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ADVANCED SAMPLE IONIZATION METHOD IN ION MOBILITY SPECTROMETER

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Abstract. *A new method for the corona discharge ignition in ion mobility spectrometer has been developed. It substantially improves stability and increases device resolution because sample controlled ionization causes a stable flow of ion-exchange processes. The implemented circuit simplifies the design of the proposed ion source and an electronic control circuit. This controlling circuit allows forming a corona discharge without using any additional ignition electrodes.*

Key words: *ion mobility spectrometer, corona discharge, ionization source*

1. INTRODUCTION

Ion mobility spectrometry is a method of detection and identification of chemical compounds vapors based on the ions separation on the criterion of mobility in a weak electric field in a gaseous medium at atmospheric pressure [1-5]. The conventional pattern of the device (Figure 1) includes the following components: ionization chamber where the sample is being ionized; gate, for the formation of ion clusters; the drift chamber, where ions are being divided by mobility while moving in a constant electric field; detecting node where the ion current measurement is performed; storage and data processing system.

An ion cluster is formed by means of the gate from the ions in the ionization chamber. The cluster is injected into the drift chamber and moved in the direction of the collector under the influence of electrostatic field. Ions with different mobilities reach the collector at different times, besides, the time structure of the collector current corresponds to the ions propagation speed in the drift region. The resulting ion mobility distribution spectrum makes it possible to detect and identify chemical substances contained in the gas sample.

Radioactive radiation, corona discharge, laser radiation, ultraviolet or X-ray radiation [6] are used to ionize air samples in ion mobility spectrometry.

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Ionization source is an important part of the system responsible for system stability, resolution and sensitivity of ion mobility spectrometer. The ionization source can operate in continuous or pulse modes. When the ionization source operates in pulse mode (pulse corona discharge, pulse laser), formation of ionic clusters occurs directly during ionization, which in some cases does not require an ion gate.

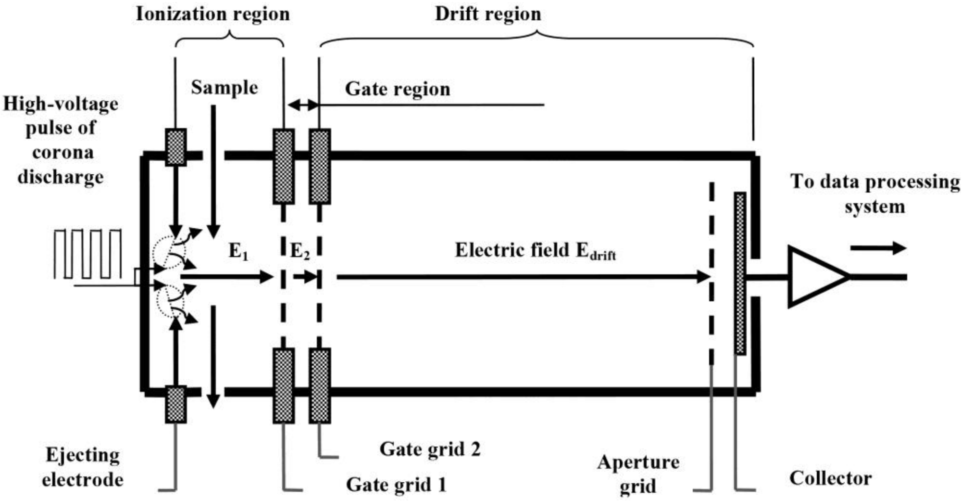


Fig. 1 The spectrometric cell of ion mobility spectrometer with ionization source and electrostatic gates.

The choice of a corona discharge for air samples ionization is related to the following advantages:

- Lack of radioactive materials;
- Possibility of generating both positive and negative ions;
- Simplicity and low cost of manufacturing;
- Low power consumption.

