A Thermistor Based Method for Measurement of Thermal Conductivity and Thermal Diffusivity of Moist Food Materials at High Temperatures

by

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A THERMISTOR BASED METHOD FOR MEASUREMENT OF THERMAL CONDUCTIVITY AND THERMAL DIFFUSIVITY OF MOIST FOOD MATERIALS AT HIGH TEMPERATURES

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(ABSTRACT)

The purpose of this research was to assess the suitability of the thermistor based method for measuring thermal conductivity and diffusivity of moist food materials at high temperatures. Research focused on aspects of calibration, thermal contact in solid food materials, natural convection in liquid media and the performance in moist food materials at high temperatures.

Thermistor probes were constructed in house and calibrated in three materials of known thermal conductivity and diffusivity, water, glycerol, and a heat transfer fluid, HTF 500. With few exceptions, the calibrated probe estimated thermal properties with an error of less than 5%, over the range of thermal properties spanned by the those of the calibration media. An alternate calibration using two media was also investigated. It was found to give better accuracy over a more limited range.

Thermal contact in potato and lean beef was investigated through a comparative study that used a miniature line heat source probe as a reference method. The food materials were measured at 25, 50 and 100 °C. Good agreement was found between the measurements with the line heat source probe and the bead thermistor probe, indicating adequate thermal contact at the thermistor probe.

The effect of fluid viscosity and the magnitude of the temperature step on the occurrence of natural convection was studied for aqueous solutions of a thickening agent. During a sample time of 30 seconds, convection was absent in solutions with a viscosity of 25 cp or greater, when measured with a temperature step of 1.5 and 2.5 °C, and in solutions with a viscosity of

50 cp or greater, when measured with a temperature step of 5.0 °C. A Rayleigh number was defined to study the notion of a critical Rayleigh number at the onset of convection. This study found that when the Rayleigh number was below 43, convection could not be demonstrated. For a Rayleigh number of 84 and higher, convection was observed.

The performance at high temperatures in food materials was studied through tests in tomato concentrate and in a liquid food supplement. Tomato puree and tomato paste were sampled at 100, 130 and 150 °C. The thermal conductivity of tomato puree at 100, 130 and 150 °C was measured as 0.638, 0.645 and 0.647 W/m°C respectively. The thermal diffusivity was 1.63, 1.64 and 1.62 $10^{-7}m^2/s$ respectively. For tomato paste at 100, 130 and 150 °C, a thermal conductivity was obtained of 0.590, 0.597 and 0.534 W/m°C respectively. The thermal diffusivity was 1.63, 1.84 and 2.36 $10^{-7}m^2/s$ respectively. With some notable exceptions the results of this study agreed well with Choi and Okos (1983). A liquid food supplement was also studied at 95 and 150 °C. The thermal conductivity of the food supplement decreased with increasing solids content from 0.62 W/m°C at a solids level of 15% to 0.41 W/m°C at a solids level of 50%.

The results of this study indicate that the thermistor based method was suitable for measuring thermal conductivity and diffusivity of moist food materials at high temperatures. However, the type of thermistor used in the research, a glass encapsulated thermistor, was too fragile for routine work. In particular the high temperature use of the glass thermistor was impacted by its susceptibility to fracture.

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CHAPTER 1

INTRODUCTION

The primary goal of the food processing industry is to supply the market with safe products. One common means of attaining this is food preservation by means of thermal processing. The application of heat can induce favorably product changes, deactivate enzymes, and kill micro-organisms. The result is a product, hopefully of appetizing quality, with an extended shelf-life and safe to consume. Unfortunate side effects of product heating involve nutritional and textural losses. Underprocessing of food may lead to health hazards whereas overprocessing may decrease a product's quality as well as constitute a wasteful use of energy and other resources. Heat transfer studies seek to find processing regimes that satisfy the markets' requirement for a high quality product but with an optimal utilization of production resources. These studies require the knowledge of thermal properties of food materials.

Various methods exist to thermally process food materials. Which method is used for a particular food material depends on several factors (product characteristics, available technology, costs, logistics, market factors) most of which are outside the scope of this work. Two commonly used thermal processes are in-can processing and aseptic processing.

With in-can processing, the conventional method of canning, a non-sterile food product is filled into a non-sterile container and hermetically sealed. Subsequently, the container and product are subjected to a heat treatment to obtain a commercially sterile product. Product heating is usually non-uniform and a temperature gradient will exist between the product near the can wall and at its cold point. As a result, part of the can contents will be overprocessed before adequate sterility is obtained at the cold point.

During aseptic processing, product and container are treated separately from each other. The product is sterilized or pasteurized in a continuous heat-hold-cool system. Rapid heating takes place in a heating heat-exchanger. The product is then held in the holding tube long enough to ensure adequate lethality. A cooling heat-exchanger rapidly cools the product after which it is transferred to an aseptic filler, where under a sterile atmosphere the product is packaged in separately sterilized containers. Where this can be applied, aseptic processing can significantly shorten the process time and yield a higher quality product then can be obtained with the conventional canning method. The product is also more uniformly processed than in a conventional system. Aseptic processing of homogeneous liquid products has become more common in the food industry. Liquid foods containing particles posed problems in the design of aseptic processing system. As of 1997, only one process has been filed with the FDA (Palaniappan, 1997).

One of the requirements to file an aseptic process of a low-acid liquid food containing particulates with the FDA, is to have the process established by a processing authority. This involves, among other things, that the filing party can demonstrate that the process delivers the selected lethality to the slowest heating zone (cold spot) of the particle by the time it reaches the end of the holding tube. Heat penetration measurements and biological methods, as used for process establishment of conventionally canned foods, are impractical for an aseptic system. Temperature measurement of the cold spot of a particle while it travels through a continuous aseptic system encounters tremendous experimental difficulties. Biological methods to validate the process are likewise complex to implement for an aseptic process of a liquid food containing particulates (de Ruyter, 1973). A possible approach to process establishment is through modeling (Chandarana, 1989)

Models seek to predict the lethality delivered to the product, and in particular that to the cold point of the particle, as it travels through the continuous heat-hold-cool aseptic system. Early models were developed by De Ruyter and Brunet (1973) and Manson and Cullen (1974). These models were based on some simplifying assumptions and did not study all the parameters involved in an aseptic process. Both models assumed temperature independent thermophysical properties for the particle and an infinite heat transfer coefficient at the particle boundary. Later models were both mathematically more advanced and more inclusive in testing for the effect of variation in parameter values. Lee (1988) and Chandarana

(1989) used their models to study the effect of variation in the thermophysical properties of the particle on the time to receive adequate lethality at the particle center. Their models demonstrated an effect of particle diffusivity on the process time. Larkin (1990) performed a sensitivity analysis of a one-dimensional heat transfer model for a heat-hold-cool aseptic system of food products containing particulates. The model system consisted of a fixed processing system with constant heater length and diameter and constant hold tube length. Particulates were modeled as spheres. The exit temperature of the fluid from the heater was kept constant by varying the steam temperature of the heater. Eighteen different design, product and process control variables were considered, and apart from the direct effect of fluid specific heat, all were found to significantly affect the amount of lethality delivered to the product. With respect to particle properties he wrote: "Very little work has been done on measuring the thermal properties of particulates and on any changes in the thermal properties that may result during the processing of a food product. [...] Considering the importance of the thermal properties of fluid and particulates and the lack of any research in this area [measurement of properties at aseptic processing temperatures], work in this area should be initiated."

The thermal properties that are generally considered in the context of heat transfer are: specific heat, thermal conductivity, thermal diffusivity, enthalpy, and surface heat transfer coefficient. The latter is not a thermal property of a material *per se* but it is influenced by thermal properties. Thermal conductivity is a measure of the ability of a material to conduct heat. In foods, the thermal conductivity is primarily dependent on composition, but also on any factor that affects the heat flow paths such as porosity and shape, size and arrangement of void spaces, homogeneity, fibers and their orientation (Sweat 1986). Thermal diffusivity relates the ability of a material to conduct heat to its ability to store heat. It is used in the analysis of transient heat transfer in solids. For lack of accurate methods to determine it directly, Sweat (1986) recommended calculation of thermal diffusivity from thermal conductivity, density and specific heat.

The majority of the research on thermal conductivity and diffusivity of food materials has been conducted in the low temperature range. Aseptic processing generally takes place at high temperatures, above 100 °C but rarely exceeding 150 °C. Extrapolation of data obtained at lower temperatures may fail to take into account the effect of temperature on thermal properties, be it related to temperature alone or to temperature induced changes in the product (moisture loss, protein denaturation, starch gelatinization). Few researchers have measured thermal properties at temperatures above 100 °C. Baghe-Khandan and Okos (1981) measured the thermal conductivity of beef through the temperature range 30 - 120 °C. Choi and Okos (1983) measured the thermal conductivity and thermal diffusivity of tomato concentrate. The measurements were performed over the range from 20 to 150 °C. Kravets (1988) measured the thermal conductivity of milk and cream from 25 to 125 °C. The thermal conductivity of starch gels was measured over the range 80 - 120 °C (Wang, 1992). Gratzek and Toledo (1993) measured the thermal conductivity of potato and carrot from 25 to 130 °C. As this brief summary shows, there is a very limited amount of thermophysical property data available in temperature ranges applicable to aseptic processing.

High temperature thermal property measurement of moist food materials demands a method that is both applicable to moist foods and adaptable to use at high temperatures. Steady state methods for thermal conductivity measurement require long equilibration times and are therefore not suitable for food materials in which moisture migration may take place during the measurement. Aseptically processed foods fall in that category. Also, these methods only yield a value for thermal conductivity. Independent measurements of density and specific heat at aseptic temperatures are required in order to calculate thermal diffusivity. These measurements are no small task. Transient state methods have the advantage of being rapid. They are therefore better suited for measuring moist food materials. Measurement above the atmospheric boiling point of water poses design problems for some of the transient methods. The direct measurement of thermal diffusivity of food materials at high temperatures has been done with methods that were based on: heat penetration, the line heat source probe, the bead thermistor. These methods will be evaluated with one further constraint in mind. The method should be capable of measuring small samples.

The thermal diffusivity of carrot cubes was determined at UHT temperatures (130 - 150 °C) from heat penetration data (Chang and Toledo, 1990). Cubes of 2 cm were subjected to flowing water at 140 °C. The center temperature was monitored. Analysis of time-temperature data was done with a finite difference scheme. A Biot number was assumed. Thermal diffusivity was found by trial and error. The same researchers determined thermal diffusivity and heat transfer coefficient simultaneously for 1 and 2 cm carrot cubes in a packed bed, placed in flowing water of 140 °C. Sample temperatures were measured at the center and at a point midway between the center and the surface. Trial and error solutions with the finite difference method yielded both heat transfer properties. Thermal diffusivity found through both measurements were in agreement, $1.88 \cdot 10^{-7}$ and $1.94 \cdot 10^{-7}$ m^2/s respectively. The corresponding thermal conductivities, were 0.74 and 0.77 W/m°C. These values are somewhat higher than the value of water at that temperature, 0.69 W/m°C. This method is computation intensive and demands great accuracy in the placement of the temperature sensor. The latter becomes more critical as the sample size decreases.

Among the transient state methods, the line heat source probe is most commonly used for measurement of thermal conductivity, both at low and at high temperatures. Sweat and Haugh (1974) developed a miniature line heat source probe for the measurement of thermal conductivity of small cylindrical samples. Choi and Okos (1983) and Casada and Walton (1989), used an additional temperature sensor with known distance to the probe for direct determination of thermal diffusivity. The drawback of this procedure is that the distance between the sensor and the probe has to be known accurately. For a solid food this may give experimental difficulties as insertion into the sample can alter its location relative to the probe. The additional temperature sensor for thermal diffusivity measurement will increase the sample diameter, making it less suited for measurement of small particles.

A method that can simultaneously measure thermal conductivity and diffusivity is the thermistor probe method. The method was developed by researchers in the biomedical field for measuring thermal conductivity and diffusivity of human tissue (Chato, 1968; Balasubramaniam, 1974; Valvano, 1981). Its use for measurement of food thermal properties is limited to one study; thermal conductivity of liquid milk products was measured over the temperature range 25 to 125 °C (Kravets, 1988). The thermistor based method utilizes a small thermistor probe whose active region approximates a sphere. Because of the small diameter of this region, beads with diameters of 2.54 mm and smaller are commonly used, it is applicable to small samples. Kravets (1988) concluded that samples could be as small as 5 mm in diameter. The thermistor is most suited for measurement of materials that can close tightly around or wet the probe, ensuring a low thermal contact resistance (Balasubramaniam, 1975). Fluids and human or animal tissue have been the most frequent test materials. Woodbury (1984) and Dougherty (1987) also measured the thermal conductivity of insulation materials. The composition and rheological properties vary between solid foods and can be temperature dependent for a given material. These food characteristics may affect the adequacy of thermal contact between probe and food and can ultimately determine the suitability of the thermistor based method of thermal property measurement of those food materials.

The thermistor based method is not an absolute method. It requires calibration with materials whose thermal conductivity and diffusivity are well documented. Available reference materials whose thermal conductivity is comparable to that of moist food materials are liquids. A thermal property measurement with the thermistor involves establishing a thermal gradient in the test medium. For a valid measurement, heat penetration has to occur solely by conduction. It has been observed that the temperature gradient will induce convection in certain liquid media. Balasubramiam (1975) noticed the departure of measurement data for water from those for agar-gelled water and ascribed that to convection. Dougherty (1987) noted that the thermistor based method may not be suitable for low viscosity fluids because of convection. Approaches traditionally taken to prevent or minimize the occurrence of natural convection use thickeners or flow inhibitors (angel hair). In both cases, an additional material is introduced with the potential of altering the thermal properties of the material under investigation. In general, the concentrations of these convection inhibitors are low and are assumed to have near negligible effect on the measured properties. No studies were found that attempt to relate fluid properties and heating power to the occurrence of convection and its onset time.

Thermal property data of food materials are relevant for the establishment of aseptic processes. However, they are scarce. The thermistor based method holds promise as a method for simultaneously measuring thermal conductivity and diffusivity at high temperatures. In particular the latter is an advantage as it avoids the independent determination of density and specific heat. Whether the method is suitable for use with solid food materials is a question that merits answer. Adequate thermal contact between the very small thermistor bead and the food material can be a problem, because of either inherent product characteristics or those effectuated by heating at high temperatures. Thermal contact is no issue when a fluid is sampled with a thermistor. Convection can however disrupt a measurement. Its occurence is related to fluid properties and method variables that have not been the subject of previous investigations. The following objectives were formulated to address the issues discussed in the foregoing.

Objectives:

1. Investigate the suitability of the thermistor based method for measurement of thermal conductivity and diffusivity at temperatures up to 150 °C,
2. Investigate the adequacy of thermal contact during bead thermistor probe thermal property measurements in solid foods,
3. Assess the effect of medium viscosity and heating power on the quantification of medium thermal properties,
4. Measure the thermal conductivity and diffusivity of moist food materials at temperatures above the atmospheric boiling point of water.

CHAPTER 2

LITERATURE REVIEW

This chapter presents the results of the literature research. Some methods for measuring thermal conductivity and/or diffusivity of food materials will be discussed. These methods can roughly be divided in steady state and transient methods. The research reported in this thesis uses the thermistor probe method. Literature pertaining to this method for measurement of thermal conductivity and diffusivity will be treated in great detail. However, the heat transfer model and its application is omitted here and presented in the next chapter. When the thermistor probe is used with liquid media, natural convection can be an unwanted phenomenon. The thermistor probe relies on liquid media as calibration materials as they are the most suited for this purpose, making natural convection of particular interest.

2.1 STEADY STATE METHODS FOR MEASUREMENT OF THERMAL CONDUCTIVITY

2.1.1 Introduction

Methods that employ steady state measurement of thermal conductivity apply Fourier’s law of heat conduction:

$$Q = kA\frac{\Delta T}{\Delta x} \tag{2.1}$$

where:	Q	=	heat flow	[W]
	k	=	thermal conductivity	[W/m°C]
	A	=	area perpendicular to heat flow	[m^2]
	ΔT	=	temperature difference	[°C]
	Δx	=	thickness	[m]

When rewritten, the thermal conductivity of a material can be expressed as a simple function of surface temperatures or heat fluxes and sample dimensions. Different methods are based on steady state heat flow. Underlying all is the attempt to simplify the mathematics by reducing the heat transfer problem to a one-dimensional problem. The results

are methods that use the infinite slab, the infinite cylinder or sphere as model.

2.1.2 Guarded Hot Plate

The guarded hot plate uses the infinite slab as heat transfer model. Since sample dimensions are finite, guard heaters are used to facilitate uni-directional heat flow. It is considered the most accurate and most widely used method for the measurement of thermal conductivity of poor conductors of heat (Mohsenin, 1980). It is most suitable for dry homogeneous samples that can be formed into a slab. The sample is sandwiched between a heat source and a heat sink. Thermal guards are kept at the same temperatures as their adjacent surfaces (heat source, heat sink) to prevent heat leakage from heat source, sample and heat sink, thus ensuring uni-directional heat flow. The heat input is monitored. After steady state has developed, as shown by stable temperatures of the heating and cooling plate, the thermal conductivity can be calculated from the heat input, the temperature differential across the sample, and the sample dimensions thickness and heat transfer area. Since steady state conditions may take several hours to develop, this method is unsuitable for use with material in which moisture migration may take place. The method has been used for measuring the thermal conductivity of dried or frozen foods.

2.1.3 Radial Heat Flow Method

Whereas the guarded hot plate is generally used for measuring the thermal conductivity of samples that can be formed into a slab, radial heat flow steady state methods are more commonly used with powdered or granular material.

A cylindrical test device employs a central line (or cylindrical) heat source. End effects are assumed negligible due to either the large length to diameter ratio of the test apparatus or the use of end guard heaters. After steady state has been established, the thermal conductivity can be calculated from the heating power, the length of the cylinder, the temperature differential between two internally (to the medium) located sensors and their radial position.

Alternatively, the cylindrical sample can be bordered by the heater on one side and a reference material on the other side. Temperatures on all surfaces are monitored. The thermal conductivity of the test material is calculated from the temperatures, the radial position of the sensors and the thermal conductivity of the reference material.

2.2 TRANSIENT STATE METHODS

2.2.1 Introduction

A disadvantage of steady state methods are the long measurement times involved. Materials containing moisture may experience moisture migration before steady state conditions develop. Consequently, a steady state method will fail to measure representative properties. Therefore, transient methods are preferred for measuring the thermal conductivity of moist food materials. They are rapid as data are obtained in minutes or even less compared to hours for a steady state measurement.

Steady state methods are only capable of measuring thermal conductivity. When the measured properties are to be used in the study of transient heat transfer, density and specific heat have to be found independently. They are combined with thermal conductivity to find the thermal diffusivity, the material property of interest. For lack of accurate methods of direct measurement of thermal diffusivity, this approach is recommended (Sweat in Rao, 1986). Methods based on transient heat transfer have the potential of directly determining thermal diffusivity, but they are not as accurate as steady state methods with dry materials (Mohsenin, 1980).

Three transient methods will be treated. The Fitch method has applications for small samples but is not practical for use at high temperatures. It is mainly included here for completeness. The line heat source probe is widely used for measurement of thermal conductivity of food materials. This report contains a comparative study between the line heat source probe and the focus of this research, the thermistor probe.

2.2.2 Fitch Method

The Fitch method was developed by Fitch in 1935 (Mohsenin, 1980) and uses a plane source of heat. It is applicable to poor conductors of heat that can be formed into a slab. The Fitch apparatus consists of a heat source and a heat sink. The heat source is a constant temperature vessel, insulated on the sides and with a highly conductive bottom. The heat sink is a copper block, insulated on all sides but the one facing the vessel. The heat transfer areas are smooth to minimize contact resistance. The roles of heat sink and heat source are reversed when the vessel is maintained at a temperature lower than that of the copper block. Initially the sample is in thermal equilibrium with the copper block. The vessel, maintained at a temperature different - typically by about 20 °C - from this temperature, is brought into contact with the sample. Thermocouples record the temperature history of the copper block, which is assumed to have a uniform temperature distribution, and the temperature of the bottom of the vessel. The model assumes a linear temperature profile, negligible heat storage in the sample, and negligible surface contact resistance. Heat transfer between the copper block and its insulation is assumed negligible. Using these assumptions, an expression was derived for the temperature of the copper block:

$$\ln\left(\frac{T_0 - T_\infty}{T - T_\infty}\right) = \frac{kA}{Lm_c c_{pc}} t, \tag{2.2}$$

where: A = heat transfer area, [m]

k = thermal conductivity of sample [W/m°C]

L = thickness of sample [m^2]

m_c = mass of copper block [kg]

c_{pc} = specific heat of copper [J/kg°C]

t = time [s]

T = temperature of copper block [°C]

T_0 = initial temperature [°C]

T_∞ = constant temperature of vessel bottom [°C]

The plot of the dimensionless temperature against time on semilog paper is linear with an initial curvilinear part. The thermal conductivity of the sample is calculated from the slope of linear part of this plot, the heat capacity of the copper block, and the thickness and heat transfer area of the sample.

Murakami et al. (1984), described a modified Fitch apparatus. The apparatus had a largely reduced heat transfer area compared to the regular Fitch apparatus. The heat sink and heat source both were 6.35 mm in diameter. This setup was suitable for measuring small disc shaped food particles. Measurements of thin, 3.25 mm, samples of cork showed a sensitivity to variations in sample homogeneity.

Zuritz et al. (1989) used a modified Fitch apparatus very similar to that of Murakami et al. (1984), to measure the thermal conductivity of kidney beans. Model error analysis showed that the errors associated with sample thickness and heat transfer area had the strongest influence on the error in sample conductivity. Ensuring good contact between sample and heat source and sink was mentioned as being critical.

Rahman (1991), used a modified Fitch apparatus with a 15 mm-diameter heat transfer area for measurements of moist food materials above and below freezing and reported an accuracy of 5 and 9% respectively (as compared to measurements with a line heat source probe). The effect of sample thickness was investigated, and was shown to have a significant effect on the quantification of thermal conductivity.

The assumptions of linear temperature profile and negligible heat storage favor a small sample thickness. On the other hand, a larger thickness will have lower measurement error. Also, Zuritz et al. (1989) mention that a fast response decreased the linear portion of the graph (for a modified Fitch apparatus). Optimum sample thickness for the Fitch apparatus is given as 6.4 to 13 mm (Mohsenin, 1980). The modified Fitch apparatus were used with much thinner samples. Thickness varied from 1.1 mm slabs of kidney bean (Zuritz, 1989) to 4-7 mm for moist food samples (Rahman, 1991). The latter tested samples of 15 mm in diameter.

The sample times for the regular Fitch apparatus are in the range of 10-20 minutes (Mohsenin, 1980). Modified Fitch apparati lose linearity for longer sample times probably due to heat transfer between the copper block and the insulation (Murakami, 1984). These apparati were generally used with sample times less that 8 minutes.

2.2.3 Transient Hot Wire

This is one of the most commonly used transient methods in particular with granular materials (Mohsenin, 1980). It is also known as the line heat source method. The theory is based on an linear heat source of infinite length and infinitesimal diameter. The line heat source is embedded in the material whose thermal conductivity is to be measured. From a condition of thermal equilibrium, the heat source is energized and heats the medium with constant power. The temperature response of the medium is a function of its thermal properties. The thermal conductivity is found from the temperature rise measured at a known distance from the heat source.

An often used implementation of the line heat source method for the measurement of thermal conductivity of food materials is the line heat source probe also known as the thermal conductivity probe.

2.2.4 Line Heat Source Probe

The line heat source probe is based on the theory of the line heat source method. Probes are constructed around a rigid straight rod like, e.g. a metal tube. A heating element and a thermocouple are placed inside, or on the outside of, the tube or rod. Internal placement makes the probe more robust. External placement of the heater and thermocouple has been reported to yield data of higher accuracy and with lower standard deviation (Baghe-Khandan, 1981b) than internal placement for a comparable sized probe. Large probes of about 47 cm length and 0.47 cm in diameter were used for measurements in soil (Hooper, 1950). For measurement of thermal conductivity of small food samples Sweat and Haugh (1974) used a miniature probe. Their probe was made from a narrow tube like a hypodermic needle. The probe was 38 mm long and had an outside diameter of 0.81 mm. An insulated heater wire (0.0762 mm diameter with 0.0762 mm teflon coating) was inserted along the full length of the tube. Constantan wire was used because of its small temperature dependence of resistance. An insulated thermocouple (Type E, chromel-constantan, 0.0762 mm diameter) was located inside the tube at the halfway point. The tube was bonded to an Omega miniature thermocouple connector.

To make a measurement, the probe was embedded in the material of interest. From thermal equilibrium, the probe heater was energized and heated the medium with constant power. The temperature rise at the heat source was monitored. Following a brief transient period, the plot of the temperature versus the natural logarithm of time became linear. The slope was equal to $Q/(4\pi k)$. The thermal conductivity could be calculated from the relation:

$$k = Q\,\frac{\ln\left[(t_2 - t_0)/(t_1 - t_0)\right]}{4\pi(T_2 - T_1)}, \qquad (2.3)$$

where: k = thermal conductivity of sample [W/m°C]

Q = power dissipation by heater wire [W/m]

t_1 = time since probe heater was energized [s]

t_2 = time since probe heater was energized [s]

t_0 = time correction factor [s]

T_1 = temperature of probe thermocouple at time t_1 [°C]

T_2 = temperature of probe thermocouple at time t_2 [°C]

The time correction factor t_0 compensates for the finite size of the probe and for differences in properties between sample and probe material. Its value is calculated from the data. Sweat and Haugh (1974) did not require time correction factors when measuring the thermal conductivity of meat at temperatures above freezing. At those temperatures, the heat capacity of the probe was reasoned to be similar to that of food. Also the small diameter probe they used (0.81 mm) closely approximated a line heat source.

Another source of error with the line heat source probe is axial flow error due to its finite length. Hooper (1950) recommend a length to diameter ratio of no less than 100. Sweat and Haugh (1974) found no statistical difference, at the 10% level, between probes with ratios varying from 93 down to 31 when testing glycerin. In line with these findings were those obtained by them when measuring agar-water samples that were shorter than the probe length. Samples of different length were measured. They were centered on the location of the thermocouple junction. The samples were bounded on both ends by teflon which has approximately half the thermal conductivity of water. No statistical effect was noticed for samples as small as half the probe's length.

The line heat source probe has the advantage of being a rapid method. Sweat (1986) reports measurements times from 3 seconds for liquid to 10 to 12 seconds for most solid foods. Besides the advantage of being rapid, the probe requires only a small sample size. Although the theory requires the medium to be of infinite size, in practice the temperature field is limited to a narrow range around the probe. Vos (1955) showed that when the expression $4\alpha t/d^2$ is greater than 0.6, an error will be noticeable due to the small sample diameter. In the above expression, α is the thermal diffusivity of the sample, t is the time since the heater was energized and d is the shortest distance between the probe and the sample boundary. For the probe of 38 mm length and 0.81 mm in diameter a sample diameter of 19 mm will suffice when measuring a thermal conductivity close to that of water.

Although often reported as an absolute method, it is recommended to calibrate the probe. Calibration also takes care of inaccuracies in measured resistance of heater wire and of temperature effects on resistance of wire. Agar-gelled water and glycerin are commonly used as thermal references. The line heat source probe is probably no more accurate than 2% (Sweat, 1986). Sweat and Haugh (1974) estimated the accuracy for measurements above 0 °C to be about 5%.

The line heat source probe is mainly used for measurement of thermal conductivity. Choi and Okos (1983) used an additional temperature sensor with known distance from the probe to measure thermal diffusivity of tomato juices. Using only a single probe, thermal diffusivity was estimated by numerical methods with heating and/or cooling data by Lan and Sweat (1992).

2.2.5 Thermistor Based Method

A thermistor is a temperature dependent resistor. Those used for thermal property measurement have a negative temperature coefficient of resistance, indicating that their resistance will decrease when their temperature is increased. Being resistive devices, a thermistor will heat when a current is passed through it. Both phenomena are exploited in the thermistor based method for thermal property measurement. The thermistor is used both as a temperature sensor and as a point heating source. The relationship between temperature and resistance is non-linear and is usually described by the empirical Steinhart-Hart equation (Thermometrics, 1987):

$$\frac{1}{T} = a_0 + a_1 \ln(R) + a_2 [\ln(R)]^3 \qquad (2.4)$$

where: T = temperature, [K]

R = resistance, [Ω]

a_0, a_1 and a_2 = derived constants.

The constants a_0, a_1 and a_2 are obtained in a calibration procedure.

In most studies concerning the measurement of thermal conductivity and diffusivity, a glass coated probe was used. Figure 2.1 shows a typical probe as was used in this research.

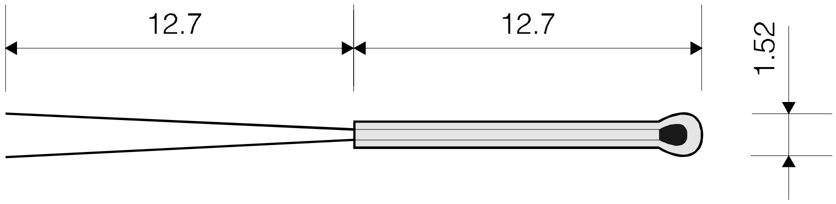

Figure 2.1 Glass coated bead thermistor probe. All dimensions in mm.

Early work on the use of a thermistor for measuring thermal conductivity took place in the biomedical field. Chato (1968) developed a transient method for measuring thermal conductivity and thermal inertia, $k \cdot \rho \cdot c_p$, of biological materials. The thermistor was modeled as a spherical heat source, with negligible thermal capacitance and negligible surface contact resistance, embedded in an infinite homogeneous and isotropic medium. The medium was treated as a semi-infinite solid. He solved the heat conduction equation in the medium for the case in which, starting from an equilibrium situation, the surface temperature of the thermistor is suddenly elevated with a predetermined increment and held constant at the elevated temperature. The temperature solution for the medium is given by:

$$\frac{T - T_0}{T_a - T_0} = \frac{a}{r} \operatorname{erfc}\left(\frac{r - a}{2\sqrt{\alpha t}} \right) \tag{2.5}$$

and the heat dissipation by the medium is given by:

$$q = -k\,4\pi a^2\left(\frac{\delta T}{\delta r}\right)_{r=a} = 4\pi ak(T_a - T_0) + 4a^2\sqrt{(\pi k\rho c_p)}\,(T_a - T_0)\,t^{-1/2} \tag{2.6}$$

where: a = radius of thermistor bead [m]
c_p = specific heat of medium [J/kg°C]
k = thermal conductivity of medium [W/m°C]
q = heat dissipation function [W]
r = radial coordinate [m]
t = time [sec]
T = temperature in medium [°C]
T_a = surface temperature of bead for $t > 0$ [°C]
T_0 = initial temperature [°C]
α = thermal diffusivity of medium [m^2/s]
ρ = density of medium [kg/m^3]

The heat dissipation by the thermistor is thus seen to be linear in the inverse square root of time. Linear regression of measurement data can be used to find the thermal conductivity (from the intercept of regression), and the thermal inertia (from the slope of regression).

This method required calibration with a medium of known thermal conductivity to find the effective bead radius. Beads were calibrated with agar-gelled water (1.5 and 1.75%) and paraffin. Chato (1968) was successful only in measuring thermal conductivity for which he reports an accuracy of 20%. Thermal inertia could not be determined due to inconsistent calibration results. Furthermore, the slopes of regression were much more sensitive to experimental error than the intercept. The method was rapid. Thermal properties could be measured within two minutes.

Balasubramaniam (1974, 1975, 1977) and Bowman (1976) improved on Chato's heat transfer model by acknowledging thermal gradients in the thermistor bead: both thermistor and medium were treated as distributed thermal masses. The thermistor was modeled as a sphere embedded in an infinite homogeneous and isotropic medium with no surface contact thermal resistance. This coupled heat transfer problem was solved for the case where starting from a thermal equilibrium, the temperature of the thermistor was raised instantaneously to, and maintained at, an elevated temperature. The required heat generation was assumed to take place uniformly throughout the bead. This heat generation was experimentally determined to be of the form $\Gamma + \beta \cdot t^{-1/2}$. The temperature distributions of thermistor bead and surrounding medium were presented as indefinite integrals which had to be solved numerically. At steady state a simple equation was obtained for measuring thermal conductivity, k_m:

$$\frac{1}{k_m} = 4\pi a \frac{\Delta T}{P_{ss}} - \frac{0.2}{k_b} \tag{2.7}$$

In the above equation, $\Delta T / P_{ss}$ is the ratio of temperature step and the steady state power dissipation in the thermistor required for maintaining ΔT. Calibration with two materials of known thermal conductivity was necessary to find values for the effective probe radius, a, and effective probe thermal conductivity, k_b. Medium thermal diffusivity was determined simultaneously through a somewhat involved procedure which required knowledge of the bead thermal diffusivity (Balasubramaniam, 1974, 1975, 1977), Bowman (1976). Sample times were short, 20 to 60 seconds. The method was reported to be capable of estimating thermal conductivity and diffusivity with an accuracy of 1 - 2% and 10% respectively.

Valvano (1981) mathematically showed the heat generation function to be of the form of $\Gamma + \beta \cdot t^{-1/2}$. Closed form approximations for the temperature distributions were presented where Balasubramaniam had given them as indefinite integrals (see the next chapter for a more detailed treatment of the heat transfer model). Valvano also showed that while the thermal conductivity of the bead plays a role in determining the medium thermal conductivity, the thermal diffusivity of the medium could be calculated without knowledge of the bead thermal diffusivity. However, an additional calibration with two media of known thermal diffusivity was required. Agar-gelled (1.5%) water and glycerol were used as calibration media to find the probe properties. Valvano (1984) tested a thermistor probe as an interpolating instrument. After calibration with agar gelled water and glycerol, the thermistor was used to estimate the thermal conductivity and diffusivity of three mixtures of water and glycerol. The thermal property measurement was found to be accurate within 2% and reproducible to 1%. Valvano (1984, 1985) used a sample period of 20 seconds with data analysis by linear regression over 4 - 18 seconds. Tests with longer periods (30, 60 and 120 seconds) yielded no different thermal properties (Valvano, 1985). Tests with different levels of agar (0.5 - 5%) showed no discernible effect of concentration on thermal properties (Valvano, 1985). Tests over the temperature range 3 - 45 °C (every 7 °C) on biological tissues showed that temperature dependence of the tissues followed that of water (except for fat, lung and cancer tissues) (Valvano, 1985).

Woodbury (1984) used self-heated thermistors to measure the thermal conductivity of building insulation with varying degree of wetness. He employed teflon coated probes with a diameter of 2.79 mm. Balasubramaniam and Valvano had used smaller glass encapsulated (and some bare) probes. Small probes heat up faster, more closely mimicking a step change in temperature. Large probes increase the sample volume, reduce the effect of imperfect contact at the thermistor medium interface and are more durable. Woodbury noticed two linear parts in the plots of power versus the inverse square root of time, an observation not reported by previous researchers. The first linear part was initially used as calibration interval (10 to 20 seconds). It was followed by a concave part. For long times, larger than 60 sec. for glycol and larger than 200 sec. for the other two materials (both insulation materials), the plot became linear again. Regression over the first linear part gave smaller values for the intercept, and thus for the 'steady state' power consumption, than regression over the second linear part. Woodbury considered the intercept as found from this latter part of the data the true estimator of steady state power consumption. The difference between the intercepts found with the two parts of the data was related to the thermal conductivity of the medium. Larger differences were found for media with smaller thermal conductivities. Long term tests were done with all probes in all calibration media and correction ratios (CR's) were found. The CR is the ratio between 'true' V_{ss}^2 and V_{ss}^2 found from regression over 10 - 20 seconds. A linear relationship was assumed between CR and k_m. Linear regression on the CR-k_m data for several probes showed that for a medium thermal conductivity of 0.40 - 0.50 [W/m°C] the value of CR would be unity. For larger medium thermal conductivities, the graph should display a convex part instead of a concave part. Tests with agar-gelled water at 25 °C (k_m is 0.61 W/m°C) confirmed this. Probe parameters were recalculated with the 'true' values of V_{ss}^2. Calibration error (error in estimating the thermal conductivity of the calibration media in a 3-media calibration) was given as 4.6%.

Larger probes and stem losses were put forward to explain the observed two-part graph. Balasubramaniam and Valvano had used small glass encapsulated probes; Woodbury used large teflon encapsulated probes. Heat loss through the probe stem was probably larger in his study because the thermal conductivities of the test media (0.03 - 0.25 W/m°C) were far lower then encountered by the previous researchers, who dealt with animal and human tissue (0.3 - 0.6 W/m°C), and the probes had larger diameter lead wires and a metal support rod in the stem.

