




## Glow Discharge Plasma as a Cause of Changes in Aqueous Solutions: The Mass Spectrometry Study of Solvation Processes of Ions

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A new apparatus for inducing changes in the properties of water in closed dielectric vessel by subjecting it to pulsed direct current glow discharge plasma is designed and constructed. It has been hypothesized that the action of plasma on the structure of water consists in resonance excitation of water aggregates. As a result of resonance excitation, aggregates of high molar masses are broken down into low molecular mass aggregates. Analysis of the ESI MS spectra revealed that in all tested aqueous solutions after exposure to plasma, the concentration of low-molecular solvated ions  $[M(H_2O)]^+$  and  $[M(H_2O)_2]^+$  significantly increased, while the concentration of the ions of high molecular masses  $[M(H_2O)_{6-10}]^+$  solvated by water aggregates decreased, relative to their concentrations in the water solutions not subjected to plasma irradiation. According to our measurements also a significant change in pH occurs. The presented results clearly show that it is possible to process a liquid that changes its structure without involving high processing energy and, unexpectedly, the obtained change of parameters is significant and stable over time.

**Keywords:** Pulsed direct current glow discharge plasma, Electromagnetic radiation resonance, Plasma noise, Solvation.

### INTRODUCTION

Low temperature plasmas have been used in various plasma processing applications for several years [1-14]. Non-thermal plasma generated at room temperature is a gas mixture composed of ions, electron, photons and free radicals [3,9,13]. The high reactivity of plasma is a result of different plasma components emitting electromagnetic radiation and noise, ions, electrons, free radicals as well as reactive chemical species to the environment.

Plasma produces large amounts of short- and long-lived molecules including oxygen, such as ozone ( $O_3$ ), superoxide anion ( $O_2^-$ ), hydrogen peroxide ( $H_2O_2$ ), hydroxyl radicals ( $HO^\bullet$ ) and other generating-ROS species, which are used for modification of different materials [3,13]. To ensure interaction of plasma with a given material, various types of plasma generators are currently used. Plasma reactors can be sorted into three categories:

i) Based on direct discharges in liquids,

ii) Discharges in the gas phase over a liquid, including the case when the conductive liquid is an electrode,

iii) Based on discharges in multiphase environments such as discharges in bubbles inside liquids or discharges contacting liquid spray mist or foams.

All these solutions are mainly based on the transfer of ions, electrons and radicals to the surface of the processed material. The existing solutions do not use electromagnetic radiation or noise generated in plasma and applied through dielectric barrier for modification or processing of different materials. The sole use of radiation enables eliminating the interaction of ions and electron radicals present in the plasma and opens up the new possibility of modification of liquids by treatment with plasma.

This paper concerns a new area of using low temperature plasmas at atmospheric pressure for modification of materials by non-contact methods. The idea is based on the possibility of tuning the plasma parameters to match the needs of materials to be modified by non-thermal effects and interaction between

electromagnetic field and noise at very low energy consumption. This process is studied in particular for aqueous solutions, because this method allows interference with the structure of water and bioorganic compounds in biological systems.

### EXPERIMENTAL

Pure water obtained from double reverse osmosis with water demineralization, (Conductivity  $0.053 \pm 0.002 \mu\text{S cm}^{-1}$ ), formic acid (98-100%) and silver(I) nitrate ( $\geq 99.0\%$ ) were the commercial products (Sigma-Aldrich, St. Louis, MO, USA). Physiological saline solution (0.9%) in closed ampoules was used as medicine commercial product (Darnitsa, Pharmaceutical Company).

The pH measurement was performed using a pH meter CP-505 with an EPS-1 measuring electrode (Elmetron). The liquid density was determined by gravimetric method using a 2 mL pycnometer.

**ESI MS measurements:** The electron spray ionization (ESI) mass spectra were recorded on a Waters/Micromass (Manchester, UK) ZQ mass spectrometer equipped with a Harvard Apparatus syringe pump. The ESI spectra of water solutions of salts at concentration of  $10^{-5} \text{ M}$  were recorded. The samples were infused into the ESI source using a Harvard pump at flow rate  $20 \mu\text{d m}^3 \text{ min}^{-1}$ . The ESI source potentials were: capillary 3 kV, lens 0.5 kV, extractor 4 V. The spectra were taken at different cone voltages ( $cv = 5, 10, 15, 20, 25$  and  $30 \text{ V}$ ). The source temperature was  $120^\circ\text{C}$  and the desolvation temperature was  $250^\circ\text{C}$ . Nitrogen was used as the nebulizing and desolvation gas at flow-rates of  $150 \text{ dm}^3 \text{ h}^{-1}$ .

**Preparation of aqueous solutions for measurements using the ESI mass spectrometry technique:** Pure water before and after treatment with plasma was used for ion hydration studies to obtain 0.5 mM of formic acid and 0.5 mM of silver(I) nitrate solutions. Aqueous solutions were obtained by dissolving the corresponding compounds at  $25^\circ\text{C}$ . Physiological saline solution (0.9%) solutions in closed ampoules were used before and after treatment with plasma for sodium ion solvation studies using ESIMS. Tap water before and after interaction with plasma was subjected to ESIMS measurements without pre-treatment.

### RESULTS AND DISCUSSION

**Plasma generator:** A plasma generator was constructed using a sealed metal chamber equipped with two electrodes, of which one was the anode (A) and the other was the cathode (C), the latter had a greater diameter. Application of a proper voltage between the electrodes allows generation of plasma in a soft vacuum that was maintained using a rotary vacuum pump. The treated material was exposed to plasma while being placed on the surface of the cathode. The operating pressure was kept at a level of 0.5-1.5 hPa and an adjustable portion of fresh naturally humid air was delivered to the chamber *via* air vessel. The details of plasma generator are shown in Fig. 1, while a photo of the generator is shown in Fig. 2. Dimensions of electrodes were the following: cathode 400 mm O.D. and anode 20 mm O.D. while the anode-to-cathode distance was 500 mm.

