Journal of Thermal Analysis, Vol. 53 (1998) 685-695

DETERMINATION OF SPECIFIC HEATS USING ISOTHERMAL MICROCALORIMETRY

V.-P. Lehto[1*], *M. Rahkola*[1], *E. Laine*[1], *L. Ylianttila*[2], *P. Hyysalo*[2] *and K. Jokela*[2]

[1]Department of Physics, University of Turku, FIN-20014 Turku
[2]Radiation and Nuclear Safety Authority, P.O. Box 14, FIN-00881 Helsinki, Finland

(Received November 20, 1997; in revised form April 15, 1998)

Abstract

The specific heat capacities (c_p) for the brain and muscle equivalent liquids were determined with isothermal heat conduction microcalorimetry (IMC) and differential scanning calorimetry (DSC). IMC was found to afford an accurate technique to measure c_p for solid and liquid samples, when an appropriate reference is employed. The accuracy of obtained c_p values was estimated to be better than 0.7% with the equivalent liquids. Intercomparison with a conventional isoperibolic calorimeter showed an excellent agreement within the estimated uncertainty of the isoperibolic calorimeter (±3%). Additionally, suitability of different kinds of IMC sample vessels was tested, and the standard electrical calibration procedure of IMC was evaluated through the determination of c_p with and without a reference material.

Keywords: DSC, isothermal microcalorimetry, specific heat capacity, tissue equivalent liquid

Introduction

A well-known physiological effect of the electromagnetic radiation at radio-frequencies is the increase of temperature of the exposed tissues resulting from the absorption of the electromagnetic energy. The most basic physical quantity describing the exposure to radio-frequency fields is the specific absorption rate (SAR), which is defined by the power absorbed in an element divided by the mass of the element. Commonly it is most convenient to measure, or calculate, the external electric and magnetic fields and compare the results with the field strength limits derived from the basic SAR limits. However, in the case of the exposure to the radiation from mobile phones the only alternative for the SAR assessment is to use simulating phantoms in the place of human body. The relationship between the external fields and internal power absorption is too complex

* Author for correspondence: e-mail: vlehto@utu.fi

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

due to the vicinity of the antenna to the body. In the near-field exposure typical of mobile phones, the relevant exposure quantity is the local SAR related to the local electric field and temperature increase by the equations

$$\mathrm{SAR} = \frac{\sigma E^2}{\rho} = c\,\frac{\partial T}{\partial t} \tag{1}$$

where σ is the conductivity, ρ is the density of the averaging mass, E is the RMS value of the local electric field strength, $\partial T/\partial t$ is the rate of temperature rise and c is the heat capacity of the tissue.

According to Eq. (1) the SAR can be assessed by measuring the temperature increase, or by measuring or computing the three orthogonal components ($E^2=E_x^2+E_y^2+E_z^2$) of the local electric field strength. At the moment, the best method for SAR assessment is based on E-field scanning in liquid phantom [1] simulating human tissues by using small electric field probes [2, 3]. To calibrate a SAR probe it is placed in a precisely known electric field either calculated from the input power of the system or determined from the temperature rise of the medium by Eq. (1) the latter method being more accurate. The uncertainty of the calibration is the most significant and fundamental limitation in the accuracy of the SAR tests as was reported in the previous study [4], where a novel calibration method for SAR probes at 1 GHz frequency was developed. The uncertainty analysis showed that overall uncertainty of the calibration was ±6% from which the uncertainty of the specific heat (±3%) constituted one of the most significant error components. Thus, ascertaining the value for the heat capacity, the accuracy of the calibration of the SAR tests can essentially be improved.

Various differential scanning calorimetry (DSC) methods are routinely employed to measure specific heat capacities (c_p). The benefits of DSC techniques are the fastness to carry out, reasonable accuracy and usefulness for many kinds of sample materials at wide temperature range [5]. If more accurate results are desired other techniques like adiabatic calorimetry and drop calorimetry can be used at appropriate temperature ranges. However, analyses are time consuming and laborious. As the best results with DSC is obtained with periodic heating methods [6] the logical consequence would be to apply isothermal microcalorimetry (IMC) in precise determination of c_p. The IMC technique is suitable for most kind of samples and the results are very accurate, but the analysis time is long, the appropriate temperature range is narrow (5–95°C with the instrument used in this study) and the surroundings condition must be controlled.

