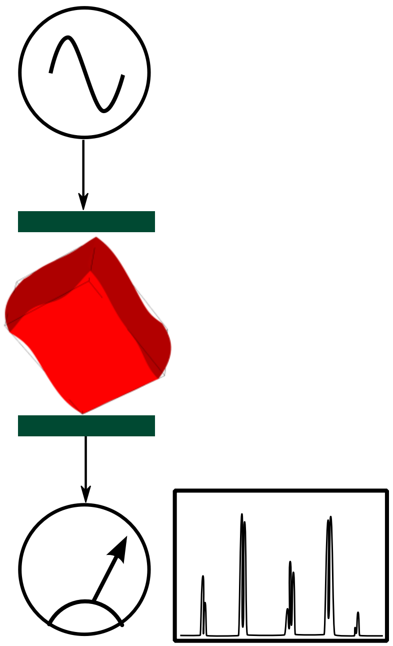
Refinement of evaluation models (FEM, Monte-Carlo simulation)

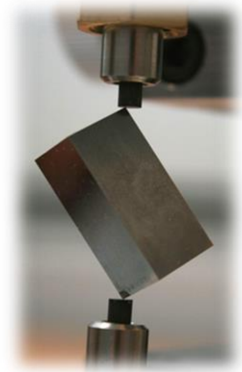
Test samples also for the insulation materials ($Al_2O_3$)

Determination of the thermal expansion coefficient and the molar specific heat capacity

adiabatic → isothermal

Resonant ultrasound spectroscopy (**RUS**):

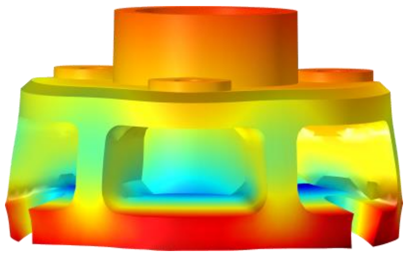




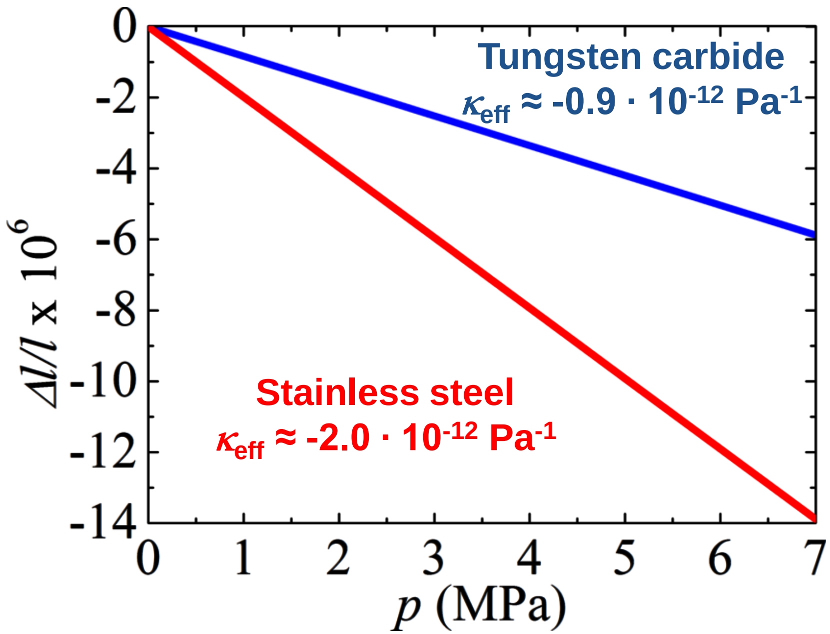
# Reducing the uncertainty of the effective compressibility

FEM calculations of effective compressibility for specific capacitor geometry

→ optimization of capacitor design



Switch from stainless steel to tungsten carbide as capacitor material




**Result (2013)**
Composite isothermal compressibility:

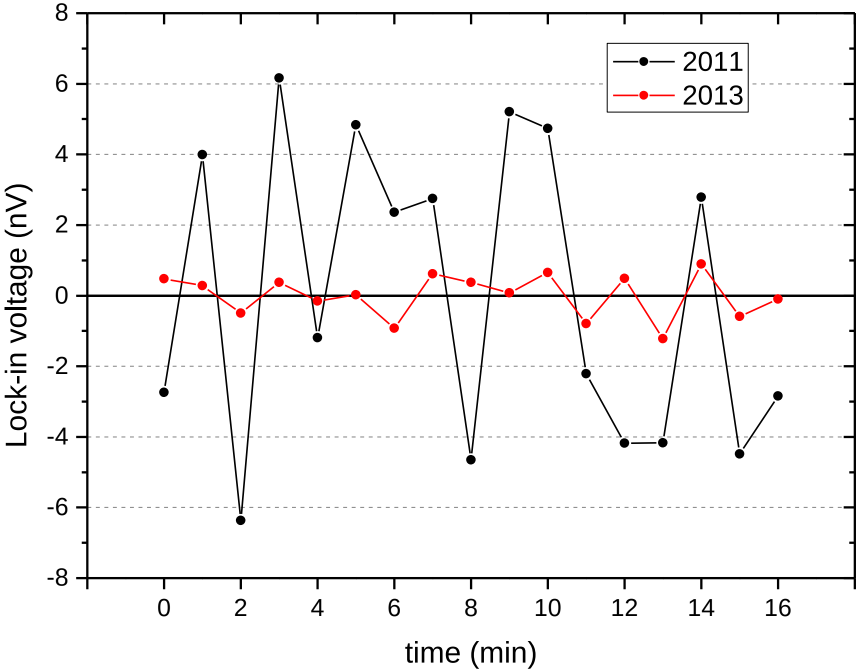
-9.370 x $10^{-13}$ Pa$^{-1}$ ($u_{rel}$ = 0.17%)

# Reducing the uncertainty of the susceptibility


Careful analysis of the capacitance measuring network (chokes) and switch to low noise cables

Only one cable for the zero detector (increase of the sensitivity by nearly a factor two)

Measurement of the unbalanced signal of the null detector with a bandwidth of 0.01 Hz



# Purity of the measuring gas

**99.99999% Helium**
(Linde AG)

↓

**Gas purifier (adsorber)**
(Micro Torr SP70, SAES Pure Gase, Inc.)

↓

**Helium purifier (getter)**
(HP2, Valco Instruments, Co. Inc.)

| Component | Certificate Gas (ppb) | Specification Getter (ppb) | Specification Adsorber (ppb) |
|---|---|---|---|
| $H_2$ | < 30 | < 10 | < 0.1 |
| $H_2O$ | < 50 | < 10 | < 0.1 |
| $O_2$ | < 30 | < 10 | < 0.1 |
| CO | < 30 | < 10 | < 0.1 |
| $CO_2$ | < 30 | < 10 | < 0.1 |
| $N_2$ | | < 10 | |
| Hydro-carbons | < 1 | < 10 | < 0.1 |
| Noble gases | | | |