Following physical processes occur while igniting a corona discharge. In the air of the ion source there is always a certain number of "background" ions and electrons caused by natural radiation. When voltage is applied between the tips of the discharge electrodes with a small curvature radius, the electric field may exceed the air gap breakdown level. The presence of primary "background" charge carriers contributes to the rapid process of secondary avalanche ionization.

The ions formation process of a detectable substance is a multi-stage process. Initially, the formation of the so-called reactant ions takes place due to air molecules ionization. Next, through a series of ion-molecule interactions (chemical ionization at atmospheric pressure) reactant ions transfer their charge to the impurities molecules, and in particular, to the molecules of detectable substances.

2. CORONA DISCHARE IONIZATION SOURCE

Ionization source based on corona discharge represents a 1 mm thick conductive substrate called an ejecting electrode and thin sharp electrodes, placed over the substrate. Corona discharge plasma is formed between these electrodes at high voltage (Fig. 2). Limiting resistance R_{lim} is used for smoothing the burning corona current.

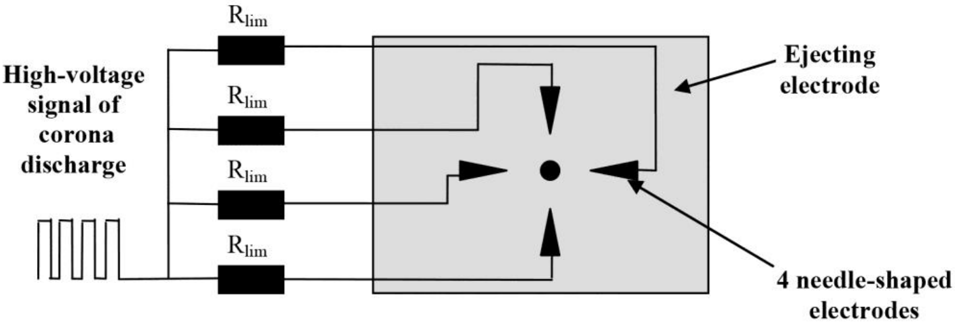


Fig. 2 Corona discharge ion source schematic.

The ionization source used in this paper operates in pulse mode. As a result, short clusters of ions are formed. Typically, the ionization chamber design is such that the ignition electrodes are located in high electric field areas to entrain the resulting ions from the ionization region to the gate. At the same time, "background" natural ions (arising due to the action of cosmic radiation, fluorescence, local fluctuations and temperature), initiating the discharge occurrence, are constantly carried out of the area between the tips of the corona source, which makes the ignition of the corona difficult. This is expressed in the instability of the discharge and the need to increase the duration and amplitude of the ignition pulse voltage. Discharge instability causes the dispersion of the ion charge in the cluster and instability of spectrum, which lead to an increased probability of malfunctioning. Stabilization of the results requires averaging of the spectrum over large time intervals, which increases the time to obtain reliable results and affects sensitivity. Therefore, an important task is to create an environment, in which air samples ionization would be processed under controlled conditions to ensure the ignition process stabilization. And as a result, this could lead to increasing the sensitivity and reducing the malfunctioning time of the device.

One way to solve this problem is proposed in [2], serving to use corona ionization source with additional ignition electrodes (Fig. 3).

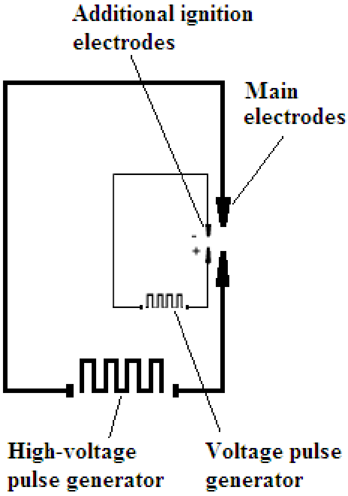


Fig. 3 Ionization source with two igniters.

