ACOUSTIC MEASUREMENTS OF THE THERMODYNAMIC TEMPERATURE BETWEEN THE TRIPLE POINT OF MERCURY AND 380 K

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Summary. This communication reports the results of a joint research project between IEN and IMGC-CNR concerning the determination of (T-T_{90}), the difference between the Kelvin thermodynamic temperature and the temperature of the International Temperature Scale of 1990 (ITS-90), on nine isotherms between the triple point of mercury and 380 K. For the present measurements the standard uncertainty of (T-T_{90}) ranges from 0.9 mK at 234 K to 1.7 mK at 380 K. Without reference to ITS-90, these results obtained by means of a primary acoustic thermometer, redetermine the triple points of mercury T_{Hg} and gallium T_{Ga} with the results: $T_{\mathrm{Hg}}/T_{\mathrm{w}} = (0.8577860 \pm 0.0000031)$ and $T_{\mathrm{Ga}}/T_{\mathrm{w}} = (1.1089478 \pm 0.0000037)$, where $T_{\mathrm{w}} = 273.16$ K exactly. The experimental method is based on the measurement of the acoustic resonance frequencies of an argon-filled spherical cavity and the microwave resonance frequencies of the same cavity when evacuated. This method is similar to that followed in the last few years by two other research groups at NIST and UCL, to determine deviations of ITS-90 from the thermodynamic temperature, respectively in the ranges 217 to 303 K [1] and 90 to 300 K [2].

Principles of the method

The principle of acoustic thermometry is based on the well theoretically founded connection between the zero-pressure limit of the speed of sound u_0 and the thermodynamic temperature T according to the relation $u_0^2(T) = \gamma^0 \mathrm{R}\mathrm{T}/M = A_0(T)$, where γ^0 is the ratio of the ideal gas heat capacities, R is the molar gas constant and M the molar mass.

The International System of Units assigns the exact value 273.16 K to the temperature of the triple point of water T_{w}. The Kelvin thermodynamic temperature of a gas can then be determined from the zero-pressure limit of the ratio of speed of sound measurements at T and T_{w} from $T/T_{\mathrm{w}} = u_0^2(T)/u_0^2(T_{\mathrm{w}})$.

The zero-pressure value of speed of sound $u_0(T)$ can be obtained by the extrapolation of a series of measurements $u(p,T)$ at different pressures along an isotherm, where each experimental value of u is obtained from the resonance frequencies f_a of a number of purely radial acoustic modes of a spherical cavity of radius $a_0(T)$, according to the simplified relation $f_a(p,T) \propto u(p,T)/a_0(T)$ (where the pressure dependence of the cavity radius has been ignored). It is therefore necessary to determine for each temperature of interest the ratio $a_0(T)/a_0(T_{\mathrm{w}})$, i.e. the thermal expansion of the spherical cavity between T_{w} and T. In this work this was accomplished by measuring several microwave resonance frequencies f_m of the evacuated cavity as a function of temperature. These are related to the cavity radius by the simplified relation $f_m(T) \propto c/a_0(T)$, where c is the speed of light in vacuum and is known exactly.

Finally, the thermodynamic temperatures were computed from the working equation:

$$\frac{T}{T_{\mathrm{w}}} = \frac{A_0(T)/a_0^2(T)}{A_0(T_{\mathrm{w}})/a_0^2(T_{\mathrm{w}})} \cdot \left[\frac{a_0(T)}{a_0(T_{\mathrm{w}})}\right]^2 . \tag{1}$$

A 316L stainless-steel spherical resonator with a nominal inner diameter of 12 cm was used for the present measurements. Argon was selected as the thermometric fluid because: (1) being a monoatomic gas γ^0 takes the value 5/3 independently of temperature with negligible uncertainty; (2) its thermodynamic and transport properties, which enter in the corrections of the experimentally measured acoustic resonance frequencies, are known with high accuracy; (3) it is available with a very high degree of purity. Two capsule type standard platinum resistance thermometers were used for the determination of T_{90} during the present measurements.