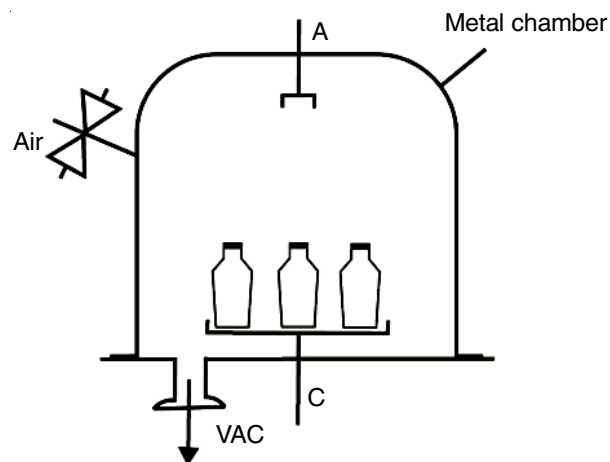


Fig. 1. Structure of the plasma generator

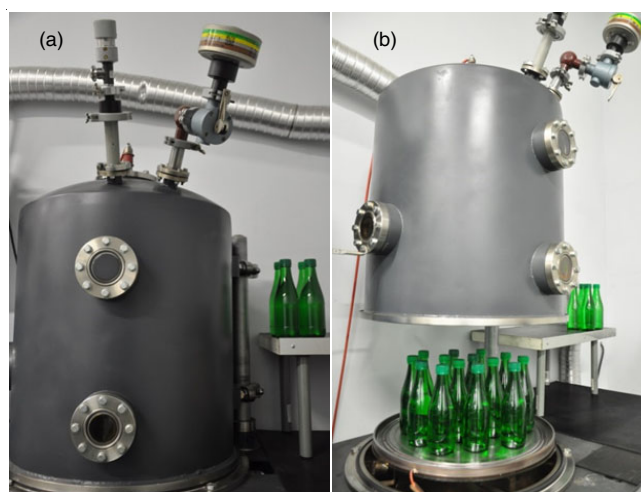


Fig. 2. Plasma generator. The closed chamber of plasma generators during operation (a), open chamber during loading of the material to be treated with plasma (b)

Plasma generating electrodes are powered by direct current (Fig. 3) with the following parameters: average voltage 1000-1500 VDC and current of about 80 mA.

**Principle of the system operation:** After placing the material to be processed (closed bottles) on the cathode surface the metal chamber was closed and the vacuum pump was started to obtain a pressure of 0.5 mbar inside the capsule. After obtaining a pressure of 0.5 mbar inside the chamber, a high DC pulsed voltage was applied to the electrodes enabling self-ignition of the plasma-generating discharge (Fig. 4) and, as a result, the current flow through the plasma started to stabilize (Fig. 5a). Due to proper tuning of voltage a noise in plasma was obtained, clearly visible on the oscilloscope (Fig. 5b) and this noise quickly transformed to separate bursts modes.

In response to changes in the level of voltage applied to the plasma generator its work can be divided in a few stages. After 15 min of further operation, this can be defined as the resonance matching time, the profile of the plasma radiation amplitude changes. When the studied material is water, the generated noise is transformed into distinct 3 to 5 modes whose shape and number depend on the type of liquid subjected to plasma radiation. The modes disappear when the physical

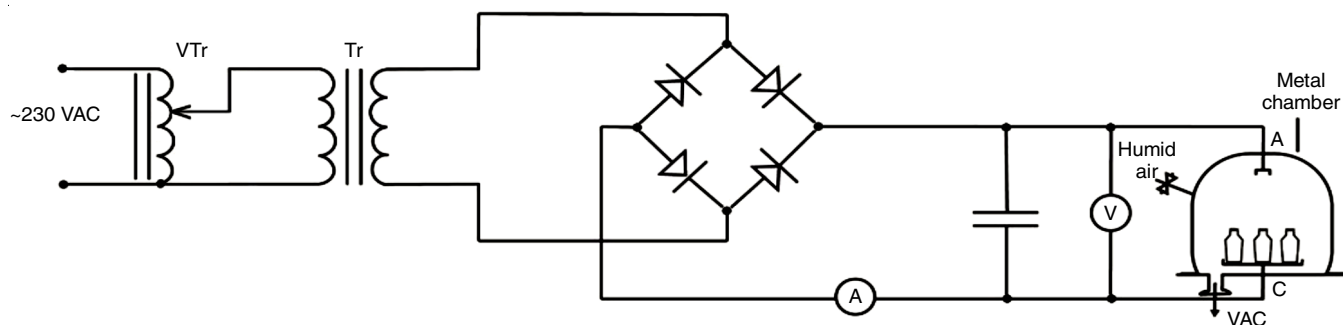


Fig. 3. Functional scheme of the simple current generator for plasma generation. VTr is a variable autotransformer, TR is a step-up isolation transformer



Fig. 4. Plasma generated in the vacuum chamber during treatment of sealed bottles with ultra-pure water. On the top the cathode glow (ion source). Below the glow of plasma surrounding the bottles with liquid

interaction of the liquid (or other material to be modified) is complete (Fig. 5d). The changes in the modes and their disappearance are convenient indicators allowing control of the process and its completion.

It should be emphasized that the first two stages of the generator work (A) and (B) are in the first run made manually, in about 2 min from starting the system. Later these stages can be automated to reliable repeatability. After finding the above-mentioned 3 to 5 modes, the system is tuned to resonance. Then, after a few minutes, usually about 15 min, the resonance considerably weakens, stages (C) and (D), which is observed as the modes decay.

It is interesting to compare resonance behaviour of other liquids different than water. Fig. 6 shows the modes obtained during treatment of diesel fuel.