# Purity of the measuring gas

**Mass-spectrometry measurements**

↓

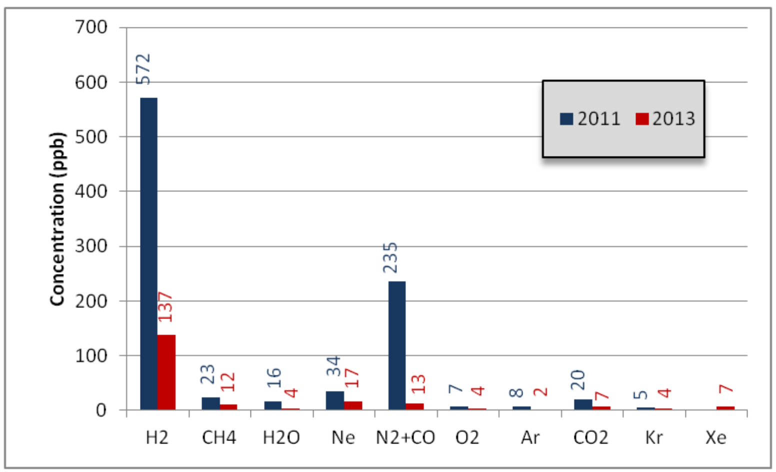
**Experiment**

(UHP gas tubing)

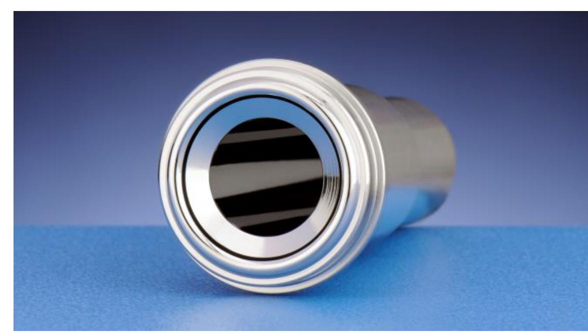
↓

**Mass-spectrometry measurements**

| Component | Detection limit (ppb) |
|---|---|
| $H_2$ | < 300 |
| $H_2O$ | < 20 |
| $O_2$ | < 10 |
| CO | < 100 |
| $CO_2$ | < 50 |
| $N_2$ | < 100 |
| $CH_4$ | < 20 |
| Ne | < 10 |
| Ar | < 10 |
| Kr | < 10 |
| Xe | < 10 |







# *Purity of the measuring gas*

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(HP2, Valco Instruments, Co. Inc.)

