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REACHABLE ACCURACY AND PRECISION FOR TRITIUM MEASUREMENTS BY CALORIMETRY AT TLK

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At Tritium Laboratory Karlsruhe (TLK) calorimetry is used as the primary method for tritium accountability and for samples ranging from micrograms to tens of grams. An accuracy of 0.3% is achievable for samples containing more than 0.5 mg tritium and the precision of each calorimeter is better than 0.5%. The results of the TLK calorimeters vary within maximum 0.6% from each other.

I. INTRODUCTION

Inside a tritium laboratory, calorimetry is an important analytical method as it is the only absolute method for determination of tritium. Because it is based on the measurement of the heat generated by the radioactive decay, the result is independent from the chemical and physical form of the sample. Another advantage is that the calibration does not require a certified tritium source. Ideally, the only uncertainty should come from the decay heat of tritium which is approx. 0.3% (Ref. 1). Therefore, at TLK calorimetry is used as the primary method for the tritium accountancy. Among the analyzed samples are gaseous mixtures from tritium reprocessing experiments, liquid tritiated water and solid materials such as samples of wall materials from experimental fusion reactors or clothes from decontamination operations.

At TLK four calorimeters are in operation², one of power compensation isothermal type (ANTECH) and three of inertial guidance controlled quasi-isothermal type³ (IGC). They were specially designed and built to allow the measurement of samples containing from $3.09 \cdot 10^{-6}$ to 30.86 g tritium. This corresponds to an activity of 10^9 to 10^{16} Bq. The specifications of these calorimeters are shown in Table I.

TABLE I. Specifications of calorimeters at TLK

| Calorimeter | Year | Volume (l) | Dynamic range (W) |
|-------------|------|------------|----------------------------------|
| ANTECH | 1995 | 1.2 | $1 \cdot 10^{-3} - 5 \cdot 10^0$ |
| IGC-A | 1998 | 0.5 | $1 \cdot 10^{-5} - 5 \cdot 10^0$ |
| IGC-V0.5 | 1999 | 0.5 | $1 \cdot 10^{-6} - 1 \cdot 10^1$ |
| IGC-V25 | 2002 | 20.6 | $5 \cdot 10^{-6} - 5 \cdot 10^0$ |

A comprehensive work has been carried out in order to recalibrate each calorimeter and determine the accuracy over the whole measurement range. In addition, a series of measurements with various tritium containing samples was performed to determine the reproducibility of the measurements for each calorimeter. Finally, a comparison was made between the results of all the TLK calorimeters.

II. CALIBRATION OF TLK CALORIMETERS

II.A. Description of the Calorimetric Measurement

An isothermal calorimeter measures the thermal power generated by a sample placed inside the calorimeter cup. This thermal power is transformed by thermopiles in an electrical signal, which is the measured signal. In order to evaluate a sample, a blank is needed, too. The blank is represented by the measurement of the empty calorimeter cup and the recorded signal represents the base line.

A continuous calibration sequence is presented in Fig. 1. The base line measurements alternate with the calibration measurements. Only the last approx. 12 hours of each measurement were shown, after the calorimeter reached a quasi-steady state when the signal was stable. However, it can take even couple of days until such a steady state could be reached.

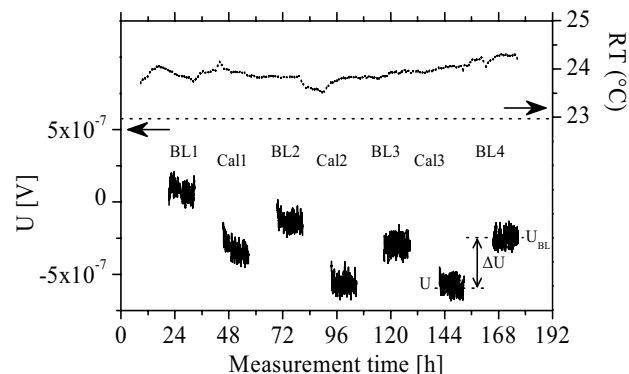


Fig. 1. Continuous calibration sequence for IGC-V0.5 at 10^{-6} W, calorimeter signal (bottom, only quasi-steady state values) and room temperature (up)

For the TLK calorimeters a signal is considered stable if the drift is less than $3 \cdot 10^{-8}$ V over the last 8 hours of measurement. In the given laboratory conditions it was seen that the temperature can vary sometimes with more than 1°C within one day. This temperature change could influence significantly the quality and the duration of a measurement. Therefore, in order to verify the stability of the calorimeter the base line is recorded before and after each measurement.

