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Theoretical calculation to create ion source using electrospray in atmosphere

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Analysis of water-containing samples has increasing demands especially in on-site investigation. Therefore, we are aiming to develop an imaging mass spectrometry in atmospheric pressure. In this paper, how to make an ion beam in atmosphere is designed and devised based on electrospray ionization (ESI) phenomena. In case of existing "desorption electrospray ionization mass spectrometry (DESI-MS)" using electrospray, specimen is dissolved in sprayed solvent, and they diffuse in it. It is possible to detect sensitively by using the solvents which is soluble in the component as long as the component in the sample is identified prior to the analysis. The condition of wet sample surface by the electrospray may affect spatial resolution of the sample depending on the combination the variety samples and solvents. We considered that the analysis can be possible regardless of the dissolved or undissolved constituents in solvents by causing physical sputtering of the sample surface using electrospray ion beam. In order to realize this sputtering phenomenon in atmosphere, it is necessary to calculate sputtering conditions. This calculation process is halfway stages for this study, and the condition for physical sputtering is mainly calculated in terms of Rayleigh limit.

1. Introduction

On-site analysis is in demand to maintain water-contain sample, e.g. lithium ion batteries, biological tissues, atmospheric aerosols and liquid crystals. We are aiming to develop an imaging mass spectrometry in atmospheric pressure based on these concepts. In this study, how to make an ion beam in atmosphere is designed and devised based on electrospray ionization (ESI) phenomena.

There is an analytical method similar to our development method among the several surface analyses in atmosphere called DESI-MS (desorption electrospray ionization mass spectrometry)[1]. This method employs electrospray to deliver small droplets onto a solid sample surface. Methanol and water are typically used as a solvent. Since the distance between sample surface and the spray emitter is short (< 5mm), the charged droplets generated by electrospray reach the solid sample surface as they are. For this reason, the solid sample surface are dissolved by the charged droplets in microscopic view. Through the charged droplets are irradiated to the sample surface by continuous spray, the

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momentum are transferred from primary charged droplets to secondary ones containing sample compounds are emitted from solvent layer on sample surface. After that, solvents of them are evaporated like ESI and become sample ion in air [2]. In DESI-MS analysis, analytes are needed to be easily dissolved in the solvent, and are diffused in the solvent layer on the sample. The condition of wet sample surface by the electrospray may affect both the lateral and depth resolution depending on the combination the variety samples and solvents [3]. These are the current problems in DESI-MS.

Our ion source currently under development is supposed to make physical sputtering of the sample surface with bombardment of molecular ions originally contained in the sprayed droplets. Therefore, it is required that sprayed droplets are rightly shrink and dried through the evaporation of the solvent and number of fissions caused by excess charge on the droplet surface until they reach the sample surface. In ideal case, a sample surface is sputtered with only the molecular ions resulting in physical sputtering. This enables us to obtain information on the raw state of the sample in atmosphere. We considered that the analysis are made possible regardless of the dissolved or undissolved constituents in solvents by causing the sputtering of the sample surface.

Figure 1 is a schematic illustration of the atmospheric ionization system considered in this study. In order to realize the sputtering phenomena in atmosphere, it is necessary to calculate sputtering conditions. This calculation process is the halfway stage for this study, and the condition for physical sputtering is mainly calculated in terms of Rayleigh limit.

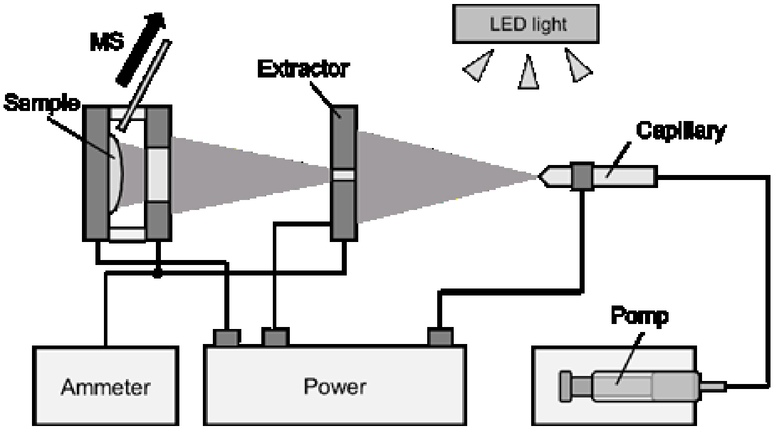

Fig.1 Schematic image of atmospheric ionization system in this study

2. Theoretical calculation

For realizing the sputtering effect in atmosphere, it is necessary to calculate both the droplet beam status and sputtering conditions. The solution, including solute molecules dissolved in a solvent, was fed to the emitter tip (made from an SUS tube) using a syringe pump. When a certain positive high voltage is applied to the emitter tip relative to the extractor at ground potential, Taylor cones is created at the emitter tip, and charged droplets are protruded over surface tension. Since the surface charge density on a droplet is too dense, the charged droplets are divided by Rayleigh limit while evaporating the charged droplets. Two kinds of charged droplets are produced in a single event. One scheme is a charged droplet having the charge of 85 % of the parent droplets and the diameter of the charged droplet is nearly unchanged. In the other scheme, about 20 small charged droplets with 0.75 % of charge of parent droplets and the diameter of the charged droplets are one-tenth [4]. In this study, the latter individual 20 charged droplets are not considered in the calculation because there is little effect on both charge and mass decreasing in the fission events. For this reason, we used the other one charged droplet to this purpose.