↓

**Mass-spectrometry measurements**

↓

**Experiment**
(UHP gas tubing)

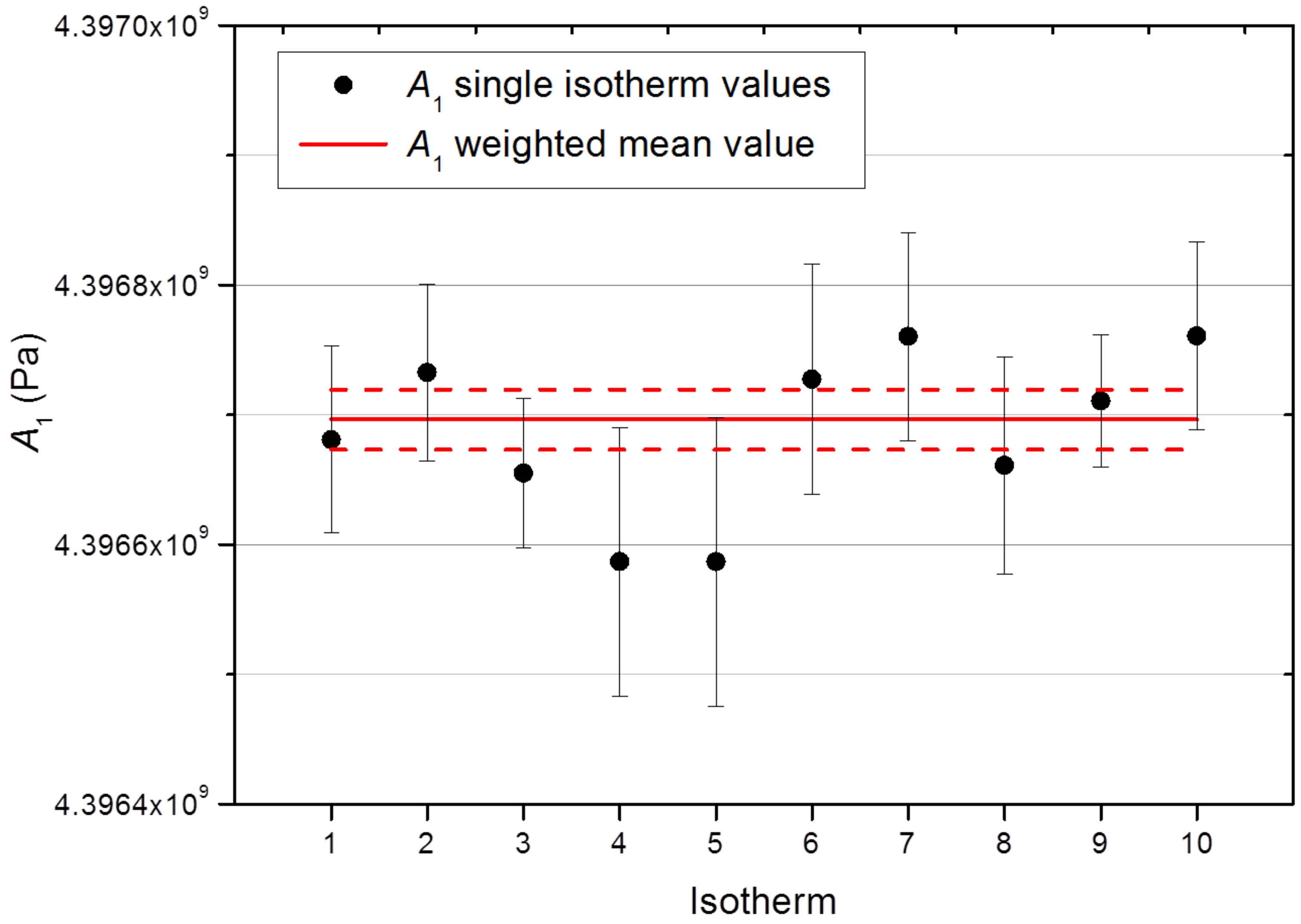
↓

**Mass-spectrometry measurements**

| Component | Mass-Spec and Getter Spec. (ppb) | Sensitivity in He | Uncertainty (ppm)* |
|---|---|---|---|
| $H_2$ | < 10 | 4 | 0.02 |
| $H_2O$ | < 10 | 160 | 0.9 |
| $O_2$ | < 10 | 10 | 0.06 |
| $CO_2$ | < 50 | 10 | 0.3 |
| $N_2$ & CO | < 100 | 8 | 0.4 |
| Ne | < 10 | 2 | 0.01 |
| Ar | < 10 | 8 | 0.05 |
| Kr | < 10 | 10 | 0.06 |
| Xe | < 10 | 16 | 0.09 |
| **Combined uncertainty** | | | **1.0** |

*(asymmetric rectangular distribution)

# Results 2013 (10 isotherms)



# Uncertainty budget DCGT 2013 (TPW)

## Typ A

| Component | $u(k)/k \cdot 10^6$ |
|---|---|
| Overall weighted mean of $A_1$ values | **2.6** (6.3) |

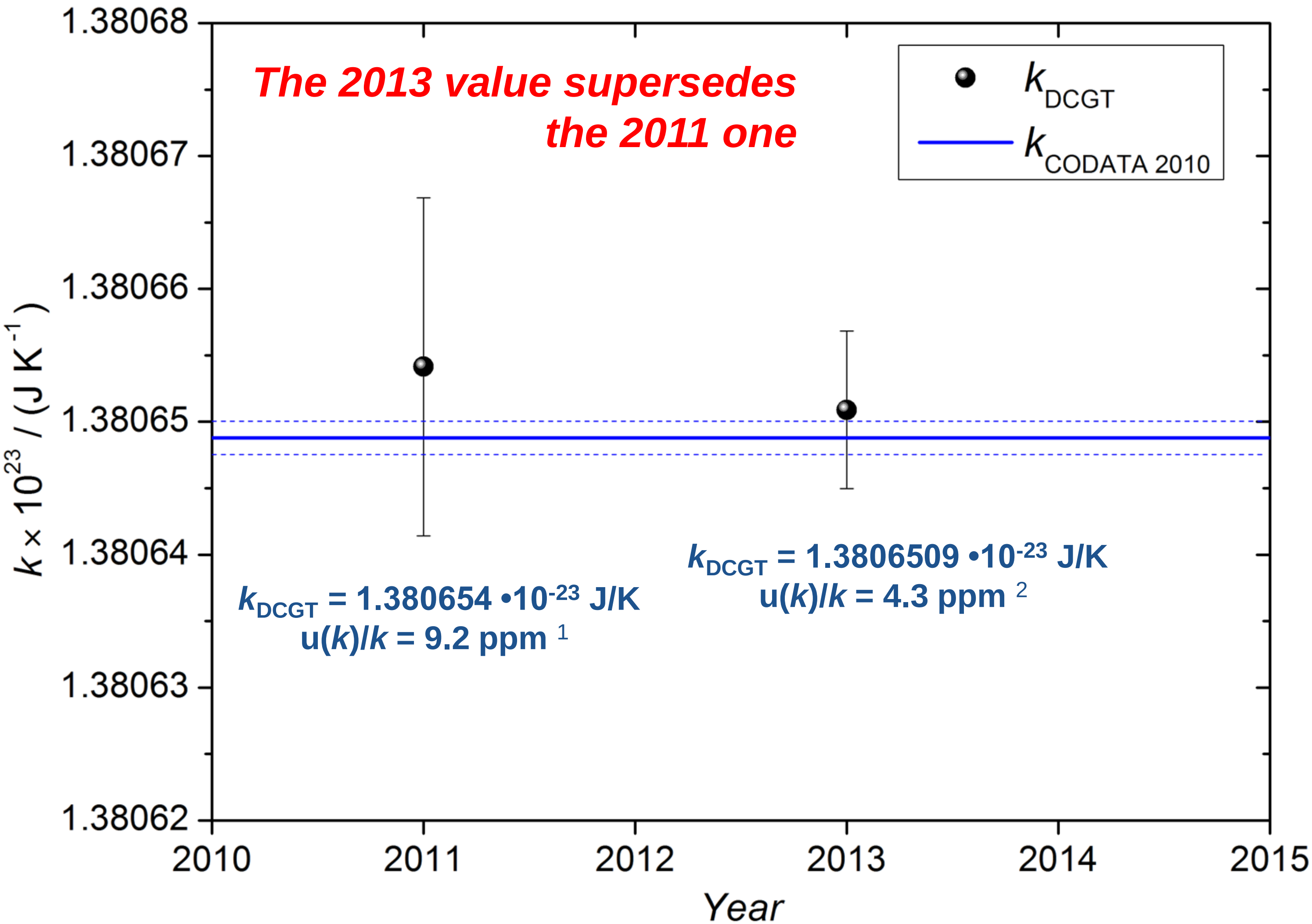
## Typ B

| Component | $u(k)/k \cdot 10^6$ |
|---|---|
| Susceptibility measurement (capacitance change) | 1.0 (1.0) |
| Pressure measurement | 1.9 (1.9) |
| Temperature | 0.3 (0.3) |
| Determination of the effective compressibility | **2.4** (5.8) |
| Head correction | 0.2 (0.2) |
| Impurities (measuring gas) | **1.0** (2.4) |
| Surface layers (impurities) | **0.5** (1.0) |
| Polarizability ab initio calculation (theory) | 0.2 (0.2) |

