„BABEŞ -BOLYAI” UNIVERSITY
FACULTY OF PHYSICS

Contact And Noncontact Photothermal Calorimetry For Condensed Matter Investigation

PhD’s thesis summary

Scientific advisor:	PhD candidate:
Prof. Dr. Viorica Simon	**Mircea Nicolae Pop**

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Kewords:

Calorimetry

Photothermal

Radiometry

Condensed state

Nondestructive investigation

Thermal properties

Thermal diffusivity

Thermal effusivity

Thermal resonant cavity

Multilayered systems

Associative mixtures

Plant extracts

Pressed powders

Nanofluids

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Contact and noncontact photothermal calorimetry for condensed matter investigation

Pop Mircea Nicolae

pop.mircea.n@gmail.com

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„BABEŞ -BOLYAI" UNIVERSITY, FACULTY OF PHYSICS

Mihail Kogalniceanu 1 Street, 400084 Cluj-Napoca
Tel : +40 (264) 405300, Fax: +40 (264) 591906
Email: phys@phys.ubbcluj.ro

Abstract

The main objective of this thesis, entitled: “**Contact and Noncontact Photothermal Calorimetry for Condensed Matter Investigation**” has been the development of new calorimetric measurement methods, based on the PPE and on the PTR photothermal techniques, in order to measure the thermal properties of condensed matter. For this purpose PPE calorimetric methods based on a liquid layer’s thickness scanning, an intermediary layer of the multilayered structure, behaving like a thermal resonant cavity, have been approached. A combined PPE and PTR method has been developed. The basic principle of the proposed method consists in the simultaneous recording of the PPE and PTR signal, both signals containing information about the thermal and geometrical parameters of the layers of the same PPE cell.

In order to accomplish these objectives, the mathematical models based on one dimensional propagation of the diffusion waves in the PPE cell have been developed. Thus the analytical expressions of the normalized PPE and PTR signals have been obtained. On the behalf of the mathematical model two PPE measurement cell configurations have been developed: **i.** a four layer configuration which allows one to measure the thermal effusivity of a bulk solid backing material and either the thermal diffusivity, the thermal diffusivity or both of these properties specific to a coupling liquid and **ii.** a five layer configuration which allows one to measure the thermal effusivity of a liquid backing and either the thermal diffusivity, the thermal diffusivity or both of these properties of a coupling liquid or of an intermediary solid layer. A generalized one dimensional heat diffusion model corresponding to a layered system composed of an infinite number of layers has been developed. Using graphical representations the behavior of the PPE and PTR signals have been studied. Using the sensitivity coefficients the influence of different known layers on the thermal parameters’ measurement precision has been evaluated.

A PPE measurement cell and a combined PPE and PTR measurement installation have been developed, using high accuracy optomechanic devices, precision piezomotors and high – stability lasers. Using measurement cells with known thermal parameters the mathematical model has been evaluated and validated. The proposed methods are able to return precise results if there is not any strong thermal mismatch among the layers of the measurement cell. The proposed methods have been used in order to measure the thermal parameters of some unknown liquids and solids. A self consistent methodology has been developed which allows the sequential measurement of both thermal parameters of a liquid layer using a five layer measurement cell.

Contents

Introduction

Photothermal techniques can be regarded as collection of methods used for nondestructive matter investigation. These techniques have been intensively developed in the last decades and nowadays they are used in the fields of material science, agricultural science, alimentary science, biochemical sciences and for fundamental research purposes. Photothermal calorimetry is mainly concerned with the measurement of the thermal properties: specific heat, thermal conductivity, thermal diffusivity and thermal effusivity and by observing the changes of these properties, it can be used to qualitatively and quantitatively evaluate matter states and changes. Thus, this type of calormetry have been largely used in the past for state transition evaluation, namely for the transition characteristic temperature measurement.

This thesis is a result of the research activity I've been developed for the last three years at INCDTIM –Cluj, in the research group headed by Dadarlat Dorin. The main objective of this work was the development of a highly sensitive and accurate method for solid state matter investigation using a PPE and PTR calorimetriy. The main specific objectives of this thesis consisted in: i. the development of a new high precision calorimetric method for thermal characterization of liquid samples, ii. The development of a method that offers the possibility of the full thermal characterization of a liquid sample, iii. The development of a calorimetric method that provides the possibility of the measurement of the thermal properties of a solid intermediary layer, iv. The development of a calorimetric method based on the simultaneous use of a contact (PPE) and a noncontact (PTR) technique. In order to accomplish this thesis two activity reports have been programmed and presented, the first one entitled, Photothermal calorimetry and the second one entitled photothermal radiometry.

Photothermal calorimetric methods using the thermal wave resonant cavity concept, along with the thickness scanning procedure of an intermediary liquid layer (coupling liquid) has been chosen since this procedure provides the most accurate results. The activity concerning the aim of this thesis has been focused on developing an analytical model that describes well enough the behavior of the FPPE measurement configuration, using multilayered measurement cells and vice versa on developing measurement cells that can ensure the attainment of the desired measurement precision. The measurement cells have been developed in such manner that a spread domain of condensed state of materials can be covered (bulk solids, composite solids, thin solids and viscous liquids, volatile liquids, etc.).

As a result of the observed similarity of the behavior of the PPE signal's components and the reported behavior of the PTR signal's components, a measurement installation has been built that allows simultaneous measurement of the PPE and the PTR signal. The aim of this work was the study of the possibilities of simultaneous use of these two signals.

Considerable efforts have been made have been made in order to being able to use the full analytical expression of the normalized PPE and PTR signals (without making any assumptions regarding the thermal thickness of the layers composing the PPE measurement cells, this simplification technique having been reported many times in literature) for the purpose of extracting the unknown thermal properties. For this purpose I've accomplished a three months research stage at KU Leuven (Belgium), where I've learned the multicurve fitting method, using more than two fitting parameters. Since a fitting technique has been used in order to extract the unknown thermal parameters, a sensitivity study of the influence of the thermal parameters variation on the PPE components behavior has been made.

The thermal properties measurement is mainly important when one intends to make a database useful for future thermal installation design or for thermal diffusion simulation or when one is interested in designing a new material with controlled thermal properties. Since the thermal properties of a material are macroscopic parameters containing information about the intimate structure and composition of a material, these properties can be used to monitor the composition and the structure of a material, like molecular associativity, ionic bounds in liquids, the alteration of a substance caused by microwave exposure and so on.