Additional ignition electrodes (Fig. 3) are managed by a Voltage pulse generator. The discharge is formed between them before the main ignition pulse, creating additional "catalytic ions". These ions contribute to a stable discharge ignition between the main electrodes controlled by a high-voltage pulse generator. It is understood that the use of additional electrodes promotes controlled and stable discharge ignition between the main electrodes in the presence of an electric field in the ionization region. A disadvantage of the method of the ion source ignition mentioned above is a structural complication of the ionization chamber, which leads to an increase in size and in complexity and deteriorates its manufacturing technology. There just remains the problem of unstable discharge firing between extra igniters, as the process occurs in an electrostatic field and the resulting primary carriers in the electrodes gaps continuously carried out of the discharge region.

In this paper the corona ignition system is considered when the ignition process is divided into two phases: preparatory and main. During the preparatory phase of ignition, the electric field in the ion source is reduced compared to the nominal level, or set to zero, which ensures the establishment of a fixed background concentration of charge carriers near the discharge gap. During the initial phase of the corona discharge, a single pulse or a series of voltage pulses are formed at the ignition electrodes, leading to the occurrence of avalanche discharge between the electrodes. Ions formed at the same time remain near ignition electrodes after the discharge termination, because there is no electric field in the ion source. By the beginning of the main phase of the ionization, the field in the ion source is set to the nominal level, and the "catalytic ions" do not have time to leave the ignition area because of low mobility. The corona ignition at the main phase is carried out, as well as on the preparatory, by single pulse or series of pulses. This ensures the stability of the corona discharge ignition due to the presence of ions in the discharge gap left since the first phase of ignition. In addition to increasing the stability, the proposed system provides manufacturability and retains the dimensions of the used ionization source without using any additional ignition electrodes. Ignition pulse generation and modulation of the electric field does not require any additional modifications to the ionization chamber and is realized by the synchronization from the ion mobility spectrometer control system.

3. CORONA DISCHARGE ION SOURCE CONTROL

To form the corona, a special control system forms high-voltage voltage that is applied to the sharpened electrodes of the corona source. The second electrode in this system is a conductive substrate – ejecting electrode. Timing diagram of the corona source is presented in Figure 4. The control system generates a sequence of several igniting pulses for each measurement cycle (Fig. 4a). The duration of the high-voltage power supply can be adjusted to the electrodes of the ionization source T_{pulse}, pause between pulses T_{pause}, as well as the number of pulses per measurement cycle (Fig. 4b).

Changing the corresponding timing intervals in the ignition system of the ionization source can achieve stable corona discharge combustion during necessary working time, change of the number of ions generated. Complete or partial filling of the ionization chamber by ions formed during one measurement cycle can be chosen.

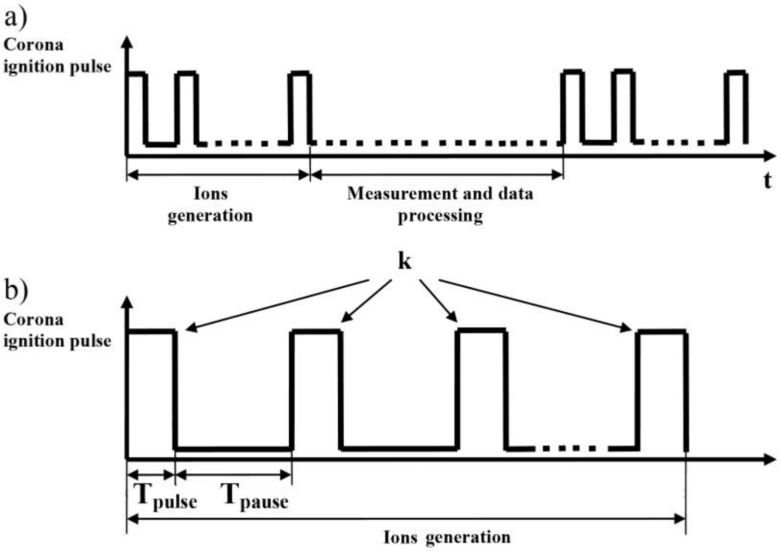


Fig. 4 Timing diagram of the ion mobility spectrometer (a); sequence of **k** ignition pulses in one measurement cycle (b).