The calibration of the commercial calorimeters is usually carried out electrically with an internal calibration resistor located inside the vessel wall in the vicinity of the actual reaction place. To achieve precise calibration it would be preferable to use a heater inserted into the reaction vessel, when it would mimic closely the conditions in the real measuring event. However, in many cases employing an external heating resistor is inconvenient and sometimes impossible.

Regardless of the procedure the calibration is carried out, the accuracy of the calibration constant should be tested by use of a well defined test reaction [7]. One way to check the validity of the calibration is to determine the heat capacity of a known sample with the instrument. The isothermal calorimeter must be used off its normal measuring mode as the sample must experience a change in temperature. Thus, the temperature change should be as small as possible not to lose the resolution however. The by-product of this work was the evaluation of the electrical calibration of the instrument.

Additionally, the specific heat capacities will be measured routinely with an isoperibolic calorimeter designed specially for the measurements of tissue equivalent liquids [4]. The aim is to improve the accuracy of the isoperibolic calorimeter by calibrating it against the isothermal microcalorimeter by using well defined tissue equivalent liquids as transfer standards.

Experimental and theoretical background

Materials

The specific heat capacities were determined for two different liquid mixtures simulating the dielectric properties of brain and muscle [4]. Both of the equivalent liquids consist of water, salt and sugar, the weight per cents being 41.2, 0.8 and 58%, consecutively, for brain equivalent liquid and 53.6, 1.4 and 45% for muscle equivalent liquid. The purified sugar was purchased from Sucros Pharma, salt was 99.5 weight % NaCl and water was de-ionized once. Alumina (α-Al_2O_3, Micromeritics part no. 004-16816-00) was also used as a calibration material. The weighing of the materials was performed with an accuracy better than 0.07%.

Isothermal microcalorimetry (IMC)

The isothermal heat conduction microcalorimeter used to determine the heat capacities was a 2277 Thermal Activity Monitor (TAM) (Thermometric AB, Sweden). The instrumentation and detection principle are described elsewhere [8]. In this work the instrument was used off its normal function mode [9]. The temperature gradient developed between the sample ampoule and the surrounding heat sink as the temperature is dropped from 25 by 1°C generates an output voltage in the Peltier elements situated between the sample and the heat sink. The voltage signal is proportional to the heat flow from the ampoule and will arise until the new set temperature is reached in the whole system. The calorimeter unit consists of the identical sample and reference sides, and as the integrated output signals from the sides are subtracted from each other, a value proportional to the difference in heat capacities of the sides is obtained. So, performing two identical measurements with a reference material (known heat capacity) and an un-

known sample, the heat capacity of the unknown sample can easily be calculated from the formula

$$c_{p,x} = \frac{m_{ref} A_x c_{p,ref}}{m_x A_{ref}} \quad (2)$$

where $c_{p,x}$ is the specific heat of the unknown sample (J (g K)$^{-1}$), m_{ref} is the weight of the reference sample (g), A_x is the integrated value of the heat flow signal (area under curve) for the unknown sample (J), $c_{p,ref}$ is the specific heat of the reference sample, m_x is the weight of the unknown sample and A_{ref} is the integrated value of the heat flow signal for the reference sample. However, as the heat capacities of the sample and reference sides containing the ampoules cannot be perfectly matched, a blank run with the empty ampoules must be performed and be subtracted from both the reference and unknown run before Eq. (2) is applied. In this way, the normal calibration of the instrument is insignificant, and the absolute accuracy depends on the accurate of the value of $c_{p,ref}$.