The research methodology consisted in the development of the mathematical models for the two techniques' specific normalized signals. The construction of the measurement installations has been performed. Then measurements on known properties materials have been made and further on, less known thermal properties materials measurements have performed.

The present thesis is structured as most of the periodical publications specific to the material thermal properties measurement domain, in hope that this structure would make it more accessible. Thus the thesis has the following structure: i. Introductive notions, ii. Theoretical fundaments, iii. Experimental installations, iv. Personal contributions to the development of contact and noncontact photothermal calorimetry and v. Final discussions and conclusions. The last section of this thesis consists in bibliographical references mentioned along the thesis' content.

Chapter 1 has the aim to present a series of introductive notions regarding to the photothermal methods, with emphasis on the PPE and PTR techniques and on some particularities of these techniques. Also the main progresses reported in the literature, considered important for the present thesis are presented.

Chapter 2 has the aim to describing the phenomenology and the mathematical descriptions of the electromagnetic radiation absorption, heat generation and diffusion with a certain emphasis on the modulated heat diffusion in multilayered structures. Thus the thermal wave concept and the thermal wave resonant cavity concept are approached. Also the PPE and PTR signals generation principles are described.

Chapter 3 was intended to describe the PPE and coupled PPE and PTR installations built and used in order to obtain the experimental results. Also, details about the PPE measurement cells are presented.

Chapter 4 was intended to describe the results obtained. Two kinds of results have been obtained: i. theoretical results consisting in the theoretical model for the PPE normalized signal and its analysis made by means of the sensitivity coefficient behavior, the theoretical model for the PTR normalized signal and ii. experimental results obtained using the PPE method. Also the results obtained using the coupled PPE and PTR measurement installation are presented in this chapter.

Chapter 5 contains final discussions and the conclusions regarding the main results obtained during my doctoral studies.

Chp. 1 General notions

Photopyroelectric calorimetry and photothermal radiometry are both photothermal methods for nondestructive matter investigation. Photopyroelectric calorimetry measurement principle is based on the pyroelectric signal's sensitivity to a heat flow through it. Photothermal radiometry measurement principle is based on possibility of an object superficial temperature measurement by measuring the intensity of the thermal radiation emitted by a material's surface.

1.1. Photothermal methods

Interaction of electromagnetic radiation with matter is accompanied by a series of effects produced by the generated energy. Electromagnetic radiation interacts with the constituent particles of the substance and causes changes of its energetic states. Much of the energy absorbed is converted directly or indirectly (by means of nonradiative dezexcitation) into heat. The phenomena accompanying the absorption of electromagnetic radiation and its conversion into heat are called photothermal effects.

1.1.1. Photothermal effects

As a result of local heat generation the substance undergoes a series of changes: **i.** local temperature increase, **ii.** "black body" emission characteristic spectrum change, iii. refractive index of the fluid medium in the vicinity optical absorption change, **iv.** local deformation of the absorbing surface, **v.** production and propagation of mechanical pressure waves, in the optical absorption and in the adjacent fluid, **vi.** local variation of the refractive index of the absorbing environment. Photothermal techniques are in fact a collection of experimental methods that exploit precisely these changes caused by the absorption of light, in order to determine the substance properties (thermal, spectroscopic, geometric, and so on).

1.1.2. Photothermal methods

As a first classification, according to the phenomenon that resides at each's technique basis, photothermal methods can be divided into the following categories: **i**. PPE techniques, **ii.** PTR techniques (based on measurement of the characteristic black body spectrum emitted by the irradiated substance changes), **iii.** photoacoustic techniques, **iv.** techniques based on changing the refractive index of the irradiated environment, **v.** techniques based on the change of the environmental refractive index, **vi.** techniques based on local expansion of the irradiated surface

1.2. Photothermal calorimetry

PT calorimetry is a technique aimed to measure thermal properties of substance: **i.** volume specific heat, **ii.** thermal conductivity, **iii.** thermal diffusivity and **iv.** thermal effusivity. Particular attention was paid in the past to the thermal properties of the substance change during a phase transition.

1.2.1. Photopyroelectric calorimetry (PPE)

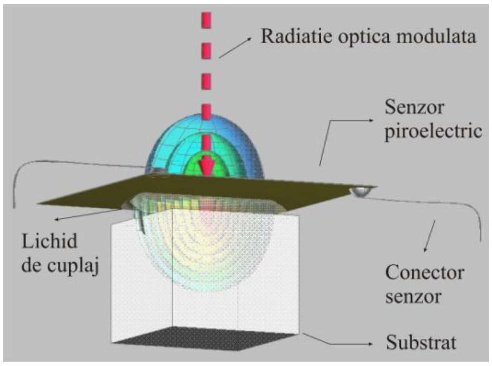

Fig. 1.1 – FPPE detection configuration

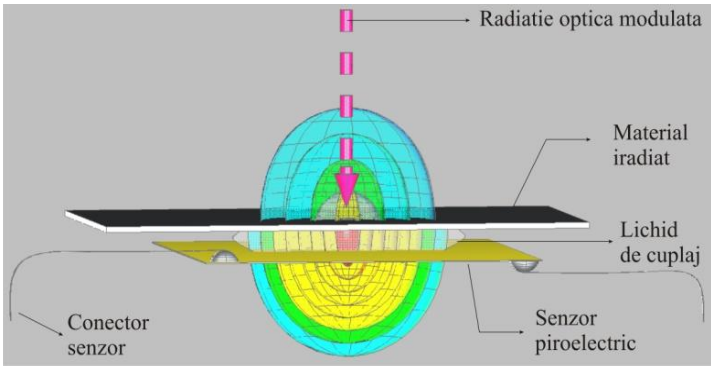

Fig. 1.2 –BPPE detection configuration

Photopyroelectric methods are based on measuring the heat flow caused by heat dissipation by means of a pyroelectric sensor. The pyroelectric sensor operation is based on the ability of a material to change its surface charge distribution when there is a temperature gradient along a specific crystal axis. In the literature various types of investigative PPE methods have been reported: i. measurement methods based on a temperature scanning procedure the, ii. measurement methods based on a radiation modulation frequency scanning procedure, iii. measurement methods based on a physical thickness of a liquid layer scanning procedure and iv. combined measurement methods (based both on a radiation modulation frequency scanning procedure and on a physical thickness of a liquid layer scanning procedure).Generally, two types of PPE detection configurations can be identified: **i.** Front PhotoPyroElectric (FPPE) measurement configuration, schematically illustrated in Fig.1.1 and characterized by the fact that the optical absorber layer is the directly shined pyroelectric sensor and **ii.** Back PhotoPyroElectric (BPPE) measurement configuration illustrated schematically in Fig. 1.2 and characterized by the fact that the optical radiation is absorbed by an opaque solid layer and the sensor located at a lower level receives a fraction of the generated heat.

