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Realization Triple Point of Carbon Dioxide at TÜBİTAK UME Laboratory

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TÜBİTAK UME Laboratuvarında Karbondioksit Üçlü Noktası Gerçekleştirimi

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Abstract
Temperature, a fundamental parameter in describing matter from the formation of the universe to the present day, has evolved with scientific advancements. Temperature measurement, crucial in everyday life, health, industry, and research, demands high precision. Innovations in temperature measurement technologies, particularly Standard Platinum Resistance Thermometers (SPRTs), have addressed this demand. The International Temperature Scale (ITS-90) defines fixed points, including the Triple Point of Water (TPW) and the Triple Point of Mercury (TP(Hg)). However, due to mercury's restrictions, alternative fixed points are sought. At the XX IMEKO World Congress on Temperature in 2012, Carbon Dioxide Triple Point (TP(CO_2)) and Sulfur Hexafluoride (TP(SF_6)) were proposed as alternatives. Recent studies have measured the triple point temperature of carbon dioxide to be around 216.591 K, with an uncertainty of less than 1 mK. This study focuses on the construction and metrological characterization of Carbon Dioxide Triple Point cells at TUBITAK UME. The measurements were conducted within the Primary Level Temperature Laboratory, performing two different methods for triple point realization. The study highlights the meticulous calibration processes and achieved precision, affirming the Carbon Dioxide Triple Point as a stable reference point. Comparisons with CCT's recommended values underline its accuracy and feasibility as an alternative to the Mercury Triple Point.

Keywords Temperature; Calibration; Fixed point; Thermodynamic; Metrology

Öz
Evrenin oluşumundan günümüze kadar maddeyi tanımlamada temel bir parametre olan sıcaklık, bilimsel gelişmelerle birlikte evrim geçirmiştir. Günlük yaşamda, sağlıkta, endüstride ve araştırmada hayati önem taşıyan sıcaklık ölçümü yüksek hassasiyet gerektirmektedir. Sıcaklık ölçüm teknolojilerindeki yenilikler, özellikle Standart Platin Direnç Termometreleri (SPRT'ler) bu talebi karşılamıştır. Uluslararası Sıcaklık Ölçeği (ITS-90), Suyun Üçlü Noktası (TPW) ve Cıvanın Üçlü Noktası (TP(Hg)) gibi sabit noktaları tanımlar. Ancak, cıvanın kısıtlamaları nedeniyle alternatif sabit noktalar aranmaktadır. 2012 yılında düzenlenen XX IMEKO Dünya Sıcaklık Kongresi'nde, Karbondioksit Üçlü Noktası (TP(CO_2)) ve Kükürt Heksaflorür (TP(SF_6)) alternatif olarak önerilmiştir. Son çalışmalar, Karbondioksit Üçlü Noktasının sıcaklık değerini 1 mK'nin altında belirsizlikle 216.591 K civarında ölçmüştür. Bu çalışma, TÜBİTAK UME'deki Karbondioksit Üçlü Nokta hücrelerinin yapımına ve metrolojik karakterizasyonuna odaklanmaktadır. Ölçümler, üçlü nokta gerçekleştirme için iki farklı yöntem kullanılarak Birincil Seviye Sıcaklık Laboratuvarı'nda gerçekleştirildi. Çalışma, özenli kalibrasyon süreçlerini ve elde edilen hassasiyeti, Karbon Dioksit Üçlü Noktasını kararlı bir referans noktası olduğunu göstermektedir. CCT'nin önerilen değerleriyle yapılan karşılaştırmalar, Cıva Üçlü Noktasına bir alternatif olarak doğruluğunu ve uygulanabilirliğini vurguluyor.

