Proc. Estonian Acad. Sci. Eng., 2007, **13**, 4, 310–319

Precise temperature measurement above 1000 °C using thermocouples

Frank Edler

Physikalisch-Technische Bundesanstalt (PTB), Abbestrasse 2-12, D-10587 Berlin, Germany; frank.edler@ptb.de

Received 2 July 2007

Abstract. Thermocouples are the most widely used electrical sensors in almost all temperature measurement applications in industry and research. Different types of thermocouples and calibration methods are described. Novel metal-carbon eutectic fixed points, usable for improved calibrations of thermocouples, and first results of their application at Physikalisch-Technische Bundesanstalt are presented.

Key words: high temperature measurement, thermocouple, eutectic fixed point.

1. INTRODUCTION

The worldwide consistent temperature measurement is assured by the International Temperature Scale of 1990 (ITS-90), which extends from 0.65 K to the highest temperatures, measurable with the aid of Planck's radiation law. The ITS-90 is based on 17 temperature fixed points, to which certain temperatures are assigned. Temperatures between the fixed points are determined from the indication of standard instruments using prescribed interpolation equations [1]. Temperatures above 1234.93 K (961.78 °C) – the freezing point of silver – are, according to ITS-90, to be measured by means of radiation thermometers, whereby the relation between the measuring signals during the measurement of the unknown radiance and the radiance of a cavity is determined on the basis of the temperature of freezing silver (1234.93 K), gold (1337.33 K) or copper (1357.77 K). The unknown temperature is then calculated by means of Planck's radiation law. Simultaneously, temperatures above 1235 K are disseminated by using thermocouples, which are used for the approximation of the ITS-90 in a large temperature range up to about 2450 K.

2. TYPES OF THERMOCOUPLES

Over the years many thermocouple materials have been developed and investigated in a large number of different environments. For most applications in industry and research, a number of material combinations, forming thermocouples of known quality and performance, are available. However, their metrological characteristics can be changed as a result of different environmental influences. Therefore, the choice of a suitable thermocouple is often a compromise by considering different boundary conditions, i.e. temperature range, working atmosphere, mechanical strain and aimed measurement uncertainty.

2.1. Noble metal thermocouples

Noble metal or rare metal thermocouples are those based on platinum metals. They have relatively low Seebeck coefficients of the order of 10 to 20 μV/K, give accuracy of 0.5 K or better, and are preferred types for standard or reference thermocouples.

2.1.1. Pt-Rh alloyed thermocouples

Thermocouples of the types S (Pt/Pt10%Rh), R (Pt/Pt13%Rh) and B (Pt6%Rh/Pt13%Rh) may be used in oxidizing and inert atmospheres continuously at temperatures up to 1300 °C (types S and R) and up to 1600 °C (type B). Contamination is one of the main causes of drift, particularly in environments with metallic vapours or reducing agents. Contamination of the thermoelements by Fe and other substances from the insulator is perhaps the most significant cause of inhomogeneity in thermocouples used above 1200 °C. Rhodium oxide is produced on the alloy wires between about 500 and 900 °C, causing a decrease in the Seebeck coefficient; the oxide dissociates above 900 °C, and the Seebeck coefficient recovers. Some thermoelectric inhomogeneity can occur during the use of thermocouples. It can be observed as dependence of the electromotive force (emf) on immersion depth (measuring and reference junctions at constant temperatures).

2.1.2. Elemental rare metal thermocouples

Besides the Au/Pt thermocouple, which can be used only up to temperatures of about 1000 °C, the Pt/Pd thermocouple has received attention in recent years for most precise uses in air and inert atmospheres up to about 1500 °C. Pt/Pd thermocouples are less susceptible to thermoelectric inhomogeneity than are the Pt-Rh alloyed thermocouples because both thermoelements are pure elements. Therefore it is not affected by lattice ordering and selective volatilization and oxidation of alloy components. The achievable accuracies are by a factor of two better than by using type S or R thermocouples. Pd undergoes reversible changes in the Seebeck coefficient in the range of 550 to 800 °C, due to oxidation of the Pd or of impurities in the wire. The Seebeck coefficient recovers within some minutes by exposure of the thermocouple to temperatures above 900 °C. Irreversible changes in Pd at temperatures beyond 900 °C were found to be small compared to reversible changes. The Pd wire should not come into contact with silicious refractories as they may form a Pd-Si eutectic with a melting temperature of 816 °C that weakens the wire. The thermal expansion coefficients of Pd and Pt are different. Therefore a stress-relieving coil at the measuring junction may help to reduce stress-related changes in the Seebeck coefficient.