1.2.2. Photothermal radiometry

The PTR technique measurement principle assumes the collection of most of the specific black body thermal radiation emitted by an object's surface with a non-zero temperature. The collected thermal radiation is then focused on the surface of a sensor with a suitable characteristic spectral sensitivity. Depending on the relative arrangement of the shined surface and the thermal radiation emitting surface, there are two types of PTR detection configurations: Back Propagation PTR detection configuration (BPPTR) , represented in Fig.1.3 that involves collecting specific black body radiation emitted by the shined surface and ii. Transmission PTR detection configuration (TPTR), represented in Fig.1.4, that involves collecting specific black body radiation emitted by the surface opposite to the shining point. Configuration detection BPPTR detection configuration is suited for a wide range of physical systems investigation.

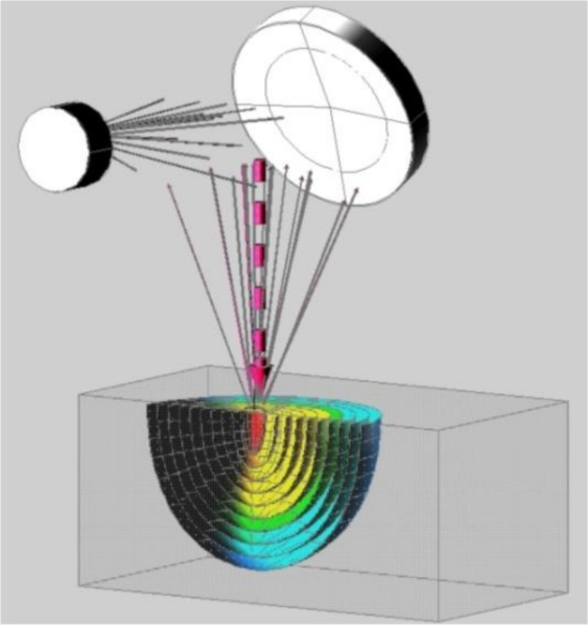

Fig. 1.3 – Back Propagation PTR detection configuration.

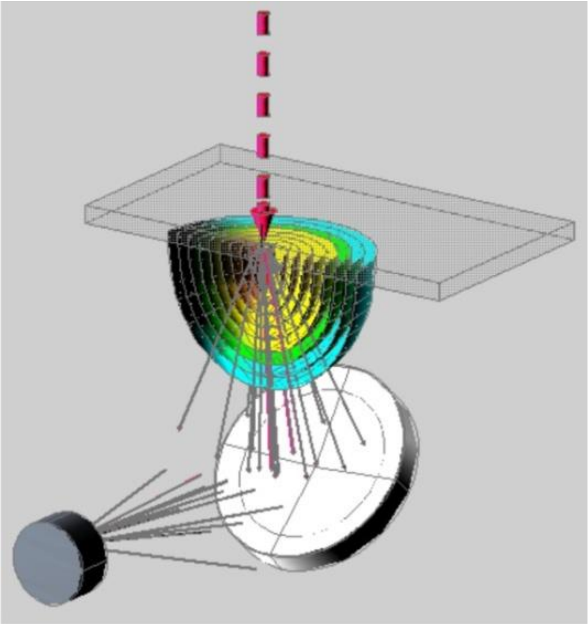

Fig. 1.4 –Transmission PTR detection configuration.

Chp. 2 The main experimental results

2.1. The self consistent method

The self-consistent measurement method allows both thermal effusivity and diffusivity measurement of a liquid [1]. The investigated liquid is inserted successively in backing and in coupling fluid’s position, alternatively with another liquid with well known thermal properties. When inserted in the backing position a scan of the phase of the FPPE signal as a function of coupling fluid’s thickness leads to the direct measurement of liquid’s thermal effusivity. Inserting then the investigated liquid in coupling fluid’s position (the backing is in this case the known liquid), a similar thickness scan leads to the measurement of its thermal diffusivity. The remaining thermal parameters can be then derived by calculation. Typical results for the normalized phase of the PPE signal for a detection cell containing water as coupling fluid and various liquids in the backing position are presented in figure 2.1, together with the best fits. The fit was performed with two fitting parameters: coupling fluid’s absolute thickness and backing’s thermal effusivity.

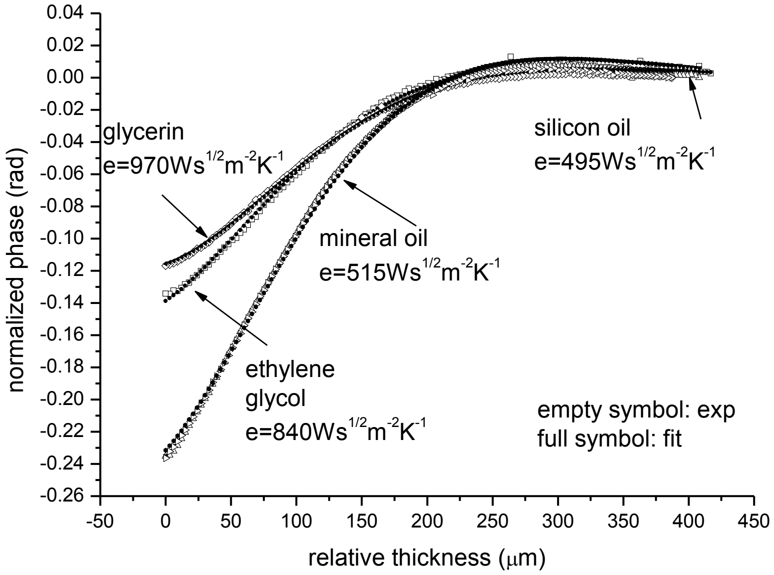

Fig. 2.1 - Normalized phases of the PPE signal for a detection cell containing water as coupling fluid and various liquids in the backing position, along with their best fits.

Figure 2.2 displays a similar graph but, in this case, water was the liquid in the backing position, and the investigated liquids played the role of coupling fluid. As presented in the theoretical section, in such a case the phase of the signal depends on both thermal effusivity and diffusivity of the coupling fluid; having the value of the thermal effusivity from the previous measurement, one can obtain the value of coupling fluid's thermal diffusivity by performing a fit with coupling fluid's absolute thickness and its thermal diffusivity as fitting parameters.

