

BOOK OF ABSTRACTS

**2nd Conference on Photoacoustic and
Photothermal Theory and Applications**

23-26 September 2014, Warsaw (Poland)

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CONFERENCE PROGRAM

TUESDAY (23.09)	
13:30 – 14:10	Registration
14:10 – 14:30	Conference opening ceremony
14:30 – 15:30	Photothermal coherence tomographies: principles and imaging applications Andreas Mandelis (plenary speech)
15:30 – 16:00	Coffee break
16:00 – 16:20	Implementation of a non-uniform FFT combined with sparse grid sampling in photoacoustic image reconstruction J. Schmid
16:20 – 16:40	A new model for frequency-dependent attenuation in photoacoustic tomography C. Shi
16:40 – 17:20	Modulated temperature profiles in dielectric nanofilms predicted by the Boltzmann transport equation: microscopic description of photothermal phenomena J. Ordonez-Miranda (invited speech)

WEDNESDAY (24.09)	
9:00 – 10:00	Time and frequency domain photothermal experiments: how to determine thermal parameter from the lateral heat diffusion Danièle Fournier (keynote speech)
10:00 – 10:20	Coffee break
10:20 – 10:40	Photoacoustic signal of soil – preliminary analysis J. Szurkowski
10:40 – 11:00	Evaluation of a contact by sub-nanosecond laser ultrasonic technique N. Chigarev
11:00 – 11:20	Thermodynamic limits of spatial resolution in active thermography P. Burgholzer
11:20 – 11:40	Detection of carbon nanoparticles in suspension by a photothermal technique S. Sel
11:40 – 12:10	Coffee break
12:10 – 12:30	Feasibility of liver fibrosis detection in ex vivo samples using an open photoacoustic cell method S. Stolik
12:30 – 12:50	Dosimetric control in phototherapy using temperature measurements and thermal imaging F. Y. López-Silva
12:50 – 13:10	Multichannel detection of photoacoustic signals: preliminary results T. Starecki
13:10 – 13:30	Application of photothermal methods for quantification of carotenoids in apricot jams O. Dóka
13:30 – 14:30	Lunch
14:30 – 15:30	Acoustic aspects of photoacoustic signal generation and detection in gases András Miklós (plenary speech)
15:30 – 16:00	Coffee break
16:00 – 18:00	Poster session

THURSDAY (25.09)	
9:00 – 10:00	Mid-Infrared semiconductor laser based trace gas sensor technologies and applications Frank Tittel (keynote speech)
10:00 – 10:20	Coffee break
10:20 – 10:40	Optoacoustic inspection of thin oil-contaminated liquid films at low energy deposits S. V. Egerev
10:40 – 11:00	Development of automated and continuous protocol for the noninvasive monitoring of liquid sample based on continuous-wave photoacoustic technique S. Camou
11:00 – 11:20	Nested cavity optical parametric oscillator in the 3.0 – 3.8 μm range for quartz enhanced photoacoustic spectroscopy G. Aoust
11:20 – 11:40	Open photoacoustic cell technique: noise analysis in frequency domain D. D. Markushev
11:40 – 12:10	Coffee break
12:10 – 12:30	Photothermal conversion of color centers in CaF_2 crystals: a process underlying use of the crystals as holographic medium A. E. Angervaks
12:30 – 12:50	Comparison of the photoacoustic effect in the IR and the UV region T. Preukschat
12:50 – 13:10	An alternative calorimetry based on the photothermoelectric (PTE) effect: application to magnetic nanofluids D. Dadarlat
13:10 – 13:30	TLM thermal modelling Z. Suszyński
13:30 – 14:30	Lunch
14:30 – 15:30	
15:30 – 21:30	City tour and gala dinner

FRIDAY (26.09)	
9:00 – 10:00	Optical and photothermal characterization of micro and nanocomposites and smart materials Juan José Alvarado-Gil (plenary speech)
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10:20 – 10:40	Quantitative thermal measurement by the use of scanning thermal microscopy J. Juszczuk
10:40 – 11:00	Thermal interface conductance of copper layers on carbon and correlation with mechanical adhesion strength J. Pelzl
11:00 – 11:20	Characterization of the O^{+6} ion implanted silicon layers using plasma waves and C-V techniques M. Maliński
11:20 – 11:50	Coffee break
11:50 – 12:10	Discussion on optimal coupling medium and its thickness in photopyroelectric calorimetry K. Strzałkowski
12:10 – 12:30	The thermal diffusivity of ZnS_xSe_{1-x} crystals as a function of composition D. Trefon-Radziejewska
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PREFACE

Intensive development of photoacoustic and photothermal techniques in the past decades has led them no longer being considered just as research topics, but as practical and unique measuring tools. The Conference on Photoacoustic and Photothermal Theory and Applications (CPPTA) has been planned to be a venue where scientists and engineers who deal with photoacoustic or photothermal techniques can share their experiences and ideas. Its scope covers virtually all the aspects of photoacoustic, photothermal and related research, including theory, instrumentation and a wide range of applications:

- theoretical considerations,
- instrumentation and methodology,
- spectroscopy, applications in chemistry,
- sensors, actuators and industrial applications (including environmental sensors, generation of ultrasound, etc.),
- applications in medicine, biology and agriculture,
- imaging (including thermography, tomography, microscopy, depth profiling, etc.),
- ultrafast, micro/nanoscale and nonlinear phenomena,
- thermophysics (including characterization of materials),
- other aspects and applications of PA / PT techniques.

The first CPPTA was organized in 2013 and showed relatively strong interest of many researchers from all over the world. Number of abstracts submitted for the 2nd CPPTA was very similar (over 60 works by over 170 authors were accepted for oral and poster presentations). We hope that these numbers will increase in the future. We strongly encourage young researchers to participate in the CPPTA conferences. They will have the opportunity not only to present the results of their research, but most of all, to learn about the latest discoveries and trends, meet the world's experts in the fields of PA / PT, and listen to speeches, during which top international scientists will summarize their experiences and talk about new ideas and perspectives of further development in the PA and PT fields.

Finally, I greatly appreciate very warm reception and a lot of support and valuable advices that I received from the participants of the first CPPTA conference. It was a great reward for our efforts and strong motivation to our work on further improvements.

Tomasz Starecki

(Conference Chair)

KEYNOTE SPEECHES

Time and frequency domain photothermal experiments: how to determine thermal parameter from the lateral heat diffusion

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In this tutorial, we introduce the photothermal experiments in both time and in frequency domains and we discuss the thermal parameters which can be deduced from experimental data. It is straightforward that multiparameter fitting of the experimental data can help to extract thermal parameters but here we want to present a “hand waving” physical approach of these experiments in order to help the “novice” to use the good geometry and the good modulation range.

In a photothermal experiment, the sample is illuminated with a pump beam which is partially or totally absorbed at its surface. The light energy deposited in the sample is converted into heat which then diffuses in the sample. The consequent temperature field is strongly dependent upon the modulation frequency or the investigated time domain, upon the dimension of the heat source, of the dimension of the sample and upon its thermal properties. A thermal diffusion length associated to the modulation frequency or to the investigated time domain has to be compared to the pump beam diameter and to the dimensions of the sample. When the heat source is almost uniform on the whole surface of the sample, heat diffusion is perpendicular to the surface while if the heat source is small compared to the lateral dimensions of the sample, heat diffusion is both parallel and perpendicular to the surface. In the first case the 1D heat diffusion equation has to be solved, while in the second case the heat diffusion equation has to be solved under cylindrical symmetry. For the usual frequency modulation and time domain ranges, the sample may be considered or not as infinite for the lateral and the perpendicular heat diffusion.

For a semi infinite bulk sample, we will underline that a 1D experiment leads to the thermal effusivity of the sample if both input heat flux and absolute value of the modulated temperature can be measured, while lateral diffusion easily allows the determination of the thermal diffusivity of the sample without absolute measurements. If the sample thickness is in the range of the thermal diffusion length, additional thermal parameters can be measured thanks to the reflection on the back.

Moreover the interesting case of layered structure has to be considered. At each interface heat is transmitted and reflected and different regimes associated with the thermal parameters of the layers and substrate can be described. For example, heat is confined in the upper layer if it is a better conductor than the substrate, or, contrarily, heat diffuses mainly in the substrate in the reverse case.

We will discuss the different geometries in the frequency domain and in the time domain and enhance the thermal parameters pertinence determination.

Finally we will compare the various experimental setups able to measure the surface temperature field and present experimental results.

Mid-Infrared semiconductor laser based trace gas sensor technologies and applications

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This talk will focus on recent advances in the development of sensors based on mid- infrared semiconductor lasers for the detection, quantification and monitoring of trace gas species and their application in atmospheric chemistry, medical diagnostics, and industrial process control as well as for use in security and defense systems. The development of compact trace gas sensors, in particular based on quantum cascade lasers (QCLs) and interband cascade lasers (ICLs) will be described. Such sensors permit the targeting of strong fundamental rotational-vibrational transitions located between 3 and 11 μm which are one to two orders of magnitude more intense than overtone transitions in the near infrared.

Trace gas optical spectroscopic sensors based on quartz enhanced photoacoustic spectroscopy (QEPAS) using either continuous wave (CW), distributed feedback (DFB) QCLs or ICLs as an excitation source will be described. QEPAS based sensor systems can achieve real time, ultra-sensitive detection of trace gas molecular species at concentration levels from the per cent level down to parts per trillion (pptv). Specifically, the spectroscopic detection and monitoring of five molecular species, such as carbon monoxide (CO), nitric oxide (NO), sulfur dioxide (SO₂), methane (CH₄) and nitrous oxide (N₂O) will be described. These molecules were detected using QEPAS based sensors, which can achieve minimum detectable absorption losses in the range from 10^{-8} to 10^{-11} cm^{-1}/Hz .

For example, a QEPAS-based sensor capable of ppbv level detection of CO, a major air pollutant will also be described. For this sensor a 4.61 μm high power CW DFB QCL that emits a maximum optical power of more than 1 W was used. A minimum detection limit (MDL) of 2 ppbv was achieved at atmospheric pressure with a 1 s acquisition time for the R6 CO line, located at 2169.2 cm^{-1} . Furthermore, the performance of 5.26 μm and 7.24 μm CW TEC DFB-QCL (mounted in a high heat load (HHL) package)-based QEPAS sensors for atmospheric NO and SO₂ detection will be reported. MDLs (1σ) of 3 ppb and 100 ppb were achieved for a sampling time of 1 s using interference-free NO and SO₂ absorption lines located at 1900.08 cm^{-1} and 1380.94 cm^{-1} , respectively [1,2]. For the targeted CH₄ and N₂O lines located at 1275.04 cm^{-1} and 1275.49 cm^{-1} MDLs of 13 ppbv and 6 ppbw were achieved [3]. Recent developments of a novel 5.26 μm intra-cavity QEPAS based NO sensor and a QEPAS sensor operating in the THz range, employing a custom-made quartz-tuning fork and a 76.3 μm CW THz quantum cascade laser will be also described.

- [1] Rice University Laser Science Group website: <http://ece.rice.edu/lasersci/>
- [2] P. Patimisco, G. Scamarcio, F. K. Tittel, V. Spagnolo, *Sensors* **14**, 6165 (2014)
- [3] M. Jahjah, W. Ren, P. Stefanski, R. Lewicki, J. Zhang, W. Jiang, J. Tarka, F. K. Tittel, *Analyst* **139**, 2065 (2014)

PLENARY / INVITED TALKS

Photothermal coherence tomographies: principles and imaging applications

A. Mandelis 

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Energy transport in diffusion-wave fields is gradient driven and therefore diffuse, yielding *depth-integrated* responses with poor axial resolution. Traditional diffusion-wave techniques, limited by the physics of parabolic diffusion, can only produce depth-integrated planar images as they are unable to generate three-dimensional subsurface imaging. This talk will present two new imaging methods developed in the CADIFT for enabling parabolic thermal-wave fields to exhibit energy localization akin to propagating hyperbolic wave-fields. This approach when used with a mid-IR camera results in *depth-selective* (or depth-resolved) photothermal imaging which not only improves axial and depth resolution, but also allows for deconvolution of individual responses of superposed axially discrete sources, opening a new field of subsurface Photothermal Coherence Tomographies (PCT) using thermal waves. In this talk I will present two novel thermal-wave imaging methodologies: pulse-compression, matched filter thermal-wave radar (TWR) and truncated-correlation photothermal coherence tomography (TC-PCT). The physical principles of these methodologies and examples of imaging applications to engineering materials and hard biotissues will be discussed.

Optical and photothermal characterization of micro and nanocomposites and smart materials

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One of the greatest challenges in materials science is to devise materials which physical properties can be controlled by the designer or final user. In the case of the thermal properties,

applications of those materials are numerous in the development of heat exchangers and smart windows in a variety of applications. Polymers, liquids and semisolids have the advantage that they can fit the form of specific objects; however those materials generally have low thermal conductivity. One of the modes of increasing the thermal conductivity is to add high conductivity particles to the fluid matrix. However, frequently the new composite material exhibits a much lower thermal conductivity than the expected using simplistic approaches. Heat transport in composite materials is a complex problem involving multiple effects related with the sizes, aspect ratio and orientation of the particles, formation of chains structures and thermal interface resistance among the matrix and the particles. In this presentation, we explore several of these possibilities showing the effects of the involved parameters in diverse systems. Particularly, the study of physical properties of smart materials, based on magnetic fluids, is presented. In this case electrical, mechanical, optical and thermal properties can be modulated in a wide range at will using an external magnetic field. It is shown that non-ferromagnetic particles can be manipulated, when they are immerse in the magnetic fluid, in response to magnetic field. Measurements of optical and thermal properties of composite materials of magnetic fluids with added carbon nanotubes and nanofibers of various sizes are presented. Results show that the increasing of magnetic particles concentration in nanofluids increases heat transfer, which can be enhanced by the use of carbon nanostructures, and that it can be made to grow even more when the structure is oriented using magnetic fields. The evolution of the optical properties of the smart fluids, induced by the magnetic orientation, is presented too. Similarly, results for the thermoelastic vibration changes, induced by magnetic field, of elastomers with charge of microparticles are presented.

Acoustic aspects of photoacoustic signal generation and detection in gases

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In this paper photoacoustic signal generation and detection in gases is investigated and discussed from the standpoint of acoustics. Three topics are considered: the effect of the intensity distribution and time profile of the light on sound generation; the effect of the acoustic properties of a resonant photoacoustic (PA) cell on the photoacoustic signal; and the effect of the microphone on the photoacoustic signal due to acoustic interaction of the PA cell and the microphone.