***Anahtar Kelimeler** Sıcaklık; Kalibrasyon; Sabit nokta; Termodinamik; Metroloji*

1. Introduction

From the formation of the universe to the present day, temperature is one of the fundamental parameters we use to describe matter. The definition of temperature has developed throughout the ages in tandem with the advancements in scientific knowledge. Temperature measurement has changed over time, beginning with Galileo's thermometer and progressing to microprocessors. There is a need for temperature measurement in everyday life, in the field of health, in industrial applications, and in scientific research. The high precision demanded by industry and scientific research has led to innovations in temperature measurement technologies. Various types of thermometers are used for temperature measurements, with Standard Platinum Resistance Thermometers (SPRTs) being among the most precise. The calibration of SPRTs, which play a significant role in precise temperature measurements, can be achieved at the millikelvin level. The International Temperature Scale (ITS), which provides specialized applications for calibration according to specific standards, replaced its previous version with ITS-90 in

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1990 (Preston-Thomas 1990). ITS-90 defines fixed points in the range of 13.8033 K to 1234.93 K for the use of SPRTs. Interpolation equations derived from ITS-90 vary depending on temperature regions, starting with the Triple Point of Water (TPW) (273.16 K). Following TPW, the Triple Point of Mercury (TP(Hg)) (234.3056 K) is used at lower temperatures. Due to its inherent high density, mercury remains in liquid form at room temperature. Its use has been restricted over time as its harmful effects on human health have become known. In the XX IMEKO World Congress on Temperature in 2012, due to the limited use of mercury and the associated challenges in transportation and storage, the aim was to use alternative fixed points. During the congress, Carbon Dioxide Triple Point (TP(CO_2)) (216.592 K) and Sulfur Hexafluoride (TP(SF_6)) (223.565 K) were proposed as alternatives due to being gases, attainable high purity, no environmental harm, no toxic effects on human health, ease of storage and transportation, low cost, and ease of acquisition, as compared to the Triple Point of Mercury(IMEKO World Congress 2012, Bedford et al. 1996; Kawamura & Nakano 2021). The Carbon Dioxide Triple Point, serving as a secondary reference point in the ITS-68 scale, was measured with an uncertainty of 1 mK at 216.58 K (Bedford et al. 1984). Recent studies (Ambrose 2002, Kartal Dogan et al. 2011, Hermier 2007, Kawamura et al. 2020, Liang et al. 2023) have determined the temperature value of the Carbon Dioxide Triple Point to be around 216.591 K. At 2020, Kawamura was measured Temperature of TP(CO2) as 216.590 90 ± 0.00036 K with 0.22 mK uncertainty (k=1) in vacuum chamber measurement systems (Kawamura et al. 2020). The last study conducted by Liang and his team in 2023; the TP (CO2) temperature was measured as 216.591 ± 0.0003 K with 0.21 mK (k=1) uncertainty (Liang et al. 2023). The Consultative Committee for Thermometry (CCT) recommended an uncertainty of 1 mK for the realization of Carbon Dioxide Triple Point, with a temperature value of 216.592 K (BIPM 2021). This study presents the construction and metrological characterization of CO2 cells at TUBITAK UME, including evaluation of the associated measurement uncertainty and proposes a new fixed point beyond ITS-90, which will be reduced by future technologies. The measurements were conducted at the TÜBİTAK UME (National Metrology Institute of Turkey) Primary Level Temperature Laboratory, which is capable of performing SPRT calibrations within the range of the Triple Point of Argon (83.8058 K) and the Silver Fixed Point (1234.93 K). The system and materials used to create the Carbon Dioxide Triple Point Cell are essentially at a level that encompasses Primary Level Temperature Laboratories

2. Measurement Method and Experimental Setup

The cells were designed as to have a thermowell of 215 mm height, 10 mm diameter, cell diameter is 50 mm and height is 235 mm, also have two vents for different measurements (Figure 1). Each cell was filled with CO_2 gas of different purities. For high purity, CO_2 gas with 99.9999% (6N) purity was obtained from Linde Gas which is impurity certificate shown at Table 1. Similarly, CO_2 gas with 99.999% (5N) purity was obtained from the UME Gas Metrology Laboratory. In addition to the two gases obtained, 6N purity gas was further purified using a Purifier Filter to obtain even purer gas (6NP). The cells were named according to their purity levels (5N-6N-6NP).