The sample signal, ΔU [V], is the difference between the measured signal, U [V], and the base line, U_{BL} [V]:

$$\Delta U = U - U_{BL} \quad (1)$$

II.B. Description of the Calibration Procedure

In order to calculate the amount of tritium inside a sample, it is necessary to convert the electrical signal into thermal power. Therefore a calibration operation is needed. The calibration doesn't require a tritium source, but some electrical components such as resistors, voltmeters and a current source. The calibration covers a range from 10^{-6} to 7.5 W, according to the specifications of each calorimeter.

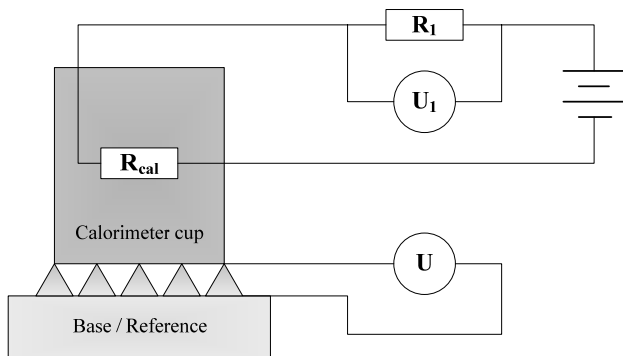


Fig. 2. Simplified schematic representation of the calorimeter calibration and measurement equipment

Each TLK calorimeter has its own onboard calibration setup (see Fig. 2). The required calibration power is generated as the result of passing an electrical current through the resistor R_{cal} [Ω]. The reference current is determined by measuring the voltage drop, U_1 [V], across the resistor R_1 [Ω]. The calibration power, P_{cal} [W], is calculated as shown below:

$$P_{cal} = R_{cal} \cdot \left(\frac{U_1}{R_1} \right)^2 \quad (2)$$

The calibration factor at a certain thermal power, $CF^{(P)}$ [$\text{W} \cdot \text{V}^{-1}$], represents the ratio between the calibration power, P_{cal} [W], and the sample signal, ΔU [V]:

$$CF^{(P)} = \frac{P_{cal}}{\Delta U} \quad (3)$$

Using linear regression, a global calibration factor, CF [$\text{W} \cdot \text{V}^{-1}$], can be determined for the whole measurement range of the calorimeter:

$$CF = a + b \cdot P \quad (4)$$

where a [$\text{W} \cdot \text{V}^{-1}$] is the theoretical value of the calibration factor at 0 W and b [V^{-1}] is the slope of the curve.

Knowing the calibration parameters and the sample signal, the thermal power a sample, P [W], can be calculated from the equality between Eq. (3) and (4):

$$P = \frac{a \cdot \Delta U}{1 - b \cdot \Delta U} \quad (5)$$

The decay heat of tritium is $0.3240 \pm 0.0009 \text{ W} \cdot \text{g}^{-1}$ (Ref. 1). The mass of tritium inside a sample, m [g], for which the thermal power was calorimetrically determined, is:

$$m = \frac{P}{0.324} \quad (6)$$

II.C. Determination of Accuracy

The accuracy of the measurement is directly related to the accuracy of the electrical components and measuring devices used for calibration. However, disturbances due to environmental changes have to be considered. Of great importance is the influence of the room temperature. The TLK calorimeters are to be operated at a stable room temperature between 20 and 25°C . A lower temperature will cause a significant increase of the measurement time and a higher temperature will make the calorimeters inoperable. It was observed that the temperature should not vary more than 0.5°C over 8 hours. A higher temperature variation over a short period of time will drive the calorimeters out of the steady state, resulting in an unstable signal. The stability of the base line before and after the measurement is very important, especially for low thermal powers (as seen in Fig. 1). Therefore, the base line value, U_{BL} [V], used for calculation is the average of the values before and after sample measurement.

For small power ranges (below 10^{-4} W) it was observed that even a difference of a few tenths of microvolts between the base line values before and after the measurement has a dramatic influence on the final result. Therefore, a measurement is to be accepted only if the absolute difference between the base line values before and after the measurement is less than 20% of the sample signal, ΔU . If this condition is not fulfilled the

measurement is not accepted. As a consequence, the first two calibration measurements shown in Fig.1 can not be accepted.

