

Joule heating effects in capillary electrophoresis - designing electrophoretic microchips

D. Witkowski ^a, J. Łysko ^b, A. Karczemska ^{a,*}

^a Institute of Turbomachinery, Technical University of Lodz,
ul. Wólczajska 219/223, Łódź, Poland,

^b The Institute of Electron Technology,
Al. Lotników 32/46, 02-668 Warszawa, Poland

* Corresponding author: E-mail address: anna.karczemska@p.lodz.pl

Received 11.09.2009; published in revised form 01.12.2009

Analysis and modelling

ABSTRACT

Purpose: Computer simulations are widely used for designing, which contributes to a cheaper equipment developing process. In the last years computer simulations have begun to be also applied in different instances of microfluidics, especially in microchip electrophoresis (where an electrophoresis process takes place in the microcapillaries manufactured on the surface of the small plate) which is interesting for us. However, there are not many commercial programs enabling simulations of microfluidics. The programs existing in the market are recently developed as microscale brings new possibilities but also unpredictable effects and challenging problems. The aim of this paper is to develop a mature technique helpful in designing electrophoretic microchips [1-4].

Design/methodology/approach: Temperature distributions occurring during capillary electrophoresis because of Joule heating effects will be calculated with use of the CoventorWare™ software.

Findings: Computer simulations with the model of capillary, with the same geometry as the real one, are presented. Numerical simulation results are compared with the real data from the capillary electrophoresis process.

Practical implications: This is the first step to create a reliable tool for designing microfluidic devices.

Originality/value: This comparison shows an ability of the CoventorWare™ software to design electrophoretic microchips.

Keywords: Capillary; Joule heating; Electrophoresis; Numerical simulations; Coventor ware

Reference to this paper should be given in the following way:

D. Witkowski, J. Łysko, A. Karczemska, Joule heating effects in capillary electrophoresis - designing electrophoretic microchips, Journal of Achievements in Materials and Manufacturing Engineering 37/2 (2009) 592-597.

1. Introduction

The term electrophoresis is generally applied to the movement of small ions and charged macromolecules in solution under the influence of an electric field. The rate of migration depends on the

size and shape of the molecule, the charge carried, the applied current and the resistance of the medium.

Electrophoresis can be performed in a capillary format. A typical system consists of two reservoirs and a capillary filled with a buffer solution. A high voltage is applied across the

capillary by using a high-voltage power supply. Very small diameter capillaries (typically 5–100 micrometers) employed in this technique allow for efficient heat dissipation. Therefore, much higher voltages can be employed than those used in the lab gel electrophoresis, leading to faster, more efficient separations. Compounds are separated on the basis of their net electrophoretic mobility.

Most often a detector is placed on line and analytes are detected as they flow past the detector. Spectroscopic detection (ultraviolet and laser-based fluorescence) is usually performed in this manner by using a capillary itself as the optical cell. Alternatively, detectors can be placed off line (behind the column). In this case, a detector is isolated from the applied electric field through the use of a grounding joint. Electrochemical detection and mass spectroscopic detection are generally accomplished in this manner, since the electric field can interfere with the performance of these detectors.

Capillary zone electrophoresis is the simplest and most widely used form of capillary electrophoresis. The capillary is filled with a homogeneous buffer, and compounds are separated on the basis of their relative charge and size. Most often, fused silica capillaries are employed. In this case, an electrical double layer is produced at the capillary surface due to the attraction of positively charged cations in the buffer to the ionized silanol groups on the capillary wall. In the presence of an electric field, the cations in the diffuse portion of this double layer move towards the cathode and drag the solvent with them, producing an electroosmotic flow. The resulting flow profile is flat rather than parabolic, which is characteristic of liquid chromatography. This flat flow profile causes analytes to migrate in very narrow bands and leads to highly efficient separations. The electroosmotic flow is also pH dependent, and it is highest at alkaline pH values.