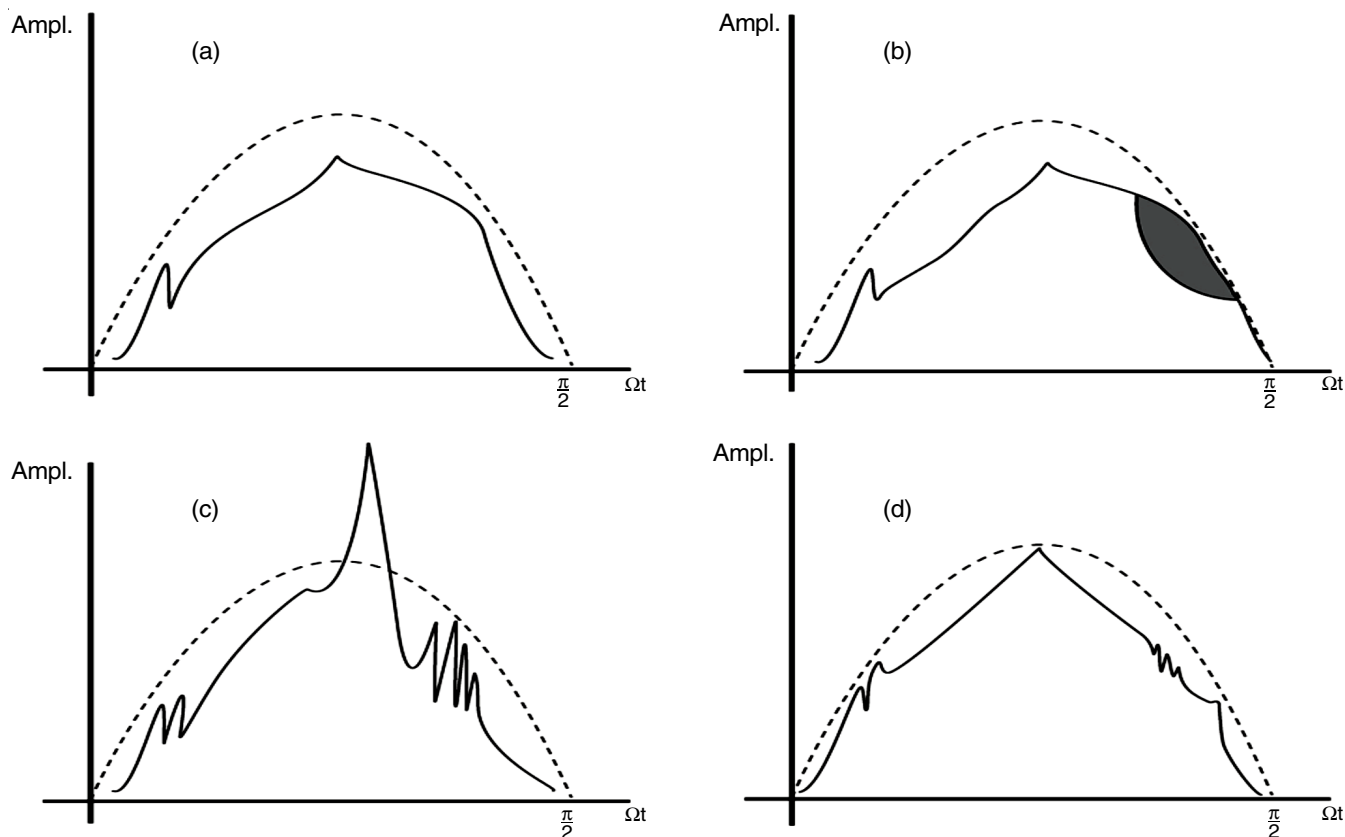


Fig. 5. Amplitude of a signal from the electric probe during the initial voltage tuning (A), further generation of noisy afterglow (B), formation of modes (C) and their decay (D). The sinus function (dashed line) is one half of rectified mains voltage given for comparison

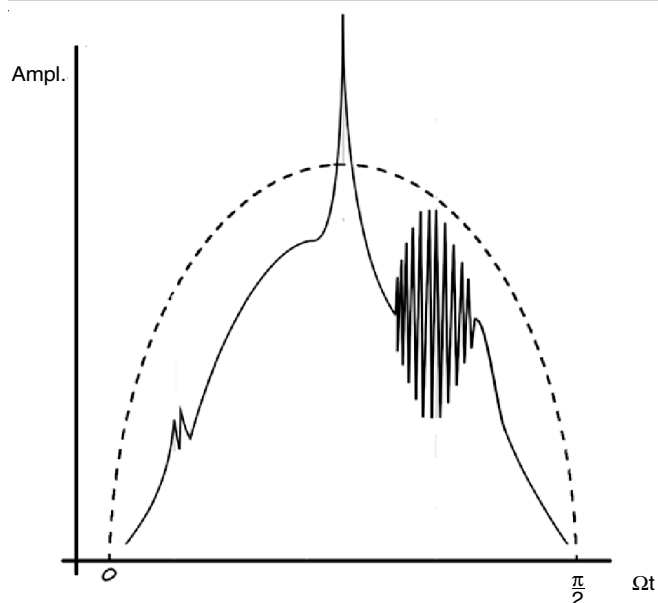


Fig. 6. Formation of modes for diesel fuel (an example)

As a matter of fact, the plasma plays a double role: as a strong source of noise which is made coherent by the presence of humidity introduced dynamically to the discharge through the air vessel and as an efficient antenna which can transmit wide band RF radiation to the surrounding. The RF noise could be measured in a wide frequency band using a spectrum analyzer. The spectra taken in the chamber as well in a glass reactor are very similar. Actually they look as shown in Fig. 7, covering the frequency range from about 100 Hz up to about 50 MHz. The electric probe of the spectrum analyzer showed greater signal at the side of lower frequencies, while the magnetic probe gave more homogenous readings with sudden drops at the ends of the bandwidth.

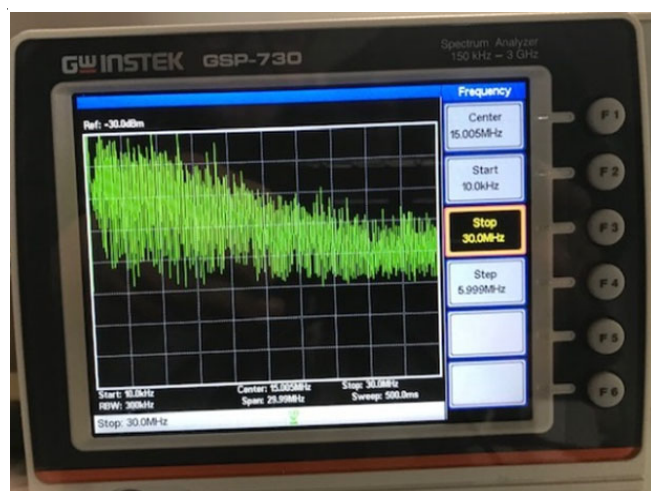


Fig. 7. Electric probe signal from the spectrum analyzer in the frequency range 100 Hz up to 50 MHz

The magnitude of the signal from the analyzer was of course a function of distance. This dependence was found to decay quicker than predicted by the quadratic law, which in fact could be expected in close proximity of the source.

**Water structures:** In recent years the structure of liquid water has been a subject of extensive research [15-24]. The water molecule is polar and shows a V-shaped order of dipoles. The aggregation of water molecules through weak interactions leads to the formation of molecular clusters. Water has random and self-complementary hydrogen bonds. In liquid water, all three atoms of every water molecule are engaged in nearly ideal hydrogen bonding interactions with the surrounding water molecules or with either hydrogen bond donors or acceptors. There is no mathematic pattern to the way the water molecules become interconnected to form different structures. In condensed phase, every water molecule acts as a donor in two hydrogen bonds and an acceptor in two hydrogen bonds. However, many natural forces can influence the degree and the stability of hydrogen bonding. The hydrogen bond network, its fluctuations and dynamics of hydrogen bonds determine the properties of water. The structure of water is best described by the cluster model in which the process of formation of clusters of different sizes and geometry as a result of dynamic processes determines its physico-chemical properties. Description of liquid water, alternative to the above model, assumes the formation of water structures, which leads to ordered structured water (water is structural) [21-25]. The classical interpretation of the structure of liquids claims that the life cycle of water clusters is very short (an order of  $10^{-12}$  s). The molecules of water are continuously moving relative to one another and the hydrogen bonds are continually breaking and reforming at intervals shorter than 200 femtoseconds. According to the water structure theory, water structures exist for a long time and these structures determine water physico-chemical properties such as the clusters sizes and the concentrations. Tereshko *et al.* [25,26] have investigated nonlinear molecular chains of water that have the potential similar to covalent and hydrogen bonds between H-O-H atoms. Applying computation methods they have shown that nonlinear oscillations of atoms in the chain were excited very intensively, which led to self-organization processes and consequently, to the displacement of atoms and their stabilization in new positions, which resulted in the formation and development of new metastable atomic groups, in particular nanoclusters. Observed electric phenomena recorded by the oscilloscope was similar to that shown in Fig. 5. We have also shown the collapse of the chains with high-energy nanocluster formation. Stabilization in new positions can be described as molecular memory.

