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Specific heat of selected graphites used in calorimetry of electron beam and its influence on the accuracy of measurement of large dose

Przemyslaw P. Panta, Wojciech Głuszewski

Abstract Calorimetry is applicable to both absolute calibration of routine dosimeters and absolute measurements of electron beam (EB) intensity (for industrial radiation processing). Advantages of graphite as the absorbing calorimetric material are a good heat capacity and negligible heat defect of this material. Knowledge of the specific heat capacities of the calorimetric core materials is fundamental in making absolute dose measurements. Two kinds of high-purity graphite used in calorimeters were analysed, i.e. Union Carbide grade AGOT and nuclear grade graphite [10]. There are some differences of specific heat of these graphites, up to 2% , which influence dosimetric response of calorimeters made of them.

Key words radiation processing • radiation sterilization • electron beam (EB) • high dose calorimetry • calibration • electron energy

P. P. Panta, W. Głuszewski✉
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warszawa, Poland,
Tel.: +48 22-8112347, Fax: +48 22-8111532,
E-mail: gluszew@ichtj.waw.pl

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Introduction

Energy absorbed in calorimetric materials such as graphite can be measured directly in terms of fundamental energy unit (usually in J/kg or kGy). Measurement accuracy depends on the energy absorption rate. With high rate characteristics of modern electron accelerators (10 kW), accuracies of 1–2% are obtainable with moderately simple apparatus and techniques. Design and use of calorimeters for heat measurements have been adequately discussed. The same principles apply to high-energy radiation absorption measurements.

In brief, the energy absorbed by a calorimeter is determined by measurement of the temperature rise of the calorimeter body (in other words – core). For graphite, for which the specific heat capacity is known, no calibration of the graphite calorimeter is needed [2]. First of all precautions are necessary to ensure that the temperature throughout the calorimetric body is as uniform as possible, particularly if the distribution of energy absorption is not uniform. Thus, liquids must be stirred, and solids must have high thermal conductivity. Secondly, it is necessary to ensure that heat exchange with the calorimeter surroundings is either negligible or known. Finally, it is frequently necessary to apply corrections for absorbed energy that is not converted to heat (so-called heat defects or thermal defects). Two types of calorimeters are most commonly used: quasi-adiabatic (or semi-adiabatic) and compensated.

Quasi-adiabatic calorimetry requires that heat transfer to or from the calorimeter be negligible. Convective heat transfer is reduced by surrounding the calorimeter with foamed plastic insulation. This method also reduces conduction loss. Conduction loss is further

reduced by using a thin wire for electrical connection to the external apparatus. In some calorimeters, radiation loss can be reduced by providing the calorimeter with a low emissivity surface and surrounding the calorimeter with a similar low emissivity radiation shield. Not all of these measures are necessary simultaneously. A quasi-adiabatic calorimeter that has been proposed as a primary standard for the absorbed dose measurement was under development at the US NBS (now NIST) and next at the UK NPL. The ICRU Report No. 35 [5] recommends a calorimeter to make absolute dosimetric measurements of high energy electron beams. In ASTM-E 1631 [2] high purity graphites are considered as calorimetric materials suitable to make standard and routine-dosimeters.

General aspects of calorimetric dosimetry for eb radiation processing

Calorimeters are considered to be primary dosimeters, because it is not usually necessary to calibrate them with another radiation measuring instruments [8]. Most chemical and solid state dosimeters, as well as most ionization chambers, require calibration in a known radiation field. The principle of operation of the calorimeter is simple. The total amount of energy that is deposited as heat inside a thermally insulated mass is measured. This measurement of the energy per unit mass yields the absorbed dose directly.

For a graphite calorimeter, the radiation induced reactions (both endo- and exothermic) are negligible [11], the deposition of the energy will totally transform into heat to be measured accurately by the balance of absorbed thermal energy. Then, the absorbed dose, D is expressed as:

$$\int dD = km \int_{T_0}^{T} C_p(T)dT \tag{1}$$

where: C_p – specific heat capacity of used graphite; dT – radiation induced increase in temperature (detected with a small calibrated thermistor embedded in the graphite core); k – correction coefficient (taking into account some different factors); m – mass of calorimetric core.

The cross-section of the Institute of Nuclear Chemistry and Technology (INCT) disc graphite calorimeter is shown in Fig. 1.

Proposed differential equations of heat transfer in disk (short circular finite cylinder) are as follows:

Steady state

$$\frac{\partial^2 T}{\partial r^2} + \frac{1\partial T}{r\partial r} = \frac{q(r)}{\lambda_1} + \frac{\alpha}{\lambda_1 d_1 + \lambda_2 d_2} T \tag{2}$$

Unsteady state

$$\frac{\partial^2 T}{\partial r^2} + \frac{1\partial T}{r\partial r} = \frac{q(r)}{\lambda_1} + \frac{\alpha}{\lambda_1 d_1 + \lambda_2 d_2} T = \frac{dT}{d\tau} \tag{3}$$

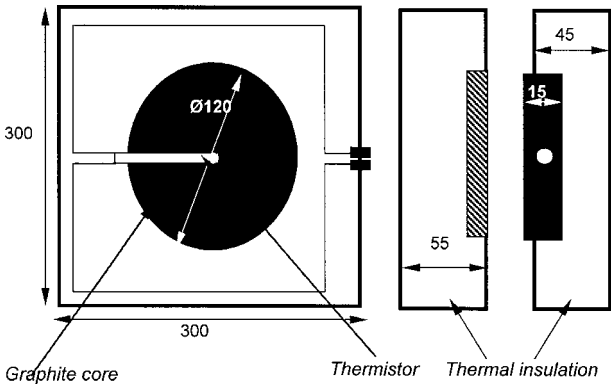

Fig. 1. The INCT calorimeter is made of high purity-nuclear grade graphite with a density of 1.69 g/cm^3. The core is a disk, 12 cm in diameter, and 1.5 cm thick. The graphite core with a small thermistor was placed in the expanded polystyrene insulation at least 5 cm thick on all sides.

where: T – temperature, K; τ – time, s; q – radiation induced thermal power, W; r – radius of calorimeter core, cm; λ_1 – heat conductivity of graphite, J/cm·s·deg; λ_2 – heat conductivity of expanded polystyrene, J/cm·s·deg; α – overall heat transfer coefficient (insulation – air), J/cm^2·s·deg; d_1 – thickness of graphite core, cm; d_2 – thickness of insulation, cm.