In most cases, the electroosmotic flow is the strongest driving force in the separation, and all analyses, regardless of charge, migrate towards the cathode. Therefore, it is possible to separate and detect positive, negative, and neutral molecules in the same electrophoretic run, if the detector is placed at the cathodic end. Negatively charged compounds are attracted to the anode but are swept up by the electroosmotic flow and elute last. Neutral molecules, which are not separated from each other in the capillary zone electrophoresis, elute as a single band with the same velocity as the electroosmotic flow. Positive compounds have positive electrophoretic mobility in the same direction as the electroosmotic flow, and they elute first. The capillary zone electrophoresis is generally employed for separation of small molecules, including amino acids, peptides, and small ions, and for separation of drugs, their metabolites, and degradation products.

In this section it is necessary to present in detail assumptions and, course of, own investigations to such an extent that a reader could repeat those works to confirm achieved results. In short papers, that information should be given in as short a version as possible.

Joule heat is a very significant but undesirable phenomenon occurring during the process of electrophoresis. It leads to the temperature and temperature gradient growth across the microfluidic chips and channels, decreasing the quality of separation in a number of ways (sample band dispersion or peak broadening, deterioration of analysis resolution and even

decomposition of thermally sensitive samples or creation of vapor bubbles in the microchannels),

$$\frac{dQ}{dt} = \frac{iV}{L_{tot}A}$$

where:

dQ/dt [W] – time of heat generation, i [A/m²] – current density, V [V/m] – voltage per length unit, L_{tot} [m] – total capillary length, A [m²] – cross section of the capillary.

2. Experiments

Numerical simulations of the capillary electrophoresis have been performed and compared with the results from the experiments. This is a first step to creating a new, reliable method of designing electrophoretic microchips.

2.1. CoventorWare™ code

The commercial code – CoventorWare™ - was used to perform numerical calculations which are described later on in this paper [7]. CoventorWare is a very modern and structured program. Its application is very wide and one can design different, sophisticated models from the very beginning. It also provides 3D analysis and design automation software for the development of micro- and nano-scale devices and systems. Our scope concerns MemCFD section which deals with (general flow, fluid mixing, thermal) module supplies, general CFD (Computational Fluid Dynamics) capabilities. The main objective is to model a capillary and simulate its flow in the air medium.

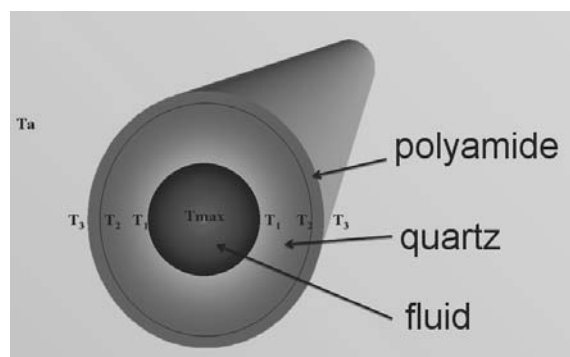


Fig. 1. 3D model of the capillary

Fluid dynamics is an essential component of microfluidics. The fundamental governing equations are Navier-Stokes equations, which are derived from the conservation of mass, momentum and energy [8]. In microfluidic devices, the surface-to-volume ratio is very high. In most cases, the length of the channel is very large in comparison to the depth and width, thus in the Navier-Stokes momentum equations, the viscous effect is dominant over the momentum effect. In microfluidic devices, the

flow is usually characterized by a low Reynolds number. Another phenomenon that distinguishes the microfluidic flow from macroscopic flows is the surface tension effect across the interfaces between different fluids, especially liquid and gas. An approach to the near-wall boundary differs as well. For macroscopic flows, it can be assumed that there is no motion of fluid particles at the fluid-to-solid boundary. However, microfluidic experiments [9] show that this assumption cannot be applied. Instead of it, in the microfluidics fluid particles at the fluid-to-solid boundary move with a slip velocity with respect to the solid surface. A magnitude of this slip velocity is linearly proportional to the shear strain rate at the fluid-to-solid boundary [10-12].