The O-H bond of water is strongly polarized, the electron density around the hydrogen atom is very low and the O-H bond is weak. Thermal fluctuations in the liquid often result in a further polarization of the O-H bond, sufficient for the hydrogen nucleus dissociation as an ion. As a consequence, dissociated water has a relatively long lifetime of about 100 ms in pure water before recombination. The spontaneous ionization of water is characterized by a dissociation constant that can be calculated from the equation:  $[H^+][OH^-]/[H_2O] = 1.82 \times 10^{-16} \text{ mol L}^{-1}$ . The structure of liquid water requires determination of hydronium ( $H_3O^+$ ) and hydroxide ( $OH^-$ ) ions presence in this structure, formed in the process of autoionization. The intact water molecule will dissociate in liquid water

within 10 h, producing hydronium ( $\text{H}_3\text{O}^+$ ) and hydroxide ( $\text{OH}^-$ ) ions [27,28]. The event is thus extremely rare on the femto-second time scale of molecular motions. But when it occurs, the system crosses a transition state region quickly, generating ions that are separated by neutral water molecules [29,30]. Volkov *et al.* [31] has proposed a model of water structure, in which the dynamics is due to diffusion of particles, neutral  $\text{H}_2\text{O}$  molecules and  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions with their periodic localizations and mutual transformations. According to this model, water contains a huge amount of short-living counter ions.

The structure of pure water changes dramatically if ions, neutral molecules or gas are introduced into it. Water molecule, being dipolar and showing hydrogen bond donating and accepting abilities, can participate in specific and nonspecific interactions with charged/dipolar solutes. The structural effect of the presence of ions/neutral molecules in water is determined by charge densities of ions or dipolar character of neutral molecules. The interactions of ions-water and water-water determine the water structure in solvents. Small ions have high charge densities so they cause strong electrostatic ordering of nearby water molecules, breaking hydrogen bonds. In contrast, large ions have low charge densities and the surrounding water molecules are largely hydrogen bonded. These strong interactions make charged/dipolar solutes miscible with water. In contrast, nonpolar solutes, because of the lack of strong interactions, self-aggregate in water. The interplay and equilibrium between various interactions such as water-water, water-solute and solute-solute govern the solubility and aggregation behaviour of solutes and the primary structure of water [32-34].

Every hydrogen atom in water molecules has a magnetic moment. When the spins on hydrogen atoms are parallel, there is a paramagnetic state called *ortho*- $\text{H}_2\text{O}$ , when two spins on the hydrogen atoms are antiparallel to each other, *para*- $\text{H}_2\text{O}$  particles are formed. Considering the *ortho/para*-magnetic spin states of hydrogen and deuterium, there are 15 different stable forms of the water molecule [35]. In liquid state water exists in two forms, *para*-water and *ortho*-water, which are distinguished by their values of the quantum number of the total nuclear spin  $I$ , with  $I=0$  and 1 for *para*- and *ortho*- $\text{H}_2\text{O}$ , respectively [36]. The apparent energy difference between the two states is significant 1-2  $\text{kJ mol}^{-1}$  [37]. Apart from their total nuclear spin, *para*- and *ortho*-water molecules also differ in other important aspects. The differences in the properties of these two forms of water are enhanced in the electric field [38]. It has been suggested that structural rearrangements can be induced by *ortho*- $\text{H}_2\text{O}$  to *para*- $\text{H}_2\text{O}$  conversion [39], because it is possible that hydrogen bonds between *para*- $\text{H}_2\text{O}$ , not having a ground state spin, are stronger and last longer than those between *ortho*- $\text{H}_2\text{O}$  [40]. It is therefore possible that *ortho*- $\text{H}_2\text{O}$  and *para*- $\text{H}_2\text{O}$  form separate hydrogen-bound clusters [41], with *para*- $\text{H}_2\text{O}$  being preferred in clusters coordinated with low-density solvent as tetrahedrons and *ortho*- $\text{H}_2\text{O}$  is preferred in high-density clusters [42], in which their rotation is easier to adjust. Liquid water is a collection of a large number of chemical individuals, between which dynamic changes take place due to the structure of the water molecule and formation

of hydrogen bond network. The amount of chemical species and the dynamics of changes increase rapidly in the aqueous solutions containing solutes (ions, salts, inert molecules of gases). Each of the structures in liquid water or water solutions is characterized by its size, mass and lifetime. To date, no single model has been developed describing the structure of liquid water and the solutions it makes.

**Effects of resonance of electromagnetic fields with water molecules:** Resonance of electromagnetic radiation is a physical phenomenon that occurs between the vibrating system and the forced vibrations, manifested as an increase in the oscillation amplitude of the vibrating system for a given frequency of the exciting signal. Resonance is the amplification phenomenon that occurs when the frequency of the periodically applied electromagnetic field is harmonically proportional to the natural frequency of the system it acts on. When an oscillatory signal is applied at the resonance frequency of a dynamic system, the system will oscillate with higher amplitude than when the same force is applied at other non-resonant frequencies. In resonance even a small periodic excitation signal can cause vibrations of considerable amplitude. An oscillating system with many degrees of freedom has many different natural frequencies and therefore resonance vibrations at each of these frequencies are possible. It is easiest to trigger resonance at the lowest frequency. What are all the resonance frequencies for liquid water that can affect the water structure? The molecules of water are characterized by low molecular weight of 18 Da and relatively large dipole moment of 1.85 D. However, in liquid water in addition to free water molecules, there are primarily agglomerates of complex molecular structures. Different groups of water molecules absorb different signals of different energies from different ranges of electromagnetic radiation. According to literature, water is capable of absorbing radiation in the terahertz range due to its energy states of molecular rotation and vibration [43-45]. In the liquid state, a water molecule has 'spare' electron pairs which could be shared with the hydrogen of another water molecule, thus forming hydrogen bond networks and allowing water to express extraordinary properties such as the coexistence of its liquid and solid phases [46]. What is important in the idea of resonance with water is to establish frequencies of signals from the emitter that would coincide with the natural frequencies of clusters or structures of water molecules. In the method proposed, plasma was used to induce structural changes in water by tuning electromagnetic radiation to the energy vibrations of water structural elements. The resonant tuning of electromagnetic radiation to the material's vibration frequencies is the basis of the process affecting the structure of the material (in this case water). Strict determination of the structures undergoing changes at this stage of research is not possible and requires further research.