When light is absorbed by a molecule and the excess energy is relaxed by collisions with the surrounding molecules the average kinetic energy, thus also the temperature of an ensemble of molecules (called “particle” in acoustics) will increase. In the case of inhomogeneous light intensity distribution the average velocity of molecules in the ensemble (“particle velocity”), which is zero in thermal equilibrium, will be nonzero. It means that the temperature and the velocity of the “particle” can increase simultaneously. Thus, two sound generation mechanisms coexist; the first one depends on the time derivative of the released heat power density, while the second one is proportional with

the gradient of the heat power density. Although this second effect is known in acoustics, it is not taken into account in the publications of the theory of photoacoustic signal generation up to date. However, this second mechanism is strongly dependent on beam geometry and may be responsible for already observed PA signal dependence on beam geometry.

Photoacoustic signal is mostly detected in a photoacoustic detector composed by acoustic resonators, buffers, filters, etc. It is not easy to interpret the measured PA signal in such a complicated acoustic system. Three problems are discussed: the effect of the resonator on PA signal amplitude and phase; the effect of PA signal generated outside the resonator (in filters, buffers), at the windows and generated by reflected and/or scattered light; and the reduction of external noise and flow noise. Moreover, the acoustic response of a PA detector to different kind of excitations (modulated cw, pulsed, periodic pulse train) will also be discussed.

The microphone for detecting the PA signal is also a part of the acoustic system; its properties have to be taken into account by the design of a PA detector. The moving membrane of the microphone absorbs acoustic energy; thus it may influence the resonance frequency and amplification of the acoustic resonator. This property may be very important by PA cells equipped with several microphones. On the other hand, microphones have a mechanical resonance, which may be utilized for increasing the sensitivity of the PA detector. Since the PA resonator and the microphone with its connecting tube form a coupled acoustic system, this system can be optimized for sensitivity. A few examples of PA detector designs will also be shown in the presentation.

Modulated temperature profiles in dielectric nanofilms predicted by the Boltzmann transport equation: microscopic description of photothermal phenomena

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The blossoming of nanotechnology involving the miniaturization of devices with enhanced rates of operation requires a profound understanding of their thermal performance. This is particularly critical in nanomaterials, in which the heat transport is not described necessarily by the Fourier's law of heat conduction.

In this talk, a nonlocal and microscopic theory for heat conduction across dielectric nanofilms under high frequency temperature fields is presented and applied to explain the reduction of their thermal conductivity observed in recent experiments. This theory is a novel and analytical solution of the Boltzmann transport equation for phonons in a dielectric film subjected to periodic heating on its surface. By considering that the mean free path (MFP) and mean free time (MFT) of phonons are

independent of the temperature and of the phonon frequency, explicit expressions for the temperature and the heat flux are derived and analyzed as a function of the film thickness and modulation frequency. It is shown that: 1) when the thickness of the film is much greater than the mean free path, the amplitude and phase of the temperature profile exhibit the typical behavior predicted by the Fourier's law. By contrast, when this thickness is comparable to or smaller than the MFP, these signals show non-Fourier oscillations, which become stronger as the film thickness is scaled down. This is described as the "dance" of phonons at the rhythm of the "music" of the modulated thermal excitation. 2) The diffusion length is still a meaningful concept in the ballistic regime and its value is given by $\mu = \sqrt{2l/3\omega\tau}$, where l and τ are the phonon MFP and MFP respectively, and ω is the modulation frequency.

Our theory facilitates the understanding of heat conduction for frequencies up to THz, and it could be used as the theoretical model to perform the microscopic characterization of nanofilms, through the determination of the MFP and MFT of phonons.

THEORETICAL CONSIDERATIONS

Comparison of the photoacoustic effect in the IR and the UV region

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The photoacoustic effect has been studied intensively using light sources emitting in the IR region. Corresponding photons lead to excitations of vibrational-rotational energy levels. Subsequent deexcitations by collisions with the surrounding molecules can increase the translational energy of these molecules. Consequently, by irradiating a gas sample with amplitude- or wavelength-modulated light, an acoustic wave can be created and recorded by means of microphones.

In case of light absorption in the UV region, however, the photon energy is too large for the before-mentioned transitions. Instead, photon absorption can induce electronic transitions or even molecule dissociation. While experiments reveal that these effects lead to a photoacoustic signal as well, investigations handling its reason were hardly published so far.

By means of a 266 nm UV laser and an IR OPO setup, respectively, photoacoustic measurements were carried out with a nitrogen-acetone gas mixture. In this presentation, both measurements are compared with each other and the fundamental processes of photoacoustic signal production in the UV region are discussed.

TLM thermal modelling

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The paper presents a method of modelling of dynamic thermal processes in homogeneous and thermally anisotropic solids. Proposed transmission line matrix models based on the electro-thermal

analogy for constant and harmonic excitation. It may be used for both analytical and numerical analysis of 1D multilayered structures and discrete models of 2D and 3D problems. Thermal circuits based on complex admittance elements and current sources are analyzed with admittance matrix method. For axially-symmetrical objects and excitations the very effective cylindrical model is presented. All models may be used for temperature fields analyzing in frequency and time domain. Examples of calculating are presented.

A new model for frequency-dependent attenuation in photoacoustic tomography

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Photoacoustic imaging is a promising imaging method that visualize biological material parameters. In a typical PAT session, the object is exposed to a short pulse of an electromagnetic wave. The object absorbs a fraction of the induced energy, heats up, and reacts with thermo-elastic expansion. This in turn produces acoustic waves, which can be recorded. The final image can show some internal structures. The mathematical formulation of PAT is an inverse problem related to the wave equation – to reconstruct the source term of the wave equation from measurements on the observation surface. PAT combines the high resolution of ultrasound waves and high contrast of EM waves. The challenge problems in this topic are to model the attenuation and to compensate its effect in image reconstruction.


The classical formulations of PAT ignores the attenuation effect within the object, which will lead to inaccurate images. To correctly model the attenuation effect in a given media, we need to investigate the relation between attenuation, dispersion, and causality. We have proved that the ill-posedness of PAT problem will increase greatly when taking into account attenuation [1]. It is known that attenuation and dispersion are connected by the Kramers-Kronig relationship. Some attenuation models are known to us, and most of them are derived from the measured power law between attenuation and frequency, but in some parameter range they don't satisfy causality. In 2011 Kowar et al. [2] proposed a new causality model in a much wider range, but it is very complicated to analyze its properties.

In this presentation, we give a new attenuation model that is causal, and approximates the power law at low frequencies. The causality of this model is proved by a simple argument. The form of this model is similar to the classical power law, but it permits the exponent to be greater than 1 without affecting causality.

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[2] R. Kowar, O. Scherzer, X. Bonnefond, Math. Methods Appl. Sci. **34**, 108 (2011)

Quantitative photoacoustic tomography with piecewise constant material parameters

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The goal of quantitative photoacoustic tomography is the determination of optical and acoustical material properties from initial pressure maps as obtained, for instance, from photoacoustic imaging. The most relevant parameters are absorption, diffusion and Grüneisen coefficients, all of which can be heterogeneous. Recent work by Bal and Ren shows that in general, unique reconstruction of all three parameters is impossible, even if multiple measurements of the initial pressure (corresponding to different laser excitation directions at a single wavelength) are available.

We propose a restriction to piecewise constant material parameters to overcome this non-uniqueness. We showed that in the diffusion approximation of light transfer, piecewise constant absorption, diffusion and Grüneisen coefficients can be recovered uniquely from photoacoustic measurements at a single wavelength. In addition, we developed a numerical scheme to recover heterogeneous material parameters from initial pressure measurements and tested it on simulated data.

[1] G. Bal, K. Ren, *Inverse Probl.* **27**, 075003 (2012)

[2] W. Naetar, O. Scherzer, “Quantitative photoacoustic tomography with piecewise constant material parameters” (preprint available at: <http://arxiv.org/abs/1403.2620>)

Implementation of a non-uniform FFT combined with sparse grid sampling in photoacoustic image reconstruction

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Photoacoustic tomography (PAT) is an imaging modality where tissue is illuminated by a short (~ns) laser pulse. The ensuing pressure wave is then recorded by an array of sensors. To obtain the initial pressure from the collected data on a planar sensor arrangement, there exists an exact analytic frequency domain reconstruction formula.

In this work we investigate the application of a non-uniform fast Fourier transform (NUFFT) for numerical image reconstruction. This is done computationally and with data acquired via a Fabry-

Pérot interferometer planar sensor. We use non-uniform grids with the goal to reduce the necessary number of acquisition points. This approach can be used to tackle the limited view problem and to sidestep sensor points with a low sensitivity. Additionally we apply the NUFFT reconstruction to regularly sampled grids. The results are compared with conventional FFT reconstruction methods.

Thermodynamic limits of spatial resolution in active thermography

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Thermal waves are very dispersive: their amplitude is decreased by more than a factor of 500 within a propagation distance of one wavelength [1]. The diffusion equation, which describes the temperature as a function of space and time (“diffusion-wave fields” [2]), is linear. Therefore the superposition law, also known as Huygens principle for optical or mechanical wave fields, is valid and limits the spatial resolution, like the Abbe diffraction limit in optics. The resolution is the minimal size of a structure which can be detected at a certain depth. It is proportional to the depth and indirect proportional to the logarithm of the signal-to-noise-ratio (SNR) of the thermographic detection system (see Fig. 1 for pulsed thermography).

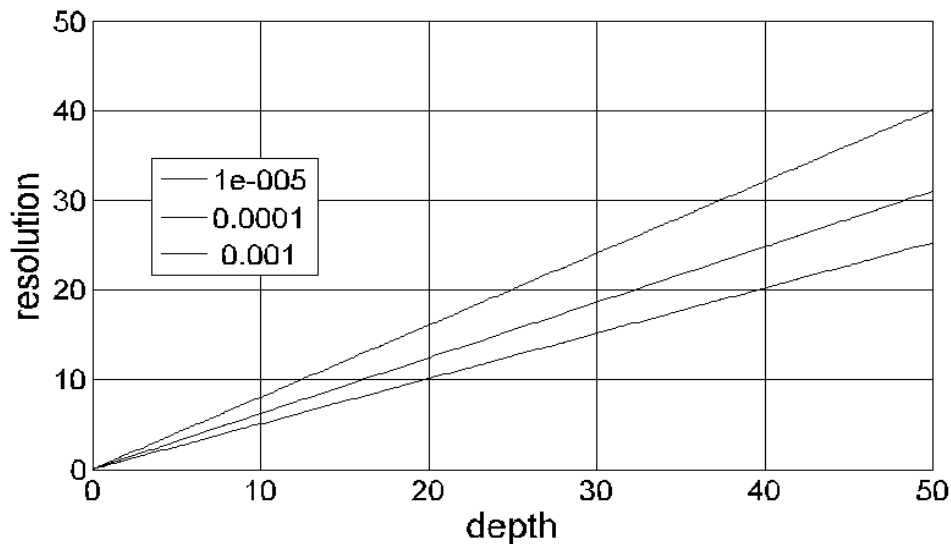


Fig. 1. Resolution for pulsed thermography as a function of depth for different SNRs.


To get the resolution in Fig. 1 the image reconstruction can be considered as the time reversal of the thermal wave. This inverse problem can be solved either by regularization methods, like Tikhonov reconstruction, or by using methods of non-equilibrium statistical physics and taking fluctuations of the temperature into account. Both methods show similar results, but describing the temperature as a random variable in a stochastic process shows the information theoretical background of the information loss due to thermal diffusion and can be applied also to other non-destructive imaging methods, like photoacoustic imaging.

Theoretical resolution limits for active thermography are compared to theoretical resolution limits for pulsed thermography and the comparison with experimental results shows the maximal potential to improve the resolution for a thermography set-up.

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- [2] A. Mandelis, *Diffusion-wave fields: mathematical methods and Green functions*, Springer-Verlag New York (2001)

INSTRUMENTATION AND METHODOLOGY

Photoacoustic signal of soil – preliminary analysis

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In the present study, an attempt was made to apply photoacoustic spectroscopy (PAS) to quantify photophysical processes in a soil sample. Our attention was paid on at least three effects mediating the photoacoustic response from soil samples while quantitatively interpreting photoacoustic signal. The first one is the soil water evaporation governed by the different ways in which water binds to soil. It is reflected well in the soil water retention curve i.e. the relationship between soil water content and hydraulic potential. We used equipment with two light beams in the measurements. One of the beams was illuminating soil samples with strong stream of non-modulated light and the second beam, with over one hundred times lower intensity, was monitoring changes proceeding in the tested samples. Obtained results indicate possibility to measurements of changes in thermal parameters of soil top layers and indirectly for assessing evaporation rate. It allows one to study water flow processes and modeling water movement through an unsaturated soil probe.

For the soil sample already without free water, the photoacoustic signal is a constant in time which makes possible to determine other soil parameters. Determination of photoacoustic signal spectra in the visible light band allows examining the chemical constitution of soil as well as its affinity to a certain agronomical category. Application of photoacoustic spectroscopy made distinguishing between soils belonging to different reaction classes to be performed. As light sources three diodes emitting at blue, green and red bands of visible light spectrum were used. The obtained dependences of photoacoustic signal amplitude versus light modulation frequency did not follow predictions of Rosencwaig-Gersho classic theory since an additional heat exchange mechanism characteristic of powdered solid samples was likely to occur. In visible light spectrum band, two independent transition processes, one exothermic and second endothermic reactions, achievable to our apparatus, were distinguished. PAS technique provided the principal parameters characterising light-soil interaction phenomenon such as: the process threshold light energy, its relative intensity, and main characteristic processes time scales.

Feasibility of liver fibrosis detection in ex vivo samples using an open photoacoustic cell method

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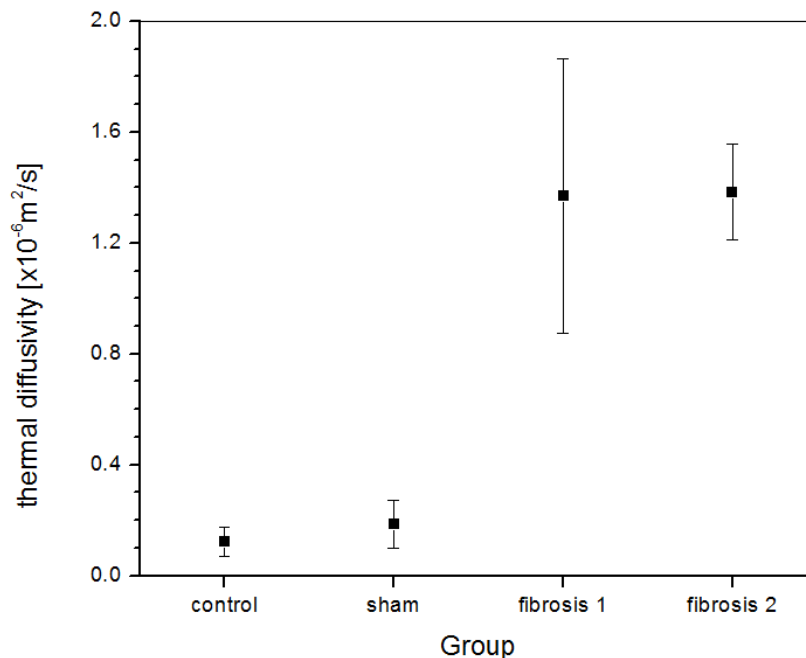
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Design of novel, non-invasive and accurate methods for liver fibrosis diagnosis has gained growing interest. However, despite hepatic biopsy may be associated with sampling error, inter-observer variability and potential complications, it is still the gold standard procedure for staging liver fibrosis.