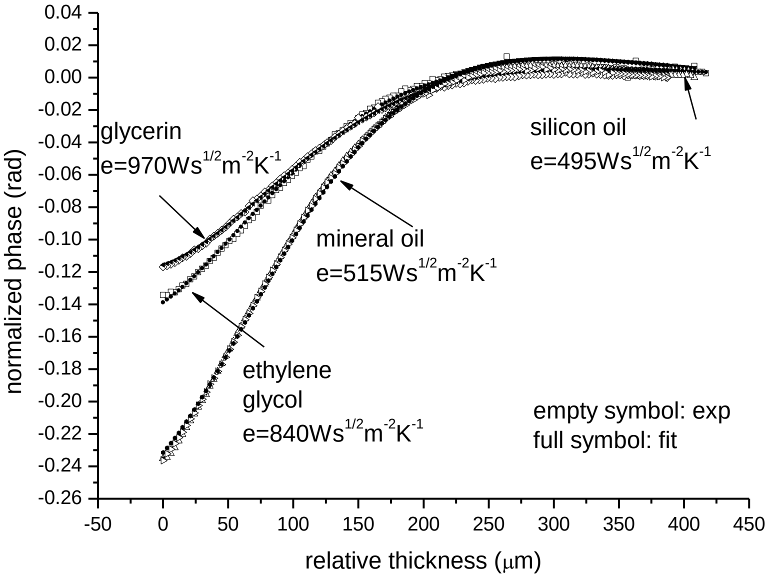

Fig. 2.2 - Normalized phases of the PPE signal for a detection cell containing water in the backing position, and the investigated liquids as coupling fluids.

Fig 2.3 presents for comparison the results (thermal diffusivity and effusivity) obtained with the method proposed in this paper together with literature data.

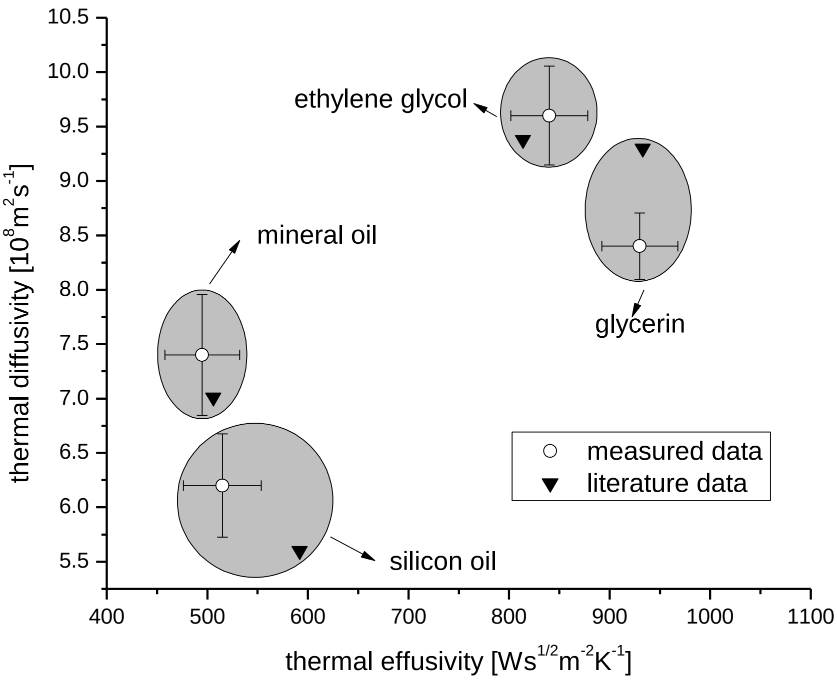

Fig. 2.2 – Thermal properties of the investigated solids compared with the literature values.

4.3. PPE calorimetry results obtained for condensed matter investigation

Massive solid materials (bulk) can be arranged as substrate in a four layered measurement cell. The experimental data was used in order to extract the thermal efusivity of the investigated material. Solid samples can be measured in this way, like raw materials, homogeneous metals, amorphous substances, etc. By means of a five layered measurement cell configuration, the thermal effusivity of pressed powders can be measured, placed in a backing position and being isolated from physical contact with fluid coupling through separator layer. Also, thin solids (on average hundreds of micrometers thick) can be placed as a separator layer in five layers measurement cell, thus the thermal diffusivity or effusivity becoming measurable.

Liquid samples, can be arranged as substrate in a five layered measurement cell thus the thermal effusivity can be measured. Since in this configuration the liquid is introduced into a designed device intended for stable liquid containment, the range of possible liquid samples becomes very wide and the measurement precision results very high.

4.3.1. PPE calorimetry applied to solid materials' investigation

In order to demonstrate the accuracy of the method for measuring the thermal effusivity of solids simple materials with known thermal properties (metals, glass, and so on) have been investigated. The obtained data was compared with those reported in the literature. Also thermal effusivity of solid dental materials prepared differently was measured and the thermal effusivity of pressed powders solid pills as a function of the applied pressure was investigated. Also the thermal diffusivity and effusivity of thin solid separator layers had been measured. Thermal diffusivity values obtained for thin solids investigated were compared with those in the literature. The proposed method was used consecutively for the characterization of a thermally thin layer obtained by electrolytic oxidation (anodization) of aluminum.

4.3.1.1. PPE calorimetry applied to pressed powders' investigation

Because some solid material of interest are in the form of powders, it was necessary to develop a PPE method for powders thermal properties measurement. The powers are generally composed of relatively complex substances or substances which cannot be obtained as a raw single crystal. Pressed powders pills obtained be introduced into a configuration as five layers, serving as substrate in order to measure their thermal effusivity. In order to being able to isolate the pill (in terms of mechanical and mass transfer) from the coupling fluid interaction, at first a fixed glass separating layer pressed on the pellet surface with a layer of silicone grease, was used. Thus, a composite substrate had been obtained.

A material that shows a growing interest for biophysics is hydroxyapatite, a crystalline material with chemical formula: $Ca_{10}(PO_4)_6(OH)_2$ present in bone tissue of mammals. This material can be deposited in thin layers on the surface of bone prostheses to ensure their biocompatibility. Thus, one aspect of biocompatibility refers to obtaining thermal properties of prostheses relatively close to the bone. For this, the knowledge of hydroxyapatite's thermal properties becomes a important.