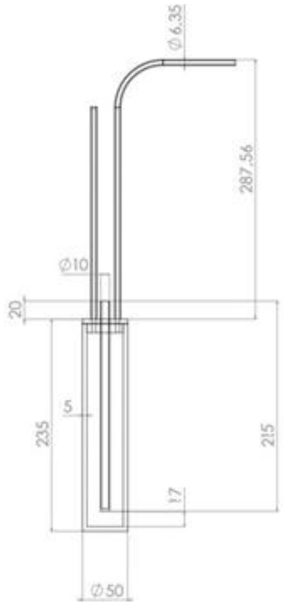

Figure 1. Cell Design

2.1 Cell Preparation

The pressure of carbon dioxide gas in a fixed volume at room temperature is approximately around 55 bar (Span & Wagner 1996). Stainless steel cells, as shown in Figure 2, were designed and produced to withstand this pressure. The maximum amount of gas to be filled was determined to be 172 grams for considering safety and storage conditions (proportion to 185 mm height). Cells have got a detailed cleaning process due to the production methods of stainless steel.

Table 1. Specification in the certificate of 6N Purity Gas

Component	Specification	Concentration
Carbon dioxide (CO_2)	99.9999 %	99.9999 %
Nitrogen (N_2)	≤0.3 ppm	<0.04 ppm DL (Detection Limit)
Oxygen (O_2)	≤0.3 ppm	0.02 ppm
Total Hydrocarbons (THC)	≤0.2 ppm	<0.02 ppm DL (Detection Limit)
Moisture	≤0.2 ppm	0.147 ppm

The cells were filled with technical acetone, ethanol, and distilled water in an ultrasonic bath for two hours each. After the ultrasonic process, they were annealed at 150 °C for 2 hours.

Figure 2. Constructed Cell with two line

2.2 Filling stage of the Cells

The chemically cleaned cells were vacuumed down to the level of 10^{-7} bar using a turbo molecular vacuum pump at the UME Gas Metrology Laboratory. Later, the cell was connected to the filling system (GC-DID) and the system was washed and vacuumed three times with using 4 g of CO_2 gas in each process to eliminate different gas impurities in the filling system. For the final wash, the cell valve was kept open, after wash complete which, the cell was vacuumed again to approximately 10^{-6} bar. The cell was filled inside an ethanol and dry ice mixture bath to facilitate gas flow to low pressure. The cells were weighed before and after filling. Three CO_2 cells were filled. Cells were filled with 172 gr CO_2. After the filling process completed, the cells were taken to Temperature laboratory to be characterized metrologically.

Figure 3. Measurement System used during comparison measurements

3. Measurement Results

3.1. Realization of the Carbon Dioxide Triple Point

During the realization of the triple point, two different methods were used. One method aimed for a slower and more stable triple point realization, while the other method involved pre-heating step to achieve a faster and more balanced plateau. These methods can be considered as freezing and melting plateaus in accordance with literature (Kawamura et al. 2020), whereas the Carbon Dioxide Triple Point was characterized solely based on the melting plateau (Liang et al. 2023). In order to measure the temperature of the Carbon Dioxide Triple Point, the inner surfaces of the cells were thermally stimulated during melting stage using a rod at room temperature, ensuring the precise realization of the triple phases (Figure 4). The induced melting increased triple point temperature of CO_2 as 0.4 mK in the beginning of the plateau and was decreased standard deviation of plateau as 0.02 mK. Without application of inner melt, a few hours are required to attain the triple point temperature.