2.2. Base metal thermocouples

Base metal thermocouples are produced in wide varieties and great quantities. They are classified in different tolerance groups depending on their temperature – emf relationship, which are defined in different international standards, for instance EN 60 584, ASTM or NIST monograph 175. Table 1 contains names, materials and application temperatures of some common base metal thermocouples.

Especially at temperatures above 1500 °C it is difficult to find reliable thermocouples. Different types of W/Re thermocouples are the only available ones, but they cannot be utilized in air and are characterized by considerable drifts (several K) and increasing brittleness. Therefore, in most cases recalibration is not recommended, at best an in-situ calibration is possible.

3. APPROXIMATION OF THE ITS-90 BY USING THERMOCOUPLES

Leaving the guidelines of the ITS-90, less complex methods of realization and dissemination of temperatures with slightly enlarged measurement uncertainties are viable, which are tolerable in most practical applications. In the temperature range above 1000 °C, thermocouples are often used to approximate the ITS-90. The traceability to ITS-90 of the thermocouples to be calibrated is often possible only by time-consuming and metrologically complex comparison measurements against radiation thermometers in furnaces, specially developed for this purpose. Calibration at fixed points at temperatures above 1000 °C (as commonly

Table 1. Base metal thermocouples

Name	Materials	Temperature range, °C
K	Ni-Cr/Ni-Al	–200–1260
N	Ni-Cr-Si/Ni-Si	–200–1260
T	Cu/Cu-Ni	–200–370
J	Fe/Cu-Ni	0–760
E	Ni-Cr/Cu-Ni	0–870
C	W5%Re/W26%Re	0–2300

performed in the low temperature range between 0 and 1000 °C) is limited by the lack of reliable high temperature fixed points. The fixed point of the ITS-90 with the highest temperature is the freezing point of copper (1084.62 °C). Besides this fixed point, only the melting points of palladium (1554.8 °C, in Argon) and platinum (1768.2 °C) are available for a fixed point calibration at temperatures above 1000 °C. The lack of reliable fixed points results in large measurement uncertainties of the calibration of thermocouples, which are caused by interpolation and/or extrapolation uncertainties, particularly in the temperature range of highest technical interest between the freezing point of copper and the melting point of palladium.

4. EUTECTIC METAL-CARBON FIXED POINTS

The implementation of high temperature fixed points of eutectic metal-carbon or metal/carbide-carbon compounds at the end of the nineties changed the situation of the limited number of reliable fixed points for the calibration of thermometers. These new fixed points were, due to their partly high melting temperatures (up to 3185 °C, HfC-C) introduced and investigated mainly for non-contact applications [2–5]. Recently, their potential for the calibration of contact thermometers, especially of thermocouples, has been also recognized [6–8].

The estimated melting temperatures of the metal-carbon eutectics Fe-C (1154 °C), Co-C (1324 °C), Ni-C (1329 °C) and Pd-C (1492 °C) are within the temperature range between the freezing point of Cu and the melting point of Pd. Some further eutectic fixed points and their melting temperatures are listed in Table 2.

Using metal-carbon compounds as fixed-point materials in graphite crucibles reduces the risk of these materials being contaminated by the material of the crucible as the graphite is a part of the eutectic compounds. On the other hand, the chemical affinity between crucible and fixed-point materials, together with their different thermal expansions, can result in a breakage of the graphite crucibles. Therefore double-wall crucibles with rounded rough edges are used. Instead of double-wall crucibles, also C/C sheets, made of pure graphite, can be used inside of a normal graphite crucible. A photograph of a eutectic fixed-point cell and a schematic diagram of the cells used for the calibration of thermocouples at PTB are presented in Fig. 1.

