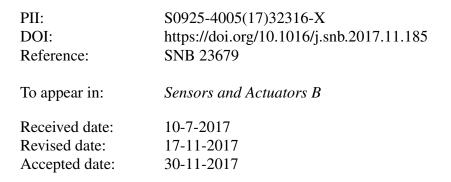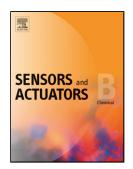# Accepted Manuscript

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Quantitative characterization of plasma treated PDMS microfluidic substrates by inverse gas chromatography

B. Mészáros[1], G. Járvás[1,2], L. Hajba[2], M. Szigeti[1,2], A. Dallos[3], A. Guttman[1,2]

[1]*Horváth Csaba Memorial Institute of Bioanalytical Research, University of Debrecen, Debrecen, Hungary*
[2]*MTA-PE Translational Glycomics Research Group, MUKKI, University of Pannonia, Veszprém, Hungary*
[3]*Department of Physical Chemistry, University of Pannonia, Veszprém, Hungary*

Highlights

- Microfluidic substrates were characterized by inverse gas chromatography.
- Recovery time of plasma treated PDMS was precisely determined.
- Hydrophobic and hydrophilic properties of PDMS surface.

Abstract

The effect of air plasma exposure time on the surface energies and acid-base characteristics of polydimethylsiloxane (PDMS) particles was studied. Polymerized PDMS powder was radio frequency induced air plasma irradiated for 2-10 seconds with the power of 500 W. The efficiency of the plasma treatments was investigated by a new generation inverse gas chromatograph, a surface energy analyzer. The dispersive component of surface energy was determined by the Dorris-Gray method describing the van der Waals interactions, while the specific component of surface energy expressed the surface ability for Lewis acid-base interactions. It was demonstrated that the air plasma treatment did not affect the dispersive and acidic parts of the surface energy and the change of surface hydrophilicity was caused by the raise of the electron-donor ability of the PDMS surface, characterized by van Oss-Good-Chaudhury's base number. The optimal plasma treatment time was found to be 5 second. Analysis of the specific surface energy and acid-base characteristics with respect to exposure time showed that partial to complete hydrophobic recovery occurred within 38 hours.

Abbreviations: PDMS – polydimethylsiloxane; IGC – inverse gas chromatography; XPS - X-ray photoelectron spectroscopy;

Keywords: PDMS, inverse gas chromatography, surface characterization, plasma treatment, hydrophobicity

1. Introduction

Microfluidic devices play important roles in the analytical and life science fields. This technology, also known as-lab-on-a-chip approach, makes to integrate analytical measurements easier, and do measurements faster amenable to use in high-throughput screening. Advantages of microfabricated devices include, but are not limited to, requirement for low sample volume, small reagents consumption, short processing time and easy integration [1-3]. Poly(dimethylsiloxane) (PDMS) is a commonly used material in fabrication of microfluidic devices due to its advantageous properties, such as elastomericity, transparency, chemical inertness, simple handling and manipulation as well as low electrical conductivity [4, 5]. PDMS is an appropriate catalyst support [6] and a very effective and low-cost air cathode catalyst binder in microbial fuel cells [7]. However, application of PDMS has limitations in microfabrication, e.g., its hydrophobic surface characteristics restricts the application of PDMS microfluidic devices with aqueous solution. Numerous methods have been developed to irreversibly or temporarily make the PDMS surface hydrophilic such as plasma treatment, UV treatment, surfactant treatment, protein adsorption, chemical vapor deposition, layer-by-layer deposition preparation of chemical coatings and their combinations [8-14]. Plasma treatment is by far the most commonly used method for PDMS surface modification [15-17]. The PDMS surface modification by plasma treatment has particular importance in the derivatization of microchips i.e. this is the initial step of many immobilization chemistries. Traditionally used analytical methods for the characterization of surface modification are contact angle measurement, scanning electron microscopy, x-ray photoelectron spectroscopy (XPS) and atomic force microscopy [18-23]. Despite of use of these characterization tools, it is still difficult to compare the effect of surface modification methods, as all of them have limitations and are not able to provide quantitative differences. For instance, the contact angle measurement of a water droplet is not taking the surface heterogeneity into account [24] and only provides a generalized measure of the sum of molecular interactions, without selective information about the strength of the dispersive and specific components of surface energy. Furthermore, this single phenomenological parameter of the surface supplied by sessile water contact angle measurement possesses a so called "observer effect" that unfortunately affects the measured surface characteristics itself. It is well known that water molecules slow the hydrophobic recovery of the PDMS surface [22] because they prefer to interact with the hydroxyl groups found on the modified surface and cover the silanol interface as a thin layer [25]. XPS determines only the ratio of the chemical elements at a small area. Please note that