In order to provide the possibility of making pellets over a wide range of pressure values, the hidroxyapatite powder was mixed with physiological paraffin in a concentration of 10%. In order to achieve high precision experimental results, measurements were made with two control parameters: frequency modulation of radiation (they used two of its values: 1 and 2 Hz) and the thickness of fluid coupling. Also, in order to increase the accuracy of the experimental results, the thermal effuzivity of the substrate was extracted by fitting both amplitude and phase normalized PPE signal. In Fig. 4.14, is the experimental PPE amplitude variation with its best fit for frequency f = 1 Hz and in Fig. 4.15 is the same component signal changes, the frequency f = 2Hz. In Fig. 4.16, is the variation in PPE experimental phase, together with its best fit for frequency f = 1 Hz and in Fig. 4.17 is the same component signal changes, the frequency f = 2Hz. Thermal effuzivity values and errors obtained for pills used as substrate are shown in Tab. 4.2.

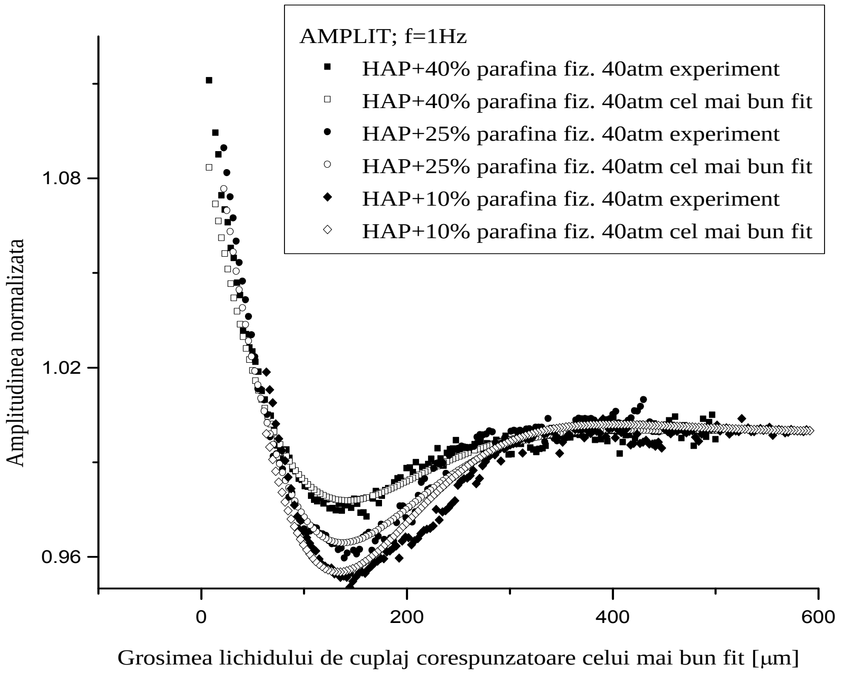

Fig. 4.14 – PPE normalized experimental amplitudes and their best fit, obtained for different HaP samples at 1Hz modulation frequency.

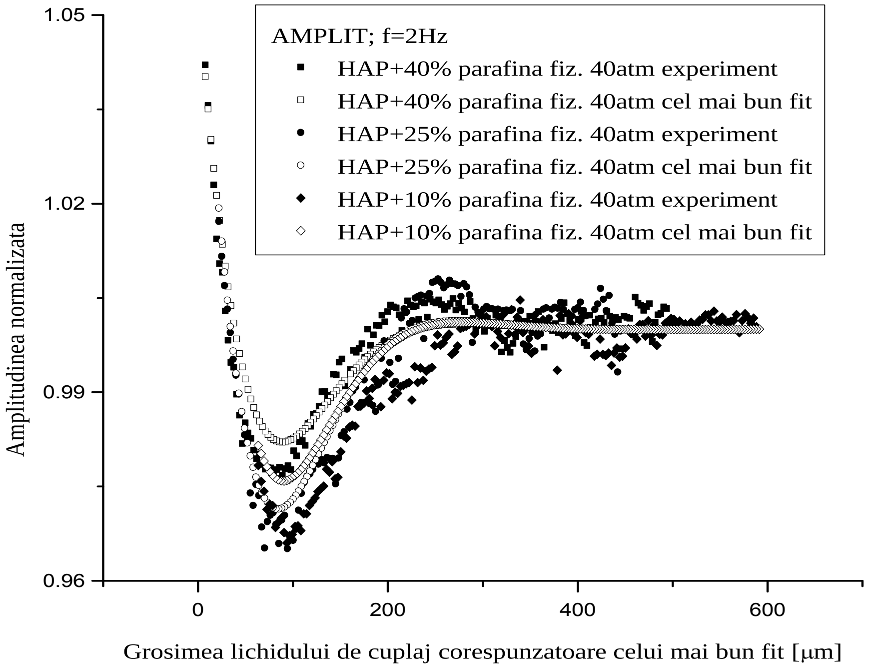

Fig. 4.15 – PPE normalized experimental amplitudes and their best fit, obtained for different HaP samples at 2Hz modulation frequency.

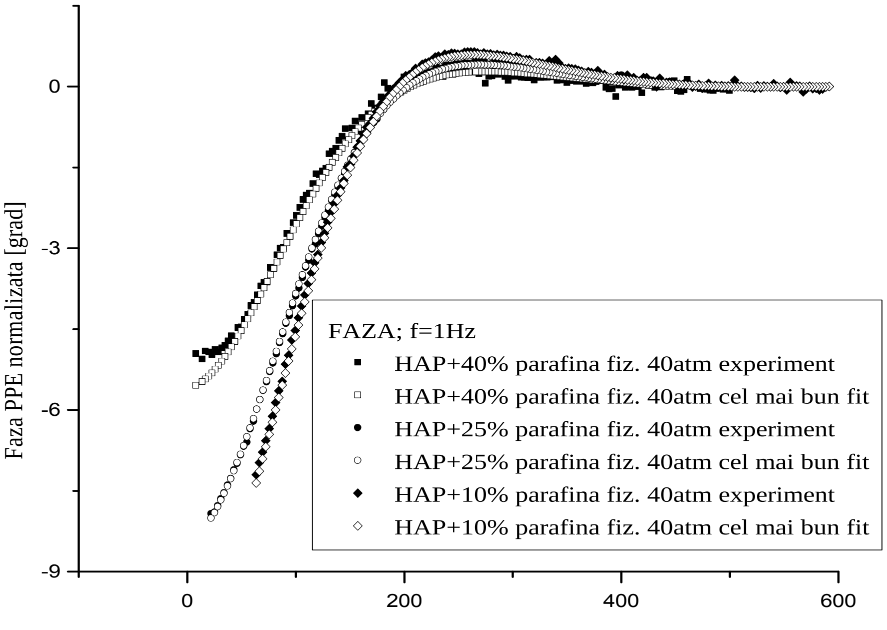

Fig. 4.16 – PPE normalized experimental phases and their best fit, obtained for different HaP samples at 1Hz modulation frequency.