Dougherty (1987) tested glass and teflon encapsulated probes with a variety of materials, ranging from low viscosity fluids like toluene to insulation materials. Glass encapsulated thermistors appeared to perform better in fluids whereas the teflon encapsulated thermistor performed better with insulation materials. Based on visual observations of test data, the researcher noted that the method may have a limited applicability due to either convection losses in low viscosity fluids or stem losses in low thermal conductivity materials. He concluded that the thermistor method is most suited for viscous liquids of higher thermal conductivity like castor oil and glycerol. An alternate approach to the probe operation was investigated. Previous researchers had used analog circuitry, developed by Balasubramaniam, to control the thermistor's temperature at the preset level. Voltage was the controlled variable. Dougherty's instrumentation used digital control to regulate the current to the probe.

Kravets (1988) was the first to use self-heated thermistors at elevated temperatures. Glass encapsulated probes were used to measure thermal conductivity of milk and cream over the range of 25 to 125 °C. This temperature range was divided in four sub-ranges because the thermistors could be used only over certain resistance - and thus temperature - range. The control circuitry limited the allowable thermistor resistance to the range 500 and 3500 Ω. The assumption of an infinite boundary, which was made in the development of the heat transfer model for the thermistor based method, was experimentally tested. A sample diameter of 5 mm was found to satisfy this assumption for a probe of 1.5 mm in diameter.

From error analysis of the measurement of thermal conductivity, Kravets concluded that: a) error in estimation of medium thermal conductivity decreases with a higher thermal conductivity of the probe; b) a temperature step of minimally 2.5 °C has to be used to minimize errors in medium thermal conductivity; c) more accurate thermal conductivity reference materials are needed to minimize the errors in estimated bead parameters.

Of the methods discussed, a self-heated thermistor promises to be the best for measurement of thermal conductivity and thermal diffusivity. The line source probe in combination with an additional temperature sensor is capable of measuring thermal diffusivity but requires a much larger sample volume than a thermistor. A disadvantage of the thermistor based method is that it is not absolute. Calibration with at least two reference materials is necessary. The calibration is required at every measurement temperature and demands thermal standards for both thermal conductivity and thermal diffusivity.

Alternate Modes of Operation of Thermistor Probes

The mode of operation of the thermistor in the foregoing was one of fixed temperature step: the thermistor is maintained at a fixed elevated temperature and the required power is monitored. Alternate modes of operation have been investigated and are briefly discussed in the following. They were developed to address the issue of perfusion in human tissue.

In the biomedical field, research into the use of thermistors for measurement of thermal conductivity focused not only on the tissue thermal conductivity itself, but also on thermal conductivity as an estimator of tissue perfusion. The thermistor based method that maintains a fixed elevated bead temperature requires a no-flow calibration in order to be able to extract intrinsic tissue thermal conductivity from the effective thermal conductivity that is measured in the presence of perfusion. Alternate modes of probe operation were investigated that would forego the no-flow calibration. Using a sinusoidal varying voltage supply, Valvano et al. (1987) , Anderson et al. (1988), and Anderson and Valvano (1989) simultaneously measured intrinsic and effective tissue thermal conductivity. Accuracy in measurement of stationary media was no better than when the probe was operated with a fixed temperature increment. Determination of thermal diffusivity was not performed.

Chen and Rupinskas (1977) measured thermal conductivity invasively with a thermistor probe by supplying the thermistor with a heating pulse and monitoring the subsequent temperature decay. The pulse-decay method is considered to be absolute, calibration should not be required. Limited results are given in the 1977 paper for three fluids. These indicate the necessity for further research before this method can be used to determine thermal conductivity with a large degree of accuracy. The pulse-decay method was later extended to predict perfusion in biological tissues as well (Chen and Holmes, 1980, Arkin et al., 1986).

The invasive probe technique causes some tissue trauma due to insertion of the probe. To measure tissue properties and perfusion non-invasively, Patel et al. (1987) developed a surface probe. A glass encapsulated thermistor was partly embedded in an insulation material to direct the heat flow downward. The bottom half was brought into contact with the medium of interest. The probe was not operated with a fixed temperature increment. Instead, a precision voltage powered the thermistor in series with a precision resistance. Power dissipation by and temperature response of the thermistor were monitored. Thermal conductivity and diffusivity could be determined simultaneously. The accuracy of the thermal properties of water-glycerin mixtures, measured with a probe that was calibrated in agar gelled water and glycerin, was comparable to that obtained with an invasive probe. Experiments with rat liver tissue, revealed a wide scatter in the data. This was attributed to poor contact between probe and surface. Valvano (1990) commenting on the surface probe method stated that it was "unreliable due to poor contact with tissue and uncertain boundary conditions at the contact surface".

2.3 NATURAL CONVECTION

One of the assumptions when using the thermistor based method is that heat transfer from the thermistor bead occurs solely by means of conduction. In a liquid medium, this assumption can be violated through natural convection. Localized heating by the thermistor bead induces density gradients in the initially isothermal and quiescent medium. The resulting buoyancy force will be opposed by a combination of inertia and viscous forces. Convection then may occur depending on the interplay of these forces. Their magnitude depends on the properties of the fluid, the size of the probe, and on the imposed temperature step. It is of interest to know if there is a means of assessing the potential for convection during a thermal property measurement with a thermistor. A literature study was undertaken to develop insight into the phenomenon of transient natural convection.

The onset of natural convection was first experimentally studied by Bénard for thin horizontal fluid layers heated from below (Chandrasekhar, 1961). Bénard's experimental work motivated Rayleigh to undertake an analytical study for the case of an infinite wide fluid layer heated from below. For a fluid layer between two horizontal boundaries and heated from below, cellular convection will be initiated once the Rayleigh number exceeds a critical value of approximately 1108. The Rayleigh number was defined as:

$$Ra = \frac{g\beta\Delta T d^3}{\alpha\nu} \qquad (2.8)$$

where: g = gravitational acceleration [m/s^2]
β = coefficient of thermal expansion [1/K]
ΔT = temperature difference between surface and fluid [°C]
d = characteristic length [m]
α = thermal diffusivity [m^2/s]
ν = kinematic viscosity = μ/ρ [m^2/s]
μ = dynamic viscosity [Pa·s]
ρ = fluid density [kg/m^3]

The onset of natural convection around a suddenly heated horizontal wire was investigated by Vest and Lawson (1972). Experiments were performed in air and water. An interfero meter registered the shape of the isotherms after application of the current. The earliest distortion of the isotherms - an indication of convection effects - were observed above the wire. Based on this observation the heating situation was taken to resemble that of the Benard problem of a fluid layer heated from below. The Rayleigh number at the onset of convection was assumed to be 1100. Vest and Lawson defined the Rayleigh number in terms of the strength of the heat source and an instantaneous heat penetration depth. The latter was found from an approximate solution to the heat transfer problem. A relationship was developed between the onset time (called the delay time) and the energy dissipation in the wire, with the fluid properties as parameters. The delay times for water agreed fairly well with the prediction. For air, though following the predicted trend, the relationship consistently underpredicted the delay time.

Parsons and Mulligan (1980) investigated the onset of natural convection in air surrounding a cylinder. A steel rod (6.3 mm diameter) was suddenly heated with an electrical current. Experimentally observed onset times of convection compared favorably against those that were predicted. The latter were calculated from the solution to the heat transfer model, and an assumed value of 1100 for the Rayleigh number at onset of convection. The Rayleigh number was numerically evaluated from the exact solution to the heat transfer problem using an effective temperature gradient, $(T_w - T_\omega)_e$. The effective temperature gradient was taken as the linearized temperature function that integrated to the same value - over the heat penetration depth - as the integrated exact solution. Although the problem was approached as that of a fluid layer heated from below, the researchers observed that localized convection currents near the vertical surfaces of the rod occurred prior to the onset of global convection.

Genceli (1980) investigated the onset of natural convection in air surrounding suddenly heated nickel plated Plexiglas cylinders with diameters of 15, 25 and 40 mm and found Rayleigh numbers at the onset of convection that ranged from about 20 for the 15 mm diameter cylinder to about 30 for the 40 mm diameter cylinder.

Wang et. al (1991) numerically studied transient natural convection from horizontal cylinders under diverse surface boundary conditions. They observed that "the onset of motion results from the natural convection along the approximately vertical portions of the cylinder surface [...], and not from a Benard type convective instability in the statically unstable conduction temperature profile near the top of the cylinder".

Jia and Gogos (1996) studied transient laminar natural convection heat transfer from isothermal spheres with a numerical method. They covered a Grashof number range of 10 to 10^7 for a fluid with Prandtl number of 0.72. The focus was mainly the developing plume. An observation pertaining to the onset of convection was that "the temperature gradient in the radial direction at $\theta = 90°$ [the equator of the sphere] seems to lead the onset of convection". Critical Raleigh numbers were calculated at the onset time of convection. The penetration depth was defined as the depth at which the medium temperature was reduced to 1% of the surface temperature. The temperature differential was taken as $T_s - T_\omega$. The critical Rayleigh numbers increased with the Grashof number from about 139 for a Grashof number of 10 to 3950 for a Grashof number of 10^8. The authors concluded that the use of the critical Rayleigh Number from the Benard problem (1100) was completely inappropriate [for the geometry of their study].

In conclusion, the literature on transient natural convection is rather limited. The above cited studies comprise about all that seemed relevant to the present study. The closest resemblance to the specific geometry of this study, that of a more or less spherical object at the tip of a downward pointing vertical rod, was the study of Jia and Gogos (1996) for isothermal spheres. As far as the expected onset times of convection are concerned, the literature was of little help. Nor could it suggest a value for the Rayleigh number that coincides with the onset of convection. That of the Benard problem is clearly not applicable because thermistor based measurements don't resemble that of a fluid layer heated from below. The idea of a critical Rayleigh number, however, was intriguing.

CHAPTER 3

PRINCIPLES OF THE THERMISTOR BASED METHOD

This chapter will discuss the principles of the thermistor based method, and the assumptions made in its development. The reality as manifested in the measurement system deviates to some extent from the model as will be pointed out. The equations used for estimation of thermal conductivity and diffusivity will be presented. These equations contain parameters which are found by calibration. The approach taken for the calibration will be outlined. Some considerations when using the thermistor based method will be discussed as they relate to the choice of samples and measurement procedure.

3.1 HEAT TRANSFER MODEL

The thermistor based method utilizes a thermistor as a point heating source. Heat emanates from the bead into the surrounding medium. The thermistor is operated with a constant temperature step: heat is generated inside the bead to maintain its temperature at a constant value above the initial equilibrium temperature. Provided some conditions are met, the power dissipated inside the thermistor bead is related to the thermal properties of the medium.

The heat transfer model acknowledges space and time dependency of temperature in both the thermistor bead and the surrounding medium. This coupled heat transfer model is based on the assumptions that:

1. the thermistor is of spherical shape,
2. the thermistor is made of isotropic and homogeneous material,
3. heat is being generated uniformly in the thermistor,
4. the surrounding medium is isotropic, homogeneous and infinite in extent,
5. no contact resistance exists between thermistor and medium,
6. the mode of heat transfer is pure conduction.

The assumptions simplified the development of the model. The reality in this research deviated from the model in several ways. Rather than being spherical, the thermistors resembled a prolate spheroid, and had a stem attached to it. Unlike the assumption, they were not isotropic and homogeneous, nor had heat generation uniformly throughout their volume. Instead, a glass shell insulated the semi-conductor core from the environment. Lead wires ran down the glass stem and attached to one side of the semi-conductor core. The electrical pathways inside the core were many with heat generation probably not completely uniform throughout. The probes used in this research were hand picked under a microscope for minimal deviations from the model. Hayes and Valvano (1985) assessed the validity of the first three assumptions with a steady state finite element model. They found "that the empirical linear relationship (between the power consumption of the probe and the inverse square root of time) remains valid when all three assumptions are significantly relaxed".

As mentioned in Chapter two, the thermally affected region is small. Kravets (1988) experimentally determined this region to be no more than 5 mm in diameter for a thermistor with a bead diameter of 1.5 mm. A sample larger than this region can be considered infinite. Whether a sample material can be seen as homogeneous and isotropic depends in general on the scale of its internal variations compared to the scale of the measurement volume. With the thermistor this volume is very small as mentioned above. The degree of homogeneity has to be evaluated with this small volume in mind.

Media that wet the surface of the thermistor minimize its contact resistance. Patel et al. (1987) developed a two dimensional transient finite element model to investigate the effect of imperfect contact between the probe and medium. A decoupler medium was introduced to model contact resistance. The error in estimated medium thermal conductivity was determined for different probe sizes and different values for decoupler thickness and decoupler thermal conductivity. They concluded that the error decreases with: a larger probe, longer heating time, thinner decoupler layer, smaller difference between medium and decoupler thermal conductivity.

The assumption of pure conduction heat transfer can be challenged when measuring the thermal properties of fluids. Localized heating by the thermistor induces temperature and density gradients in the fluid. Convection will take place if the buoyancy force resulting from the density gradient exceeds the viscous drag from the fluid. Low viscosity fluids are thus more prone to natural convection than high viscosity fluids. The low viscosity fluids are treated with either a thickener - like agar-agar in water - or a flow inhibitor, like glass fiber. The treatment level is kept to a minimum as not to change the thermal properties of the medium. In addition to that, small beads and low heating power are used in an attempt to delay the onset and minimize the effect of natural convection.

Using the assumptions the heat transfer problem can be described by the following one-dimensional heat diffusion equations:

$$\frac{1}{r^2}\frac{\delta}{\delta r}\left[r^2\frac{\delta T_b}{\delta r}\right]+\frac{q(t)}{k_b} = \frac{1}{\alpha_b}\frac{\delta T_b}{\delta t} \qquad 0 \le r \le a \qquad (3.1)$$

$$\frac{1}{r^2}\frac{\delta}{\delta r}\left[r^2\frac{\delta T_m}{\delta r}\right] = \frac{1}{\alpha_m}\frac{\delta T_m}{\delta t} \qquad r \ge a \qquad (3.2)$$

Symmetry dictates the boundary condition at the center of the thermistor to be:

$$\frac{\delta T_b}{\delta r} = 0 \qquad r = 0, \quad t \ge 0 \qquad (3.3)$$

The assumptions of pure conduction, absence of surface contact resistance and infinity of the medium gives as boundary conditions:

$$T_b = T_m \qquad r = a, \quad t > 0 \qquad (3.4)$$

$$k_b\frac{\delta T_b}{\delta r} = k_m\frac{\delta T_m}{\delta r} \qquad r = a, \quad t > 0 \qquad (3.5)$$

$$T(r,t) = T_i \qquad r \to \infty, \quad t > 0 \qquad (3.6)$$

The initial condition is given by the requirement that the thermistor and the surrounding medium should be at a thermal equilibrium at the start of a test.

$$T(r,t) = T_i \qquad 0 \le r \le a, \quad t = 0 \qquad (3.7)$$

$$T(r,t) = T_i \qquad r > a, \quad t = 0 \tag{3.8}$$

3.2 SOLUTION

The solution to this coupled heat transfer problem is taken from Valvano (1981). In order to obtain the solution, the form of the heat generation function, q(t), has to be known. A heat generation function of the form q(t) = Γ + β•f(t) is assumed. Γ is the steady state term, f(t) is the transient term which will approach zero for long times. The form of the heat generation function was experimentally verified (Balasubramaniam, 1975). The mathematics involved in solving this heat transfer problem can be found in Valvano (1981). The resulting two equations for the temperature distribution in the thermistor bead and the medium are:

$$T_b(r,t) - T_i = \frac{a^2}{k_b}\left[\frac{k_b}{3k_m} + \frac{1}{6}\left(1 - \left(\frac{r}{a}\right)^2\right)\right](\Gamma + \beta f(t)) - \frac{\Gamma a^3 f(t)}{3k_m\sqrt{\alpha_m \pi}} \tag{3.9}$$

$$T_m(r,t) - T_i = \frac{a^3\Gamma}{3k_m r}\left[\frac{(a-r)f(t)}{\sqrt{\alpha_m \pi}}\right] + \frac{\beta a^3 f(t)}{3k_m r} - \frac{\Gamma a^4 f(t)}{3k_m r\sqrt{\alpha_m \pi}} \tag{3.10}$$

Equation (3.9) describes the temperature distribution inside the bead and is used to derive equations that form the basis for the thermistor based measurement technique.

3.3 APPLICATION

3.3.1 Measurement of Thermal Conductivity

The test procedure consists of controlling the temperature of the thermistor bead at a specified increment above the initial temperature. The experimentally measured temperature of the bead, as observed from the resistance of the thermistor bead, is a spatial average over its volume. The integral of equation (3.9) over the volume of the bead will give an equation for the average bead temperature as function of time:

$$
\begin{aligned}
T_b(t) - T_i &= \frac{1}{(4/3)\pi a^3}\int_0^a \left\{ \frac{a^2}{k_b}\left[\frac{k_b}{3k_m}+\frac{1}{6}\left(1-\left(\frac{r}{a}\right)^2\right)\right](\Gamma+\beta f(t)) - \frac{\Gamma a^3 f(t)}{3k_m\sqrt{\alpha_m\pi}}\right\}4\pi r^2 dr \\
&= \frac{a^2}{k_b}\left[\frac{k_b}{3k_m}+\frac{1}{15}\right](\Gamma+\beta f(t)) - \frac{\Gamma a^3 f(t)}{3k_m\sqrt{\alpha_m\pi}} \qquad (3.11)
\end{aligned}
$$

The transient heating function f(t) will approach zero for long times. When the limit is taken of equation (3.11) with the time variable going to infinity an expression for the average steady state temperature of the thermistor bead is obtained:

$$
T_{b_{ss}} - T_i = \frac{\Gamma a^2}{3k_b}\left[\frac{k_b}{k_m}+0.2\right] \qquad (3.12)
$$

The constant internal heat generation in the bead is:

$$
\Gamma = \frac{\text{steady state power}}{\text{volume of bead}} = \frac{V_{ss}^2/R_f}{(4/3)\pi a^3} \qquad (3.13)
$$

Substituting this expression into equation (3.12) gives, after rearranging:

$$
\frac{1}{k_m} = \frac{4\pi a R_f \Delta T_b}{V_{ss}^2} - \frac{1}{5k_b} \qquad (3.14)
$$

This expression shows that when the bead parameters, a and k_b, are known, the medium thermal conductivity can be calculated from the experimentally obtained values for R_f , ΔT, and V_{ss}. The thermistor probe requires calibration with media of known thermal conductivity to estimate the bead parameters, a and k_b.

3.3.2 Measurement of Thermal Diffusivity

The temperature of the thermistor bead, as observed from its resistance, reaches a constant value shortly after energizing. As shown above, this temperature is related to the steady state heat generation term only. The terms involving the transient heat generation function f(t) in equation (3.11) must therefore sum to zero:

$$
0 = \frac{a^2}{k_b}\left[\frac{k_b}{3k_m}+\frac{1}{15}\right]\beta f(t) - \frac{\Gamma a^3 f(t)}{3k_m\sqrt{\alpha_m\pi}} \qquad (3.15)
$$

This expression can be rewritten to single out the medium thermal diffusivity, α_m, on the left side of the equal sign:

$$\alpha_m = \left[\frac{a}{\sqrt{\pi}\,(\beta/\Gamma)\left(1 + \frac{k_m}{5k_b}\right)} \right]^2 \tag{3.16}$$

The values for β and Γ of the heat generation function are found from the experimentally obtained power response of the thermistor. In the process of solving the heat transfer problem, Valvano showed that the time-function had to be of the form $t^{-1/2}$. The heat generation function can thus be described as: $q(t) = \Gamma + \beta \cdot t^{-1/2}$. Values for Γ and β are found through linear regression. The resistance of the thermistor reaches a constant value within a few tenths of a second after startup. The voltage drop across the thermistor can thus be described by $V(t)^2 = V_{ss}{}^2 + s \cdot t^{-1/2}$. Figure 3.1 shows the results of an experiment in thickened water at 100 °C. The graph depicts the square of the voltage drop across the thermistor against the inverse square root of time. The values for the probe radius and thermal conductivity in equation (3.16) are not identical as those used for estimation of thermal conductivity and have to be determined through calibration with media of known thermal diffusivity.

3.4 CALIBRATION: ESTIMATION OF PROBE PROPERTIES

Equations (3.14) and (3.16) are the working equations for the thermistor based method. The probe parameters, effective radius and effective thermal conductivity, are found through calibration with reference media. These media have well documented thermophysical properties over the temperature range of interest . Calibration is required at each temperature of future use. The results of measurements in two media can be used to solve for the probe's effective properties. Ideally, any two suitable media would yield identical probe properties. However, as observed by earlier researchers (Balasubramaniam, 1975; Dougherty, 1987; Kravets, 1988), this rarely is the case. Some of the explanations that are brought forward

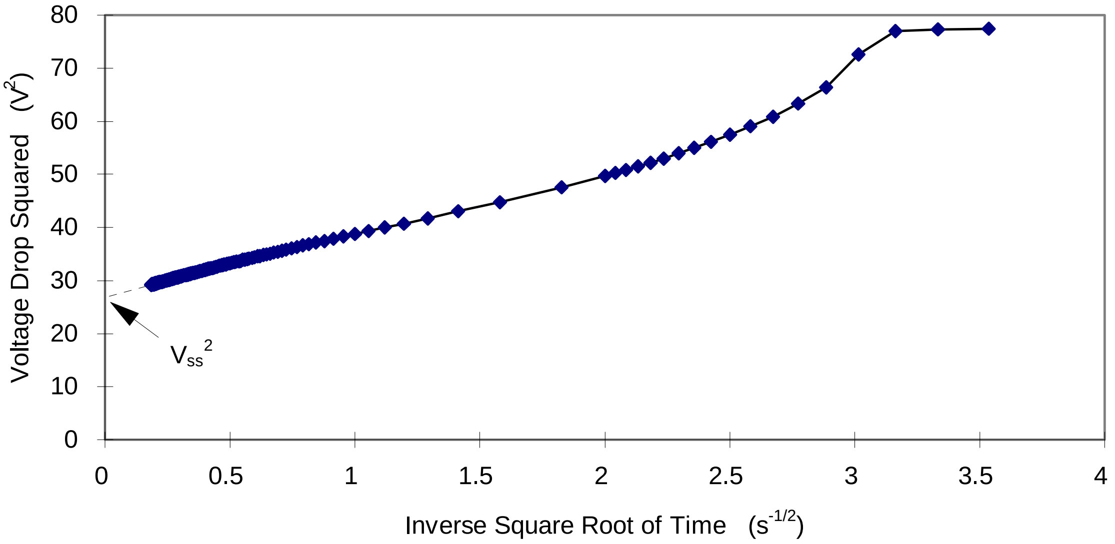

Figure 3.1 Square of voltage drop across thermistor versus the inverse square root of time for a thickened water sample at 100 °C.

mention inaccurate property data of the reference media, experimental error and stem losses (heat transfer through the stem of the probe). A three material calibration seeks to minimize the effect of the various errors. The probe's parameters are estimated by taking the average over the solutions for each two material subset.

3.5 PRACTICAL CONSIDERATIONS

When developing the procedures for the experiment, some decisions have to be made regarding the samples used and the heating power. Two of them, the required sample dimensions and the size of the temperature step used, will be discussed.

3.5.1 Sample Dimension

One of the assumptions made in the development of the heat transfer model is that the medium is infinite in extend. In reality, the temperature field generated by the thermistor probe reaches only a short distance into the medium. Probe size, temperature step, medium thermal properties and sample time will influence the size of the thermally affected region.

Balasubramaniam (1975) determined the size of the temperature field theoretically. The transient solution for the temperature distribution of the medium was used to model the temperature field in agar-gelled water, for a heating power function that caused a 3 °C temperature rise in a thermistor bead of 0.8 mm radius. A temperature rise of less than 1% of the temperature step after 60 seconds was taken as defining the infinite boundary. Under these conditions, the infinite boundary assumption was satisfied by a sample with radius of 0.25" (6.35 mm) or about eight times the bead radius. For lower medium thermal conductivity, the bead surface temperature increased (for a given value of ΔT), leading to a temperature field that extended farther into the medium.

Valvano (1985) reported an effective sample volume of 5 to 10 bead radii. This was evaluated with a steady state finite element model. The effective sample volume was taken to be bordered by a temperature contour of 10% of the average bead temperature. The effective measurement depth of a surface probe was assessed in thin layers of glycerol on agar-gelled water (Valvano, 1987). The surface probe was made from a 1.6 mm diameter glass encapsulated probe with insulating material covering the top hemisphere. Effective measurement depth was evaluated as having a measured thermal conductivity corresponding to a mixture of 95% glycerol and 5% water. Effective depth was found to increase from 0.9 radii at 20 sec., 1.3 radii at 40 sec., to 4.3 radii after 80 seconds. For a probe of 1.5 mm diameter, the effective sample volume is given as about 0.5 cc (corresponds to a sphere with radius of 5 mm). The effective sample volumes are quite a bit smaller than the 8 to 10 bead radii given by Balasubramaniam and Bowman.

Kravets (1988) determined the minimal sample size that satisfied the infinite boundary condition through experimentation. Holes of increasing diameter were drilled in an aluminum block and filled with glycerol. Sampling time and temperature step are not specified but probably similar to those used in other parts of his research: 20 seconds and 2.5 - 4 °C respectively. The infinite boundary condition was evaluated from measured conductivities in the different size holes. Tests with two different diameter probes yielded a minimal acceptable sample diameter (infinite boundary) of 5.0 mm for the thermistor with a nominal diameter of 1.52 mm and 7.16 mm for the thermistor with a nominal diameter of 2.54 mm. Expressed in bead radii, the infinite boundary assumption is satisfied by sample volumes having a radius of 3.3 and 2.9 bead radii respectively. These findings are consistent with the observations made with the surface probe by Valvano (1987).

3.5.2 Temperature Step

The size of the effective sample volume is related to the magnitude of the temperature step, ΔT. For very localized measurements, a small temperature step and short measurement times can be used. A small step will be attained fast and more closely mimicking a step change in the (average) bead temperature. Because of the possibility of natural convection, low viscosity fluids favor a small value. A larger value for ΔT will improve the accuracy of the temperature measurement and increase the accuracy of estimated thermal conductivity. A 1% error in ΔT will give a $1+0.2 \bullet k_m/k_b$ % error in k_m (Balasubramaniam, 1975), were k_m/k_b is the ratio of medium and bead thermal conductivity. For a probe with a thermal conductivity of 0.1 W/m°C, a 1% error in ΔT will give an error in the thermal conductivity of water, glycerol and castor oil of 2.2, 1.6 an 1.4% respectively.

Chato (1968) tested different values for the temperature step. A range of 3 - 7 °C was given as preferred with 5 °C being optimal. From tests in water and agar-gelled water at about 30 °C, Balasubramaniam (1975) concluded that a temperature step in the range 1.4 - 2.1 °C is best suited for water-like media. For solid biomaterials and viscous liquids, the temperature step of 5 to 10 F (2.8 to 5.6 °C) should generally work well.

Valvano (1981) investigated the effect of the temperature step on the magnitude and accuracy of thermal conductivity and diffusivity. Measurements were done in 1.5% agar-gelled water at 37 °C, with nine values for the temperature step ranging from 1 to 9 °C. It was concluded that the magnitude of the temperature step had little effect on the quantification of the thermal properties. The reproducibility was significantly better at higher values for ΔT. Valvano (1985) reports on using a value of 4 °C. Dougherty (1987) used 2 or 3 °C, without finding an effect on the measured value of thermal conductivity.

3.6 NOMENCLATURE

a = radius of thermistor bead [m]

k = thermal conductivity [W/m°C]

q = heat generation [W/m^3]

r = radial coordinate [m]

R = resistance [Ω]

s = slope of voltage squared versus inverse square root of time [$V^2s^{1/2}$]

t = time [s]

T = temperature [°C]

V = voltage drop across thermistor [V]

α = thermal diffusivity [m^2/s]

β = slope of heat generation function [$Ws^{1/2}/m^3$]

Γ = steady state power dissipation of bead per unit volume [W/m^3]

Subscripts

1 = thermal conductivity calibration (e.g. a_1)

2 = thermal diffusivity calibration (e.g. a_2)

b = bead

f = final

i = initial

m = medium

ss = steady state

CHAPTER 4

METHODS AND MATERIALS

The first part of this chapter will present the thermistors that were chosen for this research and the instrumentation that was built for making the thermal property measurements. Calibration is a requirement with this method and the way that this was accomplished will be outlined. The selection of the calibration materials is discussed.

The evaluative part of this research is presented as several studies: a) a comparative study that uses a miniature line heat source probe as reference for the thermistor, b) an investigative study into the effect of viscosity and temperature step on the quantification of thermal conductivity, c) two evaluative studies at high temperatures, one with tomato concentrate and the other with a nutritional supplement.

4.1 THERMISTORS

The thermistors in this research were glass coated probes from the P60-series of Thermometrics (Edison, NJ). They had a nominal bead diameter of 1.52 mm and an overall length of 12.7 mm. The leads were 0.203 mm in diameter. A representation of a typical thermistor used in this research was given earlier in Chapter 2 (Figure 2.1). For optimal performance of the instrumentation, to be discussed later, the resistance of the thermistor should fall in the range 500 to 3500 Ω. The temperatures encountered in this study varied from 25 to 150 °C. Thermistors exhibit a strong temperature dependence of resistance, and no single thermistor could be found for use over the entire temperature range. Experiments at low temperature, 25 and 50 °C, were performed with P60DA202M thermistors, with a nominal resistance of 2 kΩ at 25 °C. For experiments in the range 100 to 150 °C, thermistors with a nominal resistance of 50 kΩ at 25 °C, model P60DB503M, were chosen.

The thermistors were calibrated for resistance versus temperature against a thermal reference with 0.001 °C resolution (Guildline 9540 Digital Platinum Resistance Thermometer, Smith Falls, Ontario) traceable to National Institute of Standards and Technology (NIST). The probes for low temperature measurements were calibrated from 20 to 62 °C at 3 °C increments, in a circulating bath (Haake A82, Haake Buchler Instruments Inc., Saddle Brook, NJ) filled with a water-ethylene glycol mixture. The thermistors for high temperature measurements were calibrated from 95 to 155 °C at 5 °C increments, in a circulating bath (Exacal EX-251 HT, NESLAB Instruments, Inc., Newington, NH) that contained the heat transfer fluid HTF 500 (Union Carbide, Danbury, CT). For calibration, the thermistors and thermometer were placed inside a metal box 3.5 by 3.5 by 9 cm, that restricted the flow, and greatly improved the stability of the thermometer and thermistor readings. The resistance of the thermistors was determined indirectly by measuring the voltage drop resulting from a precision current of 0.1076 mA. The self heating by this current was negligible. Voltage was measured with a multimeter (Keithley 197 Autoranging Microvolt DMM, Keithley Instruments Inc., Cleveland, OH) with 0.01 mVolt resolution. Temperature was related to resistance using the following equation:

$$\frac{1}{T} = a_0 + a_1 \ln(R) + a_2[\ln(R)]^3 \tag{2.4}$$

The coefficients, a_0, a_1, and a_2, were determined by non-linear regression analysis in SAS (Statistical Analysis Software, Cary, NC).

4.2 THERMISTOR ASSEMBLY

The thermistors had a stem, approximately 12 mm long, from which two bare wires extended. The bare wires were covered with insulation that was removed from wire wrap wires. Teflon coated wires were soldered to the thermistor's lead wires and the junctions were insulated with heat shrink tubing. Completion of assembly was determined by the intended use, low or high temperature measurements.

4.2.1 Low Temperature Probes

Stainless steel tubing with an outside diameter of 6.35 mm and suited for use in a pipe fitting (Swagelock, Solon, OH) was used as a holder for the low temperature probes. They were bonded inside this tubing with epoxy (J-B Weld, J-B Weld Company, Sulphur Springs, TX), with the thermistor's bead extending about 6.5 mm from the holder. Figure 4.1 shows the probe assembly for the low temperature measurements.

Figure 4.1 Probe assembly for low temperature measurements.

4.2.2 High Temperature Probes

A significant amount of time and effort was spent on the design of a moisture and pressure resistant thermistor assembly. The high temperature probes were to be used at temperatures up to 150 °C and pressures of up to about 500 kPa. The seal around the thermistor's stem had to withstand these conditions.

Initially, a similar approach was taken as for the low temperature probes, only instead of J-B Weld, a special high temperature epoxy (Omegabond 200, Omega Engineering Inc., Stamford, CT) was used. The epoxy was cured at 150 °C for 6 hours. In use, the repeated heating and cooling, in combination with the harsh conditions to which the probes were subjected took their toll on the epoxy. It deteriorated to the point that moisture could reach the wires coming from the stem, ending the useful life of the probe. The holder was redesigned to one where the exposed surface of the epoxy was greatly reduced. However this design too failed after repeated use. Again the holder was redesigned. A thermistor-guide was constructed from a solid stainless steel rod. A hole was drilled along the axis with a 3/16 inch diameter drill bit. The hole was drilled almost to the other end. A 1.5 mm drill bit was then used to make the channel go all the way through. It allowed the thermistor to pass through the thermistor-guide as it was inserted from the side of the guide with the 3/16 inch diameter opening. The outside of the guide was partially fitted with threading. The lid to the sample chamber was designed to accept the guide. The hole in the lid was threaded at the upper end and machined to a level bottom. A narrow opening in the bottom provided access for the thermistor into the sample chamber. The bottom was only 1.5 mm thick. A rubber gasket was used to provide the seal between the thermistor, the guide and the lid. A stainless steel washer was placed between the rubber gasket and the bottom of the hole in the lid to facilitate disassembly after a measurement. Figure 4.2 shows the complete lid assembly for the high temperature measurements. This design gave an adequate seal around the thermistor. However, disassembly after a measurement, and in particular removing the rubber gasket, carried the risk of damaging the thermistor. The rubber gasket had to be replaced after almost every test. Otherwise, the gasket bonded too strongly and disassembly would damage the thermistor.

4.3 SAMPLE CHAMBER

The sample chamber consisted of three parts: a cylindrical body with top and bottom flanges, a bottom plate, and the lid. The internal diameter was 21.5 mm and the depth 44.5 mm. The lid for the low temperature measurements had a pipe fitting (Swagelock, Solon, OH) for fastening the probe. The lid for the high temperature measurements was described above and is shown in Figure 4.2. It contained a cavity to allow expansion of the test fluid. The lid and the bottom plate were bolted to the body of the sample chamber with three bolts each.
O-rings provided the seal on the contact surfaces. A representation of the sample chamber is given in Figure 4.3

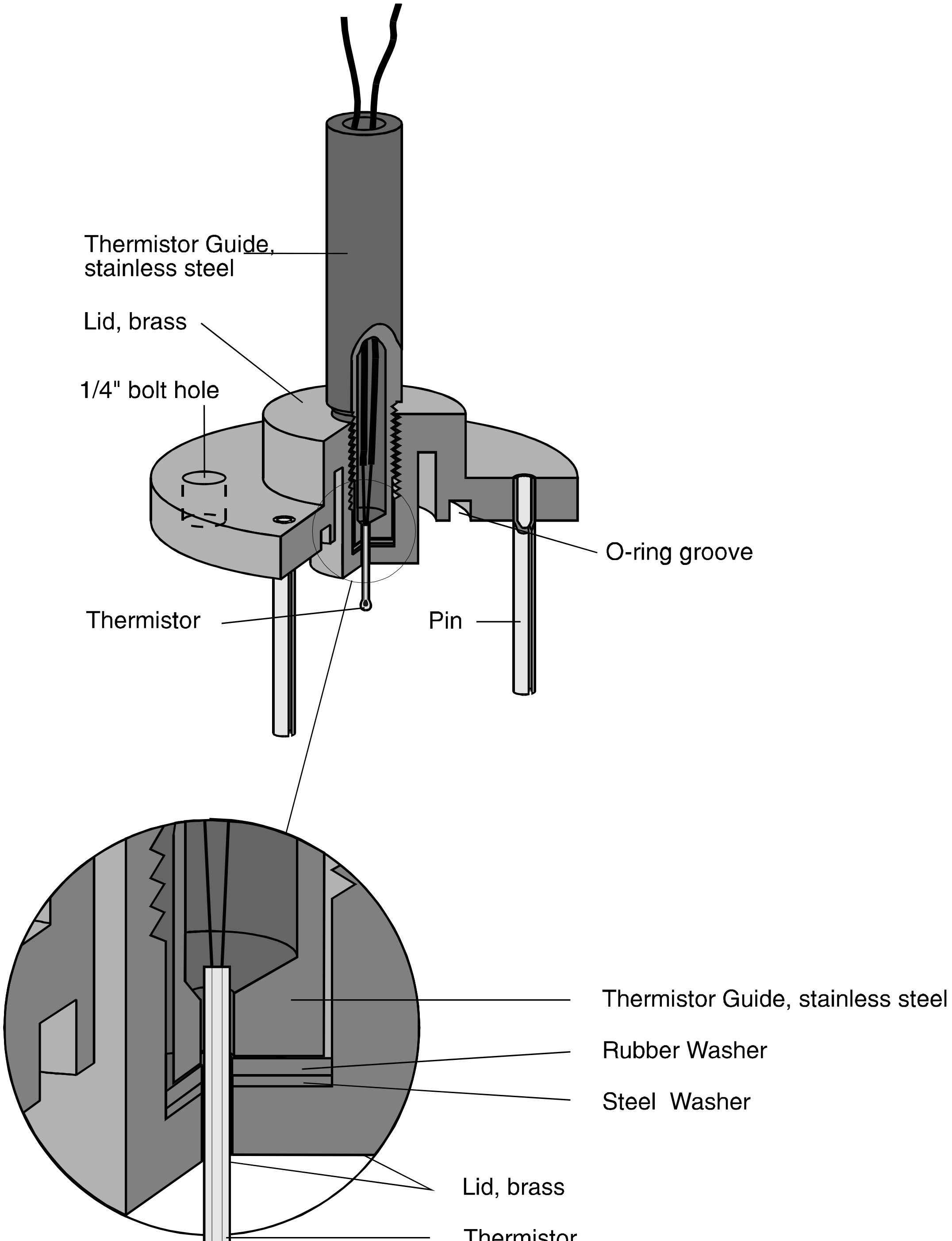

Figure 4.2 Lid assembly for the high temperature thermal property measurements.