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most of these methods require complex instrumentation with highly trained operators. In addition, it has been demonstrated in the above cited works that the hydrophobicity and hydrophilicity represent a more complex phenomena than simple oil or water wettings. Inverse gas chromatography (IGC) has recently been implemented in numerous parts of the analytical fields as it enables investigation of samples in various forms of fibers, films, powders in crystalline and amorphous state. Polymers, pharmaceuticals and composite constituents are the most extensively investigated materials using IGC, but clays and other minerals have also been analyzed [26-30]. The advent of IGC offers a fast and accurate technique for the necessary physicochemical measurements. The rapid adsorption-desorption process makes it an effective analytical method to quantitatively determine a wide range of physicochemical properties such as solubility parameter component [31], Flory-Huggins interaction parameter [32], miscibility [33], activity coefficient [34], dispersive surface energy [35], specific (acid-base) interaction [36], surface area [37], sorption enthalpy [38], sorption entropy[39], sorption free energy [40], acid/base number [41], surface energy heterogeneity [42], etc. of surfaces of diverse solid materials in various forms and morphologies [24, 43].

The aim of this paper is to characterize the surface energy changes induced on the PDMS surface by air plasma treatments in order to enhance its ability to form specific interactions. Surface energy analysis method using IGC was applied to measure the surface energies of untreated and air plasma treated real PDMS samples and to follow up the recovery time of the PDMS surface after the modification in inert atmosphere. Respective chromatograms are listed in the Supplementary material. The significant novelties of this paper are the quantitative characterization option of the effect of air plasma treatment on dispersive and specific surface energies and on the electron acceptor-donor nature of PDMS surface. Furthermore, the Lewis acid-base interpretation of hydrophilicity and hydrophobic recovery of PDMS surface was also accomplished.

2. Experimental

2.1 Sample preparation and treatment

A two-component silicon elastomeric polydimethylsiloxane (PDMS) kit (SYLGARD 184) from Dow Corning (Midland, MI, USA) was used as base material of the samples. The molar mass of the repeating monomer is 207.4 g/mol while the number-average mass of the polimer is 27000 [44]. The melting point of PDMS is ~241 K [45]. The PDMS base polymer and the curing agent were vigorously mixed with 10:1 ratio and degassed in vacuum to remove bubbles from the bulk phase. The mixture was cured at 70 °C for 1 hour. The fabricated PDMS was

subject to cryogenic grinding at liquid nitrogen temperature (–196 °C) by a CryoMill (Retsch, Haan, Germany). The cryomilling procedure included a precooling and pre-milling phase at 5 Hz vibration frequency during 5 min, and afterwards three milling steps, which were performed at 25 Hz vibration frequency for 2 min grinding time with 1.5 min intermediate cooling. The surfaces of cryomilled sample particles (mean diameter 309 μm) were treated by synthetic air plasma for 2-10 s at 500 W using a custom-made microwave plasma reactor under vacuum (3 μbar) by a G1099-80024 vacuum pump (Agilent Technologies, Santa Clara, CA, USA). Synthetic air (20.5% (V/V) oxygen, 79.5% V/V nitrogen) of 40 ml/min was introduced into the plasma reactor, controlled by a precision flow regulator (Model 5850TR, Brooks Instrument Hatfield, PA, USA). The duration of the treatment time, measured as the contact time of the sample with the plasma, was determined by an electronic stopwatch.