2.2. Capillary electrophoresis

Figure 1 presents a cross-section of the capillary which was used in the experiment. The capillary TSP530660 (Composite Metal Services Ltd.) was made of fused silica, the inside diameter was equal to $542 \pm 12 \mu\text{m}$, the outside diameter was equal to $673 \pm 25 \mu\text{m}$. The capillary was covered by polyamide, the thickness of this layer was equal to $24 \mu\text{m}$. The capillary was filled with 1% agarose gel prepared in 1xTBE buffer (pH 8,3). Total length of the capillary was equal to 17cm.

During the CE process, 3 thermocouples K (RS 205-7525 TC-08) were used to measure the external wall temperature of the capillary in three different points. The fourth thermocouple measured the ambient temperature of the air. The external temperature of the capillary wall and the internal temperature T_{max} at the capillary axis (Fig1), were also calculated with the equations described elsewhere [5]. Similarly, the temperature differences ($T_{\text{max}} - T_1$), ($T_1 - T_2$), ($T_2 - T_3$), ($T_{\text{max}} - T_3$) were calculated and the results of calculations are shown at Fig.9.

The infrared camera used for this study was Titanium series (Cedip Infrared System Corporation) with InSb as an infrared detector, the emperature range between $5 \text{ }^\circ\text{C}$ to $520 \text{ }^\circ\text{C}$, the resolution of 640×512 pixels ($25 \mu\text{m}$ pitch), the infrared wavelength between $3 \mu\text{m}$ to $5 \mu\text{m}$, cooling by electronic control of the Stirling cooler, the noise equivalent temperature difference of 17 mK at $20 \text{ }^\circ\text{C}$, the shutter speed between $10 \mu\text{s}$ to 100 ms , and the frame rate between 5 Hz to 380 Hz .

3. Results

3.1. Numerical calculations

The computer simulations [13-16], were used for the fast calculation of the temperature distribution along and across the capillaries. Figures from 2 to 5 show example distributions on the capillary with the same geometries and a different voltage value. There are temperature distributions along of the capillary model for the voltage values: 1.0kV, 1.5kV, 2kV and 2.5kV. It can be clearly seen that for all temperature profiles, the maximum temperature is in the middle of the capillary. For the voltage equal to 1.0kV, the maximum temperature obtains the value 308K, for 1.5kV – 316K, for 2.0kV – 332K and for 2.5kV – 354K.