An open photoacoustic cell technique in liver fibrosis assessment is reported in this issue. Different liver fibrosis stages were induced in Wistar rats differentially exposed to carbon tetrachloride. The liver fibrosis degree was conventionally determined by means of histological examination.

The thermal diffusivity can be accurately determined by photoacoustics from the dependence of the photoacoustic signal amplitude versus modulation frequency. This technique looks directly at the heat generated in a sample, due to nonradiative de-excitation processes, following the absorption of



light. The thermal diffusivity was measured with a home-made open-photoacoustic-cell system. Small pieces of each studied liver were taken to evaluate the feasibility of a photoacoustic measurement comparing its results with conventional techniques. The photoacoustic cell was specially designed to perform the sample measurements.

The human liver tissue shows a significant increase in the thermal diffusivity depending on the fibrosis stage. Specifically, as it can be observed in the presented figure, the liver samples from rats exhibiting hepatic fibrosis showed a higher value of the thermal diffusivity.

Temperature measurement using the surface acoustic waves velocity determination by the laser method

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Temperature measurement of the sample, which is heated by time-modulated heat source, is an effective technique that allows detection of defects and determination of thermophysical properties of the medium. Within this approach there are various ways of creating and recording temperature fields, which differ in their characteristics (speed of response, accuracy, spatial resolution, etc.).

Perspective method of temperature measurement is the use of surface acoustic wave (SAW) [1]. The method is found on SAW velocity dependence on the temperature. High accuracy was obtained through existing highly accurate methods of measuring SAW velocity. The use of laser ultrasonics opens new possibilities for the creation of new methods of measuring SAW velocity [2].

We have proposed a method of measuring the SAW velocity, which is based on a modified deflection method of the SAW detection. Its peculiarity is the use of an optical beam with a width comparable to the SAW wavelength, in contrast to the traditional method in which optical beam width is much smaller than the length of the SAW. This technique allows measuring the SAW velocity in the region of the sample, value of which is equal to the width of the optical beam. The SAW frequencies which implement this method are from 1 to 10 MHz and therefore, the measurement range size is from a few mm to fractions of a millimeter. With this technique it is possible to measure the SAW velocity in the local heating of the sample and therefore, to find its temperature. The SAW localized in a layer of the sample about 2Λ (Λ - the SAW wavelength), so by modifying SAW frequency it becomes possible to study the temperature distribution in the sample depth. The speed of response of the proposed method is limited in the SAW travel time across probing laser beam. This value in most instances is less than 1 microsecond. The method can be used for measuring dynamic temperature changes for photothermal researchers.

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- [2] S. D. Sharples, M. Clark, M. G. Somekh, Opt. Expr. **14**, 10435 (2006)

Development of automated and continuous protocol for the noninvasive monitoring of liquid sample based on continuous-wave photoacoustic technique

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In our efforts to develop a noninvasive and continuous blood glucose level (BGL) sensor, this paper demonstrates the automated and continuous monitoring of liquid samples based on the two continuous-wave photoacoustic-based protocols we proposed previously [1]. First, an automated measurement sequence was proposed, developed and tested. Comparison of results from automated and manual investigations showed good agreement. Then, the automated protocols were used to develop a continuous and operator-less system. Experimental validation was performed by monitoring water solution in static mode (no flow) for over several hours. In our efforts to develop a noninvasive and continuous blood glucose level (BGL) sensor, this paper demonstrates the automated and continuous monitoring of liquid samples based on the two continuous-wave photoacoustic-based protocols we proposed previously [1]. First, an automated measurement sequence was proposed, developed and tested. Comparison of results from automated and manual investigations showed good agreement. Then, the automated protocols were used to develop a continuous and operator-less system. Experimental validation was performed by monitoring water solution in static mode (no flow) for over several hours.

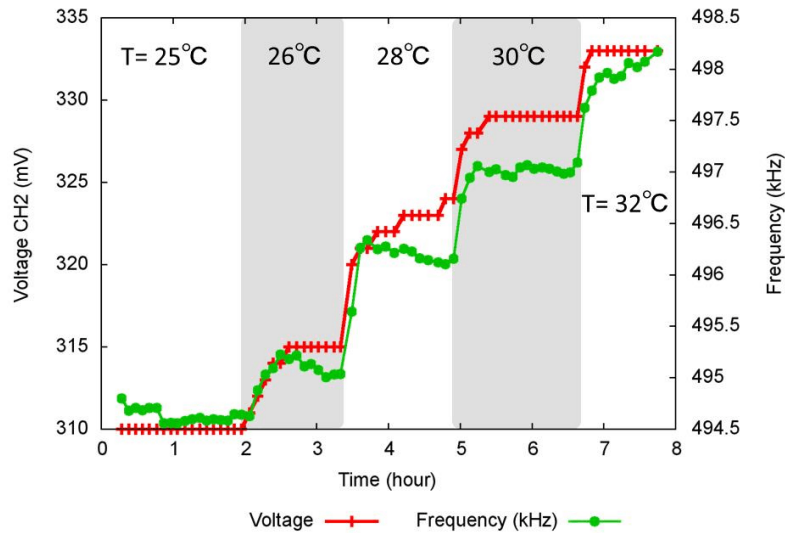


Fig. 1. Results based on FS/OPBS measurements of water sample in thermostatic bath system at several temperatures.

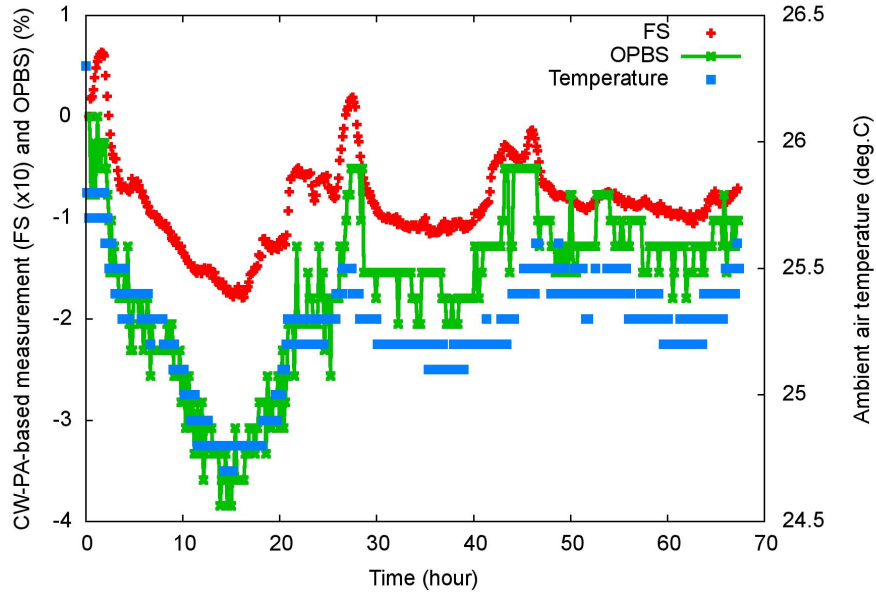


Fig. 1. Long-term FS/OPBS measurements of water sample in fluidic cell while temperature was drifting.

For the first series of experiments, the detection cell was immersed in thermostatic bath where the temperature was controlled through heater and feedback system. While the temperature was gradually increased, the CW-PA based measurements (voltage for the optical power balance shift (OPBS) and frequency for the frequency shift (FS)) showed behaviors in good agreement with temperature rises (Fig. 1).

Second set of experiments were performed in fluidic cell made of glass and filled with pure water. The system was constantly measuring for several consecutive days while monitoring the ambient air temperature simultaneously. Figure 2 shows the results for the two methods (FS and OPBS) at one frequency versus time. The experimental results exhibit wave patterns that are consistent with ambient air measurement in the room and the day/night cycle. The ambient air temperature of the experimental room varies about ± 0.5 °C within twenty four hours cycle. The real temperature of water sample inside the glass cell, which is the one that FS and OPBS were measuring, should show smaller variation, but correlation between the two temperature profiles was expected. At present time, the FS method exhibits better accuracy. However, when dealing with complex solutions, OPBS is essential for selective measurements of one compound in particular out of several solutes.

Another important point concerns the time required to perform one measurement. At the present time, one datapoint takes in average about two minutes which is consistent with the continuous BGL monitoring system on the market. However, multiplexing the optical wavelength will be necessary when dealing with complex solution, thus increasing the time consequently. Optimization will then be conducted in future towards faster and more accurate measurements.

- [1] S. Camou et al., chapter in *Pervasive and Mobile sensing and computing for healthcare*, ISBN 978-3-642-32538-0

Open photoacoustic cell technique: noise analysis in frequency domain

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In photoacoustics, noise is a general term used for all unwanted signals observed at the output of the detection system, masking the true PA signal of interest. Noise signals are usually random in both amplitude and phase, and carry no useful information. Coherent noise may also be present, interfering with the true PA signal as a consequence of the optical source modulation system influence. Both kinds of noise can be classified by their statistical properties of the

modulation frequency f power-law dependence and by how they modify the true PA signal (additive, multiplicative, etc).

Several sources of noise are found in photoacoustic measurements using an open-cell [1]. These include: a) random Brownian noise, b) flicker noise and c) coherent crosstalk noise. All represent additive types of noise and add to the underlying PA signal. Brownian, or random walk noise, is proportional to f^{-2} . Electronic flicker noise has a f^{-1} dependence. Coherent crosstalk noise is a power-law noise directly proportional to f^{+1} .

Frequency dependent noise amplitude measurements for an open photoacoustic cell are presented in Figure 1. These results show that Brownian (f^{-2}), flicker (f^{-1}) and crosstalk (f^{+1}) noise can be recognized in a

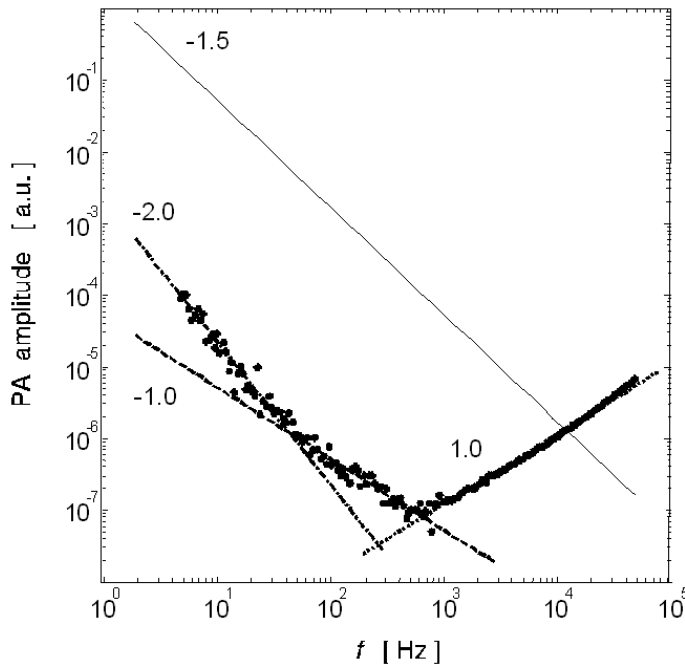


Fig. 1. Theoretically obtained PA signal with $f^{-1.5}$ slope (full line), together with noise measurements (circles): Brownian (f^{-2} , dash-dotted line), flicker (f^{-1} , dashed line) and crosstalk (f^{+1} , dotted line) noise.

wide modulation frequency range. In the case of 20 Hz – 20 kHz domain, flicker and crosstalk noise are dominant. Usually, flicker noise has negligible influence on the PA signal amplitude ($f^{-1.5}$) in the mentioned frequency range. Here, PA signal is calculated theoretically [2] in the case of Si thin plates and assuming thermal diffusion as a dominant process. Crosstalk noise is found to be coupled to the PA signal at higher frequencies (> 10 kHz). Based on the results, noise reduction is needed to remove the crosstalk signal from the measurements. One must bear in mind that noise reduction will give the signal clear from noise, but not from system deviations.

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Analysis of the photoacoustic Helmholtz resonator with conical-ended duct

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Q-factor of the photoacoustic Helmholtz cells can be improved by modification of the duct ends. The paper describes how mechanical modification of the duct ends affects frequency response of the photoacoustic Helmholtz resonator. According to previous studies linear modification of the cone parameter does not result in a linear increase of the resonator Q-factor and resonance frequency. The influence of the conical modification, cone length and angle and duct parameters length and radius was investigated by means of computer simulations based on the stepped-approximated model.

Nested cavity optical parametric oscillator in the 3.0 – 3.8 μm range for quartz enhanced photoacoustic spectroscopy

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Compact and versatile optical sensors are more and more used for indoor-air quality monitoring, green-house gases monitoring or security applications. Motivated by cost effectiveness, the demand

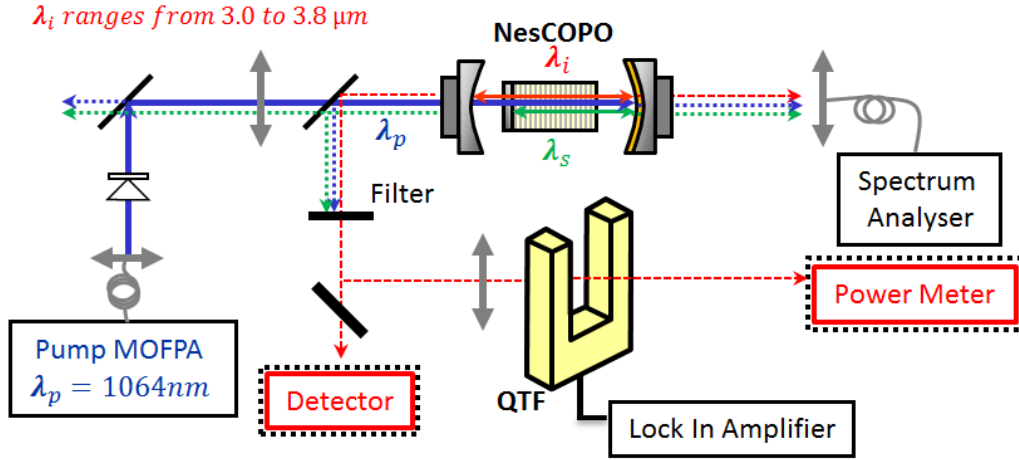


Fig. 1. Experimental Setup used for the QEPAS measurements [1].

particularly aims at multi-species trace gas detection. The 3.0–3.8 μm wavelength range is in this regard a very interesting absorption band since it allows the coverage of strong absorption lines of most green-house or VOC gas species. The combination of a single frequency, tunable optical source and a Quartz Enhanced PhotoAcoustic Spectroscopy (QEPAS) detection scheme meets such a wide spectral coverage while being simultaneously able to resolve desired absorption lines without interferences with other species.