2.2 Inverse gas chromatographic (IGC) measurements

The treated and untreated PDMS samples were investigated by a second generation inverse gas chromatograph (Surface Energy Analyzer (IGC-SEA) of Surface Measurement Systems Ltd., London, UK) equipped with a flame ionization detector (FID). IGC-SEA utilizes the so called Automated Probe Vapor Injection System, which ensures robust and highly reproducible injection. This gas phase injection system excludes the sampling errors of liquid injection method in traditional IGCs, which may result in low accuracy of retention data or exceeding the limit of concentration range. This imperfection is eliminated using the unique injection manifold and organic vapor partial pressure control of the fully Automated Probe Vapor Injection System. The probe molecules are injected in gas phase, directly from saturated headspace of solvents reservoir through a sample loop. The amount of injected vapor phase is controlled by the sample loop based on the required surface coverage and physical-chemical properties of solvents.

The powdered PDMS samples were filled into silanized cylindrical Pyrex glass tubes of I.D. = 3 mm under gentle vibration. The column packaging and the experimental setup took 80 minutes before each measurements. Surface energies were measured in dry helium gas for 36 hours in order to assess the aging of the samples and the recovery of their hydrophobicity under inert water-free conditions. A measurement cycle contained a series of eight injections and one sequence lasted 270 minutes. In each injection series all the probe compounds were injected, one after the other, in quasi-infinite dilution, at low surface coverage (Θ=0.05). IGC measurements were conducted at 303.15 K, which is well above the reported glassification temperature of PDMS (Tg~148 K) [45, 46]. This relative high temperature difference ensures the PDMS

has total amorphous structure allowing to use conventional thermodynamics. The standard flow rate of IGC technique is 10 cm^3/min. However according to our preliminary experiments the 10 cm^3/min flow rate resulted in high retention times and excessive asymmetric peak shape. Furthermore our study attempts to follow the dynamics of surface recovery with high-resolution, which requires relative short retention time i.e. the applied flow rate was 20 cm^3/min. Methane gas was used as marker for the hold-up time and high-purity-grade *n*-alkanes (*n*-hexane, *n*-heptane, *n*-octane, *n*-nonane), toluene and chloroform were as probe compounds. The synthetic air (5.0) for the FID detector was produced by Zero Air 1500-EU VWR (Radnor, Pennsylvania, USA), the helium gas (quality 6.0) and methane gas (5.0) were from Messer Hungarogáz Ltd. (Budapest, Hungary). The probe-compounds for IGC-SEA were reagent grade chemicals from Sigma-Aldrich (St. Louis, MO) with stated purity of 99 % and were applied as received. The data were recorded and analyzed by the Cirrus Plus Analysis Software (version 1.2.1.2), which is the SEA data analysis software designed and created by SMS Ltd (London, UK).

2.3 Theory

Surface energy calculations reported below were based on actual measured IGC data for each PDMS sample. Proper surface characterization required repeated injection of numerous probe molecules resulting in 48 chromatograms for a given sample. Due to page restriction, one representative chromatogram is shown in Figure 1, while the rest of the measured IGC traces can be found in the supplementary data file. Please note, in this study a total of 192 chromatograms were generated and evaluated for untreated and plasma treated PDMS samples.