4. ELECTROSTATIC GATES

Presence of two electrostatic gates allows the change of the field E1 in the ionization region (between the ejecting electrode and the gate grid 1) and field E2 in the gate region (between the gate grids 1 and 2). Changing the field E1 allows the control of the lead time of ion-molecule reactions between the reactant ions and molecules of detectable substance after ionization. Next, ions of analyzed substances are injected into the gate region. Injection takes place by the fact that the potential applied to the ejecting electrode becomes greater than the potential applied to the first gate grid. So, an electric field arises in the ionization region, which ejects ions into the gate region.

Efficiency of the electrostatic gates depends on the mode that is provided by the appropriate electronic control system. During switching-on the device, building of the initial electrostatic potentials at the gates occurs. Let us conventionally denote the first grid potential as UC1, and the ejection electrode potential as UB.

Gates functioning during one measurement cycle is divided into seven successive phases (Fig. 5):

- Phase 1 – Turning field E1 on in the ionization region, which corresponds to the beginning of the measurement cycle preparation.
- Phase 2 – Consists of two parts. During the first one, pre-ionization occurs at the reduced field E1. During the second – corona ionization is being processed, at the same time the direction or magnitude of the fields in the ionization- and the gate region are being restored. Ions movement, formed during the ionization process, occurs by the field E1, from the ejection electrode to the gate region.
- Phase 3 – The potential of the first gate grid becomes equal to the ejecting electrode potential (UC1 = UB). The field in the ionization region becomes zero,

the ions are being stopped. In the stopped cluster ion- molecule reactions take place. Reactions occur between the molecules of the examined substance and the reactant ions generated during ionization process.

- Phase 4 – Promotion of the cluster to the gate region.
- Phase 5 – Phase of ions injection into the drift region. By the field E_1 in the ionization chamber and E2 in the gate region ions are injected into the drift chamber. At the same time, a thin ion bunch can be "cut – off" by a second electrostatic gate. This significantly increases the resolution of the spectrometer.
- Phase 6 – Field E_2 direction is reversed, so the electrostatic gate is being closed. Ions left in the ionization chamber are being moved by the field E1 to the gate grid 1 and are being captured by it.
- Phase 7 – Gates condition is being restored to its original state. Field in the ionization region is absent, there is a stopping field E2 in the gate region. The system is prepared for the next measurement cycle.