TAM is equipped with four independent twin-calorimeter units. Suitability of different kinds of ampoules for the c_p measurements was evaluated. In the first channel glass ampoules were used. As an inert material glass is suitable with most of the materials, but in this case glass ampoules have disadvantages since the stoppers must be exchanged after every measurement. Because the stoppers are not identical, the exchange has an influence on heat capacity. Also, the ampoules must be cleaned exposing the ampoules to breaking. The self-made stainless steel vessels with 0.8 mm thick teflon sealing disks were used in channels two and three, and the corresponding steel vessels made by Thermometric AB with disposable sealing disks were used in channel four. The channels were calibrated electrically beforehand, but it has no influence on the results as far as the calibration remains unchanged during the measurement set, as mentioned before. The actual experimental procedure is described step by step in [9], but no glass liner was employed. Also, the baselines before and after the dropping of the temperature was measured and subtracted as linear from the actual data. The recorded heat flow signals were exported as an ASCII file, and the data handling and the calculations were done in Origin™ (Microcal, USA) and Excel™ (Microsoft, USA).

Differential scanning calorimetry

The specific heat capacities were also determined with DSC to verify the values and the methods. A Perkin Elmer DSC model 7 with a Thermal Analysis System software was used to achieve the thermograms. The scanning experiment was performed over the temperature range of 25–70°C with a heating rate of 5°C min^{-1}. Isothermal sections of 2 min before and after the temperature scan were also recorded for interpolating the baseline. The nitrogen flow of

50 ml min^{-1} was used and held steady through the measurement set. The sealed aluminum sample pans for robotic system standing 1 bar maximum internal pressure were employed. The sealing was checked performing a corresponding TG measurement with water, and no mass loss was detected. The melting endotherm of indium was used to calibrate the instrument. However, using a reference material the calibration of the ordinate is insignificant, and the value for the specific heat is obtained from

$$c_{p,x} = \frac{m_{ref}\, y_x\, c_{p,ref}}{m_x\, y_{ref}} \quad (3)$$

where y_x and y_{ref} denote the ordinate deflection for the unknown sample and for the reference sample at the same temperature, respectively. The Eq. (2) corresponds to the Eq. (3). The recorded signals were exported as an ASCII file, and the data handling and the calculations were done in Origin™ (Microcal, USA) and Excel™ (Microsoft, USA).

Results and discussion

Determinations with IMC

As neither the sample and the reference sides nor the used ampoules are thermally identical, the blank run for the set of the calorimetry unit and the ampoules must be performed. Figure 1a represents the blank run for the channel 3 with the self-made stainless steel vessels. The time when the temperature is dropped is referred as t=0 s. The signal seems to get steady in few hours but the baseline is reached just after ca. 9 h. With a corresponding measurement with a liquid sample (Fig. 1b) the signal is ca. 100 times the blank, but the baseline is reached almost in the same time. Among all the measurements the blank response was 9% at maximum of the response obtained with the sample.

The integral values of the heat flow signals for the imbalance during the temperature equilibrium are presented in Table 1 for all the measurements. As the instrument has been calibrated electrically beforehand, the approximate values for the specific heats can be calculated from the listed area values. Subtracting the blanks, converting the time and dividing by the mass the obtained values are $c_{p,alumina}$=0.7779 J $(g\ K)^{-1}$ for alumina and $c_{p,water}$=4.1962 J $(g\ K)^{-1}$ for water the standard deviations being 0.0041 and 0.0165 J $(g\ K)^{-1}$, respectively. The corresponding values in the literature are 0.7748 and 4.1798 J $(g\ K)^{-1}$ [10], respectively.

To verify the method two reference materials with known specific heat capacities were used in the measurements and calculations. The specific heats for both of the reference material were calculated utilizing the other sample (Table 2). The calculated average values are accurate down to the 3rd decimal and all

Table 1 The integrated microcalorimetric imbalance responses (μWh), when the operating temperature is dropped from 25 by 1°C for the reference and unknown samples with different sample vessels (the weights of the samples (g) in parentheses)