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The retention time of each peak was determined at the center of mass of the retention peak. The characteristic reproducibility of a derived thermodynamic property calculated from the retention time was reported to be less than 1 % [47]. The intermediate precisions of the retention time measurements of methane is RSD = 0.7%. The precision in determining the retention times and the specific retention volumes of the test samples were RSD = 0.2% and RSD = 0.5%, respectively [48]. Dispersive and specific surface energies were determined at quasi-infinite dilution with the precision of RSD = 0.3% and RSD = 1.0%, respectively [26]. The net retention volume V_w of a probe is directly related to the thermodynamic interaction with the surface. Based on the chromatograms the net retention volume can accurately be determined from the flow-rate at the column exit (F) and the residence times of the marker gas (methane)

(t_0) and the probe (t_R), respectively. The net retention volume is obtained from the measured parameters given using *Equation 1*:

$$V_w = \frac{j}{m} F_m^0 \, (t_R - t_0) \frac{T}{273{,}15}$$ (1)

where T is the column temperature, m is the sample mass, F_m^0 is the exit flow rate at 1 atm and 273,15 K, t_R is the retention time for the adsorbing probe molecule, t_0 is the mobile phase hold-up time (dead-time), j is the James-Martin correction factor for gas compressibility. More details are described in the Supplementary material.

Dispersive (Lifshitz – van der Waals) surface energies (γ_s^d) of PDMS sample surfaces has been calculated from the dispersive part of the adsorption free enthalpy change using the Dorris-Gray method [49]:

$$\gamma_s^d = \frac{1}{4\gamma_{CH_2}} \left(\frac{RT \cdot \ln\left(V_{w,nC+1} / V_{w,nC}\right)}{N \cdot a_{CH_2}} \right)^2$$ (2)

where $V_{w,n}$ is the IGC measured specific retention volume of the *n*-alkane probe with the carbon number *nC*, a_{CH_2} is the cross sectional area of an adsorbed methylene group ($6 \cdot 10^{-20}$ m^2), *N* stands for Avogadro's number, γ_{CH_2} is the surface energy of a methylene group, as constituted by close packing CH2 groups in a structure analogous to polyethylene:

$$\gamma_{CH_2} / \left(mJ \cdot m^{-2}\right) = 35.6 + 0.058 \cdot (293 - T / K) .$$ (3)

The non-polar *n*-alkane probes interact with the surface of PDMS samples by dispersive forces only thus the free enthalpy change of adsorption of the *n*-alkanes is assumed to be equal to the dispersive component of the free energy change of adsorption. The specific retention volumes of *n*-alkane vapors have been measured by IGC-SEA in quasi-infinite dilution. When plotting *RT·ln(V$_{w,nC}$)* versus carbon number *nC* for the series of *n*-alkane probes, a line is obtained and the dispersive surface free energy of the PDMS samples, γ_s^d, can be calculated from slopes.

The specific (Lewis acid-base) surface energies (γ_s^{ab}) have been estimated from the base number (γ_s^-) and the acid number (γ_s^+) of the PDMS surface:

$$\gamma_s^{ab} = 2 \cdot \sqrt{\gamma_s^+ \gamma_s^-}$$ (4)

The base number or electron-donating parameter (γ_s^-) and the acid number or electron-accepting parameter (γ_s^+) of the PDMS surface were determined from the specific parts of free enthalpy changes of adsorption ($\Delta G_{ads,i}^{ab}$) of polar probes *i*:

$$\Delta G_{ads,i}^{ab} = 2N \cdot a_i \cdot \left(\sqrt{\gamma_i^+ \gamma_s^-} + \sqrt{\gamma_i^- \gamma_s^+} \right) \tag{5}$$

using the van Oss-Good-Chaudhury approach [50] and applying the Della Volpe scale [51] . The specific parts of free energy changes of adsorption for polar probes i on PDMS surface were calculated from the difference between their total adsorption free enthalpy and their dispersive references:

$$\Delta G_{ads,i}^{ab} = \Delta G_{ads,i}^{tot} - \Delta G_{ads,i}^{d} = -RT \cdot \ln \frac{V_{w,i}}{V_{w,ref}} \tag{6}$$

where $V_{w,i}$ is the specific retention volume of polar probe i, $V_{w,ref}$ is the specific retention volume of a hypothetical n-alkane having the same selected physico-chemical property as that of the polar probe i, for example vapor pressure, normal boiling point or molar deformation polarization, P_D:

$$P_D = \frac{4}{3}\pi \cdot N \cdot \alpha = \frac{n_r^2 - 1}{n_r^2 + 2} \cdot \frac{M}{\rho} \tag{7}$$

where α is the polarisability, n_r is the refractive index, M is the molar mass and ρ is the liquid density of the probe. The specific free energy changes of adsorption of the polar probes were obtained as the vertical distances between the polar data points and their vertical projections to the reference line of the n-alkanes on the plot of $RT \cdot ln(V_w)$ versus P_D, as suggested by Dong et al. [52] and Donnet et al. [53]. Chloroform and toluene were used in this work as acceptor (monopolar Lewis acid) probe and donor (monopolar Lewis base) probes, respectively, to determine the base and acid numbers of the surface according to the van Oss concept [50].

3. Result and discussion

3.1 Effects of treatment time

The actually measured surface energies of the untreated PDMS sample are given in *Table 1*. Supplementary material contains all chromatograms and raw data of the IGC measurements along with the detailed calculation tables. The dispersive surface energy value obtained was apparently close to that was previously found by Higgins et al. [54]. The Lewis acid/base ratio was less than unity, in agreement with the report of Larsen [55] for untreated PDMS layers.

The effects of air plasma treatments on the PDMS surface can be well demonstrated by the changes of its surface energy and chemical character. *Figure 2* shows the limiting values of the differences in the specific surface energies and base numbers of the PDMS surface before and

after the air plasma treatments. The limiting values have been obtained by extrapolation of the measured surface energies at various storage times to zero time. The increase in specific parts of the surface energy and in Lewis base sites of surface energy indicated that the surface has become more hydrophilic after air plasma treatment. Our results are in agreement with the observations of other authors that the treatment of plasma on PDMS introduces polar functional groups, which are mainly silanol groups (Si-OH) [17]. Therefore, the hydrophilic nature of the modified PDMS surface can be attributed to the silanol group formation on the plasma treated sample as reported earlier by Bodas et al. [56]. *Figure 2* clearly indicates that the 2 sec treatment was not sufficient enough to appreciably modify the PDMS surface. On the other hand, the 10 sec treatment was less effective for surface modification than the 5 sec treatment. The optimal treatment time to activate the surface has been found as 5 sec.

3.2 Investigation of recovery time

Plasma treatment causes a temporary change in the molecular structure of the PDMS surface. As reported by several authors, the hydrophilicity of plasma treated PDMS without any further modification is not sustained long, as it quickly regains its original hydrophobic character [20, 22, 56, 57]. Therefore, in terms of the usage of PDMS, it is essential to understand the required recovery time. The hydrophilic stability of the modified surfaces was monitored as a function of time elapsed after treatment and quantified by IGC surface energy analysis. The samples were not exposed to air during the IGC measurements, but they were performed in inert atmosphere of helium. The specific surface energy of the samples was determined by the method of van Oss et al. [51].

Figure 3 and *4* illustrate the variation of the specific part of surface energy and the base number of the PDMS surface with time for the modification studied. Immediately after the plasma treatment, the specific part of surface energy and the base number of the PDMS surface increased probably due to the presence of polar groups at the surface.

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The surface energy values proved that the 2 sec and 10 sec air plasma treatments had minimal effect on the PDMS surface. Maximum hydrophilicity of PDMS surface was observed after 5 sec treatment with 500 W power, which significantly increased both the specific part of surface

energy and the base number of the PDMS surface. Our observations are in agreement with those of Wohl et al. [25], who reported that the oxygen plasma treatment on silicone rubbers (such as PDMS) increased its Lewis base surface energy component. However, the surface hydrophobicity was fully recovered after 38 hours in helium gas, corresponding to the experiences of others, who have shown that partial to complete hydrophobic recovery occurs independently of the exposure conditions [22]. The reason of complete hydrophobic recovery was probably due to the thinness of the oxidized PDMS layer, because the main reasons for hydrophobic recovery are assumedly the reorientation of the polar groups from the surface to the bulk, diffusion of pre-existing low-molecular-weight (LMW) species from the bulk to the surface [58, 59] and condensation of the hydroxyl groups [17]. Air plasma treated PDMS stored in helium gas stream recovered its hydrophobicity faster that of oxidized PDMS films stored in water [22].