The uncertainties of the measurement signal, $\delta_U [V]$, and of the base lines before and after the measurement have been determined from the technical specifications of the voltmeters used to measure the signals. The overall uncertainty of the base line, $\delta_{BL} [V]$, has been determined for the average value of the base line, $U_{BL} [V]$. As a consequence, the sample signal has an uncertainty, $\delta_{\Delta U} [V]$:

$$\delta_{\Delta U} = \sqrt{(\delta_U)^2 + (\delta_{BL})^2} \quad (7)$$

The uncertainty of the calibration power, $\delta_{P_{cal}} [W]$, is dependent on the uncertainty of the calibration resistor, $\delta_{R_{cal}} [\Omega]$, the uncertainty of the voltage drop U_1 , $\delta_{U1} [V]$, and the uncertainty of the resistor R_1 , $\delta_{R1} [\Omega]$:

$$\delta_{P_{cal}} = P_{cal} \cdot \sqrt{\left(\frac{\delta_{R_{cal}}}{R_{cal}}\right)^2 + \left(\frac{2 \cdot \delta_{U1}}{U_1}\right)^2 + \left(\frac{2 \cdot \delta_{R1}}{R_1}\right)^2} \quad (8)$$

The uncertainty of the calibration factor for a certain calibration power, $\delta_{CF}^{(P)} [W \cdot V^{-1}]$, is:

$$\delta_{CF}^{(P)} = CF^{(P)} \cdot \sqrt{\left(\frac{\delta_{P_{cal}}}{P_{cal}}\right)^2 + \left(\frac{\delta_{\Delta U}}{\Delta U}\right)^2} \quad (9)$$

The uncertainty of the calibration factor, $\delta_{CF} [W \cdot V^{-1}]$, also refers to the absolute difference between the measured $CF^{(P)}$ from Eq. (3) and fitted CF at the same power, from Eq. (4):

$$\delta_{CF} = \delta_{CF}^{(P)} + |CF^{(P)} - CF| \quad (10)$$

The uncertainty of the sample power, $\delta_P [W]$, can be determined from Eq. (3) using δ_{CF} from Eq. (10):

$$\delta_P = P \cdot \sqrt{\left(\frac{\delta_{CF}}{CF}\right)^2 + \left(\frac{\delta_{\Delta U}}{\Delta U}\right)^2} \quad (11)$$

The uncertainty in the determination of the tritium content, $\delta_m^{(P)} [g]$, can be calculated from Eq. (6) using the uncertainty of the decay heat for tritium¹:

$$\delta_m^{(P)} = m \cdot \sqrt{\left(\frac{0.0009}{0.3240}\right)^2 + \left(\frac{\delta_P}{P}\right)^2} \quad (12)$$

Experimentally, it was found for all calorimeters a linear correlation of the uncertainty in the determination of the tritium content (accuracy of the measurement), $\delta_m [g]$, against the tritium content in the sample:

$$\delta_m = r + s \cdot m \quad (13)$$

where $r [g]$ is the minimum achievable accuracy and s represents the slope of the accuracy curve.

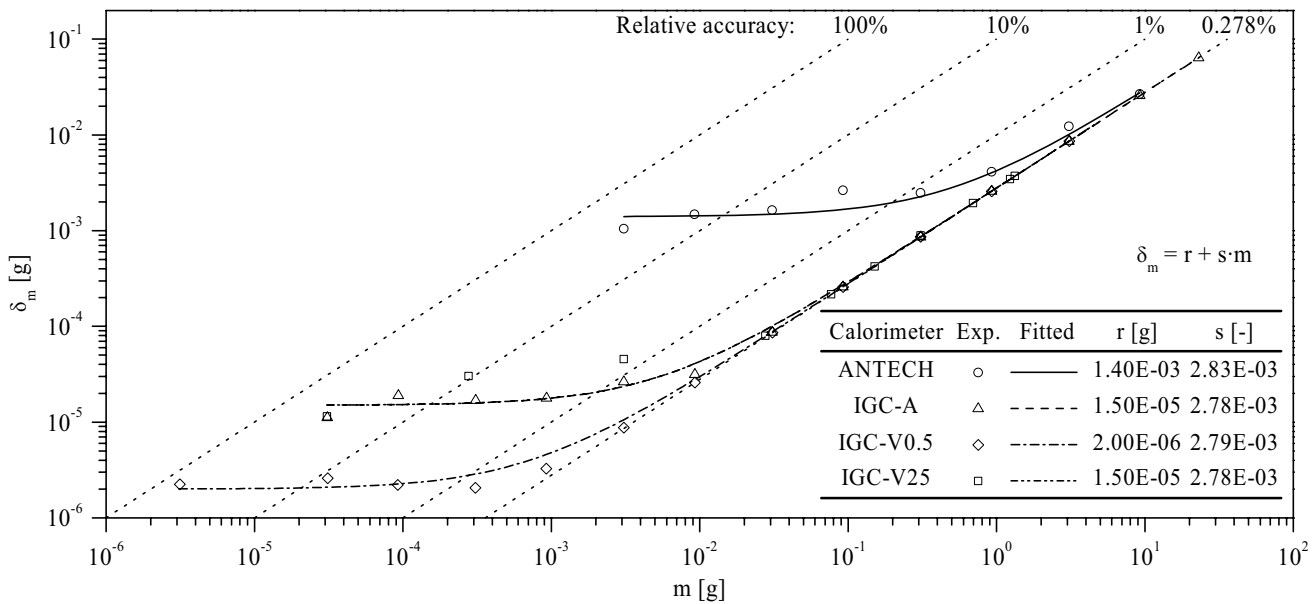


Fig. 3. Accuracy of the TLK calorimeters: markers – experimental values, lines – fitted values according to Eq. (13). Relative accuracy in percentage represented by dotted lines from 100% to the theoretical achievable minimum value of 0.278%