Here, we perform photoacoustic detection of methane and water with a combination of a commercially available Quartz Tuning Fork (QTF) and a specifically developed pulsed microsecond Nested Cavity OPO (NesCOPO) [1], tunable in the 3.0 – 3.8 μm range. The use of a Master Oscillator Fiber Power Amplifier (MOFPA) laser operating at 1064nm to pump our NesCOPO allows

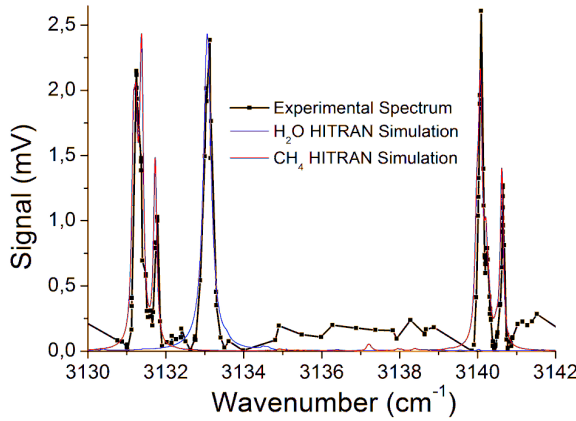


Fig. 2. Spectrum of an arbitrary mixture of methane and water, manually acquired using Vernier Effect to tune the NesCOPO wavelength [1].


to control its output power, repetition rate and temporal pulse shape and duration, and hence to make the most of the NesCOPO. The repetition rate is directly set to the tuning fork's resonant frequency, while microsecond-long pump pulses are used to maximize the generated output power [2]. The output idler pulse, whose power can be up to 100 milliwatts in our experiment, is then focused between the prongs of the QTF and a spectrum of water and methane is recorded as an example on Fig 1 and 2.

Features of a new quartz resonator will also be presented,

which has been especially designed for photoacoustic spectroscopy application. A higher quality factor than conventional QTF has already been obtained, which could lead to enhanced detection sensitivities.

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- [2] J. B. Barria, S. Roux, J. Dherbecourt, M. Raybaut, J. Melkonian, A. Godard, M. Lefebvre, Opt. Lett. **38**, 2165 (2013)

Multichannel detection of photoacoustic signals – preliminary results

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In simple photoacoustic setups signal detection is usually implemented with a single microphone or piezoelectric transducer. Use of more than one microphone (or another pressure sensor) is not very common and is limited nearly exclusively to differential setups, in which analog signals from two microphones are subtracted. A solution presented in this paper consists of an array of MEMS microphones. Each of these microphones has dedicated and individually controllable analog path, consisting of a programmable gain amplifier and an A/D converter. Further signal processing is performed in an FPGA circuit. The presented solution allows for placing over ten MEMS microphones on the area comparable to the conventional ½-inch microphone membrane area. Use of multiple microphones increases the overall signal amplitude and allows for signal to noise ratio improvement by means of noise averaging. In addition it is possible to measure not only an average value of the pressure changes, but also distribution of the pressure field inside of the photoacoustic cell. Due to small size of the microphones the array can be of virtually any shape (e.g. rectangular), thus is possible to adjust it to a particular mechanical design of the photoacoustic cell.

SPECTROSCOPY, APPLICATIONS IN CHEMISTRY

Investigations of the chemically induced changes in FT-IR photoacoustic spectra of wood

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A Fourier Transform Infrared Spectroscopy (FTIR) is a powerful tool for the materials analysis. It gives us an insight into the molecular vibrational modes and makes the detection of relatively small changes in the sample possible. However, standard FTIR cannot be used for all materials. The samples that are not IR-transparent, not IR-reflecting, and cannot be dispersed in KBr or diluted are the problematic ones. Photoacoustic spectroscopy (PAS) gives us the opportunity to investigate such materials because for the PAS measurement sample preparation is not required. Commonly this method is used to study wood-based materials [1,2], e.g. to identify softwood and hardwoods [3], to study the photodegradation of wood [4] and the impact of light induced changes on the surfaces [5].

We used the PAS FTIR to study chemically induced changes in the various wood samples. Wood was exposed to different chemical substances. The chemical reagents (like HNO₃ and CH₃COOH) and the wood preservatives were used. The influence of the drying process on the IR spectrum of the samples was also examined. The FTIR PAS spectra were recorded for all samples before and after treatment (both the exposition to chemicals and the drying process). The Jasco 6200 FTIR spectrometer equipped with the MTEC model 300 photoacoustic cell as a detector was used for that purpose. The photoacoustic cell was purged with a clean dry helium prior to every measurement. Spectra were collected in the range 7500-400cm⁻¹ with spectral resolution 8 cm⁻¹.

All the samples are characterized by distinct photoacoustic signal and the fundamental vibrations related mainly to the wood itself are clearly visible. Exposition of the samples to the chemicals or drying causes small but significant changes in their IR spectra. The most pronounced are the changes in the region were the bands related to the stretching of the OH group are observed.

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Analysis of histamine in fish by LPAS

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Histamine is a chemical compound representing a significant freshness indicator in seafood quality. The substance, not contained in fresh fish, is formed as inadequate preservation of fish. Its presence in fish is associated with symptoms of illness after the fish was eaten. In fact the presence of histamine can cause anaphylactic poisoning episodes (called scombroid poisoning). The reference method for the determination of histamine in seafood is based on HPLC technique. This technique is time consuming and requires the pre-treatment of the sample along many steps performed by skilled personnel operating in a qualified laboratory. A fast alternative detection method of histamine in fish can be based on the laser spectroscopy.

To this purpose we report the spectroscopy analysis of samples of tuna fish. The high resolution spectroscopy of certified tuna samples was performed in ENEA Frascati Laboratories (Italian National Agency for New Technologies, Energy and Sustainable Economic Development) with a home made LPAS apparatus operating in the 9 – 11 mm spectral range. A spectral comparison was performed among LPAS spectra of pure tuna, pure histamine and canned fish containing histamine. The examined samples were provided and analyzed also with HPLC UV-DAD method by the ISS (Istituto Superiore di Sanità – Italian National Institute of Health) and consisted of tuna and canned fish (FAPAS T2775) with histamine concentration value assigned by proficiency testing scheme. FTIR infrared spectra for every sample were also recorded in the 7500 – 75 cm⁻¹ range by a Bruker Optic Alpha-R interferometer equipped with a Diffuse Reflectance InfraRed Spectroscopy (DRIFT) module. This was a preliminary step in our feasibility study.

Biodiesel 2% doped with mamona and copaiba oil *in nature*

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Biodiesel is a biodegradable fuel that causes less environmental impact, thus contributing to the reduction of pollution. It can be obtained from renewable natural sources, like vegetable oils from the following species: *copaifera langsdorff* and *ricinus communis*, which are respectively copaiba and mamona oil [1].

This study was performed with spectrophotometry and photoacoustic spectroscopy (PAS) [1]. As an initial sample we used 100 ml of the 2% biodiesel and 100 ml of copaiba oil. For spectrophotometric analysis 12 samples were prepared, out of which 10 were doped with copaiba natural oil in the following concentrations: 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45% and 50%, the other two samples were pure copaiba oil and biodiesel.

The measurements were performed using a quartz cuvette with a capacity of 3 ml. The volume of the sample studied was 2.5 ml, the reading was held in new 2102UVPC spectrophotometer. The measurements were performed using experimental apparatus with monochromator Joban, lamp 1600 W in the range of 190 to 1100 nm (Fig. 1). We recorded ten absorption spectra, which were fitted with Origin software using the model of lorentzian distribution. The amount of lorentzians varied with the doping concentration in the copaiba oil. In this work we observed that each concentration gives different intensities demonstrating the validity of the technique.

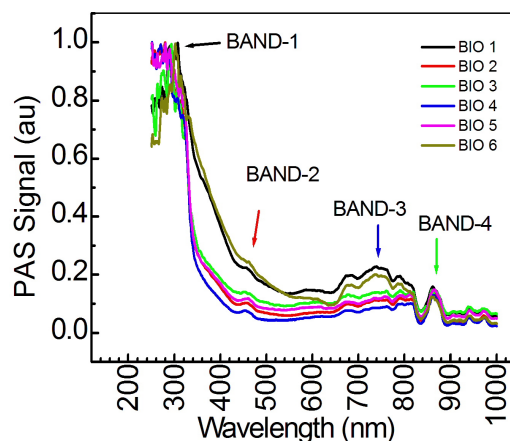


Fig. 1. PAS spectrum of several biodiesel samples.

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SENSORS, ACTUATORS AND INDUSTRIAL APPLICATIONS

Comparative analysis between thermography studies and electric measurement of partial discharges in underground power cables

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A partial discharge is a non linear phenomenon of electrical breakdown that is confined and localized in the region of an insulating medium between two conducting materials which are at different potentials. The damage of the insulating material, which is subjected to an AC voltage during the discharge process, can be directly or indirectly measured by the bombardment of energetic electrons.

In a under ground power cable installation the main point of failure are the accessories that connect it to other equipment, like terminals or splices. By this reason the onset failure is a big deal in the maintenance of under ground power installation.

In this paper a comparative study between the electrical measurements of onset PD and thermography images is presented. The study was carried out with specific faults in the installation of accessories, their evolution being monitored by inductive electric sensors and correlating the results with thermographic images taken during test development.

The thermographic image analysis is made by digital image processing algorithm. An approach is proposed to effectively analyze digital, based on texture segmentation for the detection of early failure stage. The proposed algorithm was tested and compare with the measurements obtained from electrical sensor in the failure point. The result was found to be absolutely suitable to distinguish onset failures from the background tissue using morphological operators and the extract them through machine learning techniques and a clustering algorithm for intensity-based segmentation.

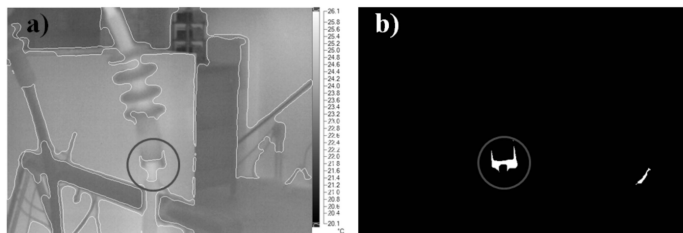



Fig. 1. Termographic image of a failure point.

The obtained results support the feasibility of the implemented configuration for measuring, monitoring, and analysis of several effects related to the partial discharges phenomena such as thermal, acoustic, and electrical, and thus to obtain important information about the insulating material status.

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Optoacoustic inspection of thin oil-contaminated liquid films at low energy deposits

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A portable optoacoustic laboratory utilizing commercially available laser source has been developed for the detection of oil contamination in thin water-based films (Fig. 1). Optoacoustic technique is promising for detecting hydrocarbons in water [1-4]. The peculiarity of the present work is that we deal with optoacoustic signal driven by small laser energy deposit 1 mJ in small liquid probes. The probe has the form of a thin layer.

Film samples with dissolved and emulsified oil components were prepared. Crude oil emulsions were prepared by ultrasonic dispersion of an oil in 100 ml of distilled water. We produced a broad range of concentrations. Optoacoustic response of crude oil is defined by the features of the constituents, such as benzene, pentane and methanol. In the present prototype, good optoacoustic contrast between water and hydrocarbons was achieved at the wavelength 527 nm. The corresponding Q-switched diode pumped solid state pulsed laser was used having pulse train frequency 1 kHz. Fiber-optic delivery of a laser beam to a sample was used.

The pick-up of the outgoing signal was provided with a thickness-mode piezoceramic transducer. The transducer output signal was processed within a frequency band up to 100 MHz. A set of 1000 successive output signals were acquired and averaged in software. This provided noticeable optoacoustic response from the probe. Acoustic selectivity for distinguishing between dissolved and dispersed hydrocarbons was due to the frequency dependence of response signal, the detection limit of the contaminating objects' concentration proved to be 10-100 ppm. This is much less than the admissible concentration level. Normally, the legislation restricts average concentration of dispersed oil to exceed 40 mg/l of discharged water.

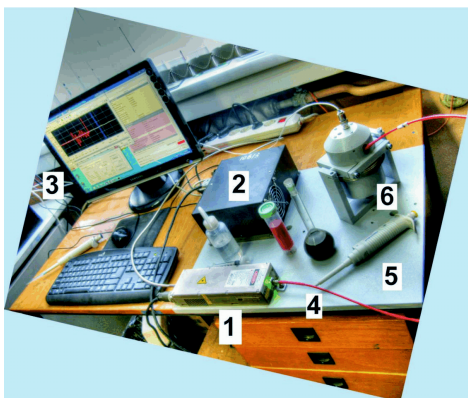


Fig. 1. A portable optoacoustic laboratory: 1 – Q-switched DPSS laser Tech-527; 2 – power supply unit; 3 – software; 4 – fiber optics guide; 5 – base plate; 6 – optoacoustic cell, including optics, sample holder, piezoceramic transducer and pre-amplifier.

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Detection of nitrous oxide emitted by diesel engine bench by photoacoustic spectroscopy


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Air pollution is a major environmental problem and has been widely discussed due to the serious damage it can cause to the environment and human health. The use of fossil fuels on a large scale, mainly from the industrial revolution, is considered the main cause of the increase in air pollution, especially diesel which is used worldwide for the transport of mass and cargo. In Brazil the road transportation network is eminently on road, so this sector seriously impacting the environment. The combustion of diesel fuel produces not only carbon monoxide and carbon dioxide, but also nitrogen oxides, especially nitrous oxide (N_2O) which is an important greenhouse gas, and have a potential approximately 300 times greater than carbon dioxide. Thus, this paper makes an assessment of nitrous oxide emitted by diesel engine bench by photoacoustic spectroscopy coupled to a quantum cascade laser (QCL). The results show that the technique used allowed the detection of gaseous species in order ppmV.