However, the air plasma treatment has no or negligible effect on the dispersive and the acidic part of the surface energy of the PDMS samples, therefore, their values did not show any changes in the time elapsed after treatment as shown in *Figure 5*. These interesting phenomena corresponded with the surface chemical modification, as the air plasma treatment was able to transform the interface silane molecules to silanol functional groups within a short reaction time as it was also experienced by Tan et al. [17] Due to these surface reactions, the air plasma treatment showed practically no effect on the dispersive component and the acid number of the PDMS surface energy, independently of the duration of the treatment. Consequently, the so called "hydrophobic recovery" process is actually considered as not a rise of hydrophobic sites of the PDMS surface, not the growth of the electron-acceptor ability (γ_s^+) of PDMS surface to bind hydrophobic molecular interactions, but the decrease of the hydrophilic sites of the PDMS surface, the lowering of its electron-donor ability (γ_s^-) to form specific interactions.

These results agree well with the observations of other authors as follows. Van Oss [60] reported that when the negatively charged biosurfaces of electron-donor and hydrophilic biopolimers were neutralized, their electron-donor parameter (γ_s^-) severely diminished, which then caused these surfaces to became hydrophobic. Van der Mei et al. [61] recognized that differences in acid–base character of microbial cell surfaces formed the basis for differences in cell surface hydrophobicity among strains: the organism surfaces having low electron-donating parameter (γ_s^-) were hydrophobic, while organism surfaces with sizeable electron-donating parameter were hydrophilic. Hamadi and Latrache [62] obtained a good correlation between the degree of hydrophobicity and Lewis acid properties of bacteria surfaces.

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4. Conclusion

IGC technique was proven as an excellent method to characterize the changes in the physico-chemical properties of PDMS surfaces after air plasma treatment. A total of 192 measurements were accomplished and all the respective data is listed in the Supplementary material. Surface energy analysis quantitatively proves that the plasma irradiation raised the hydrophilicity in terms of specific surface energy and its base component of the PDMS surface when exposed to air plasma. The inverse gas chromatography measurements provided an excellent proof for the optimal treatment time for activating the PDMS surface. These emphasized the need to accept IGC based surface energy analysis as one of the universal standard for surface hydrophilic-ity/hydrophobicity measurements. The IGC results were interpreted on the basis of van Oss-Good-Chaudhury approach, which showed that the changes of Lewis base or electron donor nature of air plasma treated PDMS surface were responsible for hydrophilicity and hydrophobic recovery of the PDMS surface.

Acknowledgment

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Biographies

Brigitta Mészáros received her MSc in chemical engineering (2016) at University of Pannonia. During her studies, she participated in the work of Department of Physical Chemistry, University of Pannonia, where she learned the bases of inverse gas chromatography. She started her PhD studies at University of Debrecen, Research Centre for Molecular Medicine in 2016. She also participates in the work of Horváth Csaba Memorial Institute of Bioanalytical Research. Her research interest is microfluidic devices for cell capturing and culturing and analysis of proteins by developing a high-resolution SDS separation gel for CGE-MS.

Gábor Járvás received his MSc in chemical engineering (2007) and PhD in chemistry (2012) at University of Pannonia. In 2013 he joined the collaboration project of Bioanalytical Instrumentation Group (Brno, Czech Republic) and MTA-PE Translational Glycomics Research Group (Veszprém, Hungary) as postdoctoral research fellow. Currently, his research interest is capillary electrophoresis based glycomics and glycoinformatics, simulation and modeling of microfabricated bioanalytical devices and development of novel CE-ESI-MS interfaces.