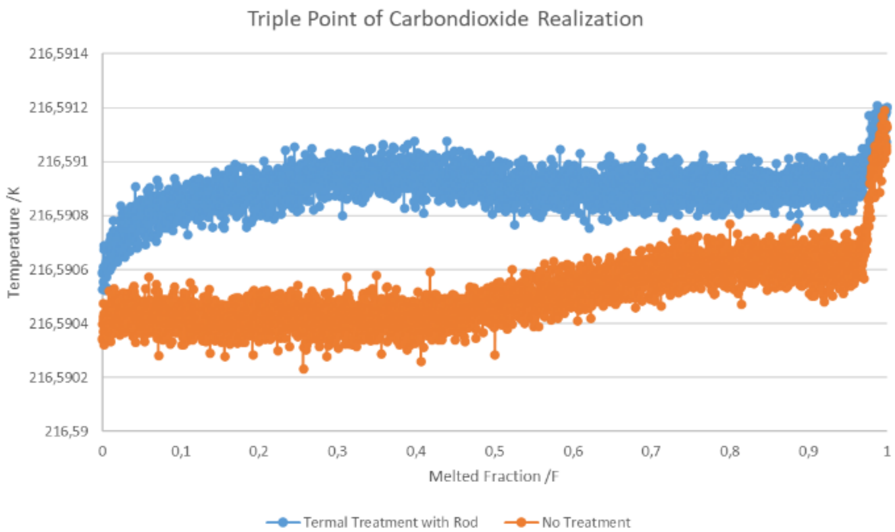

Figure 4. Thermal Stimulation of Cell 6NP

The temperature of the Carbon Dioxide Triple Point was primarily measured via resistance (Figure 5). Resistance-based measurements also served as preliminary preparations for uncertainty budget calculations. Non-Premelted Measurement had 0.12 mK standard deviation and Premelted Measurement had 0.08 mK standard deviation. Duration of Melting Plateaus approximately lasts up to 14 hours. Melting plateau analyzes provide us with a better understanding of melted fraction (Figure 6-7-8). Also linearity of 6NP plateau was shown in Figure 8. In the measurements of the melting plateau, the average values and calculations are determined within the range of 0.2 to 0.7 fractions of the amount melted.

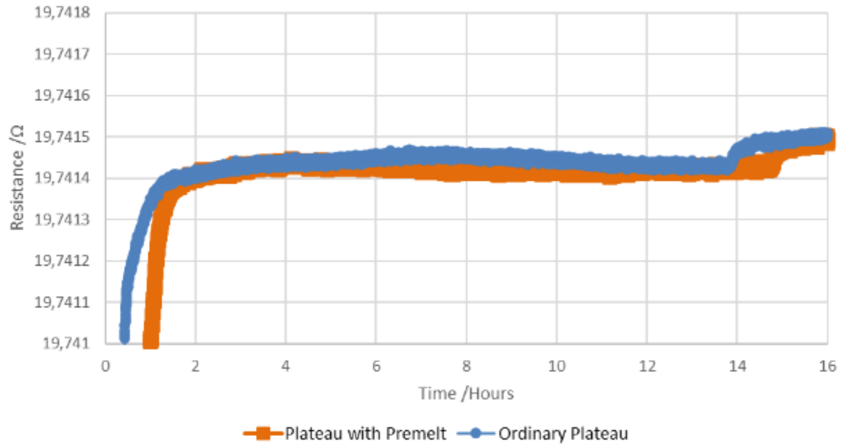

Figure 5. Melt plateaus obtained with Cell 6N.