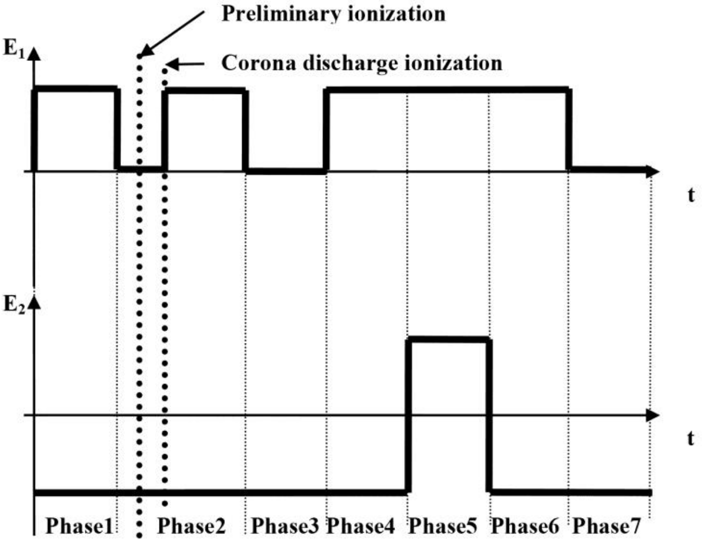
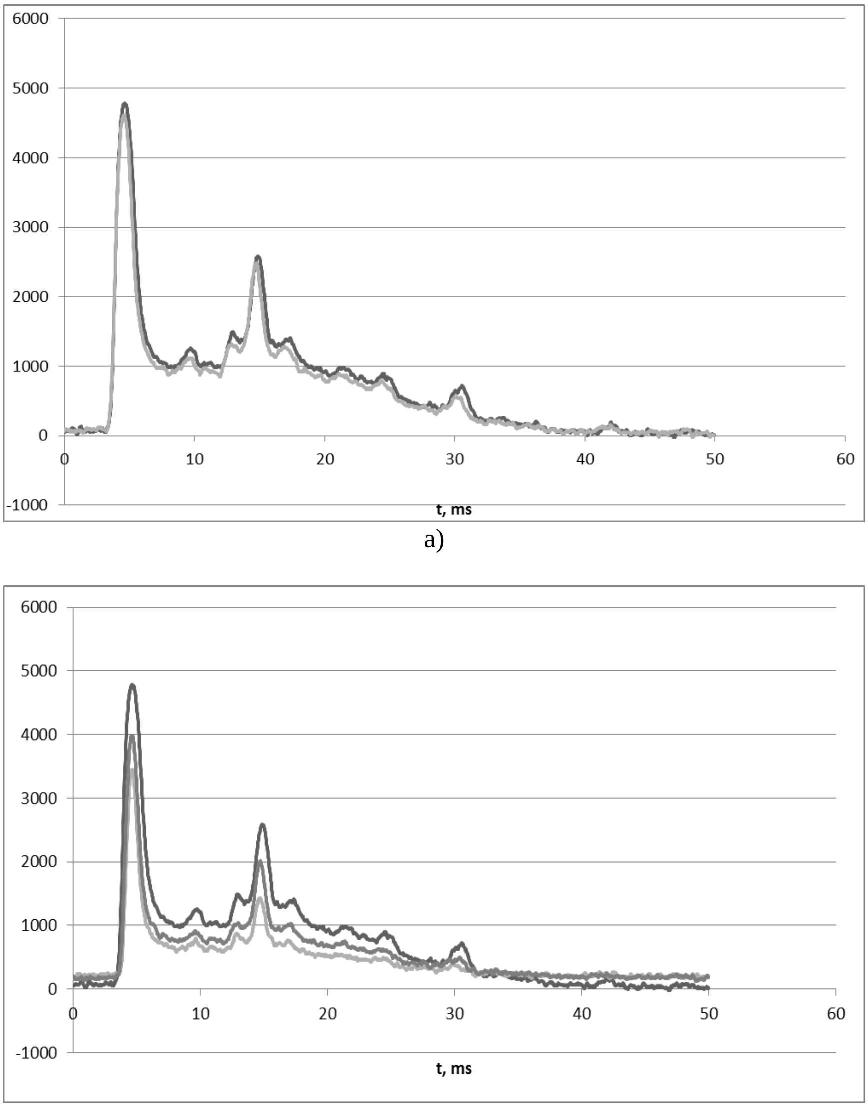


Fig. 5 Ionization- and gate region field distribution during the electrostatic gates functioning.

5. PRACTICAL EXPERIMENT

An experiment with (Fig. 6a) and without (Fig. 6b) using an advanced ignition method was performed. The spectrum altitude represents the total ion charge (normally, about 400 nC) in the drift tube. A charge deviation between the two consecutive spectrums is not more than 3% (Fig. 6a) and up to 31% (Fig. 6b).



a)

b)

Fig. 6 Experimental results with (a) and without (b) using an advanced ignition method.

Adduced electrostatic gate control circuit allows to increase or decrease the duration of the of ion-molecule reactions passage, vary the number of ions in the drift chamber, and ultimately on the collector. This opens up the possibility to improve spectrometer performance, sensitivity and resolution. With the increase of phase 3 duration, more complete charge transfer from the reactant ions to the molecules of detected substances, that have a greater proton affinity (in the case of a positive mode) or electron affinity (in the case of a negative mode), occurs. This happens due to the increase of time spent for ion-molecule reactions.

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