

The Heat Defect In The PTB Water Calorimeter: A Discussion On Uncertainty

A. Krauss and H.-M. Kramer

Physikalisch-Technische Bundesanstalt, Braunschweig, Germany

Abstract

Inside the PTB water calorimeter, the so-called H₂-system (i. e. water saturated with H₂ gas) is used for dose measurements. Model calculations for the radiolysis of this system predict a stationary state with a zero heat defect, independent of dose rate or accumulated absorbed dose. The results of calorimetric measurements using the H₂-system over a large dose range are in accordance with a constant response. The questions arise if the heat defect can be assumed to be zero and if a reasonable value for the standard uncertainty of heat defect can be given.

1. Introduction

The heat defect is one of the most important influence quantities in the water calorimetric determination of absorbed dose to water, D_W . The heat defect is due to radiation-induced chemical reactions in the water and is determined as the relative difference between the absorbed radiation energy and the energy appearing as heat in the calorimeter. Inside the plane-parallel detector vessel of the PTB water calorimeter, the design and performance of which have been described previously [1, 2], the so-called H₂-system (i.e. high purity water saturated with H₂ gas) is used. Model calculations [3, 4, 5] for the radiolysis of this system predict a stationary state with a zero heat defect, independent of dose rate or accumulated absorbed dose. Comparisons between the results of calorimetric experiments and the corresponding model calculations for the H₂-system as well as for the H₂/O₂-system [6], lead to the conclusion that the response of the PTB water calorimeter can be adequately described on a theoretical basis. Therefore, with the assumption that the heat defect for the H₂-system is zero, in the preliminary uncertainty budget for the determination of D_W in ⁶⁰Co-radiation under reference conditions no separate uncertainty contribution for the heat defect has been given besides the statistical standard uncertainty for a calorimetric experiment [1]. This led to some misunderstandings and criticism, and at an IAEA symposium in 2002 it was suggested to adopt a generally accepted consensus uncertainty estimate for the heat defect in water calorimeters [7].

In this paper, the different points of view regarding the uncertainty of the heat defect in water calorimeters are discussed in general. Based on additional experimental data for the PTB water calorimeter, possible influences regarding a deviation to the assumed zero heat defect for the H₂-system in the PTB water calorimeter are discussed in depth.

2. Uncertainty for the heat defect

The most extensive work on the subject of radiolysis and heat defect has been made by Klassen and Ross [3,4,5] at the NRC (National Research Council, Canada). By investigating the radiolysis of different systems such as pure water or water saturated either with H₂ or with an almost equal mixture of H₂ and O₂, and by performing the corresponding calorimetric measurements for these systems, it was shown that the maximum deviation between the calculated heat defects and the measured relative differences was about 0.3 % [5]. This value was accepted as the uncertainty for the heat defect in the NRC water calorimeter [8] and was similarly adopted by other authors [9, 10] for their water calorimeters. It was also shown that

the calculated heat defects for pure water and H₂-water should be zero and that both systems reach a stationary state after a small pre-irradiation dose.

For H₂-water the predictions of the radiolysis model are largely independent of the various model parameters, for example reaction rates of the different chemical reactions used in the model or G-values of the primary species. Therefore, no model-based value for the uncertainty of the heat defect for these systems can be given. This is in contrast to the H₂/O₂-system, where the calculated heat defect depends on the model parameters as well as on the dose rate, the accumulated dose and the method of analyzing the corresponding calorimetric measurement [3]. The deviation of 0.3 % observed between measurement and calculation can therefore also be attributed to the uncertainties of the radiolysis model for the H₂/O₂-system. But it cannot equivalently be used as the uncertainty for the heat defect for pure water or H₂-water when one of these systems is actually used in the water calorimeter.

This point of view is supported to some extent by the conclusion given in the latest NRC publication [4] that the uncertainty of the predicted heat defect for pure water and H₂-water would be within 0.1 % if the water in the calorimeter were as pure as the water in the model. However, assuming that the water in the calorimeter is as pure as in the model (i.e. the system reaches a stationary state) would consequently mean that the uncertainty of the predicted heat defect is zero.