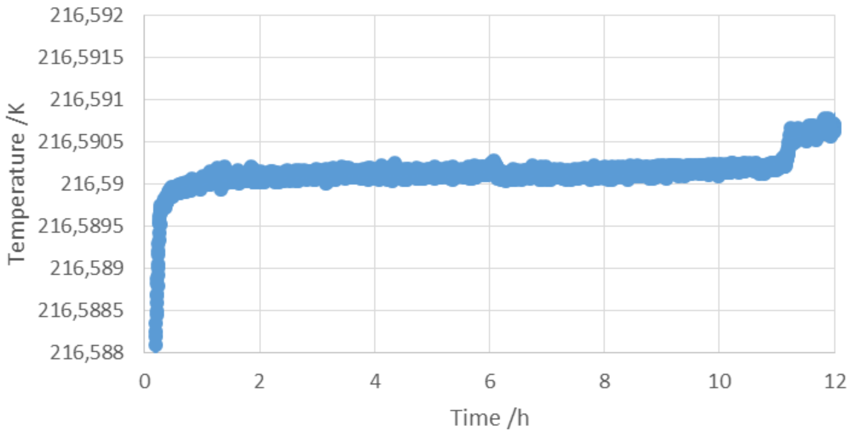

Figure 6. Melt Plateau of Cell 5N. Average: 216.5901 K & Std. Deviation: 0.07 mK

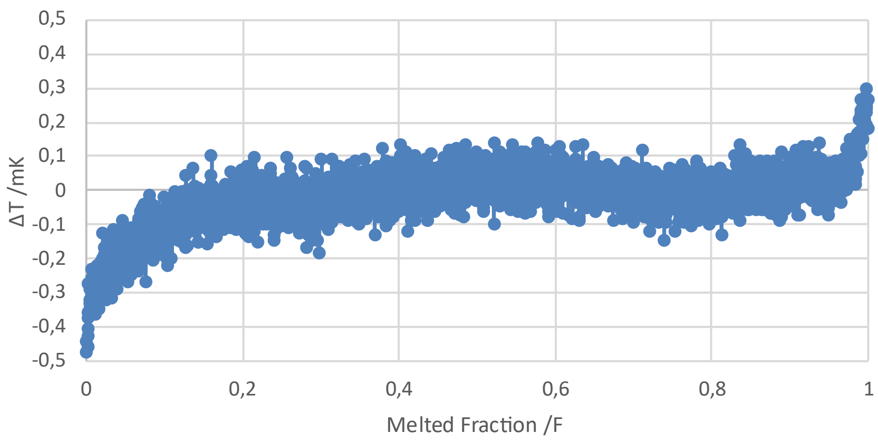

Figure 7. The melt plateau obtained with Cell 6N

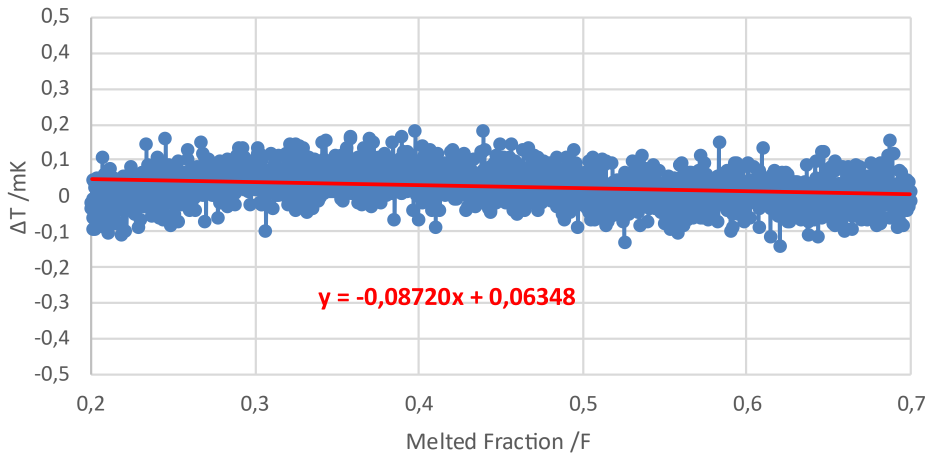

Figure 8. Analysis of Cell 6NP

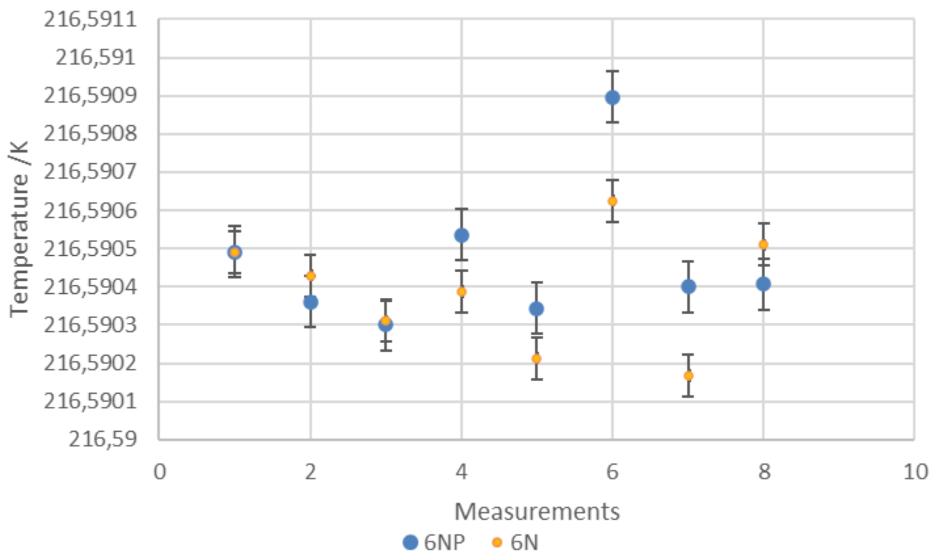

Figure 9. Total Measurements of Cell 6NP and Cell 6N as Temperature, Bars show standard deviation of plateaus

The melting range which has been considered as the temperature difference between the beginning and the end of the plateau, was observed as 0.3 mK (Figure 8). The temperature of the triple point of Carbon dioxide was measured to be 216.59055 ± 0.0005 K (Figure 9). The shape of the plateaus rise in the first half and decreases slightly in the second half that's effect of pre-melt technique and thermal stimulation.

3.2. Uncertainty Budget

Measurements were taken with 5N, 6N, and 6NP cells simultaneously at I=1 mA and I=1.42 mA to subtract zero milliamperes for the self - heating correction, as listed in the uncertainty budget (Table 2). The