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Realization of the Temperature Scale in the Range from 234.3 K (Hg Triple Point) to 1084.62°C (Cu Freezing Point) in Croatia

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Abstract This article describes the realization of the International Temperature Scale in the range from 234.3 K (mercury triple point) to 1084.62°C (copper freezing point) at the Laboratory for Process Measurement (LPM), Faculty of Mechanical Engineering and Naval Architecture (FSB), University of Zagreb. The system for the realization of the ITS-90 consists of the sealed fixed-point cells (mercury triple point, water triple point and gallium melting point) and the apparatus designed for the optimal realization of open fixed-point cells which include the gallium melting point, tin freezing point, zinc freezing point, aluminum freezing point, and copper freezing point. The maintenance of the open fixed-point cells is described, including the system for filling the cells with pure argon and for maintaining the pressure during the realization.

Keywords Croatia · ITS-90 · Realization

1 Introduction

After declaring independence in 1990, Croatia had to organize its own national metrological system. On the basis of a cost–benefit analysis, it was decided to establish a distributed system of national standards by selecting, funding, and developing standards at laboratories with an existing tradition and know-how in specific fields. The State Office for Metrology (DZM) has since coordinated the distributed system. This explains why most (7 out of 9) of the Croatian National Standards are located at the University of Zagreb. The Laboratory for Process Measurements (LPM), located at

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the Faculty for Mechanical Engineering and Naval Architecture, University of Zagreb, was selected by the State Office for Metrology to develop and maintain national standards in the fields of temperature, pressure, and humidity. At that time, LPM already had a 40-year tradition of measurements in temperature, pressure, humidity, flow, heat energy, etc. as well as a self-implemented EN 45001-based quality system. With its new role as a national laboratory, LPM decided to seek international accreditation from the European Cooperation for Accreditation (EA) in order to fulfill the needs for accredited dissemination of the temperature scale to industry and science and in anticipation of quality system requirements for NMIs at the international level. LPM achieved full EA-DKD accreditation in 2002 as a secondary laboratory disseminating the temperature scale within Croatia and in the neighboring region. Traceability was based on a set of standard platinum resistance thermometers (SPRTs) and standard thermocouples regularly calibrated at the primary laboratory of PTB Berlin.

The next step was the independent realization of selected temperature fixed points. During the past several years, LPM constructed or acquired fixed points in the range from the mercury melting point to the copper freezing point (except indium), along with the equipment needed for their realization. The sources of funding were projects of the Ministry of Science, Education and Sport (MZOS), Republic of Croatia, State Office for Metrology (DZM), several European (CARDS) programs, the metrology infrastructure program of the Republic of Germany, and from LPM's own resources as a calibration laboratory. As the new methods and equipment are implemented, the current realization capability is constantly being upgraded.

2 Equipment Used for the Realization of ITS-90

Standard platinum resistance thermometers from various manufacturers are used as interpolating instruments. One pair of them with an up-to-date PTB calibration are used only for dissemination of the scale and comparison of the fixed points, while others are used for research and as monitor thermometers. A pair of Type S thermocouples are used to disseminate the scale above 660°C, and are expected to be replaced by a pair of Pt/Pd thermocouples in the near future.

Resistance thermometers are measured with two AC bridges with accuracies of 0.5 and 0.1 ppm of the bridge ratio, coupled with their 10-channel scanners. The standard resistances, Wilkins-type 25 and 100 Ω, are kept in their temperature-controlled cabinets or in a Dewar filled with oil, in which case a resistance correction is made to every reading based on the temperature of the oil. The influence of temperature change on the reference resistor in the latter case in the calibration of the SPRT is approximately 0.25 mK.

A list of the fixed points used to realize the ITS-90 at LPM is presented in Table 1.

