White Paper

Traceable Calibration of Polarimeters

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Abstract

The traceability of polarimeter calibration is crucial in order to meet current quality management requirements. We review the most relevant standards, regulations and recommendations. As a result, for lower accuracy requirements calibration with sucrose is sufficient. For higher accuracy applications quartz control plates are recommended. They have to be traceable to national standards. Currently, the Physikalisch-Technische Bundesanstalt (PTB) is the only metrological institute maintaining such a standard.

1. Introduction

Data security and traceability plays an ever increasing role for both, users and suppliers of analytical instrumentation. Today, this is particularly driven by pharmaceutical regulations, whose main aim is to make substances entering the human body as safe as possible. Also in food-, flavour- and fragrance applications traceability quickly gains importance.

In polarimetry, the foundation to quantitative analysis and common standards has been laid by sugar industry associations in close cooperation with national metrological institutes, primarily ICUMSA[1], NIST[2] and PTB[3]. With pioneering works for "polarimetric saccharimeters" carried out several decades ago, this field of research – and money to be saved by measuring accurately – continues to be of great interest.

Also in the interaction between polarimeter suppliers and customers, the traceability of calibration is a subject that demands considerable attention. The aim of this paper is to describe best practices to calibrate polarimeters in a traceable fashion and to clarify various misunderstandings frequently encountered in the market.

2. Regulations and Standards governing Polarimeter Calibration

Polarimeter calibration has been regulated by several bodies and national institutes. For the discussion it is regarded helpful to recall the most relevant regulations in the field:

2.1. ICUMSA

The ICUMSA regulates the calibration of polarimeters in SPS-1 (2009) [1]: "To meet the requirements of the statutory authorities or the trade for absolute measurements, polarimeters need to be calibrated. This is basically possible with normal sucrose solutions which can, if necessary, be diluted stepwise to check the whole measuring range.

[1] International Commission for Uniform Methods of Sugar Analysis
[2] National Institute of Standards and Technology, agency of U.S. Department of Commerce, Gaithersburg, USA
[3] Physikalisch-Technische Bundesanstalt, Braunschweig / Berlin, Germany

However, sucrose solutions are not stable measuring standards. […] Therefore quartz control plates […] are officially prescribed for the standardisation of all polarimetric sugar analyses of an Official character. Their manufacture and fixing in suitable mounts is subject to regulations. Compliance with these regulations is checked by specialised laboratories, such as for example, the PTB, and recorded on a certificate together with the optical rotation and sugar value."

"Regulations" in this context refer to OIML standards (see 2.2).

2.2. OIML

OIML R 14 states [2]: "The calibration of the saccharimetric scale with a sugar solution is easily affected by errors due, for example, to the evaporation of the solution, to its instability, and to the considerable effect of temperature on optical rotation. It is therefore recommended that quartz plates be used for the calibration and control of saccharimeters." In addition to that, various quality parameters, form, dimensions, and tolerances are defined.

2.3. Pharmacopoeias

The European Pharmacopoeia (EUP) states "The scale is usually checked by means of certified quartz plates. The linearity of the scale may be checked by means of sucrose solutions." [3].

Concerning calibration standards, the US Pharmacopoeia (USP) suggests current lots of reference dextrose and sucrose from the Office of Standard Reference Materials, NIST, and, alternatively, quartz control plates [4].

2.4. PTB

The PTB assesses the calibration with standards solutions and quartz plates with a clear preference for the latter: "Using those [standard or normal sugar] solutions as a standard for the verification of instruments, has, however, many disadvantages, e.g. degradation due to fungi and bacterial attack and an alteration in the concentration due to evaporation. Also, the polarization rotation is very sensitive to the temperature. The search for a stable substance to act as a substitution standard led to the choice of crystalline quartz which is oriented and cut in such a way that it matches the polarization rotation of a normal sugar solution, but without bringing about the drawbacks mentioned above. Its wavelength dependence of the polarization rotation is similar to sucrose, however, it is much less sensitive to temperature variation" [5].

So the PTB agrees with ICUMSA and OIML in this respect. Additional sources of error in calibration with sugar solutions not mentioned are moisture in the sugar due to storage conditions, weighing- and other errors in sample preparation.

2.5. Summary Polarimeter Calibration Standards

In summary, the main regulatory bodies recommend quartz plates for the calibration of polarimeters. Sugar solutions are also recommended, but with certain restrictions due to their instability and evaporation of water. Significantly the sugar industry itself (ICUMSA / OIML) prefers quartz control plates to sugar solutions for highly accurate polarimeter "analyses of official character". The EUP convincingly suggests to use quartz plates for the absolute check and to use stepwise diluted sugar solutions only for linearity checks.