Detection of CO₂ and C₂H₄ released by motorcycles using photoacoustic sensors

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Atmospheric pollution is a harmful environmental issue today. Phenomena such as global warming, photochemical smog formation, acid rain are strongly related to the increased concentration of certain gaseous species in the atmosphere, are impacting all human society, being intensified since the industrial revolution. The consequences of atmospheric pollution vary from the local scale to the global scale, with deep impacts on climate and human health. Urban transportation is responsible for great part of the damaging pollutant emitted by anthropogenic sources. In Brazil, in the last 12 years, the use of motorcycles has expanded considerably, especially in large cities. Pollutant gases, as carbon dioxide (CO₂) and VOCs (volatile organic compounds), such as ethylene, are emitted in the exhaust of motorcycles. Ethylene is precursors in the generation of the troposphere ozone, greenhouse gas described in the IPCC report. In this work, traces of ethylene were measured using photoacoustic spectroscopy based on CO₂ laser, and the gas CO₂ was measured using an infrared sensor (URAS). Our results indicated that the techniques allowed the detection of the gaseous species mentioned above in ppmv range.

Detection of defects by the photothermal deflection technique when the sample is immersed in paraffin oil

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The photothermal deflection technique which is a non destructive technique may be used to study defects in materials. In this work we have used this technique to investigate a part of a circuit board card having copper strips spaced periodically and embedded in the resin. In order to avoid the use of a high power laser, the sample is immersed in paraffin oil filled cell then it is heated by a He-Ne laser of power 2mW. In fact, when the sample is heated by a powerful laser, several phenomena can occur which is often difficult to take into account in the theoretical model. The immersion of the sample in paraffin oil enhances the amplitude of the signal by a factor 500. On the other hand we have developed the theoretical model corresponding to our sample and by comparing the variations of the experimental amplitude and phase of the photothermal signal versus the displacement x of the

sample to the corresponding theoretical ones we have deduced several parameters. We have determined the width of the copper and resin strips, their thicknesses and their thermal properties. This comparison allowed also detecting some anomalies in the structure such as inhomogeneity in the width, the shape and the thicknesses of copper and resin strips.

New glass organic based on copaiba oil studied by photoacoustic diffusivity

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A new glassy material was developed in this work. We use as base oil of copaiba in condensed state. Copaiba oil is well known in the literature is extracted from the tree species *Copaifera Lansgisdorfi*. Has very important and can be used for the development of various products and applications physicochemical and biomedical characteristics [1].

In the manufacturing method of the organic glass used in the heat treatment furnace and a temperature ranging from 25° C to 220° C in steps of 12 interspersed cooling within 12 hours. The cooling process was made using a sample immersion in water at 0° C when removed from the heating source.

Photothermal measurements were performed using a diode laser source of 10 mW in the wavelength range of 600–700 nm as a function of frequency 1–800 Hz Measurements of X-ray energy dispersive were performed in the energy band 480–25400 keV to 40 keV scan band. Infrared spectroscopic measurements varying in the range from 1100 nm to 2500 nm were also performed. Other measures of structure determination and morphology form also performed as x-ray diffraction and scanning electron microscopy.

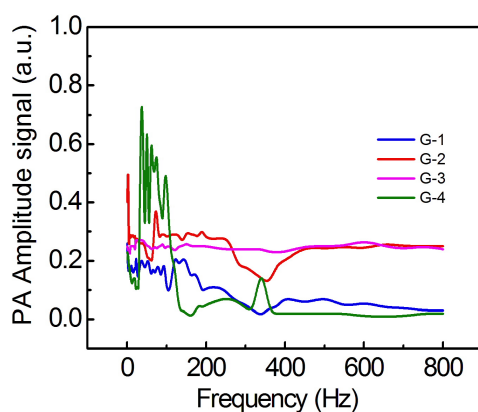



Fig. 1. PA signal amplitude vs. light modulation frequency of several samples of the new glassy material.

Specifically the measure thermal photoacoustic (Fig. 1) showed that the diffusion of radiation in glass varies according to the time spent in the thermal process and the coefficient of thermal diffusivity $a = \omega^2/4t$ [2] showed much higher values measured in *in natura* oil.

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Correlation between the emissions of nitrogen oxides from the combustion of diesel/biodiesel blends and the thermal and rheological properties using the technique of thermal lens

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In this work we present the correlation between the emission of nitrogen oxides from the combustion of diesel/biodiesel blends (B5, B10, B15, B20, B25 and B50) and the properties of viscosity and thermal diffusivity using the technique of Thermal Lens. This is a sensitive technique which is part of a set of known techniques that are based on the photothermal converting light into heat. To determine the concentration of nitrogen oxides used the electrochemical analyzers, concentrations ranged between values from 313.3 to 351.5 ppmv. It is observed that for sample of B50 was obtained value higher concentration. This result is consistent with the literature and can be related to the higher cetane number of the biodiesel thus providing a higher combustion temperatures. Furthermore, the presence of oxygen in the biodiesel molecule can also increase the rate of NOx formation. The values obtained for the property viscosity range between 3.50 to 4.15 (cP). The thermal diffusivity is the ability of the material to transmit heat, this property is strongly related to the structure and composition of the sample analyzed, as well as processing conditions, as well as having a direct relationship with the viscosity of the material medium. In this study it was possible to determine the thermal diffusivity using the technique of thermal lens, values were included among the range 0.90 to 0.94 cm² / s. We conclude from this study that the emission of oxides of nitrogen gas is strongly correlated to the rheological property of viscosity and thermal diffusivity property. The techniques are sensitive and selective detection of the properties under originated from diesel-biodiesel blends binary Furthermore, the electrochemical gas analyzer (TEMPEST) allowed obtaining the concentration of nitrogen oxides in the gas ppmv range.

APPLICATIONS IN MEDICINE, BIOLOGY AND AGRICULTURE

Characterization of *Moringa oleifera* tree by photoacoustic spectroscopy

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Different techniques have been used in the study of biological materials in order to obtain qualitative and quantitative values of some substances that compound these materials [1, 2]. Among the techniques that have been used to characterize biological materials the photothermal (PT) techniques have shown to be an alternative to determine the presence of natural pigments in plants such as anthocyanins, carotenoids, flavonoids, etc. [3]. One of the PT techniques, Photoacoustic spectroscopy (PAS), stands out for its applications in the study of biological materials. PAS is based on the photoacoustic (PA) phenomenon, in which a modulated incident light on the sample is transformed into heat and detected as a sound, by using a microphone, in a hermetically sealed PA chamber. The PA signal depends directly on the optical properties of the sample [4]. By other hand

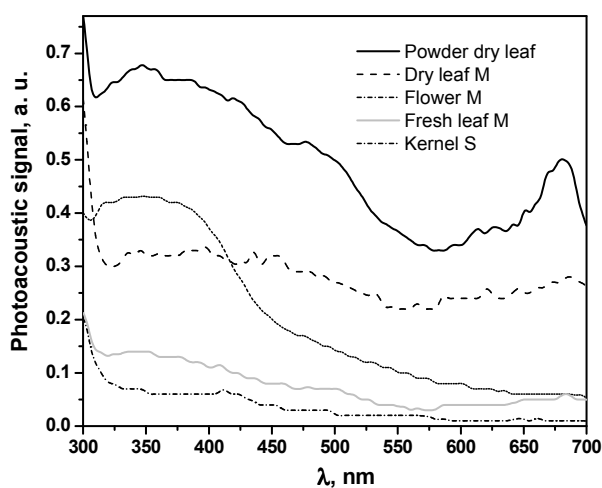


Fig. 1. Optical absorption spectra of *Moringa oleifera* samples.

Moringa oleifera tree has been studied, presenting a variety of substances in all plant parts [5]. This plant can be an alternative in nutrition and also can be used as a biofuel [6]. In the present study it was used PAS to obtain the optical absorption spectra, in the range of 300-700 nm, of different parts of *Moringa oleifera* tree (flower, dry and fresh leaf, seed). The optical spectra show different absorption bands with significant differences of $P < 0.05$, between different parts of the plant, which shows that PAS technique can be used as a reliable method for the characterization of complex biological materials with different substances in the fields of agriculture and food.

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Application of photothermal methods for quantification of carotenoids in apricot jams

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Carotenoids, natural pigments synthesized by plants and many microorganisms; are responsible for vibrant colors of many flowers and fruits. This is of particular relevance for foods because their color, often a criterion of quality, is affected by the processing. As to the human health, carotenoids were shown effective in lowering the incidence of some cancers, reducing the risk of heart disease etc. The profile as well as the total content of carotenoids (TCC) in fruits and vegetables depend on several factors such as species, variety, genetic background, growing place, meteorological conditions, maturity, postharvest storage, processing etc. The study described here explores the analytical potential of laser photoacoustic spectroscopy (LPAS) and laser opto-thermal window (OW) methods to quantify TCC of various apricot jams. Well established optical spectrophotometry (SP) and high performance liquid chromatography (HPLC) served as the two reference methods. Unlike SP or HPLC, the PAS and OW require no extraction prior to the analysis and permit rapid assessment of TCC after only a one, single initial calibration step.

The investigated jam samples were classified into two groups: The jams from the first group had the fruit content of 80 % while those from other group were characterized by 50% fruit content. Overall, there were three different samples within each specific group: the natural sample (no

additives), a sample containing 40 mg/100 g ascorbic acid and finally the sample with apple pomace content of 0.5 %. All six jams contained 1 % pectin, furthermore the samples from a first group had sugar content of 20 % as compared to 50 % sugar content of the second group.

The TCC was determined using the method of De Ritter and Purcell as modified by the Canning Research and Development Co. Ltd. [1]. After thawing, β -carotene was extracted from 1 g sample using methanol and acetone, followed by the separation with diethyl ether. The absorbance of the ethereal solution at 450 nm was measured on Hitachi U-2800A spectrophotometer.

The extraction of carotenoids from 5 g apricot jam was carried out under subdued light with 15 ml THF for 12 hours at +4°C using a shaker operating at 150 rpm. The supernatant of extraction was decanted to 1.5 ml Eppendorf-tubes and centrifuged at 8163.1xg for 5 min at -5°C. The supernatant was filtered through 0.45 μ m Millex HN syringe filter unit and finally injected onto the HPLC.

Both, the LPAS spectrometer and the OW setup used here were discussed previously [2]. The MBL-III-473 laser emitting 50 mW c.w. power at 473 nm served as a light source.

The TCC in jams was expressed in terms of β -carotene equivalents. The highest TCC (2.7 mg/100 g fresh product weight) was found in sample rich in fruit and ascorbic acid as compared to a lowest TCC value (0.8 mg/100g) for sample having low amounts of fruit and ascorbic acid. Positive linear correlations between TCC and the PA and OW signals were found. As an example, increasing TCC in 100 g fresh product by 1 mg results in 5 and 55 mV/mW increment of LPA and OW signals respectively. In conclusion, both photothermal techniques with laser excitation at 473 nm proved excellent methods for a low cost, simple and rapid assessment of TCC in apricot jams.

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Polymerization studies of giomers and evaluation of the interface between the tooth and filling using photothermal methods

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Giomers represents a new concept in restorative dentistry based on novel pre-reacted glass technology, where special glass-ionomer fillers are included in the resin matrix [1]. The purpose of this study is to investigate the polymerization process (the polymerization temperature and the variation of thermal parameters during the light-curing procedure) and to detect open cracks in cavities restored with giomer by lock-in thermography technique, using laser intensities that are safe for living teeth.

The incidence of shrinkage due to the polymerization process creates stresses within the material and its interface with the tooth structure. Accordingly, marginal failures can occur, affecting the integrity of the restoration [2]. Thin vertical cracks are usually difficult to detect by conventional optically stimulated thermography, due to heat flows being mainly generated and then propagating in a direction perpendicular to the surface. An intensity-modulated optical stimulation targeted near the dental restoration interface was selected as excitation source. The amplitude or phase images obtained after the lock-in procedure will bear information on the presence of the crack, carried by a perturbation of the amplitude or phase of the thermal wave.


Temperature rise during polymerization of light-activated comonomers with a LED unit in continuous stimulation mode (1000mW/cm^2 and applied polymerization time $2 \times 20\text{s}$) was measured with an IR camera (FLIR 7200 series, sensitive in the $1.5\text{ }\mu\text{m} - 5.1\text{ }\mu\text{m}$ wavelength range). The peak polymerization temperature of the investigated samples ranged between $27^\circ\text{C} - 61^\circ\text{C}$.

The polymerization process of the samples was also investigated by photopyroelectric calorimetry, in front detection configuration. Assuming a thermally thin regime for the sensor and thermally thick for the sample (particular case of detection in which the amplitude of the signal is proportional to the reciprocal of thermal effusivity), a calibration of the amplitude of the signal was possible by performing a room temperature frequency scan of the signal's phase in the solid state. The resulted values of thermal effusivity (around $1000\text{ Ws}^{1/2}\text{m}^{-2}\text{K}^{-1}$) showed good thermal biocompatibility of the materials both in liquid and solid state.

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Optical properties of human skin around Biological Active Points

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The physical parameter for the so called Biologically Active Points most documented in the literature is the electrical impedance. These points seem to have higher electrical conductance than their surrounding points. The stimulation of these points up to now is made not only mechanically and electrically but also optically (laser acupuncture). As far as we know, few references about optical properties of BAP's have been published in the scientific literature. We evaluated by optoacoustic technique, some skin points along the PC acupuncture meridian in the forearm region around PC5 and PC6. The measurements were performed each 0.5 cm from the wrist to complete 21 measurements (10 cm), using a Q switch NdYAG laser of 1064 nm wavelength, 5 Hz repetition rate, 9 ns pulse duration and below the security international limits for IR radiation for human tissues. The results were

compared with those from a similar “line” parallel to the meridian, one centimeter toward the internal part of the forearm. We find a slight relative increment in absorption around one meridian region which could be associated with an acupuncture point but the same case is found in the non meridian skin line non associated with any acupuncture structures. Taken into account the normal variability of the skin absorption and dispersion, we can not conclude that such points are optically special.