Sample vessel	Sample					
	blank	alumina	water	brain 1	brain 2	muscle 1	muscle 2
Glass		498.2513	1585.6998	1189.7324	1179.7208	1265.0647	1230.7753
	−56.8093						
(channel 1)		(2.5867)	(1.4127)	(1.5926)	(1.5859)	(1.5420)	(1.4931)
Steel 1a		548.0815	2316.7576	1578.2455	1594.6820	1748.8675	1793.7044
	−0.3955						
(channel 2)		(2.5347)	(1.9879)	(2.0069)	(2.0303)	(2.0347)	(2.0863)
Steel 1b		572.6555	2312.0139	1656.1871	1632.3286	1792.3775	1817.2585
	16.4405						
(channel 3)		(2.5745)	(1.9754)	(2.0889)	(2.0607)	(2.0675)	(2.0946)
Steel 2		428.1633	2247.2235	1523.3550	1497.3018	1502.6044	1647.7521
	−135.6680						
(channel 4)		(2.5946)	(2.0331)	(2.1006)	(2.0696)	(2.0142)	(2.0646)

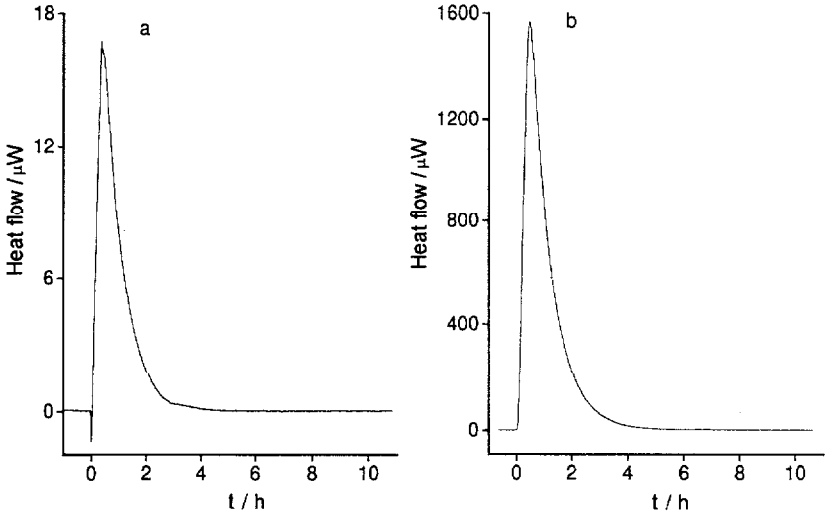

Fig. 1 Microcalorimetric imbalance response for channel 3: a) blank and b) brain equivalent liquid

the measured values are within the error limits (2σ). The glass ampoules give the greatest deviation, which presumably is due to the new stoppers used in every measurements and the adsorption of moisture in the stopper, especially when liquid samples are employed.

Table 2 Calculated specific heats for water using alumina (c_p=0.7748 J (g K)$^{-1}$ as reference, and for alumina using water (c_p=4.1798 J (g K)$^{-1}$ as reference (standard deviation in parentheses)

Sample vessel	$c_{p,water}$/J (g K)$^{-1}$	$c_{p,alumina}$/J (g K)$^{-1}$
Glass (channel 1)	4.1981	0.7714
Steel 1a (channel 2)	4.1737	0.7759
Steel 1b (channel 3)	4.1675	0.7771
Steel 2 (channel 4)	4.1789	0.7750
Average	4.1796 (0.0115)	0.7749 (0.0021)

The specific heats for the brain or muscle equivalent liquids calculated using alumina and water as the reference do not differ significantly (Tables 3 and 4). The average of the 16 values for the brain equivalent liquid is $c_{p,brain}$= 2.8160 J (g K)$^{-1}$ (0.0051) and for the muscle equivalent liquid $c_{p,muscle}$=3.0859 J (g K)$^{-1}$ (0.0098) where the standard deviations are in parentheses. The uncertainty of the results is excellent, better than ±0.7% (2σ) at least.

