Int. J. Metrol. Qual. Eng. **6**, 303 (2015)

DOI: 10.1051/ijmqe/2015016

Thermoelectric properties of currently available Au/Pt thermocouples related to the valid reference function

F. Edler[1*], N. Arifovic[2], G. Atance[3], C. Dinu[4], C.J. Elliott[5], C. Garcia Izquierdo[3], N. Hodzic[6], S. Kalisz[7], J.V. Pearce[5], S. Simic[8], R. Strnad[9], and D. Taubert[1]

[1] Physikalisch-Technische Bundesanstalt (PTB), Abbestraße 2-12, 10587 Berlin, Germany
[2] Turkiye Bilimsel ve Teknolojik Arastirma Kurumu (TUBITAK), Turkey
[3] Centro Español de Metrología (CEM), C/del Alfar 2, 28760 Tres Cantos, Madrid, Spain
[4] Biroul Roman de Metrologie Legala (BRML-INM), Romania
[5] National Physical Laboratory (NPL), Hampton Road, Teddington, Middlesex, UK
[6] Institute of Metrology of Bosnia and Herzegovina (IMBIH), Augusta Brauna 2, 71000 Sarajevo, Bosnia and Herzegovina
[7] Główny Urząd Miar, ul. Elektoralna 2, 00-139 Warszawa, Poland
[8] Directorate of Measures and Precious Metals, Mike Alasa 14, 11000 Belgrade, Republic of Serbia
[9] Cesky Metrologicky Institut Brno (CMI), Czech Republic

Received: 14 March 2015 / Accepted: 9 June 2015

Abstract. Au/Pt thermocouples are considered to be an alternative to High Temperature Standard Platinum Resistance Thermometers (HTSPRTs) for realizing temperatures according to the International Temperature Scale of 1990 (ITS-90) in the temperature range between aluminium (660.323 °C) and silver (961.78 °C). The original aim of this work was to develop and to validate a new reference function for Au/Pt thermocouples which reflects the properties of presently commercially available Au and Pt wires. The thermoelectric properties of 16 Au/Pt thermocouples constructed at different National Metrological Institutes by using wires from different suppliers and 4 commercially available Au/Pt thermocouples were investigated. Most of them exhibit significant deviations from the current reference function of Au/Pt thermocouples caused by the poor performance of the Au-wires available. Thermoelectric homogeneity was investigated by measuring immersion profiles during freezes at the freezing point of silver and in liquid baths. The thermoelectric inhomogeneities were found to be one order of magnitude larger than those of Au/Pt thermocouples of the Standard Reference Material® (SRM®) 1749. The improvement of the annealing procedure of the gold wires is a key process to achieve thermoelectric homogeneities in the order of only about (2–3) mK, sufficient to replace the impracticable HTSPRTs as interpolation instruments of the ITS-90. Comparison measurements of some of the Au/Pt thermocouples against a HTSPRT and an absolutely calibrated radiation thermometer were performed and exhibit agreements within the expanded measurement uncertainties. It has been found that the current reference function of Au/Pt thermocouples reflects adequately the thermoelectric properties of currently available Au/Pt thermocouples.

Keywords: Au/Pt thermocouple, reference function, temperature scale

1 Introduction

The current International Temperature Scale of 1990 (ITS-90) is defined by means of platinum resistance thermometers calibrated at specified temperature fixed points and by using interpolation procedures at temperatures between the triple point of hydrogen (13.8033 K) and the freezing point of silver (961.78 °C) [1]. Above the triple point of water, metal melting or freezing transitions are used as calibration points for Standard Platinum Resistance Thermometers (SPRT). In the temperature range between the freezing temperatures of aluminium (660.323 °C) and silver, special High Temperature Standard Platinum Resistance Thermometers (HTSPRT) are used to realize the ITS-90. Their susceptibility to contamination, lack of stability and poor repeatability are well-known problems. Furthermore, to reach highest accuracy after exposing them to temperatures above about 700 °C a special heat treatment procedure is recommended before making a measurement at lower temperatures [2].

Elemental thermocouples made of pure gold and platinum are discussed as an alternative to replace HTSPRTs because of their excellent thermoelectric stability and homogeneity. Different reports [3–5] state small calibration uncertainties of Au/Pt thermocouples in the order of about ±10 mK, which are in the same order of magnitude

* Correspondence: frank.edler@ptb.de

reachable by using HTSPRT. Different reference functions for Au/Pt thermocouples [4,5] based on different sources of pure gold and platinum wires have been generated. The currently accepted reference function based on the measurements of Burns et al. [5] (1992) and published in reference [6] has become the standard generally used for the application of Au/Pt thermocouples. The disadvantage of this current reference function is that the equations and reference tables relating the temperature to electromotive force (emf) relationship of Au/Pt thermocouples are not based on a representative sample of Au/Pt thermocouples: instead being based on only two Au/Pt thermocouples chosen from a group of seven measured Au/Pt thermocouples. Furthermore, the thermoelectric behavior of wires from different batches/providers available today, exhibits enormous variation among themselves and partly from wires used by Burns et al. [5]. Therefore, it could be profitable to develop and validate a new reference function which better reflects the properties of commercially available Au and Pt wires, to reduce the measurement uncertainty. To reflect the variety of high quality Au/Pt thermocouples currently available, this requires the investigation of a number of different Au/Pt thermocouples with proven stability and homogeneity, constructed of wires from different sources and with different assembly techniques.

Coleman et al. [7] presented the results of the calibration of 8 new Au/Pt thermocouples made of wires of three different suppliers at fixed points of the ITS-90 (Ag, Al, Zn and Sn). The emfs of the resulting contemporary "best available" Au/Pt thermocouples varied significantly and the uncertainties caused by their thermoelectric inhomogeneity were, in some parts, higher by an order of magnitude than those of the Standard Reference Material® (SRM®) 1749, reported in reference [8]. The SRM® 1749 is a lot of 18 specially-constructed and annealed Au/Pt thermocouples, each calibrated on the ITS-90 and supplied with integral lead wires and protective sheath. Their expanded measurement uncertainties ($k = 2$) is less than 8.3 mK in the temperature range from 0 °C to 962 °C [8].