A sealed mercury fixed point from Isotech is kept in a parallel-tube bath filled with ethanol. The temperature stability of the bath is around 0.010°C, allowing a plateau of 8 h duration. The realization of the melting plateau was also tested by putting the mercury triple point into a Dewar filled with ethanol, over which liquid nitrogen was poured to cool the alcohol below −40°C. In addition to the commercially available Hg MP used to realize the scale, LPM filled and sealed a mercury multientrance fixed

Table 1 List of LPM fixed-point cells with their combined uncertainties

Fixed-point cell	Manufacturer, purity	Immersion depth (mm)	Uncertainty (mK)
Hg TP	Isotech, 7N	200	0.83
H_2O TP	Isotech, n/a	270	0.52
Ga MP	Isotech, 8N	260	0.81
Sn FP	Isotech, 6N5	200	2.60
Zn FP	Isotech, 6N5	200	5.04
Al FP	Isotech, 6N5	200	12.2
Ag FP	Isotech, 6N5	200	130
Cu FP	Isotech, 6N5	200	153

point to investigate the feasibility of decreasing the thermal gradients of comparison calibrations [1].

Two Isotech Type A11 water triple-point cells, one with a known temperature deviation due to its isotopic composition, realize the reference temperature of 0.01°C at LPM. The triple-point cells are kept in a large Dewar filled with ice made from demineralized water, while a small aquarium pump connected to an electronic timer is used to pump excess water from the Dewar every 6 h. Triple points can be kept this way up to 3 weeks after being made, but it is not convenient for triple-point cells with integrated glass handles. A new water bath for the water triple points is being ordered. Three other water triple-point cells have temperature depressions larger than 100 μK, and are not used. LPM also sealed one small-diameter water triple point, which is used to demonstrate the supercooling of water to students attending measurement lectures at the Faculty.

The gallium melting-point cell is of Isotech design, and is kept in its original gallium apparatus. Two other gallium cells (which were constructed at CNAM [2]) are of the open design, thus allowing for pressure control. They contain gallium of lower purity and are kept for crosschecking and research.

Fixed points in the range from tin to copper are all commercially available Isotech open cells. Open cells were chosen not only to allow smaller uncertainties due to being able to measure the pressure during the plateau, but also due to the ease of repair in certain ‘unplanned circumstances,’ as occurred on two occasions. In the case of a small crack in the cell envelope or in the re-entrant thermowell, flushing the cell with a flow of argon should prevent air from entering the cell. Low-, medium-, and high-temperature furnaces along with a fluidized bath are used to realize fixed-point plateaux. A membrane pump is used to evacuate the system, while a mechanical pressure regulator in conjunction with a needle valve is used to regulate the flow and pressure of 6N-purity argon. The system, Fig. 1, is mounted on two frames with ample space to accommodate eight furnaces with fixed points, with connections to the vacuum/argon pressure system for each furnace. Smooth stainless-steel tubes are mounted on the frames, connecting the vacuum pump/argon port to the eight ports leading to the fixed points. At all eight ports, KF mounting flanges are welded to allow connection of corrugated flexible tubes to the metal tops of the freezing points. In this way, the fixed point can be pulled from the furnace at any time, while the internal argon pressure is maintained, for inspection or to start a freeze (for example, in the case of deeply supercooling tin). Cold traps can be added to the argon side to prevent