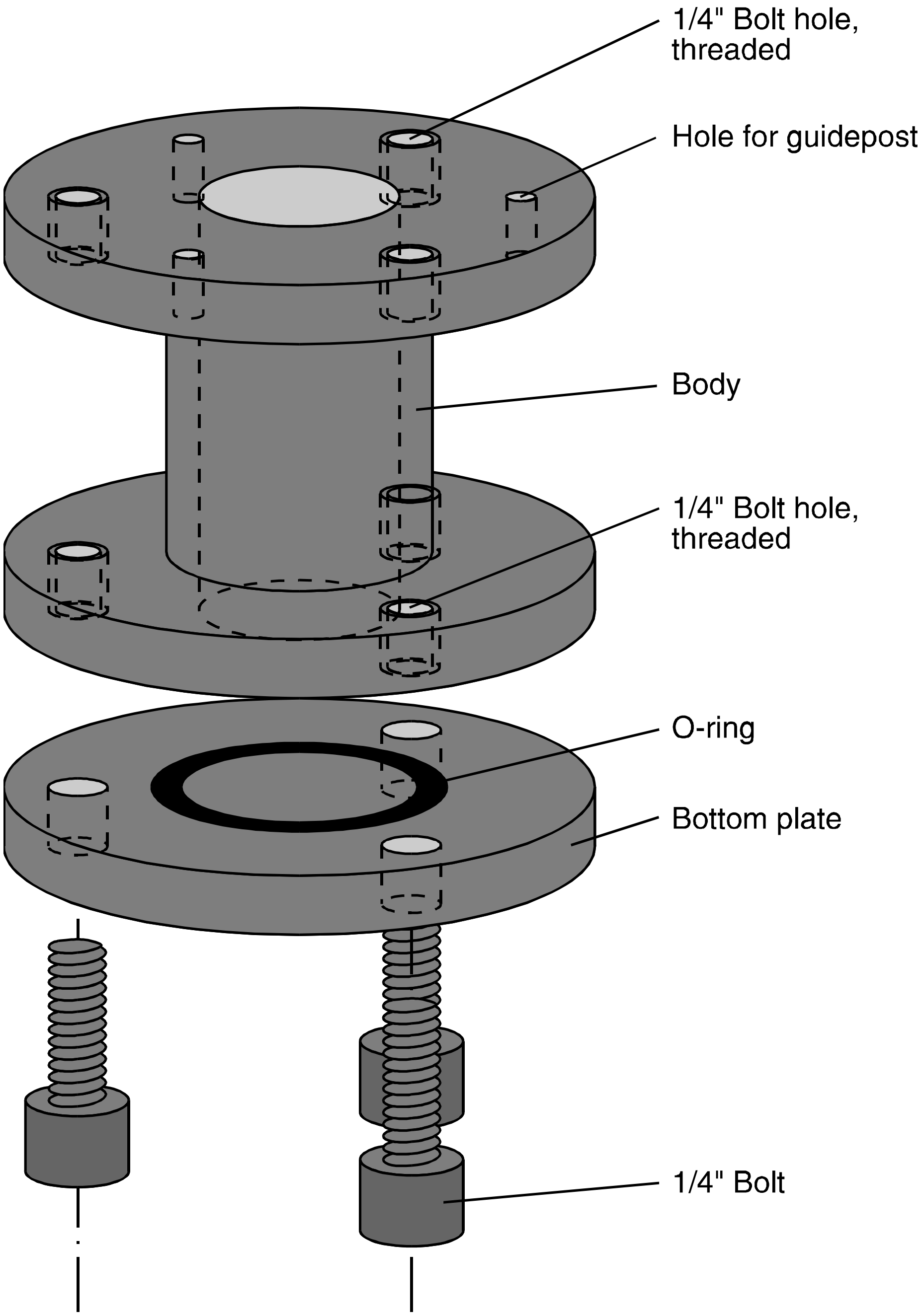

Figure 4.3 Sample chamber for thermal property measurements.

4.4 CONTROLLER

Thermal property measurement was performed with a fixed temperature step of the thermistor. The temperature of the thermistor bead had to be raised almost instantaneously to a temperature above the initial equilibrium temperature and kept at this elevated temperature for the duration of the test. An electronic circuit performed this task. It was taken from Valvano (1981) who had modified the original design of Balasubramaniam (1975). The circuit (Figure 4.4) is best described as a resistance equilibration circuit. Once activated, it will match the resistance of the thermistor to that of a resistor bank, provided that entails a resistance reduction (the circuit is incapable of increasing the resistance of the thermistor). The resistor bank consisted of nine resistors (metal film 1% precision resistors, 1/4-W rating). Eight resistors could be individually short circuited by computer controlled relays (EAC D1A05A). The value of these resistors were chosen to be powers of two, with the lowest value being 1 Ω . The resistors were hand picked as close approximations of their intended value. All eight resistors in series would give a resistance of approximately 255 Ω . The ninth resistor was permanently part of the circuit. This resistor had to be changed manually to accommodate a thermistor resistance from 500 to 3500 Ω . The resolution of the resistor bank allowed the actual temperature step to be within 0.03 °C of its intended value. Zener diodes were added to the circuit to attenuate the output of the circuit and prevent overpowering the thermistors. They reduced the maximum output of the operational amplifiers (OpAmps) from 12 to 9 Volt. The circuitry was interfaced to a Personal Computer (PC) with an input-output board (PIO-12, MetraByte Corporation, Taunton, MA), and a data acquisition board (DAS-20, MetraByte Corporation. Taunton, MA). A passive low-pass filter consisting of a capacitor (0.047 μF) and a resistor (1000 Ω) was used at the signal connections to the data acquisition board. The resistor was placed between one of the signal leads and the binding post. The capacitor was placed across signal leads. Measurement control and data acquisition took place through software written in Turbo Pascal 4.0 (Borland International, Scotts Valley, CA) running on the PC.

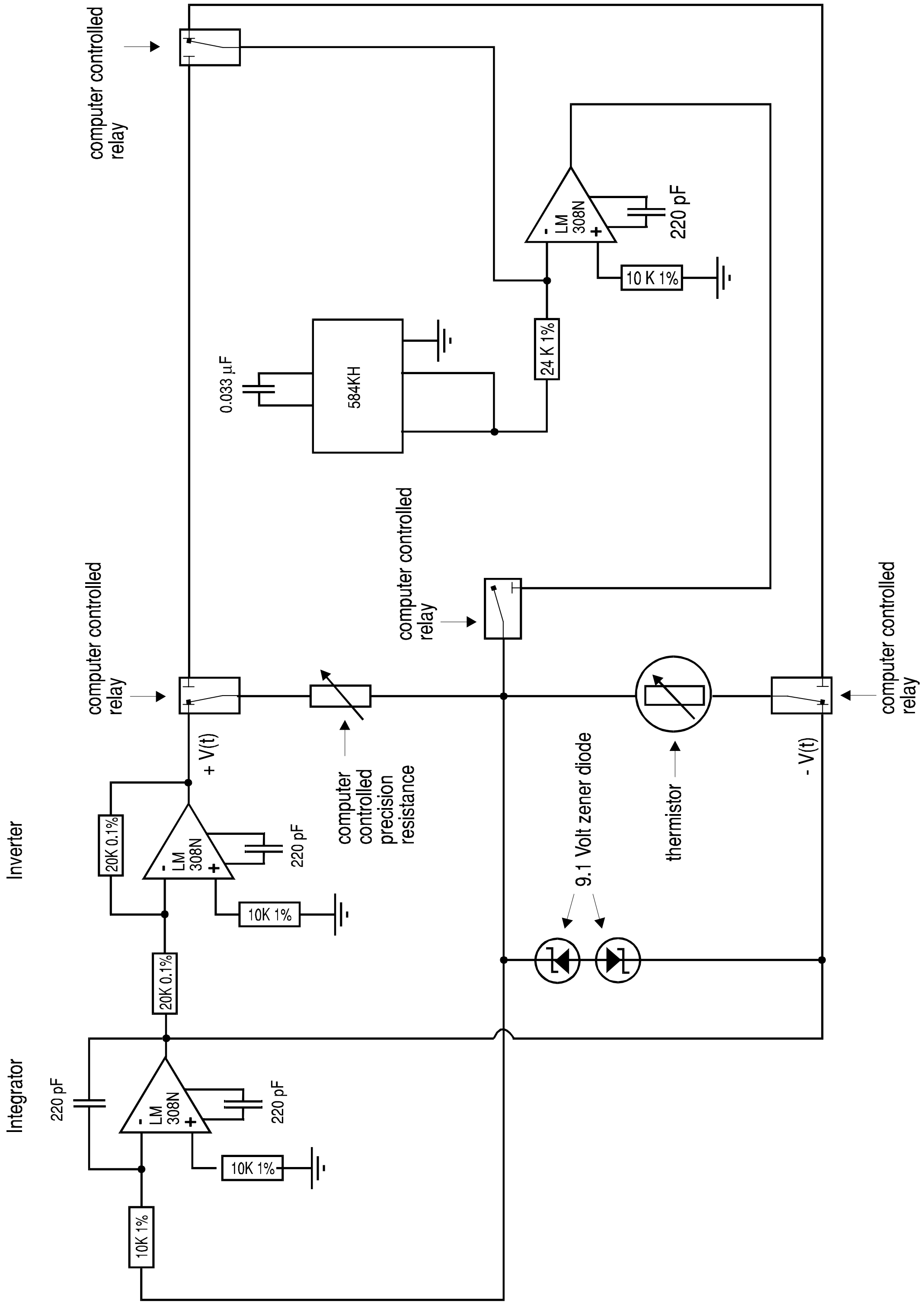

Figure 4.4 Control circuit for thermal property measurements.

4.5 THERMAL PROPERTY MEASUREMENT

A thermal property measurement started from thermal equilibrium. The temperature was measured by placing the circuit in resistance measurement mode. A precision current of 0.1076 mA was fed through the thermistor. The resulting voltage drop was measured with the ADC. The resistance was calculated and converted to a temperature with equation (2.4). The chosen temperature step, 2.5 °C in this research, was added to the equilibrium temperature and this final temperature was converted to the corresponding resistance of the thermistor. The resistor bank was set to the closest match of this resistance by switching the appropriate relays. The resistance was measured so the realized temperature step could be calculated. The circuit was then placed into thermal property measurement mode: the master switch was thrown, which connected the output of the OpAmps to the thermistor and the resistor bank; voltages of equal size but different sign were applied across the thermistor and the resistor bank as shown in Figure 4.4 with $-V(t)$ and $+V(t)$. The initial unbalance in resistance caused a non-zero voltage at the junction of thermistor and resistor bank. This voltage formed the (error signal) input for the integrator. The circuit reduced the error signal to zero which was accomplished by matching the thermistor's resistance to the value of the resistor bank. The circuit response was very fast, with equilibration typically taking place within 0.1 second, closely approximating a step change in temperature.

The voltage across the thermistor was sampled at a rate of 100 Hz for a period of 30 seconds and stored to disk. The realized temperature step and the final resistance of the thermistor were stored for each measurement.

4.6 EFFECTIVE PROBE PROPERTIES

The bead properties effective radius and effective thermal conductivity of equations (3.14) and (3.16) were estimated from measurements in reference media. They have to be determined at each temperature of intended use. Water, glycerol (Fisher Scientific, Pittsburgh, PA) and a heat transfer fluid, HTF 500 (Union Carbide, Danbury, CT), were used as reference media. The choice of these media will be discussed later in this chapter ("4.10 Thermal Standards"). Convection in water was controlled with a gelling agent, Kelset (Merck Inc., Kelco division, Rahway, NJ) in 0.9 % concentration (w/w). For the glycerol and HTF 500 samples fiberglass pipe wrap insulation (Frost King, Thermwell Products Co., Inc., Paterson, NJ) in a concentration of 1.5 % (w/v) served to control convection. This material worked better than glass wool (Fisher Scientific, Cat. No. 11-390, Pittsburgh, PA), which could not give a uniform fill of the sample chamber. The use of glass fiber in a low concentration to control convection is common practice. At such a low level it is assumed that the thermal properties of the test medium are unaffected.

The water samples required a more involved sample preparation than samples of the two other calibration materials. A 0.9 % (w/w) Kelset solution was made in de-ionized water as described in the following. Kelset was added to 80 °C water in a blender. After blending, the solution was heated to 85 °C, and placed under vacuum (600 mg Hg) to expel entrapped air. The solution was allowed to cool. The sample chamber was filled with the lukewarm solution. With glycerol and HTF 500, the glass fiber insulating material was placed in the sample chamber. The fluid was heated to 80 °C to reduce its viscosity, and introduced in the sample chamber. The sample was placed under vacuum (600 mm Hg) to remove any entrapped air. The prepared samples were hermetically sealed into the sample chamber with the lid which held the probe.

The low temperature probes were calibrated at 25 and 50 °C, with three samples of two calibration fluids. Since the research for which probe #L4 was calibrated involved materials with thermal properties that were known to fall between those of water and glycerol, a deviation from the three-fluid calibration used in the rest of this research was made in that a two-fluid calibration was used instead. This expedited the pace of the work and was deemed appropriate and acceptable in light of the objective of this part of the research. Also, a calibration with water and glycerol only, was not unprecedented, as Valvano (1981) had done exactly this in his research. The calibration took place with the sample chamber submerged in a circulating bath (Haake A82, Haake Buchler Instruments Inc., Saddle Brook, NJ), filled with a water-ethylene glycol mixture, and maintained at either 25 or 50 °C.

Calibration of the high temperature probes was performed over the range 100 to 150 °C at 10 °C increments with samples of water, glycerol and HTF 500. Each sample was used over the entire temperature range. The sample chamber was submerged in the circulating bath (Exacal EX-251 HT, NESLAB Instruments, Inc., Newington, NH). The bath was started and heated the sample to the starting temperature. With the gelled-water samples, the first test started at 100 °C after which the temperature was incremented 10 °C until the final temperature was attained, 150 °C. The glycerol and HTF 500 samples were started at 150 °C after which the temperature was decreased. This approach was taken because of experience gained in earlier tests. Prior experiments had revealed a risk of probe failure. The epoxy, though rated for high temperature, deteriorated as a result of the harsh conditions to which it was subjected. Extra protection was supplied by a coat of polyurethane varnish that was applied at the base of the glass stem. The coating would not hold up long and was reapplied frequently. By starting at 150 °C, the worst conditions were met by a coating that was still fresh, thus stronger. The water samples however could not be started at 150 °C. Kelset browns at about 130 °C. It does however form a sort of rigid matrix and regains it convection controlling characteristics albeit not as adequate as at lower temperatures (under 130 °C). With the final design of the thermistor assembly, that used the replaceable rubber gaskets as seal, all calibration sessions were started at 100 °C.

The standard protocol at each temperature was to take three measurements (repeats) with each sample. The repeats were separated by adequate time to allow the system to return to equilibrium, typically 8 minutes. Sampling was performed at a rate of 100 Hz for 30 seconds. As mentioned before, a temperature increment of 2.5 °C was used in all the tests. About 70 min. were allowed between successive temperatures for the bath and sample to equilibrate.

4.7 ADEQUACY OF THERMAL CONTACT

4.7.1 Introduction

The small size of the thermistor allows measurement of small particles, or localized properties (see the discussion of the infinite boundary condition in chapter 3 ("3.5.1 Sample Dimension")). It also indicates a very small heat transfer area. Good thermal contact on this area is critical. Homogeneous liquid media can be measured with good repetition, provided convection is effectively controlled. With solid media, imperfect contact between thermistor and medium may give inaccurate findings.

The suitability of the thermistor based method for measuring the thermal conductivity of food materials of different texture was investigated. The thermistor based method was compared to a line heat source probe, a widely used method for measuring the thermal conductivity of food materials. The line heat source probe has a sampling volume many times that of the thermistor and can deal more adequately with slightly inhomogeneous media or media that do not provide a perfect contact. Two materials were chosen for this study, potato and lean beef. Potato is a very homogeneous material. Lean beef is less homogeneous and due to its fibrous nature probably not isotropic, and may not close well around the thermistor bead. Temperature will affect the properties of the test materials. The methods were compared at 25, 50 and 100 °C.

4.7.2 Sample Material

Two brands of potatoes were used, Idaho and California White. The potatoes were obtained from a local grocery store (Kroger). Measurements at 25 and 50 °C used both brands. Only Idaho potatoes were tested at 100 °C. Six potatoes were sampled at each temperature. The thermal conductivity of each potato was measured with both methods, using separate samples.

Two slabs of lean beef (top round steak), 18 and 50 mm in thickness, were procured from a local grocery store (Kroger). They were sequential cuts to minimize variability in composition of the slabs. Six samples were used for each method at each temperature.

4.7.3 Thermistor Based Measurements

Two thermistors were used in the study. Low temperature measurements were done with a 2-kΩ probe, designated #L4. For the measurements at 100 °C, a 50-kΩ probe, designated #H2, was used.

Sample Preparation, Potato

All samples were cut with a cylindrical open bore, that gave samples with a diameter of 20.5 mm. The samples were taken, parallel to the longitudinal axis of the potato and at least 10 mm removed from the skin. Separate samples were taken from each potato for measurements with the thermistor and the line heat source probe. Samples were measured at only one temperature.

Samples for measurement at 50 °C were cut after the whole potato had undergone a hot water treatment at 50 °C for 60 minutes. The samples for use at 25 and 50 °C were trimmed to a length of about 15 mm. They were lightly dried with a paper towel. The thermistor probe was carefully inserted along the longitudinal axis of the sample. The sample was immobilized on the probe with dental floss and beeswax - through a dip in molten wax. The beeswax also sealed in the moisture, and prevented the heat transfer fluid from reaching the thermistor bead.

Samples for measurement at 100 °C were taken from fresh potato. They were trimmed to a length equal to the depth of the sample container, 45 mm. Prior to measurement they were sealed in the sample container and subjected to a heat treatment of 60 minutes at 100 °C. After the heat treatment, the container was removed from the bath and its lid was replaced by the lid with the thermistor. Guideposts assured thermistor insertion along the sample axis.

The guideposts minimized lateral movement of the thermistor, thereby reducing the effect of the insertion procedure on thermal contact. The sample chamber was returned to the bath for the measurement of thermal conductivity.

Sample Preparation, Beef

The meat was frozen to ease the process of cutting samples. Samples were taken parallel to the muscle fibers, with the same cylindrical bore as was used for the potato samples. Samples for measurement at 25 and 50 °C were taken from the 18 mm thick slab, those for measurement at 100 °C from the 50 mm thick slab. Care was taken to avoid the inclusion of fat in the samples. The samples were wrapped in Saran wrap and stored overnight in a sealed container in a refrigerator.

Samples for measurement at 50 and 100 °C were heat treated immediately prior to measurement. They were sealed in the sample chamber and submerged in a circulating bath for 60 minutes at 50 or 100 °C. The fresh and 50 °C treated beef samples were attached to the thermistor probe with the same procedure as described for the low temperature potato samples. After the heat treatment at 100 °C, the sample chamber was removed from the bath and its lid was replaced by the lid with the thermistor. The heat treatment at 100 °C made the samples shrink. Some pennies were used to prop them up. The sample chamber was returned to the bath for the measurement of thermal conductivity.

Measurement of Thermal Conductivity

Thermal conductivity of the potato and beef samples was measured in a circulating bath. The bath was maintained at the temperature at which the thermal conductivity was to be evaluated (25, 50 or 100 °C). The sample was submerged in the circulating bath. Adequate time was allowed for thermal equilibration, as could be observed from reading the thermistor, about 20 minutes. Thermal conductivity was measured according to a standardized protocol. A single measurement lasted 10 seconds. Data were sampled at a rate of 100 Hz. A temperature step of 2.5 °C was used. Three repeats were done with the described protocol. Adequate time was allowed between the repeats for the sample to return to thermal equilibrium, typically 8 minutes. After the measurement of thermal conductivity, the samples were dissected. The contact area of the thermistor and potato was inspected for quality of contact.

4.7.4 Measurements with the Line Heat Source Probe

Equipment

A miniature line heat source probe was used for measuring thermal conductivity. The probe is described in Chapter 2 ("2.2.4 Line Heat Source Probe"). The sensor part was 38 mm long and had an outside diameter of 0.81 mm. The probe was connected to a cold junction compensator (OMEGA CJ, Omega Engineering, Stamford, CT). The output of the CJC was connected a circuit that was designed to amplify and filter the CJC signal. This circuit was interfaced to a PC through an I/O board (PIO-12, MetraByte Corporation, Taunton, MA), and a data acquisition board (DAS-20, MetraByte Corporation. Taunton, MA). Measurement control and data acquisition were performed with software (Turbo Pascal 4.0, Borland International). Heating power was supplied by a precision power supply (B & K Precision 1630), capable of maintaining constant current levels between 0 and 3 Ampere at a voltage between 0 and 30 volt. The voltage setting was adjusted for each test material to a level that gave a 6 °C temperature rise in 30 seconds. For agar-gelled water and glycerol the voltage setting were 2.9 and 2.3 Volt respectively. The line heat source probe was evaluated in 1.6% agar-gelled water and glycerol. A correction factor was deemed unnecessary (Wolters, 1992).

Sample Chamber

The sample chamber consisted of a sample container and a lid. The container was machined from solid brass, to an internal diameter of 21.5 mm and a depth of 44.5 mm. The top had a flange that contained an o-ring which sealed against the lid. The lid was also machined from solid brass. The one-piece lid consisted of a cylindrical plate with a thickness of 3.2 mm with a cylinder attached to it. The cylinder was 48 mm long and had internal and external dimensions of 19.1 and 27 mm respectively. It was centered on the plate. A hole in the center of the plate allowed the probe to be inserted into the sample container. The purpose of the cylinder was two-fold. It provided support for the probe which was set tight with two set screws towards the top of the cylinder and it shielded the probe from the heat transfer medium in the circulating bath.

Experiments

The potato and beef samples were taken with the same bore as described earlier. The beef samples were taken from the 50 mm slab only. The potato samples for measurement at 100 °C, and the beef samples at 50 and 100 °C were cooked in the sample chamber for 60 minutes at the evaluation temperature. To make a measurement, the lid used during cooking, was replaced with the lid for the probe. The lid was tightened on the sample container and the probe was inserted through the hole and set tight with the screws. The chamber was returned to the bath. The bath was set to a temperature 3 °C below the evaluation temperature to allow for a temperature rise of approximately 6 °C during the measurement. After temperature stabilization, the test would start. The probe was energized for 30 seconds with sampling taking place over that period at a rate of 100 Hz. The heater voltage was sampled simultaneously with the temperature data enabling exact calculation of the power dissipation in the heater wire. Each sample was measured three times. These repeats were done about eight minutes apart to allow the temperature to stabilize.

4.8 NATURAL CONVECTION

4.8.1 Introduction

Whether convection will occur within certain time depends both on the fluid properties and on the imposed temperature step. The effect of one fluid property, viscosity, on the onset of convection was studied for different values of the temperature step. It was accomplished by comparing test data for fluids that differed only in viscosity. Water was a suitable medium for this purpose. It can be thickened with minimal change in its thermal properties. Generally accepted is the use of the thermal conductivity and diffusivity of pure water for aqueous solutions of up to 2% thickener (by mass). When convection effects are absent, and assuming negligible effect of the thickening agent on the thermal properties of interest, measured values of thermal conductivity and diffusivity are independent of viscosity. The test-hypothesis was: no effect of viscosity for a given magnitude of the temperature increment.

As viscosities were selected, 1, 5, 25, 50, 100 and 150 cp. The 150 cp solution would not experience convection. Prior tests with this viscosity gave results that were identical to those obtained with the much more viscous Kelset solution that was used for calibration. The values for the temperature step were chosen to fall within a practical range (see "3.5.2 Temperature Step"), yet be different enough to expect a demonstrable effect; as values for the temperature step were selected: 1.5, 2.5 and 5.0 °C.

The study design for the thermal property experiments was a split-plot design with two independent factors. Factor A, the viscosity was the whole plot factor. It had 6 levels. Factor B, the temperature step, had 3 levels. The value of each level for both factors was mentioned above. For each level of factor A (viscosity), two independent samples were made. Hence a total of 12 samples were tested. With each sample all three temperature steps were used and each temperature step was done in triplicate. The nine tests on each sample were randomized with aid of a random table (Ott, 1988, Appendix table 8). Sequencing the 12 samples was done in like manner.

Under model conditions, when heat transfer is by conduction only, the power dissipation in the bead was shown to be linear in the inverse square root of time (Chapter 3). Therefore, linear regression of the square of the voltage drop across the thermistor against the inverse square root of time will yield identical values of slope, S, and intercept, V_{ss}^2, regardless of what part of the data (e.g. 5 to 10 seconds, 20 to 30 seconds) is used. Convection will distort this linearity. This is seen as an upward curvature in the power dissipation towards increased duration. It can be demonstrated by comparing regression results from data late in a measurement to those from data earlier in the same measurement. Alternatively, two samples of the same material can be compared, whereby convection in one sample is controlled. The increased heat transfer due to convection will result in an increase in the intercept of regression, V_{ss}^2, and a decrease in the ratio of slope and intercept, S/I.

The data files were compared on the values for the terms $R_f\Delta T/V_{ss}^2$ and S/I. These are the terms that were used to calculate thermal conductivity and diffusivity (equations 3.14 and 3.16). V_{ss}^2 is the intercept, I, of linear regression of V^2 against $t^{-1/2}$ and S is its slope. In the absence of convection, the values of $R_f\Delta T/V_{ss}^2$ and S/I, calculated from an identical regression interval, should be comparable for all values of viscosity (since their thermal conductivity and diffusivity are the same). Convection in a less viscous solution would result in values for $R_f\Delta T/V_{ss}^2$ and S/I that are significantly lower (indicative of an apparent higher thermal conductivity and diffusivity) than for the more viscous solutions that experienced no convection. Estimation of onset time was done by performing successive regressions over a short interval and using the results in a multiple-comparison procedure. A regression interval of 2 second length was used. This interval slid down the time axis with 1 second increments until a start time of 12 seconds was attained and with increments of 2 seconds from thereon. A short interval was necessary in order to estimate the onset time of convection. A shorter interval than 2 seconds would have been too sensitive to the noise in the data; a longer interval would have reduced the resolution with which the onset time of convection could be estimated. The results of the regression analysis ($R_f\Delta T/V_{ss}^2$ and S/I) for each regression interval formed the input for a multiple-comparison procedure, Tukey's W, with SAS (Statistical Analysis Software, Cary, NC). A type 1 error of 0.05 was used.

4.8.2 Sample Preparation

Solutions were made from de-ionized water with a gelling agent. Preliminary testing was done to find a gelling agent which would yield solutions with Newtonian fluid behavior. The test results were negative. All solutions were non-Newtonian (pseudo-plastic). Two sodium alginates, Keltone LV and Keltone HV (Merck & Co. Inc., Kelco Division, Clark, NJ) gave the best results, yielding solutions that were close to Newtonian. Solutions were made with these alginates, with consistency coefficients, K, as close as possible to the chosen viscosities. For ease of writing, the word viscosity will be used from hereon in place of consistency coefficient.

The 1 cp fluid was in fact pure de-iononized water. The solutions with viscosities 5, 25 and 50 cp were made with Keltone LV. Keltone HV was used in preparation of the 100 and 150 cp solutions. All solutions were made with an identical procedure. De-ionized water was heated to 80 °C on a hot-plate and 400 grams were poured into the cup of a blender (Waring commercial blender). While blending, the appropriate amount of gelling agent, weighed on a digital analytical balance (Sartorius model 1712 MP8 silver edition, Brinkmann Instruments Inc., Div. of Sybron, Westbury, NY), was gradually added. After thorough mixing, the solution was poured into a 1000 ml beaker. The solution was heated on the hot-plate to 80 °C under continuous stirring. It was then placed under 600 mg Hg of vacuum to deaerate. Three samples were taken for viscosity tests, and one for measurement of thermal conductivity and diffusivity. To account for evaporative and transfer losses (blender cup to beaker), weights were taken throughout the process. These measurements allowed calculation of the concentration of the solutions, but more importantly assured proper replication. All weighing, except of the amount of thickener, was done with a Mettler balance (Mettler PM6, Mettler Instrument Corporation, Hightstown, New Jersey), with a resolution of 1 g.

4.8.3 Measurement of Viscosity

Viscosity was measured with a Brookfield LV viscometer (Brookfield Engineering Laboratories, Stoughton, MA). The type of cup and spindle was determined by the viscosity of the sample. For the solutions of 50 cp and below, the UL adapter was used. The 100 and 150 cp solutions required the small sample adapter (SC4-18/13R). All viscosity measurements were done at 50 °C. To accomplish this, the UL adapter was lowered into a circulating bath, maintained at 50 °C. The small sample adapter had a flow jacket. It was connected to the ports of the circulating bath through insulated tubing. The viscometer was programmed to take data at shear rates over its full operational range. An up and down ramp was used to check for shear thinning or thickening behavior. The consistency coefficient and flow behavior index were calculated from the data with a spreadsheet program (SuperCalc 5.0, Computer Associates International, Inc.). Viscosity was measured in triplicate.

4.8.4 Measurement of Thermal Properties

Thermal conductivity and diffusivity were measured with a 2-kΩ probe, designated #L4. A sample time of 30 seconds was used. All measurements were performed at 50 °C. Temperature control was attained by submersion of the sample chamber in a constant temperature bath (Haake A82, Haake Buchler Instruments Inc., Saddle Brook, NJ), filled with a water-ethylene glycol mixture, maintained at 50 °C. The measurement procedure was identical as described earlier in this Chapter ("4.6 effective Probe Properties").

4.8.5 Rayleigh Number Calculation.

Rayleigh numbers were calculated by numerical evaluation of the exact solution for the temperature distribution in the medium as given by Balasubramaniam (1975). The evaluation was done with software written in Turbo Pascal 4.0 (Borland International, Scotts Valley, CA). The infinite integrals of the solution were evaluated with Romberg integration. The procedures for the integration were taken from "Numerical Recipes in Pascal" (Press, 1989).

The boundaries of integration were set to 10^{-30} and 10^{30}. Program input consisted of the bead parameters, the medium properties and the size of the temperature step. For the bead parameters, the calibrated values were used except for the bead thermal diffusivity, which could not be found from the calibration. A value of $1.3 \cdot 10^{-7}$ m^2/s, given by Balasubramaniam (1975), was used. Balasubramaniam had used that value for the estimation of thermal diffusivity (his method required knowledge of the bead's thermal diffusivity, whereas the present method does not). The bead thermal diffusivity was calculated from the thermal conductivity of the bead and its density and specific heat. Balasubramiam's value for the thermal diffusivity falls between those experimentally found by Valvano (1981). Valvano obtained the bead's thermal diffusivity by monitoring its temperature as the bead was quickly moved from a well stirred bath at 17.5 °C to one at 38 °C. Four thermistors were tested in this manner. Bead thermal diffusivity ranged from 0.958 to 1.636 [$10^{-7}m^2/s$].

Temperature profiles in the medium were generated with a resolution in the radial variable of 1/50 of the bead radius. They were generated at 0.5 second intervals and the Rayleigh number was calculated with the time dependent heat penetration depth and effective temperature gradient. The criterion for the penetration depth was chosen as the distance at which the temperature rise in the medium extinguished to below 1% of the surface temperature of the thermistor bead. The effective temperature gradient over the penetration depth was calculated as the linearized temperature gradient that integrated to the same value as the integrated simulated temperature profile. Rayleigh numbers were calculated for those combinations of temperature step and viscosity that exhibited signs of convection.

4.9 EVALUATION AT HIGH TEMPERATURE

4.9.1 Introduction

Few food materials have documented values of thermal conductivity and diffusivity above 100 °C. Data for tomato concentrate had been collected by Choi and Okos (1983) with the line heat source probe over the range 25 to 150 °C. Being a paste like material, it was thought to be a good material for evaluation of the thermistor based method. A paste was expected to provide good surface contact with the thermistor bead.

Thermal conductivity of liquid food is strongly influenced by its water content. Liquid nutritional supplements with various solids content were tested. These materials came without reference data. They were used to test if the probes would measure thermal conductivity that followed the expected downward trend with solids content.

4.9.2 Tomato Concentrate

Thermal conductivity and thermal diffusivity of the tomato puree and tomato paste were determined with the thermistor probe. The tomato concentrate was supplied by Van Den Bergh Foods Co. (Roxbury, CT) in size 10 cans. Three temperatures were chosen for thermal property evaluation; 100, 130 and 150 °C. Two cans per material (puree, paste) were used and from each can two samples were taken for measurement of thermal conductivity and thermal diffusivity. Each sample was used at all temperatures. A sample of the tomato product was carefully placed in the sample chamber. Care was taken not to create air pockets which would alter the thermal properties. The sample chamber was hermetically sealed with the lid with the probe (#H3) mounted to it. The sample chamber was then submerged in a constant temperature bath (Exacal EX-251 HT, NESLAB Instruments, Inc., Newington, NH) and bath and sample were heated to 100 °C. Measurements were performed with the protocol as outlined in "4.6 Effective Probe Properties". Three measurements were taken at 100 °C. After the third measurement, the sample was heated to 130 °C for three measurements at that temperature and subsequently to 150 °C for a final set of measurements. After this final set, the sample was allowed to cool to room temperature and visually inspected for heating induced changes.

In order to compare the results of the thermal property measurement to the data reported by Choi and Okos (1983), the solids content of the material needed to be known. Factory supplied values for solids content were checked. The refractive index was obtained with a refractometer (ABBE MARK II digital refractometer, Reichert-Jung). Tomato paste was diluted with water in the ratio 1:2 before measuring the refractive index. The refractive index, which is a measure of soluble solids, was related to total solids with aid of a table (Pearson, 1973, Table 9.5).

4.9.3 Nutritional Supplement

A fluid nutritional supplement was supplied for testing by Abbott Labs/Ross Products Division (Columbus, OH). Products of different solids content and different composition (e.g. fat, protein, carbohydrates) were tested. Some of these products were viscous enough that natural convection was deemed unlikely. For the others, fiberglass pipe insulation was used at 1 - 1.5% (w/v) as a convection inhibiter/reducer. These low concentrations were assumed to have no influence on the thermal properties. Care was taken in the sample preparation to limit air inclusion in the samples as much as possible. The samples that used the pipe insulation were heated to reduce their viscosity. Using a pipette, the sample was introduced at the bottom of the sample chamber. After filling, the sample chamber was placed in a vacuum desiccator, under 600 mg Hg of vacuum, for a few minutes to remove entrapped air, if present. It was assumed that this procedure gave negligible moisture loss from the samples. Four different products were tested, designated at "TC1", "TC2", "TC3" and "TC4". Each product was supplied in various solids contents. The products were tested at two temperatures, 95 and 150 °C. Duplicate samples were used for all but product "TC2". The combinations of product, solids content and temperature that were tested were specified by the supplier and can be found in Table (5.23) in the results. The samples were submerged in the bath, already at measurement temperature. Doing so minimized the heat-up time. Approximately 20 minutes were required, after submersion, for temperature equilibration to take place. Property measurement was performed with the protocol as described in "4.6 Effective Probe Properties".

4.10 THERMAL STANDARDS

Thermistor probes require calibration to obtain their effective properties. Calibration takes place with thermal standards, media of known thermal conductivity and diffusivity. The accuracy of the thermistors in subsequent use is dependent on the accuracy of property data of the calibration media. One of the conclusions reached by Kravets (1988) was the need for well defined thermal reference materials in the range of food products. Dougherty (1987) observed that probe parameters found from a calibration with water and ethylene glycol were different from those found for the same probe with water, glycerol and toluene. This dependency of probe properties on thermal standards was partly attributed to inaccurate literature data.

A potential calibration material should meet a number of criteria:

1. Its thermal conductivity and diffusivity should be similar to the values found in moist food materials,
2. Its thermophysical properties must be well documented over 20 - 150 °C,
3. The transfer of energy in the fluid by means other then conduction (convection, radiation) should be minimal.

Literature was searched for liquid thermal standards that would meet the criteria. Finding materials that are viscous enough to be used at high temperatures and have well documented properties proved difficult. The starting point were the media used by prior researchers: water, glycerol, castor oil, toluene and ethylene glycol.