Resonance vibrations of structural elements of materials occur when a natural frequency is equal to or close to the frequency of irradiation. If these frequencies are equal or close, small vibrations in a given material are substantially enhanced by resonance. Increase in the strength of vibrations in water clusters may lead to breaking up of the hydrogen bonds con-

necting ions in the clusters so that a metastable state of charge separation is reached. This process changes the structure of liquid water. Resonance amplification of the strength of vibration of a structural element of a material (water) leads to a permanent changes in its physico-chemical properties. A dissociation of a water molecule in liquid water is the fundamental event in acid-base chemistry, determining the pH of water. Nagata *et al.* [47] proposed a non-equilibrium molecular dynamics algorithm that provides a detailed picture of water vibrational dynamics by generating non-equilibrium vibrational excited states at targeted vibrational frequencies. The approach presented in this work uniquely disentangles the effects of the four contributions: delocalization of the O-H stretching mode, structural dynamics of the hydrogen bond network, intramolecular coupling within water molecules and intermolecular coupling between water molecules (near-resonance energy transfer between O-H groups) on the vibrational dynamics. Our results illustrate that intermolecular energy transfer and the delocalization of the O-H stretching mode are particularly important for the spectral diffusion in H<sub>2</sub>O. There is rich literature on the effects of electromagnetic radiation on biological objects [43,47-50] that interact with alternating electromagnetic fields in a range of different frequencies. The biological response is varied and depends on the organism, tissue, molecular composition of the particular cell as well as on the parameters of the electromagnetic field: frequency, intensity, modulation, polarization, pulsing mode, instantaneous and average power and total energy absorbed [43]. For testing purposes, we used pure water and a water solution containing 0.9% NaCl. Water samples were placed in the reactor and subjected to plasma treatment. Each experiment study was repeated 10 times. In order to determine which physico-chemical parameters of water change during plasma treatment, selected water parameters were determined before and after the treatment. The data obtained are presented in Table-1.

After water exposure to plasma in the reactor, no increase in the amount of radicals in the water sample was observed. However, the water sample after the treatment was noted to show unusual gas absorption capacity (nitrogen, CO<sub>2</sub>, oxygen) relative to that of untreated water sample. The amount of gas absorbed by water was about 10 times higher at a given temperature compared to that of the untreated water sample. The amount of gas absorbed by water subjected to plasma treatment depended on the type of gas. In all cases, a slight decrease in the density of aqueous solutions after exposure to plasma as well as a clear change in the pH value of the solution were observed. The direction of the recorded changes depended on the type of solution. It was also found that as a result of

exposure to plasma precipitation of the crystalline hydroxide or salt took place. The amount of crystalline precipitate depended on the content of metal ions in the treated water.

If, as hypothesized, the exposure to plasma results in disintegration of larger water agglomerates into smaller ones, the effect should be changes in the ion solvation in water. We used electrospray ionization mass spectrometry method (ESI MS) to observe these changes in solvation of ions by water molecules. The electrospray ionization (ESI) is a soft molecule ionization technique using an electrospray in which a high voltage is applied to a liquid to create an aerosol. This method used because it overcomes the propensity of these molecules to fragmentation when ionized and because solution-phase information can be retained in the gas-phase [51,52]. The use of ESI MS in the studies of solutions is particularly important when using a variable cone voltage, because of the possibility of observing complexes with different durability in the solution [53-55]. Changes in cone voltage energy allow observation of low-energy chemical species in a solution in the ESI MS spectra. The increase in cone voltage energy allows observation of spectra of water complexes of different stoichiometry. Ultrapure water before and after plasma treatment was used to study changes in the H<sup>+</sup> and Ag<sup>+</sup> ion solvation process using the ESI MS technique as a function of cone voltage (5-30 V) in the *m/z* range 5-250 D. ESI MS spectra are presented in Figs. 8 and 9. Changes in hydration of proton or silver ions in water after different plasma treatment durations were also investigated. The observed changes are presented in Figs. 10 and 11.

ESI MS spectra recorded at different cone voltages of a 0.5 mM formic acid solution prepared from water before and after treatment with plasma differ significantly. Proton water agglomerates give a mass spectrum with signals at *m/z* 19 [H(H<sub>2</sub>O)]<sup>+</sup>, 37 [H(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup>, 55 [H(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup>, 73 [H(H<sub>2</sub>O)<sub>4</sub>]<sup>+</sup>, 91 [H(H<sub>2</sub>O)<sub>5</sub>]<sup>+</sup>.... We analyzed these signals to determine the effect of plasma on water structure. In all recorded spectra, an increase in the concentration of solvated protons in the presence of smaller mass water agglomerates was observed. The amount of ions with low molar mass increased, as evidenced by the signals at *m/z* 19 [H(H<sub>2</sub>O)]<sup>+</sup>, 37 [H(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup>, 55 [H(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup> while the concentration of ions with big molar mass decreased *e.g.* 181 [H(H<sub>2</sub>O)<sub>10</sub>]<sup>+</sup>. For detailed analysis, we chose the spectra recorded at *cv* = 20 V for water treated with plasma for 10 s and 1000 s. Changes in the abundance of signals of protonated water agglomerates in the ESI MS spectrum (Fig. 10) show a significant increase in the concentration of [H(H<sub>2</sub>O)]<sup>+</sup>, [H(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> while the concentration of aggregates [H(H<sub>2</sub>O)<sub>6-11</sub>]<sup>+</sup> is reduced. To confirm the observation that lower mass water agglomerates (H<sub>2</sub>O)<sub>n</sub> form after treatment with plasma, we examined the

TABLE-1  
PHYSICO-CHEMICAL PARAMETERS OF WATER BEFORE AND AFTER PLASMA TREATMENT

	Pure water		Water solution 0.9% NaCl		Tap water	
	Before	After plasma interaction	Before	After plasma interaction	Before	After plasma interaction
Density d <sup>20</sup> (g/cm <sup>3</sup> )	0.998 ± 0.001	0.967 ± 0.001	1.015 ± 0.002	1.006 ± 0.002	0.998 ± 0.002	0.967 ± 0.002
pH	7.3 ± 0.1	6.6 ± 0.1	7.6 ± 0.1	7.9 ± 0.1	6.8 ± 0.1	6.5 ± 0.1
Precipitate	–	–	–	–	–	7.3 ± 0.1 (After 24 h) CaCO <sub>3</sub> , CaCl <sub>2</sub>