Table 2. Eutectic metal-carbon and metal/carbide-carbon fixed points

Eutectic point	Rh-C	Pt-C	Ru-C	Ir-C	MoC-C	TiC-C
T_{90}, °C	1656.9	1737.9	1953.1	2291	2583	2761

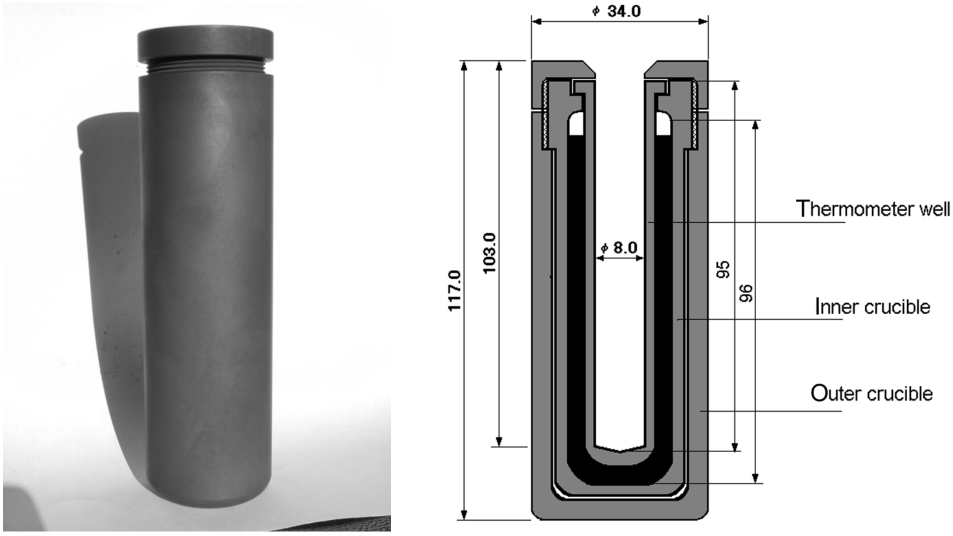

Fig. 1. Photograph and schematic diagram of a eutectic fixed-point cell.

Figure 2 shows the phase diagram of the Ni-C eutectic as a typical example of a metal-carbon eutectic system. The lowest temperature of the liquid phase is detected at the eutectic composition. Therefore additional graphite of the crucible does not cause a further decrease of the freezing temperature. Lowering the temperatures of the liquid phase, a possible excess of graphite contained in the liquid phase becomes solid at the liquidus line (point A) and the concentration of graphite in the liquid phase is decreasing. If the eutectic composition is reached during further decreasing of the temperature, at the horizontal line, 1329 °C, both components of the eutectic system – metal and carbon – start to freeze simultaneously but separately. Therefore, the solid phase consists of two single solid phases, the metal and the graphite.

In contrast to conventional fixed points of pure metals, metal-carbon eutectic fixed points are characterized by a different melting and freezing behaviour. The melting and freezing temperatures differ from each other by some tenths of a degree (depending on the material), both plateaus are less flat than the corresponding plateaus of pure metals and the freezing temperature often depends on different parameters, i.e. on the freezing rate, on the set temperature below the freezing plateau and on the heat treatment of the fixed-point cell before accomplishing the freeze. Therefore, according to an agreement among the temperature community and based on the highest reproducibility found for the inflection point of a melting curve, the corresponding emf of the inflection point of the melting curve is used to define the melting temperature of the eutectic system. The maximal emf, measured after supercooling, is taken as the freezing temperature of the eutectic compound. Figure 3 shows a typical melting and freezing curve of a Ni-C eutectic, measured by means of a Pt/Pd thermocouple.

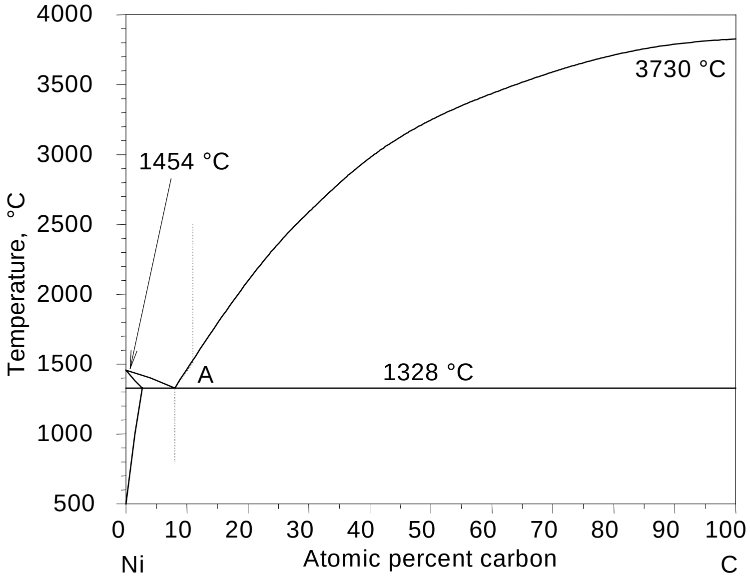

Fig. 2. Phase diagram of Ni-C eutectic.