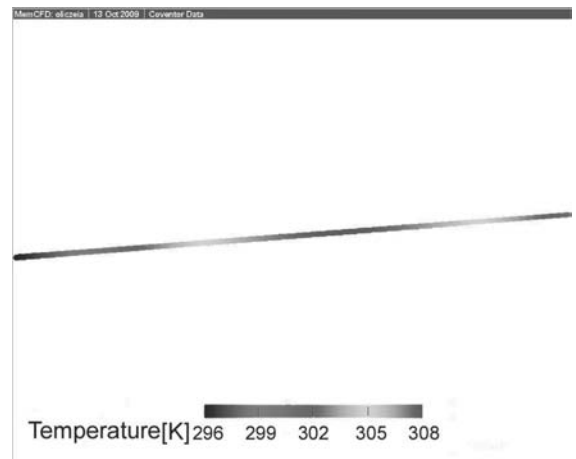


Fig. 2. Temperature distributions, cross-sections of the capillary model, 1.0kV

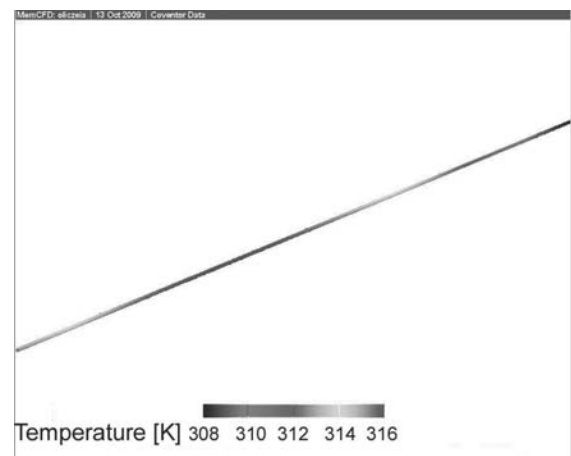


Fig. 3. Temperature distributions, cross-sections of the capillary model, 1.5kV

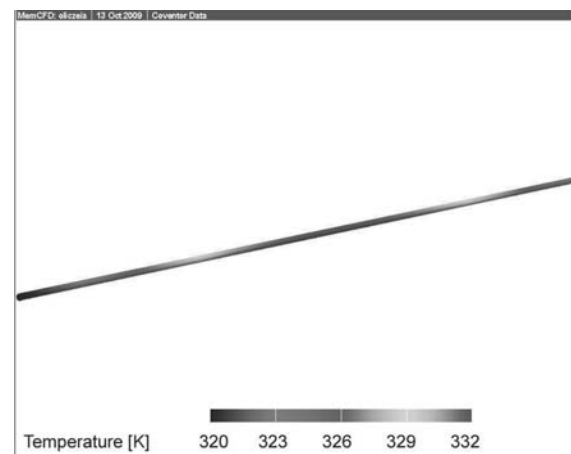


Fig. 4. Temperature distributions, cross-sections of the capillary model, 2.0kV

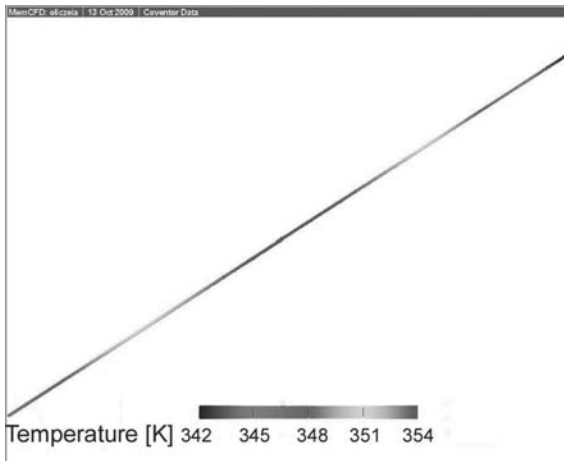


Fig. 5. Temperature distributions, cross-sections of the capillary model, 2.5kV

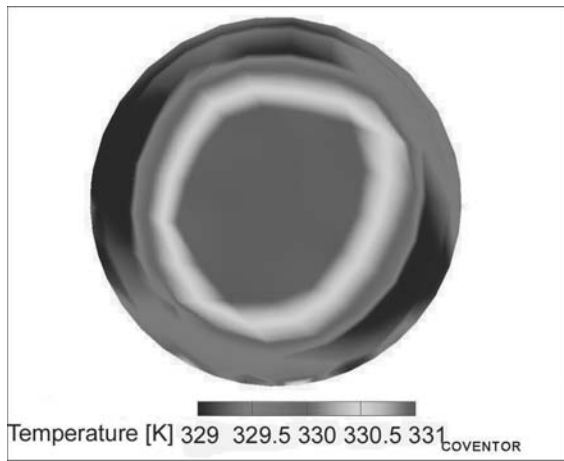


Fig. 6. Temperature distributions, cross-sections of the capillary model, 2kV

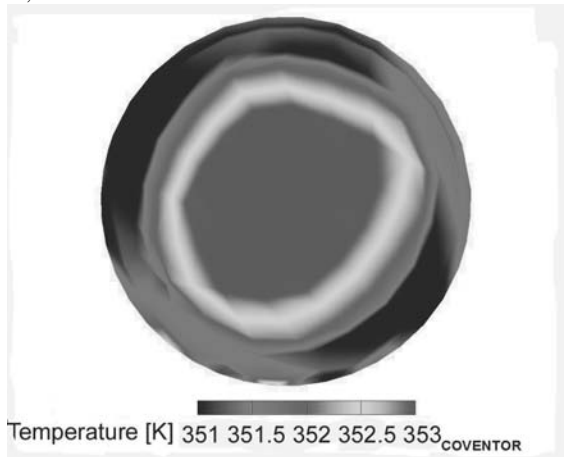


Fig. 7. Temperature distributions, cross-sections of the capillary model, 2.5kV

Results from the numerical calculation, a cross-section of the capillary are visible in Figures 6 and 7. In the middle of the capillary there is the highest value of temperature, 331K (fig.6) and 353K (fig.7). The first result was obtained for the voltage value equal to 2kV, the second result for the voltage value equal to 2.5kV. A difference between the middle of the capillary and walls is close to 1K. Generally, the temperature is too high, when we compare this result with the result from the experiment. It is necessary to compare and obtain similar results from the numerical calculations and from the experiment. When it is achieved, it will be possible to design a new capillary with different geometries and a different material to find the best solution to minimize the influence of Joule heating.