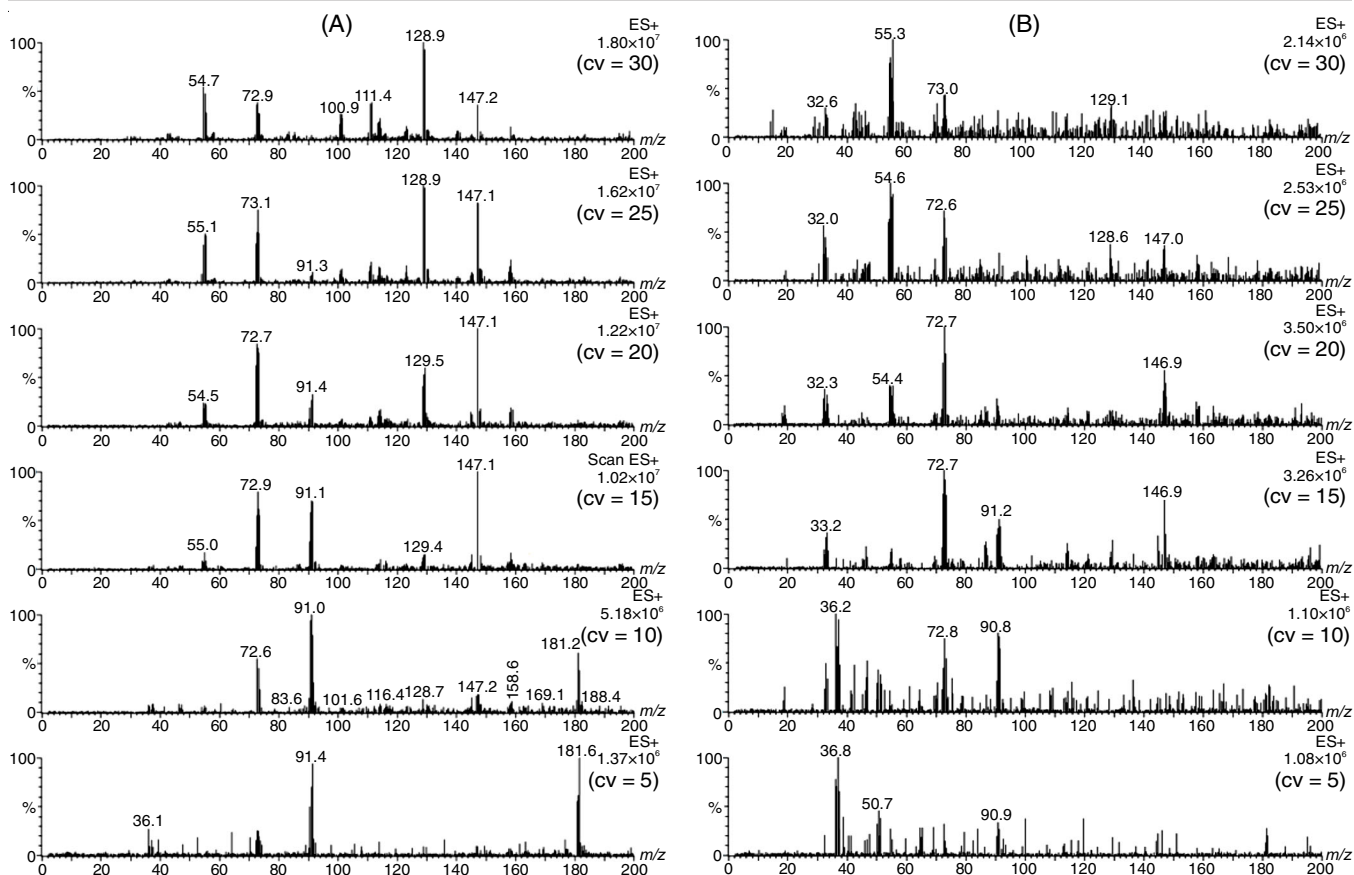


Fig. 8. ESI mass spectra of water with 0.5 mM of formic acid before (A) and after (B) plasma treatment at various cone voltages

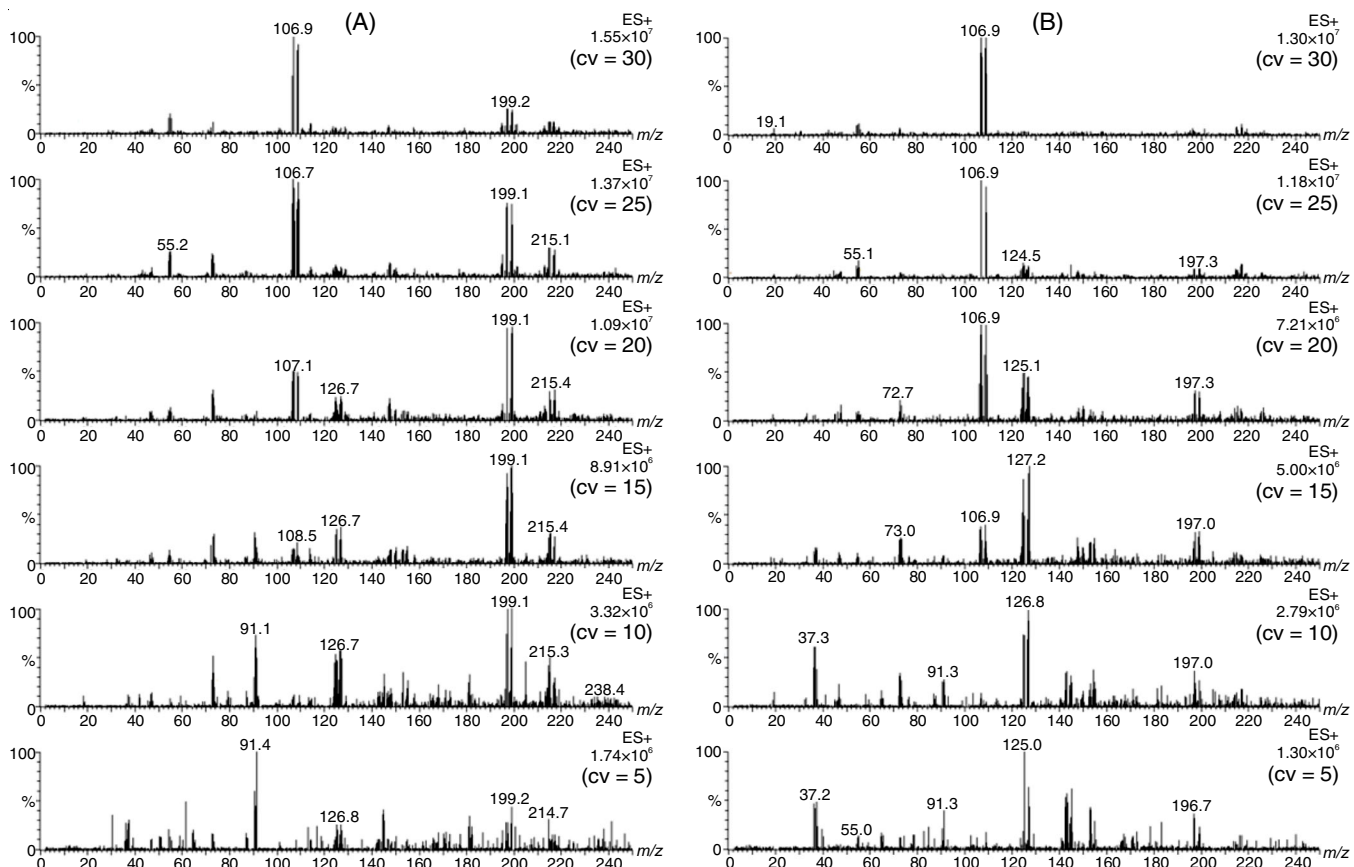


Fig. 9. ESI mass spectra of water with 0.5 mM of silver(I) nitrate before (A) and after (B) plasma treatment at various cone voltages