comparison results were considered during the estimation of uncertainty arising from chemical impurities. As a result of the measurements, it was observed that the difference occurred between the cells filled with 5N grade and 6N grade CO_2 as 0.15 mK which formed the basis for impurity effect in uncertainty budget. On the other hand, the temperature difference between 6N and 6NP cells was found to be 0.04 mK which is not significant considering the measurement uncertainty. The comparison results between 6N and 6NP cells are shown in Figure 10.

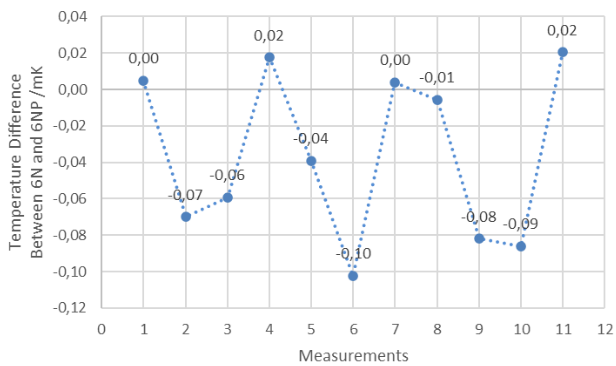

Figure 10. Comparison Measurements of 6NP and 6N cells.

The parameter of repeatability was calculated using measurements taken after recalibration. FLIR thermal images of the frozen cell showed CO_2 gas distributed throughout the cell (Figure 11). For the hydrostatic correction, immersion depths in measurements (Figure 12) yielded values close to those in the Clapeyron

Equation which defines temperature change in depth and the Clapeyron Value of CO2 is 0.0246 mK/cm (Liang et al 2023).