**Combined standard uncertainty: 4.3 ppm (9.2 ppm)**

B. Fellmuth *et al*., *Metrologia* **48**, 382-390 (2011),
C. Gaiser *et al*., *Metrologia*, **50,** L7-L11 (2013)

# Determination of k with DCGT (TPW)

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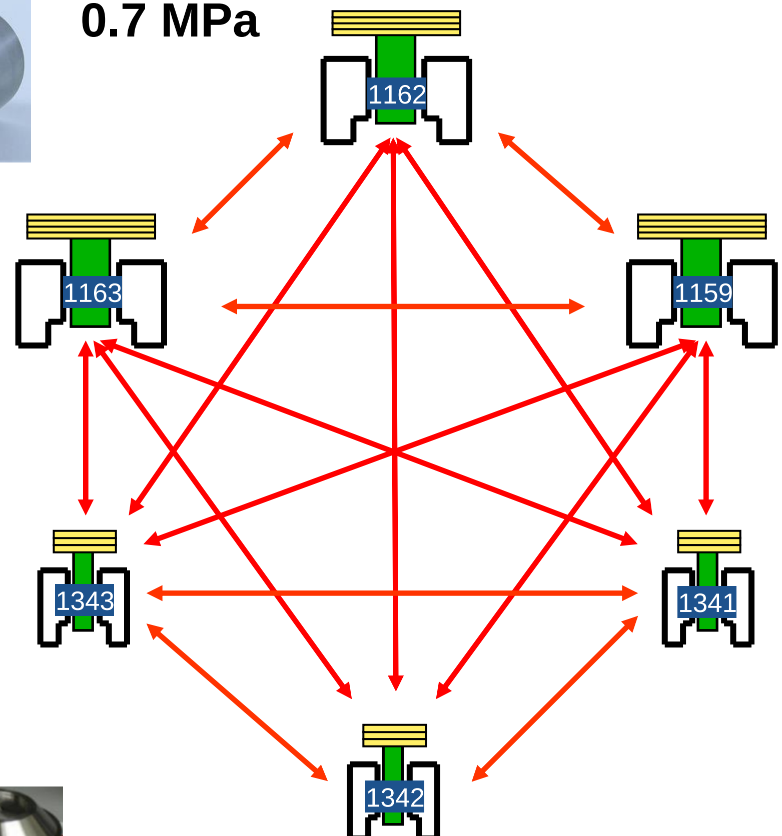
[2] C. Gaiser *et al.*, *Metrologia*, **50,** L7-L11 (2013)