The optical absorption coefficient of barley seeds investigated by photoacoustic spectroscopy and their effects of biostimulation laser

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The laser light as biostimulator has been applied in the agriculture, where some scientific reports evidence its usefulness [1-4], where the knowledge about a seed's optical parameters is of great

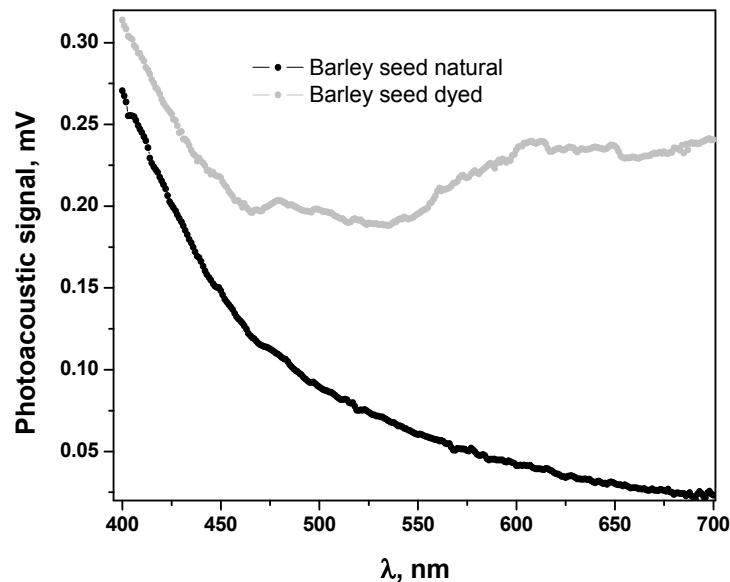


Fig 1. Optical absorption spectra of barley seeds.

relevance in the biostimulation process, could provide information about its absorption. Of this way, the objective of the present study was to determine the optical absorption coefficient β for barley malt seeds in two conditions: Seeds in their natural color (I) and seeds dyed with methylene blue (II), by means of the photoacoustic spectroscopy (PAS). The seeds were biostimulated by laser treatment (650 nm) to evaluate the effects of pre-sowing biostimulation in mycobiota naturally associated to different irradiation times by laser (0, 60, 180, 240 and 480 seconds). The biostimulation effects showed that the seed samples with a higher optical penetration length had a positive biostimulation, in the percentage of mycobiota total naturally associated to the seed, obtaining an diminish of @ 40% compared to the control to the irradiation times of 180 and 480 seconds.

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Total lycopene content in optically highly dense products derived from the thermally processed tomatoes: evaluation and comparison of several non-destructive methods

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Tomato (*Lycopersicum esculentum*) is agricultural commodity used worldwide by the food and canning industries to produce a wide range of processed products. Examples are tomato juice, tomato puree, tomato paste, ketchup etc. Unlike tomato paste that is made from tomatoes that have been cooked for several hours, tomato purée (also termed concentrate) was boiled only briefly before being strained. It is a liquid with a consistency ranging between that of crushed tomatoes and tomato paste. Most important constituent in tomatoes is lycopene, the fat soluble carotenoid. This red pigment in tomatoes is considered responsible for protecting the cells against oxidative damage thereby reducing the risk of several diseases.

Routine quantification of total lycopene content in various tomato products and in tomato waste is an important issue [1]. In practice this is usually achieved by spectrophotometry (SP) and high pressure liquid chromatography (HPLC); however these methods are in turn destructive and as such intrinsically laborious and expensive. On the other hand in food colorimetry, which is essentially the non-destructive approach, one performs reflectance measurements of *external* (optical) characteristics (colour of specific commodity).

When trying to use classical spectrophotometry (SP) to analyze optically dense samples, the very low amount of radiation transmitted through the specimen precludes recording of *internal* (optical) characteristics). Using techniques such as the attenuated total reflection (ATR-IR) and the group of non-destructive methods classified under the name photoacoustic and photothermal spectroscopies might prove promising in dealing with difficulties of that kind [2]. In the work described here photoacoustic spectroscopy (PAS), optothermal window (OW), photothermal radiometry (PTR) and the infrared thermography (IRT) were applied to quantify total lycopene content directly (neither extraction, nor separation and purification is required) in a variety of commercially available processed tomato commodities. In addition, the performance of each of these methods was compared to that of colorimetry and the near infrared spectroscopy [3].

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Dosimetric control in phototherapy using temperature measurements and thermal imaging

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In recent years, several therapeutic methods based on the application of light have been developed. A common problem to these methods is the dosimetry. The absorption of the photon energy will be transformed into heat generation, among other processes, resulting in a temperature rise.

Twenty eight mice were irradiated with a red light with a wavelength of 630nm. The irradiance was of 218 mW/cm² and two energy density doses were used (150 mJ/cm² and 250 mJ/cm²). These are typical parameters to perform ALA-mediated photodynamic therapy. The measured temperature rise is presented in Fig. 1. An important temperature decrease is observed after the anesthesia of almost 3°C. After irradiation the temperature of the tissue increases almost 6°C.

The temperature of the irradiated tissue is a parameter that usually is not considered in dosimetry. However, it might play a significant role during the photochemical reactions associated to the therapy. Two temperature monitoring systems were developed to corroborate the feasibility of temperature rise measurements to perform a dosimetric control of delivered light.

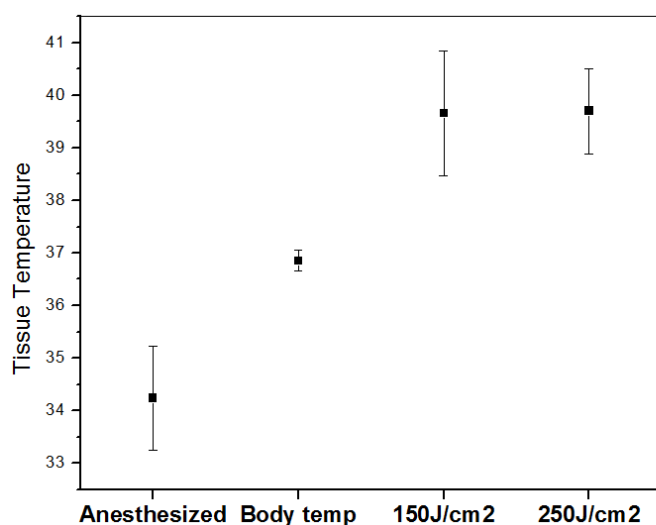



Fig. 1. Measured tissue temperature.

The first system includes an IR detector to measure the temperature in a specific irradiated spot. The second one uses an image detector to detect the thermal distribution to compare it with the fluorescence image related to the distribution of treated lesions.

Application of photoacoustic spectroscopy in transdermal delivery studies

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Studying the mechanism of drug transport through human skin is of considerable interest for understanding the barrier function of the stratum corneum as well as for many medical and cosmetic applications. Permeation studies were performed on the model system: drug dithranol dissolved in vaseline (4% w/w) and artificial skin barrier – dodecanol-collodion membrane (thickness ~25 μm). The time-dependent PA measurements were performed for 20 modulation frequencies, which corresponds to the different depths in the sample. Signal amplitude differentiation led to experimental drug distribution in the membrane.

There are, at least, two mechanisms responsible for the drug motion in the system. First one, called the diffusion, is the net movement of a substance caused by its concentration gradient in the medium. Second, the advection, is transport phenomena that utilize bulk motion in the system. For low Reynolds numbers, the advection flux may be introduced as a creeping flow approximation of Navier-Stokes equation. Mass balance equation for the described system also accounts terms

responsible for the chemical reaction (or metabolic depletion) in the medium. The governing equation of the model may be introduced as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \mu C + \gamma \quad (1)$$


where C stands for the concentration, D , v , μ and γ are diffusion, advection, first-order reaction and zero-order reaction parameters respectively, x is the distance measured normal to the surface, and t stands for the time.

Four models of different complexity of (1) were taken into consideration: classical diffusion model (v , μ and $\gamma = 0$), diffusion-advection model (μ and $\gamma = 0$), diffusion-advection model with zero-order reaction ($\mu=0$) and diffusion-advection-reaction model (no constraints on eq. (1)). During verification tests, much improvement was noticed between every step of model expansion (ex. the diffusion model's Residual Sum of Squares (RSS) = 5.32, the diffusion-advection-reaction RSS = 1.19).

Combination of experimental results and theoretical computations allowed to determinate the transport dynamics parameters. Also, the role of external forces in transport phenomena was specified. Since the advection process was included in the model, it is broadly applicable across diverse external factors affecting the transport process, for example in iontophoresis.

IMAGING

Thermal effects of laser light on maize seeds evaluated by thermography

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There are several hypotheses concerning possible mechanisms of laser radiations, which are assumed to contain substances with very narrow absorption bands. A selective excitation of chromophores of molecules of such substances initiates some biochemical reactions [1] In the biostimulation in pre-sowing seed, among molecules that are excited are the phytochromes [2-4] where the seeds first absorb the light energy and then transform it into chemical energy and use for their subsequent growth processes. Of this way, the laser radiation broke the kinetic equilibrium of seed germination and increased the internal energy of seeds [6]. Temperature effects on seed due to the visible wavelength laser are supposed to emit very little heat [2]. But it is important to know the temperature changes that the seed has to be irradiated with laser light because almost not been studied and could have substantial practical and theoretical importance because some authors agree that the effects of laser treatment on an organism involve almost others effects, temperature effect [7]. Thus, in this study the temperature changes produced by laser light in maize seed to be irradiated for one minute and subsequently decay temperature for one minute after power off were determined. Flourey maize seeds were used in its natural color (N) and dyed of black (D) and temperature changes were measured by an infrared camera. The results indicate temperature changes detected by an infrared camera, increasing changes in seed dyed of black. Thus, it is found that there is a thermal component in the mechanisms associated with laser biostimulation

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Automatic digital breast thermography segmentation for breast cancer detection

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One in eight deaths worldwide is due to cancer. Cancer is the second leading cause of death in developed countries and the third leading cause of death in developing countries. In 2009, about 562,340 Americans died of cancer, more than 1,500 people a day. Approximately 1,479,350 new cancer cases were diagnosed in 2009. In the United States, cancer is the second most common cause of death, and accounts for nearly 1 of every 4 deaths [1]. The chance of developing invasive breast cancer at some time in a woman's life is about 1 in 8 (12%) [2]. Breast cancer continues to be a significant public health problem in the world. Approximately 182,000 new cases of breast cancer are diagnosed and 46,000 women die of breast cancer each year in the United States [3]. Thus, the incidence and mortality of breast cancer are very high, so much so that breast cancer is the second leading cause of cancer death in women. Although breast thermography has its limitations in sensitivity and specificity and it is dependent on examination conditions, it provides valuable information about the physiological condition of the breasts. Its ability to detect early physiological changes in breasts due to cancer formation can be used to detect patients whom require more thorough examinations, thus making the treatment more effective.

This paper presents an approach for detecting in digital thermography not only the detection and early stage of tumors can also detectable The first step of the cancer signs detection should be a segmentation procedure able to distinguish masses and micro calcifications from background tissue using Morphological operators and finally fuzzy c- means clustering (FCM) algorithm has been implemented for intensity – based segmentation. The implemented algorithm is absolutely capable to identify and subsequently isolate the area of interest taking into account the result of the texture ana-

lysis of the image. The proposed technique shows better results. The method was tested over several images of image databases taken from Digital Database for Screening Mammography (DDSM) for cancer research and diagnosis. Results allow us to see the effectiveness of the proposed method.

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Analysis of thermal imaging for the detection of failures in transmission lines

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The infrared images show the temperature scale based on the previous calibration of the camera thus allowing measuring the temperature over several regions of the test terminal. Despite an accurate contactless temperature measurement can be achieved by a good calibration of the infrared camera, the proposed image processing is not based on this calibration but on the textures defined by the gray levels that naturally arise due to thermal effects. In order to orientate the analysis of the thermal effects to the region of interest (ROI), infrared images of the experimental setup where digitally processed by using segmentation and extraction algorithms based on texture and morphological image analysis [1-4].

These processes, through which the ROI (i.e. region where the partial discharges are induced) is discriminated from the entire environment, allow not only having a calibrated measure of the temperature over several regions of the experimental setup but also accurately extracting the physical location where the failure is occurring.

The results are very promising, as they allow us to identify a fault in a transmission line if you need to have it offline, ie keeping the energized line.

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ULTRAFAST, MICRO/NANOSCALE AND NONLINEAR PHENOMENA

Photothermal magnetic diffusivity observed in gel essential oil

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We have developed a magnetic gel based in natura an oil extracted from the seed of the plant *Piper hispidum* popularly known as long pepper. The essential oil (EO) was removed by simple distillation using a source coupled to a cooling condenser itself. EO was used to prepare magnetic-based magnetite nanoparticles gel.

The magnetite nanoparticle was characterized by electron microscopy whose average diameter was 4.6 nm and polydispersity of 0.2 nm. The nanoparticles were coated with oleic acid and

dispersed in a row were in essential oil by varying the concentration of magnetite nanoparticles in the range 10^{14} – 10^{16} nanoparticles/cm³. Using ultrasonic diffusion was possible to introduce the nanoparticles in a polymer matrix forming a magnetic condensation gel.

Five samples and characterization was by FTIR, X-ray energy dispersive, infrared measurements in the range 1100 to 2500 nm and thermal diffusivity measurements in the region of 1 were prepared at 800 Hz thermal diffusivity measurements showed a variation the propagation of thermal energy in the material structure as shown in Fig. 1 for the FGM samples 1 to 5 [1].

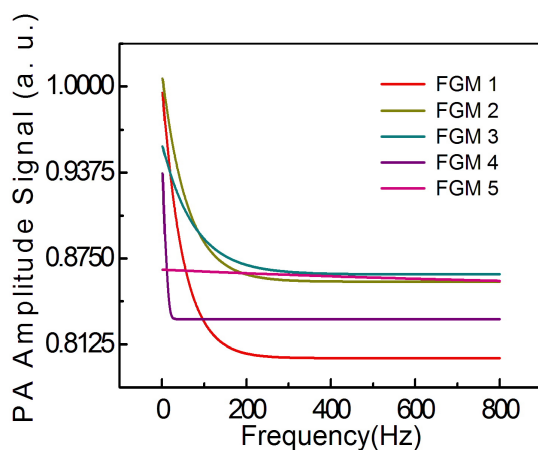



Fig. 1. PA amplitude vs. light modulation frequency for several FGM samples.

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Detection of carbon nanoparticles in suspension by a photothermal technique

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In this article a photothermal technique is presented to detect carbon nanoparticles in suspension and determine their concentration. The main methods of the technique are the photothermal lens effect and the photothermal beam deflection. Both are well researched and described in corresponding literature. The experimental setup consists of a pump and a probe laser and optical devices for beam guidance and signal detection. First, an optical setup to generate both effects in a suspension simultaneously is described. To detect the beam deflection respectively the beam expansion of the measuring beam, different optical detectors were applied, moreover a graphical CMOS-camera based method was developed. The dependence of the photothermal effect on the absorption of the pump laser beam is discussed, particularly by varying the concentration of carbon nanoparticles in suspension. It is shown, that the absorption of the pump beam and thus the photothermal effects can be modified by setting the laser power or also by changing the concentration of carbon nanoparticles. The measurements with this system are showing that especially with the graphical method a determination of the concentration in the low ppb range is possible.

Investigations of thermal transport properties in porous silicon by photoacoustic technique

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Improvement of low-dimensional structures is still important direction of modern materials research. This is due with the fact that nanostructured materials are widely used in various areas of nowadays technology. In particular, nanostructured porous silicon (PSi) and its different modifications are successfully applied in micro-, nano-optoelectronics, medicine, sensorics etc.