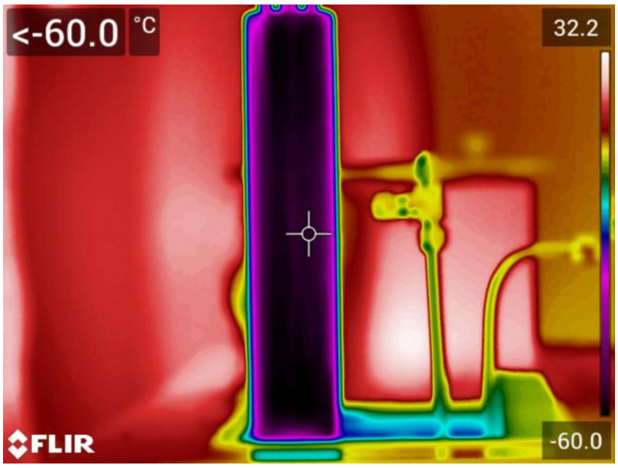

Figure 11. Thermal Observation of Cell 6NP with FLIR

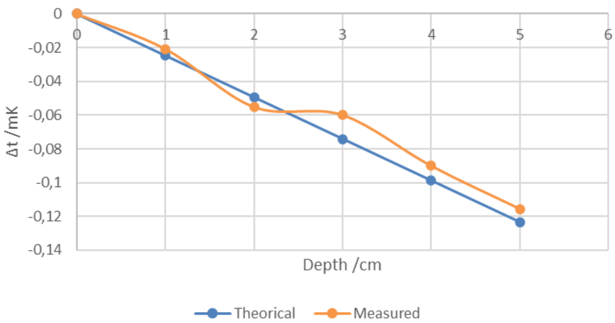

Figure 12. Immersion Profile of Cell 6NP with Theorical value

The uncertainty budget and relevant parameters related to SPRT calibration at CO2 cell are given in Table 2. The most effective parameter was found to be chemical impurities and its assessment were carried out as mentioned above.

All measurements were carried out with very high accuracy resistance bridge through 25 Ohm standard resistors which were calibrated at TUBITAK UME Impedance Laboratory before measurements.

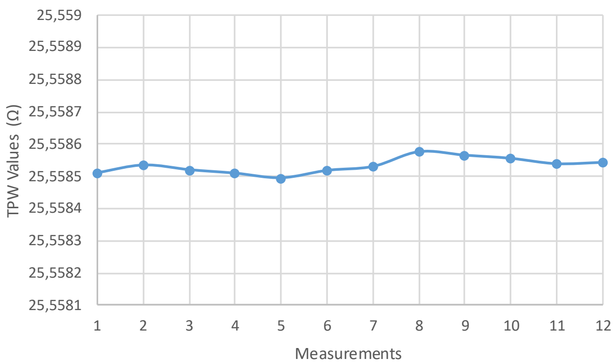

Figure 13. The four-year TPW (Triple Point of Water) values of the SPRT used in the measurements.

The uncertainty propagation related to TPW measurements was also considered as an additional parameter since SPRT calibration was of concern. The stability of SPRTs at TPW were regularly checked during the study. The uncertainty at TPW was calculated as 0.1 mK and propagated uncertainty at CO2 TP was evaluated considering the W value (Typically around 0.8) (Figure 13). Last four TPW measurements were taken during TP(CO2) measurements.

Table 2. Uncertainty Budget

Unit	**mK**
Phase Transition Realization Repeatability	0.09
Bridge (repeatability, non-linearity, AC quadrature)	0.02
Reference resistor stability	0.01
Plateau Interpretation	0.10
Chemical Impurities	0.15
Hydrostatic-head	0.03
Propagated TPW	0.08
SPRT self-heating	0.03
Heat Flux	0.02
Combined Standard Uncertainty	0.22
Expanded Uncertainty (*k*=2 level)	**0.45**

4. Conclusions

In this study, the measured Carbon Dioxide Triple Point realization temperature is determined to be 216.59055 ± 0.0005 K, with an associated expanded uncertainty (k=2) of 0.45 mK. The temperature recommended by CCT is 216.592 ± 0.001 K (BIPM 2021). The Carbon Dioxide Triple Point can be easily established in Primary Level Temperature Laboratories with basic methods (Kalemci et al. 2015, Kalemci et al. 2018). Creating the Mercury Triple Point requires complex systems and processes (Hill 1994, Kalemci et al 2009). Considering prior studies and this research, the Carbon Dioxide Triple Point can be utilized as a stable reference point instead of the Mercury Triple Point.

Declaration of Ethical Standards

The authors declare that they comply with all ethical standards.

Credit Authorship Contribution Statement

Author 1: Investigation, Methodology Study, Experimental Study, Analyses, Writing
Author 2: Investigation, Supervision, Resource, Writing, Validation
Author 3: Analyses, Methodology, Study design
Author 4: Experimental Study
Author 5: Supervision, Validation

Declaration of Competing Interest

The authors have no conflicts of interest to declare regarding the content of this article

Data Availability Statement

All data generated or analyzed during this study are included in this published article.

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