Márton Szigeti received his MSc in environmental engineering (2014) at University of Pannonia. In 2014, he became a PhD student at University of Debrecen, Research Centre for Molecular Medicine. He also participates in the work of MTA-PE Translational Glycomics Research Group (Veszprém, Hungary) as a research fellow. His main research interest is glycan analysis development and automation for CE and CE-ESI-MS platforms.

László Hajba holds a PhD in analytical and environmental chemistry from University of Pannonia, awarded in 2008. Later he carried out research in the field of biospectroscopy and chemometrics at the university. In 2010 he joined the biotechnology research group at Research Institute of Chemical and Process Engineering, University of Pannonia. In 2013 he started his work in the field of microfluidics and bioseparations at the MTA-PE Translational Glycomics Research Group under the supervision of Prof. András Guttman.

András Dallos PhD has served as associate professor of physical chemistry at the University of Pannonia (1995-2017). He has his expertise in experimental and computational physical chemistry: measurement and modelling of bulk and surface properties of pure compounds, mixtures,

macromolecules, nanomaterials and composites. His research activities focus to the inverse gas chromatographic and calorimetric determination of intermolecular interactions, which are relevant to the design of nanocomposites and to the calculations of phase equilibria and separation processes. He is author and co-author of 57 scientific publications and presented 185 scientific conference papers and posters. He is a consultant of 10 companies and government agencies and a reviewer for leading academic periodicals.

András Guttman, external member of the Hungarian Academy of Sciences, holds the MTA-PE Lendulet professorship of Translational Glycomics, heads the Horvath Laboratory of Bioseparation Sciences in University of Debrecen (Hungary) and leads the separation application efforts at Sciex. He held visiting professorships at Northeastern University (Boston, MA), The Scripps Research Institute (La Jolla, CA) and UCSD (San Diego, CA). The industrial background of Dr Guttman includes positions at Novartis, Genetic BioSystems, and Beckman Instruments, working on capillary and microfluidics based electroseparation methods. Dr. Guttman graduated from the University of Veszprem (Hungary) in chemical engineering, where he also received his doctoral degree.
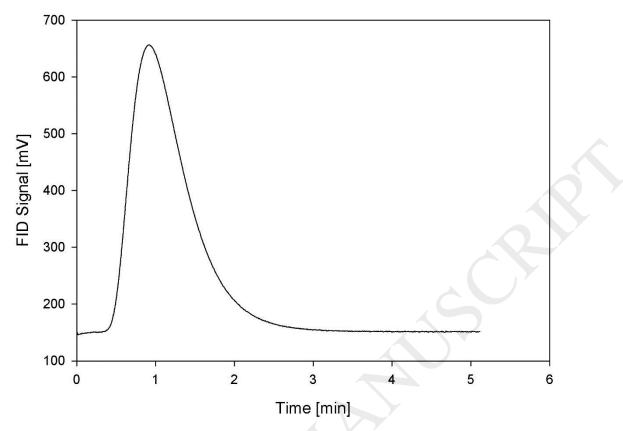
Figure 1 Representative IGC chromatogram of n-hexane probe molecule on the untreated PDMS sample at low surface coverage (Θ=0.05), 303.15 K temperature with a helium carrier gas flow of 20 cm^3/min
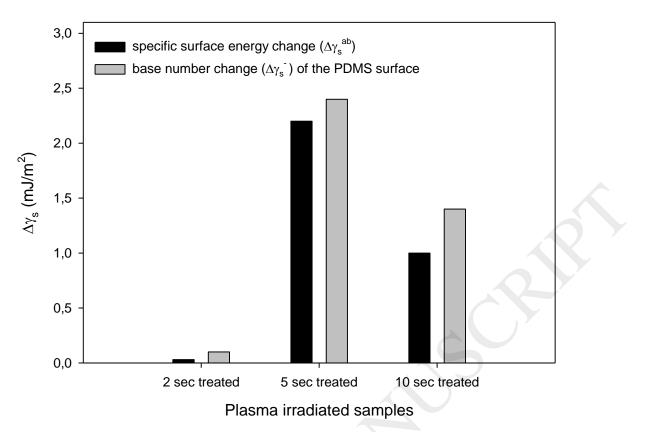
Figure2. Effects of air plasma treatments on the changes of the specific part of the surface energy and the base number of the PDMS surface at 303.15 K
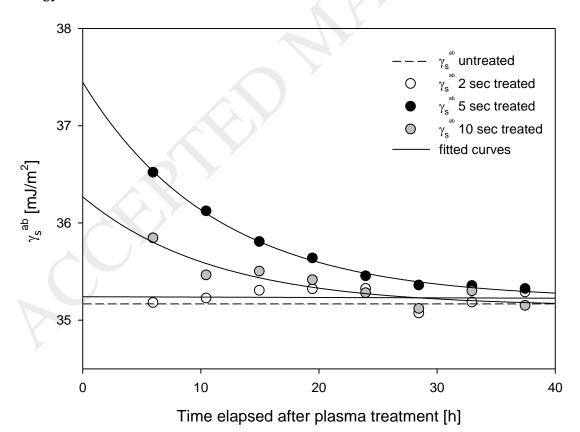