In the frame of the European Metrology Research Programme project SIB10 "Novel techniques for traceable temperature dissemination" (NOTED) the partners Centro Español de Metrología (CEM, Spain), Cesky Metrologicky Institut Brno (CMI, Czech Republic), Physikalisch-Technische Bundesanstalt (PTB, Germany) and Turkiye Bilimsel ve Teknolojik Arastirma Kurumu (TUBITAK, Turkey) constructed a set of 16 Au/Pt thermocouples of partly different designs by using currently available Au and Pt wires of different suppliers. Furthermore, 4 commercially available Au/Pt thermocouples from 4 different manufactures (M1, M2, M3 and M4) obtained by NPL were included in the investigations. All Au/Pt thermocouples were calibrated at ITS-90 fixed-points and the thermoelectric homogeneity was investigated at the freezing point of silver and partly in liquid baths and in a heat pipe furnace. Almost all of the constructed Au/Pt thermocouples exhibited significant deviations from the currently accepted reference function for Au/Pt thermocouples [6] and their thermoelectric homogeneity was too poor to perform reliable and high precision measurements – leading to uncertainties of the order of 100 mK or higher.

2 Au/Pt thermocouples

2.1 Construction

Information about the thermowires used for the construction of the Au/Pt thermocouples is listed in Table 1. The diameter of all wires was 0.5 mm. Ceramic insulation tubes of pure alumina (Al_2O_3, 99.7%) of 4 mm outer diameter (CMI, TUBITAK) and 4.5 mm outer diameter (CEM) with bores of 1.2 mm (CMI) and 1.5 mm (CEM, TUBITAK) were used to electrically insulate the thermoelements against each other. The different expansion coefficients of Au and Pt, and hindered free movement of the thermowires, can induce mechanical stresses resulting in local changes of the Seebeck coefficient: to overcome this, a stress-relieving coil is often used at the thermocouple hot junction. The Au/Pt thermocouples constructed at PTB were equipped with four-hole quartz glass insulation tubes instead of ceramic tubes: the smoother surface of the inner holes of quartz glass compared to alumina and their inner diameter of 1.5 mm are intended to allow an easier movement of the thermowires inside the tube and should therefore make the use of stress relieving coils as measuring junctions needless. Quartz glass (PTB) or alumina (Al_2O_3, 99.7%) tubes of 7×5 mm in diameter (CEM, CMI and TUBITAK) closed at one end provided protection from environmental influences. Some of the thermocouples were equipped with a stress-relieving coil made of thin platinum wire, and on the thermocouple "Au/Pt D3" of CMI a coil made of 0.5 mm diameter gold wire was used (see Tab. 1). The thermoelements of all Au/Pt thermocouples were welded by using hydrogen-oxygen flames.

2.2 Annealing procedure

The project partners applied different annealing procedures on the thermowires before and after assembling them to thermocouples. Table 2 gives an overview of these annealing procedures. The platinum wires were annealed electrically in air by passing a current through them. The gold wires have an inadequate mechanical strength to anneal them electrically therefore they were mounted in alumina insulation tubes and annealed in horizontal furnaces (a vertical furnace was used at CEM). The whole length of the gold wires of TUBITAK was inserted into a cleaned U-bended quartz glass tube. Then the quartz glass tube with the Au wire was placed in the most homogeneous zone of a horizontal furnace and was annealed. Depending on the length of the temperature uniform section in the furnace, several annealing steps were needed to anneal the Au thermoelement, in segments, over its whole length. After assembling the thermocouples, a horizontal furnace annealing was performed to remove physical defects introduced during the assembly and to improve the thermoelectric stability and homogeneity of the thermoelements.

Table 1. Providers and purities of the thermoelements of the Au/Pt thermocouples.

Thermo-couple Name	Institute of manufacture	Wires			Measuring junction type (coil wire diameter, d)
		Supplier	Purity	Length/ mm	
CEM-2013-1	CEM	Alfa Aesar	Au: 99.999% Pt: 99.997%	1500	without coil
CEM-2013-2	CEM				without coil
CEM-2014-1	CEM				Pt-coil, $d = 0.1$ mm
CEM-2014-2	CEM				Pt-coil, $d = 0.1$ mm
Au/Pt D1	CMI	Alfa Aesar	Au: 99.999% Pt: 99.997%	1250	without coil
Au/Pt D2	CMI				without coil
Au/Pt D3	CMI				Au-coil, $d = 0.5$ mm
AuPt 12-01	PTB	Au: M&K (12-01/12-02)	(M&K): 99.999%	2000	without coil
AuPt 12-02*	PTB	Au:BMHW (12-02/12-03)	BMHW: unknown		without coil
AuPt 13-03	PTB	Pt: Alfa Aesar	Pt: 99.997%		without coil
Au/Pt 1	TUBITAK	Au: Sigmund Cohn Pt: Leico	Au: 99.999% Pt: 99.999%	1500	without coil
Au/Pt 2	TUBITAK				Pt-coil, 0.3 mm
Au/Pt 1-14	TUBITAK			1800	without coil
Au/Pt 2-14	TUBITAK				without coil
Au/Pt 3-14	TUBITAK				Pt-coil, 0.3 mm
Au/Pt 4-14	TUBITAK				Pt-coil, 0.3 mm

*AuPt 12-02 consists of two Au-wires of different suppliers M&K GmbH and Berliner Metallhütten- und Halbwerkzeuge (BMHW) welded directly to the Pt-wire (Alfa Aesar).

Table 2. Annealing procedures.

