# NOVEL TECHNIQUES FOR TRACEABLE TEMPERTURE DISSEMINATION AN EUROPEAN JOINT RESEARCH PROJECT

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**Abstract:** In the frame of the European Metrology Research Program (EMRP) a new joint research project focused on the development of new advances techniques for providing improved traceability to the kelvin, to support its wider and simpler dissemination to the users, is being carried out. This project (SIB10 NOTED) is supported by EURAMET and the European Commission as part of the targeted program "SI Broader Scope" aimed to underpin the needed development of the SI system through Metrology R&D for fundamental and applied metrology. This paper presents a general description of the SIB10 NOTED technical program.

**Keywords:** Temperature, thermometer, ITS-90, traceability, fixed points.

## 1. INTRODUCTION

The Mise en Pratique for the definition of the kelvin (_MeP_-K) was created in 2006 by the Consultative Committee for Thermometry (CCT) to provide definitive guidance for the practical realization of the unit in accordance with the International System of Units (SI). The _MeP_-K opens new and flexible ways of updating and expanding the range of recognized thermometry methods beyond those currently in use. In addition future versions of the _MeP_-K will include: the redefinition of the kelvin in terms of the Boltzmann constant, the realization (and where possible dissemination) of the kelvin by primary methods and by indirect approximations capable of exceptionally low uncertainties or increased reliability. The expected outcome is greater flexibility in traceable temperature measurement. It is also foreseen that the International Temperature Scale of 1990 (ITS-90) (the current temperature scale in use

throughout the world) will continue to be in use because it is a robust and reliable tool. Nevertheless it has some limitations and some pending questions that need to be solved; a number of the most pressing of these are addressed in this project.

This project aims at answering the needs and solving the weaknesses identified by the CCT and some NMIs of the present established methods for the dissemination of the kelvin [1-6] and prepares the thermal metrology community for the forthcoming redefinition of the temperature unit. The main objectives are:

a) The development of new interpolation instruments and techniques and, through implementing practical primary thermometers, the calibration of Standard Platinum Resistance Thermometers (SPRT) directly to the new kelvin definition.

b) Solve current outstanding questions related to the ITS-90 temperature fixed points to clarify the discrepancies in their realization thus facilitating a reduction of their uncertainty.

The works are structured into five technical workpackages (WP) as follows:

• WP 1 Reducing the uncertainties related to the realisations of the defining fixed points.

• WP 2 SPRT and capsule type SPRT calibration procedures and temperature scale non-uniqueness.

• WP 3 New fixed points for improved dissemination and future International Temperature Scales.

• WP 4 Approximation to the kelvin between aluminium and silver fixed points.

• WP5 E Exploring new methods to establish traceability to the kelvin.

## 2. WP 1: REDUCING THE UNCERTAINTIES RELATED TO THE REALISATIONS OF THE DEFINING FIXED POINTS

The presence of impurities in a fixed point substance influences the temperature of its liquid-solid phase transformation. As the purity of fixed point substances is typically 6N or better (very high-purity), a fixed point substance containing $N$ different impurity species $i$, each one with molar concentration $c_i$, can be treated as a superimposition of $N$ independent diluted binary systems, in which the solvent is the fixed point substance and the solute is the impurity species $i$. Under certain freezing conditions, the elevation or depression of freezing points caused by impurities can be described using Van't Hoff's equation, which allows to evaluate the temperature shift produced by each impurity species $i$ with respect to the ideally pure fixed point substance, in terms of the slope of the liquidus line in the phase diagram with respect to the concentration of impurity $i$ and the concentration $c_i$ of the same impurity $i$ [1].



**Figure 1.** Triple point of water cell

Clearly, the uncertainty component arising from impurities could be substantially reduced if the liquidus slopes of all possible impurities of all fixed point substances would be known. Liquidus slopes of all possible impurities are currently, with few exceptions, unknown and this task represents a relevant contribution to the experimental determination of such liquidus slopes through appropriate doping experiments. Unfortunately this picture is complicated by the fact that some still unknown binary systems (so called "zero-systems") exhibits a phase transformation at very low solute (impurity) concentration and, for such systems, the Van't Hoff theory described above fails. In order to asses this effects doping experiments in water, Hg, Ga and Al fixed point cells will be performed.