Results

The present results for (T-T_{90}) are listed in Tab. 1 and are compared with other recent results from primary acoustic thermometry experiments in Fig. 1.

Tab. 1. Values of the differences (T-T_{90}).

T_{90}/K	(T-T_{90})/mK
234.3156	–2.77 ± 0.92
253.1136	–2.58 ± 0.83
288.1883	1.85 ± 1.04
302.9166	3.58 ± 1.01
318.1487	4.61 ± 1.08
333.1499	7.00 ± 1.15
348.1746	8.30 ± 1.31
363.3052	10.20 ± 1.37
380.0081	9.91 ± 1.70

The present results agree within the remarkably small combined uncertainties with both NIST acoustic thermometry [1] and UCL acoustic thermometry [2] in the overlapping temperature range.

Using Eq. (1), we determined:

$T_{\mathrm{Hg}}/T_{\mathrm{w}}$	=	0.8577860 ± 0.0000031
$T_{\mathrm{Ga}}/T_{\mathrm{w}}$	=	1.1089478 ± 0.0000037

Table 2 lists the important components of the standard uncertainty u_{s} in the determination of (T-T_{90}) from the measurement of the quantities in Eq. (1). Here we briefly outline the phenomena that contributed to u_{s}.

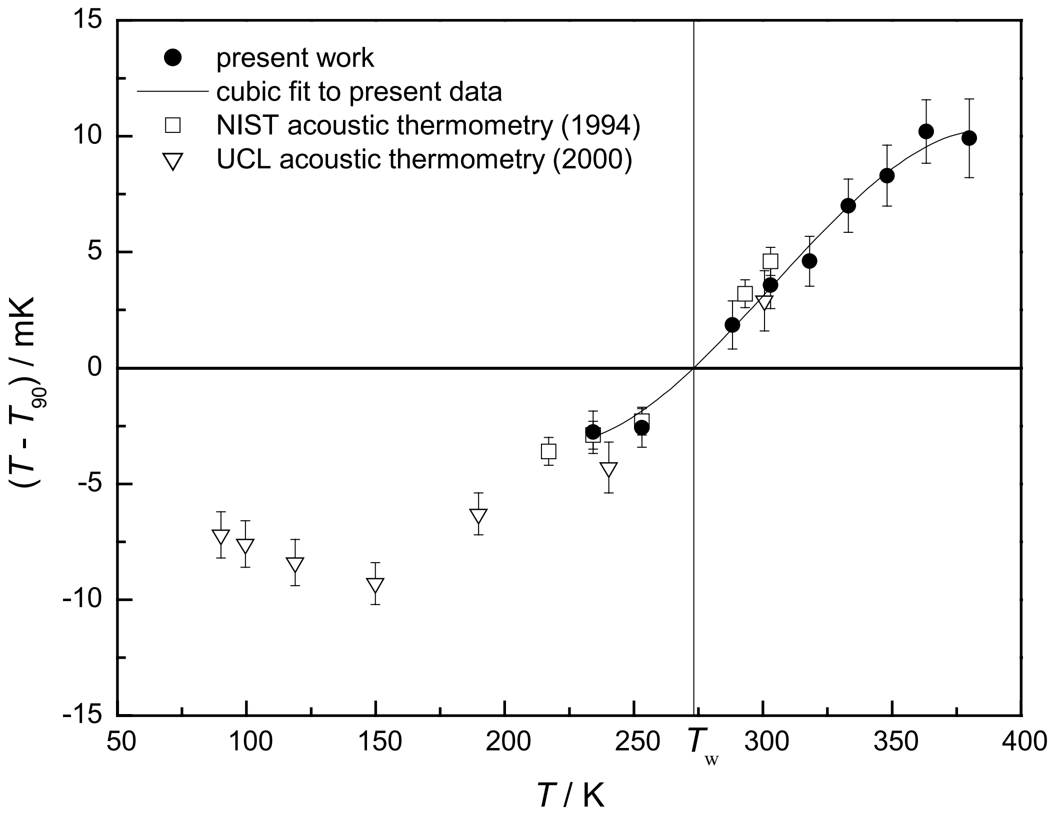

Fig. 1. Comparison between the differences (T-T_{90}) measured in this work and other primary acoustic thermometers [1, 2].