Thermocouple Name	Institute of manufacture	Pt: electrical annealing		Au: furnace annealing		Annealing after assembling	
		Temperature/°C	Duration/h	Temperature/°C	Duration/h	Temperature/°C	Duration/h
CEM-2013-1	CEM	1300 450	10 1	1000 1000→450 450 °C	10 8 20	450	20
CEM-2013-2	CEM					1000	1
CEM-2014-1	CEM					1000→450	8
CEM-2014-2	CEM					450	12
Au/Pt D1	CMI	950*	1*	950	1	No further annealing	
Au/Pt D2	CMI						
Au/Pt D3	CMI						
AuPt 12-01	PTB	1300	7	1000	7	1000	6
AuPt 12-02	PTB		10		10	1000	5
AuPt 13-03	PTB		7		7	800/1000	15/6
Au/Pt 1	TUBITAK	1300 450	10 1	1000** 450	10 16	1000	1
Au/Pt 2	TUBITAK						
Au/Pt 1-14	TUBITAK						
Au/Pt 2-14	TUBITAK						
Au/Pt 3-14	TUBITAK						
Au/Pt 4-14	TUBITAK						

* Pt wires exposed only to a furnace anneal. ** Au wires of thermocouples Au/Pt 1 and Au/Pt 3-14 (TUBITAK) were exposed to large temperature gradients (temperature differences of about 6 K over a length of 10 cm).

2.3 Thermoelectric stability

The PTB Au/Pt thermocouples were thermoelectrically stabilized by a further thermal treatment, after annealing and construction. Figure 1 shows the measured emfs at the freezing point of Ag to test the thermoelectric stability of the PTB thermocouples Au/Pt 12-02 and Au/Pt 13-03 after various thermal treatments. The annealing temperatures for the thermocouple Au/Pt 12-02 were chosen between 750 °C and 1000 °C, the annealing of the thermocouple Au/Pt 13-03 was performed at a temperature of 970 °C exclusively. The last annealing step applied to the thermocouple Au/Pt 02-12 was finished with a 450 °C annealing for 1 h. In general the emfs measured at the freezing point of silver were stable within a temperature equivalent of better than ±0.1 K. Furthermore, the

Table 3. Maximum emf changes measured over the given range for each thermocouple at the freezing point of silver and/or in a liquid bath.

Name	Institute of manufacture	Ag (961.78 °C)		Liquid bath		
		Δemf/μV	range/cm	Δemf/μV	range/cm	T/°C
CEM-2013-1	CEM	1.32	7	2.00	22	200
CEM-2013-2	CEM	1.36	7	2.60	22	200
CEM-2014-1	CEM	3.68	7	1.70	14	200
Au/Pt D1	CMI	2.18	6			
Au/Pt D2	CMI	2.70	5			
Au/Pt D3	CMI	1.87	5			
AuPt 12-01	PTB	2.30	10			
AuPt 12-02*	PTB	1.50	10	0.48/0.39	20	250
AuPt 13-03	PTB	1.10	12	0.09	20	250
Au/Pt 1	TUBITAK	13.5	10			
Au/Pt 2	TUBITAK	0.39	10	1.74	10	300
Au/Pt 1-14	TUBITAK	0.22	10	0.29	10	300
Au/Pt 2-14	TUBITAK	0.78	10	0.52	10	300
Au/Pt 3-14	TUBITAK	1.36	10			
Au/Pt 4-14	TUBITAK	0.45	10	0.56	10	300

*AuPt 12-02 consists of two Au-wires of different suppliers M&K and BMHW welded directly to the Pt-wire (Alfa Aesar).

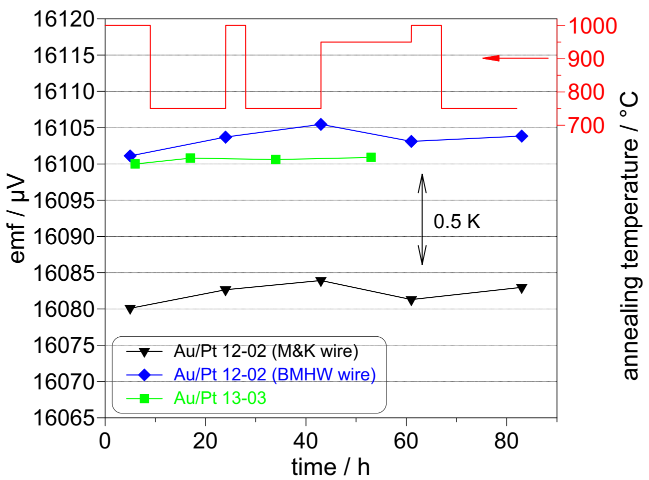

Fig. 1. Measured emf at the freezing point of silver for two Au/Pt thermocouples; each measurement is taken after a thermal treatment (with the temperature and duration indicated) to monitor the thermoelectric stability of Au/Pt thermocouples constructed at PTB.

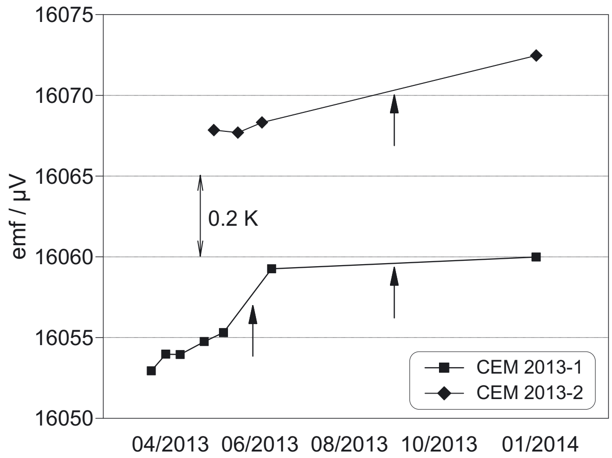

Fig. 2. Measured emfs at the freezing point of silver to test the thermoelectric stability.

similar behavior of the emf measured by using the thermocouple Au/Pt 12-02 with each of the two Au wires from different suppliers (M&K and BMHW) indicate that the obtained emf changes are probably caused by changes of the Seebeck coefficient of the shared Pt wire.