The thermal conductivity and diffusivity of water is well documented at high temperatures. Convection is a potential problem with water, and agar, an effective agent at low temperatures, breaks down at the high temperatures encountered in the present study. An alternative was found in Kelset, a sodium alginate. This material proved to control convection satisfactory in low enough concentrations, 1%, as not to alter the thermal properties of water. Glycerol is a high viscosity fluid at room temperature but at 150 °C its viscosity is only slightly higher than water at room temperature. However, with glass fiber material to suppress convection, it tested well at 150 °C. Castor oil is not documented at high temperatures. Toluene is a recommended thermal conductivity reference material (Marsh, 1987). Its thermal conductivity is low, around 0.13 W/m°C, making it a good complement to water (0.61) and glycerol (0.30) in covering the range of values found in food materials. Its viscosity however is very low. Even with aid of fiber glass material, it failed to perform well. Ethylene glycol has a thermal conductivity comparable to that of glycerol. Its thermal conductivity is documented at high temperatures, but thermal diffusivity data were neither found nor could be calculated from thermal conductivity, specific heat and density for lack of data for the latter two properties. Of the four (liquid) recommended thermal conductivity reference materials (Marsh, 1987), only water was considered to meet the criteria formulated earlier.

A heat transfer fluid was chosen as third calibration fluid. HTF 500 (Union Carbide, 1989) has a thermal conductivity below 0.2 W/m°C. Glass fiber material sufficiently suppressed convection to allow HTF 500 to be used as a calibration material. Thermophysical properties were obtained from the manufacturer. Their accuracy were not verified. Tables 4.1 through 4.3 list the properties of the calibration fluids used in this research. In all cases, thermal diffusivity was calculated from thermal conductivity, density and specific heat. Thermal conductivity and specific heat values for glycerol were taken from CINDAS (1988) and its density was measured (Appendix A).

Table 4.1 Thermophysical Properties of Water

Temperature [°C]	Thermal Conductivity[1] [W/m°C]	Density[2] [kg/m^3]	Specific Heat[2] [J/kg°C]	Thermal Diffusivity[3] [10^{-6}m^2/s]
20	0.5981	998.5	4181	0.1432
25	0.6067	997.1	4180	0.1456
30	0.6149	995.5	4179	0.1478
40	0.6297	992.0	4179	0.1519
50	0.6426	987.8	4181	0.1556
60	0.6535	983.1	4184	0.1589
70	0.6624	977.7	4190	0.1617
80	0.6694	971.7	4197	0.1641
90	0.6744	965.1	4207	0.1661
100	0.6790	958.2	4218	0.1680
110	0.6816	950.8	4229	0.1695
120	0.6832	942.8	4244	0.1707
130	0.6838	934.5	4263	0.1717
140	0.6834	925.6	4285	0.1723
150	0.6820	916.4	4311	0.1726

[1] Nieto de Castro (1986), 20 - 90 °C; adapted from Sengers et. al (1984), 100 - 150 °C.

[2] Adapted from Incropera and DeWitt (1985).

[3] Calculated as $\alpha = k/\rho \bullet C_p$, α = thermal diffusivity, k = thermal conductivity, ρ = density, C_p = specific heat.

Table 4.2 Thermophysical Properties of Glycerol.

Temperature [°C]	Thermal Conductivity[1] [W/m°C]	Density[2] [kg/m^3]	Specific Heat[1] [J/kg°C]	Thermal Diffusivity[3] [10^{-6}m2/s]
20	0.2843	1260.9	2354	0.0958
25	0.2850	1257.7	2381	0.0952
30	0.2856	1254.6	2407	0.0946
40	0.2869	1248.1	2458	0.0935
50	0.2882	1241.6	2505	0.0927
60	0.2895	1235.0	2549	0.0920
70	0.2908	1228.3	2588	0.0915
80	0.2921	1221.5	2625	0.0911
90	0.2934	1214.6	2658	0.0909
100	0.2947	1207.6	2687	0.0908
110	0.2960	1200.5	2712	0.0909
120	0.2973	1193.3	2733	0.0911
130	0.2986	1186.0	2751	0.0915
140	0.2998	1178.5	2764	0.0920
150	0.3011	1171.0	2774	0.0927

[1] CINDAS (1988).

[2] Measured (Appendix A).

[3] Calculated as $\alpha = k/\rho\, C_p$, α = thermal diffusivity, k = thermal conductivity, ρ = density, C_p = specific heat.

Table 4.3 Thermophysical Properties of HTF 500

Temperature [°C]	Thermal Conductivity[1] [W/m°C]	Density[1] [kg/m^3]	Specific Heat[1] [J/kg°C]	Thermal Diffusivity[2] [10^{-6}m^2/s]
20	0.1679	1038.9	1940	0.0833
25	0.1671	1035.3	1958	0.0824
30	0.1663	1031.8	1976	0.0816
40	0.1647	1024.6	2010	0.0800
50	0.1632	1017.5	2043	0.0785
60	0.1616	1010.4	2074	0.0771
70	0.1600	1003.2	2104	0.0758
80	0.1584	996.1	2132	0.0746
90	0.1569	988.9	2158	0.0735
100	0.1553	981.8	2182	0.0725
110	0.1537	974.7	2205	0.0715
120	0.1522	967.5	2226	0.0706
130	0.1506	960.4	2246	0.0698
140	0.1490	953.2	2264	0.0691
150	0.1475	946.1	2280	0.0684

[1] Adapted from manufacturer supplied graphs (Union Carbide, 1989).

[2] Calculated as $\alpha = k/\rho \bullet C_p$, α = thermal diffusivity, k = thermal conductivity, ρ = density, C_p = specific heat.

CHAPTER 5

RESULTS AND DISCUSSION

The first part of this chapter discusses the calibration of the thermistors. Subsequently, the results of the comparative study are given. These are followed by those for the study into natural convection. In the last part of the chapter, the high temperature measurement of two types of food material are discussed.

5.1 TEMPERATURE-RESISTANCE CALIBRATION

The results of temperature-resistance calibrations are given in Table 5.1. The table shows the probes that were calibrated, the temperature range over which a probe was calibrated, the value of the coefficients of equation (2.4), and the value of the χ^2 statistic. The values of χ^2 for the low temperature probes were far lower than those for the high temperature probes. This indicated a much better fit of the equation to the data for these probes. The agreement between the equations and the data was better than 0.006 °C for the low temperature probes, and better than 0.05 °C for the high temperature probes. This excellent agreement between the equations and the data attest to the correctness of equation (2.4), and to the accuracy of both the temperature and resistance measurement.

$$\frac{1}{T} = a_0 + a_1 \ln(R) + a_2 \ln(R)^3 \qquad (2.4)$$

Not all the probes of Table 5.1 were used after they were calibrated. The temperature-resistance calibration was the first step of the two-step process of calibrating a thermistor probe for thermal property measurements. This first step was the least time-consuming part, and could be done for four probes simultaneously. The second step, in which the effective probe properties were determined, was a fairly lengthy endeavor. It had to be done for each probe separately. Therefore, just one low and one high temperature probe were completely calibrated at a given time. Only in case of probe failure would another probe be taken through the second step.

Table 5.1 Calibration coefficients and value of the χ^2 statistic for the temperature-resistance function of the probes

Range of Calibration and Probe	a_0	a_1	a_2	χ^2
20 - 62 °C				
#L1	1.30486 E-03	2.58926 E-04	1.33393 E-07	6.0 E-05
#L2	1.27912 E-03	2.58769 E-04	1.33874 E-07	4.3 E-05
#L3	1.30103 E-03	2.60179 E-04	1.32498 E-07	1.1 E-04
#L4	1.28409 E-03	2.59543 E-04	1.37882 E-07	6.1 E-05
95 - 155 °C				
#H1	8.63309 E-04	2.11965 E-04	1.52697 E-07	6.5 E-03
#H2	8.46124 E-04	2.14167 E-04	1.52067 E-07	6.8 E-03
#H3	8.80808 E-04	2.09922 E-04	1.60020 E-07	3.3 E-03
#H4	8.81477 E-04	2.10426 E-04	1.59332 E-07	3.9 E-03
#TT1	8.31390 E-04	2.19282 E-04	1.17724 E-07	1.2 E-02
#TT2	8.42144 E-04	2.20328 E-04	1.14475 E-07	1.1 E-02
#TT3	8.71597 E-04	2.16516 E-04	1.25304 E-07	1.6 E-02
#TT4	8.34315 E-04	2.18145 E-04	1.11302 E-07	1.3 E-02

5.2 EFFECTIVE PROBE PROPERTIES

5.2.1 Low Temperature Probes

The effective probe properties were determined in the second step of the calibration for thermal property measurement. The probe parameters (a_1, k_{b1}, a_2, k_{b2}) as required by equations (3.14) and (3.16) were estimated from measurements in reference media.

$$\frac{1}{k_m} = \frac{4\pi a_1 \Delta T R_f}{V_{ss}^2} - \frac{0.2}{k_{b1}} \tag{3.14}$$

$$\alpha_m = \left[\frac{a_2}{\sqrt{\pi}\ (S/I) \left(1 + \frac{k_m}{5k_{b2}}\right)} \right]^2 \tag{3.16}$$

Of the low temperature probes, only probe #L4 was calibrated for use in thermal property measurements. It was calibrated with water and glycerol. Regression analysis yielded values for V_{ss}^2 (replaced by I in the equation 3.16) and S. I and S represent the two parameters of the model that described the voltage drop across the thermistor, $V(t)^2 = I + S \bullet t^{-0.5}$. The values of R_f and ΔT were known constants for each measurement. Linear regression used the data of the interval 3 to 9 seconds. The regression results were used to generate values for the terms $R_f\Delta T/V_{ss}^2$, and S/I. The sample average at each temperature was found by averaging these terms over the three measurements that were done on each sample at that temperature. The medium average was found as the average of the three sample averages. The replication was good. The largest difference between sample averages was 0.6%, which was for S/I of water, at 25 and 50 °C. The replication was marginally better for the term $R_f\Delta T/V_{ss}^2$, with 0.5% being the largest difference. The regression results are given in Appendix B. The medium averages, and the reference data for the calibration media, were substituted into the two equations to find the properties of the probe. The properties of probe #L4 at 25 and 50 °C are given in Table 5.2.

Table 5.2 Properties for low temperature probe #L4, corresponding to the regression interval 3 to 9 seconds.

Temperature	a_1	k_{b1}	a_2	k_{b2}
[°C]	[mm]	[W/m°C]	[mm]	[W/m°C]
25 °C	0.9874	0.1032	0.7467	0.1185
50 °C	0.9707	0.1080	0.7602	0.1168

The radius as obtained for estimation of thermal conductivity is larger than the physical radius of 0.76 mm. This is in agreement with findings of other researchers (Balasubramaniam, 1975, Valvano, 1981, Dougherty, 1987). The radii found for estimation of thermal conductivity, a_1, were also larger than those for estimation of thermal diffusivity, a_2. Valvano (1981), the only other researcher who calibrated probes for measurement of thermal diffusivity found that as well. Inaccuracies in the reported reference data as well as stem losses were given as likely causes for the differences in probe properties. The values for the calibrated thermal conductivity of the probe fall within reported values.

5.2.2 High Temperature Probes

High temperature probes were calibrated with three calibration media. During the calibration of the low temperature probes it was noticed that the response of the thermistor in water and glycerol deviated somewhat from the model, in particular when data early in the measurement were used in regression. At longer times, the response more closely followed the model. This suggested the use of long sample times. However, the duration of the test in low viscosity fluids was limited by the onset of natural convection, despite efforts to delay that as much as possible. Thus, a regression interval had to be found that excluded initial effects and also ended before convection effects disrupted the measurement.

Software was written in Turbo Pascal (Borland International, Scotts Valley, CA) to perform the linear regression. The software performed linear regression on successive intervals. Input to the program consisted of the length of the regression interval, the start time of the first interval and the magnitude of the step with which the start time was incremented. The length of the regression interval was chosen as 10 seconds. The first interval started at 1 second. For each successive interval the start time was incremented by 1 second. Linear regression as described above was done on the data files that were collected for calibration. For each data file, the program would generate a table with regression results. In those, regression statistics were tabulated for the successive regression intervals. Included for each regression interval were the secondary statistics $R_f\Delta T/V_{ss}^2$ and S/I. The probe properties were obtained much like that done for the low temperature probe. Software was used to calculate the probe properties for each of the three two-media calibrations, (water-glycerol, water-HTF 500, and glycerol-HT 500). Those were averaged to find the properties for the three media calibration. They were calculated for each regression interval. The parameters of probe #H3 at 100 °C for estimation of thermal conductivity are given in Table 5.3, those for estimation of thermal diffusivity in Table 5.4.

The calibrated probes were used to estimate the thermal properties of the calibration media. The difference between the estimated medium properties and their reference values is shown in Tables 5.3 and 5.4 as estimation errors. Ideally, each of the three combinations of two calibration media would have yielded identical probe properties, and all estimation errors would have been zero. This was not the case, and the calibration accuracy could be assessed from the estimation errors. These errors are also shown in Figure 5.1 for estimation of thermal conductivity and Figure 5.2 for estimation of thermal diffusivity.

Table 5.3 Radius and thermal conductivity of the #H3-probe, calibrated for the measurement of thermal conductivity at 100 °C. The error in estimation of medium thermal conductivity for the calibration media is given. Regression interval was 10 seconds.

Start Time of Regression Interval [sec]	Probe Radius [mm]	Probe Thermal Conductivity [W/m°C]	Error[a] in estimation of Water [%]	Glycerol [%]	HTF 500 [%]
1	0.9528	0.0968	-1.93	0.35	-0.70
2	1.0106	0.0844	2.18	-0.95	0.80
3	1.0374	0.0801	3.18	-1.94	1.19
4	1.0514	0.0780	3.50	-2.55	1.33
5	1.0596	0.0768	3.62	-2.93	1.39
6	1.0647	0.0761	3.68	-3.20	1.42
7	1.0684	0.0755	3.70	-3.39	1.44
8	1.0711	0.0751	3.72	-3.57	1.45
9	1.0731	0.0748	3.72	-3.72	1.46
10	1.0746	0.0746	3.72	-3.86	1.47
11	1.0759	0.0744	3.72	-4.00	1.47
12	1.0777	0.0742	3.71	-4.09	1.47
13	1.0784	0.0741	3.70	-4.16	1.48
14	1.0785	0.0740	3.70	-4.18	1.48
15	1.0786	0.0740	3.70	-4.17	1.48
16	1.0783	0.0740	3.71	-4.15	1.48
17	1.0778	0.0740	3.71	-4.07	1.47
18	1.0780	0.0740	3.71	-4.08	1.47
19	1.0778	0.0739	3.71	-4.08	1.47

[a] A positive value indicates overestimation by the thermistor based method

Table 5.4 Radius and thermal conductivity of the #H3-probe, calibrated for the measurement of thermal diffusivity at 100 °C. The error in estimation of medium thermal conductivity for the calibration media is given. Regression interval was 10 seconds.

Start Time of Regression Interval	Probe Radius	Probe Thermal Conductivity	Error[a] in estimation of		
			Water	Glycerol	HTF 500
[sec]	[mm]	[W/m°C]	[%]	[%]	[%]
1	1.2025	0.0505	13.47	29.77	7.21
2	0.9326	0.0714	-4.60	9.15	-2.25
3	0.8474	0.0858	-6.28	4.93	-2.54
4	0.8073	0.0962	-5.86	3.48	-1.98
5	0.7844	0.1041	-5.20	2.88	-1.47
6	0.7701	0.1102	-4.52	2.55	-1.00
7	0.7598	0.1153	-3.91	2.34	-0.62
8	0.7522	0.1196	-3.22	2.19	-0.21
9	0.7466	0.1236	-2.57	2.09	0.17
10	0.7424	0.1269	-1.86	2.02	0.57
11	0.7395	0.1296	-0.90	2.00	1.11
12	0.7342	0.1333	-0.41	1.99	1.36
13	0.7322	0.1354	0.10	2.00	1.63
14	0.7311	0.1370	0.12	1.99	1.63
15	0.7300	0.1380	-0.06	1.97	1.51
16	0.7301	0.1384	-0.24	1.96	1.41
17	0.7304	0.1378	-0.97	1.95	1.00
18	0.7290	0.1392	-1.06	1.94	0.94
19	0.7288	0.1403	-1.13	1.94	0.89

[a] A positive value indicates overestimation by the thermistor based method

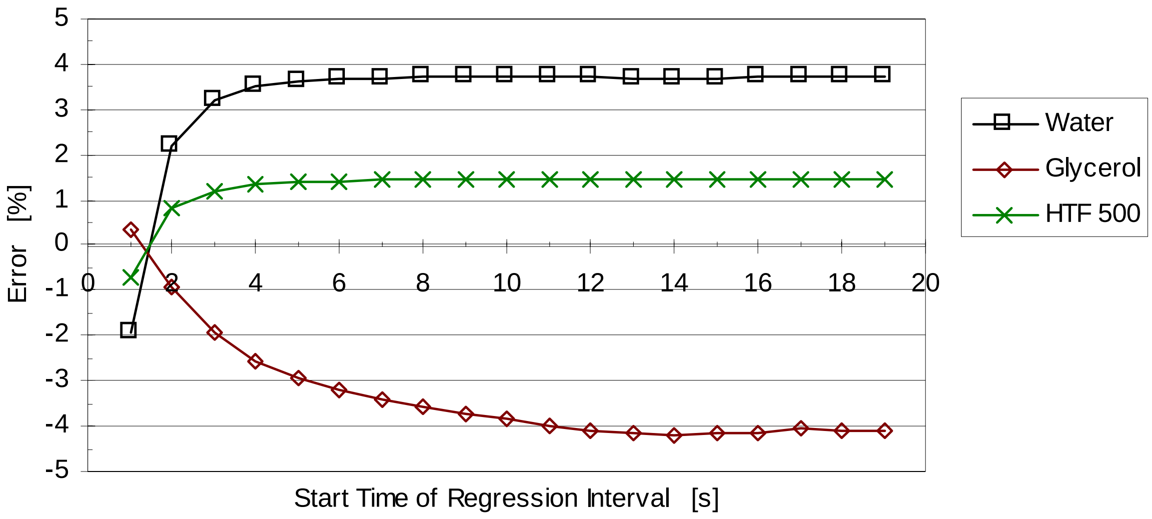

Figure 5.1 Error in estimation of thermal conductivity of the calibration media for Probe #H3 at 100 °C.

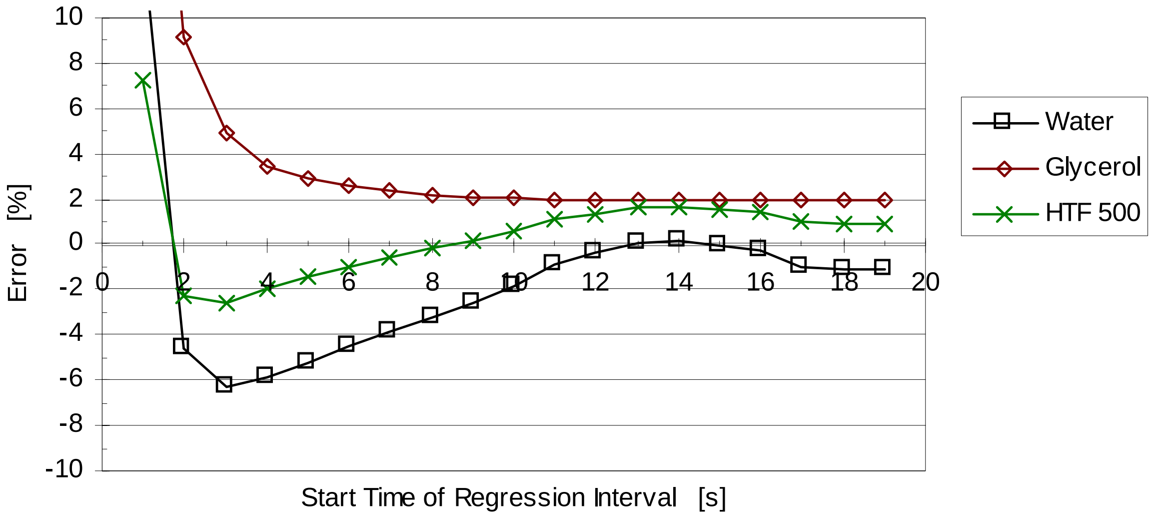

Figure 5.2 Error in estimation of thermal diffusivity of the calibration media for Probe #H3 at 100 °C.

The tables and the figures show the trends in the probe parameters and estimation errors with the successive regression intervals. The tables show that the properties of the probe changed rapidly for successive intervals for small values of the start time of the regression interval and more or less stabilized for larger values of the start time. The estimation errors reflected that pattern. The estimation errors for the estimation of thermal conductivity were the smallest for the interval 1-11 seconds. For later intervals, the estimation errors increased rapidly first, then more or less stabilized. The estimation errors for glycerol were the largest, up to 4.2%, water followed with -3.7%, and HTF 500 was best at 1.5%. As was the case with the low temperature probe #L4, the radii for estimation of thermal conductivity were larger than the physical radius and larger than the radii for estimation of thermal diffusivity. The finding that the lowest estimation errors were found for the interval 1-11 seconds was not expected from the theory. Equation 3.14 requires a value for the steady state power dissipation in the probe. The power dissipation in the probe towards the end of a measurement should give a better estimate of steady state power dissipation than early, yet was associated with larger errors in the estimated thermal conductivity of the calibration media. It is possible that for longer times heat flow along the stem of the probe exerted a stronger effect. Inaccuracies in the reference data could have been another factor. When the probe properties were calculated with a 8% higher thermal conductivity of HTF 500, the result was quite different from that displayed in Figure 5.1. The lines for water and HTF 500 shifted downward whereas the line for glycerol became nearly horizontal. The interval 1-11 seconds had far from optimal estimation errors as the thermal conductivity of water was under predicted by almost 15%. However, the estimation errors for all three media were below 1% for all intervals beyond 5-15 seconds. This illustrates the importance of accurate reference data for the calibration.

Estimation of medium thermal diffusivity tended to improve by using data later in the experiment. The estimation improved up to a start time of 11 seconds. Estimation errors corresponding to the interval 11-21 seconds were equal to or below 2% for each material. Medium thermal diffusivity was however calculated with an estimated value for thermal conductivity for that interval, which could be deduced from Figure 5.1, was different from the reference value. When the literature value for thermal conductivity was used, optimal estimation took place for interval 7-17 seconds. The estimation errors increased for later intervals. Compared to Figure 5.2, the lines for water and HTF 500 were shifted up and the line for glycerol shifted down by an amount reflecting their estimation errors for thermal conductivity (Figure 5.1). Unfortunately, the intervals giving the smallest estimation errors for thermal conductivity and diffusivity didn't coincide. The best interval for thermal conductivity gave poor estimation of thermal diffusivity.

In the foregoing, the results for probe #H3 at 100 °C, were discussed. Results at the higher temperatures, 110 to 150 °C, were similar to those at 100 °C. The estimation errors for thermal conductivity showed hardly a trend with temperature. For all temperatures, the interval 1-11 seconds gave the best estimation of thermal conductivity. For later intervals, the trend in the estimation errors replicated that seen at 100 °C. The magnitude of the errors changed marginally. The maximum estimation errors for glycerol gradually worsened with increasing temperature to about -6% at 150 °C (Figure 5.3). Those in water for long times decreased with temperature to about 3.1% at 150 °C, whereas the maximum errors in HTF 500 gradually increased to about 1.8% at 150 °C.

Estimation of thermal diffusivity showed a larger change with temperature. The interval for which the estimation errors were the smallest, moved towards earlier intervals (Figure 5.4). At 150 °C, the interval with a start time of either 3 or 4 seconds yielded the smallest estimation errors. When estimation used the reference values for thermal conductivity, the interval 2-12 seconds gave optimal results. The errors increased rapidly for intervals beyond that of optimal estimation. This was probably caused by convection. The deterioration in estimation for intervals beyond that of optimal estimation, became noticeable for temperatures above 120 °C. The viscosity of the calibration materials was strongly reduced at these high temperatures. The small amount of pipe insulation may not have been sufficient to restrict convection for a long time. If convection was the main cause for the deterioration, then the term S/I was more sensitive to its effects than the term $R_f\Delta T/V_{ss}^2$. Convection will lead to a decrease in the slope, S, and an increase in the intercept, I (= V_{ss}^2). The relative change in S/I will thus be larger than in $R_f\Delta T/V_{ss}^2$.

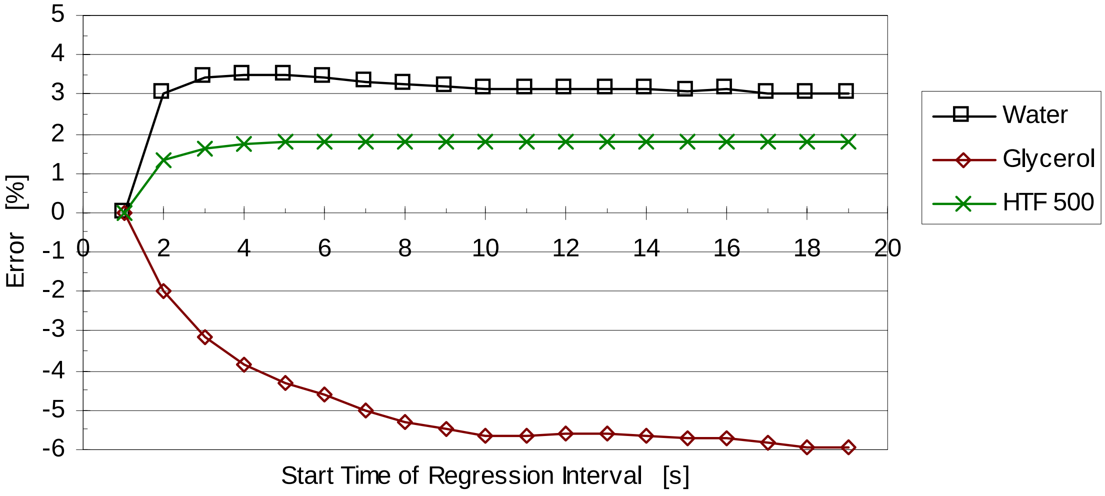

Figure 5.3 Error in estimation of thermal conductivity of the calibration media for Probe #H3 at 150 °C.

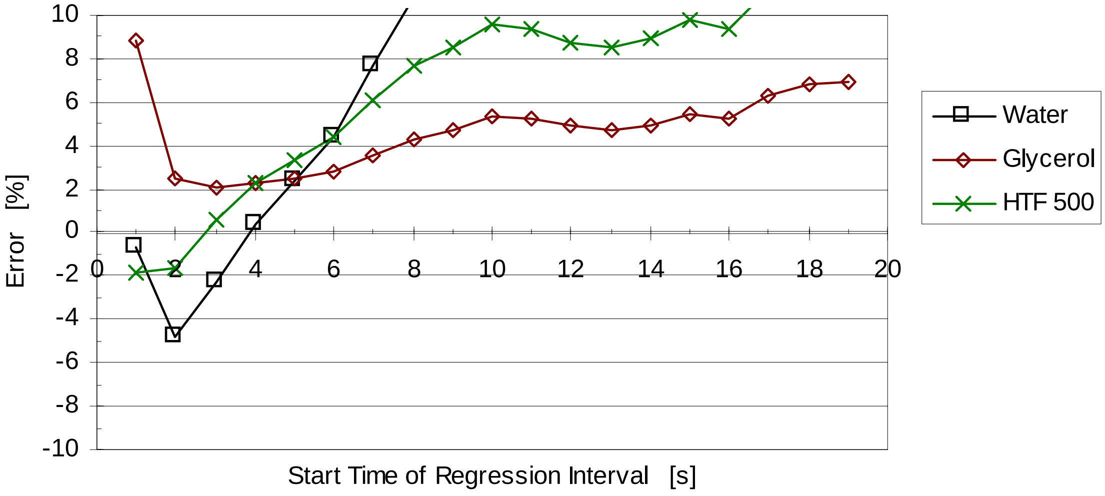

Figure 5.4 Error in estimation of thermal diffusivity of the calibration media for Probe #H3 at 150 °C.

The optimal intervals were dependent on the data for the calibration media as was shown with the hypothetical example under the discussion of the estimation errors for thermal conductivity at 100 °C. Reference data for thermal properties can vary with the literature source. While this research was in progress, property data for glycerol were found that were more recent, and supposedly more accurate. Initially property data for the thermal conductivity and specific heat were taken from Touloukian (1970a, 1970b). When a more recent source of reference for these properties was found (CINDAS, 1988), the probe properties were re-estimated. These latter properties were shown in Table 5.3 and 5.4. The difference in thermal conductivity data between the two sources was minor. The CINDAS data were 1% lower than those given by Touloukian over the temperature range 25 to 150 °C. The difference in specific heat data however was small at low temperatures but substantial at high temperatures. At 25 and 50 °C, the difference was well below 1%. At 100 °C, the CINDAS data were 4% lower than those given by Touloukian. At 150 °C, this difference had grown to 10%. The effect of this change in reference data on the estimation errors is best illustrated by Figures 5.5 and 5.6 that show the estimation errors for probe #H3 at 150 °C, when calibrated using the glycerol data that were taken from Touloukian. Comparison of Figure 5.5 to Figure 5.3 showed that the more recent relationship given by CINDAS yielded smaller maximum estimation errors for thermal conductivity. On the other hand, comparison of Figures 5.6 and 5.4 indicated a better calibration result for estimation of thermal diffusivity when the data from Touloukian were used. The use of more recent and supposedly more accurate reference data had led to an improvement in the calibration for thermal conductivity but a deterioration in the calibration for thermal diffusivity.

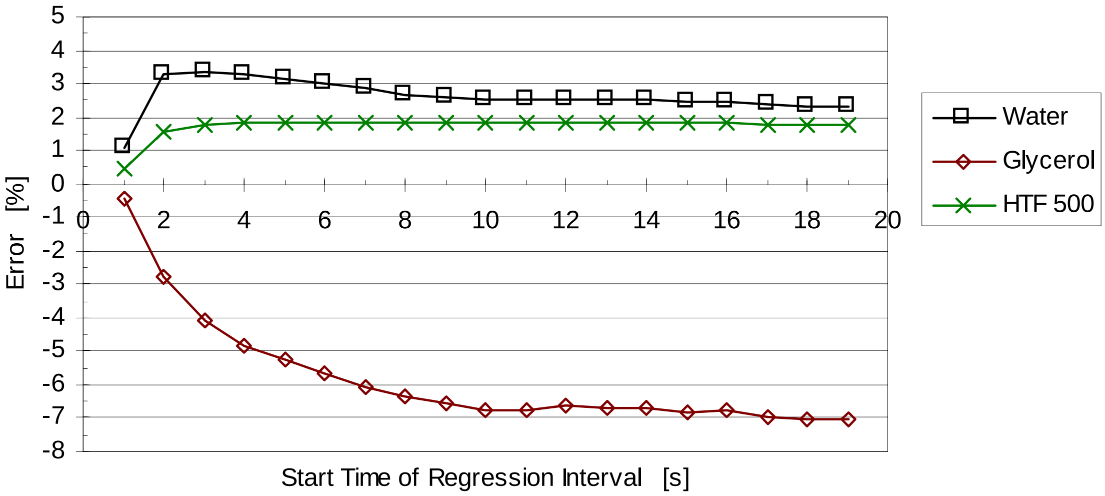

Figure 5.5 Error in estimation of thermal conductivity of the calibration media for Probe #H3 at 150 °C, when using reference data for the thermal conductivity of glycerol from Touloukian (1970).

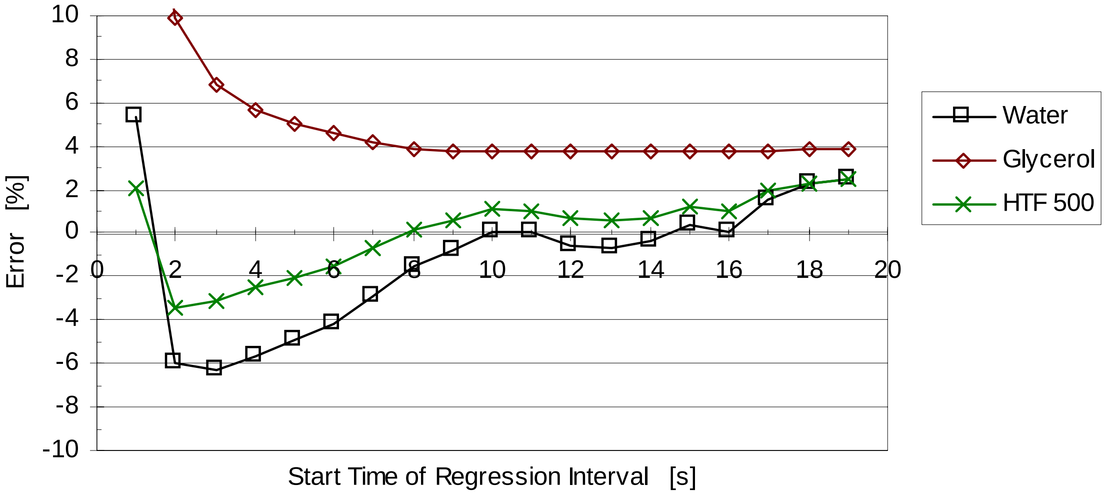

Figure 5.6 Error in estimation of thermal diffusivity of the calibration media for Probe #H3 at 150 °C, when using reference data for the thermal conductivity and specific heat of glycerol from Touloukian (1970).

5.3 ADEQUACY OF THERMAL CONTACT

5.3.1 Introduction

The thermal conductivity of potato and lean beef was measured with a miniature line heat source probe and the bead thermistor probe. The objective was to assess the adequacy of thermal contact for the bead thermistor during measurements in materials of different textural properties. The line heat source probe was used as a reference method. Thermal contact was evaluated by a comparison of the test results for both methods.

The accuracy of the line heat source probe was assessed from measurements in thickened water and glycerol at temperatures from 23 to 93 °C. Agreement with published data was better than 3% for temperatures up to 88 °C. Based on these results, the probe was used without a calibration factor (Wolters, 1992). The data for thickened water at 93 °C were inconsistent, and largely overestimated the thermal conductivity of water. The over estimation was ascribed to convection as the sample chamber was not pressureable. Line heat source measurements were standardized to 30 seconds sample time. Thermal conductivity was calculated over the data of the interval 10 to 30 seconds.

5.3.2 Potato Measurements

During the early potato measurements with the bead thermistor probe, all at 25 °C, a slight decrease in thermal conductivity was observed with successive measurements on the same sample. The decrease was small, but seemed systematic. It was decided to change the experimental design somewhat. Instead of using one sample of each potato and measure that sample three times, two samples were taken of each potato, and measured twice. This approach was followed for the remaining potatoes at 25 °C and for all potatoes at 50 °C. These later measurements did not consistently confirm the suspected effect of repeat measurements on the apparent thermal conductivity. At 100 °C, the original approach of one sample per potato with three measurements per sample was again used. This inconsistency in measurement protocol is mentioned for completeness, and as clarification as to why in Appendix D (Tables D.2 and D.3) three values are given for some potatoes, and four for others. The effect on the overall results of this protocol switch was minute. Analysis of the data showed that regardless of protocol, the standard deviation within samples was much smaller than between samples.

Figure 5.7 shows the properties for potato as measured with both methods at the three temperatures. The data are given in Appendix D (Table D.1). Included in the figure is thermal conductivity of water, taken from literature (Nieto de Castro, 1986). The thermal conductivity of moist foods is strongly dependent on moisture content and, barring significant changes in product composition, is expected to follow the trend for water with temperature. The measurement data for both methods followed this trend, as can be seen from Figure 5.7. An exception to this were the results for the line heat source probe at 50 °C. At that temperature the data appeared to follow a dichotomous distribution, whereby about half of the samples were centered around a value that was lower than measured at 25 °C.

The agreement between both methods was good at 25 and 50 °C, and fair at 100 °C. At all temperatures, the bead thermistor probe measured lower values than the line heat source probe. The average thermal conductivity at 25 °C with the bead thermistor was 0.5517 W/m°C, 7.4% lower than the value of 0.5957, measured with the line heat source probe. At 50 °C, the average thermal conductivity for the bead thermistor was 0.5842 W/m°C. This was 4.5% lower than the average for the line heat source probe, 0.6117 W/m°C. At 100 °C, the difference between the methods was 15%. The bead thermistor probe yielded an average value of 0.6015 W/m°C, and the line heat source probe an average of 0.7075 W/m°C. The latter value seems rather high as it exceeds the thermal conductivity of water at 100 °C (0.6779). The cause for the high value was sought in evaporative heat loss. The sample chamber for the line heat source probe was not pressureable. In an initial test with the circulating bath at 97 °C, an even larger apparent thermal conductivity was measured (0.77 W/m°C). All subsequent measurements were done with the bath at 94 °C. This may have only partly cured the problem. Both methods measured the thermal conductivity with good replication.