<u>Microwave measurements</u>

Microwave measurement are used to determine the ratio $(a_0(T)/a_0(T_w))^2$ in the temperature range 234 to 380 K. Four triply degenerate microwave modes TM11, TM12, TM13 and TM15 in the frequency range from 2 to 12 GHz, were considered. At each temperature the cavity radius was determined from the average frequency of the triplet according to the relation:

$$a_0(T) = \frac{c\nu_m}{2\pi(\hat{f}_m(T) + g_m(T))}, \tag{2}$$

in which ν_m is a microwave eigenvalue, $\hat{f}_m$ is the average frequency of the triplet and g_m is the calculated halfwidth of the microwave resonances, which is determined by the penetration of the electromagnetic field into the inner surface of the resonator wall and therefore calculable if the electrical resistivity of the wall material is known as a function of temperature. The corresponding values of $(a_0(T)/a_0(T_w))^2$ were then fitted to a cubic polynomial function of (T_w - T).

Row 1 of Tab. 2 accounts for the different values of $(a_0(T)/a_0(T_w))^2$ obtained from the four different microwave triplets investigated. In Row 2 the components of u_s due to the uncertainty in available experimental data of the electrical resistivity of steel (approximately 4%), are reported. If instead of using the calculated values of the halfwidths, the experimental values had been used, different values for the penetration length of the field would have been obtained; the difference in these two alternative approaches contributes to u_s as reported in Row 3 of Tab. 2.

Tab. 2. Standard uncertainties u_s (in ppm) in the determination of (T-T_{90}).

source	**234 K**	**253 K**	**288 K**	**303 K**	**318 K**	**333 K**	**348 K**	**363 K**	**380 K**(*)
				microwave values for $[(a(T)/ a(T_w))^2]$					
1) discrepancies among different microwave modes	0.33	1.10	2.19	1.88	1.77	1.64	2.28	2.35	2.62
2) electrical resistivity	0.06	0.03	0.03	0.04	0.06	0.09	0.11	0.13	0.16
3) difference between experimental and calculated halfwidths	2.03	0.49	0.17	0.56	0.96	1.38	1.39	0.94	0.43
				Acoustic isotherm fits for $[(A_0(T)/ a^2]$					
4) uncertainty of $A_0(T_w)/a^2$	2.20	2.20	2.20	2.20	2.20	2.20	2.20	2.20	2.13(*)
5) uncertainty of $A_0(T)/a^2$	1.94	1.80	1.40	1.34	1.40	1.37	1.13	1.43	2.52
				Thermometry					
6) temperature gradient	1.35	0.95	1.08	0.53	0.39	0.28	0.35	0.41	1.08
7) fixed points calibration	0.56	0.21	0.12	0.28	0.31	0.39	0.47	0.54	0.62
8) SPRTs stability at T_w	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
9) difference between calibrations	0.11	0.02	0.03	0.09	0.20	0.26	0.30	0.35	0.40
				Other sources					
10) thermal conductivity	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
11) pressure	0.15	0.08	0.15	0.18	0.21	0.23	0.25	0.26	0.27
				Total					
total (ppm)	3.91	3.29	3.63	3.35	3.39	3.46	3.75	3.78	4.48
total (mK)	**0.92**	**0.83**	**1.04**	**1.01**	**1.08**	**1.15**	**1.31**	**1.37**	**1.70**

(*) The isotherm at 380 K and a corresponding isotherm at 273.16 K have been obtained with a different experimental configuration of the acoustic resonator.