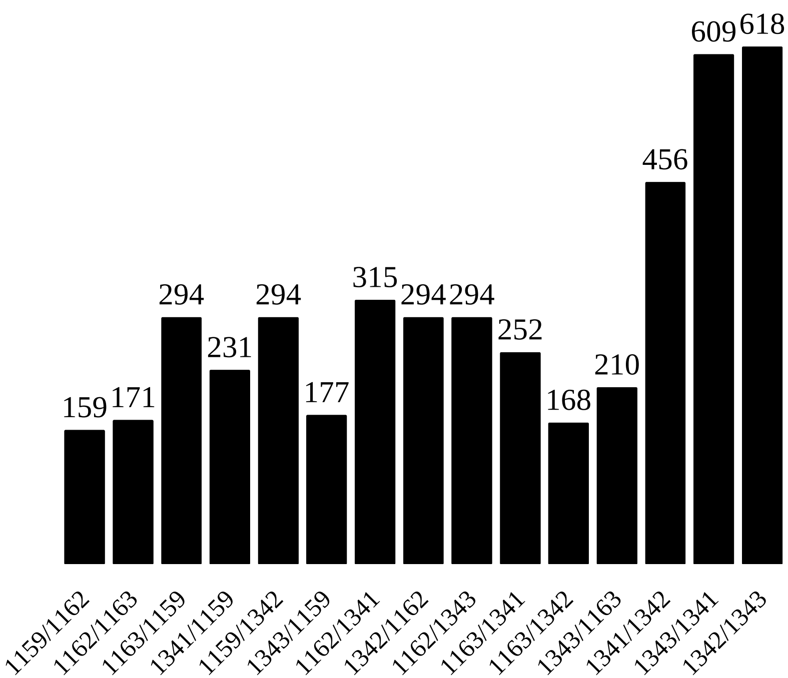
# Improved pressure standard

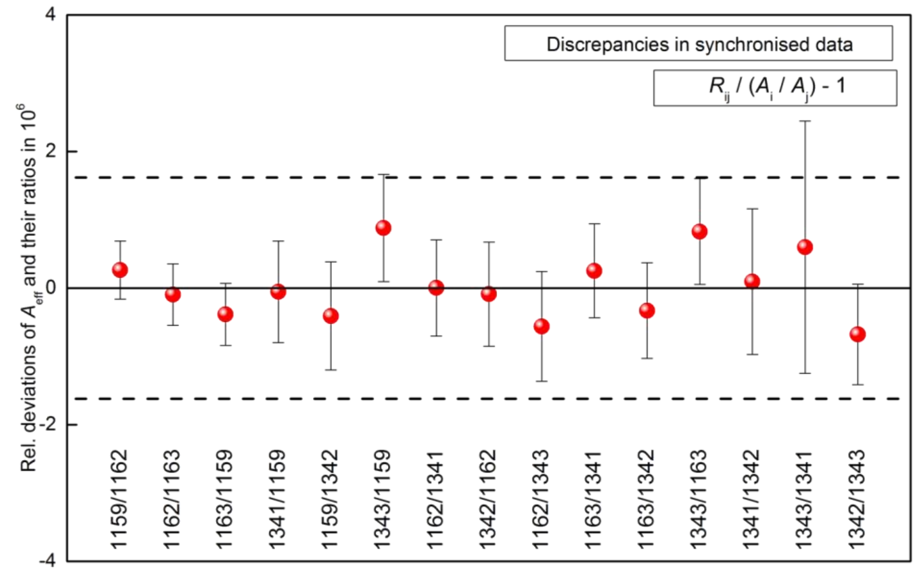
**20 cm² – Systems**
**0.7 MPa**




**2 cm² – Systems**
**7 MPa**

# Cross-float measurements

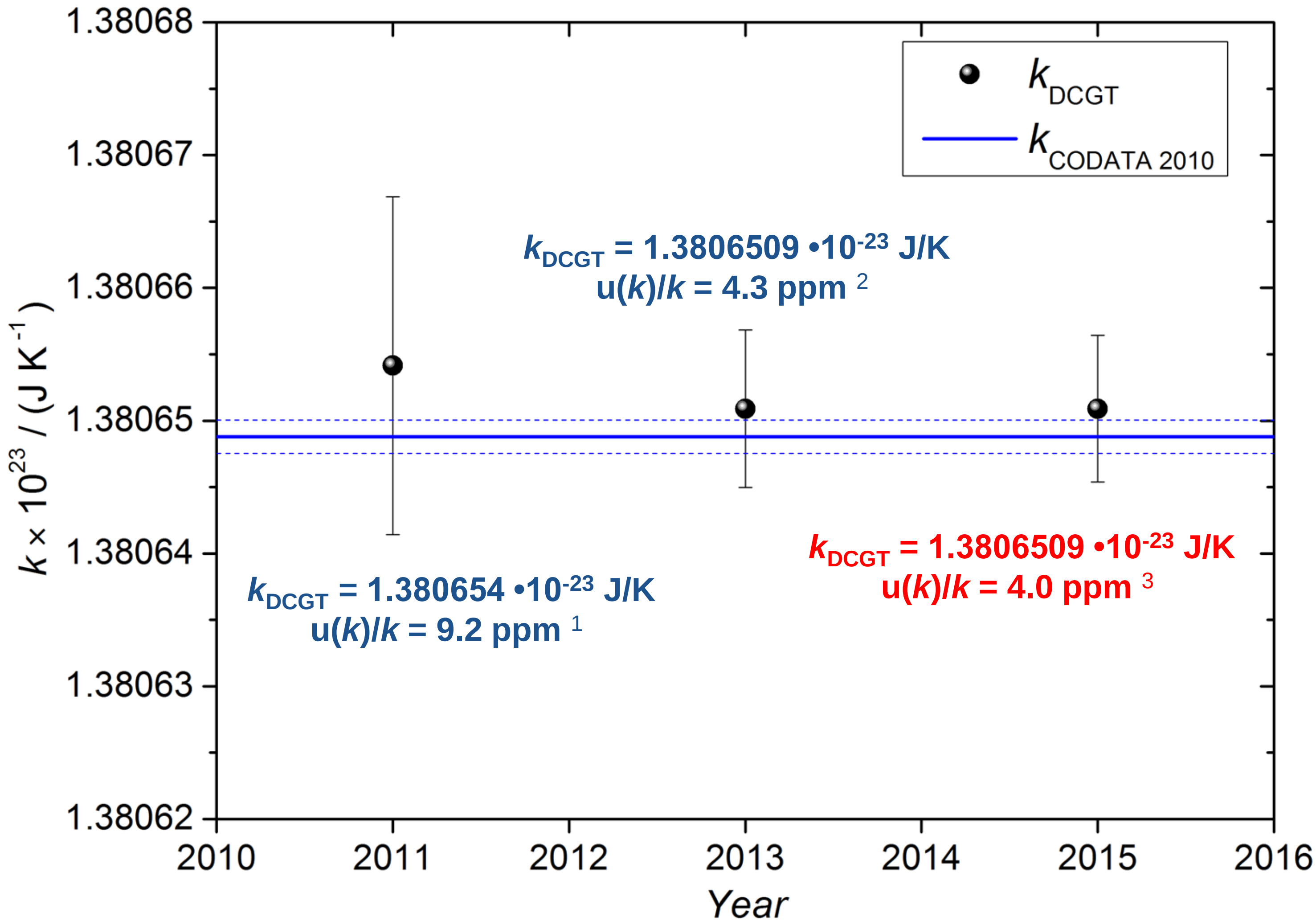



$u_{2013}(p)$=1.9 ppm→ $u_{2015}(p)$=1.0 ppm

T. Zandt *et al.*, *Metrologia*, **Special-issue on *k*** (2015)

# Determination of k with DCGT (TPW)

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[2] C. Gaiser *et al.*, *Metrologia*, **50,** L7-L11 (2013)
[3] C. Gaiser *et al.*, *Metrologia*, **Special-issue on *k*** (2015)

# Remaining potential of uncertainty reduction

## Type A

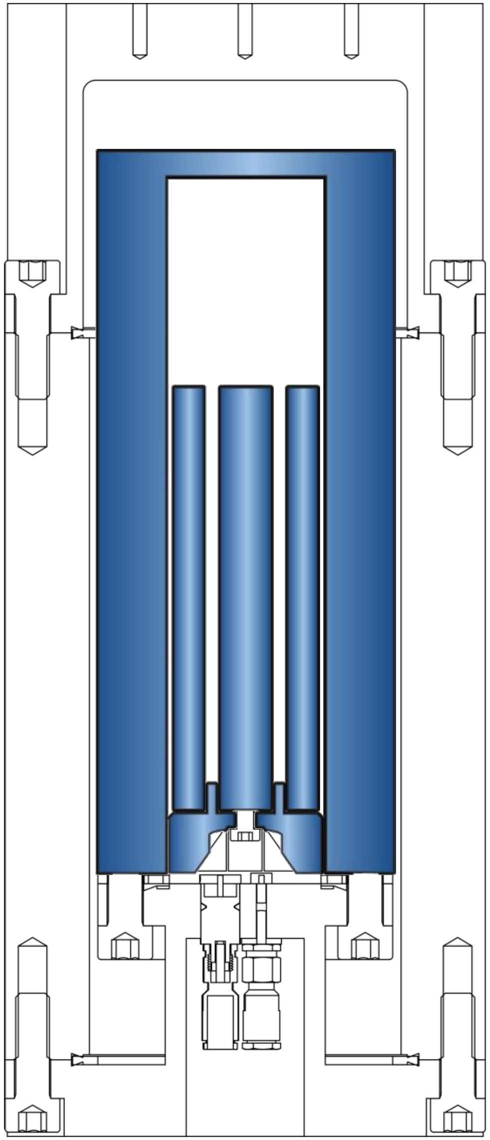
| Component | $u(k)/k \cdot 10^6$ |
|---|---|
| Overall weighted mean of $A_1$ values | 2.6 |

**What is next:**
DCGT measurements with two new different tungsten carbide cylindrical capacitors
**Hope:**
Extremely stable results → reduction in the Type A uncertainty.
Consistent results → reduction of $u(\kappa_{\text{eff}})$

## Type B

| Component | $u(k)/k \cdot 10^6$ |
|---|---|
| Susceptibility measurement (capacitance change) | 1.0 |
| Pressure measurement | 1.0 |
| Temperature | 0.3 |
| Determination of the effective compressibility | 2.4 |
| Head correction | 0.2 |
| Impurities (measuring gas) | 1.0 |
| Surface layers (impurities) | 0.5 |
| Polarizability ab initio calculation (theory) | 0.2 |