These equations can be solved numerically, see Fig. 2.

Specific heat capacity of high purity graphites

The theoretical description of solids was made by Debye [4]. The Debye theory considers the specific heat of solids as due to the thermal vibrations of the crystal lattice, and the molar heat capacity, C_v, is given by this theory in terms of the Debye temperature, Θ, the relation being:

$$C_v = 3 \cdot N_A \cdot k \cdot f(\Theta/T) \tag{4}$$

where: $f(\Theta/T)$ – the Debye function (which is tabulated); N_A – the Avogadro's number; k – the Boltzmann

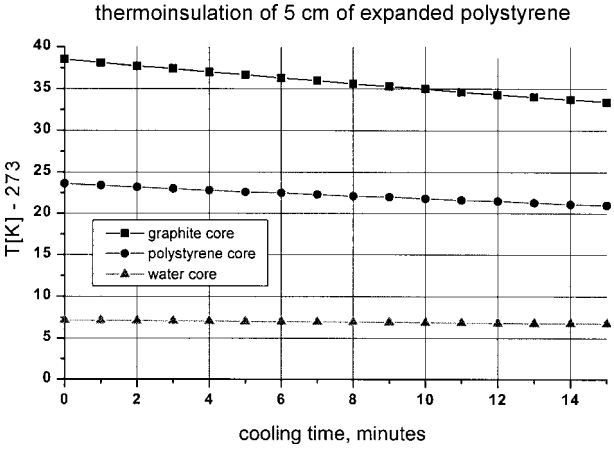

Fig. 2. Cooling curves of calorimetric cores after the dose of 30 kGy.

constant; Θ – the characteristic temperature of a given solid; T – temperature, K.

At high temperatures, this relation leads to the Dulong-Petit law, $C_v \approx 3R = 24.9435$ J/K·mol (or 6 cal/K·mol). An important feature of the Debye theory is that only a single parameter, Θ, is required to characterize a material. By choosing the temperature scale properly, all heat capacity data can be fitted to a single universal curve [9, 12].

There are significant discrepancies in the opinion of different authors about the value of graphite Debye temperature (i.e. from 760 to over 1000 K) [4]. The best fitting of theoretical Debye's curve to experimental results occurs to the Θ value at about 1500 K.

Some interesting classical works were devoted to study the specific heat of graphite in the fifties of the last century [3, 6, 7]. In the case of high-purity Acheson graphite, these results are very close to the present values.

According to ASTM [2], the value of specific heat capacity of various types of graphites of 2.86T-136.68 (kg/J·C) is recommended in the range of 273 to 333 K.

This value must, however, not be considered as universal value. For the nuclear grade graphite, the ASTMC [1] proposes that the following complex equation may be used for the temperatures between 300 and 3000 K as follows:

$$(5)\quad C_{p\text{graphite}} = 8.1353\times 10T^{-2} - 6.2119\times 10^{5}T^{-1} + 1289.2 + 2.6326T - 2.5559\times 10^{-3}T^{2} + 1.2376\times 10^{-6}T^{3} + 2.9593\times 10^{-10}T^{4} + 2.7904\times 10^{-14}T^{5}\ \text{[J/kg·K]}$$

$$300\ \text{K} < T < 3000\ \text{K}\ (\pm 0.1\%).$$

In the working calorimetric range of 273 to 333 K (0 to 60°C), it can be approximated by a simple, parabolic expression:

$$(6)\quad C_{p\text{graphite}} = -0.0011T^{2} + 3.25T - 163$$

The specific heat of the nuclear grade graphite used in this study has been measured as a function of temperature at the Warsaw Technical University, Poland. Measurements were made using the technique of differential scanning calorimetry and the obtained data agree with the above parabolic formula.

In Fig. 3, are shown the values of specific heats of reactor grade graphite [12] and of other kinds of pure graphites [2]. One can see that the differences are of about 2%. These differences should be taken into account in the case of comparative measurements with the use of calorimeters made of such kinds of graphites.

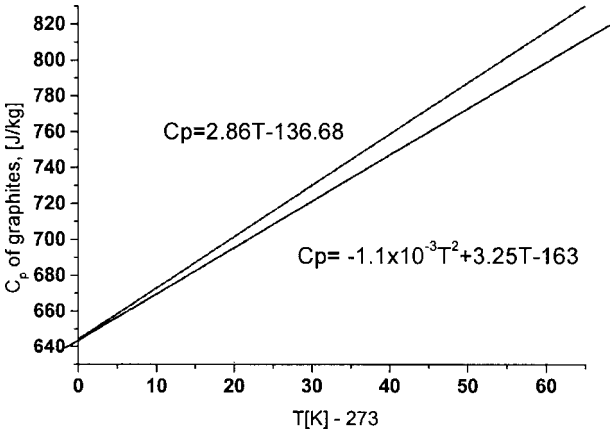

Fig. 3. Comparison of the specific heat capacity of different kinds of graphite.

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