Table 3 Specific heats for the brain and muscle equivalent liquids using alumina as the reference sample (standard deviation in parentheses)

Sample vessel	$c_{p,brain1}$/ J (g K)$^{-1}$	$c_{p,brain2}$/ J (g K)$^{-1}$	$c_{p,muscle1}$/ J (g K)$^{-1}$	$c_{p,muscle2}$/ J (g K)$^{-1}$
Glass (channel 1)	2.8262	2.8153	3.0953	3.1138
Steel 1a (channel 2)	2.8166	2.8131	3.0783	3.0784
Steel 1b (channel 3)	2.8151	2.8122	3.0805	3.0833
Steel 2 (channel 4)	2.8159	2.8132	3.0770	3.0799
Average	2.8159 (0.0045)		3.0858 (0.0128)	

Table 4 Specific heats for the brain and muscle equivalent liquids using water as the reference sample (standard deviation in parentheses)

Sample vessel	$c_{p,brain1}$/ J (g K)$^{-1}$	$c_{p,brain2}$/ J (g K)$^{-1}$	$c_{p,muscle1}$/ J (g K)$^{-1}$	$c_{p,muscle2}$/ J (g K)$^{-1}$
Glass (channel 1)	2.8138	2.8030	3.0818	3.1002
Steel 1a (channel 2)	2.8207	2.8172	3.0828	3.0829
Steel 1b (channel 3)	2.8234	2.8204	3.0896	3.0924
Steel 2 (channel 4)	2.8166	2.8138	3.0777	3.0805
Average	2.8161 (0.0063)		3.0860 (0.0075)	

Determinations with DSC

When the c_p values are calculated with the Perkin Elmer software, no reference scan is allowed in the analysis, only the baseline scan with empty pans and the sample scan is employed. This way the analysis is exposed to many errors and the results are quite poor as is represented for water in Table 5. Reliable results are obtained just after few degrees as the system is reached its equilibrium after the temperature scan has been started [11]. The errors can be reduced applying Eq. 3, but the same effect is achieved applying correction factors obtained by comparing the values in Table 5 with the corresponding literature value of water at each temperature. Water was used as the reference material since alumina gave great difference in the c_p values compared with the literature values indicating poor accuracy of the results determined with DSC. Furthermore, the values decreased as a function of temperature the true values acting reverse behavior. In this case, water is advisable for the reference material since the physical state of the sample is the same as with the equivalent liquids. The corrected c_p values (Table 6) increase as a function of temperature, and the first reliable results seems to be 2.767 J (g K)$^{-1}$ (0.017) for the brain equivalent liquid and 3.015 J (g K)$^{-1}$

Table 5 Specific heats obtained with DSC for water (standard deviation in parentheses)

T/ °C	c_p/J (g K)$^{-1}$				
	sample 1	sample 2	sample 3	sample 4	average
30	4.000	3.989	4.036	4.112	4.034 (0.056)
35	4.106	4.096	4.139	4.216	4.139 (0.055)
40	4.126	4.112	4.155	4.225	4.155 (0.051)
45	4.135	4.120	4.162	4.220	4.159 (0.045)
50	4.135	4.114	4.152	4.205	4.152 (0.039)
55	4.138	4.112	4.136	4.197	4.146 (0.037)
60	4.132	4.106	4.120	4.172	4.133 (0.029)
65	4.133	4.104	4.109	4.158	4.126 (0.025)
70	4.134	4.104	4.101	4.142	4.120 (0.021)

Table 6 Corrected specific heats obtained with DSC for the brain and muscle equivalent liquids (n=4, standard deviation in parentheses)

T/°C	$c_{p,brain}$/J (g K)$^{-1}$	$c_{p,muscle}$/J (g K)$^{-1}$
30	2.767 (0.017)	3.015 (0.026)
35	2.785 (0.015)	3.039 (0.030)
40	2.808 (0.014)	3.060 (0.030)
45	2.833 (0.012)	3.082 (0.029)
50	2.857 (0.011)	3.103 (0.027)
55	2.882 (0.010)	3.133 (0.029)
60	2.907 (0.009)	3.153 (0.021)
65	2.933 (0.008)	3.175 (0.018)
70	2.959 (0.010)	3.202 (0.017)

(0.026) for the muscle equivalent liquid at 30°C. As the standard deviation of the correction factor is taken into account, the precision of ±2% at least for the values is obtained. However, the deviations from the results obtained with IMC are great.