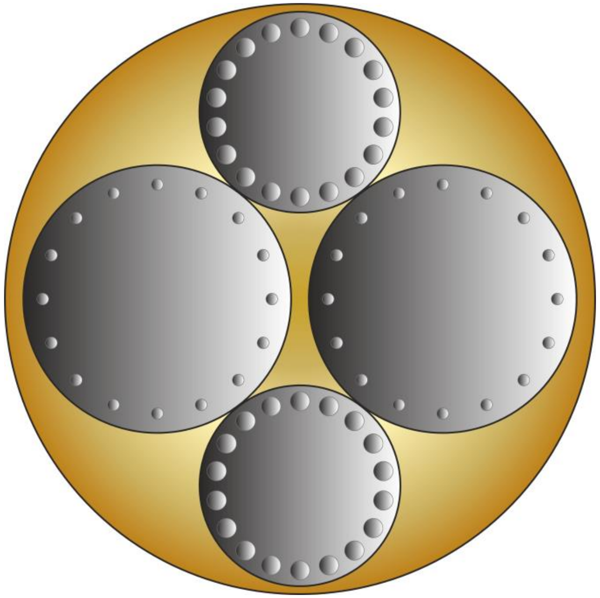
# Improvements since 2014



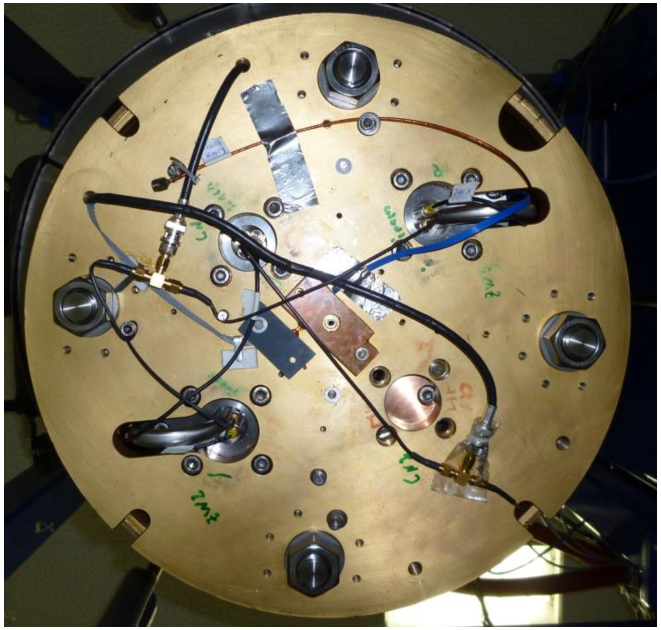
New massive shielding of the capacitor electrodes and more stable insulating discs

Parallel measurement of 2 different capacitors against two different types of reference capacitors

*top:*



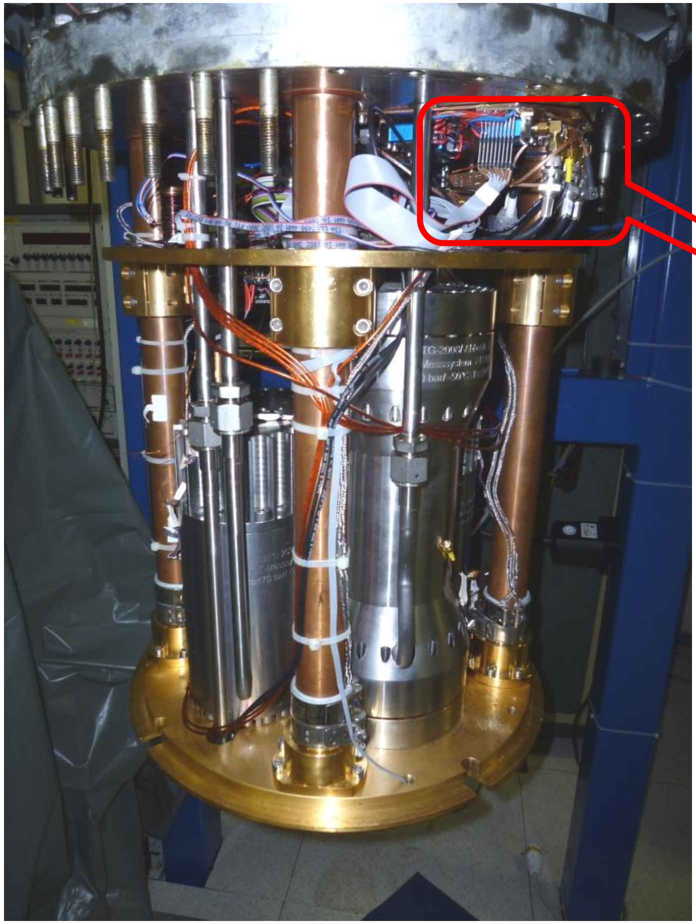
*bottom:*

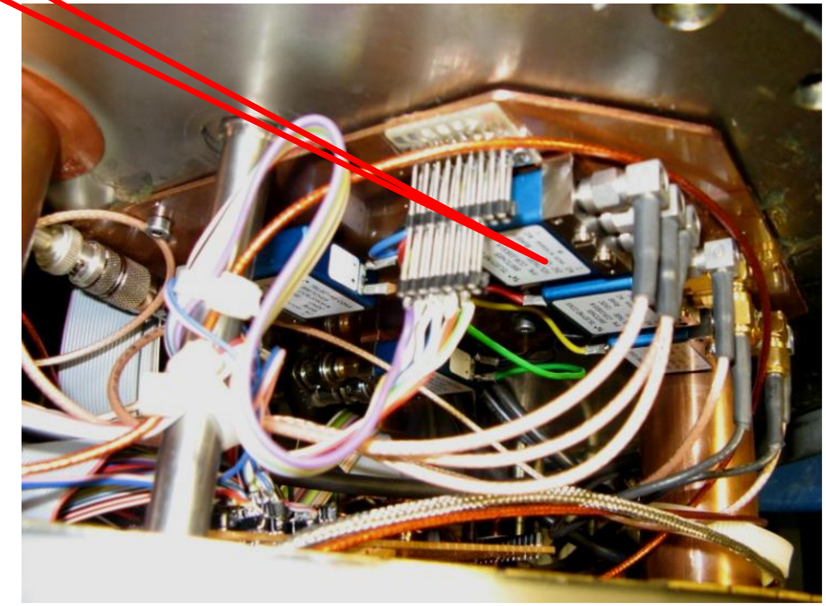


# Improvements since 2014: Type A

Improved stability due to switches inside the measurement system

Reduction of Type A uncertainty by a factor ≈ 2





# Improvements since 2014: compressibility

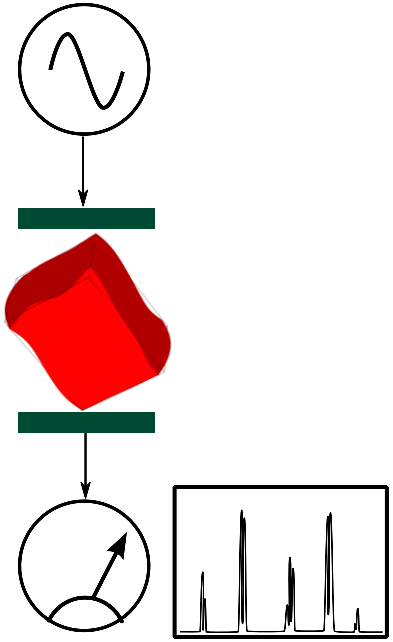
Use of two different types of tungsten carbide $\Delta\kappa_{\mathrm{eff}} \approx 6\ \%$