3.2. Temperature distributions in capillary electrophoresis

Figure 8 presents a temperature comparison, results from the stand and the theoretical calculations. Temperatures Tc1, Tc2 and Tc3 represents the three measuring points (with thermocouples) on the stand, temperature Ts is the room temperature, T3 is the temperature from the theoretical calculation, Tmax is the temperature in the centre of the capillary (also the theoretical calculation). It is seen that the results from the stand and theoretical calculations are convergent.

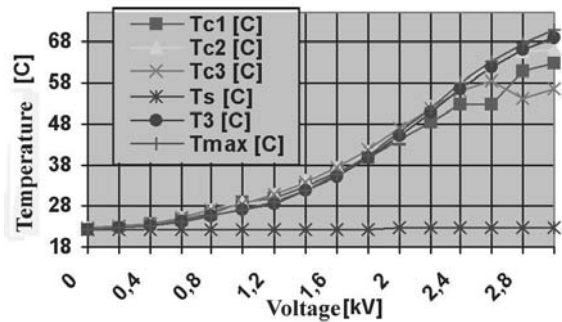


Fig. 8. Temperature comparison, results from the stand and calculations, temperature of the capillary wall as a function of voltage [5]

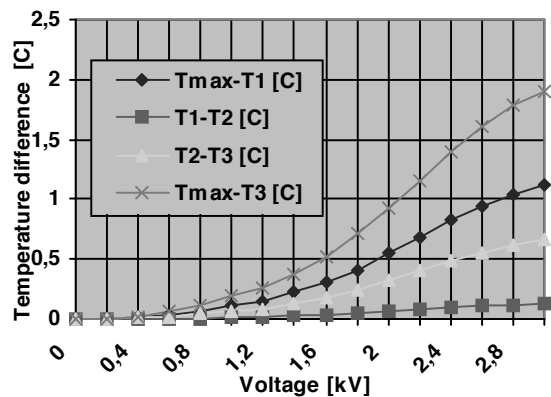


Fig. 9. Temperature differences ($T_{max} - T_1$), ($T_1 - T_2$), ($T_2 - T_3$), ($T_{max} - T_3$) versus voltage applied [5]

Figure 9 shows other calculations, especially important is the temperature difference ($T_{max}-T_1$) that should not exceed 1K. It is seen that to the 3.0kV $T_{max}-T_1$ is less than 1K. Over 3.0kV this differences is more than 1K.

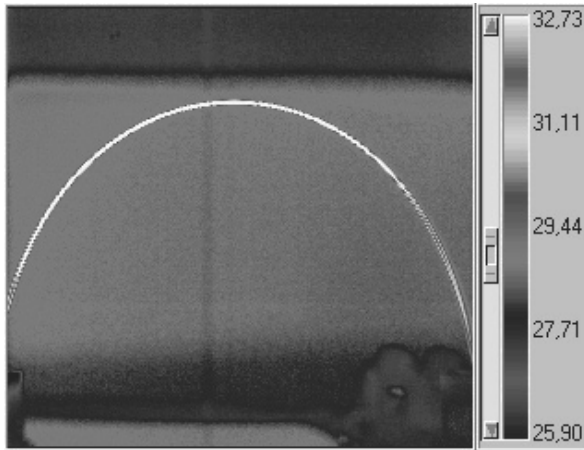


Fig. 10. Capillary photos, results from the infrared camera for the voltage equal to 1.6kV [5]

Figures 10 and 11 present results from the infrared camera for the voltage value equal to 1.6kV (Fig.10) and 1.8kV (Fig.11), respectively.