As the heat defect cannot be determined in absolute terms from the calorimetric experiments, the question remains whether there are experimental evidences that the water in the calorimeter does not behave like the model water during irradiation. In the case of H₂-water, for example, small amounts of oxygen leaking into the detector vessel can cause a significant change in the response of the calorimeter. Generally, the oxygen concentration in this case as well as other impurity concentrations in the water which could affect the heat defect may depend on the individual detector design and on the preparation and filling procedure of the detector vessel. Therefore it seems to be evident that everyone carrying out absolute dose measurements by means of a water calorimeter has to investigate the heat defect for the specific system actually being used in the calorimeter. This is the same, as everyone has to determine the individual correction factors, as an example for heat conduction effects, which depend on the individual calorimeter geometry and the individual measurement procedure. Consequently, from this point of view it seems not to be reasonable to adopt a consensus uncertainty estimate for the heat defect.

3. Experimental data for the H₂-system

3.1. Single experiment

Newly prepared detectors of the PTB water calorimeter initially contain the H₂/O₂-system with a concentration ratio of hydrogen to oxygen greater than 10. The response of this system, which shows a pronounced dependence on the accumulated absorbed dose over about 230 Gy, is taken as a check for the preparation method and the water quality [6]. After this pre-irradiation the radiation chemistry in the detector is characterized by the pure H₂-system with a stable response for all following irradiations. As an example, fig. 1 shows the result of a calorimetric experiment performed over a dose range of about 1.2 kGy (after the pre-irradiation) with successive 120 s irradiations. The relative standard uncertainty of the single measurements and of the mean value is about 0.9 % and 0.03 %, respectively and is mainly due to the low dose rate of the ⁶⁰Co-γ-source used for the experiments. Any long-term change of the calorimeter response with accumulated absorbed dose could be ascribed to a change of

the heat defect. However, the corresponding slope of a linear fit to the data of Fig. 1 is about 8×10^{-5} % per Gy with a relative estimated standard uncertainty of 90 %.

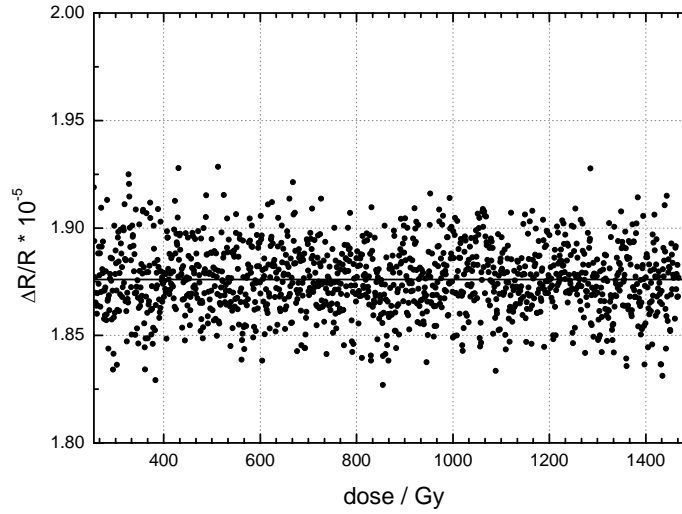


Figure 1. Relative resistance change of the thermistors as a function of absorbed dose for the H_2 -system during 120 s irradiations over a dose range of 1.2 kGy. The solid line indicates the mean value of the single measurements.

To analyse the data for the existence of short-term variations of the heat defect, the moving average over a certain dose range has been investigated. As the lowest dose range used for an calorimetric experiment is about 75 Gy (see section 3.2), the moving average over such intervals has been calculated and compared to the corresponding moving averages of several random distributions having the same standard uncertainty. The resulting distributions of the calculated mean values have a standard uncertainty of about 0.1 % both for the random data and for the data of Fig. 1. No evidence has been found for systematic changes of the moving average with accumulated dose, which could not be explained as pure statistical effects.