Typically, PSi is obtained by anodic etching of mono-crystalline silicon substrate. Clearly that this process is stochastic, and as a result, even under the same etching conditions and regimes the properties of resulting material can vary. Due to significant influence of morphology of low-dimensional systems on their thermal properties [1], this difference can be used as an informative marker for development of PSi diagnostics methods. However, a non-availability of systematic approaches for theoretical evaluation of heat transport properties in disordered systems makes a usage of these methods extremely difficult. So the systematic experimental studies of thermal transport characteristics in different composite systems are completely important.

In this paper we present the results of an experimental study of photoacoustic transformation in composite systems “porous matrix – liquid”, where the PSi with different values of porosity was used as the matrix. To investigate the thermal conductivity of the composite system a photoacoustic method with gas-microphone registration in classical configuration was used [2]. As a result of experimental research the increase of thermal conductivity (up to twice) of the composite system “porous silicon – liquid” (compared to porous silicon) has been stated. This increase was explained by improved thermal contact between the crystallites in matrix as the result of the second order pores filling by liquid [3,4].

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An alternative calorimetry based on the photothermoelectric (PTE) effect: application to magnetic nanofluids

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Among the photothermal (PT) contact methods, the photopyroelectric technique (PPE) is probably the most used for calorimetric purposes [1]. In the PPE calorimetry, a sample is irradiated with an optical beam and the heat, generated in the sample due to the absorption of radiation, is measured with a pyroelectric sensor which is in good thermal contact with the sample. Recently, it

has been proved that similar results can be also obtained with thermoelectrics (TE) [2]. In this case, the physical mechanism relies on the Seebeck effect. The efficiency of the material depends on its characteristics such as Seebeck coefficient (S_0), thermal (k) and electrical (σ_0) conductivities. In this paper we propose to use a TE material with large Seebeck coefficient (TiS_3) as radiation sensor and the resulted photothermoelectric (PTE) effect for thermal characterization of some particular liquid samples (magnetic nanofluids). The “front” detection configuration coupled with TWRC method (scan of the liquid’s thickness), is used for thermal effusivity measurements and the “back” detection, together with the chopping frequency scan, for thermal diffusivity investigations.


The thermal properties of a particular magnetic nanofluid (carrier liquid: transformer oil, surfactant: oleic acid, nanoparticles’ type Fe_3O_4) have been investigated as a function of nanoparticles’ concentration. Small increases of thermal diffusivity (from $9.14 \times 10^{-8} \text{ m}^2/\text{s}$ to $10.33 \times 10^{-8} \text{ m}^2/\text{s}$) and thermal effusivity (from $450 \text{ W s}^{1/2} \text{ m}^{-2} \text{ K}^{-1}$ to $530 \text{ W s}^{1/2} \text{ m}^{-2} \text{ K}^{-1}$) with increasing concentration of Fe_3O_4 nanoparticles (from 0 to 0.623 mg $\text{Fe}_3\text{O}_4/\text{ml}$ fluid) were observed.

Due to the fact that PTE is very similar with PPE, a comparison of the performances of the two techniques is made. Finally, both techniques proved to be suitable calorimetries for a complete thermal characterization (measurement of all static and dynamic thermal parameters) of magnetic nanofluids.

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Evaluation of a contact by sub-nanosecond laser ultrasonic technique

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Contactless sub-nanosecond laser ultrasonic (LU) technique [1,2], provides excellent opportunities for non-destructive evaluation of elastic properties of different materials. It has been applied recently for the probing of laser-induced crack closure [3], which is interesting for non-destructive testing. Meanwhile, the parameters of naturally produced cracks, necessary for the verification of the theoretical models [4] are usually unknown. For this reason, the use of a contact between light-transparent and light-absorbing plates could be proposed for the simulation of some properties of cracks and delaminations, because some of the parameters of this contact could be measured optically and predicted theoretically. It is worth noting that the contact of a sphere with the substrate under variable external loading has been already tested by picosecond laser ultrasonics with bulk longitudinal acoustic waves [5].


The technique is based on the excitation of surface, interface and surface/interface skimming bulk acoustic waves by a sub-nanosecond laser and their subsequent detection by a continuous laser beam using a well-know deflection method. The excitation is produced by a linear source with a size of

100x5 μm and the detection is realized by Gaussian beam of 5 μm diameter. The signals are detected by a 1 GHz photo-detector for their subsequent visualisation on a 18 GHz oscilloscope. The automatic scan of photo-acoustic signals is obtained by the displacement of the excitation beam relative to the detection one. The value of sound velocity is obtained from the fit of arrival time of the acoustic pulse as a function of distance between the beams. The sample is installed on the displacement stage, allowing the study of different parts of the contact. It is worth noting that the acoustic waves, propagating along the surface of a contact, could be studied in the transmission or reflection configuration [3].

In the simplest configuration, a contact between a cylindrical lens and a light absorbing plate has been studied using this technique. Then, the realization of experiments with the materials of different elastic properties and with different quality of surface polishing allows to test the situation with real contacts. The amplitude and the profile of different acoustic waves propagating near the surfaces in contact should provide the opportunity of evaluation of the parameters of the contact. The application of variable force allows us to change the parameters of the contact. An additional heating beam from a powerful continuous laser could be introduced to change locally the distance between the surfaces of the contact. This method has been already validated in laser ultrasonic experiment with a crack in light-absorbing glass [3]. Possible nonlinear regimes of acoustic pulses propagation, when the distance between the surfaces of the contact is comparable with the displacement in the wave, are particularly interesting. The results of this work should find the applications in the area of the adhesion characterization and the mapping of damages and cracks in different materials.

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Microcomposite ash organic complexed with laterite

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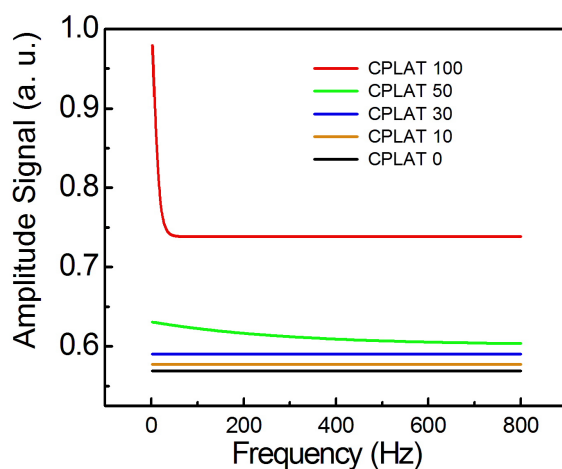
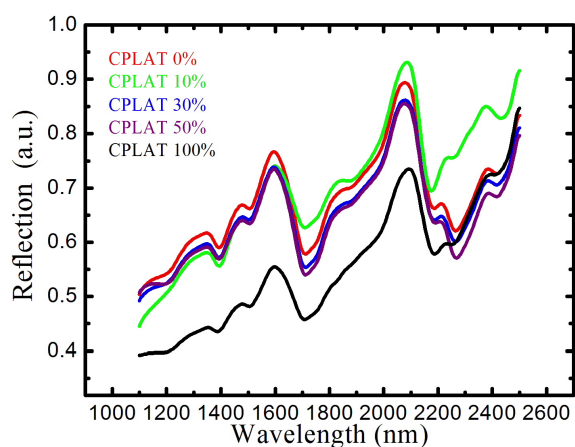
Materials in micro scale can present several interesting physical and chemical properties for some applications. In this way microcomposites have been studied in recent years with either amorphous, crystalline, or non-magnetic in order to observe phenomena intrinsic characteristics.

To synthesize micro composite materials that may have some property to physical applicability is necessary to choose the raw material to be used. Organic ashes are generally obtained by firing at high temperature (900° C) and are materials that can be applied in mixtures with other proportional to give consistency to the final outcome.

Another type of material found in abundance in some soils of laterite rock is a rock that is formed by iron hydroxides and aluminosilicates characterized by the occurrence of leaching, which is the process of extracting a substance present in solid components by dissolving a liquid (rain or irrigation) and is found in the region of hot and humid (Amazon) climate [1].

Therefore, this work describes the preparation and characterization of microcomposite complexed with organic ashes microcrystals rock treated laterite at ambient temperatures, 150, 300, 450, 600 and 750° C, 75 micron in diameter was made. Were analyzed using the techniques of infrared and x-ray fluorescence and photoacoustic diffusivity by the frequency region 1–800 Hz [1].

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THERMOPHYSICS

Photothermal conversion of color centers in CaF_2 crystals: a process underlying use of the crystals as holographic medium

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Heating of CaF_2 crystals in the reducing atmosphere of metal-cation vapor (“additive coloring” of crystal) results in diffusion of two flows, anion vacancies and electrons, into the crystal bulk. Recombination of these components form a quantity of color centers differing by the number of these components. They are divided into “simple” centers, which are formed, respectively, by one to four anionic vacancies with a corresponding number of electrons, and “highly aggregated” centers with larger quantity of these components. The latter include “colloidal” centers, which in fact are two dimensional metallic calcium inclusions into the crystal lattice, they contain from thousands up to tens of thousands of atoms. Another type of highly aggregated centers are “quasi-colloidal” centers. The structure and constitution of these centers are unknown at moment; probably they take an intermediate position between simple and colloidal centers by the number of vacancies/electrons.

Color centers have characteristic bands in the absorption spectrum of additively colored crystal. They overlap all visible and infrared (IR) range of the spectrum up to the end of lattice absorption of the crystal ($\sim 10 \mu\text{m}$). At the room temperature, T , illumination in these bands does not change the composition of centers present in the crystal since arising electron is captured by the photo-ionized center. However, at high temperature ($T > 70^\circ\text{C}$) the anion vacancy may segregate off such center and diffuse over the crystal. Its recombination with electron may take place at another center. Thus, the combined action of illumination and temperature results in modification of centers composition. Its character depends on both the wavelength of actinic radiation and the temperature; the duration of photothermal influence is also substantial.

The high-temperature photosensitivity makes it possible to use additively colored CaF_2 crystals as a holographic medium. The diffusion-drift mechanism of hologram recording in CaF_2 includes centers conversion and their redistribution over the crystal bulk. The modification of the absorption spectrum of the crystal at hologram recording is tied with modification of the dispersion of its refractive index. Depending on the readout wavelength, it is possible to read out amplitude, amplitude-phase or phase holograms. The unique feature of holograms in CaF_2 crystals is the opportunity of their transformations with modification of centers types via post-exposure photothermal treatment by use of incoherent radiation [1, 2]. Tough treatment does not lead to any noticeable decay of the hologram. This fact shows the exceptionally high resistance of holograms recorded in these crystals with respect to heating and optical radiation. Such hologram stability is tied with the

diffusion-drift mechanism of the photo-induced spatial redistribution of color centers over the crystal bulk during the hologram recording and its post-exposure illumination with incoherent radiation.

The stability of holograms and the opportunity to record thick holograms (up to 10–15 mm), which ensures their high angular selectivity (~ 1 arcmin), enabled creation of holographic measure of plane angle. Wide transparency gap of CaF_2 crystal coupled with the existence of convertible color centers absorption bands allows formation of narrow-band transmitting and reflecting holographic filters. It is especially important for the mid-IR range due to absence of holographic media suitable for formation of such filters for the wavelength range more than 3 μm .

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Photothermal radiometry analysis of NiO/Ni selective coatings

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Selective coatings have received increasing interest due to their application in solar thermal technology. The adequate selection of the appropriate selective coating on a given surface can guarantee the best performance of the heat generation system of the heater. Photothermal radiometry is based on the illumination of a given surface by a light source, the subsequent heating of the surface and the emission of infrared radiation with a maximum wavelength corresponding to the black body radiation spectra at the temperature of the sample. Therefore photothermal radiometry can be expected to be a technique especially suited to measure the emissivity of the surface of the illuminated material [1]. Several efforts have been made to achieve this objective, however given that the emissivity is frequently coupled to the absorbed radiation this is not a simple goal to reach [2]. In this work, selective coatings of NiO/Ni, deposited on 316 stainless steel, are studied by front illumination and detection. The photothermal signal is generated by illuminating by 1W, 808 nm laser source with a spot of about 5mm, modulating the laser intensity in the frequency range between 3 and 2003 Hz. The photothermal signal amplitude and phase NiO/Ni were normalized with the measured signals of the steel substrate. Measuring the optical reflectance using a conventional UV-VIS, the thermal emissivity of the selective coating can be obtained. Additionally, in order to determine the effect of the layered structure on the photothermal radiometry signal, simulations in two layers systems is performed and compared with the experimental data.

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Study of grain boundaries in polycrystalline silicon sample by photothermal deflection technique

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In this study we examined the grain boundaries in polycrystalline silicon sample by photothermal deflection technique. For this purpose the sample is immersed in a glass cell filled with paraffin oil and heated using a 2mW He-Ne laser modulated at the frequency of 67 Hz. Photothermal signal variations as a function of micrometric displacement of the sample has been studied. The pump beam is perpendicular to sample surface however the probe laser beam skimming the sample surface remains at a fixed distance from the sample surface. A change in the amplitude and phase of the photothermal signal has been observed when the beam pump passes through the area where there is the grain boundary. Thus by comparing the experimental curves of the amplitude and phase of the photothermal signal to the corresponding theoretical curves one can determine the size of the grain boundary as well as its thermal properties.

Discussion on optimal coupling medium and its thickness in photopyroelectric calorimetry

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In this paper different coupling fluids inserted between a solid sample and a pyroelectric sensor have been investigated. The measurements of the thermal diffusivity of the specimen were performed in the standard photopyroelectric back configuration (BPPE) with frequency scanning procedure [1] and infrared lock-in thermography (IRT) [2].

The PPE method in the back configuration (the solid sample placed onto the sensor is excited by the incident radiation) requires a thin layer of the coupling medium between the sample and the pyroelectric sensor. The presence of thin (but uncontrolled in thickness) additional layer changes the slope of the phase curve, and consequently obtained value of thermal diffusivity is always underestimated [3]. The influence of the coupling medium in pyroelectric measurements of solids

becomes significant especially for high conductive samples and at high modulation frequency of the incident radiation.

The research has been focused on searching for an optimal coupling medium. Obtained results lead to conclusion that the type of the coupling medium is not as important as its thickness. To minimize the influence of the coupler, some improvements of experimental BPPE setup were proposed. After the modification both methods lead to similar results.