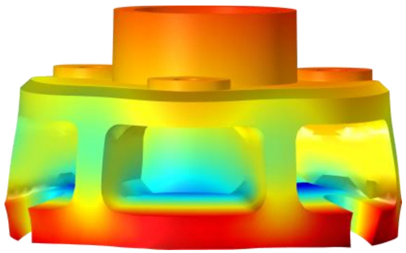
Refinement of evaluation models (FEM, analytic approximation)

RUS measurements on many samples > consideration of $\kappa_{\mathrm{vol}}(\rho)$

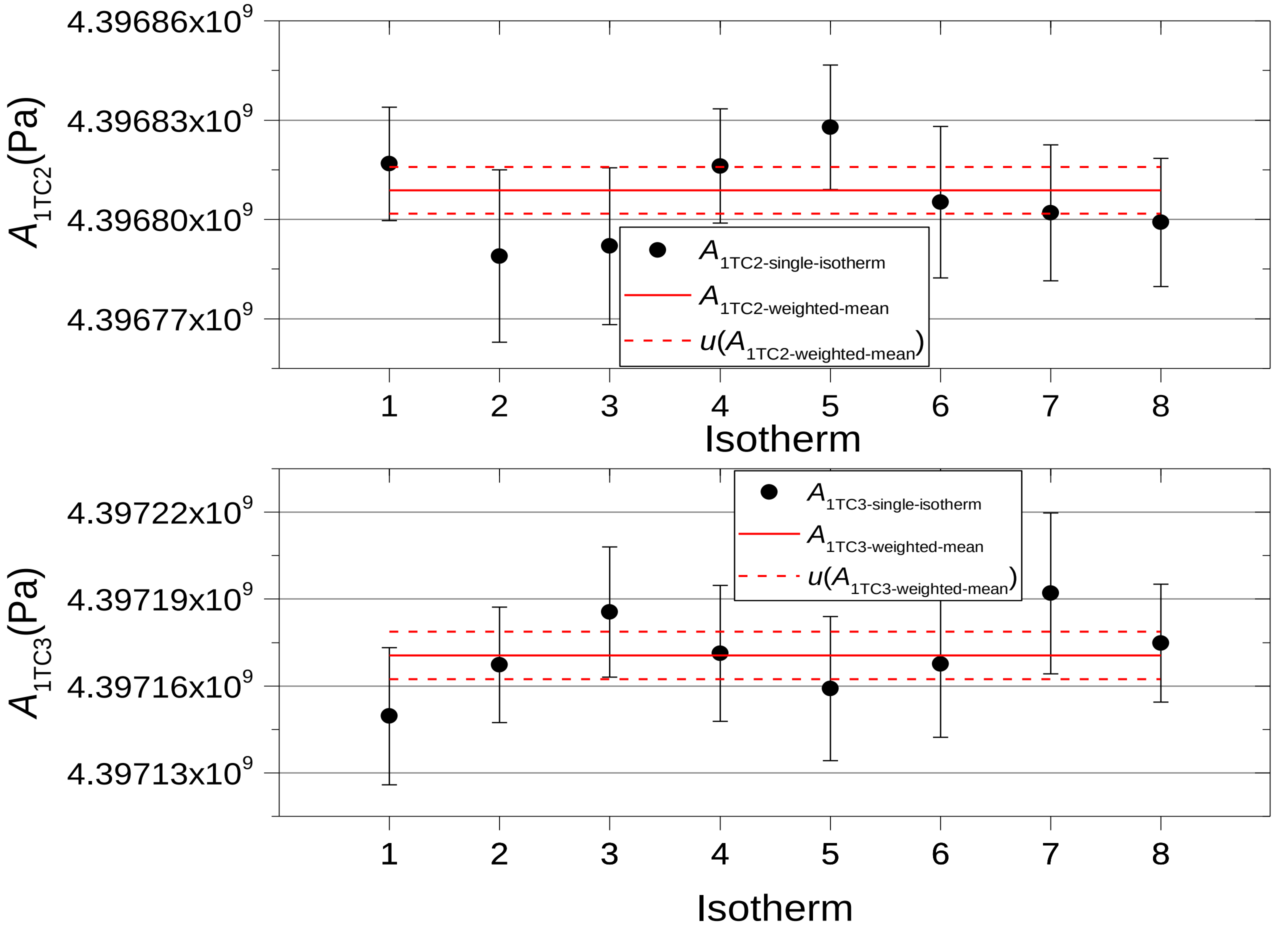
Consistent results for the two capacitors led to reduction of $u(\kappa_{\mathrm{eff}})$ by a factor of $\approx 2$

Resonant-ultrasound spectroscopy (**RUS**):





# Results 2017 (8 isotherms, 2 capacitors)



# Uncertainty Budgets (ppm)

| Component | TC1 (2013) | TC2 (2017) | TC3 (2017) |
|---|---|---|---|
| **Type A estimate** | 2.62 | 1.60 | 1.86 |
| **Type B estimates** | | | |
| Susceptibility measurement ($\Delta C/C$) | 1.00 | 0.40 | 0.40 |
| Determination of the compressibility $\kappa_{\text{eff}}$ | 2.35 | 0.65 | 1.53 |
| Temperature $T_{\text{TPW}}$ (traceability to the TPW) | 0.30 | 0.30 | 0.30 |
| Pressure measurement (7 MPa) | 1.00 | 1.00 | 1.00 |
| Head correction (pressure of gas column) | 0.20 | 0.20 | 0.20 |
| Impurities (measuring gas) | 1.00 | 1.00 | 1.00 |
| Surface layers (impurities) | 0.50 | 0.50 | 0.50 |
| Polarizability from *ab inio* calculations (theory) | 0.20 | 0.10 | 0.10 |
| **Combined standard uncertainty** | **3.97** | **2.36** | **2.89** |