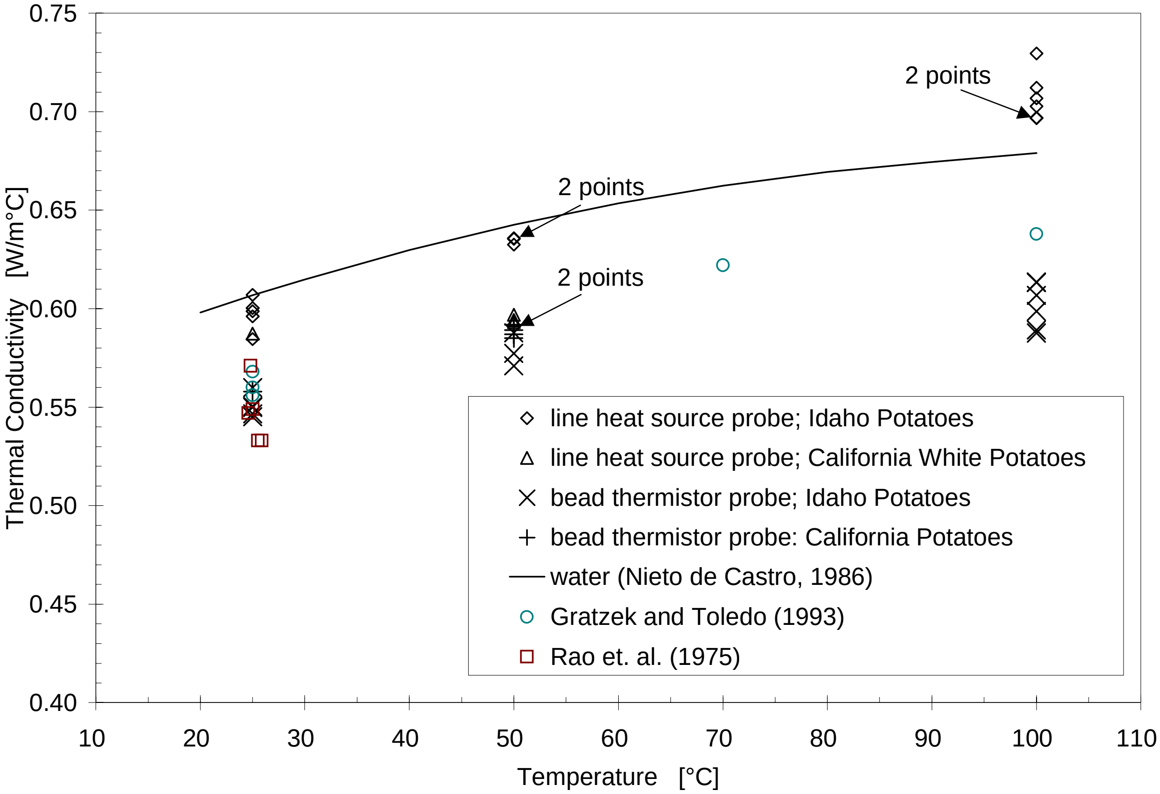

Figure 5.7 Thermal Conductivity of Potato at 25, 50 and 100 °C, measured with the Line Heat Source Probe and the Bead Thermistor Probe.

At 50 °C, the data for the line heat source probe fell in two distinct groups. The two groups corresponded to the two brands of potato, California White and Idaho. The bead thermistor probe however could not distinguish between the two brands. A brand effect is possible, but clouded by the fact that at 25 °C, the line heat source probe did not distinguish the one sample of California White from the samples of Idaho potato. Statistically, it would be more likely that the one sample (at 25 °C) was an outlier than three samples (at 50 °C). That would imply that there was a measurable difference between the two varieties. Rao et. al. (1975)

found significant differences between potato varieties, when measured at 25 °C, despite similar moisture contents. However, the value measured for the California White potatoes at 50 °C, 0.5946 W/m°C, was lower than the average at 25 °C. One would expect a higher value because of the positive effect of temperature on the thermal conductivity.

Literature data for potato are given for comparison in Figure 5.7. The values for the bead thermistor probe are closer to the literature data than those of the line heat source probe. At all three temperatures, the line heat source probe measured a thermal conductivity that was higher than the literature data. Yamada (1970) reported values of 0.485 at 10 °C, to 0.556 at 75 °C, and mentioned that the thermal conductivity of potato followed the trend in water with temperature. The data from Rao et. al. (1975) and Gratzek and Toledo (1993), both shown in Figure 5.7 were also much lower than those found with the line heat source probe in this study. Not shown in the figure are the results of two studies that report a thermal conductivity of potato higher than that of water. Lamberg and Hallström (1986) measured the thermal conductivity of potato (moisture content 80% w.b.) with the transient hot-strip method. They report an equation for thermal conductivity: $k = 0.624 + 1.19 \cdot 10^{-3} T$ W/m°C where T is in °C, valid over the range 20 to 85 °C. The transient hot-strip method used had not been used with food materials before (according to the authors). As an unestablished method for food thermal property measurement, one can not give too much weight to the data it yielded. Califano and Calvelo (1991) obtained the thermal conductivity of potato (moisture content 80% w.b.) from heat penetration data. The data were fitted to a 2nd order polynomial: $k = 1.05 - 1.96 \cdot 10^{-2} T + 1.90 \cdot 10^{-4} T^2$ W/m°C, valid for the range 50 to 100 °C, T in °C. The equation from Califano and Calvelo is at odds with most of the published data for moist food materials in that it has a positive coefficient for the quadratic term. In general, the thermal conductivity is shown to curve downward with temperature, much like the thermal conductivity of water.

Based on the comparison of both methods, it was concluded that thermal contact was adequate for the bead thermistor during the measurements of potato. This conclusion was supported by visual examination of the samples after the measurements, where the sample was sliced in half at the insertion point. The samples showed evidence of a thight fit around the thermistor.

5.3.3 Beef Measurements

Figure 5.8 shows the thermal conductivity of beef. The data can be found in Appendix D (Tables D.5 to D.8). Six samples were measured at each temperature. The values in the figure represent the average thermal conductivity for each sample, found from three measurements. Because some samples gave nearly identical values, their associated data markers can be hard to distinguish. The sample averages are listed in Appendix D (Table D.5). Two samples were excluded from contributing to the average, one sample at 25 °C with the bead thermistor probe, and one sample at 50 °C with the line heat source probe. Both samples had a substantially lower apparent thermal conductivity than the other samples. Post-test examination of all samples revealed the presence of fat near the probe only in the two samples that had shown a much lower thermal conductivity than the others.

Both methods show a larger variation than when used with the potato samples. This was expected as the beef samples were less homogeneous than the potato samples. Surprisingly, both methods measured with comparable replication. It was expected that the line heat source probe would show better replication because of its larger sample volume. As was the case with the potato samples, the line heat source probe yielded values that were higher than those from the bead thermistor probe. The differences between the methods, as judged by the average at 25 and 50 °C, was similar to those seen with potato. At 25 °C, the average for the bead thermistor probe was 0.4937 W/m°C, 7.3% lower than the value of 0.5326 W/m°C for the line heat source probe. At 50 °C, the bead thermistor probe measured an average value of 0.5084 W/m°C, 7.3% lower than the value of 0.5482 W/m°C, found with the line heat source probe. At 100 °C, agreement between both methods was the best (quite unlike with the potato samples). The average value of 0.4656 W/m°C with the bead thermistor probe is only 2% lower than measured with the line heat source probe (0.4750 W/m°C). A possible explanation as to why the line heat source probe tests with beef at 100 °C (actual bath temperature, 94 °C;

temperature rise during test was about 6 °C) did not give the inflated values as it did with potato may be found in the textural differences. The elasticity of beef might have provided a tighter seal around the probe whereas insertion into the cooked potato might have created a small gap between the probe and the tissue. Agreement between the bead thermistor probe measurements and the data given by Baghe-Khandan (1981a) for whole round beef is good. The difference was less than 4%.

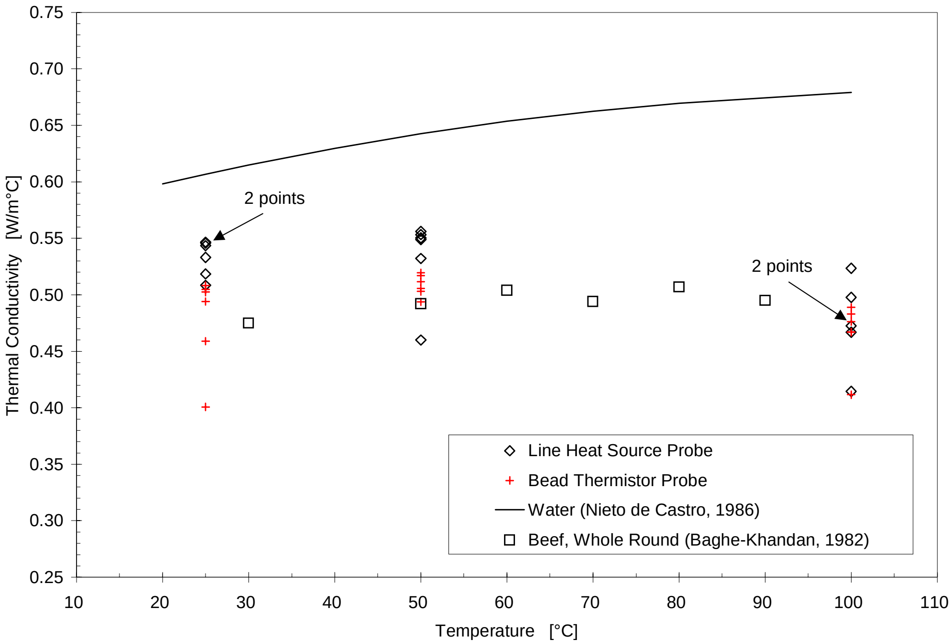

Figure 5.8 Thermal Conductivity of Lean Beef at 25, 50 and 100 °C, measured with the Line Heat Source Probe and the Bead Thermistor Probe.

The thermal conductivity of beef appeared to show no clear trend with temperature. The bead thermistor measured a slight increase in thermal conductivity from 25 to 50 °C. The same can be said for the line heat source probe. At 50 °C, the composition and texture of beef was still unchanged from that at 25 °C, and any effect of heating induced changes was not expected. Denaturation of meat proteins did not take place until higher temperatures. Baghe-Khandan (1981a) reported denaturation of beef muscle protein between 60 and 70 °C, leading to shrinkage and a decreased moisture content. In the present experiments it was observed that the beef samples shrunk and lost moisture as a result of the cook at 100 °C. The decrease in thermal conductivity at 100 °C was attributed to the moisture loss that occurred as a result of the heating. Other heating induced effects might not have played a role. Perez and Calvelo (1984) took room temperature thermal conductivity measurements of beef samples that were either subjected to a heat treatment at temperatures between 80 and 180 °C, or vacuum dried at low temperatures. They concluded that "both the apparent density and thermal conductivity of cooked beef are dependent on the water content of the product, being independent of the thermal history to which it has been submitted".

5.3.4 Conclusion

Good agreement was found between the bead thermistor probe and the miniature line heat source probe for the thermal conductivity of potato and lean beef at 25 and 50 °C. The agreement between both methods at 100 °C was very good for beef and fair for potato. The latter was attributed to problematic measurements with the line heat source probe. Based on the results of the comparative study, thermal contact between the thermistor probe and both potato and lean beef was considered adequate. Examination of the samples after the tests supported this conclusion. The bead thermistor probe measured the thermal conductivity of both materials with replication that was comparable to that of the line heat source probe.

5.4 NATURAL CONVECTION

5.4.1 Viscosity Measurements

The intended viscosities were 1, 5, 25, 50, 100 and 150 cp. The consistency coefficients of the solutions in this study came close to these values. In the following discussion the intended values are used. It should be understood that these refer to the corresponding actual solutions. Data on the solutions are given in Table 5.5. The solutions below 100 cp were almost Newtonian in behavior as witnessed from their near unity flow behavior indices. The replication was good.

Table 5.5 Viscosity of sodium alginate solutions

Intended viscosity	Measured value, first sample[1]		Measured value, second sample[1]		Average
	consistency coefficient, K	flow behavior index, n	consistency coefficient, K	flow behavior index, n	consistency coefficient, K
[cp]	[10^{-3} N·s^n/m^2]		[10^{-3} N·s^n/m^2]		[10^{-3} N·s^n/m^2]
1	0.55 [2]		0.55 [2]		0.55
5	4.7	1.010	4.9	1.009	4.8
25	24.9	0.993	24.2	0.998	24.6
50	48.6	0.991	47.9	0.998	48.3
100	101.6	0.970	101.4	0.963	101.5
150	151.4	0.967	154.2	0.968	152.8

[1] Average of triplicate measurement.

[2] Literature value (Incropera and DeWitt,1985, Appendix 6).

5.4.2 Effect of the Viscosity

The discussion pertains to analyses performed at a given value of the temperature step, ΔT. The overall effect of viscosity, not differentiated with respect to ΔT is a meaningless statistic in the context of this research.

The results of the multiple-comparison procedure with SAS are shown in Tables 5.6 and 5.7. They present the Tukey's W groupings based on $R_f\Delta T/V_{ss}^2$ and S/I respectively. The columns in the tables show the groupings for a particular value of the starting time of the regression interval. Each of the three blocks in a column corresponds to one value of the temperature step. The viscosities within each block are ordered by descending value of their associated value of $R_f\Delta T/V_{ss}^2$ and S/I respectively. Those values can be found in Tables 5.8 and 5.9. Viscosities within a block that are marked with the same letter did not test different. Statistical differences between viscosities in a block were most likely caused by natural convection.

An idea of the onset time of convection for the different viscosities and temperature steps, could be obtained from Tables 5.9 and 5.10. When a solution of certain viscosity tested significantly different from the more viscous solutions for successive start times of the regression interval, the earliest start time at which that occurred could be used to make an estimate of the onset time of natural convection in the solution of that viscosity. The start times of these earliest intervals at which the solutions tested different (from the more viscous) are shown in Table 5.10.

Table 5.6 Tukey's W grouping for viscosity for each of the three temperature steps and different values for the start time (ST) of the regression interval; SAS analysis was performed on the means of $R\Delta T/V_{ss}^2$ (Table 5.8) corresponding to viscosity (and ΔT); the means of $R\Delta T/V_{ss}^2$ originate from linear regression over a 2 second wide interval.

ST [s]	1	2	3	4	5	6	7	8	9	10	11	12	14	16	18	20	22	24	26
1.5 [°C]	100^{A}	100^{A}	100^{A}	5^{A}	100^{A}	5^{A}	100^{A}	100^{A}	100^{A}	100^{A}	150^{A}	100^{A}	100^{A}	150^{A}	150^{A}	100^{A}	150^{A}	150^{A}	150^{A}
	5^{A}	5^{A}	5^{A}	150^{A}	5^{A}	100^{A}	5^{A}	5^{A}	150^{A}	150^{A}	50^{A}	25^{A}	50^{A}	50^{A}	100^{A}	150^{A}	25^{A}	100^{A}	50^{A}
	150^{AB}	150^{A}	150^{A}	100^{A}	25^{A}	25^{A}	150^{A}	25^{A}	25^{A}	50^{A}	25^{A}	150^{A}	25^{A}	25^{A}	50^{A}	25^{A}	100^{A}	50^{A}	25^{A}
	100^{AB}	25^{A}	50^{A}	25^{A}	150^{A}	150^{A}	25^{A}	50^{A}	5^{A}	25^{A}	100^{A}	50^{A}	150^{AB}	100^{A}	25^{AB}	50^{A}	50^{A}	25^{A}	100^{A}
	50^{AB}	50^{A}	25^{A}	50^{A}	50^{A}	50^{A}	50^{A}	150^{A}	50^{A}	5^{A}	5^{A}	5^{A}	5^{B}	5	5^{B}	5	5	5	5
	1^{B}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

ST [s]	1	2	3	4	5	6	7	8	9	10	11	12	14	16	18	20	22	24	26
2.5 [°C]	25^{A}	150^{A}	25^{A}	150^{A}	100^{A}	25^{A}	150^{A}	150^{A}	100^{A}	25^{A}	150^{A}	25^{A}	50^{A}	100^{A}	25^{A}	150^{A}	150^{A}	150^{A}	100^{A}
	150^{A}	25^{A}	150^{A}	25^{A}	50^{A}	150^{A}	25^{A}	100^{A}	50^{A}	50^{A}	50^{A}	150^{A}	100^{A}	150^{A}	50^{A}	100^{A}	50^{A}	100^{A}	150^{A}
	5^{A}	5^{A}	50^{A}	100^{A}	25^{A}	50^{AB}	100^{A}	25^{A}	150^{A}	150^{A}	100^{A}	100^{A}	150^{A}	50^{A}	150^{A}	50^{A}	100^{A}	50^{A}	50^{A}
	100^{A}	50^{A}	5^{A}	50^{A}	150^{A}	100^{AB}	50^{A}	50^{A}	25^{A}	100^{A}	25^{A}	50^{A}	25^{A}	25^{A}	100^{A}	25^{A}	25^{A}	25^{A}	25^{A}
	50^{A}	100^{A}	100^{A}	5^{A}	5^{A}	5^{B}	5	5	5	5	5	5	5	5	5	5	5	5	5
	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

ST [s]	1	2	3	4	5	6	7	8	9	10	11	12	14	16	18	20	22	24	26
5.0 [°C]	5^{A}	150^{A}	150^{A}	150^{A}	150^{A}	100^{A}	150^{A}	50^{A}	150^{A}	150^{A}	100^{A}	100^{A}	100^{A}	50^{A}	150^{A}	100^{A}	150^{A}	150^{A}	150^{A}
	50^{A}	25^{A}	25^{A}	25^{A}	50^{A}	150^{A}	50^{A}	150^{A}	100^{A}	50^{A}	150^{A}	150^{A}	150^{A}	150^{A}	100^{A}	150^{A}	100^{A}	100^{A}	100^{AB}
	100^{B}	5^{A}	50^{A}	50^{A}	100^{A}	50^{A}	100^{A}	100^{A}	50^{A}	100^{A}	50^{A}	50^{A}	50^{A}	100^{A}	50^{AB}	50^{A}	50^{A}	50^{A}	50^{B}
	150^{BC}	100^{A}	100^{A}	100^{A}	25^{A}	25^{A}	25^{A}	25^{A}	25^{A}	25^{A}	25^{A}	25	25	25	25^{B}	25	25	25	25
	25^{BC}	50^{A}	5^{A}	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
	1^{C}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

Table 5.7 Tukey's W grouping for viscosity for each of the three temperature steps and different values for the start time (ST) of the regression interval; SAS analysis was performed on the means of S/I (Table 5.9) corresponding to viscosity (and ΔT); the means of S/I originate from linear regression over a 2 second wide interval.

ST [s]	1	2	3	4	5	6	7	8	9	10	11	12	14	16	18	20	22	24	26
1.5 [°C]	5^{A}	25^{A}	100^{A}	5^{A}	25^{A}	50^{A}	100^{A}	50^{A}	25^{A}	100^{A}	150^{A}	25^{A}	50^{A}	150^{A}	150^{A}	150^{A}	150^{A}	150^{A}	150^{A}
	150^{A}	5^{A}	5^{A}	150^{A}	5^{A}	25^{A}	150^{A}	100^{A}	50^{A}	50^{A}	50^{A}	100^{A}	100^{A}	50^{AB}	100^{A}	100^{A}	25^{A}	100^{A}	50^{A}
	25^{A}	150^{A}	50^{A}	25^{A}	100^{A}	5^{A}	25^{A}	5^{A}	150^{A}	150^{A}	25^{AB}	50^{A}	25^{A}	25^{AB}	50^{A}	25^{A}	100^{A}	50^{A}	25^{A}
	50^{A}	100^{A}	25^{A}	50^{A}	50^{A}	150^{A}	5^{A}	25^{A}	100^{A}	25^{A}	100^{AB}	150^{A}	150^{A}	100^{B}	25^{AB}	50^{A}	50^{A}	25^{A}	100^{AB}
	100^{AB}	50^{A}	150^{A}	100^{A}	150^{A}	100^{A}	50^{A}	150^{A}	5^{A}	5^{A}	5^{B}	5^{A}	5	5	5^{B}	5	5	5	5^{B}
	1^{B}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

ST [s]	1	2	3	4	5	6	7	8	9	10	11	12	14	16	18	20	22	24	26
2.5 [°C]	25^{A}	150^{A}	50^{A}	150^{A}	50^{A}	25^{A}	50^{A}	150^{A}	100^{A}	25^{A}	50^{A}	25^{A}	50^{A}	100^{A}	25^{A}	150^{A}	50^{A}	150^{A}	100^{A}
	150^{A}	50^{A}	25^{A}	50^{A}	100^{A}	150^{A}	25^{A}	100^{A}	50^{A}	50^{A}	150^{A}	100^{A}	100^{A}	150^{A}	50^{A}	100^{A}	150^{A}	100^{A}	150^{A}
	100^{A}	25^{A}	150^{A}	100^{A}	25^{AB}	50^{A}	150^{A}	50^{A}	150^{A}	100^{A}	100^{A}	50^{A}	150^{A}	50^{A}	150^{A}	50^{A}	100^{A}	50^{A}	50^{A}
	50^{A}	100^{A}	100^{A}	25^{A}	150^{AB}	100^{A}	100^{A}	25^{A}	25^{A}	150^{A}	25^{A}	150^{A}	25^{A}	25^{A}	100^{A}	25^{A}	25^{A}	25^{A}	25^{A}
	5^{A}	5^{A}	5^{A}	5^{A}	5^{B}	5	5	5	5	5	5	5	5	5	5	5	5	1	1
	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	5	5

ST [s]	1	2	3	4	5	6	7	8	9	10	11	12	14	16	18	20	22	24	26
5.0 [°C]	5^{A}	25^{A}	25^{A}	25^{A}	150^{A}	100^{A}	150^{A}	50^{A}	100^{A}	150^{A}	100^{A}	100^{A}	100^{A}	50^{A}	150^{A}	100^{A}	150^{A}	100^{A}	150^{A}
	50^{A}	150^{AB}	150^{A}	150^{A}	50^{A}	150^{A}	50^{A}	150^{A}	150^{A}	100^{AB}	150^{AB}	50^{A}	150^{A}	150^{A}	100^{A}	150^{A}	100^{A}	150^{A}	100^{AB}
	100^{B}	100^{AB}	100^{A}	100^{A}	100^{A}	50^{A}	100^{A}	100^{A}	50^{A}	50^{AB}	50^{AB}	150^{A}	50^{A}	100^{A}	50^{AB}	50^{A}	50^{A}	50^{A}	50^{B}
	150^{BC}	50^{AB}	50^{A}	50^{A}	25^{A}	25^{A}	25^{A}	25^{A}	25^{A}	25^{B}	25^{B}	25^{B}	25	25	25^{B}	25	25	25^{B}	25
	25^{BC}	5^{B}	5	5	5	5	5	5	5	5	5	5	1	1	1	1	1	1	1
	1^{C}	1	1	1	1	1	1	1	1	1	1	1	5	5	5	5	5	5	5

Table 5.8 Values of $R_f\Delta T/V_{ss}^2$ as related to temperature step and start time of the regression interval. The regression interval was 2 seconds wide. Values are ordered, per temperature step, in decreasing value from top down. The corresponding values for viscosity can be found in Table 5.6.

ST [s]	1	2	3	4	5	6	7	8	9	10	11	12	14	16	18	20	22	24	26
1.5 [°C]	274.4	280.0	283.7	284.0	285.4	286.3	287.6	288.0	287.6	289.1	288.9	289.5	290.0	291.8	292.1	290.1	292.0	292.3	293.9
	274.3	279.9	283.1	283.9	285.1	286.3	286.9	287.4	287.2	286.8	288.1	288.6	289.4	290.1	290.5	289.9	291.3	291.2	291.7
	274.1	279.6	282.5	283.8	284.6	285.8	286.8	286.8	287.1	286.6	287.8	288.1	288.3	289.5	288.4	289.0	289.8	289.5	289.7
	273.5	279.4	282.2	283.3	284.5	285.8	286.3	286.7	287.0	286.3	287.4	287.9	288.1	288.5	287.3	287.7	287.7	286.8	287.7
	273.4	278.7	282.2	283.1	283.9	285.7	286.1	286.6	286.5	285.7	285.6	285.5	283.5	281.9	281.5	275.9	279.0	275.7	277.6
	272.0	270.5	263.1	252.0	241.4	231.9	226.1	220.5	220.2	219.3	220.3	220.7	223.1	225.1	225.4	229.3	224.0	226.7	227.8
msd	2.25	3.01	3.85	4.19	4.46	4.34	3.51	3.99	3.62	4.10	3.64	5.60	4.86	3.84	5.96	9.43	7.05	7.51	8.98
% of max	0.8	1.1	1.4	1.5	1.6	1.5	1.2	1.4	1.3	1.4	1.3	1.9	1.7	1.3	2.0	3.3	2.4	2.6	3.1

ST [s]	1	2	3	4	5	6	7	8	9	10	11	12	14	16	18	20	22	24	26
2.5 [°C]	269.6	274.7	276.9	278.8	279.8	280.2	280.5	281.3	281.7	282.7	282.6	281.9	281.8	283.9	284.4	284.8	282.4	283.9	284.2
	269.6	274.5	276.6	278.2	279.8	279.8	280.4	280.9	281.3	281.4	282.5	281.5	281.7	283.3	282.9	283.1	282.2	283.2	283.8
	269.6	274.4	276.5	278.1	279.2	279.0	280.1	280.9	281.3	281.3	281.8	281.2	281.3	282.4	282.6	282.1	280.7	282.5	281.1
	269.2	274.2	276.3	278.0	279.0	278.8	280.1	280.8	280.0	281.1	281.1	281.1	280.3	282.1	282.0	281.7	280.3	278.6	280.1
	269.0	273.9	276.1	277.5	278.4	277.5	276.9	275.3	274.9	273.8	271.3	268.9	264.4	258.8	253.9	253.9	249.9	249.1	246.2
	264.9	257.8	242.9	227.3	216.3	210.0	209.0	209.0	211.5	213.1	214.8	214.4	216.5	216.2	217.4	217.7	218.5	219.7	216.4
msd	1.36	1.73	1.99	2.32	1.49	1.98	1.80	2.34	2.40	2.47	2.40	4.05	2.85	3.45	4.38	3.72	4.23	5.56	5.05
% of max	0.5	0.6	0.7	0.8	0.5	0.7	0.6	0.8	0.9	0.9	0.8	1.4	1.0	1.2	1.5	1.3	1.5	2.0	1.8

ST [s]	1	2	3	4	5	6	7	8	9	10	11	12	14	16	18	20	22	24	26
5.0 [°C]	283.6	276.1	274.6	274.1	274.7	275.0	275.2	275.8	275.9	276.6	275.9	275.6	276.5	276.0	276.7	276.4	278.5	276.9	276.9
	279.6	276.0	274.5	274.0	274.5	274.9	275.1	275.5	275.8	275.8	275.8	275.2	275.9	275.6	275.4	276.2	276.5	276.8	274.8
	272.4	274.9	273.7	273.8	274.1	274.6	274.7	274.8	275.3	275.7	275.6	275.2	275.7	275.0	272.8	274.8	275.1	274.1	272.4
	268.3	274.8	273.7	273.7	274.0	274.3	274.3	273.6	274.7	274.2	273.4	272.5	272.3	270.8	269.7	269.1	267.5	265.8	263.9
	267.8	274.1	272.9	270.5	266.7	262.7	257.8	252.6	247.1	242.0	238.4	234.4	229.9	226.9	226.1	226.8	226.2	227.5	228.2
	263.1	242.1	214.8	201.2	199.5	201.8	205.0	206.5	206.8	207.1	207.5	207.1	208.3	207.8	208.3	208.1	207.7	206.5	208.5
msd	6.84	3.33	2.48	1.92	2.12	2.21	2.48	2.61	2.60	2.64	2.63	2.50	2.64	2.72	4.15	3.97	3.62	4.49	3.78
% of max	2.4	1.2	0.9	0.7	0.8	0.8	0.9	0.9	0.9	1.0	1.0	0.9	1.0	1.0	1.5	1.4	1.3	1.6	1.4

Table 5.9 Values of S/I as related to temperature step and start time of the regression interval. Regression interval was 2 seconds wide. Values are ordered, per temperature step, in decreasing value from top down. The corresponding values for viscosity can be found in Table 5.7.

ST [s]	1	2	3	4	5	6	7	8	9	10	11	12	14	16	18	20	22	24	26
1.5 [°C]	0.4272	0.4687	0.4950	0.5027	0.5157	0.5291	0.5365	0.5403	0.5425	0.5552	0.5612	0.5647	0.5811	0.6084	0.6150	0.5771	0.6165	0.6230	0.6579
	0.4265	0.4677	0.4945	0.5025	0.5136	0.5278	0.5338	0.5403	0.5378	0.5389	0.5597	0.5614	0.5705	0.5931	0.5789	0.5720	0.6142	0.5911	0.6276
	0.4264	0.4655	0.4931	0.5025	0.5117	0.5269	0.5337	0.5400	0.5374	0.5331	0.5527	0.5567	0.5610	0.5793	0.5652	0.5710	0.5658	0.5855	0.5850
	0.4261	0.4648	0.4917	0.5010	0.5089	0.5216	0.5333	0.5397	0.5360	0.5319	0.5321	0.5505	0.5488	0.5459	0.5421	0.5512	0.5505	0.5285	0.5222
	0.4244	0.4643	0.4901	0.4959	0.5087	0.5215	0.5329	0.5311	0.5341	0.5173	0.5162	0.5140	0.4833	0.4575	0.4503	0.3496	0.4065	0.3443	0.3819
	0.4167	0.4059	0.3436	0.2399	0.1314	0.0260	-0.0422	-0.1136	-0.1175	-0.1293	-0.1143	-0.1088	-0.0685	-0.0349	-0.0288	0.0493	-0.0594	-0.0018	0.0226
msd	0.0082	0.0135	0.0202	0.0280	0.0278	0.0297	0.0247	0.0336	0.0334	0.0500	0.0421	0.0778	0.0560	0.0588	0.0980	0.1557	0.1294	0.1406	0.1718
% of max	1.9	2.9	4.1	5.6	5.4	5.6	4.6	6.2	6.2	9.0	7.5	13.8	9.6	9.7	15.9	27.0	21.0	22.6	26.1

ST [s]	1	2	3	4	5	6	7	8	9	10	11	12	14	16	18	20	22	24	26
2.5 [°C]	0.4429	0.4792	0.4989	0.5167	0.5314	0.5329	0.5360	0.5451	0.5550	0.5663	0.5684	0.5560	0.5585	0.5921	0.5997	0.6033	0.5635	0.5872	0.6021
	0.4420	0.4788	0.4988	0.5136	0.5309	0.5266	0.5354	0.5450	0.5516	0.5524	0.5623	0.5480	0.5547	0.5743	0.5765	0.5791	0.5582	0.5805	0.5850
	0.4411	0.4787	0.4955	0.5128	0.5217	0.5227	0.5352	0.5442	0.5451	0.5469	0.5565	0.5475	0.5437	0.5684	0.5622	0.5621	0.5342	0.5714	0.5413
	0.4406	0.4753	0.4944	0.5109	0.5187	0.5192	0.5350	0.5417	0.5304	0.5450	0.5440	0.5472	0.5308	0.5595	0.5596	0.5534	0.5273	0.4934	0.5228
	0.4381	0.4735	0.4892	0.5008	0.5095	0.4994	0.4935	0.4729	0.4681	0.4540	0.4191	0.3835	0.3150	0.2222	0.1370	0.1371	0.0596	0.0715	-0.0075
	0.4185	0.3651	0.2368	0.0864	-0.0315	-0.1037	-0.1159	-0.1168	-0.0809	-0.0569	-0.0302	-0.0365	-0.0008	-0.0069	0.0166	0.0247	0.0425	0.0451	-0.0150
msd	0.0081	0.0104	0.0128	0.0175	0.0128	0.0178	0.0201	0.0242	0.0298	0.0307	0.0308	0.0547	0.0437	0.0560	0.0714	0.0689	0.0776	0.1110	0.1044
% of max	1.8	2.2	2.6	3.4	2.4	3.3	3.8	4.4	5.4	5.4	5.4	9.8	7.8	9.5	11.9	11.4	13.8	18.9	17.3

ST [s]	1	2	3	4	5	6	7	8	9	10	11	12	14	16	18	20	22	24	26
5.0 [°C]	0.5987	0.5532	0.5398	0.5359	0.5401	0.5480	0.5467	0.5544	0.5590	0.5645	0.5596	0.5552	0.5700	0.5585	0.5681	0.5682	0.6035	0.5773	0.5724
	0.5764	0.5523	0.5392	0.5339	0.5386	0.5431	0.5459	0.5500	0.5555	0.5581	0.5534	0.5458	0.5553	0.5502	0.5519	0.5587	0.5713	0.5722	0.5354
	0.5289	0.5431	0.5338	0.5336	0.5378	0.5394	0.5444	0.5462	0.5474	0.5538	0.5516	0.5456	0.5536	0.5447	0.5025	0.5371	0.5430	0.5239	0.4876
	0.4968	0.5337	0.5302	0.5313	0.5353	0.5387	0.5387	0.5309	0.5445	0.5377	0.5268	0.5129	0.5108	0.4861	0.4671	0.4562	0.4275	0.3930	0.3531
	0.4952	0.5322	0.5153	0.4920	0.4521	0.4066	0.3488	0.2836	0.2100	0.1393	0.0865	0.0255	0.0299	0.0208	0.0310	0.0255	0.0168	-0.0106	0.0375
	0.4726	0.3070	0.0638	-0.0743	-0.0930	-0.0642	-0.0222	-0.0017	0.0036	0.0086	0.0153	0.0085	-0.0461	-0.0983	-0.1122	-0.0984	-0.1114	-0.0842	-0.0667
msd	0.0460	0.0208	0.0128	0.0115	0.0161	0.0171	0.0191	0.0272	0.0221	0.0258	0.0288	0.0298	0.0348	0.0401	0.0721	0.0702	0.0643	0.0835	0.0778
% of max	7.7	3.8	2.4	2.1	3.0	3.1	3.5	4.9	4.0	4.6	5.1	5.4	6.1	7.2	12.7	12.4	10.7	14.5	13.6

Table 5.10 Earliest start time of regression interval (of 2 seconds wide) at which a viscosity would test different (at the 5% level) of the more viscous solutions. Times are given for both the analysis of $R_f\Delta T/V_{ss}^2$ and S/I

Viscosity	1		5		25	
	on $R_f\Delta T/V_{ss}^2$	on S/I	on $R_f\Delta T/V_{ss}^2$	on S/I	on $R_f\Delta T/V_{ss}^2$	on S/I
1.5 °C	2	2	16	14		
2.5 °C	1	1	7	6		
5 °C	x[1]	x[1]	4	3	12	12

[1] Initial transients for the temperature step of 5 °C lasted longer than one second. These transients served to overcome the heat capacity of the thermistor. The analysis at 1 second therefore is not given any weight.

Since Tukey's W groupings are shown at the start time of the regression interval, significant differences reflect effects occurring within the following two seconds. A non-significant difference compared to a more viscous solution could be interpreted as the absence of natural convection up to the time shown. The analysis on S/I shows effects of convection for earlier start times than the analysis for $R_f\Delta T/V_{ss}^2$. Table 5.11 gives the estimated onset time of convection in thickened water at 50 °C, based on the analysis of S/I.

Table 5.11 Estimated onset time of convection in thickened water at 50 °C, [s].

Viscosity, cp	1	5	25
1.5 °C	< 3	15	
2.5 °C	< 3	7	
5 °C	< 3	4	13

Table 5.11 shows the delaying effect of an increase in viscosity on the onset of convection, and an accelerating effect of an increase in the temperature step. According to the statistical analysis, thickened water samples with a viscosity of at least 50 cp can be measured with a

temperature step of up to 5 °C, without significant convection. For a temperature step of 1.5 or 2.5 °C, this threshold can be lowered to 25 cp.

5.4.3 Effect of the Temperature Step

Table 5.8 suggested that the temperature step had an effect on the value of $R\Delta T/V_{ss}^2$. This was noticed when these values were compared for the 150 cp solution, in which convection had not taken place. The model for the thermistor based method did not predict such an effect. In order to determine if there was a statistical correlation between the magnitude of the temperature step and the value of $R\Delta T/V_{ss}^2$, the data of the 150 cp solution were used in a multi-comparisons test. The procedure was much like the one that was used for estimating the onset of convection. A regression interval of 10 seconds was used to smooth the effect of the noise in the data. The linear regression was done on successive intervals whose start time was incremented by one second, until it reached the value of 19. The regression results formed the input to Tukey's W test, with a type 1 error of 0.05.

According to the theory, the steady state power dissipation of the probe should be a linear function of the temperature step, ΔT. If that were the case, and when convection was negligible, the values for $R_f\Delta T/V_{ss}^2$ and S/I should be independent of the size of the temperature step. The values of $R_f\Delta T/V_{ss}^2$ and S/I are shown in Figures 5.9 and 5.10 respectively. The data in the figures originated from the above described regression procedure. If measurement followed theory, the lines for the three temperature steps would be (nearly) identical. They were not and the difference between the lines was statistically significant for times larger than 2 seconds (Table 5.12).