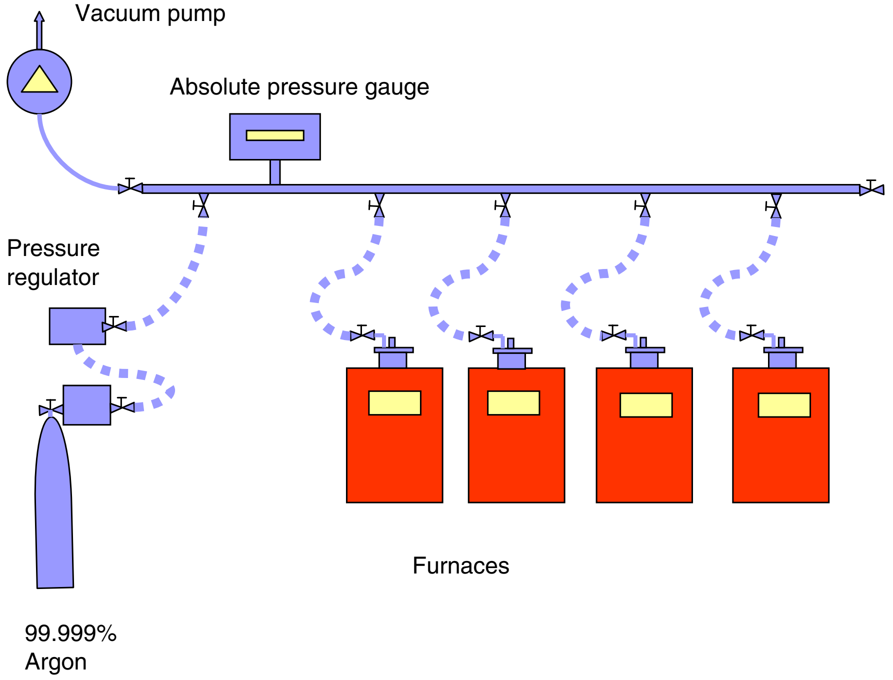

Fig. 1 Diagram of the LPM gas handling system for the fixed points

any moisture from the argon from entering the cells. An absolute pressure gauge with an uncertainty of 100 Pa is used to monitor the pressure in the cell during the plateau. The implementation of a dedicated electronic pressure controller to the system is being considered, in order to maintain a constant overpressure of 5 kPa during the heating, phase transition, and cooling of the freezing points.

3 Measurement Techniques and Uncertainties

Realizations of the fixed points in the range from the triple point of mercury to the gallium melting point is rather straightforward, as those fixed points are sealed. The mercury triple point is frozen overnight at a temperature of −40°C, and then the set point of the bath controller is raised 0.4°C above the phase-transition temperature. When the temperature observed by the monitor thermometer stops rising, indicating melting of the mercury, a 6-mm diameter stainless-steel rod is inserted for 1 min, creating an inner melt around the thermometer well. The thermometer, almost at room temperature, is then inserted into the cell and left to stabilize. The duration of the plateau is approximately 8 h. Triple-point-of-water cells are left overnight in an ice bath to cool prior to realization. Then, a small amount of crushed ice is poured into the Dewar flask to create a cushioning bed for the cell's bottom, the cell is inserted into the flask, and the rest of the flask is filled with crushed ice to minimize heat loss during creation of the mantle. The stainless-steel rod, pre-cooled in liquid nitrogen, is used to nucleate formation of the mantle, which is then completely formed with the use of an Isotech alcohol-filled heat pipe. The cell is slowly and continuously turned to maintain a symmetrical mantle. The top of the cell protrudes from the crushed ice, thereby preventing the formation of an ice bridge at the surface of the cell and facilitating observation of the water level against a mark on the glass. After the water level has risen 6.5 mm, indicating the percentage of ice in the cell is around 50%, the alcohol is removed from the re-entrant thermowell, cold water is poured into the thermowell, and a sponge stopper is placed at the bottom of the thermowell. The cell is left to stabilize at least 2 days before measurements are taken. To realize the gallium melting point, the regulator on the thermostatted cabinet is switched to "AUTO" and an inner melt is formed by inserting a stainless-steel rod heated to approximately 50°C.

All open fixed-point cells in the range from tin to copper are realized in a similar manner (except tin, due to its notorious supercooling).

The operating procedure for the vacuum system when the cell is newly connected to the system is as follows. As the stainless-steel tubes fixed on the frame are exposed to air (and moisture from the air) every time cells are mounted or dismounted from the system, the system is flushed with argon and evacuated five times before opening the valve to the cell. During the first pumping, the system is checked for leaks by monitoring the absolute pressure attainable by the membrane pump, which is approximately 150 Pa (absolute), and the system should hold the pressure as long as it is being tested. The cell is also checked in the same manner after every opening, and the maximum allowable pressure rise is approximately 3 kPa in 30 min. After cleaning, the system is filled with argon at a pressure of approximately 101.3 kPa and the valve to the cell is slowly opened to prevent argon bursts into or out of the cell. Then, the system with the cell connected is evacuated, kept at the minimum pressure for 3 min (approximately 300 Pa pressure rise is allowed) to check the cell again. When the cell is connected to the system, the maximum rate of pumping or flushing with argon is approximately 300 Pa per second, as a faster rate would produce larger argon speeds and turbulence in the system and would leave all 'sediment' at the lowest point of the system, in the cell itself. After five pumping/argon flushing sequences, the system is left at a pressure above atmospheric and the furnace is turned on. During heating, the argon pressure will rise, so the pressure has to be checked regularly and adjusted to be always between atmospheric and 109 kPa absolute. If the melt plateau is to be measured, then the argon pressure is regulated to 2 kPa above atmospheric pressure before the melt, or if a calibration is to be made only on the freeze plateau, then the pressure is regulated before the cold rods are inserted into the re-entrant thermowells. A slight overpressure gives an indication of any leak in the cell at high temperature and also, in the case of a crack, creates an outgoing stream of argon to prevent contamination of the cell. After the measurement, the cell is left to cool with the regulator on the argon bottle adjusted to bleed pressure at approximately 3–4 kPa above atmosphere, so fresh argon from the bottle enters the cell as the pressure in the cell and the system drops. After cooling to room temperature, the valve on the cell is closed and the cell can be stored until its next use at a slight overpressure above atmospheric. The only exception to the abovementioned procedure is the tin cell, which has to be pulled from the furnace to start crystallization. To avoid the pressure in the cell dropping below atmospheric, the pressure is regulated at 109 kPa absolute before pulling the cell from the furnace. For