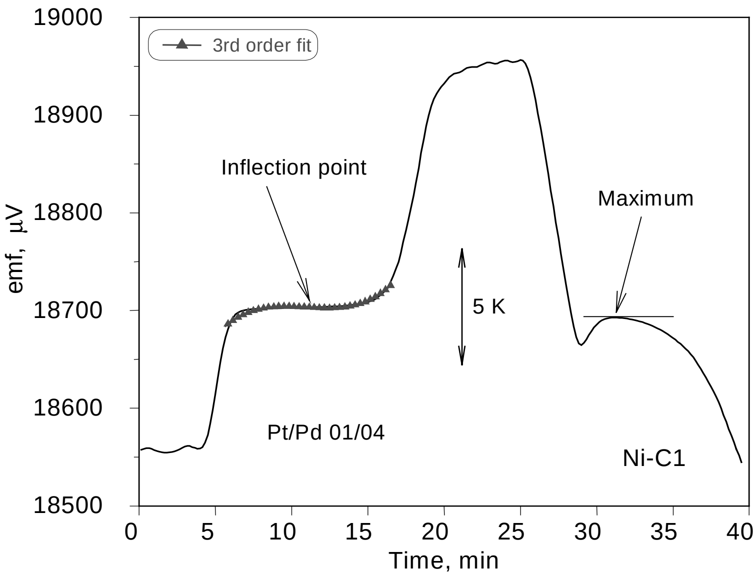

Fig. 3. Melting and freezing curves of Ni-C.

5. CALIBRATION OF THERMOCOUPLES

The calibration of thermocouples includes the measurement of their emfs at a sufficient number of known temperatures and a homogeneity test. The calibration may be performed in different ways depending on the temperature range and the required accuracy. Standard laboratory thermocouples (noble metal thermocouples) are commonly calibrated at fixed points of the ITS-90 and/or by comparison against platinum resistance thermometers in bathes (low temperature range) or against pyrometers (high temperature range). Base metal thermocouples may be calibrated by comparison with noble metal thermocouples in furnaces.

Independent of the calibration method used, the differences of the measured emfs at the calibration points from the corresponding reference function are used to calculate low order deviation functions, which, together with the reference function, describe the individual properties of the thermocouples under calibration.

By means of the new metal-carbon eutectic fixed points, the calibration of thermocouples on the basis of the fixed-point method can be extended smoothly to temperatures above 1000 °C. In this way, measurement uncertainties may be reduced by a factor of about two. Without using the novel metal-carbon fixed points, for instance, the best measurement capability of the calibration of noble metal thermocouples (types R, S, or B) is about ±0.3 °C at 1000 °C, rising to ±1.5 °C at 1500 °C and to ±2 °C at 1600 °C. This large uncertainty is due to interpolation uncertainties caused by the large temperature interval between the available calibration points, the freezing point of copper and the melting point of palladium. Furthermore, calibrations at the melting point of Pd are normally performed using the wire bridge method or miniature fixed points. This calibration technique is partly destructive and linked with high measurement uncertainties due to problems of heat flux.

Figure 4 shows the individual emf–temperature relationships (solid lines) of three type B thermocouples, which were calibrated firstly at the melting point of palladium and at the conventional fixed points of the ITS-90, Cu, Ag and Al (closed symbols). Here, the emf deviations, Δemf, at the fixed points from the reference function (zero-line) are presented. The open symbols mark the emf deviations from the reference function at the melting temperatures of the eutectic fixed points Fe-C, Co-C and Pd-C, measured following the calibration at the conventional fixed points. The variations at the Fe-C and Pd-C eutectics from the individual emf–*T* relationships of the three thermocouples are not larger than a temperature equivalence of at most 0.3 K. The emfs, measured at the melting point of Co-C, are systematically higher (between about 0.5 and 1 K) than calculated and expected using calibrations at conventional fixed points. Considering the uncertainties of the eutectic fixed point temperatures of about 0.2 to 0.3 K and the uncertainties of the determined emf–*T* relationships of about 1.0 to 1.5 K ($k = 2$) using calibration at conventional fixed points, an agreement of the results can be confirmed within these uncertainties in the temperature range between 1100 and 1500 °C.