Intercomparison with the isoperibolic calorimeter

The c_p values for the tissue equivalent liquids were also measured with the isoperibolic calorimeter, which consisted of a stainless steel thermos flask (dewar), an electrical heating coil, stirrer and three temperature sensors [4]. The volume of the calorimeter was 1 dm^3. No thermostated bath was used. The heating

Table 7 Comparison of the c_p values (J (g K)$^{-1}$) for the brain and muscle equivalent liquids

	IMC (25°C)	DSC (30°C)	Isoperibolic calorimeter (25°C)	Literature [12]
Brain	2.82	2.77	2.84	2.85
Muscle	3.09	3.02	3.11	–
Uncertainty	±0.7%	±2%	±3%	–

power was determined by measuring the voltage and current of the heating coil by using precision resistors (0.1%) and an A/D converter. Temperature and heating power were controlled by a computer. The minor error due to a slight temperature drift before and after the heating period was corrected mathematically afterwards. The measured specific heats were $c_{p,brain}$=2.84 and $c_{p,muscle}$= 3.11 J (g K)$^{-1}$ for the brain and muscle equivalent liquids, respectively, with an uncertainty of 3% (2σ). The c_p values obtained with different methods have been compiled in Table 7. The results are consistent with each other IMC giving the most accurate values.

Conclusions

The c_p values for alumina and water calculated directly from the microcalorimetric imbalance response using no reference differ about 0.4% from the values calculated with reference. This indicates that the procedure of the electrical calibration for closed ampoules is valid and causes only minor errors in the values of heats obtained from heat flow signals.

Two different methods, IMC and DSC, was employed to achieve the values of c_p for the brain and muscle equivalent liquids to compare the methods and verify the results. The benefits of DSC are the rapidity of the analysis and the precision good enough to distinguish the equivalent liquids. Unfortunately the results of DSC own quite a low accuracy and an unexpected temperature dependence. On the contrary, the accuracy and the precision of the IMC results are excellent. As a disadvantage, the time needed for the measurements is long. The values for specific heats are $c_{p,brain}$=(2.82±0.02) J (g K)$^{-1}$ for the brain equivalent liquid and $c_{p,muscle}$=(3.09±0.02) J (g K)$^{-1}$ where the error limits are twice the standard deviation. The accuracy of the results is thus better than 0.7%. The c_p values obtained in this study for the equivalent liquids show excellent agreement IMC giving the most accurate value.

In this study, the samples were not pure substances and the weighing of the components and the preparation of the samples increased the errors for their parts. It is advisable to use stainless steel ampoules, which are exactly identical from a measurement to another, in IMC measurements since with glass ampoules

the stoppers have to be replaced and glass is fragile. With careful handling of samples and precisely designed measuring procedure an uncertainty of ±0.7% in specific heat can readily be reduced significantly.

* * *

This work was supported by a research grant to V-P. L. from Graduate School of Materials Research financed by the Ministry of Education, Finland.

The authors are grateful to Mr. T. Hoppela for the assistance in IMC measurements and calculations.

References

1 T. Schmid, O. Egger and N. Kuster, IEEE Trans. Microwave Theory Tech., 44 (1996) 105.
2 H. I. Bassen and G. S. Smith, IEEE Trans. Antennas Propagat., 31 (1983) 710.
3 R. R. Bowman, IEEE Trans. Microwave Theory Tech., 24 (1976) 43.
4 K. Jokela, P. Hyysalo and L. Puranen, IEEE Trans. Instr. Meas., submitted (1997).
5 M. J. O'Neill, Anal. Chem., 38 (1966) 1331.
6 G. K. Demensky and O. A. Teplov, J. Therm. Anal., 32 (1987) 451.
7 L.-E. Briggner and I. Wadsö, J. Biochem. Biophys. Methods, 22 (1991) 101.
8 J. Suurkuusk and I. Wadsö, Chemica Scripta, 20 (1982) 155.
9 P. F. Bunyan, Thermochim. Acta, 130 (1988) 335.
10 Handbook of Chemistry and Physics, CRC Press, Boca Raton 1992, p. 6–10.
11 J. L. Ford and P. Timmins, Pharmaceutical Thermal Analysis, John Wiley & Sons, Chichester 1989, p. 32.
12 K. Meier, M. Burkhardt, T. Schmid and N. Kuster, IEEE Trans. Microwave Theory Tech., 44 (1996) 1954.