The thermocouples assembled at CEM were checked at the freezing point of silver several times just after the initial heat treatment. The measured emfs are presented in Figure 2. Additional heat treatments were applied to the thermocouple CEM-2013-1 in order to improve its stability and homogeneity (marked by the arrows in Fig. 2). The heat treatment consisted of an 1 h annealing at 1000 °C, 8 h of cooling down from 1000 °C to 450 °C and 12 h at 450 °C. This treatment results in an emf increase of about (5–7) μV which corresponds to a temperature equivalent of about (0.2–0.3) K. The same heat treatment were applied later to both thermocouples without any influence on CEM-2013-1 at the silver fixed point but the emf of the thermocouple CEM-2013-2 increased by about 4 μV.

2.4 Thermoelectric homogeneity

Immersion profiles at ITS-90 fixed points and in liquid baths were measured to evaluate the thermoelectric homogeneity of the Au/Pt thermocouples. The maximum emf deviation, Δemf, obtained during each immersion profile measurement (from the emf measured at the deepest immersion) is presented in Table 3. Most of the Au/Pt thermocouples exhibit inhomogeneities in the order of (1 to 2) μV at the freezing point of silver. The corresponding

Table 4. Maximum emf changes measured by using the Au/Pt thermocouples of TUBITAK in liquid baths and in a sodium heat pipe furnace.

Name	Liquid bath			Heat pipe furnace				
	200 °C	300 °C	400 °C	500 °C	600 °C	760 °C	860 °C	900 °C
	Δemf/μV	Δemf/μV	Δemf/μV	Δemf/μV	Δemf/μV	Δemf/μV	Δemf/μV	Δemf/μV
Au/Pt 1	–	–	–	0.47	4.29	–3.74	2.36	–0.14
Au/Pt 2	–3.17	–1.74	–0.20	2.86	0.91	–4.82	–3.33	–6.14
Au/Pt 1-14	1.30	–0.29	–0.68	1.35	0.87	–6.85	–1.57	–2.01
Au/Pt 2-14	–1.06	–0.52	–0.82	0.82	1.12	–4.73	–2.68	–1.65
Au/Pt 3-14	–	–	–	0.12	3.70	2.57	–1.22	–1.18
Au/Pt 4-14	–0.49	–0.56	0.24	0.47	0.81	–4.87	–3.97	–6.07

contribution to the measurement uncertainty at the freezing point of silver (typically 0.5 μV) leads to combined uncertainties (typically 0.7 μV) which are larger by about almost one order of magnitude compared to those of Au/Pt thermocouples of the SRM® 1749 (typically 0.1 μV). In comparison, using the NIST Au/Pt thermocouple 95-17 (SRM® 1749), PTB has measured maximum emf differences of only 0.09 μV and 0.35 μV at 400 °C over 18 cm, in a salt bath and at the freezing point of silver, respectively.

The thermoelectric homogeneity of the Au/Pt thermocouples of TUBITAK was tested more comprehensively in baths at 200 °C, 300 °C and 400 °C and in a sodium heat pipe furnace at 500 °C, 600 °C, 760 °C, 860 °C and 900 °C. TUBITAK used a vertical comparator similar to that used by NPL for the comparison of Au/Pt thermocouples against calibrated HTSPRTs (Sect. 4). The total immersion depth in the heat-pipe furnace was 45 cm. SPRTs or HTSPRTs were used to correct the emf recorded for local and temporal temperature changes in the course of the immersion profile measurements which were performed over a length of 10 cm by withdrawing the thermocouples from the baths/furnaces. The results presented in Table 4 were ambiguous and no definite relationship between the measured maximum emf changes at different temperatures (emf) according to the common correlation, (Δemf/emf), established by Jahan and Ballico [9] could be proven. The inhomogeneities of the various Au/Pt thermocouples correspond to temperature equivalents between 13 mK and 52 mK at 400 °C and to temperature equivalents between 6 mK and 260 mK at 900 °C.

The thermoelectric homogeneity of the Au/Pt thermocouples of TUBITAK (excluding Au/Pt 1 and Au/Pt 3-14) when tested at the freezing point of silver, was better by a factor of 3 to 5 than the Au/Pt thermocouples constructed by using Alfa Aesar wires (Tab. 3). This indicates a better performance of the thermoelements delivered by Sigmund Cohn and Leico. Nevertheless, the thermoelectric homogeneity of Au/Pt thermocouples described in SRM® 1749 is far better still, and in the order of about 0.1 μV at the freezing point of silver [8].

2.5 Calibration at fixed points

All Au/Pt thermocouples were calibrated at the ITS-90 fixed points of Ag, Al, Zn, Sn, and partly at the freezing point of In, the melting point of Ga and at the ice point. The emf at each fixed point was compared with that obtained by calibrating a Au/Pt thermocouple from the SRM® 1749 (PTB's Au/Pt 95-17) and other commercially available Au/Pt thermocouples in the same fixed points. Figures 3 and 4 show the deviations of the measured emfs at the fixed-points from the currently accepted reference function [6]. Additionally measurements by using the triple point of water as reference temperature instead of the ice point were performed at TUBITAK, but no remarkable differences were determined.