Together with the impurities, the thermal fluxes are the other major source of uncertainty during the realization of the ITS-90 fixed points. The idea at the basis of any fixed point realization is to establish a solid-liquid interface in the fixed point substance that completely surrounds the thermometer and maintains it at the temperature of the solid-liquid interface itself. This ideal situation can be closely approached currently only in the cryogenic fixed points (triple points of $H_2$, Ne, $O_2$ and Ar) using the calorimetric technique, in which the fixed point is maintained in an adiabatic environment and simple experiments enable the quantification of background heat fluxes and empirical modelling of the first-order thermal response of the fixed point, which in turn allow to correct thermal errors and minimize the uncertainty arising from thermal effects.

In contrast with cryogenic fixed points, which operate adiabatically in vacuum and at very low temperatures, the metal fixed points are operated in air at higher temperatures, so that the thermal resistances between the furnaces and the fixed-point cell are very much lower and it is difficult to reduce the heat fluxes below a few watts. The usual solution is to rely on the establishment of two solid-liquid interfaces in the fixed point cell. With this practice, the outer interface provides the temperature regulation for the inner interface, which is then in near-isothermal conditions but many complications arise including freezing initiation, SPRT immersion effects and impurity segregation. A few experiments have investigated operating procedures that approximate adiabatic conditions [2], but the full understanding of thermal effects and their impact on uncertainty was not achieved yet.

To deepen in this problem, a mixed deductive and phenomenological approach is chosen. On one side, models that describe the time evolution of the phase transformation (essentially the evolution of the solid-liquid interface) as a function of given theoretical assumptions and given parameters (furnace thermal gradients, freezing initiation type of furnace, furnace thermal gradients, ambient temperature and insulation) will be adopted. On the other side, the validity of the adopted models by observing the impact of the selected parameters on the observed corresponding melting curves will be verified experimentally.

Moreover, the thermal effects in $O_2$, Ar. Hg and water triple points will be investigated with the calorimetric technique allowing (for the first time) to observe their phase transitions with long stem SPRTs under quasi-adiabatic conditions.

Finally, the time evolution of the solid fraction and melt fraction along the phase transformation will be followed using a newly developed method based on the difference of the electrical conductivity of solid and liquid metals.

## 3. WP 2 SPRT AND CAPSULE TYPE SPRT CALIBRATION PROCEDURES AND TEMPERATURE SCALE NON-UNIQUENESS

The principal purpose of the ITS-90 is to provide a practical mean for approximating thermodynamic temperature using practical thermometers. Instead of directly measuring thermodynamic temperature, these practical thermometers relate to some other parameter which is a function of temperature, such as resistance.. They are

calibrated at specified fixed points, whose temperatures are defined on the ITS-90, and rely on defined interpolation schemes to yield the temperature between fixed points.

Capsule SPRTs have been used as ITS-90 interpolation instruments at low temperatures for many years, and due to their compact form factor they are also very often employed with thermodynamic thermometers such as acoustic resonators, to determine the difference between thermodynamic temperature $T$ and ITS-90 temperature $T_{90}$. They have played a large role in all methods and apparatuses involved in the Boltzmann constant determination to transfer the water triple point temperature [3]. The calibration of Capsule SPRTs (CSPRT) in conventional fixed point cells is often performed in a very different environment to that when they are used in thermodynamic temperature devices so there remains much work to be performed to characterise the influence of e.g. gas, oil, and vacuum environments on the CSPRT performance. One of the objectives of this WP is to evaluate this influence. Particular attention will be paid to self-heating effects which are likely to differ between CSPRTs and SPRTs and from one measuring environment to another. The objective is to assess the equivalence of the ITS-90 realisations performed with these two different sensor types.

