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Application of electrospray mass-spectrometry for nanoparticle investigations: Simulation of ion movement in a supersonic jet.

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Introduction: The assessment of nuclear waste repositories requires detailed knowledge of chemical and physical properties of radionuclides, in particular of their behavior in the environment. It is known that metal ions, in particular tri- and tetravalent actinides, have a high tendency to hydrolyze, form polyspecies, adsorb to natural nanoparticles (colloids, 10-800 nm) and are transported within the aquifer. To carry out investigations of nanoparticles suspended in water by mass-spectrometry, it is possible to use electrospray, a well known method of transferring ions from solution to vacuum which was implemented in our system. Picture 1 shows its general layout: 1. ESI source. 2. Linear trap. 3. Ion guide. 4. Laser system. 5. Time-of-flight mass-spectrometer. The key feature of our system is the ability to work with very heavy particles. The mass/charge range is [100 – 1011 amu/q].

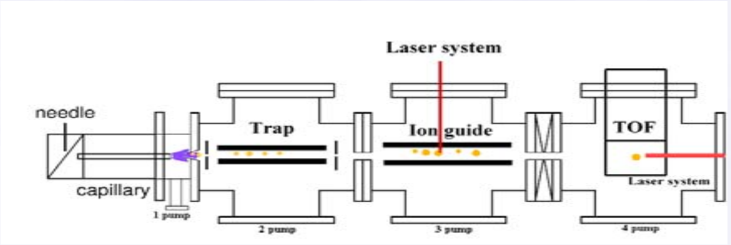
Objective: This study was conducted to determine the behavior of ions in a supersonic jet (region orifice-skimmer, pictures 2, 3) and to define parameters (emittance) of ions behind the skimmer.

Methods: The model of ion movement in the supersonic jet under influence of an electrical field combines the **Monte-Carlo methodology** (MCm) and the **Large particle** method (numerical model of supersonic jet).

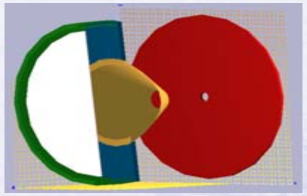
The Large particle method: Supersonic jet, formed by gas flowing from a high pressure region to a low pressure region, exhibits a large degree of unhomogenity. Parameters of the jet can significantly vary along the direction of gas flow. Therefore, it is necessary to use special methods of calculation of systems of differential equations that allow calculation of gap or shock waves. Gas movement is described by Euler's equations.

Method of solution of equations (Euler's equations): the whole space is divided up into many cells. The solution of the equations is based on principles of splitting of physical processes. It means that the calculation consists of many iterations in time, but variation of physical parameters at each time step is made in two stages. Stage 1: parameters are changed only according to pressure. It means that only inner conditions of cell are changed. Such cell is named *large particle*. Second stage: effects of mass, momentum and energy redistribution are calculated. The scheme of system of equations is conservative. It means that conservation of energy for each cell is taken into account, which leads to an increase of the calculation quality.

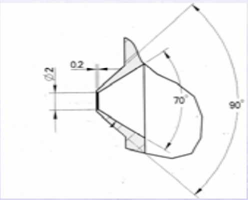
Results of simulation by Large particle method are arrays of density, temperature, pressure and velocity of gas. Examples of simulation are presented on pictures 4, 5. Those arrays describe the constant regime of the supersonic jet, where the main parameters (pressure, density, temperature, velocity of jet) are unequivocally determined by the distance from the orifice and can be used for simulating ion movement in SIMION. To simplify the usage of this simulation in SIMION, those arrays were approximated by the isentropic model (see formulas). As an advantage of the isentropic model the main parameters are parameterized by analytical expressions. **Therefore we apply the isentropic model for modeling the supersonic jet and the coefficients are obtained from simulations by the "large particle model".**



Picture 1. Layout of whole system.

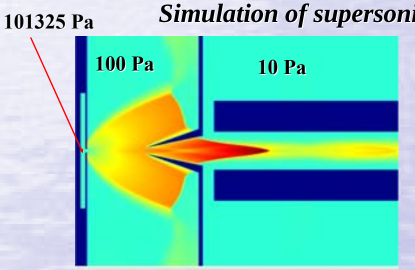


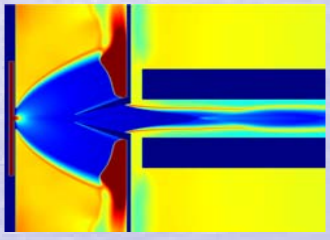
Picture 2. 3D geometry of orifice - skimmer