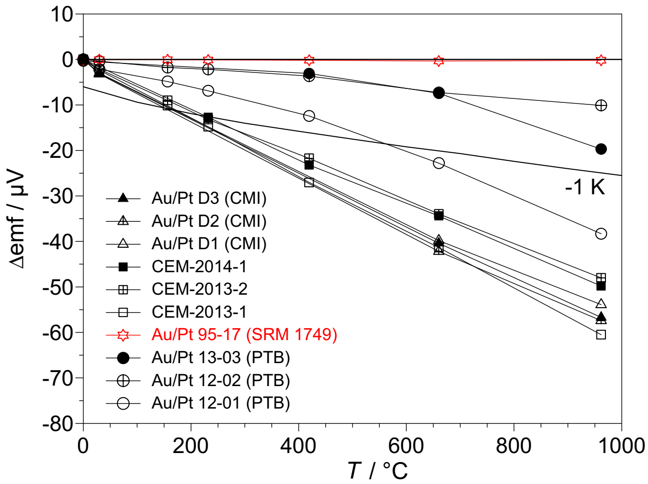

Fig. 3. Emf deviations from the current reference function of Au/Pt thermocouples measured at fixed points of the ITS-90 by using Au/Pt thermocouples constructed by the project partners.

The uncertainty of the measured emfs, $u(E_X)$, at fixed points of the ITS-90 can be calculated according to

$$u\left(E_X\right)^2 = u(E_{\mathrm{RP}})^2 + u(E_{\mathrm{el}})^2 + u(E_{\mathrm{FP}})^2 + \left(u(t_0 \cdot S_0)\right)^2 + \left(u(E_{\mathrm{Hom}}) \cdot \frac{E_X}{E_{\mathrm{ref}}}\right)^2$$

where E_X is the emf indicated at the voltmeter at the corresponding fixed point, E_{ref} is the emf at the temperature T_{ref}, at which the homogeneity check was performed, and S_0 is the Seebeck coefficient at the ice point (6 μV/K). The combined measurement uncertainty of E_X is obtained by

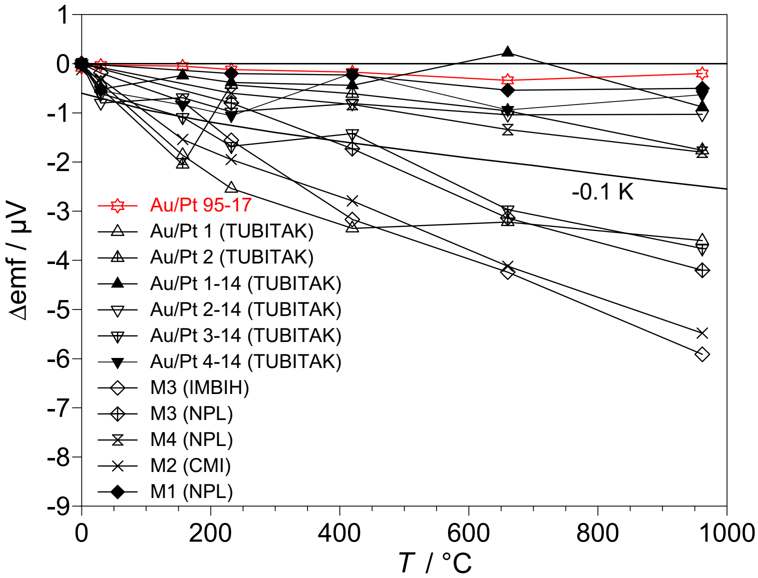

Fig. 4. Emf deviations from the current reference function of Au/Pt thermocouples measured at fixed-points of the ITS-90 by using Au/Pt thermocouples constructed by the project partners and by using commercial available Au/Pt thermocouples.

squared summing the following uncertainty contributions (in brackets typical values):

- $u(E_{\mathrm{RP}})$: repeatability of emf measurements (0.1 μV);
- $u(E_{\mathrm{el}})$: electric emf measurement (0.4 μV);
- $u(E_{\mathrm{FP}})$: fixed point realisation (0.1 μV);
- $u(t_0)$: temperature of the reference junction (0.05 μV);
- $u(E_{\mathrm{Hom}})$: thermoelectric homogeneity at T_{ref} (0.5 μV).

This results in a combined uncertainty ($k = 1$) of about 0.7 μV at the freezing point of silver.

Generally, the emfs of the Au/Pt thermocouples measured at the fixed points were lower than the emfs specified by the current reference function [6]. The thermocouples of CEM and CMI made of gold and platinum wires both supplied by Alfa Aesar show the largest and even almost the same deviations (about –50 μV (–2 K) at the freezing point of silver) despite a complete different heat treatment of the thermoelements. The thermoelements of the CMI thermocouples were annealed only for one hour before assembling and no further heat treatment was followed after assembling in contrast to the annealing procedure performed at CEM (Tab. 2) which was more comprehensive. The three Au/Pt thermocouples constructed at PTB by using platinum wire supplied by Alfa Aesar but gold wire of different suppliers show deviations from the reference value at the freezing point of silver between –10 μV and –40 μV. This clearly indicates the emf dependence of the Au/Pt thermocouples on the thermoelectric properties of the Au thermoelements used. Furthermore, the platinum wire delivered by Alfa Aesar was compared to the Standard Thermocouple Material, Pt 67: SRM® – 1967 [10] at the freezing point of silver at PTB and only a deviation of +0.9 μV was found. Therefore, it can be concluded, that the performance of the Au/Pt thermocouples essentially depends on the thermoelectric properties of the Au wire used.

The Au/Pt thermocouples of TUBITAK were constructed by using gold wire from Sigmund Cohn and platinum wire delivered by Leico. The deviations from the reference value [6] at the freezing point of silver were found to be less than –2 μV with the exception of the thermocouples Au/Pt 1 and Au/Pt 3-14 for which the Au thermoelement was exposed to large temperature gradient during wire annealing. The commercially available Au/Pt thermocouples of the manufactures M2, M3 and M4 show deviations from the reference value at the freezing point of silver between –4 μV and –6 μV (–0.15 K to –0.2 K) whereas the Au/Pt thermocouple of the manufacturer M1 offers only a very small deviation of less than –1 μV. It is summarized that significant deviations from the valid reference function of Au/Pt thermocouples arise except the Au/Pt thermocouples of TUBITAK and of the manufacturer M1.