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Evaluation of physico-chemical properties of biodiesel subjected to ultraviolet radiation and thermal degradation: using thermal lens spectrometry

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Biodiesel is no longer a promise to become a reality in the global scenario, since this biofuel comes from a renewable energy matrix and that can complement or replace dependence on fossil fuels. Brazil currently has consolidated as a potency on the world stage in the production of biodiesel, however, with increasing demand for biodiesel, is necessary a suitable choice of materials to be used for its production. Therefore, the characterization of this fuel becomes relevant because these properties are essential for the evaluation of the composition of raw materials and products obtained, being essential, for example, determine the thermal stability, storage period and temperature.

In this work we performed a study of evaluation of physico-chemical properties of soybean biodiesel subjected to ultraviolet radiation and thermal degradation using thermal lens spectrometry. The physical properties were viscosity and the thermal diffusivity (α) using a conventional technique and Thermal Lens Spectrometry (TLS), respectively. The viscosity expresses the resistance to flow or deformation of a fluid and the thermal diffusivity (α) expresses the ability of a material to transmit heat [1].

The TLS occurs when heat is deposited in the sample by absorbing light. The generation of heat induces a change in the intensity of the laser beam center that propagates through the sample and is

detected in a time interval, resulting in a gradient of refractive index with temperature (dn/dT) [2]. This variation depends on the properties of the material analyzed, such as the optical absorption coefficient and the thermal diffusivity.

Due to the complexity of the degradation process, which is crucial to check the thermal stability of biodiesel, the results of thermal properties will be compared with those obtained by the technique of gas chromatography to analyze the compounds.

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Thermal properties of low-density polyethylenes evaluated by photoacoustics

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Thermal diffusivity and thermal conductivity have been investigated for low-density polyethylenes at room temperature, using photoacoustic frequency measurement. These thermal properties have been evaluated by both amplitude and phase frequency characteristics. Very good agreement with values reported in the literature has been obtained.

Contrast methods in photothermal measurements

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Physical phenomena, kind and properties of detector used for the measurement, transmittance of amplifier and signal processing may change temperature signal form and magnitude in photo-thermal measurements. Such kind of signal changes is classified as linear distortions and it may be especially troublesome during analyzing of object's properties in frequency or time domain. In the case of photothermal examination the various methods of energetic stimulation and temperature measurement are commonly used. Each time, it causes the changes in frequency spectra of signal. In order to reproduce the actual shape and magnitude of the temperature signal the character of total

transmittance of all measured system have to be known. It is usually necessary condition for quantitative measurements of thermal parameters. However, very often the knowledge about changes (contrasts) of temperature signal in comparison to the signal detected for reference object of known properties is sufficient for determining of thermal traits of measured object. If the measuring position for reference and measured objects is the same the contrast signal may be independent of its transmittance.

Generally, a few kinds of contrasts (i.e. amplitude, phase or complex ones) and reference objects may be used in measurements. So, it is very important how do results and accuracy of measurements depend of them. In the paper a few of contrast techniques for various types of contrasts and reference objects are analyzed from that point of view.

Determination of structural parameters of thin-film photocatalytic materials by BDS

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In the photothermal beam deflection spectroscopy (PDS) an intensity-modulated beam of light illuminates an absorbing sample. As a result of nonradiative deexcitation heat pulses (thermal waves) are generated. Thermal waves diffuse into the sample and the adjacent medium resulting in a modulated temperature and consequently refractive index gradients that leads to the intensity change of another light beam (probe beam) passing through the adjacent medium grazing the sample surface [1].

The photodeflection (PD) signal contains information about the thermo-optical parameters of the examined sample which, in turn, are determined by its structural characteristics as porosity [2] or surface roughness [3]. This is because the surface roughness strongly influences the propagation of thermal waves (ThW) by distorting their wave fronts. Such an influence is the stronger, the higher modulation frequencies f of ThW are used during the experiment [3]. This effect is important especially in case of thin films deposited on bulk support when the use of high f is necessary to get information about the samples properties without the influence of its support.

The sample's porosity determines the heat exchange, as well as the heat conduction in the material, thus define the values of its thermal diffusivity and conductivity. The thermal parameters of porous films decrease with increasing porosity as a result of decrease in heat conduction, as well as heat radiation in the fluid throughout the pores and throughout the sample's material [2].

The goal of this work is to extract information, from BD measurement, about structural properties of some photocatalytic materials by comparing the measured results with theoretical values obtained by the use of theoretical description based on the complex geometrical optics equations [4], according to which the PB interaction with the field of ThW consist of two effects: its deflection and phase change. Deflection is a result of refractive index gradient in the fluid above the sample's surface that

changes the trajectory and divergence, thus the amplitude of PB. The change in PB phase is due to the change of the PB's optical path which result from its deflection on refractive index gradients or/and the change in fluid refraction index.

Samples of the commonly used photocatalytic materials (eg. TiO_2) in a form of thin films deposited on bulk support, were chosen for examination. For this type of materials, their surface roughness and porosity are important properties that determine their effectiveness as photocatalysts in water purification processes.

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Temperature dependent photothermal studies of biodiesel and precursor oils

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Biodiesel is a promising option for alternative fuels since it derives from natural and renewable materials, it is biodegradable and less polluting than fossil fuels. A gradual replacement of diesel by biodiesel has been adopted by many countries, making necessary the investigation of the physical properties of biodiesel and of its mixture in diesel as well. Photothermal techniques, specifically photopyroelectric technique (PPE), have proved to be suitable in the characterization of biodiesel and of its precursor oils, as well as of the biodiesel/diesel mixtures.

In this paper we investigate thermal properties of some biodiesel and precursor oils as a function of temperature, aiming to characterize the freezing/melting interval and the changes in the physical properties from the solid to the liquid phase. The supercooling effect was detected for samples with higher viscosity values. Measurements with coconut oil and biodiesel, babassu oil and animal-fat based biodiesel are discussed with emphasis. Thermal diffusivity, effusivity and conductivity measurements of the samples at room temperature are also presented. The samples were prepared using the transesterification method, by the ethylic route. Optical transmittance experiments were carried out in order to confirm the phase transition interval and the supercooling effect detection.

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Characterization of the O⁺⁶ ion implanted silicon layers using plasma waves and C-V techniques

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This paper presents investigation of optical properties of the high energy O⁺⁶ ion implantation using combination of optical (photothermal radiometry (PTR) and modulated free carrier absorption (MFCA)) and electrical methods (Capacitance-Voltage (CV)). The recombination parameters of silicon samples implanted by energy O⁺⁶ ion implantation were investigated in paper [1]. In this paper we propose simple relation between the thickness of the implanted layer d and the optical absorption coefficient of this layer β_{imp} :

$$d = - \frac{\ln k}{\beta_{imp}} \quad (1)$$

where k is the ratio of the PTR or MFCA amplitude, in the plasma wave region of the implanted sample, to the PTR or MFCA amplitude of the nonimplanted sample in the same plasma wave region. Fig. 1 presents relation between $-\ln(k)$ and four different excitation photons' energies.

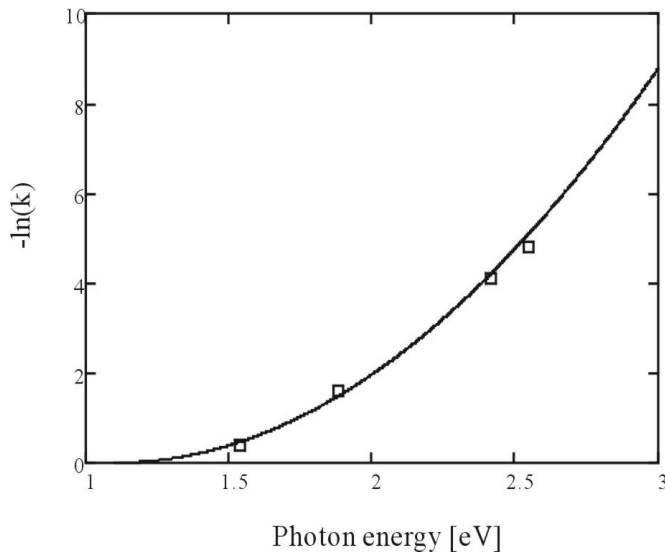


Fig.1. Dependence $-\ln(k)$ vs. energy of photons for oxygen implanted silicon sample - $\ln(k) = \beta_{imp} \cdot d = A \cdot (E_f - E_g)^2 \cdot d$, where $E_g = 1.1$ eV. Squares mean PTR or MFCA results for four different excitation photons' energies.

If the thickness of the ion implanted is known then the absorption coefficient of the ion implanted layer can be calculated.

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Thermal interface conductance of copper layers on carbon and correlation with mechanical adhesion strength

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The functioning of protective coatings is governed by the strength of the mechanical adhesion of the film on the substrate. Generally, it is assumed that the mechanical contact is directly related to the thermal contact. Therefore, measurements of the thermal interface conductance are used to judge the quality of adhesion of the film. In this work we have setup a study to explore the quantitative nature of this correlation for copper films deposited on carbon. The thermal interface conductance was determined by frequency domain photothermal radiometry (PTR). The mechanical adhesion strength (AS) of the film coating was deduced from pull-off experiments. The experiments were performed on copper-carbon flat model systems with different bonding layers between the copper film and the substrate. The Cu- films (about 1 μm thickness) and the bonding layers of B, Mo, Nb or Ti (5-10 nm thickness) were deposited by magnetron sputtering on vitreous carbon (Sigradur) substrates. One part of the samples had been subjected to a heat treatment. The experimental thermal data were analysed in the frame of heat diffusion equation for one-dimensional and three-dimensional heat transport. It was assumed that the contact of the layer is not perfectly constant across the samples. The non-perfect interfaces were modelled by two different values for the thermal interface conductance G_1 and G_2 which co-exist at different areas on the interface and are weighted according to their relative area x_1 and x_2 . With respect to the heat transport through the interface the two areas with different G values act like a parallel connection of two resistors where the one with a larger G and larger area dominates the total $G_{th} = x_1 \times G_1 + x_2 \times G_2$. However, when considering the correlation with the mechanical adhesion strength we found that one has to take into account the series connection of the interface resistances of both areas $R_{eff} = x_1 \times R_1 + x_2 \times R_2$. The adhesion strength then scales with the effective thermal conductance $G_{eff} = 1/R_{eff}$. The defective area has a much larger impact for G_{eff} than for G_{th} that controls the heat transport across the interface. For the investigated CuC-flat samples the adhesion strength (AS) as a function of the effective interface conductance G_{eff} obeys the power law $AS \propto G_{eff}^{0.60}$. The result that the adhesion strength scales more likely with G_{eff} than with G_{th} can be explained by pulling forces in the AS-experiment which are not directed perpendicular to the surface only.

Study of heat transfer regimes as a function of gas pressure in a vacuum chamber using a thermal wave resonant cavity

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Evacuated solar collector receivers are the most important components of a solar thermal system, which are designed to improve the energy conversion efficiency from sunlight to thermal energy. The structure of the collector consists of an absorber tube and a glass envelope, in which the intermediate space is evacuated from air or filled with low thermal conduction gases. Heat loss is due to three mechanisms: conduction, convection and radiation. In order to minimize conduction and convection mechanisms, the tube-glass intermediate space is evacuated to reach a vacuum pressure of about 10^{-5} Torr [1]. In this situation, only radiation heat transfer mechanism is present. In this work, we used a Thermal Waves Resonant Cavity (TWRC) [2] to study the suppression of conduction and convection heat transfer mechanisms. With this purpose we put the resonant cavity into a vacuum chamber; and the signal phase and amplitude of the pyroelectric signal was collected as a function of vacuum pressure. The results obtained show a dependence of the amplitude and phase lag of the pyroelectric signal with respect to the vacuum pressure which allows us to determine the different heat transfer mechanisms as a function of the chamber pressure.

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Quantitative thermal measurement by the use of scanning thermal microscopy

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The scanning thermal microscopy (SThM), invented in 1986 by Williams and Wickramasinghe, gives opportunities for thermal measurement with high spatial resolution. Both lateral and depth resolutions are defined by a radius of SThM probe and sample contact. In a case of nanofabricated thermal probes this radius does not exceed 100 nm. Thermal images of nanostructures confirmed the submicron spatial resolution of the measurement.

The main problem connected with quantitative thermal measurement using SThM equipment is relatively low dynamic range. Because the contact area between the probe and the sample is very small, an influence of sample thermal properties on measured signal is low. A few orders of magnitude change in the thermal conductivity of the sample results in no more than 20-30% change in the measured signal. This caused necessity of noise suppression to obtain satisfactory resolution of measurement. This goal can be reached by the use of lock-in signal detection. However it requires driving the probe by ac current which causes problems with stability of the probe sample contact. To solve this problem the measuring technique in which the probe is driven by a sum of dc and ac currents was proposed. Experiments showed that in this case periodical probe bending caused by thermally induced stresses can be avoided. The measured signal consists of dc component and 3 harmonic components at frequencies ω , 2ω and 3ω , where ω is the frequency of ac component of driving current.

An analysis of the sensitivity of the system to the thermal conductivity of the sample revealed that the highest sensitivity can be theoretically achieved when higher harmonics are measured. But from the other hand higher harmonics detection is accomplished by the fact that the amplitude consecutive harmonics considerably decrease.

The results of theoretical considerations were confirmed by experimental data. Measurements were carried out for two types of probes: the probe utilizing Wollaston wire and nanofabricated thermal probe. Measured frequency characteristics of both probes can be qualitatively explained by the lumped approximation of suspended wire. More detailed analysis showed that dependencies obtained for the nanofabricated thermal probe have more complex character. Its interpretation requires more complex model of the heat exchange in the probe-sample system.

The thermal diffusivity of $\text{ZnS}_x\text{Se}_{1-x}$ crystals as a function of composition

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$\text{ZnS}_x\text{Se}_{1-x}$ ternary crystals are solid solutions of two binary semiconductors ZnSe and ZnS. They can be potentially interesting for applications thanks to possibilities of controlling physical properties through crystal composition. It was already shown that the band gap, the electric conductivity, the optical properties etc. depend on sulphur content x . The aim of this work was to investigate the thermal diffusivity dependence on x .

Measurements were carried out by photothermal method with IR detection. A plate-like sample was illuminated by intensity modulated light ($\lambda = 532$ nm) and the temperature disturbance was registered through the IR radiation from the sample surface. Measurements for front and back illumination were carried out. As investigated samples were transparent to both illuminating light and

IR radiation a thin metal foil was attached to the sample surface for localization of heat sources and temperature measurement. An existence of these foils were taken into account in experimental data analysis.

The sulphur content varied from 10 at% to 30 at%. The results showed that the thermal diffusivity of samples decreases with the increase of sulphur content x . However proper analysis of obtained data was accomplished by the fact that the thermal diffusivity strongly depends on the concentration of phonon scattering centres. They can be produced by alien atoms in the crystal lattice but also by other defects (dislocations, grain boundaries, etc.). It causes that unambiguous interpretation of experimental results is difficult.

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