A further method of analyzing the data is to determine the so-called Allan variance. The Allan variance was initially introduced to solve the problem of characterizing the frequency stability of oscillators [11] but can similarly be used to investigate the underlying noise of a sample of experimental data [12], although the method is not sensitive to long-term linear drifts. The Allan variance is given as one half of the average over the sum of the squares of the differences between successive values of moving averages over a sampling interval of length τ .

$$\sigma^2(\tau) = \frac{1}{2(N-2\tau-1)} \sum_{i=1}^{N-2\tau+1} [Y(i+\tau) - Y(i)]^2, \text{ with } Y(k) = \frac{1}{\tau} \sum_{j=k}^{k+\tau-1} y(j) \quad (1)$$

In the formula shown above the symbol N denotes the total number of measurement data. The calculated square root of the Allan variance as a function of the sampling interval τ for the data of Fig. 1 is presented in Fig. 2 and shows an almost linear decrease with increasing τ . The negative slope of a linear fit to the data is 0.46, which is fairly close to the value of 0.50 expected for the case of an ideal statistical distribution (“white noise”) of experimental data.

The different kind of analysis presented in this section for the example of the data presented in Fig. 1 has also been carried out for other H_2 -experiments. As a result, no evidence can be found that the data of the corresponding single measurements over a large dose range deviate

from a constant calorimeter response. This is in agreement with the model prediction for the H₂-system.

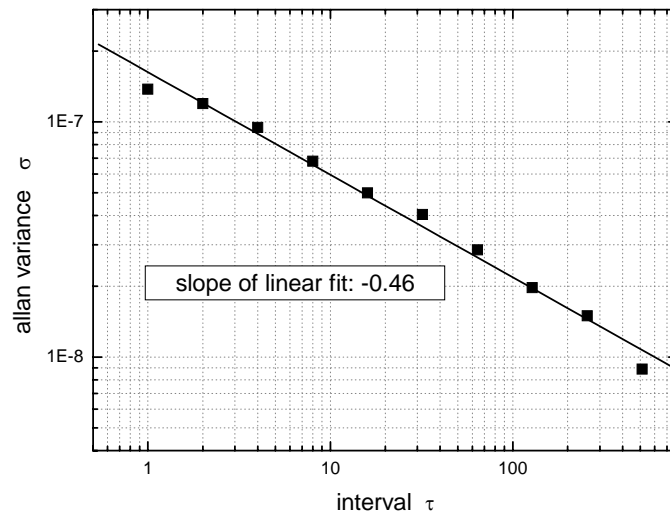


Figure 2. Square root of the Allan variance for the data of figure 1 as a function of the sampling interval. The solid line indicates the result of a linear fit.

3.2. Different experiments

During the past few years several calorimetric experiments for the H₂-system (partly with newly prepared detectors) have been carried out which encompassed in total more than 7000 single measurements. Between successive experiments with the same detector, the detector was removed from the calorimeter and stored in dark surroundings. The mean values of the absorbed dose to water determined during each experiment are shown in Fig. 3 as a function of the number of experiment. The given standard uncertainties for each experiment reflect the combination of several uncertainty contributions, for example the number of measurements and the calibration of the thermistors and of the resistance bridge, respectively. The results are in accordance with a constant value for the response of the H₂-system within a relative standard uncertainty of about 0.1 % with respect to the single experiment.

As these variations between the experiments are in the same order as the standard uncertainty of the single experiments it can be concluded that any uncertainty contribution due to the heat defect must be much lower than 0.1 %, if present at all. The variations shown in Fig. 3 further support the conclusion of a stable calorimeter response for the H₂-system in the PTB water calorimeter. The data offer no reasonable basis for the statement of a separate uncertainty contribution for the heat defect. It has to be concluded that any uncertainty contribution due to the heat defect is already considered within the standard uncertainty of a single H₂-experiment.