3 Comparison measurements at PTB

The temperature to emf relationship of three Au/Pt thermocouples constructed at PTB and one of the Au/Pt thermocouple of the SRM® 1749 (95–17) were determined against a calibrated near-infrared (1.6 μm) radiation thermometer of PTB by using a high accuracy double sodium heat pipe blackbody [11] in the temperature range between 520 °C and 960 °C. The schematic set up for the comparison measurements with the blackbody source in a horizontal arrangement is presented in Figure 5. Three of the four through-holes of the inner heat pipes were used for the Au/Pt thermocouples, whereas one HTSPRT was inserted into the fourth hole for the fine control of the temperature of the inner heat pipe. The thermocouples and the HTSPRT were additionally protected by using alumina tubes and thin sleeves made of platinum.

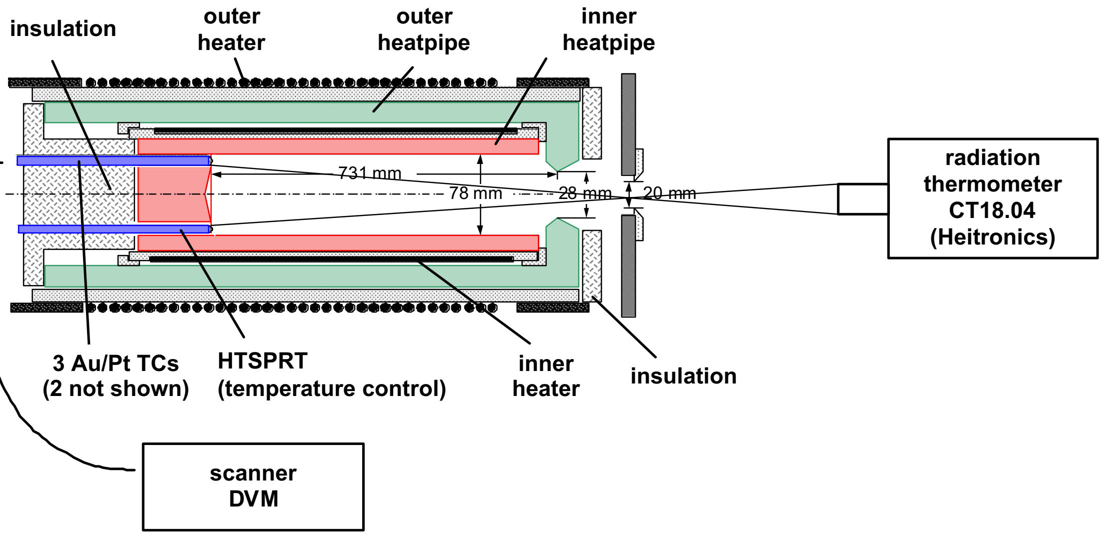

Fig. 5. Schematic view (not true to scale) of the measurement set up of the comparison measurements at PTB.

The axial temperature homogeneity within the bottom of the inner sodium heat pipe was better than ±2 mK over a length of about 20 cm around the position of the measuring junctions of the thermocouples. Radial temperature differences between the four holes of the inner heat pipe within an axial range of about 2 cm (i.e. the indefiniteness of the position of the measuring junctions) were less than about 5 mK measured by using HTSPRT.

The measurements were performed starting at 520 °C by raising temperatures in steps of 20 K. In each case two measurements were performed successively after reaching the thermal equilibrium (about 3 h–4 h) at any temperature. The measurements started by recording the emfs of the thermocouples every 20 s over a period of about 17 min (50 values) by using a Keithley 2182 voltmeter and a Switch System 7001 with a 7168 Nanovolt scanner card. The two thermocouples Au/Pt 95-17 (SRM® 1749) and Au/Pt 13-03 were measured twice at each temperature but the Au/Pt 12-02 with the two different Au thermoelements and the shared Pt thermoelement was measured alternately. The radiation temperature was recorded simultaneously and measured with a standard deviation of about ±1 mK.

The results of the comparison measurement are presented in Figure 6. The deviations of the thermocouple temperatures from the reference temperature given by the calibrated radiation thermometer Heitronics CT18.04 are presented. The expanded measurement uncertainty of the radiation temperature was between 0.11 K and 0.24 K for $k = 2$ (dotted lines). The temperatures of the thermocouples were calculated on basis of the calibration at the freezing points of Ag, Al and Zn before and after finishing the comparison measurements with uncertainties ($k = 2$) in the temperature range between 520 °C and 960 °C of about 0.09 K (Au/Pt 95-17), 0.15 K (Au/Pt 12-01 and Au/Pt 13-03) and 0.24 K/0.28 K for Au/Pt 12-02 with the two Au thermoelements from BMHW / M&K, respectively.

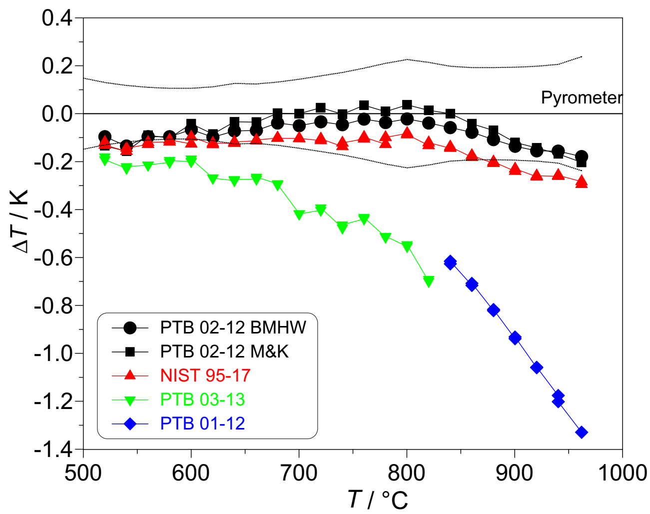

Fig. 6. Difference of the temperature indicated by the calibrated Au/Pt thermocouples from the reference temperature given by the radiation thermometer in K.