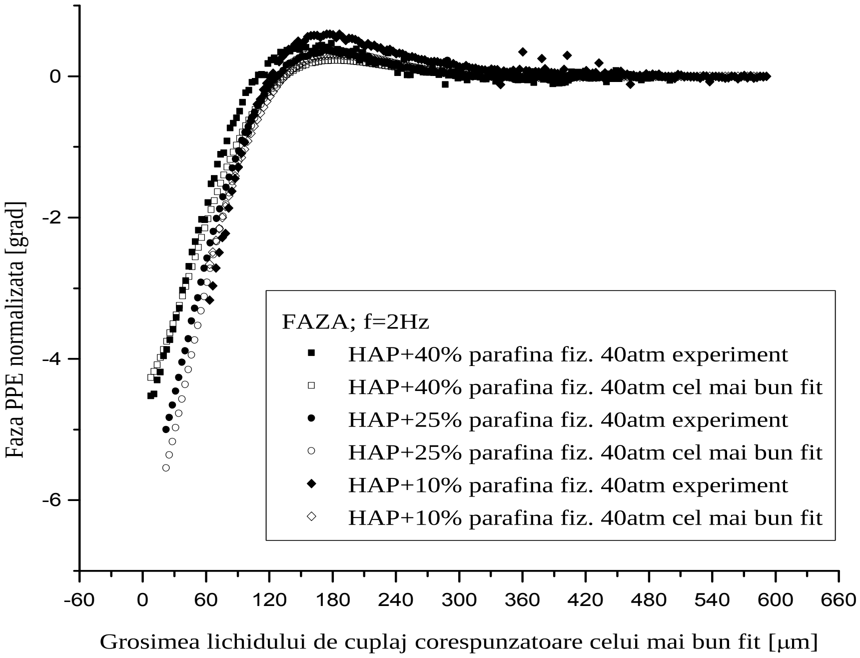

Fig. 4.17 – PPE normalized experimental phases and their best fit, obtained for different HaP samples at 1Hz modulation frequency.

Tab. 4.2 – Backing's thermal effusivity results obtained for different presure values used for powders pressing.

	p=10 atm (p=103.28 tonef/m^2)	p=25 atm (p=258.2 tonef /m^2)	p=40atm (p=413.1 tonef /m^2)
Efuzivitatea termică [Ws$^{1/2}$m^{-2}K^{-1}]	259.2(±1,5)	318.4(±3,2)	475.5(±4,5)

From Tab. 2 the pellets' effusivity increase as a function of applied pressure can be observed.

4.3.1.3. PPE calorimetry applied to thin solid investigation

In order to perform the experiment need for the thin solid separator layer, the coupling fluid and backing layer were the same liquid, ethylene glycol (e_2= 814Ws$^{1/2}$m^{-2}K^{-1}; α_2= 9.36x10^{-8}m^{2}s^{-1}). Several thin solid foils were used as separators between the coupling fluid and liquid backing. Their thickness and the value considered for thermal effusivity are listed in Table. 3.

Typical plots of the behaviour of the normalized phase of the FPPE signal as a function of relative thickness of the coupling fluid, for two different thin solid layers (good thermal conductor-150µm thick Al, and low thermal conductor-100µm thick glass) are displayed in Figs. Figs. 4.18 and 4.19. The chopping frequency of radiation was 1 Hz. Figs. 4.18 and 4.19 contain also the best fit of tthe experimental curves.

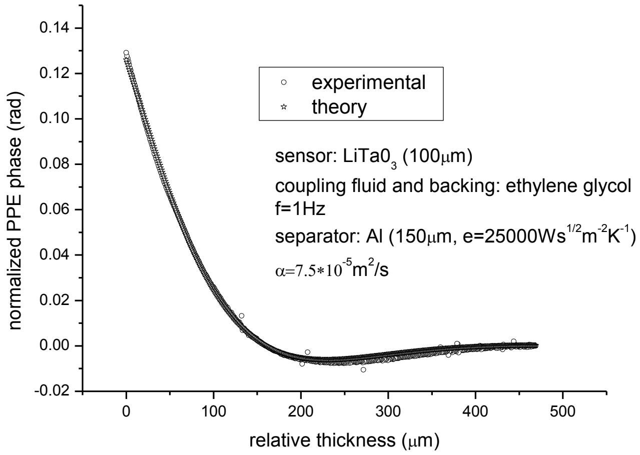

Figure 4.18. The experimental behaviour of the normalized FPPE phase as a function of coupling fluid's thickness, for a detection cell with 150µm thick Al foil as separator. The best theoretical fit is also displayed.

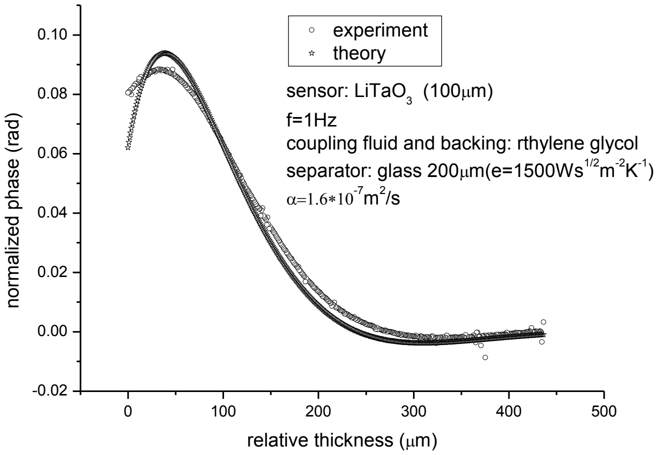

Figure 4.19 The experimental behaviour of the normalized FPPE phase as a function of coupling fluid's thickness, for a detection cell with 100µm thick glass foil as separator. The best theoretical fit is also displayed.