Another important objective in this WP is to improve the calibration procedures for long-stem SPRTs. Use of physical understanding of the phase transition and thermal behaviour of fixed points gained by numerical modelling and experiments will be directed at providing a practical method for e.g. impurity correction which can be used by the end-user, particularly primary calibration laboratories. Furthermore, the influence of the SPRT itself on the calibration will be evaluated by examination of oxidation and annealing effects, the improvements afforded by employing different kinds of bushings, and better approaches to minimise the extrapolation to zero measuring current. The calibration scheme will also be investigated, particularly by evaluating the optimum combination of fixed points to use for a desired temperature range of calibration.

Because the interpolating instrument is a resistance thermometer there is a need for interpolating functions to relate temperature to resistance between the defining fixed points. However, the functional form of these equations does not take into account the many physical effects associated with real thermometers, and so SPRT calibration equations are always subject to interpolation error of the order of 0.5 mK [4]. This so-called 'type 3 non-uniqueness' arises from the differences in interpolated values between fixed points between different SPRTs. It affects all the ITS-90 subranges but it is particularly severe in the range between 660.323 °C – 961.78 °C [5]. In this range there is very limited data on type 3 non-uniqueness because of the drift and oxidation of SPRTs. The type 3 non-uniqueness arising from SPRTs having non-ideal physical characteristics not incorporated in the interpolating equations will be studied. The behaviour of SPRTs between fixed points will be examined by studying the statistical behaviour of a population of SPRTs with calibration data between fixed points.

## 4. WP 3 NEW FIXED POINTS FOR IMPROVED DISSEMINATION AND FUTURE INTERNATIONAL TEMPERTURE SCALES

In the realization of the ITS-90, new fixed points can be used as secondary fixed points, mainly to reduce uncertainties in temperature ranges where large temperature gaps exist between established defining fixed points. Examples of large temperature gaps are between the triple point of argon (-189 °C) and the triple point of mercury (-39 °C) and between the freezing point of zinc (420 °C) and the freezing point of aluminium (660 °C). By adding one or more secondary fixed points in these intervals, uncertainties in the realization of the ITS-90 at the highest degree of accuracy can be reduced by up to a factor two [6].

In future Temperature Scale implementations, new fixed points are likely candidates to be incorporated as new defining fixed points, either as additional or as substitutive fixed points, with the objective of improving the accuracy of temperature standards.



**Figure 2.** On the left, prototype of a sealed copper cell for the realization of the triple point of water in quasi-adiabatic conditions. On the right multi-compartment cell

Potential new temperature fixed points have been studied and tested few years ago, but further research is necessary to get uncertainty levels suitable to improve current and future temperature standards. This work package intends to carry out this research work on a subset of most promising temperature fixed points recently studied, as well as on some novel ones.

The aim of this work package is to develop new temperature fixed points to improve the realization and the dissemination of the ITS-90 below 1000 °C, and possibly to contribute to the implementation of a future edition of the International Temperature Scale.

Below 0 °C potential candidates that would allow the reduction of the ITS-90 uncertainty by a factor of approximately two are the triple point of xenon (Xe, 111.745 °C) and hexafluoroethane ($C_2F_6$, 100.07 °C). To replace the triple point of mercury in the ITS-90 definition, due to the increasing difficulties in the supply of pure mercury samples and to the problems in conveying mercury cells for international comparisons, possible candidates are the triple point of carbon dioxide ($CO_2$, 56.558 °C), carbon

dioxide liquid-to-vapour phase transitions above 56 °C, and the triple point of sulphur hexafluoride (SF$_6$, 49.595 °C). Studies on these fixed points are included in the project together with studies on the Al-Cu eutectic point (548.16 ºC) and the I$_2$ triple point (114.7 ℃) to increase their repeatability.

## 5. WP 4 APPROXIMATION TO THE KELVIN BETWEEN ALUMINIUM AND SILVER FIXED POINTS

The aim of this WP is to develop new and improved approximation techniques for the kelvin in the temperature range from 500 °C to 1000 °C to overcome the limitations of the present approximation according to the ITS-90 which is based on SPRTs. The work will focus on the approximation of the kelvin with primary detector-based radiation thermometry and vapour pressure temperature scales.
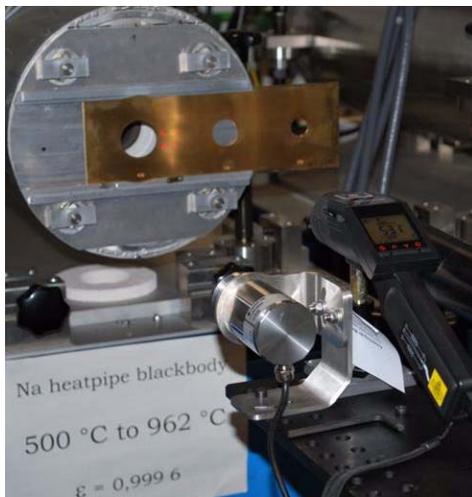