4 Comparison measurements at NPL

NPL designed and constructed a vertical comparator for comparison of commercially available Au/Pt thermocouples against calibrated HTSPRTs (which provide a link to ITS-90). To date, the temperature to emf relationship of four Au/Pt thermocouples has been measured in two separate runs. Each Au/Pt thermocouple was calibrated at the silver, aluminium, zinc and tin fixed points of the ITS-90 before starting the comparison measurements. These pre-run calibration values were used to calculate the temperature of each thermocouple from the measured emfs.

The results presented in Figure 7 were taken over the course of a week (7 days), where the Au/Pt thermocouples were continuously cycled between 660 °C and 960 °C, at random temperatures within that range – the reference

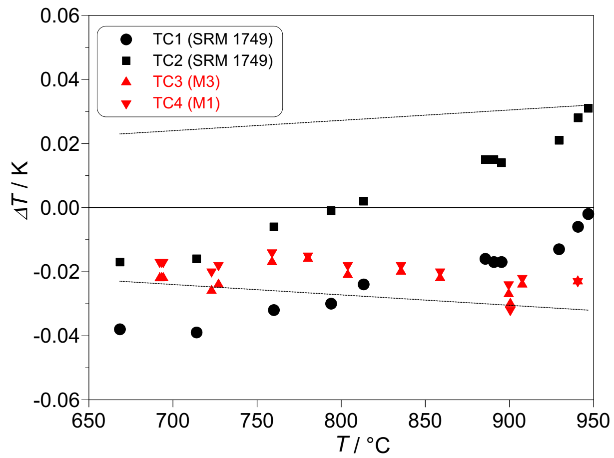

Fig. 7. Difference of the temperature indicated by the calibrated Au/Pt thermocouples from the reference temperature given by the HTSPRT in K.

temperature recorded is shown, but the sequence is not. The reference temperature is measured using a stable HTSPRT and the holding time at each temperature was of the order of 10 h for each point. The furnace was only cooled down to below 660 °C when the first two Au/Pt thermocouples were replaced by the third and fourth. The measurement uncertainty ($k = 2$) of the HTSPRT amounts to about 5 mK at 660 °C and rises up to about 7 mK at 960 °C. The expanded uncertainties ($k = 2$) of the Au/Pt thermocouples were in the order of 22 mK at 660 °C and increased linearly to 31 mK at 960 °C. The dotted lines mark the range of the expanded uncertainties of the temperature difference between the Au/Pt thermocouples and the reference HTSPRT.

5 Discussion

Emf deviations from the current reference function up to temperature equivalents of about −2.5 K at the freezing point of silver were measured by using the newly constructed Au/Pt thermocouples. On the one side, this confirms the preliminary assumption that currently available thermoelements did not meet the present reference function. On the other side, the thermoelectric properties and especially the poor thermoelectric homogeneity of most of the constructed Au/Pt thermocouples were insufficient to allow reliable and high precision measurements. Therefore the aim to establish a new reference function which better reflects the properties of currently available Au and Pt wires was not accomplished.

The thermoelectric homogeneity of the investigated Au/Pt thermocouples constructed in the frame of the EMRP project NOTED was approximately lower by an order of magnitude than those of Au/Pt thermocouples of SRM® 1749. Their thermoelectric homogeneities are typically in the order of 0.1 μV at the freezing point of silver. Only one of the new Au/Pt thermocouples, Au/Pt 1-14 of TUBITAK, exhibit a similar thermoelectric homogeneity at the freezing point of silver. The other Au/Pt thermocouples constructed at TUBITAK by using wires of the same suppliers (Au, Sigmund Cohn; Pt, Leico) are less homogeneous. It should be noted, that the Au wires of the two thermocouples Au/Pt 1 and Au/Pt 3-14 of TUBITAK were exposed to large temperature gradients during wire annealing in a furnace in contrast to the other four Au/Pt thermocouples of TUBITAK. This explains their larger thermoelectric inhomogeneities found at the freezing point of silver compared with the other Au/Pt thermocouples of TUBITAK and other partners. The three thermocouples of CMI, which were annealed for only an extremely short period (1 h) exhibit also huge inhomogeneities, measured at the freezing point of silver (Tab. 3) and at other fixed points. This clearly indicated that an adequate annealing procedure must be applied to improve the thermoelectric homogeneity of Au/Pt thermocouples. An improved and agreed annealing procedure of the gold wire is the key to reach better thermoelectric homogeneities. The use of different measuring junctions of the Au/Pt thermocouples seemed to have no influence on their thermoelectric properties, but maybe interfered by more significantly effects, for instance caused by an insufficient annealing procedure of the gold wires.

The comparison of Au/Pt thermocouples of PTB against an absolutely calibrated radiation thermometer in the temperature range between 520 °C and 960 °C is dominated by the relatively large – compared to contact thermometry – measurement uncertainty of the radiation thermometer as reference. The measured temperatures by using the thermocouples Au/Pt 95-17 (SRM® 1749) and Au/Pt 12-02 with the both Au wires (BMHW, M&K) agree with the radiation temperature within their measurement uncertainties. The deviations of the thermocouple temperatures from the radiation temperature could be fitted by a polynomial of second order with minimum deviations at around 800 °C. This indicates a possible inconsistency of the present reference function of Au/Pt thermocouples [6] between the temperatures the freezing points of Al and Ag which is normally not noticed when a calibration only at fixed-points is performed. However the large measurement uncertainty did not allow a serious estimation of this effect.

The larger deviations with increasing temperatures found for the thermocouples Au/Pt 12-01 and Au/Pt 13-03 were construction-conditioned (quartz glass insulation tube) and were investigated in a separate topic.