Significant differences between temperature profiles of the voltage equal to 1.6kV and 1.8kV are well visible. The maximum temperature for 1.6kV is equal to 32.73 Celsius degree (305.72K), for 1.8kV is equal to 37.86 Celsius degree (310.86K). A influence of the voltage value on the Joule heating generation, can be clearly seen.

4. Discussion

The theoretical results, the results of numerical simulations and the data from measurements (thermocouples and an infrared camera) show some degree of similarities. However, the numerical simulations up to now have shown slightly higher values of temperature that the real results from experiments and theoretical calculations.

To compare results from the experiment, theoretical calculations, and infrared camera, the maximum difference is about 8.2%. For example, for the voltage value equal to 1.6kV, the result from the experiment is 35°C for the theoretical calculations 32°C and for the infrared camera 32.7°C. For the voltage value equal to 1.8kV the result from the experiment is 38°C for the theoretical calculations 35°C and for the infrared camera 37.9°C. When we add the results from the numerical calculations, the differences are bigger. For instance, for the voltage value equal to 1.0kV the result from the numerical calculation is 35°C, for the the experiment 27°C it is about 29%. For the voltage value equal to 1.5kV the result from the numerical calculation is 43°C, for the experiment 33°C, it is about 30.3%.

There is too significant difference but it is possible to reduce it to less than 10%. While preparing the calculation it was necessary to create some presumption, which cause these differences. This presumptions have to been improved.

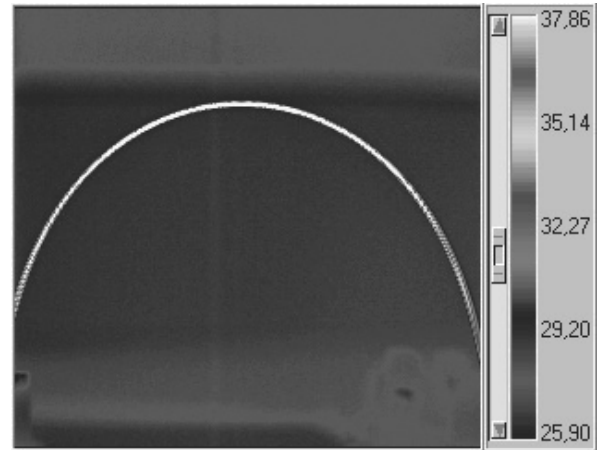


Fig. 11. Capillary photos, results from the infrared camera for the voltage equal to 1.8kV [5]

It is still much to be done with numerical simulations in case of microfluidic systems. There are not many commercial programmes including possibilities of microfluidics calculations. The authors of this paper are not sure how reliable are these programmes. There is a necessity to apply numerical simulations to different areas of microfluidics, it is especially important during designing new microfluidic devices. Modelling of such devices can lower the costs of their manufacturing and lead to new solutions. But there is also a need to check these programmes, and their accuracy with real systems.

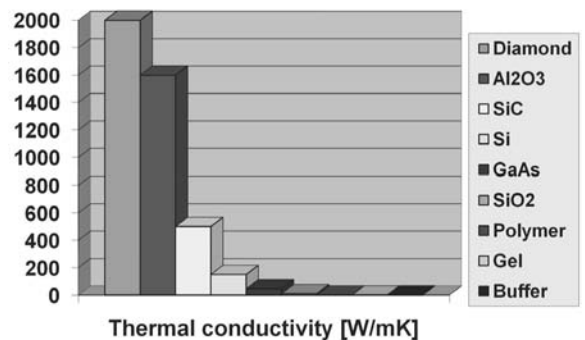


Fig. 12. Thermal conductivity of materials – comparison [5]

Figure 12 presents thermal conductivity coefficients of different materials, some of them are commonly used for manufacturing electrophoretic microchips. The best material is diamond, from the point of view of thermal properties. Thermal conductivity of diamond is equal to 2000 W/mK. It is 5 times higher than for copper. Additionally, diamond, thanks to its exceptional physical, bio-chemical and mechanical properties, has

been recognized recently as a very promising material for different biological sensing systems, [4, 6, 8]. Its highest known thermal conductivity makes diamond the best material choice for the applications in different microfluidic devices based on the electrophoresis process (microchip electrophoresis – MCE).