First, the diameter D of the first droplet with the stable state of spray is expressed by

$$D=\left(\frac{\gamma\varepsilon_0{}^2}{\rho K^2}\right)^{\frac{1}{3}} \qquad (1)$$

, where ε_0, γ, ρ and K are vacuum permittivity, surface tension, density of solution and conductivity of solution, respectively [4]. The charge q_R to mass m ratio of a droplet is expressed by

$$\frac{q_R}{m}=\frac{12\sqrt{2}}{\rho}\sqrt{\frac{\varepsilon_0\gamma}{D^3}} \qquad (2)$$

, where V is accelerating voltage [5]. From this condition, the initial speed of the first droplet v_0 is

$$v_0=\sqrt{\frac{3}{2\pi}}\times\sqrt{\frac{q_R V}{\left(\frac{D}{2}\right)^3\rho}}. \qquad (3)$$

In case of droplet of charge number and mass are 85 % and 98 % from droplet before disruption, number of times of disintegrate n until target valence k is expressed by

$$log_{0.85}\frac{k}{q_R}=n. \qquad (4)$$

The spray solution for the ion source was prepared using tris-(8-hydroxyquinoline) aluminum (Alq_3) dissolved in chloroform diluted by acetone. The reason for using acetone was the rapid evaporation from the emitter tip to sample surface, and the solute contains Al atom suitable for physical sputtering. Table 1 summarizes the calculated result when the first charged droplet of acetone and the number of times of disintegrate until singly-charged droplet are 62 times. In case of a solute molecule of Alq_3 are dissolved in acetone, we considered that a solute molecule of Alq_3 of the charge number in this case is calculated.

As for the kinetic energy of droplet E_{kn}, it can be calculate from the initial speed v_0 and mass m_0, and does not depend on the charge number and but on the air resistance during flight. In this case, $E_{kn}(n)$ is expressed by

$$E_{kn}(n)=\frac{1}{2}m_0\left(\frac{98}{100}\right)^n v_0{}^2. \qquad (5)$$

For example, the disintegrated time of the droplets t is constant to be 5 μs, the time of the disappeared solvents of the charged droplet is 50 μsec. When the number of the times to disintegrate n is 10, $E_{kn}(10)$ was estimated to be 3.77×10^{-12} kgm^2/s^2 when these conditions are assumed. Figure 2 shows E_{kn}, and the charge number as a function of n, respectively until singly-charged droplet. Calculated in Rayleigh limit, it considered that the sputtering conditions is mainly required to select a balance of the number of times to disintegrate *n* and the charge number because the decrement of the charge number is greatly decreased.

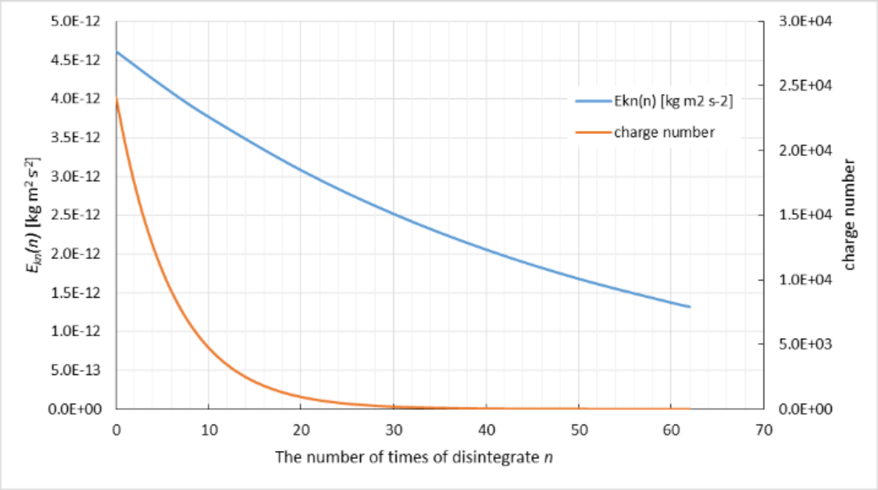

Figure 2. The graph relating $E_{kn}(n)$ and charge number to the number of time to disintegrate until monovalent droplet.