Figure 2. Specific surface energy curves on the PDMS surface at 303.15 K as a function of exposure time in helium gas
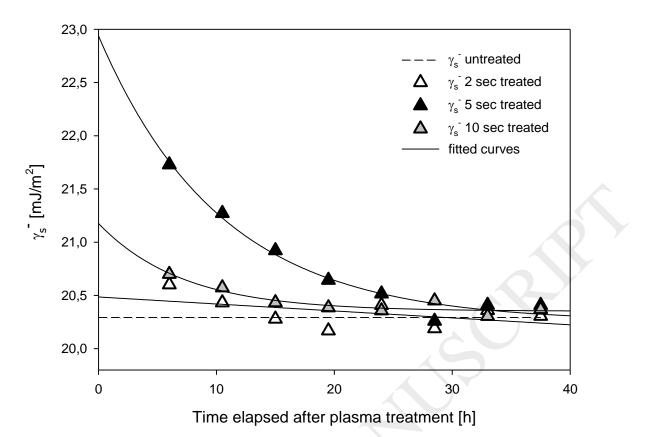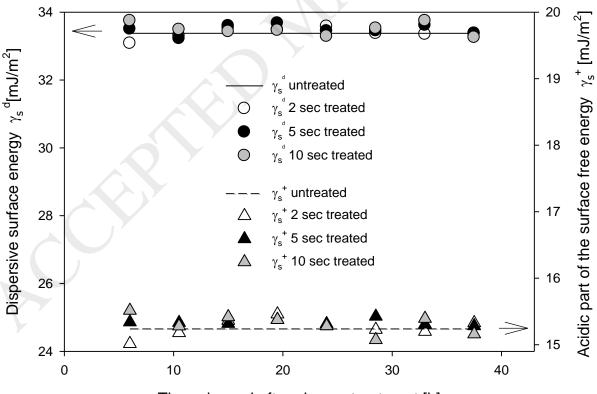
Figure 3. The base number curves of the PDMS surface at 303.15 K as a function of exposure time in helium gas

Figure 5. Effects of air plasma treatments on the changes of the dispersive part of the surface energy and of the acid number of the PDMS surface at 303.15 K

Table 1. Surface energies of the untreated PDMS sample at 303.15 K

Dispersive surface energy γ_s^d [mJ/m^2]	Specific surface energy γ_s^{ab} [mJ/m^2]	Base number of the surface γ_s^-[mJ/m^2]	Acid number of the surface γ_s^+ [mJ/m^2]	Lewis ratio	acid/base
33.38	35.17	20.29	15.24	0.75	