Acoustic measurements

The acoustic measurements were made on 10 isotherms from near T_{Hg} up to 380 K. Along each of the isotherms measurements were performed at 11 different pressures (between a minimum of 16 kPa and a maximum of 523 kPa) which corresponded to approximately the same density values for all the isotherms. At every state point the frequencies and halfwidths of the lowest five radial modes were measured. The experimental frequencies were corrected to account for the presence of a thermal boundary layer near the inner surface of the resonator wall, for the effect of coupling of gas and shell motion, and for the perturbations caused by a small opening in the wall through which the gas was admitted into the cavity. The entity of thermal correction is far above the other two corrections. From the corrected frequencies divided by the corresponding eigenvalue, values of (u/a_0) were obtained. Each value of $(u/a_0)^2$ deduced from the different modes was then weighted inversely by the square of its estimated standard deviation, which takes into account the uncertainty of the single frequency measurement and its deviation from the average of the results of the five different investigated modes. The values of $(u/a_0)^2$ were then fitted by the expansion in powers of the pressure [1]:

$$(u/a_0)^2 - (A_3/a_0^2)p^3 = (A_0/a_0^2) + (A_1/a_0^2)p + (A_2/a_0^2)p^2 + (A_4/a_0^2)p^{-1} \quad (3)$$

from which A_0/a_0^2 was obtained. The uncertainties in the determination of this parameter contribute to u_s as reported in Rows 4 and 5 of Tab. 2.

The thermal boundary layer term in the correction of the experimental frequencies is mainly determined by the thermal conductivity of the gas, which was obtained from literature with an estimated relative uncertainty of 0.3%. This correction affects u_s as reported in Row 10 of Tab. 2.

The standard uncertainty of a single measurement of the pressure of argon was estimated to be approximately 33 Pa (mainly due to changes in zero-pressure indication of the pressure transducer). For each isotherm the corresponding contribution to u_s was estimated by multiplying the uncertainty of the pressure by the linear term of Eq. (3), that is A_1, and is reported in Row 11 of Tab. 2.

Temperature measurements

In the present work, two capsule standard platinum resistance thermometers (SPRTs) have been used to measure the temperature T_{90} of the resonator. The two SPRTs have been manufactured for this specific purpose by Hart Scientific. They are 25-Ω thermometers with a 18 mm long sensor in a glass-sheath of 35 mm length. These dimensions allow the entire SPRT to be encased in the resonator pole. The resistances of each thermometer were measured before and after each measurement of acoustic or microwave frequency and the temperature calculated as the average of the readings of the two thermometers. During the acoustic measurements a small vertical temperature gradient existed in the resonator, whose contribution to u_s was estimated on the basis of the mean value of the gradient over a complete isotherm and is reported in Row 6 of Tab. 2.

Before and after the acoustic and microwave measurements in the resonator, the SPRTs were calibrated at the ITS-90 fixed points, between the mercury triple point and the indium freezing point, as maintained at IMGC-CNR [3]. The propagation of the uncertainties from the fixed points to the Hg-Ga range and to the Ga-In range has been evaluated. The same reference cells and measuring procedures for the realization of the triple point of Hg, triple point of H_2O, melting point of Ga and freezing point of In, previously used by IMGC-CNR for the CCT-K3 Key Comparison [4], were also used in the present work. Therefore, the fixed point uncertainties were assumed to be the same total uncertainties as declared for the CCT-K3, increased (in quadrature) by the SPRT drift of the triple point of water measured immediately before and after each fixed point. Since the SPRTs used in the present work were very stable and very reproducible, their drifts during the two calibrations were very small and the resulting total uncertainties were almost identical to those declared for the CCT-K3. (Tab. 2, Row 7). The uncertainties due to the SPRTs stability at the triple point of water (Tab. 2, Row 8) take into account all the data measured for the two SPRTs during the calibrations. The differences resulted from the two fixed point calibrations, carried out before and after the microwave and acoustic measurements, have been examined. The uncertainty values reported in the Row 9 of Tab. 2. are based on the maximum observed change for the two thermometers. Finally, the uncertainty contribution due to the non-uniqueness of ITS-90 could not be evaluated, since all the available non-uniqueness data refer to sub-ranges which are different from the one considered in this work; however it should be noted that the ITS-90 ranges used here (the Hg-Ga range for measurements between 234 and 303 K, and the 0.01 °C-In range from 318 to 380 K) are supposed to be the most accurate of the entire Scale.

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