CMC review protocol for calibration of high-temperature fixed points

Scope

To provide a method of reviewing thermometry CMCs in the sub-field of secondary fixed point cells for acceptance in Appendix C of the KCDB. Covers service category numbers 2.1, 2.5.1 and 2.8.3 of the "CMC Service Categories for Temperature and Humidity (October 2009)" in the KCDB.

This protocol for the review of industrial thermometer CMCs supersedes the version of 25 September 2009.

Metal-carbon eutectics (service categories 2.1 and 2.5.1)

Preliminary notes

- Metal carbon eutectic fixed-point cells for thermometry and radiometry have been studied and approximate transition temperatures have been published, but definitive values are not yet determined.
- As unique transition temperature, the minimum of the first derivative of the melting process with respect to time is defined (inflection point of symmetrical part of the melting curve).

Metal-carbon eutectics as secondary reference points

Secondary reference points must fulfil the following criteria [1]:

- high reproducibility
- multiple measurements of the temperature value
- uncertainty of the assigned temperature
- stated purity (>99,99%)
- references must be given

Reproducibility:

- fixed point: temperature are determined by a physical process → no difference between different cells → to be checked by comparisons: i.e. multiple cells of different materials, designs and manufacturers
- the difference between the melting temperatures should agree within the comparison uncertainty ($k = 2$)
- a summary of comparisons performed including reproducibilities can be found in [2]
- reproducibilities in the order of about 0.1 K were achieved

Values of inflection point of melt:

- Approximate ITS-90 temperatures for some metal-carbon fixed points are given in different publications. A summary can be found in [3]. Recent measurements of absolute melting temperatures [4] were consistent with the corresponding ITS-90 temperatures (see table below).

Eutectic	T / °C [3]	T / °C [4]	T_{max} - T_{min} / °C [3, 4]
Co-C	1324.0	1324.0	0.7
Pd-C	1491.7	1491.9	0.8
Pt-C	1737.9	1738.6	1.3
Ru-C		1954.0	1.6
Re-C	2474.2		2.0

- The rightmost column in the above table shows the difference between the highest and lowest temperatures of the inflection point of the melt reported in [3] and [4].
- The temperatures presented in the above table are measured by pyrometers or filter radiometers. Alternative methods to determine melting temperatures of metal-carbon eutectics by using Pt/Pd

thermocouples [5] or infrared thermometry [6] on basis of extrapolation methods were also applied.

Uncertainties:

- The uncertainties of melting temperatures of eutectic fixed points differ considerably. Published uncertainties (k = 2) of low temperature eutectics (Fe-C, Co-C and Ni-C) usable also for the calibration of contact thermometers are in the order of 0.2 K - 0.4 K. In the mid range (Pd-C, Pt-C, Rh-C, Ru-C) uncertainties of 0.3 K - 0.7 K can be found. At higher temperatures, above 2000 °C, uncertainties in the order of 1 K are common.

Review criteria

The NMI must have approved CMCs for the thermometers used to calibrate the fixed points.
No Key Comparisons have been performed in this sub-field.

Uncertainty limits of CMC entries for calibration of eutectic fixed point cells (k = 2):

Eutectic	RMO review	WG8 review
Fe-C	< 0.7 K	< 0.3 K
Co-C	< 0.7 K	< 0.3 K
Ni-C	< 0.7 K	< 0.3 K
Pd-C	< 0.8 K	< 0.3 K
Pt-C	< 1.3 K	< 0.5 K
Ru-C	< 1.6 K	< 0.7 K
Re-C	< 2.0 K	< 0.8 K

Suggested scrutiny elements for reviewers

- methods of determination of the temperature values of the inflection point of the melt
- uncertainty budget
- verification of the purity of the fixed-point materials used
- results of inter-comparisons involving the source of traceability of temperature measurement (e.g., the NMI's own metal-carbon eutectic cell, a filter radiometer measuring thermodynamic temperature, or a radiation thermometer measuring T_{90}): if the NMI's own eutectic cell is used as the source of traceability, the NMI should have a proven measurement system (e.g., T_{td} filter radiometer or T_{90} radiation thermometer), with an approved CMC, to verify the eutectic cell's temperature
- results of internal comparisons of at least two different eutectic fixed-point cells

Pure metal fixed points (service categories 2.1, 2.5.1 and 2.8.3)

Preliminary notes

- Pure metal fixed points at temperatures above 1000 °C are the freezing point of gold (1064.18 °C) and copper (1084.62 °C) and the melting points of palladium (1554.8 °C, in argon), platinum (1768.2 °C), rhodium (1963 °C), iridium (2446 °C), molybdenum (2622 °C) and tungsten (3414 °C) [1] (basically, only the first three fixed points are used for the calibration of thermocouples and should be considered furthermore).
- Calibration of thermocouples is performed using a conventional fixed-point cell design for the freezing points of gold and copper, and using the wire method or miniature crucibles at the melting points of palladium and platinum.

Pure metal fixed points as secondary reference points

The pure metal fixed points listed above are accepted as secondary reference points, with the exception of the freezing points of gold and copper, which are defining fixed points of the ITS-90. (This protocol deals with the use of gold and copper to calibrate thermocouples, therefore the Au and Cu points are here grouped together with secondary fixed points.)

The standard deviation of the consensus values of the secondary fixed points can be found in [1]. The temperatures and their uncertainties were obtained using "large" cells and pyrometric methods. A one-to-one propagation of these uncertainties to the calibration of thermocouples would underestimate the uncertainties involved.
(Note: CMCs for the calibration of thermocouples using high temperature fixed points are discussed in the industrial thermometer CMC review protocol.)

- Key Comparisons have not been performed so far, but two EUROMET projects (624, 844) were performed to compare the freezing temperatures of different fixed-point cells of copper by using Pt/Pd thermocouples [7, 8]
- Uncertainty budgets are available

Uncertainty limits of CMC entries of pure metal fixed points (service categories 2.1, 2.5.1 and 2.8.3) (k = 2):

Fixed point	RMO review	WG8 review
Au	< 0.15 K	< 0.1 K
Cu	< 0.15 K	< 0.1 K
Pd	< 1.2 K	< 0.4 K
Pt	< 2.4 K	< 0.8 K

Suggested scrutiny elements for reviewers

- uncertainty budget
- results of inter-comparisons (in the case of a WG8 review)
- results of internal comparisons of at least two different miniature cells or wire probes

References

[1] Bedford R.E., Bonnier G., Maas H., Pavese F., "Recommended values of temperature on the ITS-90 for a selected set of secondary reference points", *Metrologia*, 1996, **33**, 133-154.

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[6] Battuello M., Girard F., Florio M., "Metal-carbon eutectics to extend the use of the fixed-point technique in precision IR thermometry", *Int. J. Thermophys.*, Vol. 29, No.2, 2008.

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[8] F. Edler, "Intercomparison of copper fixed-point cells by using Pt/Pd thermocouples", Final report 844, 2007, www.euramet.org.