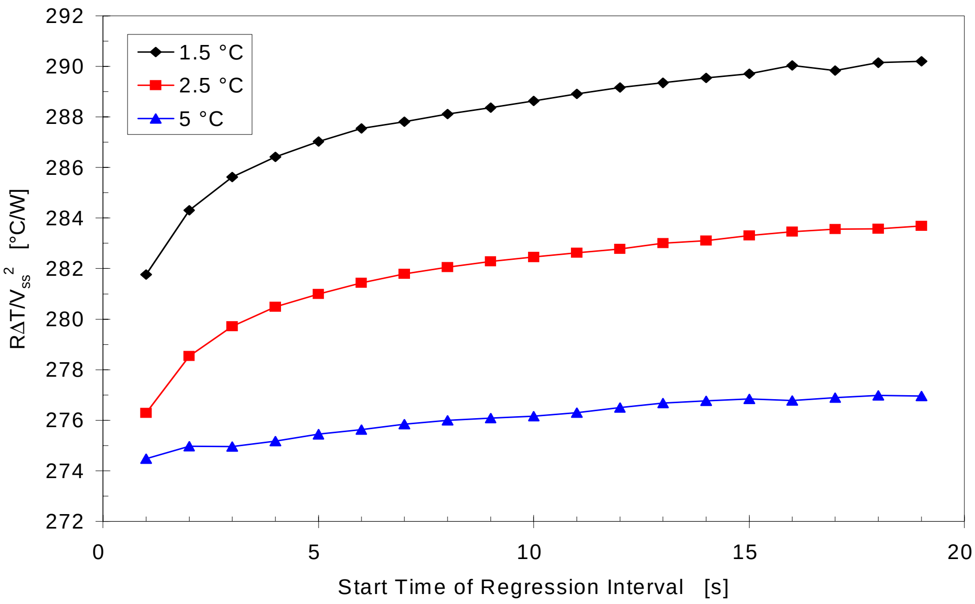

Figure 5.9 $R_f\Delta T/V_{ss}^2$ for the 150 cp solution and temperature steps of 1.5, 2.5 and 5 °C. Data originated from linear regression over a 10 second interval. They are the average of 2 samples.

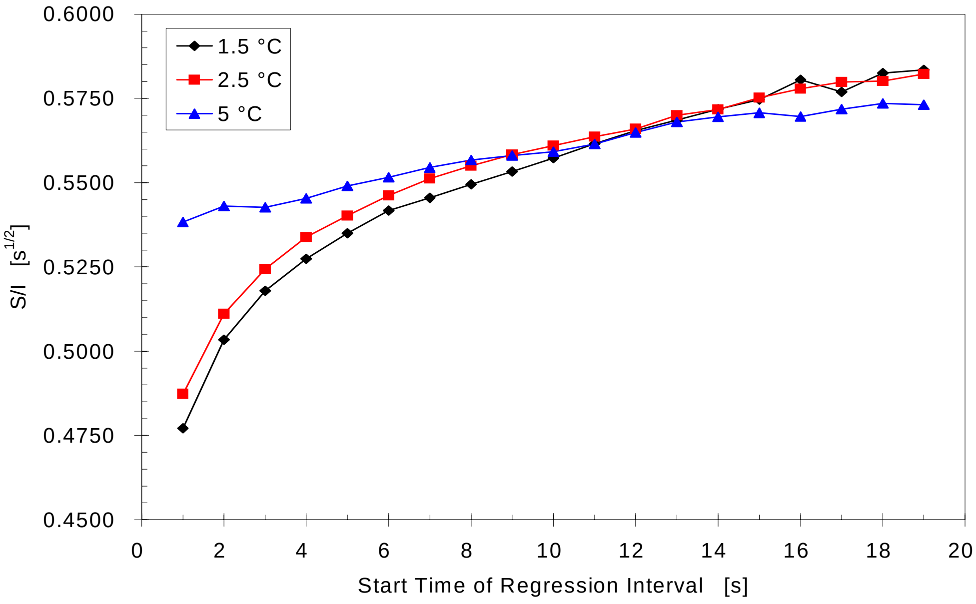

Figure 5.10 S/I for the 150 cp solution and temperature steps of 1.5, 2.5 and 5 °C. Data were obtained from linear regression over 10 second intervals, with an increment in its start time of 1 second. They are the average of two samples.

Figure 5.9 shows three lines that are almost equidistant from 4 seconds on. The lines for 1.5 and 5 °C are about 2% higher and lower respectively than the line for 2.5 °C. The differences between these lines was significant according to the multiple-comparison procedure, Tukey's W. This effect of the magnitude of the temperature step had not been reported by other researchers. Valvano (1981) measured the thermal conductivity and diffusivity of water with a temperature step ranging from 1 to 10 °C. He found no effect of the magnitude of the temperature step on the observed thermal properties. Reproducibility, however, increased with the magnitude of the temperature step. Dougherty (1984) found no difference in measured thermal conductivity when using either 2 or 3 °C as temperature step. Based on this study however, the probe should be used with the same temperature step as during calibration. If the probe had been calibrated at 1.5 °C, and used with a step of 5 °C, the thermal conductivity of water would be overestimated by about 10%. A probe calibrated at 2.5 °C can be used over the range 1.5 to 5 °C, with a temperature step induced error from about -4-5 to +4-5% in estimated thermal conductivity of water.

The estimation of thermal diffusivity did not display the same sensitivity to the size of the temperature step. Figure 5.10 shows how the lines - and thus the response of the thermistor - displayed very much the same trend for the temperature step of 1.5 and 2.5 °C and converge for longer times. The difference between the lines before convergence is only about 2%, but statistically significant, at the 5% level, up to a starting time of 10 seconds (an exception are the results for a starting time of 6 seconds). The line for the 5 °C temperature step doesn't follow a similar trend as the others, and seemed to cross them after about 12 seconds. From 10 seconds on, all temperature steps tested the same at the 5% level.

The 100 cp solution was basically convection free as well. As such it could be used to test the results of the 150 cp solution on representativeness. When the results for the 100 cp solution were added to Figures 5.9 and 5.10, they confirmed those of the 150 cp solution.

The cause of the observed effects was unknown. It could be either that model inaccurately predicted a linear relationship between the temperature step and the power dissipation in the probe, or that the observed differences were caused by the instrumentation. Either way, it appears advisable to use a probe with the same temperature step as in calibration. This research did confirm Valvano's conclusion that a higher value for the temperature step improved the reproducibility, as indicated by the lower values of msd for higher values of the temperature step (Table 5.8 and 5.9).

Table 5.12 Tukey's W grouping for 150 cp solution for the effect of the magnitude of the temperature step on the value of $R\Delta T/V_{ss}^2$ and S/I

Effect of Temperature Step on Value of $R\Delta T/V_{ss}^2$								Effect of Temperature Step on Value of S/I							
ST [s]	ΔT[1] [°C]			$R\Delta T/V_{ss}^2$ [°C/W]			msd [°C/W]	ST [s]	ΔT[1] [°C]			S/I [$s^{1/2}$]			msd [$s^{1/2}$]
1	1.5	2.5	5.0	281.8	276.3	274.5	0.92	1	5.0	2.5	1.5	0.5383	0.4873	0.4771	0.0080
2	1.5	2.5	5.0	284.3	278.5	275.0	0.50	2	5.0	2.5	1.5	0.5430	0.5111	0.5034	0.0032
3	1.5	2.5	5.0	285.6	279.7	275.0	0.52	3	5.0	2.5	1.5	0.5427	0.5244	0.5180	0.0032
4	1.5	2.5	5.0	286.4	280.5	275.2	0.58	4	5.0	2.5	1.5	0.5453	0.5339	0.5274	0.0032
5	1.5	2.5	5.0	287.0	281.0	275.5	0.56	5	5.0	2.5	1.5	0.5490	0.5402	0.5350	0.0038
6	1.5	2.5	5.0	287.5	281.4	275.6	0.65	6	5.0	2.5^A	1.5^A	0.5516	0.5462	0.5417	0.0046
7	1.5	2.5	5.0	287.8	281.8	275.8	0.60	7	5.0^A	2.5^A	1.5	0.5545	0.5512	0.5455	0.0042
8	1.5	2.5	5.0	288.1	282.1	276.0	0.56	8	5.0^A	2.5^A	1.5	0.5567	0.5550	0.5495	0.0038
9	1.5	2.5	5.0	288.4	282.3	276.1	0.61	9	2.5^A	5.0^A	1.5	0.5583	0.5581	0.5533	0.0042
10	1.5	2.5	5.0	288.6	282.5	276.2	0.60	10	2.5^A	5.0^A	1.5^A	0.5610	0.5592	0.5573	0.0046
12	1.5	2.5	5.0	289.2	282.8	276.5	0.62	12	2.5^A	1.5^A	5.0^A	0.5660	0.5655	0.5649	0.0063
15	1.5	2.5	5.0	289.7	283.3	276.8	0.84	15	2.5^A	1.5^A	5.0^A	0.5752	0.5747	0.5707	0.0110
18	1.5	2.5	5.0	290.1	283.6	277.0	1.06	18	1.5^A	2.5^A	5.0^A	0.5825	0.5802	0.5735	0.0150
19	1.5	2.5	5.0	290.2	283.7	277.0	0.87	19	1.5^A	2.5^A	5.0^A	0.5835	0.5823	0.5732	0.0113

[1] Values that are marked with the same letter are not different at 5% level (Tukey)

5.4.4 Rayleigh Number Correlation

Rayleigh numbers were calculated for the viscosity-temperature step combinations that appeared to exhibit natural convection. Figure 5.11 shows the Rayleigh numbers as function of time. An attempt was made to find a critical Rayleigh number above which convection would be likely. Table 5.11 was compared to Figure 5.11. The Rayleigh number corresponding to estimated onset time of convection was, in increasing order, 43 (5 cp and 5 °C), 45 (25 cp and 5 °C), 48 (5 cp and 2.5 °C), and 84 (5 cp and 1.5 °C). In light of the coarseness of the procedure with which the onset times were estimated, this range was considered to be narrow. It appears then, that when the simulated Rayleigh number remained under 43, convection had negligible effect.

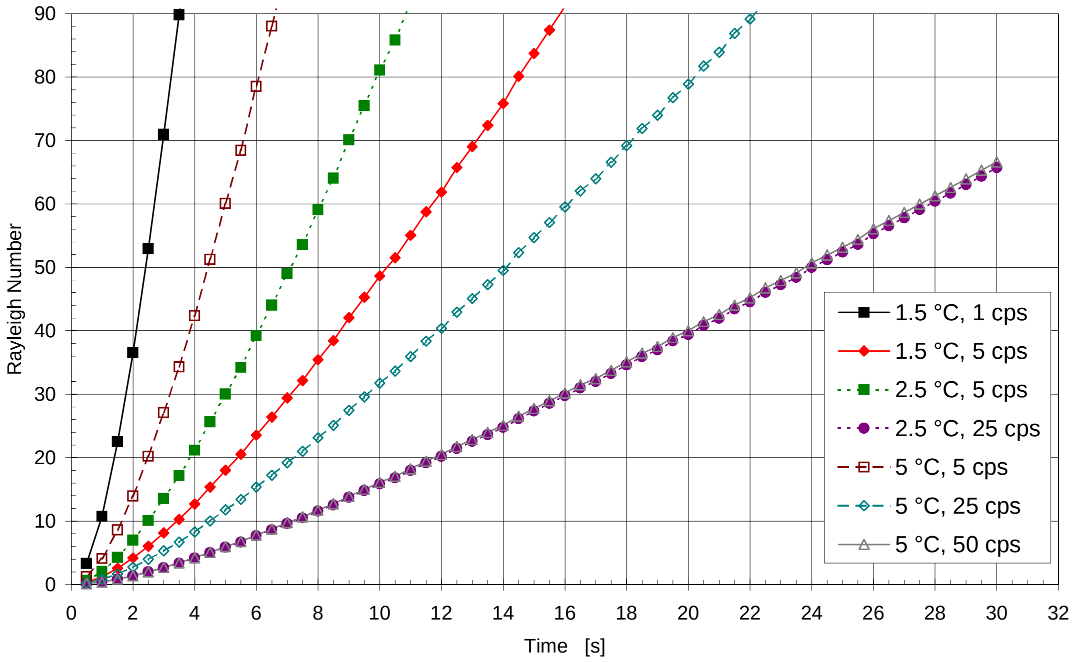

Figure 5.11 Simulated Rayleigh numbers for viscosity-ΔT combinations that appeared to exhibit signs of convection during measurement of thickened water of various viscosity.

5.4.5 Validation of Rayleigh Number Correlation

The Rayleigh number of 43, below which convection seemed unlikely, was derived from the experiments in thickened water, and for a specific probe. Data gathered with another probe in glycerol were scrutinized to investigate whether this Rayleigh number of 43 could be applied to a different probe and a different test medium. A sample of glycerol was measured over the range 100 to 150 °C in 10 °C increments, without any means of controlling convection in the sample. The power response in the sample was compared to that in two other samples of glycerol that were measured at the same temperatures, with the same probe and whereby convection was inhibited (or limited) with 'angel hair' (in concentrations small enough as to be considered of negligible impact on the thermal properties of interest). The onset time of convection in sample #1 was estimated from comparison to samples #2 and #3. Linear regression was performed over a two second wide interval with all the data files gathered. The starting time of the regression interval was incremented by 1 second until it reached the value of 27. The regression results were used in a t-test (Excel 97, Microsoft Corporation, Seattle, WA) with type 1 error of 0.05. A significant difference between the mean of sample #1 and that of samples #2 and #3 combined, was taken as indicative of convection in sample #1. Onset time for convection in sample #1 was estimated from the regression results. Table 5.13 contains the estimated onset times for the 6 temperatures at which the glycerol was tested.

Next the temperature distribution in the medium was simulated to find the Rayleigh numbers corresponding to the onset times of Table 5.13. The results for S/I were slightly more sensitive to convection. The estimates listed in that column were used. The relevant input parameters and their values for simulation of the Rayleigh number are given in Table 5.14. The probe parameters correspond to the regression interval 10-20 seconds. Rayleigh number calculations were done at temperatures from 100 to 150 °C.

Table 5.13 Estimated onset time of convection in Glycerol sample #1, measured with probe #H1.

	Estimated onset time of convection	
Temperature [°C]	on RΔT/V_{ss} [s]	on S/I [s]
100	12	10
110	9	8
120	8	7
130	7	6
140	6	5
150	5	4

Table 5.14 Parameter values for simulation of temperature profiles in Glycerol with program MEDTEMP.PAS

Parameter	Simulation Temperature, °C					
	100	110	120	130	140	150
k[1], W/m°C	0.2947	0.2960	0.2973	0.2986	0.2998	0.3011
α[2], $10^{-7} m^2/s$	0.908	0.909	0.911	0.915	0.920	0.927
ρ[3], kg/m^3	1207.6	1200.5	1193.3	1186.0	1178.5	1171.0
β[4]$\cdot 10^4$, 1/°C	5.85	5.97	6.09	6.21	6.33	6.46
μ[1], cp	15	10.8	8.1	6.2	4.8	3.8
a_1, mm	1.0687	1.0694	1.0778	1.1034	1.0991	1.1074
k_{b1}, W/m°C	0.07332	0.07507	0.07566	0.07715	0.07964	0.07968
a_2, mm	0.7609	0.7687	0.7718	0.7464	0.7661	0.7661
k_{b2}, W/m°C	0.11081	0.11093	0.11066	0.13936	0.13957	0.14820

[1] Adapted from CINDAS (1988).

[2] Calculated as $\alpha = k/\rho \cdot C_p$, α = thermal diffusivity, k = thermal conductivity, ρ = density, C_p = specific heat.

[3] Measured (Appendix A).

[4] Appendix A.

Figure 5.12 shows the Rayleigh numbers in glycerol at temperatures from 100 to 150 °C. Rayleigh numbers corresponding to the estimated onset times of Table 5.13, vary from a low of about 46 at 110 °C to a high of 55 at 140 °C.

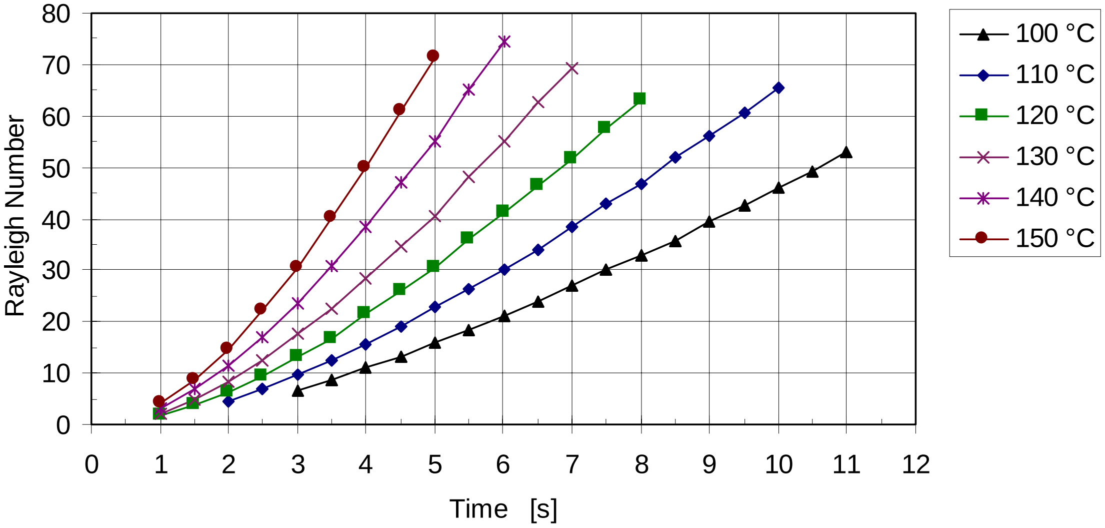

Figure 5.12 Simulated Rayleigh numbers for measurements in glycerol at temperatures from 100 to 150 °C, with a temperature step of 2.5 °C.

The Rayleigh numbers at the onset of convection in water varied from 43 to 82, those for the sample of glycerol between 45 and 55. Considering the coarseness with which the onset time of convection was estimated, this was considered a good result. A comparison of the numbers to literature is of limited value. The Rayleigh numbers of this study are dependent on the values of the input parameters. If for instance the penetration depth had been defined as 1/1000th of the surface temperature instead of 1/100th, much larger values of the critical Rayleigh number would have resulted. Using different probe parameters will give a different outcome. However when probes of the same series were used and their properties were taken from the same interval, the variation in Rayleigh numbers was small. The properties of four different probes were taken from the same regression interval. Rayleigh numbers were generated for each probe in glycerol at three temperatures. Rayleigh numbers for different probes were only 1 or 2% different. A larger effect was found when the properties of an extreme interval were used. That resulted in a 10-15% change in the simulated Rayleigh numbers. The net effect of that was a time shift of about 0.5-1 seconds before a Rayleigh number of 40 was reached (or 30, 50, 60). Whether the correlation can be used for a larger diameter probe is not sure. It is felt however, that similar values for the critical Rayleigh number will be found.

5.5 EVALUATION AT HIGH TEMPERATURE

5.5.1 Tomato Concentrate

The solids content of tomato concentrate was found from refractometry to be 86% for the tomato puree and 74% for the tomato paste. These values were used to compare the measured values for the thermal properties of this study to those calculated with the equations from Choi and Okos (1983).

The thermal properties of tomato concentrate were calculated from the results of linear regression. Based on the results for the calibration of probe #H3, a regression interval of 1-11 seconds was used for estimation of thermal conductivity. The interval for estimation of thermal diffusivity depended on the temperature as was discussed earlier in this Chapter ("5.2.2 High Temperature Probes"). At 100 °C, the interval 11-21 seconds was used, at 130 °C the interval 6-16 seconds, and at 150 °C the interval 3-13 seconds.

Thermal Conductivity and Thermal Diffusivity of Tomato Puree

The thermal conductivity and diffusivity of tomato puree are given in Tables 5.15 and 5.16. The table lists the average for each sample over the three measurements that were taken with each sample at each temperature. The coefficient of variation (COV) of the three measurements is included in the table. A low value is an indication of unchanged conditions during the test. A high value may suggest that the product was experiencing changes as a result of the high temperature cook, or that the instrumentation malfunctioned.

Table 5.15 Average thermal conductivity and coefficient of variation (COV) of tomato puree (solids content 14% w/w), at high temperature

	100 °C		130 °C		150 °C	
Sample Number	Thermal Conductivity [W/m°C]	COV [%]	Thermal Conductivity [W/m°C]	COV [%]	Thermal Conductivity [W/m°C]	COV [%]
1	0.6310	0.1	0.6476	0.6	0.6282	0.7
2	0.6293	0.3	0.6480	0.5	0.6455	1.5
3	0.6257	0.4	0.6409	0.7	0.6617	1.8
4	0.6256	0.4	0.6409	0.5	0.6623	0.6
Average	0.6279		0.6443		0.6494	
StdDev.	0.0027		0.0040		0.0162	
Choi and Okos (1983)	0.6176		0.6305		0.6335	
Difference, %	1.7		2.2		2.5	

The thermal conductivity is close to the values predicted by the equation for Choi and Okos. The measured values are 1.7, 2.2 and 2.5% higher than the literature values at 100, 130 °C and 150 °C respectively. The difference between the sample means at each temperature increased from about 1% at 100 °C to about 4% at 150 °C. This is reflected in the increasing value for the standard deviation.

Table 5.16 Average thermal diffusivity and coefficient of variation (COV) of tomato puree (solids content 14% w/w), at high temperature

	100 °C		130 °C		150 °C	
Sample Number	Thermal Diffusivity $[10^{-7}m^2/s]$	COV [%]	Thermal Diffusivity $[10^{-7}m^2/s]$	COV [%]	Thermal Diffusivity $[10^{-7}m^2/s]$	COV [%]
1	1.55	0.2	1.53	0.9	1.52	0.5
2	1.59	0.6	1.56	0.3	1.53	2.0
3	1.74	0.8	1.80	0.5	1.74	2.8
4	2.07	10.4	1.86	7.0	2.36	2.9
Average[1]	1.63		1.63		1.60	
StdDev.[1]	0.10		0.15		0.12	
Choi and Okos (1983)	1.52		1.58		1.60	
Difference, %	7.2		3.2		0.0	

[1] The average and standard deviation excludes sample #4.

The measurement of thermal diffusivity was less repeatable than that of thermal conductivity as shown by the standard deviation of the sample means. One sample (#4) was an outlier, and excluded from the average and standard deviation at each temperature. With this sample removed, the average values at each temperature compared favorably to the literature values. The thermal diffusivity in this study was 7.2 and 3.2% higher at 100 and 130 °C respectively. At 150 °C, the measured value and literature value were identical.

Thermal Conductivity and Thermal Diffusivity of Tomato Paste

A total of six samples were used in the tests. The main reason for exceeding the initially planned total of four were the poor results obtained with two of the samples. These two outliers were removed from the analysis. A cause for the poor results could have been the inclusion of air pockets near the probe. The remaining four samples gave acceptable results at 100 °C. At higher temperatures a few gave acceptable results, others not. Product changes due to prolonged heating at high temperatures were suspected as the cause for the large variability in the results. Some samples were re-tested at 100 °C following the tests at 150 °C to see if the heating had caused irreversible effects. Not surprisingly the results of these measurements differed greatly from the earlier tests at 100 °C. The apparent thermal conductivity of the samples had increased substantially. Inspection of the tested tomato paste samples showed that the paste had hardened to a brittle material. Some samples had a fracture near the location of the bead suggesting the existence of water air/gas pockets there (pressure buildup inside the chamber was noticed on several occasions).

The procedure had been to measure a given sample at 100 °C, then at 130 °C, and finally at 150 °C. The samples were thus subjected to prolonged heating. In an alternative approach, a few samples were tested by placing the room temperature samples in the bath at 150 °C. Doing so reduced the time during which the product was subjected to the high temperature to the 20 minutes required for thermal equilibration. This approach however did not improve the measurements.

The thermal conductivity and diffusivity of tomato paste is given in Tables 5.17 and 5.18. At 100 and 130 °C, the thermal conductivity compared well against the literature data. At 100 °C, a mean value of 0.5828 W/m°C was measured, which was only 3.3% higher than that calculated with the equation from Choi and Okos. The mean value of 0.5942 at 130 °C was only 1.8% higher than the literature value. The coefficient of variation (COV) for the samples and the standard deviation of the sample means at 100 and 130 °C were also good. The overall mean at 150 °C, 0.5457 W/m°C, was 7.8% lower than that found from the equation of Choi and Okos. The sample means at this temperature showed a large variation. Samples #2 and #3 had a low apparent thermal conductivity. Sample #4, on the other hand had a high thermal conductivity. The low values for samples #2 and #3 may have been caused by changes of the paste (hardening) which led to a localized drop in moisture content. The fairly high value of sample #4 could have been caused by similar effects but with the formation of a water filled cavity near the thermistor.

Table 5.17 Average thermal conductivity and coefficient of variation (COV) of tomato paste (solids content 26% w/w), at high temperature

	100 °C		130 °C		150 °C	
Sample Number	Thermal Conductivity [W/m°C]	COV [%]	Thermal Conductivity [W/m°C]	COV [%]	Thermal Conductivity [W/m°C]	COV [%]
1	0.5817	0.4	0.5909	0.7	0.5820	1.6
2	0.5826	0.5	0.5646	0.3	0.4166	0.3
3	0.5835	0.1	0.6097	0.1	0.4987	1.3
6	0.5836	0.4	0.6114	0.7	0.6856	0.5
Average	0.5828		0.5942		0.5457	
StdDev.	0.0009		0.0218		0.1151	
Choi and Okos (1983)	0.5643		0.5836		0.5920	
Difference, %	3.3		1.8		-7.8	

Table 5.18 Average thermal diffusivity and coefficient of variation (COV) of tomato paste (solids content 26% w/w), at high temperature

	100 °C		130 °C		150 °C	
Sample Number	Thermal Diffusivity [$10^{-7}m^2/s$]	COV [%]	Thermal Diffusivity [$10^{-7}m^2/s$]	COV [%]	Thermal Diffusivity [$10^{-7}m^2/s$]	COV [%]
1	1.67	2.3	1.69	1.7	1.75	2.6
2	1.71	1.5	2.17	1.7	2.51	7.5
3	1.55	0.3	1.75	2.4	2.47	3.3
6	1.59	1.4	1.79	1.1	3.95	17.0
Average	1.64		1.85		2.67	
StdDev.	0.08		0.22		0.92	
Choi and Okos (1983)	1.38		1.46		1.50	
Difference, %	18.8		26.7		78.0	

The thermal diffusivity of tomato paste was very different from the literature data. At 100 °C, the measured data exceeded the literature value by 18.8%. At 130 and 150 °C the difference with the literature data was 26.7 and 78% respectively. Heating induced changes in the tomato paste were the cause of the large discrepancies between the measured values and the literature data. These changes were mentioned earlier. The effect of these changes on the measurement of thermal diffusivity were much more pronounced than on the measurement of thermal conductivity because of the way by which each property is calculated (Chapter 3).

Conclusion

The measurements of tomato puree gave better results than the measurements of tomato paste. The higher moisture content of puree probably prevented formation of the hard lumps that were noticed in the tomato paste samples upon examination after the measurements. The puree thus remained more homogeneous. The measurement of thermal properties of the tomato paste might have been more successful if the paste could have been heated faster. The measurement of thermal diffusivity was more sensitive to (suspected) product variations and other sources of variation (like noise) than the measurement of thermal conductivity.

5.5.2 Nutritional Supplement

Problems with the thermistor probes were encountered during the measurements. About halfway into the research with the nutritional supplement, the calibrated probe (#TT2) suffered catastrophic failure. No other calibrated probe was available. Time constraints, dictated by the limited shelf life of the products, prohibited calibrating another probe. An uncalibrated probe (#TT5) was used, with the intention to calibrate it after all the tests were done. Unfortunately, this probe failed before it could be calibrated.

The properties of the uncalibrated probe at 150 °C were estimated using the results of the two products that were measured with both the calibrated and uncalibrated probe ("TC3", 40% solids, and "TC4", 30% solids). Property values of previously used probes were tried for the uncalibrated probe. Those that yielded thermal conductivity values that best matched those found with the calibrated probe were used to calculate the thermal conductivity at 150 °C for all the samples that were measured with the uncalibrated probe. The closest match was found with the properties of probe #H3. The probe whose calibrated properties at 150 °C were substituted for those of the uncalibrated probe, also supplied the probe properties for the uncalibrated probe at 95 °C. These properties were however obtained through calibration at 100 °C.

Thermal conductivity values for the fluid nutritional supplement as related to solids content and temperature are given in Table 5.23. Reference values for water are given for comparative purposes. The thermal conductivity of moist foods is strongly influenced by their water content. Data gathered with the uncalibrated probe are indicated with a superscript. Because of the assumed probe properties for the uncalibrated probe, the thermal conductivity values obtained with it are less reliable than those found with the calibrated probe.

For the nutritional supplement, no published thermal property data were available. The accuracy of the values obtained thus can not be directly assessed. The values appear to be reasonable. They follow an expected trend with respect to the effect of the solids content. An increase in solids content appears to decrease the thermal conductivity of the products. This finding is consistent with the commonly found positive relationship between thermal conductivity and moisture content (Sweat, 1986). The replication is excellent (within 1%) for the measurements at 95 °C at all solids levels and for those at 150 °C at solids levels of 25% and below. The replication at 150 °C for the higher solids levels is worse than those at lower solid levels and temperature. This is probably due to heat induced changes in the product which are more pronounced at higher solids levels. A similar effect was observed with tomato concentrate. Tomato paste yielded less accurate data (as compared to the literature data) and displayed worse replication than tomato puree.

Table 5.19 Thermal Conductivity of "TC1", "TC2", "TC3" and "TC4" at High Temperatures, [W/m°C]

	TC1		TC2		TC3		TC4	
Solids content [% wb]	95 °C	150 °C	95 °C	150 °C	95 °C	150 °C	95 °C	150 °C
15		0.6216		0.6152				0.6034
		0.6170						0.6031
25						0.5594		
						0.5575		
30		0.5527	0.5520	0.5501			0.4955	0.5230
								0.5194[b]
35				0.5342				
40	0.4864[a]	0.5047[b]	0.5048	0.5092		0.4575	0.4549[a]	0.4625[b]
	0.4856[a]	0.4912[b]				0.4663[b]	0.4534[a]	
50					0.4132[a]	0.4330[b]		
					0.4116[a]	0.4204[b]		
water, literature value	0.6762	0.6820	0.6762	0.6820	0.6762	0.6820	0.6762	0.6820

a) Measured with probe #TT5, properties taken from probe #H3 at 100 °C.
b) Measured with probe #TT5, properties taken from probe #H3 at 150 °C.

5.5.3 Conclusions of High Temperature Measurements

The thermistor based method was found to be suitable for the measurement of thermal conductivity and thermal diffusivity of tomato concentrate and of the nutritional supplement at temperatures up to 150 °C. For the most part, the measurement data for tomato concentrate agreed well with the published values. For those data, predominantly at 150 °C, were this was not the case, the cause of disagreement was more likely related to heating induced changes in the product, than to problems with the thermistor based method itself. The nutritional supplement was measured with good replication. Measured values for thermal conductivity followed the expected trend with moisture content.

CHAPTER 6

REMARKS ON CALIBRATION

The calibrated probe properties at high temperature, discussed in the previous Chapter ("5.2.2 High Temperature Probes"), depend on the part of the data (regression interval) that was used for estimating the properties. The estimation errors of the calibration media also varied with the regression interval. The dependency of these estimation errors on the regression interval led to the selection of a certain intervals for the evaluation of thermal properties in subsequent measurements of tomato concentrate and the nutritional supplement. These intervals, dubbed optimal intervals, were selected based on the low estimation errors obtained in the calibration. The optimal interval for the estimation of thermal conductivity was different from the optimal interval for estimation of thermal diffusivity. Also, the optimal interval for estimation of thermal diffusivity was different for the each of the six temperatures of calibration. An evaluation interval that depends on the property of interest and on the temperature is impractical. It was of interest to investigate the cause of the observed dependency of estimation errors on the regression interval. A more practical calibration procedure might follow out of that investigation.

The response characteristics of the thermistor in the three calibration media was analyzed. A plot of the voltage response for different media doesn't show the differences very well. The derived properties $R\Delta T/V_{ss}^2$ and S/I much better illustrate the differences between the media. Figures 6.1 and 6.2 show the values for these terms for the three calibration media. They were used in estimating the probe properties of probe #H3 at 100 °C. Figures 6.3 and 6.4 present these data in a different format. The values for each interval are compared to those for the interval 10-20 seconds.

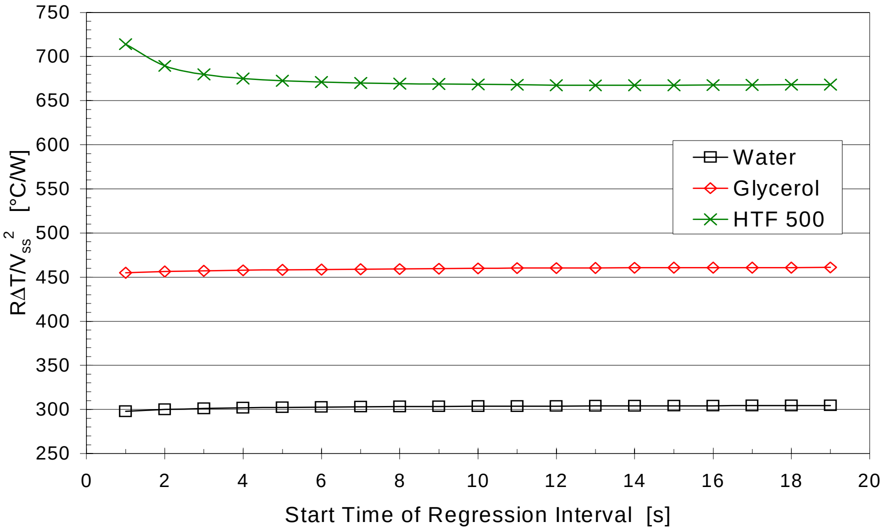

Figure 6.1 Value of $R\Delta T/V_{ss}^{2}$ for Probe #H3 at 100 °C for the three calibration materials and a regression interval of 10 seconds. The average of three samples is shown.

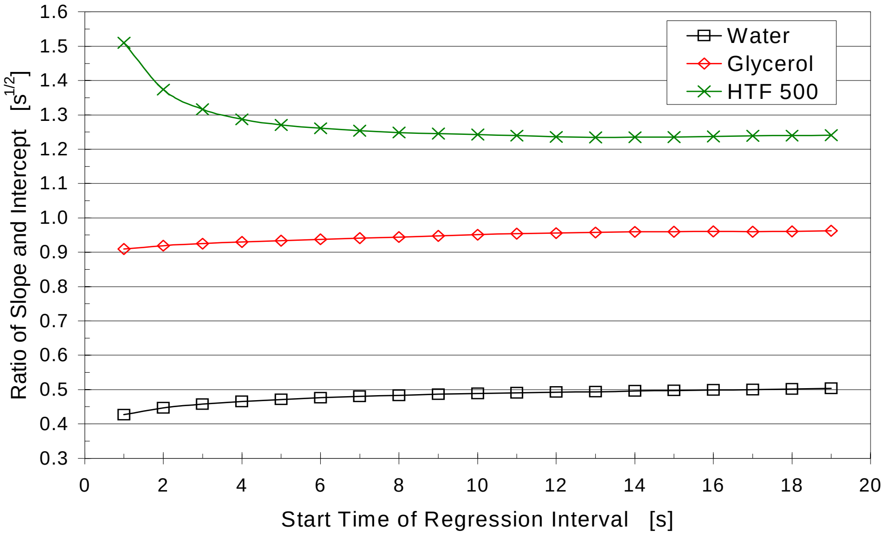

Figure 6.2 Ratio of Slope and Intercept, S/I, for Probe #H3 at 100 °C for the three calibration materials and a regression interval of 10 seconds. The average of three samples is shown.