Picture 3. Skimmer's parameters

Simulation of supersonic jet by Large particle model





Picture 4. Velocity distribution (m/sec) Picture 5. Temperature distribution (K)

Approximation of velocity for skimmer

$$V = 331 \cdot \sqrt{\frac{2}{\gamma - 1} \cdot (1 - [A \cdot (\frac{d}{r})^2]^{\gamma-1})}$$

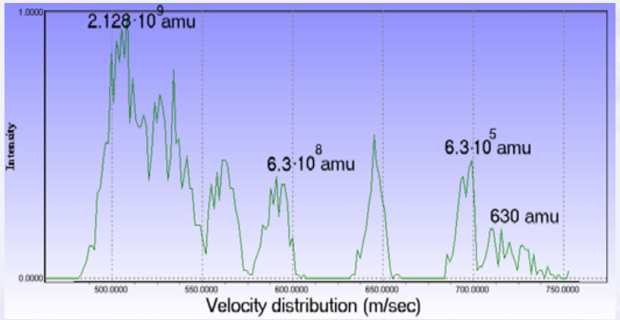
$$V(m/sec) = \begin{pmatrix} A = 0.1, r \in [3 - 9.5mm], \\ A = 0.3, r \in [9.5 - 17.8mm], \\ A = 15, r \in [17.8 - 22mm]. \end{pmatrix}$$

Approximation of temperature distribution

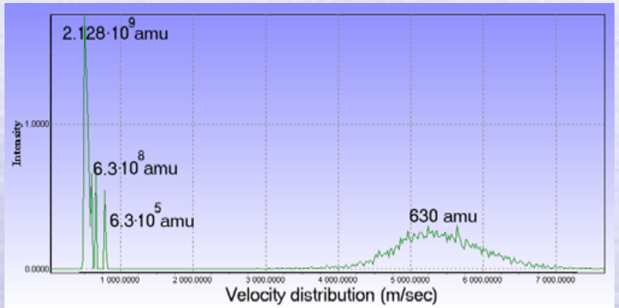
$$T = 300 \cdot [A \cdot (\frac{d}{r})^2]^{\gamma-1}$$

$$T(K) = \begin{pmatrix} A = 0.1, r \in [3 - 9.5mm], \\ A = 0.3, r \in [9.5 - 17.8mm], \\ A = 15, r \in [17.8 - 22mm], \end{pmatrix}$$

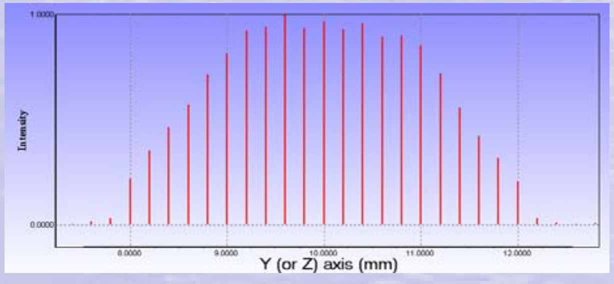
Monte-Carlo method: The ion movement and collisions in gas can be modeled by the *direct Monte-Carlo method*, based on the following idea: the environment in the nozzle-skimmer region is regarded as medium (consisting of gas flow, electrical field, and electrodes) and a statistical ensemble of ions. This medium is described by four parameters: 1. Density/pressure of gas flow in space. 2. Temperature distribution in space. 3. Velocity distribution in space. 4. Electrical field. The medium is divided up into many cells each of which stores local density/pressure (n/P), temperature (T), and the vector of velocity (V) (isentropic approximation). The ion movement between collisions is a straight line. The simulation of the collisions of ions and neutral molecules is based on the hard spheres model. The velocity of neutral molecules before collisions is the sum of jet velocity (local cell, isentropic approximation) and thermal velocity (defined in Boltzman distribution). Therefore on the one hand, our model of ion movement in gas takes into account the key features of supersonic jet, and, on the other, it comprises a Monte-Carlo method, which gives best results in numerical simulation of gas.



Picture 6. Ions distribution behind skimmer (no potentials).



Picture 7. Ions distribution behind skimmer (1 kv between orifice and skimmer).



Picture 8. Ions distribution behind skimmer (perpendicular to jet direction). Mass/charge ratio [100; 10^{11}]

Results

1. Simulation of supersonic jet for different pressure ratio is made.
2. The influences of supersonic jet and electrical field on ion movement are estimated.
3. The effect of slipping energy of ions in mass range [100 – 10^{11} amu] in supersonic jet is evaluated.
4. Emittance of orifice-skimmer region with effect of supersonic jet is calculated.
5. Acceptance of quadrupole (based on emittance of orifice-skimmer) is evaluated.