Table 2. Results obtained with FPPE-TWRC method for the thermal diffusivity of the investigated samples, together with results reported in the literature. Column 3 contains the values of the thermal effusivity used in the fitting procedure.

material	thickness (µm)	thermal effusivity [ref] ($Ws^{1/2}m^{-2}K^{-1}$)	thermal diffusivity x10^{-6} (m^2/s)	
			experiment	literature
Cu (alloy)	50	37000	61.4	32.9-117.3
Al (alloy)	150	25000	75.2	35.1-87.9
steel	80	7200	3.3	3.5-19.7
glass	200	1500	0.65	0.31-0.74

Concerning the accuracy of the method, as stated in previous papers [17, 22], for this type of investigations, it depends on the relative effusivity ratio solid layer/coupling fluid (backing layer).

The suitability of the method was demonstrated with investigations on several solids with different thicknesses (50-150µm) and values of thermal diffusivity (glass, steel, aluminium, copper). If we refer to the thicknesses of the investigated solids, they are not enough thin to be obtained by direct deposition on the pyroelectric sensor and not enough thick to be investigated by other PPE detection schemes. Consequently, in the authors' opinion, the method presented in this paper is a complementary one. No restriction is imposed to the optical properties of the investigated sample.

4.3.2.PPE calorimetry for liquid investigation

PPE measuring cell with five layers was used to measure thermal properties of liquids arranged as substrate [7]. Liquid substrate was composed of binary mixtures of water - ethylene glycol and water - ethanol and water - DMSO (dimethyl sulfoxide). Because specialized devices were made for liquid containment placed as substrate, thermal properties of solvents with high volatility (ether, chloroform, etc.) could be measured. Further on, the proposed method had been found suited for basil extracts effusivity measurement which has evidenced differences among the chemical composition of the extracts. Also, using these devices the measurement of highly corrosive chemicals was possible. Also differences between thermal properties of mixtures of water and salt at different measurement concentrations had been possible.

4.3.2.1. PPE calorimetry applied to fluid mixtures' investigation

Water – solvent liquid mixtures had been investigated in order to test the backing's thermal effusivity method's ability to detect the presence of molecular association phenomena.

In all experiments, the coupling fluid was water (e_2= 16.0x10^{2}Ws$^{1/2}$m^{-2}K^{-1}; α_2= 14.6x10^{-8}m^{2}s^{-1}) and binary mixtures of water with ethylene glycol, ethanol and DMSO, were inserted as backing materials. Several foils (glass, quartz, mica) were tested as separators between the coupling fluid and liquid backing. Finally we selected a 100μm thick glass foil (e_3= 15.0x10^{2}Ws$^{1/2}$m^{-2}K^{-1}; α_3= 8.3x10^{-7}m^{2}s^{-1}).

Typical results obtained for the phase of the FPPE signal for a detection cell with water as coupling fluid and water based binary mixtures with ethylene glycol, ethanol and DMSO respectively, are displayed in Figs. 4.20, 4.22, 4.24, and the corresponding dependence of the thermal effusivity as a function of binary mixture composition, in Figs. 4.21, 4.23, 4.25.

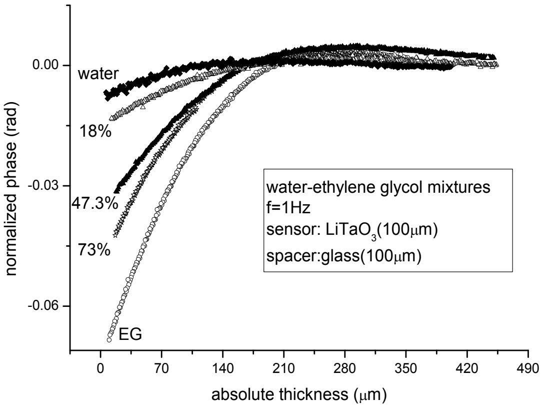

Fig. 4.20 – The experimental behaviour of the normalized FPPE phase as a function of coupling fluid's thickness, for water-ethylene glycol binary mixtures, inserted as backing.

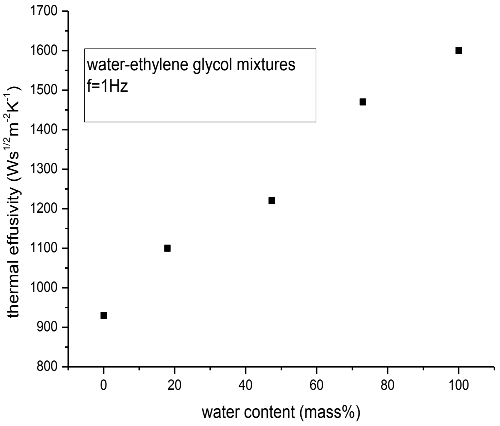

Fig. 4.21 – Room temperature values of thermal effusivity for different compositions of water-ethylene glycol mixtures.

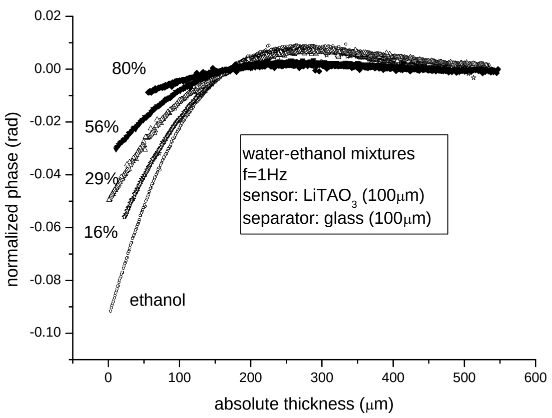

Fig. 4.22 – The experimental behavior of the normalized FPPE phase as a function of coupling fluid's thickness, for water-ethanol binary mixtures

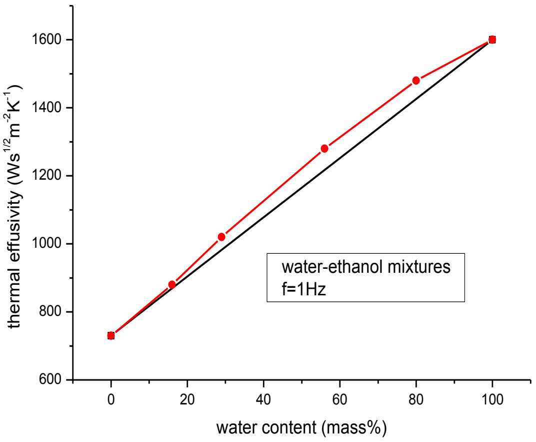

Fig. 4.23 – Room temperature values of thermal effusivity for different compositions of water-ethanol mixtures.