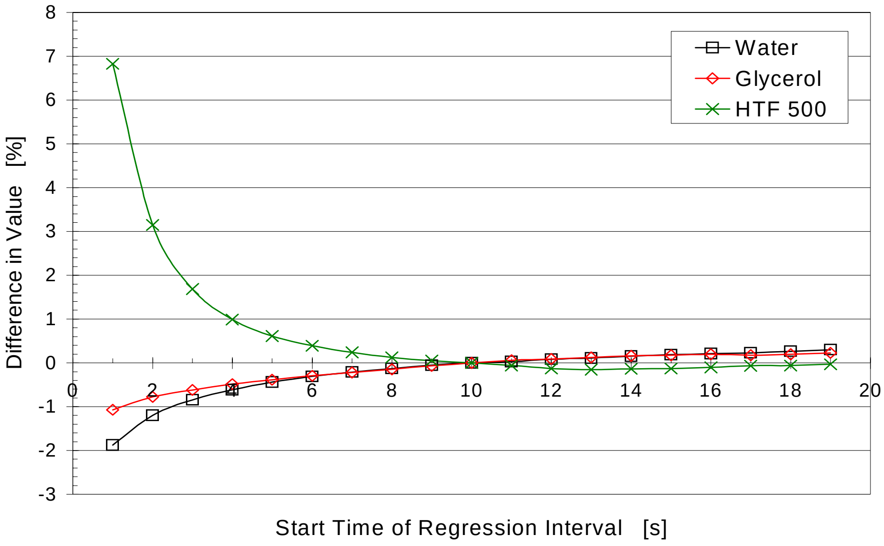

Figure 6.3 Difference in the value of $R\Delta T/V_{ss}^2$ from its value at ST = 10 seconds at 100 °C for the three calibration materials. The average of three samples is shown.

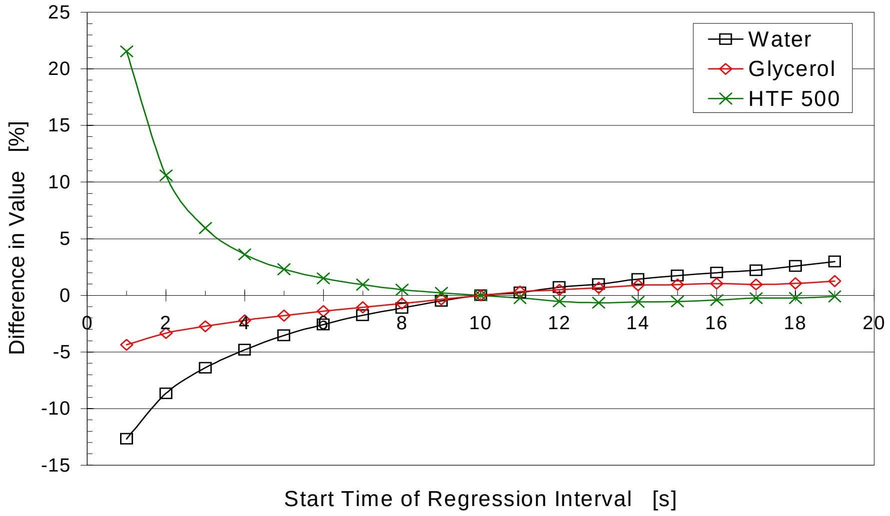

Figure 6.4 Difference in the value of S/I from its value at ST = 10 seconds at 100 °C for the three calibration materials. The average of three samples is shown.

Some conclusions can be drawn from these figures. According to the model, the power dissipation in the probe should be linear in the inverse square root of time. In that case, the linear regression results should have been independent of the regression interval; the lines in Figures 6.1 through 6.4 should have been horizontal, with those of Figures 6.3 and 6.4 coinciding with the x-axes. The deviation from the model is most noticeable for early intervals. At later times, the response in all fluids appeared to follow the model more closely. The values of S/I showed a larger relative change with successive regression intervals than the values of $R\Delta T/V_{ss}^2$. The response in the low thermal conductivity fluid, HTF 500, is fundamentally different from that in either of the two fluids with a higher thermal conductivity. The cause of this was not clear. The practical implication is that the calibration of a probe for use with moist food materials might be better done with water and glycerol only. The thermal properties of moist foods generally fall between those of water and glycerol.

Tomato puree was measured in a study discussed earlier. The data from one sample were used to compare the calibration of a probe (#H3) with water and glycerol only, to one where HTF 500 was added as calibration material. Figures 6.5 to 6.8 show the apparent thermal properties of tomato puree at 100 °C. The probe (#H3) was calibrated with water and glycerol (Figures 6.5 and 6.6) or with water, glycerol and HTF 500 (Figures 6.7 and 6.8). Markers indicating a plus or minus 1% deviation from the graphed values are shown in the figures to aid in the interpretation.

Figures 6.5 and 6.6 clearly show that the response of the thermistor in the tomato puree sample was quite similar to that in water or glycerol. The measured value of thermal conductivity is virtually independent of the interval used to calculate the value. The thermal diffusivity shows more variation with interval, but the variation is very small up to the interval 18-28 seconds.

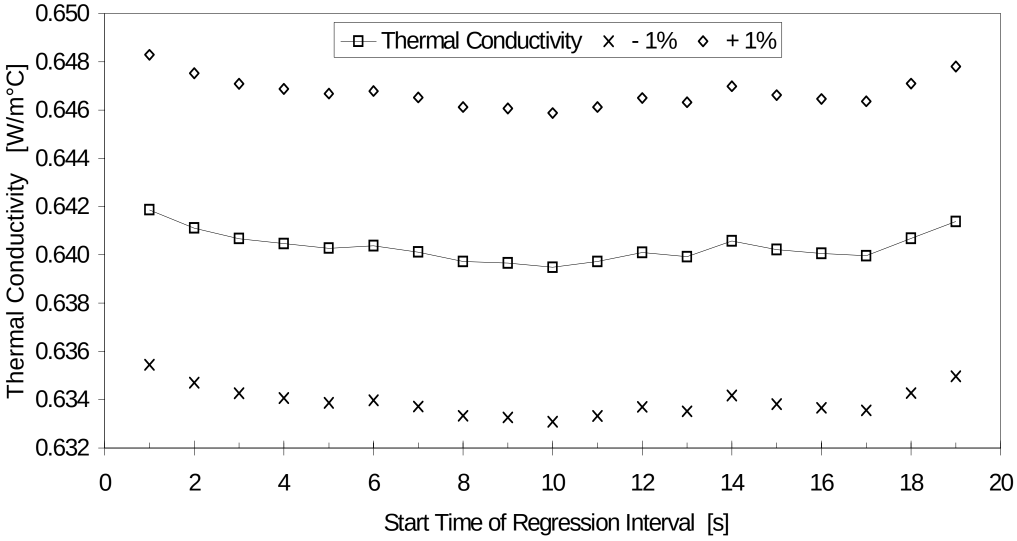

Figure 6.5 Thermal Conductivity of Tomato Puree at 100 °C, measured with a probe (#H3) that was calibrated with water and glycerol.

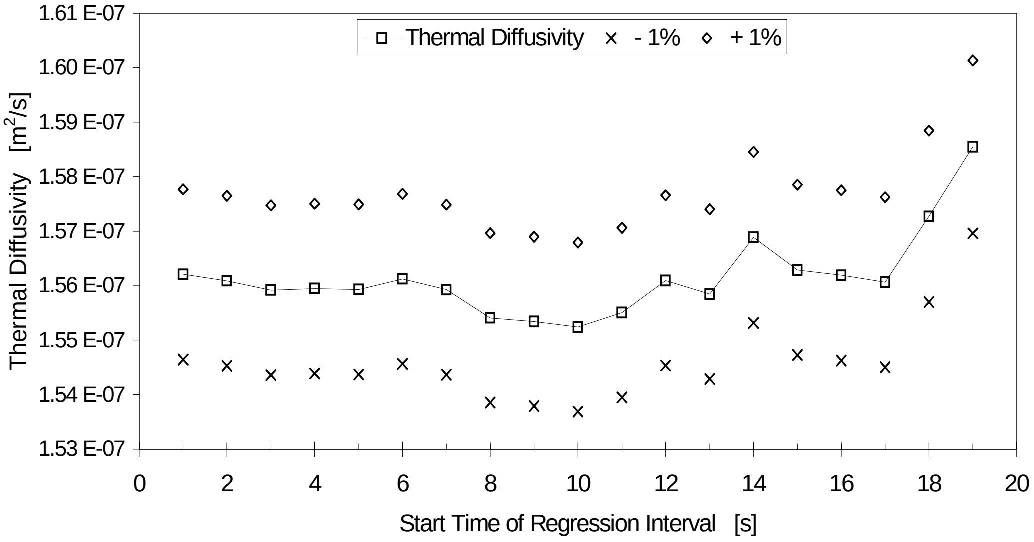

Figure 6.6 Thermal Diffusivity of Tomato Puree at 100 °C, measured with a probe (#H3) that was calibrated with water and glycerol.

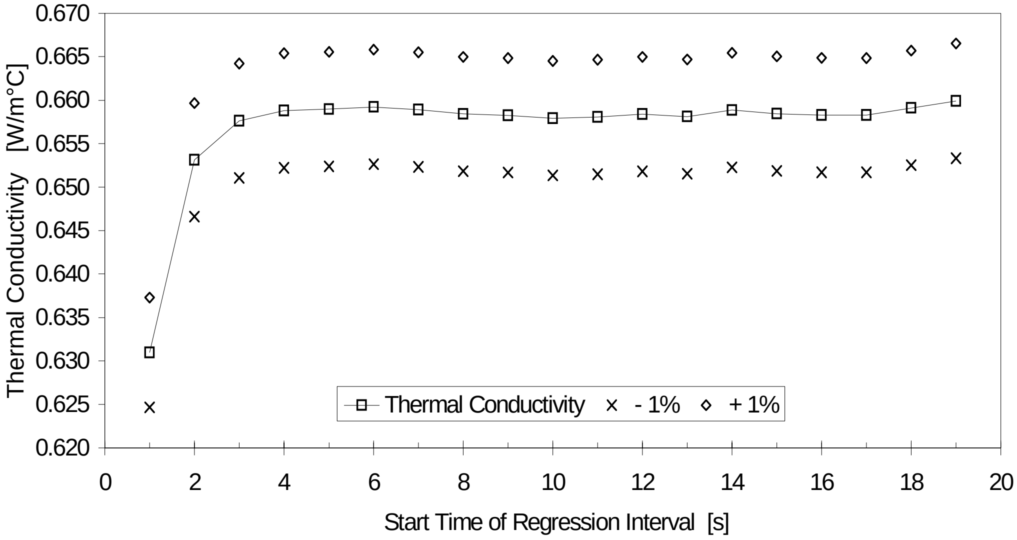

Figure 6.7 Thermal Conductivity of Tomato Puree at 100 °C, measured with a probe (#H3) that was calibrated with water, glycerol and HTF 500.

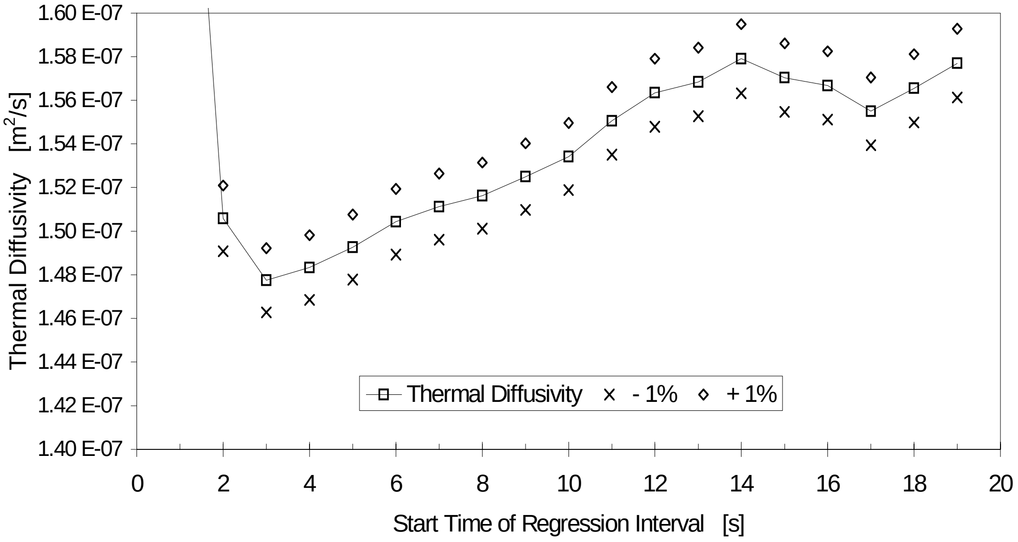

Figure 6.8 Thermal Diffusivity of Tomato Puree at 100 °C, measured with a probe (#H3) that was calibrated with water, glycerol, and HTF 500.

Figures 6.7 and 6.8 demonstrate the effect of adding HTF 500 as calibration material. The line in Figure 6.7 resembles that of the estimation errors for water that were shown in Figure 5.1. Except for the first two intervals, the calculated properties are only mildly dependent on interval, and probably overestimated the actual values. The thermal conductivity of the tomato puree sample found with the three-media calibration was about 3% higher than found with the two-media calibration (excluding the values for starting times 1 and 2 seconds). The value for thermal diffusivity was dependent on the interval from which it was obtained. As was the case for the thermal conductivity, the graph resembles that shown for the estimation errors for water (Figure 5.2). This reflects the high water content of tomato puree, approximately 86%. The difference between the low value, at a starting time of 3 seconds, and the high value, at a starting time of 14 seconds, was 6.9%. Figure 5.2 suggested the use of an interval with a starting time in the range 10 to 19 seconds (this reduced all estimation errors to below 2%). Doing so yielded thermal diffusivity values in the range 1.53 to 1.58 [$10^{-7}m^2/s$]. In comparison, the two-media calibration yielded values in the range 1.55 to 1.58 [$10^{-7}m^2/s$] (excluding the value for the last interval).

When the thermal properties of a tomato puree sample at 130 °C were calculated, similar results were obtained as in Figures like 6.5 to 6.8. Again, the two media calibration showed hardly any (estimation of thermal conductivity) to some (estimation of thermal diffusivity) variation with the interval used for calculation. Estimation of thermal diffusivity with the three-media calibration displayed a stronger relationship with regression interval than at 100 °C.

These findings suggest that a two media calibration with water and glycerol will give better results when the thermistor probe is calibrated for thermal property measurements of moist foods. With a two media calibration there was no need to pick an optimal regression interval for each different temperature, as was the case with the three media calibration.

The accuracy with which the calibrated probe can determine the properties of a medium is related to the accuracy of the data for the reference materials. The properties of water are well documented. Those of glycerol were probably somewhat less accurate. The data for the third material, HTF 500, were supplied by the manufacturer. The manufacturer could not give the accuracy of the thermal property data. With the accuracy of the properties of HTF 500 uncertain, this too might suggest that the use of this material should be limited to the calibration of a probe for low thermal conductivity applications.

An independent means of evaluating the accuracy of the probe for thermal property measurement is to measure the properties of a material with well documented properties. There were very few materials available for the evaluation. Ethylene glycol and dimethyl phthalate were chosen. The thermal conductivity of dimethyl phthalate was taken from literature (Marsh, 1987). The thermal diffusivity was calculated from the thermal conductivity, the density and the specific heat. The last two properties were measured (Appendix A and C). The thermal conductivity and specific heat for ethylene glycol were taken from literature (CINDAS, 1988). The data covered temperatures from room temperature to beyond 150 °C. Density data were found only up to 100 °C (Incropera, 1985). Measurement of thermal diffusivity could thus only be evaluated at that temperature.

One sample of dimethyl phthalate and one sample of ethylene glycol were measured at 100, 130 and 150 °C. Convection in the samples was restricted with fiber glass pipe insulation in a 1.5% (w/w) concentration. Thermal properties were calculated and compared to the reference data. Comparison was performed for results obtained with the three possible two-media calibrations and the three-media calibration. The results are presented in Table 6.1 for ethylene glycol and in Table 6.2 for dimethyl phthalate. Calibration of the probe with three media used the interval 1-11 seconds for estimation of thermal conductivity at each temperature, and for the estimation of thermal diffusivity the intervals 11-21 seconds, 6-16 seconds, 3-13 seconds at 100, 130 and 150 °C respectively. These intervals appeared to yield optimal estimation errors for the calibration media. For the two-media calibration, the interval 7-17 seconds was used. The choice was somewhat arbitrary. Calculation of the thermal properties used the same interval as used to calibrate the probe.

Table 6.1 Thermal Properties of Ethylene Glycol at 100, 130 and 150 °C, measured with probe #H3.

Thermal Conductivity					
Temperature [°C]	Literature[1] [W/m°C]	WGH [W/m°C]	WG [W/m°C]	WH [W/m°C]	GH [W/m°C]
100	0.2555	0.2640	0.2659	0.2509	0.2615
		3.3[3]	4.1	-1.8	2.
130	0.2560	0.2649	0.2646	0.2496	0.2625
		3.5	3.4	-2.5	2.
150	0.2550	0.2639	0.2675	0.2472	0.2610
		3.5	4.9	-3.1	2.

Thermal Diffusivity					
Temperature [°C]	Literature[2] [m^2/s]	WGH [$10^{-8}m^2/s$]	WG [$10^{-8}m^2/s$]	WH [$10^{-8}m^2/s$]	GH [$10^{-8}m^2/s$]
100	8.67	9.04	8.89	9.14	8.90
		4.3	2.5	5.4	2.
130	not available	8.95	8.76	8.77	8.76
150	not available	8.93	8.92	8.54	8.79

[1] CINDAS (1988)

[2] Calculated as $\alpha = k/\rho \cdot C_p$

[3] The values in italics give the difference from the literature value in %.

WGH	Calibration with Water, Glycerol and HTF 500; estimation interval for thermal conductivity at each temperature: 1-11 seconds; estimation interval for thermal diffusivity: 11-21 seconds at 100 °C, 6-16 seconds at 130 °C, and 3-13 seconds at 150 °C.
WG	Calibration with Water and Glycerol; estimation interval 7-17 seconds.
WH	Calibration with Water and HTF 500; id.
GH	Calibration with Glycerol and HTF 500; id.

Thermal conductivity of ethylene glycol was most accurately estimated from the calibration with glycerol and HTF 500. The difference from the literature data was 2.3% at 100 °C, 2.5% at 130 °C, and 2.4% at 150 °C. Compared to the other calibrations, the estimated value also changed the least if another interval was used for evaluation of the thermal properties. Regardless of interval (in the range 3-13 to 19-29 seconds), the calculated value deviated by no more than 0.3% from the value for the interval 7-17 seconds (the value shown in Table 6.1 . Since the thermal conductivity of ethylene glycol fell between those of glycerol and HTF 500, it was expected that the calibration with these two media would give the best estimation. The other calibrations gave acceptable results. The largest deviation was 4.9% for the water-glycerol calibration at 150 °C. In terms of amount of variation in estimated thermal conductivity with regression interval, the water-glycerol calibration was second to the glycerol-HTF 500 calibration, followed by the three media calibration and the water-HTF 500 calibration.

The thermal diffusivity of ethylene glycol at 100 °C was more accurately estimated with the water-glycerol calibration (accurate to 2.5%) than with the glycerol-HTF 500 calibration (accurate to 2.7%). The latter however showed a little less variation with regression interval. The maximum inaccuracy was 5.4%, for the water-HTF 500 calibration. This calibration also had the strongest dependence on regression interval.

Table 6.2 Thermal Properties of Dimethyl Phthalate at 100, 130 and 150 °C, measured with probe #H3.

Thermal Conductivity

Temperature [°C]	Literature[1] [W/m°C]	WGH [W/m°C]	WG [W/m°C]	WH [W/m°C]	GH [W/m°C]
100	0.1373	0.1373	0.1506	0.1399	0.1390
		0.0[3]	*9.7*	*1.9*	*1.2*
130	0.1326	0.1338	0.1494	0.1365	0.1355
		0.9	*12.7*	*2.9*	*2.2*
150	0.1293	0.1307	0.1477	0.1336	0.1326
		1.1	*14.2*	*3.3*	*2.6*

Thermal Diffusivity

Temperature [°C]	Literature[2] $[m^2/s]$	WGH $[10^{-8}m^2/s]$	WG $[10^{-8}m^2/s]$	WH $[10^{-8}m^2/s]$	GH $[10^{-8}m^2/s]$
100	6.98	6.67	6.40	6.60	6.62
		-4.4	*-8.3*	*-5.4*	*-5.2*
130	6.68	6.71	6.77	6.60	6.58
		0.4	*1.3*	*-1.2*	*-1.5*
150	6.47	6.44	7.16	6.49	6.45
		-0.5	*10.7*	*0.3*	*-0.3*

[1] CINDAS (1988)

[2] Calculated as $\alpha = k/\rho \cdot C_p$

[3] The values in italics give the difference from the literature value in %.

WGH Calibration with Water, Glycerol and HTF 500; estimation interval for thermal conductivity at each temperature: 1-11 seconds; estimation interval for thermal diffusivity: 11-21 seconds at 100 °C, 6-16 seconds at 130 °C, and 3-13 seconds at 150 °C.

WG Calibration with Water and Glycerol; estimation interval 7-17 seconds.

WH Calibration with Water and HTF 500; id.

GH Calibration with Glycerol and HTF 500; id.

The thermal properties of dimethyl phthalate fell outside the range for which the probe was calibrated. The calibration material with the most similar thermal conductivity and diffusivity was HTF 500. It was therefore expected that a calibration that used that material would yield a more accurate estimate of the thermal properties of dimethyl phthalate, than the calibration with only water and glycerol. Indeed the water-glycerol calibration gave the most inaccurate results. The three media calibration gave the most accurate estimation of thermal conductivity and diffusivity of dimethyl phthalate. The largest difference between the measured values for thermal conductivity and the literature values was 1.1%, at 150 °C. For thermal diffusivity, the worst estimation was at 100 °C (-4.4%). At 130 and 150 °C, the difference from the literature was 0.4 and -0.5% respectively. The water-HTF 500 and glycerol-HTF 500 calibration gave good results. The measured values for thermal conductivity and the literature values were at most 3.3% different. The inaccuracy in thermal diffusivity was the largest at 100 °C (5.4% maximally) and within 1.6% at 130 and 150 °C. The variation in measured values with regression interval was small for the two-media calibrations that used HTF 500 as one of the calibration values. Calculation of thermal conductivity from a different interval than 7-17 seconds (in the range 3-13 to 19-29 seconds) gave values that were at most 0.6% (100 and 130 °C) or 1% (150 °C) different from the tabulated values. The estimation of thermal diffusivity was more sensitive to the choice of regression interval, in particular at 150 °C. The apparent thermal properties increased as later intervals were used. This could have been caused by convection. Convection will increase the apparent thermal properties of the medium. The amount of convection a the lower temperatures seemed limited as the apparent thermal diffusivity increased only little with later intervals.

Conclusions

Since only one sample of ethylene glycol and dimethyl phthalate was used to evaluate the different calibrations, conclusions have to be drawn with caution. The three-media calibration gave good results for both ethylene glycol and dimethyl phthalate. Those good results were obtained by using specific intervals for the evaluation of the properties. The use of measurement data outside these intervals could result in significant inaccuracies in the measured values.

The accuracy obtained with the two-media calibration was comparable to that for the three-media calibration, provided the properties of the test material fell between those of the calibration materials or were at least close to those of one of them. The advantage over the three-media calibration was the low sensitivity of the measured property values to the choice of regression interval. The results for ethylene glycol suggests that a two-media calibration over a small thermal conductivity range around the test material gives the best results.

CHAPTER 7

SUMMARY AND CONCLUSIONS

The thermistor based method was investigated for its suitability to measure the thermal conductivity and diffusivity of moist food materials at high temperatures. The following summarizes the conclusions of this research. The conclusions are used to outline a recommended calibration procedure for the thermistor.

- Calibration of the thermistor with three standards, water, glycerol and HTF 500, gave good results provided the optimal interval of 1-11 seconds was used for estimation of thermal conductivity. The optimal interval for estimation of thermal diffusivity depended on the temperature at which the probe was calibrated. The use of an interval other than the optimal interval would result in marked loss of accuracy. The magnitude of this loss increased as the temperature increased from 100 to 150 °C.

- Thermal contact between the thermistor and both potato and beef was found to be adequate for the measurements at temperatures of 25, 50 and 100 °C. A comparison of the bead thermistor probe to a reference method, the line heat source probe, showed good agreement between both methods, except for potato at 100 °C. The latter was attributed to problematic measurements with the line heat source probe. Visual examination of the samples after the tests showed evidence of good contact between the thermistor and the potato and beef samples.

- Natural convection occurred in samples of thickened water during the sample interval of 30 seconds. Statistical analysis of measurements in samples of thickened water demonstrated convection in samples with a viscosity of 5 cp and less, when measured with a temperature step of 1.5 and 2.5 °C, and in samples with a viscosity of 25 cp and less, when measured with a temperature step of 5 °C. A Rayleigh number was defined and its value at the onset of convection was numerically evaluated. For the four samples that experienced convection, the Rayleigh number at the onset fell in the range 43 to 84. For samples of glycerol, measured with a different probe, similar values for the Rayleigh number were found at the onset of convection. Although extrapolation to probes of slightly different size and to different test media is debatable, it is felt that onset for those conditions will be characterized by a Rayleigh number of similar values as found in this research.

- The size of the temperature step had an effect on the outcome of a thermal property measurement. The use of a different size temperature step then used during calibration led to a marked loss of accuracy.

- The high temperature thermal property measurement of tomato puree gave better results than that of tomato paste. Product alterations and noticeable inhomogeneity were noticed in the tomato paste samples after the measurements. The tomato puree experienced less product alterations and remained almost homogeneous. The measurement of thermal properties of tomato paste might have been more successful if the paste could have been heated faster. The measurement of thermal diffusivity was more sensitive to (suspected) product variations and other sources of variation (like noise) than the measurement of thermal conductivity.

- For the nutritional supplement at high temperature, the thermistor measured a decreased thermal conductivity with increasing solids content. The data from the thermistor thus followed the expected trend with respect to the effect of the solids content. The replication was good for the measurements at 95 °C at all solids levels and for those at 150 °C at solids levels of 25% and below. The replication at 150 °C for the higher solids levels was worse than those at lower solid levels and temperature. This was probably due to heat induced changes in the product which are more pronounced at higher solids levels.

- The construction of a durable seal around the glass stem of the thermistor remained unresolved at the end of this research. The epoxy, that was used initially, could not withstand the repeated exposure to the test media at high temperatures. The final design that used a rubber gasket to provide the seal led to loss of thermistors as well.

- The power response of the thermistor probe deviated from the model function in a way that was related to the fluid thermal properties. The response in materials with a thermal conductivity below 0.2 W/m°C had a different character than that in materials with a thermal conductivity of 0.26 W/m°C and higher.

- Estimation of the thermal properties of a test medium was best accomplished when the probe was calibrated with two thermal standards whose properties were close to that of the test medium. The estimation deteriorated when the thermal properties of the standards were more divergent from that of the test medium, or when three standards were used. A calibration with two media did not show the sensitivity to regression interval that the three media calibration did.

Recommended procedure for thermal property measurement with the thermistor probe.

1. Calibrate the probe with two materials whose thermal conductivity and diffusivity are accurately known, and bracket the range of intended application.
2. The interval used for evaluation of the probe properties has to be used for the evaluation of the thermal properties of a test medium. When calibrating to measure the properties of a low viscosity medium in which convection is likely to occur, standardization on a early interval is the preferred approach. If adequacy of thermal contact is of concern, as can be with a solid test material, a later and possibly longer interval is preferred.
3. It is recommended to use the thermistor probe with the same size temperature step as used during its calibration.

4. One measurement per sample should suffice in most cases. Multiple measurements can be done to either average over random instrument error or check for the stability of the test conditions.
5. Perform the linear regression with successive intervals. Evaluate the power response of the thermistor from the regression results for the successive intervals. The trend in the results should be similar to that for the calibration materials. A strong upward trend in the intercept is indicative of convection. A waving plot may indicate inadequate surface contact and/or inhomogeneity.

RECOMMENDATIONS

The following recommendations were formulated based on the research of this study.

- An alternative to the glass probes of this research should be developed. This alternative should meet the following criteria. It uses a small spherical resistance heater as heat source and temperature sensor. A uniform thin coating will insulate electrically the heat source from the test medium. The coating as well as the heater should be good heat conductors. A slender stem, both thermally and electrically an insulator, carries the lead wires of the heater. While having the dimensions of the glass probes of this research, the improved probe should be made of a material with superior strength and should be impact resistant. Also, it should be manufactured as one piece so that it can be mounted into a system that can withstand repeated exposure to high temperature and pressure.
- A rapid means of heating food materials should be implemented in order to minimize the heat up time. For fluid products a flow system with a tubular heat exchanger and valves can be used. Thermal property measurement can take place after closing a valve to block the flow. For solid food materials, a sample chamber with dimensions only slightly larger than required to satisfy the infinite boundary condition can be used.

REFERENCES

Anderson, G.T., Valvano, J.W. and R.R. Santos. 1988. A self-heated thermistor technique to measure perfusion. Proceedings of the IEEE Engineering in Medicine and Biology Tenth Annual Meeting, New Orleans, pp. 776-777.

Anderson, G.T. and J.W. Valvano. 1989. An interlobular artery and vein based model for self-heated thermistor measurements of perfusion in canine kidneys. ASME Winter Annual Meeting, San Francisco, HTD Vol. 126, BED Vol. 12, pp. 29-35.

Arkin, H., Holmes, K.R., Chen, M.M. and W.G. Bottje. 1986. Thermal pulse decay method for simultaneous measurement of local thermal conductivity and blood perfusion: a theoretical analysis. J. of Biomechanical Engineering, Trans ASME, Vol. 108, pp 208-214.

Baghe-Khandan, M.S. and M.R. Okos. 1981a. Effect of Cooking on the Thermal Conductivity of Whole and Ground Lean Beef. Journal of Food Science, Vol. 46, pp 1302-1305.

Baghe-Khandan, M.S. and M.R. Okos. 1981b. Improved Line Heat Source Thermal Conductivity Probe. Journal of Food Science, Vol. 46, pp. 1430-1432.

Balasubramaniam, T.A. and H.F. Bowman. 1974. Temperature field due to a time dependent heat source of spherical geometry in a infinite medium. Journal of Heat Transfer, Transactions ASME Vol. 99, Series 3, No.3, pp. 296-299.

Balasubramaniam, T.A. 1975. Thermal conductivity and thermal diffusivity of biomaterials: a simultaneous measurement technique. Ph.D. dissertation, Northeastern University, Boston MA.

Balasubramaniam, T.A. and Bowman, H.F. 1977. Thermal conductivity and thermal diffusivity of biomaterials: a simultaneous measurement technique. Journal Biomechanical Engineering, Transactions ASME Vol. 99, pp. 148-154.

Bowman, H.F. and T.A. Balasubramaniam. 1976. A new technique utilizing thermistor probes for the measurement of thermal properties of biomaterials. Cryobiology Vol. 13, pp. 572-580.

Califano, A.N. and A. Calvelo, 1991. Thermal conductivity of potato between 50 and 100 °C. Journal of Food Science, Vol. 56 (2), pp. 586-588.

Casada, M.E. and L.R. Walton, 1989. New model for determining thermal diffusivity with the thermal probe. Transactions of the ASAE, Vol. 32 (3), pp. 973-976.

Chandarana, D.I., Gavin, A III and F.W Wheaton. 1989. Simulation of parameters for modeling aseptic processing of foods containing particulates. Food Technol. Vol. 43, pp. 137-143.

Chandrasekhar, S. 1961. Hydrodynamic and hydromagnetic stability. Oxford University Press, London.

Chang, S.Y., and R.T. Toledo, 1990. Simultaneous determination of thermal diffusivity and heat transfer coefficient during sterilization of carrot dices in a packed bed. Journal of Food Science, Vol. 55 (1), pp. 199-205.

Chato, J.C. 1968. A method for the measurement of the thermal properties of biological materials. In "Thermal Problems in Biotechnology", ASME, NY, pp. 16-25.

Chen, M.M. and V. Rupinskas. 1977. A simple method for measuring and monitoring thermal properties in tissues. Advances in Bioengineering, ASME paper No. 77-WA/HT-42.

Chen, M.M and K.R. Holmes. 1980. The thermal pulse-decay method for simultaneous measurement of thermal conductivity and local blood perfusion rate of living tissues. Advances in Bioengineering, ASME, pp. 113-115.

Choi, Y. and M.R. Okos. 1983. The thermal properties of tomato juice concentrates. Transactions of the ASAE Vol. , pp. 305-311.

CINDAS, 1988. Properties of inorganic and organic fluids. CINDAS Data Series on Material Properties Volume V-1, C.Y. Ho (ed.), Hemisphere publishing corporation, New York, London.

de Ruyter, P.W. de and R. Brunet. 1973. Estimation of process conditions for continuous sterilization of foods containing particulates. Food Technology, Vol. 27, pp. 44-49.

Dougherty, B.P. 1987. An automated probe for thermal conductivity measurements. MSc thesis in Mechanical Engineering, Virginia Polytechnic Institute and State University.

Drouzas, A.E., Maroulis, Z.B., Karathanos, V.T. and G.D. Saravacos. 1991. Direct and indirect determination of the effective thermal diffusivity of granular starch. Journal of Food Engineering, Vol. 13, pp. 91-101.

Genceli, O.F., 1980. The onset of manifest convection from suddenly heated horizontal cylinders. Wärme und Stoffübertragung, Vol. 13, pp. 163-169.

Gratzek, J.P. and R.T. Toledo, 1993. Solid food thermal conductivity determination at high temperatures. Journal of Food Science, Vol. 58 (4), pp. 908-913.

Hayes, L.J. and J.W. Valvano. 1985. Steady-State Analysis of Self-Heated Thermistors Using Finite Elements. Journal of Biomechanical Engineering, Vol. 107, pp. 77-80.

Hooper, F.C. and F.R. Lepper. 1950. Transient heat flow apparatus for the determination of thermal conductivities. ASHVE Transactions, Vol. 56, pp. 309.

Incropera, F.P. and D.P. DeWitt. 1985. Fundamentals of Heat and Mass Transfer, 2nd ed., John Wiley & Sons, New York.

Jia. H. and G. Gogos, 1996. Transient laminar natural convection heat transfer from isothermal spheres. Numerical Heat Transfer, Part A, Vol. 29, pp. 83-101.

Kravets, R.R. 1988. Determination of thermal conductivity of food materials using a bead thermistor. Ph.D. thesis in Food Science and Technology, Virginia Polytechnic Institute and State University.

Kustermann, M.K. Scherer, R and H.D. Kutzbach. 1981. Thermal conductivity and diffusivity of shelled corn and grain. Journal of Food Process Engineering, Vol. 4, pp. 137-153.

Lamberg, I. and B. Hallström, 1986. Thermal properties of potatoes and a computer simulation model of a blanching process. Journal of Food Technology, Vol. 21, pp. 577-585.

Lan, Y. and V.E. Sweat. 1992. Simultaneous determination of thermal conductivity and thermal diffusivity with probe. ASAE Paper No. 92-6597, ASAE, St. Joseph, MI 49085.

Larkin, J.W. 1990. Mathematical analysis of critical parameters in aseptic particulate processing systems. Journal of Food Process Engineering, Vol. 13, pp. 155-167.

Lee, J.H. and R.K. Singh. 1988. Determination of lethality in a continuous sterilization system containing particulates. ASAE Paper No. 88-6600, ASAE, St. Joseph, MI 49085.

Manson, J.E. and J.F. Cullen 1974. Thermal process simulation for aseptic processing of foods containing discrete particulates. Journal of Food Science, Vol. 39, pp. 1084-1089.

Marsh, K.N. (ed.) 1987. Recommended reference materials for the realization of physicochemical properties. Blackwell Scientific Publications, Oxford.

Mohsenin, N.N., 1980. Thermal properties of foods and agricultural materials. Gordon and Breach Science Publishers, NY.

Murakami, E.G., Sastry, S.K. and C.A. Zuritz, 1984. A modified Fitch apparatus for measuring thermal conductivity of small food particles. ASAE Paper No. 84-6508, ASAE, St. Joseph, MI 49085.

Nieto de Castro, C.A., Li, S.F.Y., Nagashima, A., Trengove, R.D. and W.A. Wakeham. 1986. Standard reference data for the thermal conductivity of liquids. Journal Phys. Chem. Ref. Data, Vol. 15 (3), pp. 1073-1086.

Pearson, D., 1973. Laboratory Techniques in Food Analysis. Butterworth & Co. (Publishers) Ltd., London.

Ott, L. 1988. An Introduction to statistical methods and data analysis. Third ed., PWS-Kent Publishing Company, Boston. Table 8, Appendix A-23.

Palaniappan, S. and C.E. Sizer, 1997. Aseptic process validated for foods containing particulates. Food Technology, Vol. 51 (8), pp. 60-68.

Parsons, J.R. Jr., and J.C. Mulligan, 1980. Onset of natural convection from a suddenly heated horizontal cylinder. Journal of Heat Transfer, Vol. 102, pp. 636-639.

Patel, P.A., Valvano, J.W., Pearce, J.A., Prahl, S.A. and C.R. Denham. 1987. A self-heated thermistor technique to measure effective thermal properties from tissue surface. Journal of Biomechanical Engineering, Transactions ASME, Vol. 109, pp. 330-335.

Perez, M.G.R. and A. Calvelo, 1984. Modeling the thermal conductivity of cooked meat. Journal of Food Science, Vol. 49, pp. 152-156.

Press, W. H., Flannery, B.P., Teukolsky, S.A. and W.T. Vetterling, 1989. Numerical Recipes in Pascal; The Art of Scientific Computing, Cambridge University Press, Cambridge.