5. Conclusions

This is the first step to create a reliable tool for designing microfluidic devices. While preparing the capillary model some presumptions were introduced, which at present cause some discrepancy of the results. These presumptions have to be improved, which permits to increase the convergence of results obtained from the numerical calculations and experiment. Such a method which is to produce microfluidic devices, allows us to minimize the experiment costs, process of device creating, stand preparation and experiment realization. Verification of the numerical calculations and experiments is, of course, an indispensable part of the research.

Acknowledgements

Supported by the project “Diamond Microfluidic Devices for Genomics and Proteomics”, ERA –NET MNT/98/2006.

References

- [1] D. Erickson, Towards numerical prototyping of labs-on-chip: modelling for integrated microfluidic devices, *Review, Microfluid Nanofluid 1* (2005) 301-318.
- [2] D. Paul Grossman, C. Joel Colburn; *Capillary Electrophoresis - Theory and Practice*; Copyright Academic Press, INC, USA, 1992.
- [3] *Introduction to Capillary Electrophoresis*; Beckman Instruments, Inc., 1994.
- [4] H. Björkman, C. Ericson, S. Hjertén, K. Hjort, Diamond microchips for fast chromatography of proteins, *Sensors & Actuators B 79* (2001) 71-77.
- [5] A. Karczemska, D. Sideris, J. Hassard, K. Józwiak, E. Mitura, Electrophoretic chips for DNA and protein separations – Joule heating dissipation, *Proceedings of the VI Symposium Modelling and measurements in medicine MPM, Krynica, 2004.*
- [6] A. Karczemska, A. Sokołowska, Materials for DNA sequencing chip, *Journal of Wide Bandgap Materials 9/4* (2002) 243.
- [7] Coventor inc. *Microfluidics Reference*, 2008.
- [8] G.K. Batchelor, *An introduction to fluid dynamics*, Cambridge University Press, 2000 in: Coventor inc. *Microfluidics Reference*, 2008.
- [9] C.H. Choi, K.J.A. Westin, K.S. Breuer, Apparent slip flows in hydrophilic and hydrophobic microchannels, *Physics of Fluids 15/10* (2003) 2897-2902 (in: Coventor inc. *Microfluidics Reference*, 2008).
- [10] C.L.M.H. Navier, *Mémoire sur les lois du mouvement des fluides*, *Mémoires de l'Académie Royale des Sciences de l'Institut de France*, 6, (1823) 389-440 (in: Coventor inc. *Microfluidics Reference*, 2008).
- [11] J.C. Maxwell, On stresses in rarified gases arising from inequalities of temperature, *Phil. Trans. R. Soc. Lond.*, 170 (1879) 231-256 (in: Coventor inc. *Microfluidics Reference*, 2008).
- [12] E. Lauga, H.A. Stone, Effective slip in pressure-driven Stokes flow, *Journal of Fluid Mechanics 489* (2003) 55-77 (in: Coventor inc. *Microfluidics Reference*, 2008).
- [13] J. Lysko, D. Witkowski, D. Obidowski, A. Karczemska, Numerical simulation of diamond microfluidic device for biomolecules' electrophoretic separations, 19th European Conference on Diamond, Diamond-Like Materials, Carbon Nanotubes, and Nitrides, Sitges, Spain, 2008.
- [14] D. Witkowski, D. Obidowski, J. Lysko, A. Karczemska, 3D Simulations of Microfluidic Devices, *Thermal Flow Machiner- Turbomachinery 133* (2008) 359-368.
- [15] A. Karczemska, D. Witkowski, V. Ralchenko, A. Bolshakov, D. Sovyk, J.Hassard, Diamond Microfluidic Devices manufactured with the replica method, Perspective technologies and methods in MEMS design, *Proceedings of the Vth International Conference MEMSTECH 2009*, Polyana, Ukraine 2009
- [16] J.M .Lysko, D. Witkowski, D. Obidowski, A. Karczemska, Numerical Simulations of Diamond Microfluidic Device for the Biomolecules Electrophoretic Separations.