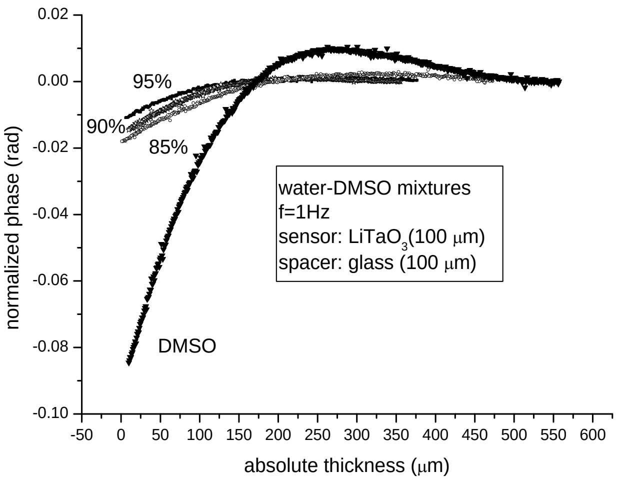

Fig. 4.24 – The experimental behavior of the normalized FPPE phase as a function of coupling fluid's thickness, for water-DMSO binary mixtures

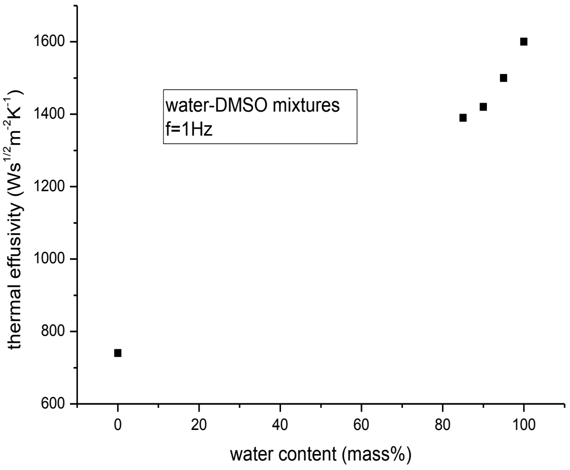

Fig. 4.25 – Room temperature values of thermal effusivity for different compositions of water-ethanol mixtures.

The behaviors of the thermal effusivity as a function of the mass composition for the investigated binary liquid mixtures are in good agreement with the results previously obtained with PPE and PA investigations – frequency scanning procedures. As reported before, if in the case of non-associative liquid mixtures (water-ethylene glycol for example) the additivity rule is respected (the thermal effusivity depends linearly on the mass composition of one component), for associative liquid mixtures (water-ethanol and water-DMSO), deviations from this additivity rule are observed.

4.3.2.4. PPE calorimetry for nanofluids' investigation

Nanofluids are a new class of fluids composed of a carrier fluid and nanometric size in suspension (colloidal) particles (nanoparticles, nanofibers, nanotubes, filaments, rods, sheets or drops), ideally stable over time. Nanofluidele SiO2 particles were prepared by mechanical mixing water and SiO2 nanoparticles in such aerosil ® 300, manufactured by Evonik Degussa Corporation, with the average size of 7nm. Nanofluid with nanoparticle mass concentrations of 1% and 3% in water were prepared at KU Leuven, were arranged as fluid coupling and a test facility with four layers: air - PZT sensor - fluid coupling - substrate metal. In the first sequence, we used water as the fluid coupling and made a fitting parameter fit right multicurve using thermal effuzivity substrate.

Conclusions

1. A mathematical model that assumes one-dimensional diffusion of thermal perturbations in a multilayer system has been developed. Two fitting methods that make use of the mathematical model can be applied:
   - i. A simple fitting algorithm applied to experimental data obtained by scanning of a single control parameter, thus enabling the extraction of the backing's thermal effusivity.
   - ii. A complex algorithm fitting algorithm applied to experimental data obtained by scanning of two control parameters, thus allowing the extraction of the thermal diffusivity and/or of the thermal effusivity of an intermediate layer of a five layer measurement cell.

2. The proposed method applied to extract a single thermal parameter was used to obtain:

i. the thermal effusivities of solid materials with known thermal properties, placed as a backing layer of a four layers measurement cell with

ii. the thermal diffusivity or the thermal effusivity or solids disposed as an intermediate layer of a five layered measurement cell

iii. the thermal effusivities of a backing layer in a five layered measurement cell

This measurement method returns thermal values of the thermal parameters close to those reported in the literature, if the measuring cell there is no strong thermal mismatch.
3. The proposed method was applied to investigate the backing layer of the measurement cell in order to:

- i. find the thermal effusivity of dental materials obtained by different methods and with different compositions. The proposed method revealed the difference in thermal effusivity of the investigated materials.
- ii. find the thermal effusivity of HAP pressed powder pellets at different pressure values. The proposed method revealed an increase of the pellets' thermal effusivities as the applied pressure increases, in accordance with reported results using a different PT technique.

iii. find the thermal effusivity of liquids mixtures. The proposed method revealed the molecular associative phenomena for mixtures of substances that exhibit this behavior.

iv. find the thermal effusivity of aqueous solutions of simple ionic substances. The proposed method revealed the difference among thermal effusivities of acidic aqueous solutions (water + HCl), of alkaline pH (water + NaOH) and of neutral pH (water + NaCl with various concentrations) and thus revealed the different influences of different ions on heat diffusion in the solutions investigated.

v. find the thermal effusivity of nanofluids with different concentrations of SiO2 nanoparticles and nanofluids with different concentrations of Au nanoparticles with different average sizes. In case of SiO2 based nanofluids, the proposed method revealed the thermal effusivity increased with increasing concentrations of nanoparticles.

vi. find the thermal effusivity of basil extracts obtained by different extraction methods in different solvents and mixtures thereof. The proposed method allowed the detection of compositional differences of the investigated solutions by observing differences between measured values of thermal effusivity.

4. The proposed method was applied to investigate the measuring cell separator layer and allowed measurement of its thermal diffusivity or of its thermal effusivity assuming that the other thermal property of the solid separator is known.

5. The proposed method was applied for the purpose of extracting both thermal parameters of SiO2 nanoparticles based nanofluid disposed as a coupling liquid in a four layer measurement cell.

6. A self- consistent method for both thermal parameters of a liquid sample has been developed.

7. A coupled PPE and PTR measurement installation has been built which allowed the simultaneous measurement of both signals corresponding to the same PPE measurement cell. The possibility of simultaneous usage of both signals for thermal properties measurement has been studied.

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