3. Traceability to National Standards

A calibration with a reference standard is only meaningful, if the standard can be traced back to a national standard or normal, cf. VIM [6]: Traceability is "the property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties."

3.1. Traceability of Liquid Standards

A liquid standard for polarimetry generally referred to is sucrose solution. Sugar solutions have to be prepared locally for individual calibrations, as they are not stable and cannot be kept over time. For achieving traceability, it is thus required to have sucrose with a traceable specific rotation that has not absorbed moisture during storage, a traceable balance for weighing in the sucrose, sufficiently pure water, and most careful sample preparation and handling avoiding human errors, evaporation etc.

Traceable sugar is available from NIST under the trade name SRM 17f - Sucrose Optical Rotation. The certificate states an optical rotation value for a normal sugar solution of 17.305° ± 0.035° at a wavelength of 589.440 nm and 100mm optical path length [7]. This uncertainty is 35 times larger than that of PTB-certified quartz plates.

It has to be emphasized that tracing the calibration of a polarimeter to NIST sugar does not comply with the accuracy requirements of ±0.01° specified in the EUP.

3.2. Traceability of Quartz Plates

While historically quartz control plates could be certified by a number of national metrological institutes – namely PTB (GER), NIST (US), NPL[4] (UK), LNE[5] (FR) – today this service is only available from the PTB in Germany. According to our knowledge, NIST stopped calibrating quartz control plates around 2007 [8].

Prior to the measurement of the optical rotation, the PTB checks the compliance of the quality of the quartz plate with regard to OIML requirements for dimensions, optical pureness, flatness, parallelism of the faces and optical axis errors.

The calibration of optical rotation is carried out with the PTB's high precision polarimeters and certified with an extended uncertainty (k02) of ± 0.001° [9].

Fig. 1 High precision polarimeter at the PTB. Source: [9]

4. Market Misconceptions

4.1. Quartz plates are permanent standards

Historically, quartz control plates were referred to as permanent standards. This was based on the assumption that the optical properties of solids do not change over time. Mechanical damage or dirt can be a source of error, changing the optical rotation values, though.

[4] National Physical Laboratory, Teddington, UK
[5] Laboratoire national de métrologie et d'essais, Paris, France

Hence the PTB recommends a recalibration of the optical rotation after three years [10].

If a quartz plate is mounted and equipped with an internal temperature sensor, the temperature sensor also has to be recalibrated in regular intervals. Typical intervals for temperature sensor recalibrations are one year.

4.2. NIST Traceability of Quartz Plates

Some suppliers of polarimeters and quartz plates emphasize the NIST traceability of their quartz plates. However, the NIST stopped calibrating quartz plates around 2007. So the NIST traceability can a) refer to a certificate which is as per 2015at least eight years old or b) refer to NIST sugars.

a) According to the recommendation of the PTB, the only national institute currently capable of calibrating quartz plates, a recalibration should be done after three years. Consequently, by today's standards, an eight year-old quartz plate certificate is outdated and therefore not traceable.

b) The second possible traceability path via NIST sugar leads to an uncertainty of ± 0.035° (at 589 nm, 100mm path length and 20°C). This is by far too inaccurate to calibrate today's polarimeters up to their typical instrument specification of ±0.002° in the absolute value of the optical rotation. Neither does the achievable accuracy meet the requirements of EUP, OIML or ICUMSA.

5. Conclusion and Recommendation

Following the above arguments, we are convinced that for calibrating polarimeters to state-of-the-art accuracies and to the requirements by EUP, ICUMSA and OIML the only traceability path leads to PTB certified reference quartz plates.

In contrast to historical believe, Quartz plates are today no longer regarded as permanent standards with indefinite lifetime. Currently the PTB is the only national metrological institute offering competence and advice concerning quartz plates; PTB suggest recalibration after three years in order to maintain traceability. Hence quartz plates exceeding a recalibration interval of three years cannot be regarded traceable.

In case suppliers of polarimeters and quartz plates claim NIST traceability of their quartz plates, we strongly advise to demand a seamless documentation of the traceability path including corresponding certificates. If certificates do not contain recalibration intervals, the calibration cannot be regarded state-of-the-art. In this case we recommend re-establishing traceability with PTB-certified quartz plates.

References

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