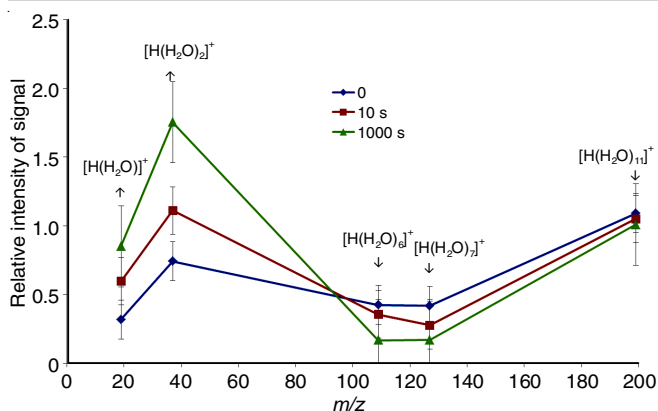


Fig. 10. Concentration of hydration form in water vs. times of plasma treatment. Spectra of ESI MS recorded at  $cv = 20$  V

process of solvation of silver ions by water before and after the exposure to plasma. For silver ions in the mass spectrum we observe signals at  $m/z$  107  $[Ag]^+$ , 125  $[Ag(H_2O)_2]^+$ , 197  $[Ag(H_2O)_5]^+$ , 215  $[H(H_2O)_6]^+$ . We analyzed these signals to determine the effect of plasma on the water structure. In all recorded spectra we observed an increase in the concentration of non-solvated and solvated silver ions by lower water agglomerates. For detailed analysis, we chose the spectra recorded at  $cv=20$  V for water treated with plasma for 10 s and 1000 s. Changes in the abundance of the signals at  $m/z$  107, 125, 197 and 215 in the ESI

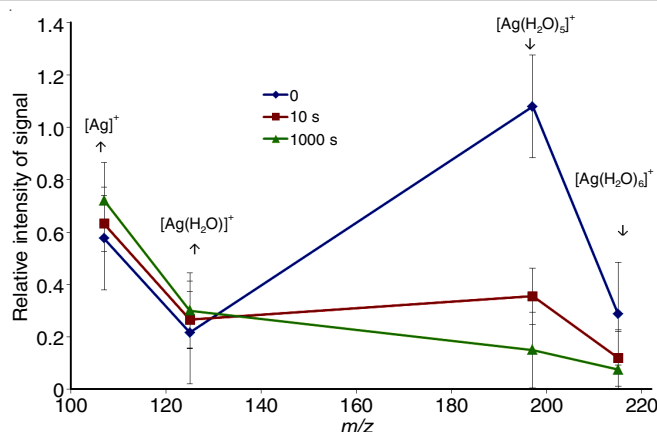


Fig. 11. Concentration of hydration form of Ag(I) in water vs. times of plasma treatment. Spectra of ESI MS recorded at  $cv = 20$  V

MS spectrum (Fig. 11) show a significant increase in the concentration of  $[Ag]^+$ ,  $[Ag(H_2O)]^+$  ions while the concentration of the aggregates  $[Ag(H_2O)_{5-6}]^+$  is reduced. We also examined physiological saline solution in closed ampoules before and after exposure to plasma. Fig. 12 presents the ESI mass spectra of water with 0.9% of sodium chloride before and after treatment with plasma at various cone voltages.

In order to confirm the hypothesis that smaller mass agglomerates  $(H_2O)_n$  form after water treatment with plasma, we

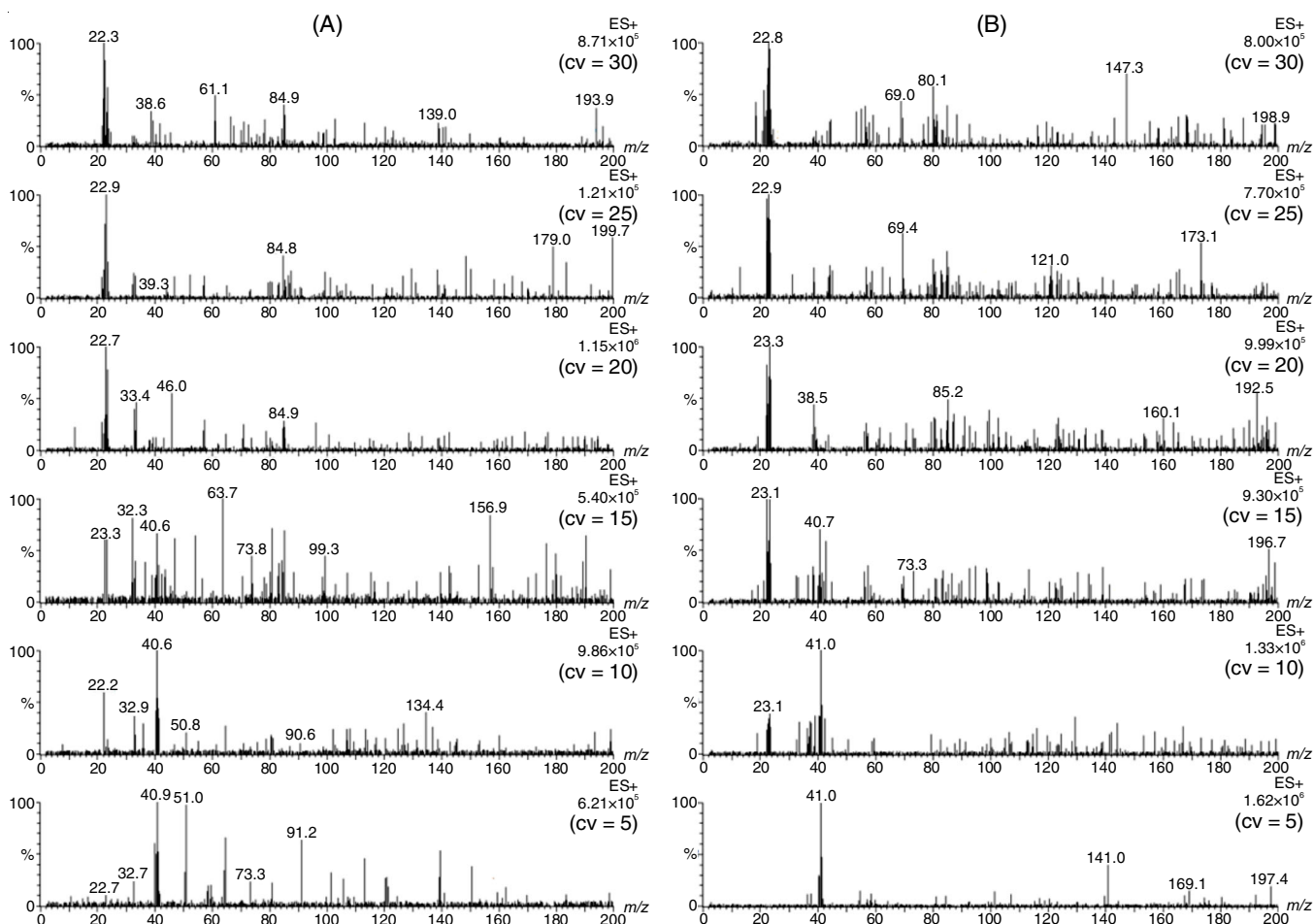


Fig. 12. ESI mass spectra of water with 0.9% of sodium chloride before (A) and after (B) plasma treatment at various cone voltages