More calibration measurements were made in order to determine the calibration factors and also the curves for the uncertainty of the calibration factors. The resulted values were then used to determine the accuracy. In Fig. 4 the accuracy is shown as the as a function of the tritium mass. It can be observed that for tritium amounts below 10^{-5} g the accuracy is in the same order of magnitude as the sample mass. However, the accuracy is improved drastically as the measured tritium amount increases. For samples containing more than 0.5 mg of tritium, a relative mass uncertainty of 0.3% is achievable using IGC-V0.5, close to the uncertainty of the decay heat of tritium.

III. REPRODUCIBILITY OF MEASUREMENTS AND COMPARISON BETWEEN CALORIMETERS

Two uranium getter beds, UTB 4065 containing approx. 31 mg and UTB 5009D containing approx. 2.3 g tritium, were measured several times in each calorimeter in order to determine the reproducibility of the measurements, which gives information about the precision of the calorimeters. In Table II and III the measurement results are shown, after correction due to tritium decay. The terms average, accuracy, trueness and precision are used according to ISO 5725-1:1994.

TABLE II. Calorimetric measurements of UTB 4065

| Measurement | Tritium content [mg] | | | |
|---------------|----------------------|-------|----------|---------|
| | ANTECH | IGC-A | IGC-V0.5 | IGC-V25 |
| 1 | 31.83 | 30.81 | 31.10 | 30.98 |
| 2 | 31.77 | 30.80 | 31.10 | 30.99 |
| 3 | 31.00 | 30.85 | 31.16 | 31.21 |
| 4 | 31.06 | 30.86 | 31.17 | - |
| 5 | 30.64 | 30.89 | 31.20 | - |
| Average | 31.26 | 30.84 | 31.14 | 31.06 |
| Trueness | 1.54 | 0.10 | 0.09 | 0.10 |
| Precision | 0.52 | 0.04 | 0.05 | 0.13 |
| TLK average | 31.08 | | | |
| TLK deviation | 0.18 | | | |

TABLE III. Calorimetric measurements of UTB 5009 D

| Measurement | Tritium content [g] | | | |
|---------------|---------------------|-------|----------|---------|
| | ANTECH | IGC-A | IGC-V0.5 | IGC-V25 |
| 1 | 2.316 | 2.284 | 2.301 | 2.295 |
| 2 | 2.307 | 2.281 | 2.302 | 2.298 |
| Average | 2.311 | 2.283 | 2.302 | 2.296 |
| Trueness | 0.008 | 0.006 | 0.006 | 0.006 |
| Precision | 0.007 | 0.002 | 0.001 | 0.002 |
| TLK average | 2.298 | | | |
| TLK deviation | 0.012 | | | |

In addition, for each calorimeter the average value, the trueness (accuracy determined using the average measured value) and the precision (standard deviation of

the results around the average value) are shown. Also, the TLK average (mean value of the results from all four calorimeters) and the TLK deviation (standard deviation of the results around the TLK average value) are shown.

For both getter beds the precision of each calorimeter was better than 0.5%, except the ANTECH calorimeter for which the precision in the case of UTB 4065 was 1.6%. Nevertheless, the comparison of the results between calorimeters showed a very good agreement. A variation of 0.6% at most between the calorimeters results was observed after the correction due to tritium decay.

IV. SUMMARY AND CONCLUSIONS

An investigation was made in order to determine the reachable accuracy and precision of the existing calorimeters at TLK.

It was observed that the calibration and measuring devices influence the accuracy. Also temperature variations over short periods of time can influence the stability of the calorimeter during measurements.

Around the lowest detection limit a lower accuracy was observed for each calorimeter. However, increasing the thermal power improved significantly the accuracy, up to 0.3%.

More measurements were made using tritium getter beds in order to determine the precision of the calorimeters. A good reproducibility was observed and the comparison of the results between calorimeters showed a very good agreement.

In summary, accurate and precise measurements of samples containing very small amounts of tritium (independently of sample physical and chemical form) are possible at TLK using the existing calorimeters. Therefore, one of the basic requirements for the operation of a tritium laboratory is fulfilled.

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