The failed approach of PTB by using only quartz glass as insulation materials also indicated, that a minimum insulation resistance is necessary to perform reliable and traceable measurements. The replacement of the quartz glass insulation tubes by ceramic insulation tubes made of pure alumina (Al_2O_3, 99.7%) resulted in increased emfs measured at the freezing point of silver and in a less extent at the freezing point of Al whereby the emf at the freezing point of Zn remains nearly unchanged as shown in Table 5.

The comparison measurements of commercial available Au/Pt thermocouples against a HTSPRT at NPL resulted in an agreement of the measured temperatures

Table 5. Emfs measured at fixed points of ITS-90 before and after replacement of the quartz glass insulation tubes for Au/Pt 12-01 and Au/Pt 13-03.

Fixed point	Au/Pt 12-01			Au/Pt 13-03		
	emf/μV (Quartz)	emf/μV (Al_2O_3)	Δemf/ μV	emf/μV (Quartz)	emf/μV (Al_2O_3)	Δemf/ μV
Ag	16084.9	16091.7	6.8	16101.6	16113.1	11.5
Al	9299.3	9300.6	1.3	9312.6	9315.0	2.4
Zn	4933.2	4934.0	0.8	4942.6	4943.0	0.4

within about ±30 mK (660–950) °C. The Au/Pt thermocouples of the manufactures M1 and M3 show only a slightly increasing deviation from the ITS-90 temperature represented by the HTSPRT of about –20 mK at 660 °C and –25 mK at 960 °C. This confirms excellently the characteristic of the temperature to emf relationship of the present reference function, even if an absolute offset exists. The cause of the deviations of the two Au/Pt thermocouples of SRM® 1749 is ambiguous, but nearly within the combined measurement uncertainty of the temperature differences. Further tests with these thermocouples including exposure for an additional three weeks (continuously) is planned and will be reported later. This is expected to show how the thermocouples may change with use.

6 Conclusion

The best Au/Pt thermocouples of SRM® 1749 generally have the potential to replace HTSPRTs as defining standard interpolating instrument of the ITS-90 in the temperature range between 660.323 °C and 961.78 °C. For newly constructed Au/Pt thermocouples a very careful preparation is needed including an adequate heat treatment to reach the performance of the best Au/Pt thermocouples of SRM® 1749. The most essential starting point is an improvement of the annealing procedure for the gold wires (which have inadequate mechanical strength to be annealed electrically). Up to now, an optimal solution has not yet been found.

A relationship between thermoelectric homogeneity and deviation from the reference function which is caused by the composition or lower purity of the wires used was also found. Au/Pt thermocouples of CEM and CMI showed the largest deviations from the current reference function and exhibit also the largest thermoelectric inhomogeneities. However this relationship is weaker than the relationship between heat treatment and thermoelectric homogeneity. Concluding from these points, more work needs to be done to investigate these both relationships in detail.

The current reference function of Au/Pt thermocouples is a suitable basis to characterize the performance of Au/Pt thermocouples. Limited deviations of single Au/Pt thermocouples are tolerable as long as adequate thermoelectric homogeneities are accomplished (less than a temperature equivalent of (2–3) mK at the freezing point of silver. Combined uncertainties of Au/Pt thermocouples of less than (5–10) mK in the temperature range between 660 °C and 962 °C are required to replace the impracticable HTSPRTs in this temperature range.

Acknowledgements. This work is funded by the European Metrology Research Programme (EMRP) and national metrology research program. The technical assistance of Jayne Gray (NPL) and Arti Rani (NPL India) is gratefully acknowledged.

References

1. H. Preston-Thomas, The International Temperature Scale of 1990 (ITS-90), Metrologia **27**, 3–10 (1990)
2. BIPM, Supplementary Information for the International Temperature Scale of 1990, Pavillon de Breteuil, 92312 Sevres, 1997, ISBN 92-822-2111-3
3. E.H. McLaren, E.G. Murdock, *The Pt/Au thermocouple, NRCC 27703* (National Research Council of Canada, Ottawa, 1987), p. 111
4. M.Gotoh, K.D. Hill, E.G. Murdock, Rev. Sci. Instrum. **62**, 2778 (1991)
5. G.W. Burns, G.F. Strouse, B.M. Liu, B.W. Mangum, Gold versus platinum thermocouples: Performance data and an ITS-90 based reference function, in *Temperature: Its Measurement and Control in Science and Industry*, edited by J.F. Schooley (American Institute of Physics, New York, 1992), Vol. 6, pp. 531–536
6. IEC 62460 ed 1.0 Temperature – Electromotive force (EMF) tables for pure-element thermocouple combinations, Technical Committee 65B, 2008
7. M.J. Coleman, T.J. Wiandt, T. Harper, *A comparison of contemporary gold versus platinum thermocouples with NIST SRM 1749 based thermocouples and reference function* (Tempmeko, 2013)
8. D.C. Ripple, G.W. Burns, NIST Special Publication 260-134 – Standard reference material 1749: Au/Pt thermocouple thermometer (National Institute of Standards and Technology, 2002)
9. F. Jahan, M. Ballico, A study of the temperature dependence of inhomogeneity in platinum-based thermocouples, In *Temperature: Its Measurement and Control in Science and Industry*, edited by D.C. Ripple (American Institute of Physics, New York, 2003), Vol. 7, pp. 469–474
10. R.L. Powell, L.L. Sparks, J.G. Hust, NBS Special publication 260-56 – Standard reference materials: Standard thermocouple material, Pt-67: SRM-1967 (National Bureau of Standards, 1978)
11. M. Stock, J. Fischer, R. Friedrich, H.J. Jung, B. Wende, The double-heatpipe black body: a high-accuracy standard source of spectral irradiance for measurements of $T - T_{90}$, Metrologia **32**, 441–444 (1995)