Table 1. The calculated result of acetone

D [m]	q_R/m [C/kg]	Charge number	Initial speed v_0 [m/s]
2.52×10^{-6}	2.44	2.41×10^{4}	76.31

Actual behavior of the droplets emitted by electrospray are affected by the drag due to air. For that reason, it is required to calculate the losing energy caused in atmosphere in addition to the calculation shown in formula (5). The energy at the arbitrary point is calculated by subtracting the losing energy used the calculation of the drag. Two conditions are assumed arbitrary values of the droplet size and accelerating voltage after evaporating from first droplet. The calculation of the drag is described as:

$$D = \frac{1}{2}\rho V^2 S C_D. \tag{6}$$

, where C_d is drag coefficient, ρ is air density, S is maximal area of a droplet, and V is relative speed between the fluid and the body [6]. We calculated the distance l when the droplet size decreases to be 10 nm during evaporating assuming using as the solvent is acetone.

Figure 3 shows the relationship between the kinetic energy of a droplet and the distance l when a constant speed V was assumed. We calculated under the conditions where the relative speed V is 1 m/s and the distance l is varied from 0.01 m to 0.16 m. The result of the calculation (Fig.3) showed that the energy of the droplet is largely affected by the drag due to air and the energy is too low to cause the sputtering. Moreover, the energy

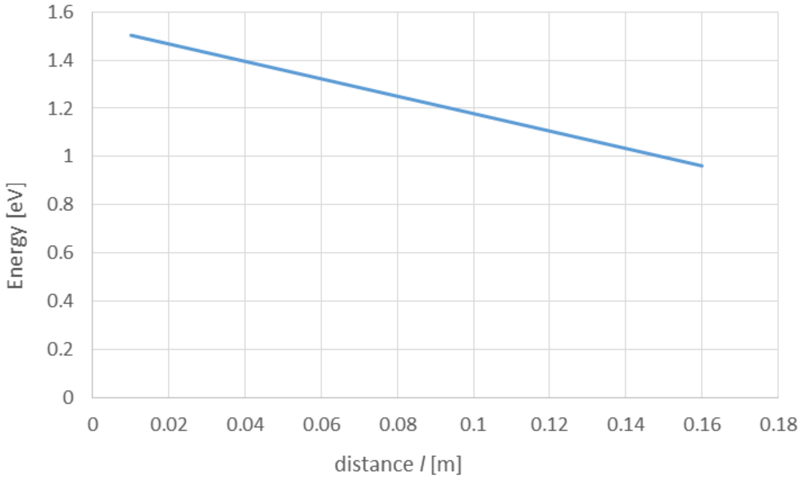

Figure 3. Energy of droplet with a diameter of 10 nm as a function of the distance *l* .

decreased with increasing *l*, but this effect was not so large. This is because of the energy is not related to the acceleration voltage, but the drug.

By this reason, the instrument of electrospray which can deliver droplets involving Alq_3 with a diameter of less than 10 nm (ideally not a droplet, but an Alq_3 molecule) is possible by re-acceleration the droplet (or an Alq_3 molecule) towards the sample surface using another electrode just in front of the sample. For physical sputtering, each of atoms in the droplet or solute Alq_3 should have at least 10 eV [7]. In case of an Alq_3 molecule, it consists of 52 atoms containing 5 kinds of elements. Very rough estimation if an Alq_3 molecule has 520 eV, the threshold of 10 eV/atom is fulfilled. This means re-acceleration should have at least 520 V potential difference between the re-acceleration electrode and the sample surface. In this situation, mean free path of Alq_3 in air. Mean free path λ [m] is generally expressed by the following formula,

$$\lambda = 3.11\text{x}10^{-24}\, T/(PD)^2 \,. \tag{7}$$

, where T [K] is temperature, P [Pa] the pressure, and D [m] the diameter of the molecule. Considering current situation, λ is calculated to be 4.2x10^{-5} nm (4.2x10^{-14} m). Beam intensity (number of Alq_3 molecules/s) I after re-acceleration is expressed by,

$$I = I_0 \exp(-x/\lambda) \tag{8}$$

, where x is the distance between re-acceleration electrode and the surface. If x is 10^{-3} m, I/I_0 is close to zero. However, it is noted that if an Alq_3 molecule collide with air (O_2, N_2), its scattering angle is thought to be small, and accelerated again if the molecule is not neutralized by the collision. There is a possibility to make Alq_3 beam with a condition of 10 eV/atoms causing physical sputtering in air.

3. Conclusion

It is conducted that the initial calculation sputtering conditions using mainly Rayleigh limit for the sputtering effect in atmosphere. Since it calculated by standard electrospray phenomenon, we will confirm the physical sputtering effect in atmosphere through the future directions.

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