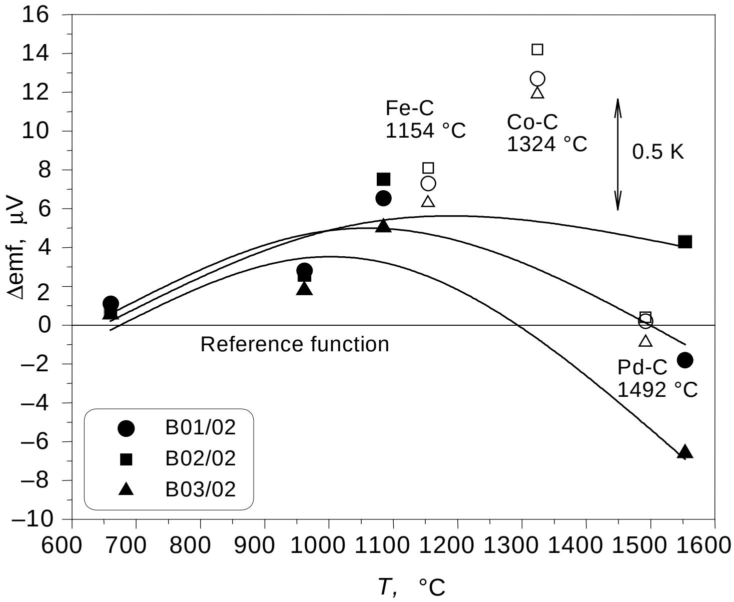

Fig. 4. Emf–*T* relationships (solid lines) of three type B thermocouples.

The benefit of the eutectic fixed points, especially for the calibration of the most stable Pt/Pd thermocouples at temperatures above 1000 °C, becomes evident if realizing that, on one hand, no conventional fixed point is available at temperatures between 1100 and 1500 °C, but, on the other hand, the upper temperature limit of Pt/Pd thermocouples is about 1500 °C. Therefore a required extrapolation to temperatures above the freezing point of copper would result in large measurement uncertainties.

Recent comparison measurements of metal-carbon fixed points, constructed for contact thermometry applications, have shown unprecedented agreement in this temperature range – within about 0.2 K – indicating that these high temperature fixed points will be able to serve as practical and repeatable standards [[9,10]]. Figure 5 shows as an example the measured emfs at the melting points of different Fe-C eutectic fixed-point cells, measured in two different high temperature furnaces by using a Pt/Pd thermocouple. The error bars mark the expanded uncertainties of the single measurements for $k = 2$.

The specification of temperature values of the different eutectic compounds, used for the calibration of thermocouples by the Consultative Committee for Thermometry, would allow the use of such fixed points for traceable calibrations. Eutectic fixed-point cells, based on metal-carbon eutectic alloys, could be used as adequate transfer standards for the dissemination of temperatures at temperatures above 1000 °C.

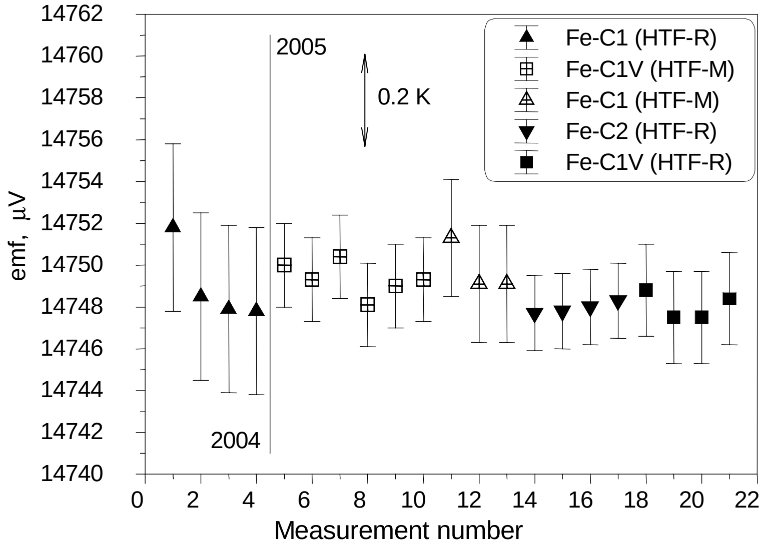

Fig. 5. Measured emfs at the melting points of different Fe-C eutectic fixed-point cells using a Pt/Pd thermocouple.