**Figure 3.** Radiation thermometers calibration set-up

Assessing the range from 500 °C to 1000 °C with absolute radiation thermometry requires radiation thermometers (RTs) operating in the near infrared (NIR) wavelength range. These types of radiation thermometers are routinely calibrated according to the ITS-90 via SPRT/blackbody based facilities. At present, no NMI performs a detector based characterisation of these devices in the NIR wavelength range, in terms of their absolute radiance responsivity i.e. thermodynamic temperature. This task will therefore establish beyond state-of-the art techniques and facilities enabling absolute radiometric characterisation of NIR radiation thermometers to be applied for a first time for the approximation and dissemination of the kelvin below 1000 °C. The radiometric characterisation will include the determination of the key parameter for thermodynamic temperature determination, the absolute radiance responsivity with relative uncertainties below 0.1 % ($k$=1), the radiation thermometer short term stability and the investigation of the linearity within the dynamic range of the radiation thermometers.

At the same time, a NIR radiation thermometer with a tuneable operating wavelength will be developed specifically engineered to facilitate laser calibration of its absolute spectral radiance responsivity. The calibration of this instrument will be much more simplified compared to filter radiometer based techniques as it is spectrally tuneable. This new type of radiation thermometer will be characterised and it is anticipated that it will be more stable than a conventional, optical grating based spectroradiometer as it does not use any moving mechanical parts.

Recent studies on the evaluation of the uncertainties budgets on temperature measurements by means of high temperature SPRTs showed that at present, between the Al and Ag fixed points the overall uncertainty attainable is close to 10 mK in the whole range. The use of vapour pressure temperature scales can fill this temperature range by a continuous thermodynamic phase transition curves. This task aims at reducing that uncertainty to the order of 1 mK.

## 6. WP5 EXPLORING NEW METHODS TO STABLISH TRACEABILITY TO THE KELVIN

The aim of this WP is to develop new instrumentation which, while maintaining the accuracy of a primary thermometer and the precision of fixed points, would be highly simplified allowing new practical ways to give traceability to the kelvin.

High temperature SPRTs are defined as standard interpolating instrument of the ITS-90 in the temperature range between 660.323 °C and 961.78 °C. Their susceptibility to contamination, the lack of stability, and the poor repeatability of measurements are well known problems. Modern techniques for the production of wires of pure noble metals allow the application of Au/Pt thermocouples (tcs) as possible candidate to replace HT-SPRTs. Au/Pt thermocouples have a higher sensitivity (Seebeck coefficient) which is larger by about a factor of two than the Seebeck coefficient of the Pt-Rh alloyed thermocouples, and they have a better thermoelectric homogeneity and stability. Furthermore, they are much more robust, are more easily manageable thermometers, and are much cheaper that HT-SPRTs.

A unique investigation of only one lot of Au/Pt thermocouples has been made to determine their reference function published in the international document IEC 62460 [7], that specifies its equation and reference tables relating the temperature to EMF (electro-motive force) relationships. The problem nowadays is that the thermoelectric behaviour of wire from different batches/providers exhibits enormous variation, and it seems to be necessary to develop and validate a new reference function which better reflects the properties of commercially available Au and Pt wire, in order to enforce their repeatability, and, at the same time, to lower the measurement uncertainty. This will be realized by investigating a number of different thermocouples, with proven stability and homogeneity, constructed with wires from different sources and with different assembly techniques. The relationship between temperature and electromotive force should be determined using different procedures to allow its validation. In addition a comparison with HT-SPRTs has to be undertaken.