**DCGT > second primary thermometry method with $u_r(k)$ < 3 ppm**

→

**Second condition of the CCT for the new definition of the kelvin fulfilled!**

# Weighted mean considering fully correlations

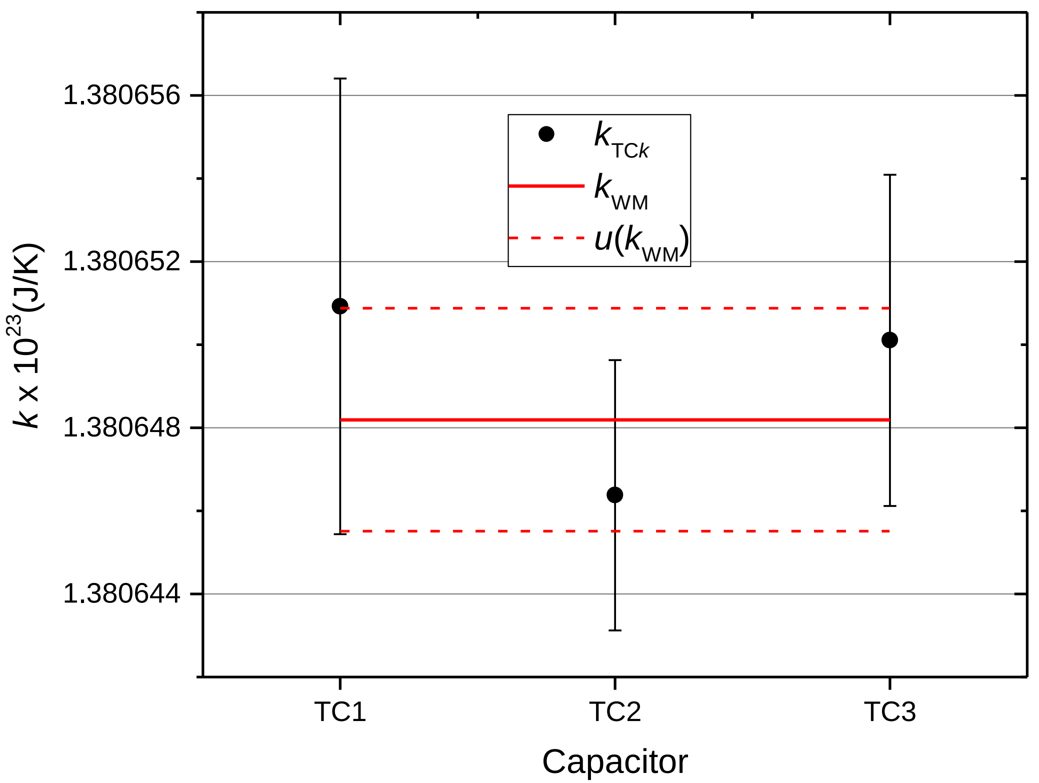
| **Component** | **Correlation** |
|---|---|
| Type A estimate | Partial |
| Susceptibility measurement ($\Delta C/C$) | Complete |
| Determination of the compressibility $\kappa_{eff}$ | Partial |
| Temperature $T_{TPW}$ (traceability to the TPW) | Complete |
| Pressure measurement (7 MPa) | Complete |
| Head correction (pressure of gas column) | Complete |
| Impurities (measuring gas) | No (independent) |
| Surface layers (impurities) | No (independent) |
| Polarizability from *ab inio* calculations (theory) | Complete |

**$k_{WM}$ = 1.3806482 with $u_r(k)$ = 1.94 ppm**

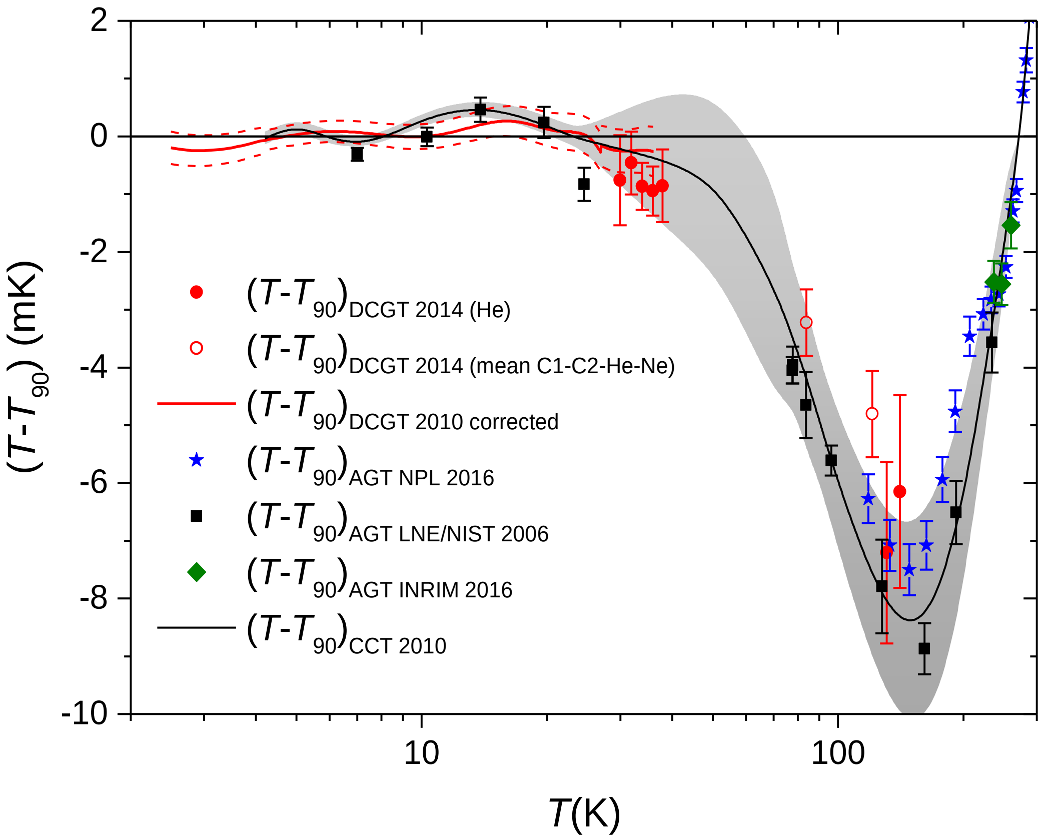
(≈ 0.2 ppm smaller than CODATA 2014)

(Relative standard uncertainty without consideration of correlations: 1.66 ppm, i.e. smaller by about 20%)

# Comparison of the three $k_{TCk}$ values



# Results at low temperatures




Gaiser, Fellmuth, Haft: *Metrologia* **54**, 141 (2017): *Primary thermometry from 2.5 K to 140 K applying dielectric-constant gas thermometry*

Gaiser, Fellmuth: *Phys. Stat. Sol.* ***B*** **253**, 1549 (2016): *Method for extrapolating compressibility data of solids from room to lower temperatures*