4. Heat defect of the H₂-system

During the discussion so far it has been assumed that the heat defect of the H₂-system in the PTB water calorimeter is zero. Principally it cannot be ruled out with certainty, that also a stable but non-zero heat defect could cause the measured stable response. Hypothetically, this could be due to unknown impurities with a concentration high enough to create a stable heat defect over a large dose range or for example by a catalytic process in the water during irradiation. Besides this, the most likely source which specially affects the heat defect of the H₂-system is the contamination of the water with small amounts of oxygen [3, 7]. This case is discussed in the following.

Oxygen leaking into to detector vessel and diffusing into the water at a constant rate could lead to an exothermal heat defect for the H₂-system. The balance between the oxygen leakage rate and the dose rate would in this case determine the value of the heat defect. Furthermore, the heat defect would be independent of the accumulated absorbed dose if the successive measurements were performed at constant time intervals. By calculating the oxygen leakage rate necessary to produce an exothermal heat defect of about 0.2 % [1] for the dose rate used for the experiments presented in Fig. 3, it is easily shown that an interruption of the experiments for some days would cause the oxygen concentration to increase such that the heat defect would amount to several per cent for the following irradiations. Such a scenario can be ruled out as even a much longer interruption of two or three weeks in the case of H₂-experiments performed with the same detector yielded no significant response change of the calorimeter.

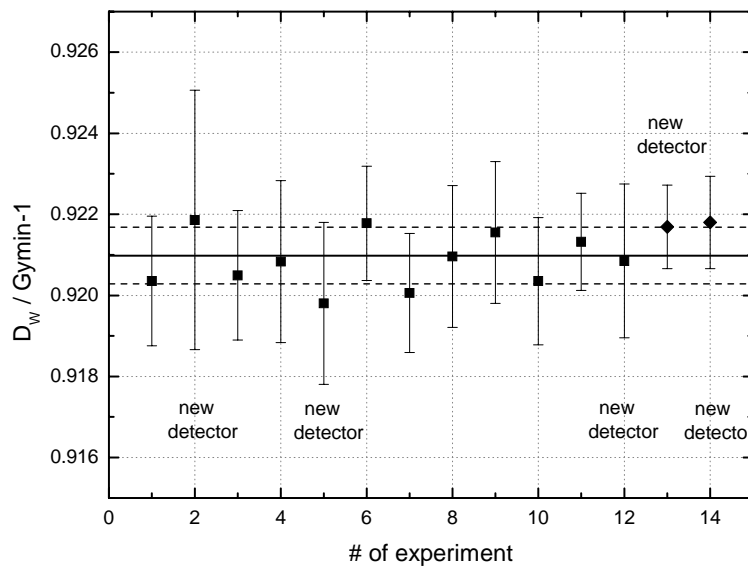


Figure 3. Measurements of the rate of absorbed dose to water at ⁶⁰Co radiation with the PTB water calorimeter using the H₂-system. No corrections for heat conduction or radiation field perturbation have been applied. The solid and the dashed line indicate the mean value and the standard uncertainty, respectively.

However, if it is assumed that the nature of the oxygen contamination is radiation-induced, then a non-zero heat defect for the H₂-system could be achieved which is independent of an interruption of the experiment. The only reasonable source of a radiation-induced oxygen contamination would probably be due to the direct interaction of the radiation with the glass materials of the detector, i.e. the glass walls of the vessel and the walls of the glass pipettes. During irradiation, the oxygen hypothetically produced in the glass would diffuse into the water and would exothermally react with the hydrogen. For oxygen produced in the glass walls of the vessel, this reaction occurs at a position far away from the position of the temperature measurement. As no oxygen remains to further diffuse to the position of the temperature sensors, only a negligible influence on a calorimetric measurement due to heat conduction can be assumed in this case.