Table 2 Current LPM uncertainty budget (in mK) for calibration of an SPRT at the Al fixed point

Repeatability of readings	0.31
Purity	1.50
Hydrostatic pressure correction	0.03
Perturbing heat exchanges	3.00
SPRT self-heating correction	0.20
Bridge linearity	0.25
AC/DC current	5.00
Gas pressure	0.01
Propagation from TPW	0.55
Stability of reference resistor	0.50
Temperature of reference resistor	0.25
Resistance ratio (W_t) scatter	0.41
Standard combined uncertainty, $k = 1$	6.1
Expanded combined uncertainty, $k = 2$	12.2

the freeze plateau, a 1°C temperature offset below the freezing temperature is used (except for tin, where a 0.1°C offset is used after the cell is returned into the furnace).

The LPM uncertainty budget for the calibration of SPRTs at the fixed points takes into account contributions from the fixed point itself, contributions from the electrical measurement, and contributions from the SPRT, as elaborated extensively in [3]. Generally, for every point the budget includes the repeatability of readings, the influence of chemical impurities, the uncertainty associated with the hydrostatic head, the uncertainty of the SPRT self-heating correction, the uncertainty due to perturbing heat exchanges, the nonlinearity of the bridge, differences in AC/DC measurements, the uncertainty in measuring the gas pressure during the realization, the stability and temperature of the standard resistor, and the propagation of uncertainty from the water triple point. The current uncertainty budget for the calibration of SPRTs in the range from the mercury triple point to the aluminum freezing point is presented in Table 1. As can be seen from the uncertainty budget for the calibration of SPRTs at the aluminum freezing point, presented in Table 2 for Euromet Project 820 [4], the limiting factor is the uncertainty due to the DC/AC current, which is affected by the available power source. The laboratory is located where an ever-growing number of nonlinear electrical loads (such as computers, air conditioning systems, etc.) create a very noisy power supply for the sensitive AC bridges. Electrical work on the infrastructure has started and in the near future a power line with separate grounding directly from the transformer for bridges and multimeters will be available. Upon finishing this work, and with cells characterized with the new F18 bridge, some components of the budget will be improved.

Although not part of the ITS-90 contact thermometry definition, the LPM copper cell was intercompared by means of thermocouples with those of other laboratories as part of the Euromet Project 844, and the results of the intercomparison have been reported [5].

4 Future Development

Plans for the future include both extension of the range and refinement of the uncertainty budget. The calibration range will be extended down to the argon triple point, which has been ordered together with its Dewar. The uncertainties in realizing the scale will be affected through the purchase of new equipment (water triple-point bath, standard resistor bath) and through infrastructure work, particularly the availability of a new, clean power supply. Also, to better characterize the silver and copper freezing points, we plan to purchase Pt/Pd thermocouples. Further, we plan to take part in all intercomparisons in the range from the argon triple point to the copper freezing point to test the realization of the ITS-90 in Croatia.

5 Conclusion

The LPM, although small in manpower, is putting lots of effort into advancing its capabilities in temperature metrology. From a quality secondary laboratory, a new primary laboratory has emerged, thus fulfilling all requirements of industry and science in Croatia regarding contact temperature calibration. This article describes the current achievements in this ongoing process, which is greatly supported by colleagues from other laboratories to whom we express our gratitude.

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