examined the process of sodium ion solvation in physiological saline before and after the treatment. For sodium ions in water in the ESI MS mass spectrum, we observe signals  $m/z$  23  $[\text{Na}]^+$  and 41  $[\text{Na}(\text{H}_2\text{O})]^+$ , we analyzed these signals to determine the effect of plasma on the structure of water. We observed an increase in the concentration of non-solvated Na ions in all recorded spectra. We examined tap water before and after plasma treatment analysis to the signals at  $m/z$  19, 37 and 55. ESI mass spectra ( $cv = 20$  V) of tap water before and after plasma treatment are shown in Fig. 13. After the treatment of tap water with plasma, an increase in the abundance of the signals at  $m/z$  19 and 37 characteristic of proton solvation by one or two water molecules is observed. To sum up, in all tested aqueous solutions after exposure to plasma, we observe in the ESI MS spectrum a significant increase in the concentration of low-molecular water agglomerates solvating the studied ions, with a simultaneous decrease in the concentration of ions solvated by water aggregates with higher molar masses.

### Conclusion

We presented a new type of apparatus for inducing changes in water properties in closed vessels as a result of treatment with plasma generated by Pulsed direct current glow discharges, hypothesizing that the action of plasma on the structure of

water consists in resonant excitation of water aggregates. As a result of resonance excitation, aggregates of high molar masses are broken down into low mass molecular aggregates. To confirm the hypothesis we examined the solvation of ions in water before and after treatment with plasma, placed in closed vessels without direct plasma.

On the basis of the ESI MS spectra we found that in all tested aqueous solutions after exposure to plasma, a significant increase in the concentration of low-molecular  $[\text{M}(\text{H}_2\text{O})]$  and  $[\text{M}(\text{H}_2\text{O})_2]$  water agglomerates solvating the ions tested took place, while the concentration of ions solvated by water aggregates of high molar masses  $[\text{M}(\text{H}_2\text{O})_{6-10}]$  decreased, relative to the corresponding values for untreated water.

The presented method is characterized by the transmission of electromagnetic radiation generated by plasma generated by pulsed direct current glow discharges formed in special conditions. Influence of plasma takes place through a dielectric shield and can cause changes in the composition of aqueous solutions in closed vessels; therefore this method can be used to change the amount of chemical species present in water in biological systems (cells). In addition, the method can also be used to improve water and wastewater parameters on an industrial scale [56].

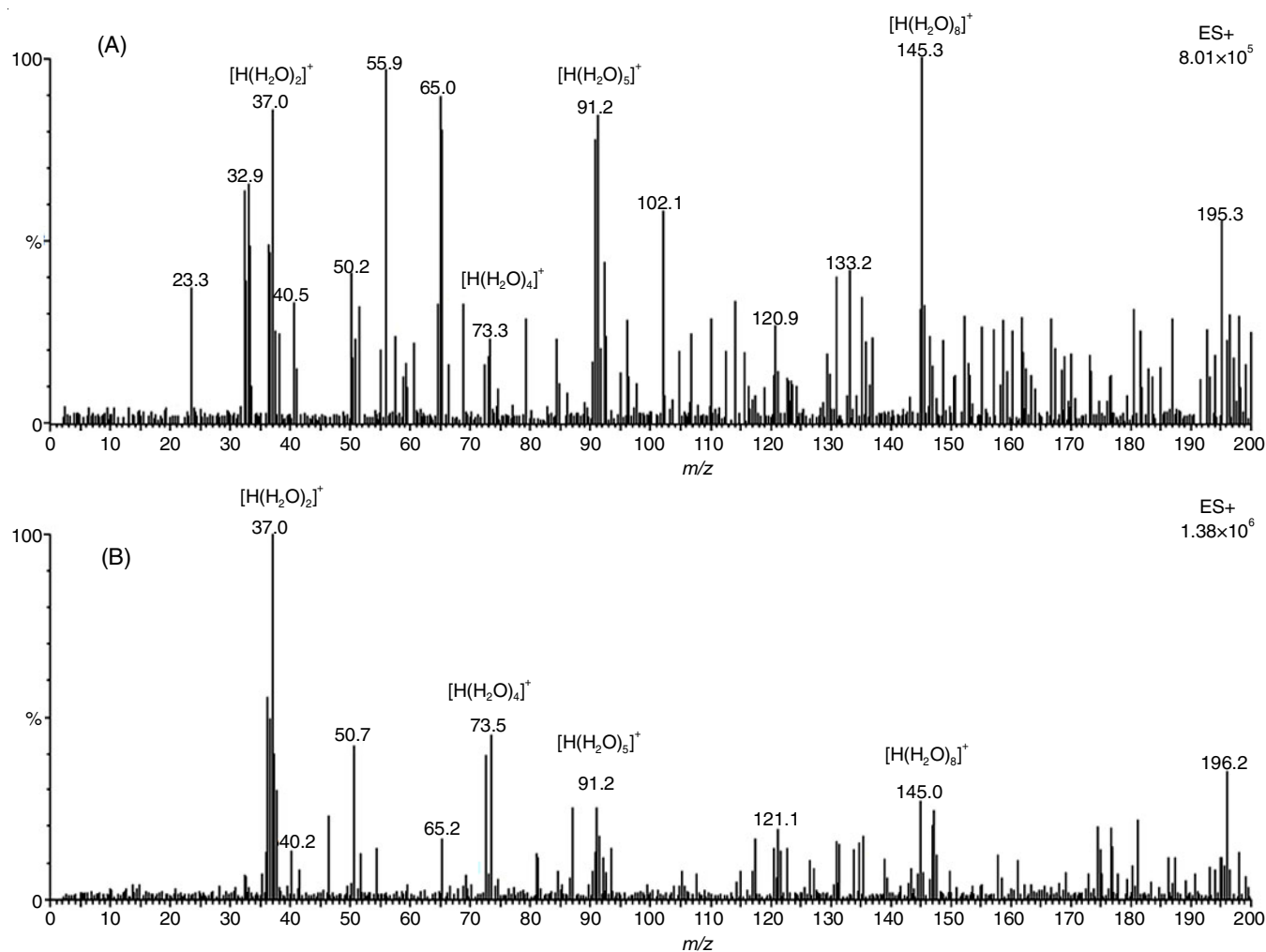


Fig. 13. ESI mass spectra of tap water before (A) and after (B) plasma treatment at  $cv = 20$  V

### CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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