Rahman, Md. S. 1991. Evaluation of the precision of the modified Fitch method for thermal conductivity measurement of foods. Journal of Food Engineering, Vol. 14, pp. 71-82.

Rao, M.A., Barnard, J. and J.F. Kenny, 1975. Thermal conductivity and diffusivity of process variety squash and white potatoes. Transactions of the ASAE, Vol. 18, pp. 1188-1192.

Sengers, J.V., Watson, J.T.R., Basu, R.S. and B. Kamgar-Parsi, 1984. Journal Phys. Chem. Ref. Data, Vol. 13, table 1.6, p 925.

Sweat, V.E. and C.G. Haugh. 1974. A thermal conductivity probe for small food samples. Transactions of ASAE, Vol. 17, No 1, pp. 56-58.

Sweat, V.E. 1986. Thermal properties of foods. in "Engineering properties of foods", Rhao, M. and S.S.H. Rizvi (ed.), Marcel Dekker, New York.

Thermometrics. 1987. Thermistor sensor handbook. Thermometrics Inc., NJ.

Touloukian, Y.S., Liley, P.E. and S.C. Saxena. 1970a. Thermal Conductivity: Nonmetallic Liquids and Gases. The TPRC data series, Vol. 3, IFI/Plenum Press, New York.

Touloukian, Y.S. 1970b. Specific Heat: Nonmetallic Liquids and Gases. The TPRC data series, Vol. 6 Suppl., IFI/Plenum Press, New York.

Touloukian, Y.S., Kirby, R.K., Taylor, R.E. and P.D. Desai, 1975. Thermal Expansion: Metallic Elements and Alloys. The TPRC data series, Vol. 12., IFI/Plenum Press, New York.

UCON Heat Transfer Fluid 500. 1989. Union Carbide Chemicals and Plastics Company Inc., Specialty Chemicals Division, Danbury, CT.

Valvano, J.W. 1981. The use of thermal diffusivity to quantify tissue perfusion. Ph.D. thesis in Medical Engineering, Harvard University - MIT Division of Health Sciences and Technology.

Valvano, J.W., Patel, P.A. and L.J Hayes. 1983. A Finite Element Analysis of Self-Heated Noninvasive Thermistors. Advances in Bioengineering, ASME, pp. 149-150.

Valvano, J.W., Allen, J.T. and H.F. Bowman. 1984. The simultaneous measurement of thermal conductivity and perfusion in small volumes of tissue. Journal of Biomechanical Engineering, Transactions ASME, Vol. 106, pp. 192-197.

Valvano, J.W., Cochran, J.R. and K.R. Diller. 1985. Thermal conductivity and diffusivity of biomaterials measured with self-heated thermistors. Int. Journal of Thermophysics,Vol. 6, pp. 301-311.

Valvano, J.W., Badeau, A.F. and J.A. Pearce. 1987. Simultaneous measurement of intrinsic and effective thermal conductivity. Heat Transfer in Bioengineering and Medicine, ASME Winter Annual Meeting, Boston, HTD Vol. 95, BED Vol. 7, ed. Chato, Diller, Diller, Roemer, pp. 31-36.

Valvano, J.W., Nho, S. and G.T. Anderson. 1990. A Weinbaum-Jiji model of steady state heated thermistors in the canine kidney cortex. Advances in measuring and computing temperatures in biomedicine: thermal tomography techniques, bioheat models. ASME Winter Annual Meeting., Dallas, TX, HTD Vol. 147, ed. Roemer, Valvano, Hayes, Anderson, pp. 51-57.

van Gelder, M.F and K.C. Diehl. 1996. A thermistor based method for measuring thermal conductivity and thermal diffusivity of moist food materials at high temperatures. Thermal Conductivity 23: Proceedings of the Twenty-Third International Thermal Conductivity Conference, Technomic Publishing Co. Inc., Lancaster, PA.

Vargaftik, N.B., 1975. Tables on the Thermophysical Properties of Liquids and Gases: in Normal and Dissociated States, Hemisphere Publishing Corp., Washington.

Vest, C.M. and M.L. Lawson, 1972. Onset of convection near a suddenly heated horizontal wire. Int. Journal of Heat and Mass Transfer, Vol. 15, pp. 1281-1283.

Wang, J. and K. Hayakawa, 1992. Thermal conductivity of foods at high temperatures as influenced by moisture content. Act. Rep. R & D. Assoc., Research and Development Associates for Military Food and Packaging Systems, San Antonio, TX.

Wang, P., Kahawita, R. and D.L. Nguyen, 1991. Transient laminar natural convection from horizontal cylinders. Int. Journal of Heat and Mass Transfer, Vol. 34 (6), pp. 1429-1442.

Wolters, R.J.H., 1992. Development of a computer controlled method for measuring thermal conductivity in small food samples. (unpublished), Virginia Polytechnic Institute and State University .

Woodbury, K.A. 1984. An experimental and analytical investigation of liquid moisture distribution in roof insulating systems. Ph.D. thesis in Mechanical Engineering, Virginia Polytechnic Institute and State University.

Yamada, T. , 1970. The thermal properties of potato. (in Japanese) J. Agr. Chem. Soc. of Japan 44:587, (Abstract in Food Science and Technology Abstracts, 1973, 5:Abstract No. 12j2011).

Zuritz, C.A., Sastry, S.K., McCoy, S.C., Murakami, E.G. and J.L. Blaisdell. 1989. A modified Fitch device for measuring the thermal conductivity of small food particles. Transactions ASAE Vol. 32(2), pp. 711-718.

APPENDIX A

DENSITY OF GLYCEROL AND DIMETHYL PHTHALATE

A DENSITY OF GLYCEROL AND DIMETHYL PHTHALATE.

A.1 INTRODUCTION

In the initial stage of the research, dimethyl phthalate was considered as a calibration material. Its thermal conductivity was well documented as it was included in a list of recommended reference materials for thermal conductivity measurements (Marsh, 1987). Its thermal diffusivity however was not documented. It could not be calculated from published values for specific heat and density since those weren't found for the temperature range of interest (100 - 150 °C). A project was undertaken to measure the density of dimethyl phthalate at temperatures up to 150 °C. A second objective was to obtain high temperature density data for glycerol in order to calculate its thermal diffusivity. Thermal diffusivity of glycerol was not available from literature at high temperature. Density data were limited and old.

The density of fluids can be found by several methods. A simple approach is to weigh a volume, measured with a graduated cylinder. Other methods use calibrated beads of known density or an hydrometer. These methods however are limited to a narrow temperature range. Graduated cylinders are calibrated for a certain temperature. Thermal expansion will negatively impact their accuracy at the high temperatures intended in this study. The same remarks could be made with regard to calibrated beads and the hydrometer. This research looked to the specific gravity balance as a possible method.

A.2 METHOD

A specific gravity balance is generally used to measure the specific gravity, or the density of a sample of solid material. In order to determine the density of a solid sample with the specific gravity balance, the sample is first weighed suspended in air. Subsequently, the sample is submerged in a liquid of known density and its weight is recorded again. The difference between the two values (suspended in air versus suspended in the liquid) yields the buoyancy of the liquid (the buoyancy of air is assumed negligible). The volume of the sample can be calculated from the buoyancy and the known density of the liquid. Finally, the density of the sample is found from its volume and dry weight.

For this research, the method was adapted. The unknown was the density of the fluid. An object needed to be manufactured with an accurately known volume. The material for this object had to be temperature and chemical resistant. Metal seemed a logical choice. Stainless steel rod of known specifications was available. The object was manufactured from a stainless steel (SS 304) rod (9.6 mm in diameter). The length was 51.5 mm. The bottom of the object was rounded to prevent air bubbles from being trapped underneath. The top was tapered and a hole was drilled to hang the object from a hook. The hole was machined such that it would not retain any air. The temperature dependence of the volume of the object was found by applying equations given by Touloukian (1975). The expansion of type SS 304 stainless steel could be described by the equation:

$$\frac{L_1 - L_0}{L_0} = -0.00358 + 9.472 \bullet 10^{-6} T + 1.031 \bullet 10^{-8} T^2 - 2.978 \bullet 10^{-12} T^3 \qquad (A.1)$$

where: L_1 = Length at temperature T_1, [m]

L_0 = Length at T_0, T_0 = 20 °C, [m]

T = Temperature [K]

The equation gives the expansion as a fraction of the length at 20 °C. The result of equation A.1 is used to find the mean coefficient of linear expansion, defined as:

.

$$\alpha = \frac{L_1 - L_0}{L_0(T_1 - T_0)} \qquad (A.2)$$

where: L_0, L_1 = Length, at Temperature T_0 and T_1 respectively [m]

T_0, T_1 = Temperature [°C]

The volumetric thermal expansion coefficient, β, is approximately three times the value of α. The value of α is referenced to 20 °C. The volume of the object at other temperatures can be calculated with the expression:

$$V(T) = V_{20}(1 + 3\alpha\Delta T) \tag{A.3}$$

where: $V(T)$ = Volume of object at temperature T, [cm^3]

V_{20} = Volume of object at 20 °C, [cm^3]

α = mean coefficient of linear thermal expansion, [$°C^{-1}$]

ΔT = T - 20. [°C]

The volume of the object was determined by triplicate measurement in water. The density of water taken from Incropera (1985).

A.3 EQUIPMENT

All weight measurements were taken with a digital analytical balance (Sartorius Model 1712 MP8 Silver edition, Brinkmann Instruments Inc., Div. of Sybron, Westbury, NY), with a resolution of 0.1 mg. The balance had a hook underneath the weighing platform, allowing it to be used as a specific gravity balance. The balance was placed on a stand, 29 cm above the workbench. An opening in the stand gave access to the hook. A piece of thin wire with ends shaped as hooks was hung from the hook under the balance. A similar shaped second piece of wire was hung from the first one. The object was hung on this second piece of wire. The volume of the submerged part of the wire was determined from its diameter and length.

The test fluid was contained in the sample cup borrowed from a viscometer (Brookfield LV, Stoughton, MA). The cup had a diameter of 20.9 mm and a depth of 60.2 mm. The cup came with a flow jacket for temperature control. The flow jacket was connected, through insulated high temperature silicon tubing, to a circulating temperature bath (Exacal EX-251 HT, NESLAB Instruments, Inc., Newington, NH). The bath contained a heat transfer fluid for high temperature applications (HTF 500, Union Carbide, Danbury, CT). The viscosity of this fluid at low temperatures was too high for the circulating bath to properly function. For this reason, measurements were started at 35 °C. The sample cup was covered with a plastic top (accessory to the small sample adapter) to minimize evaporation and heat loss from the sample. The temperature of the test fluid was monitored with a thin thermocouple (24 ga. copper-constantan). The thermocouple was connected to a cold junction compensator (OMEGA CJ, Omega Engineering, Inc., Stamford, CT). The output of the cold junction compensator was read with a voltmeter (Keithley 197 Autoranging Microvolt DMM, Keithley Instruments Inc., Cleveland, OH). The thermocouple was calibrated against a thermal standard with 0.001 °C resolution (Guildline 9540 Digital Platinum Resistance Thermometer, Smith Falls, Ontario), traceable to the National Institute of Standards and Technology (NIST).

The accuracy of the method was assessed with water. Distilled water was boiled and placed under a vacuum of 600 mg Hg to expel air. The density was determined at 7.5 °C intervals over the range 40 to 85 °C. Higher temperatures were not feasible due to excessive evaporation. The measurement was replicated once.

Glycerol and dimethyl phthalate were measured over the temperature range 40 to 150 °C at 10 °C increments. Each material was measured in duplicate. Prior to filling the sample cup, the glycerol was heated to approximately 85 °C to lower its viscosity, and so decrease the likelihood that air bubbles would be incorporated into the fluid upon filling the cup, or when the object was lowered into the fluid.

A.4 RESULTS

Because the circulating bath didn't allow measurements at 20 °C, the volume of the object was determined at a higher temperature. The volume of the object at 50 °C was found from triplicate measurements to be 3.3266 cm^3. By using equations A.1-A.3, the volume at 20 °C was found, 3.218 cm^3. The volume of the submerged part of the wire was 0.0035 cm^3.

The results of the density measurements in water are given in Table A.1. The replication was excellent. The combined measurement data were used in quadratic linear regression to find a prediction equation. The equation fitted the data with a mean absolute deviation of 0.04% and a maximum absolute deviation of 0.14%. The equation was used to generate density values for comparison to tabulated literature data. Compared to literature values for water given by Incropera and DeWitt (1985) over the range 310 to 360 K (37 - 87 °C) the equation underestimated the density of water by an average of 0.06% and a maximum of 0.08%. Based on these results, the method was deemed of sufficient accuracy.

Table A.1 Density of water determined with a specific gravity balance.

First Sample		Second Sample	
Temperature [°C]	Density [kg/m^3]	Temperature [°C]	Density [kg/m^3]
		34.5	993.6
39.4	991.8	39.4	991.4
46.9	988.3	46.8	988.2
54.2	985.5	54.1	984.8
61.6	983.0	61.7	981.3
69.1	977.7	68.9	977.3
76.5	973.6	76.2	973.4
83.8	969.5	83.4	970.4

Density of Glycerol

The data of the two measurements are given in Table A.2 and Figure A.1. The combined measurement data were used in quadratic linear regression to find a prediction equation.

$$\rho = 1273.18 - 0.60577\,T - 5.01 \bullet 10^{-4} T^2 \qquad (A.4)$$

where: ρ = Density [kg/m^3]

T = Temperature [°C]

Equation A.4 fitted the data with a mean absolute deviation of 0.05% and a maximum absolute deviation of 0.1%. The equation was compared to literature data given by Vargaftik (1975) over the range 20 to 140 °C. The difference with these data is less than 0.25% up to 100 °C, -0.44% at 120 °C, and -1% at 140 °C. The measurement data and the reference values from Vargaftik are given in Figure A.1. Equation A.4 was used the estimate the coefficient of thermal expansion, β: $\beta(T) = -1/\rho(T) \bullet (\delta\rho/\delta T)_T$. The estimated values for the coefficient of thermal expansion deviated less that 5% from those given by Incropera (1985) over the range 273 - 320 K.

Table A.2 Density of Glycerol with a specific gravity balance

First Sample		Second Sample	
Temperature [°C]	Density [kg/m^3]	Temperature [°C]	Density [kg/m^3]
39.4	1247.5	49.5	1242.0
49.1	1242.6	59.2	1235.7
59.3	1235.6	69.0	1229.4
68.9	1229.6	78.9	1222.8
78.4	1222.7	88.6	1215.9
88.6	1215.0	99.3	1208.5
98.1	1207.9	109.1	1201.8
107.9	1201.2	119.2	1194.6
118.1	1193.8	129.2	1187.1
127.7	1186.7	139.1	1180.1
137.7	1179.1	149.1	1172.4

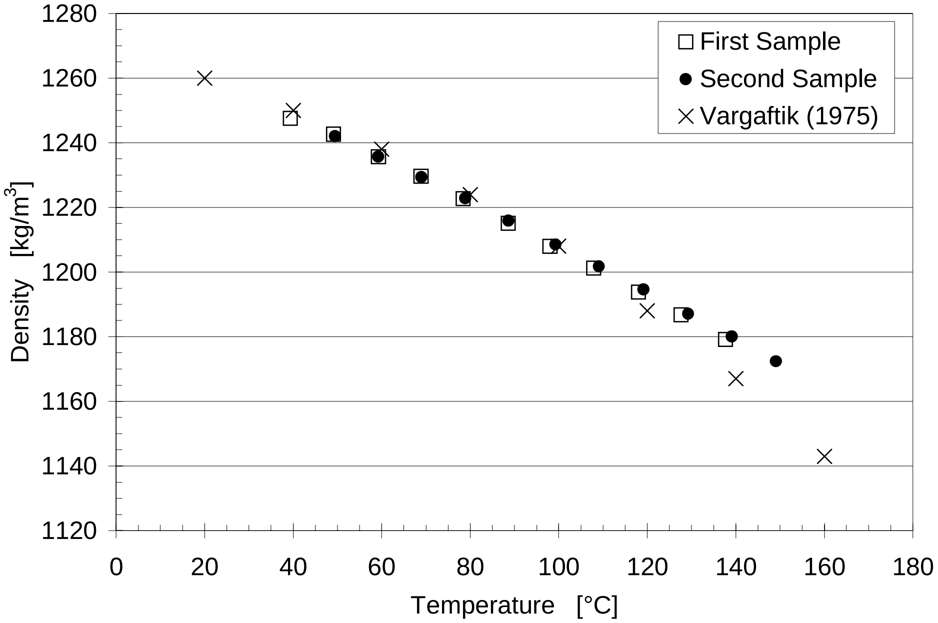

Figure A.1 Density of Glycerol with a specific gravity balance

density of dimethyl phthalate

The data of the two measurements are given in Table A.3 and Figure A.2. The combined measurement data were used in linear regression to find a prediction equation.

$$\rho = 1210.00 - 0.92027\,T \qquad (A.5)$$

where: ρ = Density [kg/m^3]

T = Temperature [°C]

The data fit the equation with an average absolute deviation of 0.02% and a maximum deviation of 0.06% (0.22 and 0.62 [kg/m^3] respectively). This excellent fit is testament of the excellent replication.

Table A.3 Density of dimethyl phthalate with a specific gravity balance.

First Sample		Second Sample	
Temperature [°C]	Density [kg/m^3]	Temperature [°C]	Density [kg/m^3]
39.2	1173.7	39.1	1174.1
49.2	1164.5	48.9	1164.4
59.0	1155.5	59.0	1155.6
69.3	1146.1	69.0	1146.6
79.6	1136.7	79.7	1137.0
90.1	1127.3	89.2	1128.5
99.9	1118.3	99.7	1118.5
110.1	1108.7	110.1	1109.1
119.7	1099.8	120.0	1099.9
129.6	1090.8	129.7	1090.7
139.7	1081.5	139.5	1081.4
149.6	1072.1	149.3	1072.0

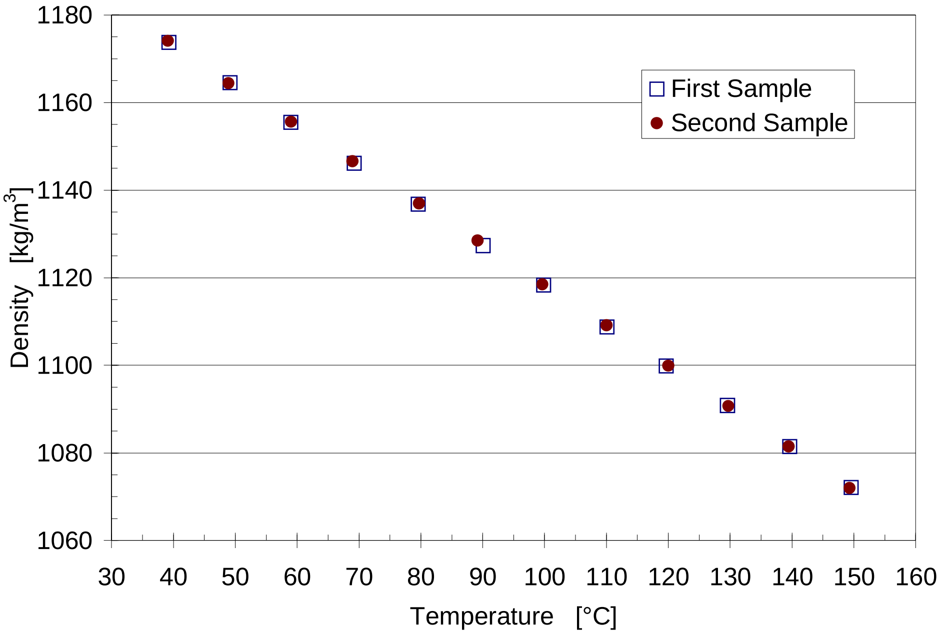

Figure A.2 Density of dimethyl phthalate measured with a specific gravity balance.

APPENDIX B

MEASUREMENT DATA FOR THE CALIBRATION OF THE LOW TEMPERATURE PROBE

Table B.1 Regression Results for Water at 25 °C with Probe #L4, from regression over the interval 3-9 seconds.

File	$R\Delta T/V_{ss}^2$	Intercept	Slope	S/I
L4W25A.D1	288.3	17.7947	9.6738	0.5436
L4W25B.D1	289.5	17.7182	9.6828	0.5465
L4W25C.B1	289.1	17.7003	9.5990	0.5423
Sample Average	**289.0**			**0.5441**
L4W25X.D2	290.8	17.6358	9.6215	0.5456
L4W25Y.B2	289.4	17.7393	9.6562	0.5443
L4W25Z.D2	289.1	17.7505	9.6906	0.5459
Sample Average	**289.8**			**0.5453**
L4W25A.D3	288.5	17.7340	9.6811	0.5459
L4W25B.D3	288.4	17.7017	9.6594	0.5457
L4W25C.D3	288.7	17.7559	9.7675	0.5501
Sample Average	**288.5**			**0.5472**
Average at 25 °C	**289.1**			**0.5456**

Table B.2 Regression Results for Glycerol at 25 °C with Probe #L4, from regression over the interval 3-9 seconds.

File	$R\Delta T/V_{ss}^2$	Intercept	Slope	S/I
L4G25A.D1	439.2	11.7065	10.7951	0.9222
L4G25B.D1	438.4	11.6589	10.7683	0.9236
L4G25C.D1	438.5	11.7142	10.8208	0.9237
Sample Average	**438.7**			**0.9232**
L4G25A.D2	439.8	11.6407	10.7545	0.9239
L4G25B.D2	439.9	11.6382	10.7290	0.9219
L4G25C.D2	440.3	11.6351	10.7597	0.9248
Sample Average	**440.0**			**0.9235**
L4G25A.D3	438.6	11.6788	10.7604	0.9214
L4G25C.D3	438.3	11.6975	10.7579	0.9197
L4G25D.D3	438.4	11.6895	10.7187	0.9170
Sample Average	**438.5**			**0.9193**
Average at 25 °C	**439.0**			**0.9220**

Table B.3 Regression Results for Water at 50 °C with Probe #L4, from regression over the interval 3-9 seconds.

File	RΔT/Vss2	Intercept	Slope	S/I
L4W50A.B1	279.7	7.3673	3.8184	0.5183
L4W50B.B1	279.1	7.3768	3.7977	0.5148
L4W50C.D1	279.5	7.3913	3.8188	0.5167
Sample Average	**279.4**			**0.5166**
L4W50A.D2	279.2	7.4098	3.8260	0.5164
L4W50B.B2	279.7	7.3960	3.8229	0.5169
L4W50C.D2	279.8	7.4102	3.8300	0.5169
Sample Average	**279.6**			**0.5167**
L4W50A.B3	279.2	7.3276	3.8115	0.5202
L4W50B.D3	280.0	7.3330	3.8121	0.5199
L4W50C.D3	279.1	7.3248	3.8009	0.5189
Sample Average	**279.4**			**0.5196**
Average at 50 °C	**279.5**			**0.5176**

Table B.4 Regression Results for Glycerol at 50 °C with Probe #L4, from regression over the interval 3-9 seconds.

File	RΔT/Vss2	Intercept	Slope	S/I
L4G50A.B1	436.9	4.6861	4.4293	0.9452
L4G50B.B1	436.1	4.6718	4.4024	0.9423
L4G50C.B1	436.6	4.6624	4.3955	0.9428
Sample Average	**436.5**			**0.9434**
L4G50A.D2	435.7	4.7915	4.5261	0.9446
L4G50B.D2	435.4	4.7841	4.5153	0.9438
L4G50C.D2	435.6	4.7742	4.5119	0.9451
Sample Average	**435.6**			**0.9445**
L4G50A.D3	436.2	4.7546	4.4600	0.9381
L4G50B.D3	437.2	4.7477	4.4789	0.9434
L4G50C.D3	437.3	4.7457	4.4774	0.9435
Sample Average	**436.9**			**0.9416**
Average at 50 °C	**436.3**			**0.9432**

APPENDIX C

SPECIFIC HEAT OF DIMETHYL PHTHALATE

C SPECIFIC HEAT OF DIMETHYL PHTHALATE

C.1 INTRODUCTION

In order to calculate the thermal diffusivity of dimethyl phthalate, values for thermal conductivity, density, and specific heat had to be found. Thermal conductivity was found from literature (Marsh, 1987). The density was determined with a specific gravity balance (Appendix A). The determination of specific heat in the temperature range 100 to 150 °C was the objective of this study.

C.2 METHODS AND MATERIALS

The specific heat of dimethyl phthalate was measured with a differential scanning calorimeter (Metler Thermal Analysis Systems TA 4000, consisting of a TC11 TA processor and a DSC 30 measuring cell). The DSC was fully calibrated prior to the experiments.

The DSC was run from 50 °C to 160 °C with a scan rate of 10 °C per minute. Four samples were tested. The samples were weighed on a digital analytical balance (Sartorius model 1712 MP8 silver edition, Brinkmann Instruments Inc., Div. of Sybron, Westbury, NY) with a resolution of 0.01 mg. Sample weight was approximately 30 mg.

C.3 RESULTS

The thermal analysis processor evaluated the specific heat at 5 °C increments over the range 80 to 150 °C. The data of the four samples are given in Table C.1. Replication was good as demonstrated by the low values of the standard deviation. The data were to a linear equation with a R^2 value of 0.944. The data fitted the equation with an average absolute deviation of 0.52% and a maximum deviation of 1.33%.

$$C_p = 1.5495 + 0.002091\,T \tag{C.1}$$

where: C_p	=	Specific Heat	[kJ/kg°C]
T	=	Temperature	[°C]

A quadratic equation improved the fit marginally, but the parameter of the quadratic term had a standard error that was of the same magnitude as the parameter itself.

Table C.1 Specific heat of Dimethyl Phthalate, kJ/kg°C

Temperature	Specific Heat					
[°C]	Sample #1	Sample #2	Sample #3	Sample #4	Average	StdDev
80	1.72	1.72	1.73	1.74	1.73	0.0096
85	1.72	1.71	1.73	1.74	1.73	0.0129
90	1.73	1.73	1.74	1.75	1.74	0.0096
95	1.74	1.73	1.76	1.76	1.75	0.0150
100	1.75	1.75	1.76	1.78	1.76	0.0141
105	1.75	1.75	1.76	1.78	1.76	0.0141
110	1.77	1.77	1.78	1.79	1.78	0.0096
115	1.78	1.78	1.79	1.80	1.79	0.0096
120	1.79	1.80	1.81	1.82	1.81	0.0129
125	1.79	1.80	1.81	1.81	1.80	0.0096
130	1.81	1.81	1.83	1.83	1.82	0.0115
135	1.82	1.83	1.84	1.84	1.83	0.0096
140	1.84	1.83	1.85	1.86	1.85	0.0129
145	1.85	1.85	1.86	1.87	1.86	0.0096
150	1.86	1.86	1.87	1.87	1.87	0.0058

APPENDIX D

THERMAL CONDUCTIVITY OF POTATO AND BEEF: MEASUREMENT DATA

Table D.1 Average Thermal Conductivity of Potato at 25, 50 and 100 °C, measured with the Line Heat Source Probe and the Bead Thermistor Probe

Measurement Temperature (°C)	Potato	Variety	Thermal Conductivity			
			Line Heat Source Probe		Bead Thermistor Probe	
			Sample Average[a] (W/m°C)	Temperature Average (W/m°C)	Sample Average[a] (W/m°C)	Temperature Average (W/m°C)
25	1	Idaho	0.5846		0.5500	
	2	Idaho	0.5986		0.5598	
	3	California White	0.5873		0.5580	
	4	Idaho			0.5503	
	5	Idaho	0.5961		0.5452	
	6	Idaho	0.6004		0.5467	
	7	Idaho	0.6070	0.5957		0.5517
50	1	California White	0.5942		0.5918	
	2	California White	0.5969		0.5891	
	3	California White	0.5932		0.5850	
	4	California White	0.5942		0.5870	
	5	Idaho	0.6355		0.5773	
	6	Idaho	0.6357		0.5878	
	7	Idaho	0.6325	0.6117	0.5710	0.5841
100	1	Idaho	0.7790			
	2	Idaho	0.7068		0.6135	
	3	Idaho	0.6970		0.5986	
	4	Idaho	0.7122		0.5892	
	5	Idaho	0.6968		0.6133	
	6	Idaho	0.7028		0.6068	
	7	Idaho	0.7296	0.7075[b]	0.5877	0.6015

[a] Average is calculated over 3 repeats.
[b] Average excludes sample #1.

Table D.2 Thermal Conductivity of Potato at 25 °C, measured with the Line Heat Source Probe and the Bead Thermistor Probe; results of individual measurements

Potato Variety	Thermal Conductivity			
	Line Heat Source Probe		Bead Thermistor Probe	
		Mean Value for Potato		Mean Value for Potato
	[W/m°C]	[W/m°C]	[W/m°C]	[W/m°C]
Idaho	0.5872		0.5495	
	0.5809		0.5505	
	0.5857	0.5846	0.5500	0.5500
Idaho	0.5985		0.5596	
	0.5981		0.5617	
	0.5993	0.5986	0.5582	0.5598
California White	0.5900		0.5588	
	0.5836		0.5570	
	0.5883	0.5873	0.5581	0.5580
Idaho	0.5961		0.5466	
	0.5951		0.5515	
	0.5970	0.5961	0.5529	0.5503
Idaho	0.6038		0.5425	
	0.6030		0.5411	
	0.5944	0.6004	0.5493	
			0.5479	0.5452
Idaho	0.6042		0.5426	
	0.6075		0.5419	
	0.6092	0.6070	0.5510	
			0.5510	0.5466
Average at 25 °C.		0.5957		0.5517
Standard Deviation of Means		0.0084		0.0060

Table D.3 Thermal Conductivity of Potato at 50 °C, measured with the Line Heat Source Probe and the Bead Thermistor Probe; results of individual measurements

Potato Variety	Thermal Conductivity			
	Line Heat Source Probe		Bead Thermistor Probe	
		Mean Value for Potato		Mean Value for Potato
	[W/m°C]	[W/m°C]	[W/m°C]	[W/m°C]
California White	0.5981		0.5920	
	0.5925		0.5894	
	0.5919	0.5942	0.5948	
			0.5911	0.5918
California White	0.6008		0.5885	
	0.5947		0.5885	
	0.5952	0.5969	0.5894	
			0.5900	0.5891
California White	0.5991		0.5847	
	0.5958		0.5837	
	0.5847	0.5932	0.5850	
			0.5866	0.5850
California White	0.5931		0.5883	
	0.5967		0.5865	
	0.5928	0.5942	0.5871	
			0.5860	0.5870
Idaho	0.6388		0.5793	
	0.6360		0.5743	
	0.6316	0.6355	0.5773	
			0.5785	0.5774
Idaho	0.6371		0.5914	
	0.6342		0.5902	
	0.6359	0.6357	0.5853	
			0.5843	0.5878
	0.6357		0.5634	
	0.6300		0.5610	
	0.6318	0.6325	0.5781	
			0.5815	0.5710
Average at 50 °C.		0.6117		0.5842
Standard Deviation of Means		0.0214		0.0074

Table D.4 Thermal Conductivity of Potato at 100 °C, measured with the Line Heat Source Probe and the Bead Thermistor Probe; results of individual measurements

Potato Variety	Thermal Conductivity			
	Line Heat Source Probe		Bead Thermistor Probe	
		Mean Value for Potato		Mean Value for Potato
	[W/m°C]	[W/m°C]	[W/m°C]	[W/m°C]
Idaho	0.7088		0.6134	
	0.6917		0.6138	
	0.7199	0.7068	0.6133	0.6135
Idaho	0.6938		0.5849	
	0.6949		0.6089	
	0.7022	0.6970	0.6020	0.5986
Idaho	0.7055		0.5930	
	0.7223		0.5911	
	0.7088	0.7122	0.5834	0.5892
Idaho	0.6958		0.6000	
	0.7018		0.6220	
	0.6927	0.6968	0.6180	0.6133
Idaho	0.7023		0.6095	
	0.6986		0.6040	
	0.7076	0.7028	0.6069	0.6068
Idaho	0.7226		0.5820	
	0.7371		0.5868	
	0.7291	0.7296	0.5943	0.5877
Average at 100 °C.		0.7075		0.6015
Standard Deviation of Means		0.0123		0.0115

Table D.5 Average Thermal Conductivity of Lean Beef at 25, 50 and 100 °C, measured with the Line Heat Source Probe and the Bead Thermistor Probe

	Line Heat Source Probe			Bead Thermistor Probe		
Measurement Temperature	Sample	Thermal Conductivity		Sample	Thermal Conductivity	
		Sample Average[1]	Temperature Average		Sample Average[1]	Temperature Average
(°C)		(W/m°C)	(W/m°C)		(W/m°C)	(W/m°C)
25	1	0.5465		1	0.5025	
	2	0.5458		2	0.4007	
	3	0.5331		3	0.4590	
	4	0.5435		4	0.5083	
	5	0.5085		5	0.5047	
	6	0.5184	0.5326	6	0.4941	0.4782
50	1	0.5321		1	0.5169	
	2	0.5504		2	0.5195	
	3	0.5532		3	0.5116	
	4	0.5488		4	0.5031	
	5	0.5562		5	0.5057	
	6	0.4600	0.5335	6	0.4938	0.5084
100	1	0.4669		1	0.4829	
	2	0.4145		2	0.4669	
	3	0.5234		3	0.4671	
	4	0.4726		4	0.4888	
	5	0.4977	0.4750	5	0.4117	
	6			6	0.4764	0.4656

[1] Average is calculated over 3 repeats.

Table D.6 Thermal Conductivity of Beef (Whole Round) at 25 °C, measured with the Line Heat Source Probe and the Bead Thermistor Probe; results of individual measurements

Sample Number	Thermal Conductivity Line Heat Source Probe [W/m°C]	Line Heat Source Probe Mean Value for Sample [W/m°C]	Bead Thermistor Probe [W/m°C]	Bead Thermistor Probe Mean Value for Sample [W/m°C]
1	0.5482		0.5040	
	0.5446		0.5010	
	0.5467	0.5465	0.5024	0.5025
2	0.5468		0.4019	
	0.5461		0.3989	
	0.5444	0.5458	0.4015	0.4008
3	0.5315		0.4532	
	0.5351		0.4622	
	0.5327	0.5331	0.4616	0.4590
4	0.5403		0.5083	
	0.5468		0.5079	
	0.5433	0.5435	0.5087	0.5083
5	0.5138		0.5045	
	0.5046		0.5034	
	0.5070	0.5085	0.5063	0.5047
6	0.5174		0.4949	
	0.5173		0.4928	
	0.5205	0.5184	0.4946	0.4941
Average at 25 °C.		0.5326		0.4782[1]
Standard Deviation of Means		0.0159		0.0420[1]

[1] After the test a lump of fat was discovered near the probe. Excluding sample number 2 from the analysis changes the average and standard deviation to 0.4937and 0.0201 respectively.

Table D.7 Thermal Conductivity of Beef (Whole Round) at 50 °C, measured with the Line Heat Source Probe and the Bead Thermistor Probe; results of individual measurements

Sample Number	Thermal Conductivity Line Heat Source Probe [W/m°C]	 Mean Value for Sample [W/m°C]	 Bead Thermistor Probe [W/m°C]	 Mean Value for Sample [W/m°C]
1	0.5309		0.5195	
	0.5308		0.5174	
	0.5347	0.5321	0.5138	0.5169
2	0.5509		0.5212	
	0.5521		0.5185	
	0.5482	0.5504	0.5188	0.5195
3	0.5566		0.5119	
	0.5510		0.5121	
	0.5521	0.5532	0.5106	0.5115
4	0.5528		0.5026	
	0.5479		0.5053	
	0.5456	0.5488	0.5013	0.5031
5	0.5543		0.5053	
	0.5625		0.5052	
	0.5519	0.5562	0.5065	0.5057
6	0.4624		0.4930	
	0.4586		0.4948	
	0.4589	0.4600	0.4936	0.4938
Average at 50 °C.		0.5335		0.5084
Standard Deviation of Means		0.0370		0.0095

Table D.8 Thermal Conductivity of Beef (Whole Round) at 100 °C, measured with the Line Heat Source Probe and the Bead Thermistor Probe; results of individual measurements

Sample	Thermal Conductivity			
Number	Line Heat Source Probe		Bead Thermistor Probe	
	[W/m°C]	Mean Value for Sample [W/m°C]	[W/m°C]	Mean Value for Sample [W/m°C]
1	0.4695		0.4885	
	0.4675		0.4778	
	0.4637	0.4669	0.4824	0.4829
2	0.4120		0.4670	
	0.4131		0.4696	
	0.4183	0.4145	0.4641	0.4669
3	0.5219		0.4655	
	0.5180		0.4745	
	0.5304	0.5234	0.4613	0.4671
4	0.4771		0.4856	
	0.4760		0.4875	
	0.4647	0.4726	0.4933	0.4888
5	0.4936		0.4147	
	0.5044		0.4095	
	0.4952	0.4977	0.4109	0.4117
6			0.4756	
			0.4738	
			0.4798	0.4764
Average at 100 °C.		0.4750		0.4656
Standard Deviation of Means		0.0406		0.0278

VITAE

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