For the situation of oxygen being produced in the glass walls of the pipettes it has been tried to determine a resulting heat defect on the basis of a simulated change of the oxygen concentration in the water near the temperature sensors. This oxygen concentration depends on the radiation-induced production rate (G-value) of oxygen in glass and on the diffusion rates of oxygen in glass and water, respectively. As no reliable data could be found for these

processes in glass, conservative assumptions were used for the simulations. The G-value was assumed to be 1×10^{-6} mol/J, which is about 20-times the value of hydrogen production in water during the radiolysis, and the diffusion coefficient was assumed to be equal to the value for helium diffusion in glass (1×10^{-13} m²/s [13]). The geometry of the glass pipettes was taken to be a solid glass rod of 0.6 mm diameter. For an infinite irradiation with a dose rate of 0.5 Gy/min the simulations, which were performed by means of a finite element diffusion model, predicted an increasing oxygen concentration in water with an almost constant rate of about 1.3×10^{-13} mol/Ls. This is too low to cause an exothermal heat defect for the H₂-system greater than 2×10^{-2} %.

5. Conclusion

The experimental data taken so far for the H₂-system in the PTB water calorimeter are in accordance with a stable heat defect over large dose ranges. The different methods of data analysis used in this paper show no evidence of response changes of the calorimeter which could be attributed to changes of the heat defect and which could be taken as the basis for a separate uncertainty contribution for the heat defect. It is concluded that any uncertainty related to changes of the heat defect is already contained within the standard uncertainty of a calorimetric experiment. Although it can not be ruled out with certainty that the heat defect in the PTB water calorimeter using the H₂-system yields a non-zero value, from several arguments pointed out in this paper it seems to be reasonable to adopt the theoretical predicted zero value. The absolute determination of the quantity absorbed dose to water by means of the PTB water calorimeter will be based on this assumption.

As the conclusions given here may be related to the individual geometry and preparation methods of the calorimetric detectors, they consequently should not be directly applied to other water calorimeters without an individual validation.

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Discussion

David Webb – I take your point about not assigning an uncertainty, but aside from that there has to be perhaps an estimate of the bound of the possible uncertainty that you might expect, even though it wouldn't go into a GUM estimate.

Michael Kramer – Yes, so if we said, “Well, let's be on the safe side”, then one could argue that part of those variations that you saw were due to variations of the heat defect. Let's assume this. In this case one would expect that the heat defect would depend on the accumulated dose or on pauses between irradiations. Such an effect can contribute only a very small fraction to the total spread of the experimental points. If there was a contribution of say 0.02%, 0.03% we could not resolve it, because it is contained in a wider statistical distribution. So, on the basis of the data shown we cannot exclude the presence of a small contribution caused by variations of the heat defect. This contribution is however completely hidden in the overall distribution. In terms of the overall uncertainty budget it doesn't matter, if there is a contribution of 0.0 something %. May I add something in view of the 0.3% which is often found for the O₂ system. In my view this figure can not be rationalised easily. I think it has quite some arbitrariness. At least, I haven't found a solid way in which this figure was derived. It could be also 0.4% or 0.1% instead of 0.3%. It's a figure which seems to fall out of the sky somehow. Maybe not quite. I'm exaggerating somewhat. *(This response clarified in proof - ed.)*

Hugo Palmans – You showed a comparison of two chemical systems, and you find a difference which you can determine with a certain accuracy. You could for example use that as a base for determining the boundary, like Dave suggested, of your uncertainty on your model. And that's actually the way it was done in the NRC. (They) used eight chemical systems. The differences between the different chemical systems showed some variation with the models, and they assumed this was a measure of the accuracy with which they know the model for the heat defect. So I think that is a reasonable basis for assigning an uncertainty to the heat defect.

Michael Kramer – I think I would agree that in systems where you have a dependence of the heat defect on the input parameters used in the rate equations one could make an analysis. But if there is a stationary state as in the H₂ system, then ‘nothing happens’ and there also is no uncertainty to it.

Hugo Palmans – If you have chemical reactions with a time constant of the same - level - as the time of your measurements, you could have a non-zero heat defect which does give a stationary state.

Michael Kramer – That's true. The idea of this presentation was to make all efforts to find any indication of whether something might be going on. All I'm saying is, that for the H_2 system we couldn't find any indication. Maybe if somebody comes up and says, "Well, you have not looked at such and such a reaction, which could occur in this system", then of course we would have to consider this, and we would certainly do so. But as things stand for the moment, we have not a shadow of a hint that something might be happening. Now that's all I'm saying.