In the mid term (likely in 2014) the kelvin will be redefined in terms of a determined fixed value of the Boltzmann constant and the thermometry community, led by the CCT, is aware of the need to manage the transition to the thermodynamic temperature $T$ [8]. At present, in the high and low temperature ranges $T$ and $T_{90}$ coexist because the equipment in use to realize both are equally reproducible, repeatable, and have the same level of complexity. But there are currently no practical means for disseminating the thermodynamic temperature $T$. Primary thermometers like the Acoustic Gas Thermometer (AGT), the Dielectric-Constant Gas Thermometer (DCGT) or the Doppler Broadening Thermometer (DBT) are complex, voluminous and generally unwieldy. They are excellent for the realization of the temperature standards at the highest degree of accuracy, but are unsuitable transfer standards. In this project, the necessary means to allow practical thermodynamic calibrations, constructing practical acoustic devices, will allow SPRT calibration direct to the thermodynamic temperature. Unlike ITS-90 calibrations, thermodynamic calibrations can be realised at any thermodynamic temperature, and are not limited to the fixed points. The number of calibration points can be chosen according to the accuracy required: in temperature ranges where high accuracies are required, the number of calibration points can be higher than in ranges were lower accuracies are needed. A calibration function specific to each thermometer can be determined, instead of the standard reference function of the ITS-90. This provides direct traceability to the thermodynamic temperature and overcomes the problems related to the propagation of the uncertainties of the fixed points.
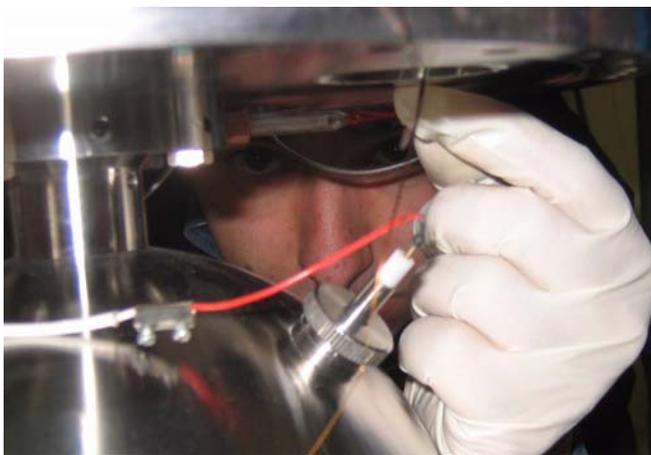


**Figure 4.** Detail of an acoustic gas thermometer

Thermometers based on the sapphire whispering-gallery-mode (WGM) resonator may be a good candidate to overcome the mechanical instabilities of PRTs in industrial applications. The intrinsic temperature dependence of the refractive index (or its near equivalent, the permittivity) of synthetic sapphire, coupled with the ease of measuring the frequencies of high-$Q$ resonant modes, allows the use of a sapphire WGM as a thermometer rather than a frequency standard. Compared to platinum, synthetic sapphire is thought to be mechanically stable up to 1800 °C and less

subject to changes in physical state (e.g., oxidation, growth of crystal defects). Due to the inherent stability issues associated with PRTs, a sapphire WGM thermometer represents a potential replacement for a PRT in industrial applications where measurement uncertainty below 10 mK is required. A sapphire WGM thermometer is expected to have stability at the ice melting point (0 °C) of 1 mK with a resolution equivalent to 0.1 mK. In this project, a sapphire WGM thermometer to cover the range from -80 °C to 180 °C will be developed

In addition dedicated electronics for the temperature control of fixed point furnaces and for the very accurate temperature control required in primary thermometry innovative devices will be developed too.

## 7. CONCLUSION

This paper presents the description of the works program of the project SIB10 NOTED entitled "Novel techniques for traceable temperature dissemination". This project is a challenge in the field of fundamental thermometry trying to solve some of the pressing weaknesses of the ITS-90 and will help establish a practical link between the thermodynamic temperature $T$ and $T_{90}$. This JRP offers solutions to the most pressing problems associated with high level practical temperature metrology, in the most widely used temperature range, from -218 ºC up to 1000 ºC.

## 8. ACKNOWLEDGMENTS

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