6. SUMMARY

In general, temperatures above 1000 °C may be measured with high accuracy by using noble metal thermocouples. At present, up to about 1500 °C, Pt/Pd thermocouples are the most stable and reliable thermocouples available. Measurement uncertainties of some tenth of a degree are accessible. For temperature measurements between 1500 °C and about 1750 °C, type B thermocouples are favoured (best measurement uncertainties of about 2 K). Higher temperatures can be measured only by using different types of W/Re thermocouples. Here drift effects of some tens of Kelvin can occur. Novel metal-carbon eutectic fixed points can be used for an improved calibration of thermocouples and as transfer standards for the dissemination of the ITS-90 in the high temperature range at temperatures above 1000 °C.

REFERENCES

1. Preston-Thomas, H. The International Temperature Scale of 1990 (ITS-90). *Metrologia*, 1990, **27**, 3–10.
2. Yamada, Y., Sakate, H., Sakuma, F. and Ono, A. Radiometric observation of melting and freezing plateaus for a series of metal-carbon eutectic points in the range 1330 °C to 1950 °C. *Metrologia*, 1999, **36**, 207–209.
3. Yamada, Y., Sakate, H., Sakuma, F. and Ono, A. High-temperature fixed points in the range 1150 °C to 2500 °C using metal-carbon eutectics. *Metrologia*, 2001, **38**, 213–219.

4. Yamada, Y., Duan, Y., Ballico, M., Park, S. N., Sakuma, F. and Ono, A. Measurement of Rh-C, Pt-C and Ru-C eutectic points by four national metrology institutes. *Metrologia*, 2001, **38**, 203–211.
5. Sadli, M., Fischer, J., Yamada, Y., Sapritsky, V., Lowe, D. and Machin, G. Review of metal-carbon eutectic temperatures: proposal for new ITS-90 secondary points. In *Proc. International Symposium on Thermal Measurements in Industry and Science – Tempmeko*. Cavtat-Dubrovnik, 2004 (Zvizdic, D., ed.), 2005, 341–348.
6. Yamada, Y., Sakuma, F. and Ono, A. Thermocouple observations of melting and freezing plateaus for metal-carbon eutectics between the copper and palladium points. *Metrologia*, 2000, **37**, 71–73.
7. Morice, R., Favreau, J. O., Morel, E., Megharfi, M. and Filtz, J. R. Realization of metal-carbon fixed points for application in contact thermometry at high temperatures. In *Proc. International Symposium on Thermal Measurements in Industry and Science – Tempmeko*. Cavtat-Dubrovnik, 2004 (Zvizdic, D., ed.), 2005, 847–852.
8. Kim, Y. G., Yang, I., Kwon, S. Y. and Gam, K. S. Features of Co/C and Ni/C eutectic transitions for use in thermocouple thermometry. *Metrologia*, 2006, **43**, 67–70.
9. Edler, F. and Baratto, A. C. A cobalt-carbon eutectic fixed point for the calibration of contact thermometers at temperatures above 1100 °. *Metrologia*, 2005, **42**, 201–207.
10. Edler, F. and Baratto, A. C. Comparison of nickel-carbon and iron-carbon euetectic fixed point cells for the calibration of thermocouples. *Metrologia*, 2006, **43**, 501–507.

Üle 1000 °C ulatuva temperatuuri täppismõõtmine termopaaridega

Frank Edler

On käsitletud mitmesuguste kõrgtemperatuuriliste termopaaride kasutamist tööstuses ja teadusuuringutes koos nende kalibreerimiseks kasutatavate meetoditega. Erilist tähelepanu on pööratud uudsele metall-süsinikeutektiliste punktide süsteemi kasutuselevõtule termopaaride kalibreerimisel. On toodud esmased katsetulemused, mis on saadud Physikalisch-Technische Bundesanstalti laborites Berliinis.