David Burns – I think some people conceptually have a problem with a zero uncertainty. It implies an infinite confidence. The problem might be resolved if you just use a very small uncertainty. Based, for example, on your last graph is a series of data points in time, and you're saying there's no indication there of a drift. That's it. But when you say no indication, actually there's an uncertainty on your data, there's an uncertainty on the gradient of that data.

Michael Kramer – Of course, but ...

David Burns – If you use the uncertainty on the gradient there, that would put an upper limit on your confidence that it's stable in time, for example. And it would be a very small uncertainty, but it wouldn't be zero.

Michael Kramer – I agree with you that that's a conceptual problem that one has with the uncertainty, but if one has a stationary state, then 'nothing happens'. And there's no uncertainty to a stationary state.

David Burns – Yes, but you can't experimentally demonstrate that. What you want is something that supports that theoretical model. And so you do a series of experiments to support that model. And your experiments themselves have an uncertainty. So you can only support your model to the extent of the uncertainty on your measurements.

Michael Kramer – Yes, I mean so ...

David Burns – So if you want to assign an uncertainty, ...

Michael Kramer – Please let me go back to one of the diagrams I showed. In the plot of the 7000 individual dose measurements there is no significant slope. Furthermore there would also be no slope, if the groups of experiments with each detector were mutually exchanged. The slopes would be different. The differences are not significant. You might say these differences have something to do with the calorimeter heat defect. I would consider this as an arbitrary decision. (*This response clarified in proof - ed.*)

Malcolm McEwen – One of the problems is that you can only after two and a half years and 7000 measurements, say, "I had a zero heat defect, for that beam". As David Burns was saying, you can't infinitely reproduce a number, and you can't get it down into the required zero uncertainty the next time you do it. Do you not need to establish your steady state for the next time you do a fill?

Michael Kramer – Yes, one has to run through this curve each time. The assumption is that after the exothermic peak, the steady state is reached in a reproducible way. So it is essential that one follows, for every new detector, this procedure. After that we had the detectors in use and out of use deliberately, to see whether there were some indications of something happening. If oxygen did diffuse in, we would see its effect. (*This response clarified in proof - ed.*)

David Burns – I think there are a number of ways you could analyse the data. That you could take the ... You've got a series of data sets like that one?

Michael Kramer – Yes.

David Burns – For each of those you could look at the gradient and deduce the uncertainty ... and then you've got a series of measurements of which you can combine statistically.

Michael Kramer – Yes.

David Burns – The other thing I wanted to say about that is I think rather than taking a moving average, you might learn something from looking at the Allen variance. It's a technique commonly used in other areas of metrology. (You) can analyse a time sequence of data to look at what type of noise you have, whether you think you have white noise or 1/f noise or some other kind of noise. You can use the Allen ...

Michael Kramer – That would be a possibility. I would have to do this also with the other detectors in order to see whether something significant comes out of it. The moving average was a crude approach I admit. I did show that nothing could be detected. What we saw so far is in line with a statistical behaviour. If the distribution contains a contribution from the heat defect, this contribution is so small that it can not be separated from the noise. Maybe some upper limit could be found there. (*This response clarified in proof - ed.*)

David Burns – Well, I think that's what you end up with. You've got a theoretical model which says zero, and there's no uncertainty, because of the nature of the theoretical model.

Michael Kramer – Yes.

David Burns – And the only way you can try and get information on the uncertainty is by making experiments. And this is one of the experiments.

Michael Kramer – Yes.

David Burns – And that will always have an uncertainty. So it puts an upper limit on how well you can justify your model. So when someone mentioned having an upper limit it would come from this data, I would think.

Michael Kramer – It would come from this data. But I'm not so sure how far one can detect in such a statistical distribution, some possibly hidden effect there.

David Burns – Well, we know it's way down below 0.07%, from the next graph, you're only going to end up with something below 0.07%.

Michael Kramer – And then it doesn't matter in the overall uncertainty budget.

David Burns – Exactly, so if you do that then everyone will be happy.

(laughter).