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Negative Corona Discharge Ion Source Under Ambient Conditions with Mini Line-cylinder Electrodes

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A novel ambient negative corona discharge ion source with mini line-cylinder electrodes is designed. The diameters of inner and outer electrode are 0.16 and 4 mm respectively. With a special assembly method, a perfect coaxiality of the two electrodes is obtained. An injection system utilizing a temperature control technique, achieves a constant and stable concentration of the sample, which is critical to the experiment. The formulas of the corona onset voltage of line-cylinder electrodes are also introduced. The experiment results show that negative substances such as formic acid and acetic acid can be ionized under ambient conditions. When combined with micro electrical mechanical system fabrication process, the volume of the ion source can be reduced dramatically, but there is an undesirable surface discharge. To solve the surface discharge problem, an improved structure was designed and tested. The simplicity of the interface of the ion source makes it suitable for mass spectrometer, micro mass spectrometer, ion mobility spectrometer, and high-field asymmetric waveform ion mobility spectrometer applications.

Key words: Line-cylinder corona discharge, Ion source, Surface discharge, Ambient mass spectrometry, Micro electrical mechanical system

I. INTRODUCTION

The analysis of narcotics, explosives and chemical warfare agents at trace levels is an important research field for security purposes. The sort and concentration of these chemical substances can be detected by chemical analyzers such as mass spectrometer (MS), ion mobility spectrometer (IMS) and high-field asymmetric waveform ion mobility spectrometer (FAIMS). The common principle under these analyzers is to ionize the chemical substances and then detect the current signal induced by the ions. That is, they convert the detection of chemical substances into the detection of electric current signals [1]. Thus, the ionization is one of the key elements to obtain a satisfactory analysis result. If the analyzer can work under ambient conditions and the size can be minimized, a rapid-response, hand-held detector of environmental contaminations for use in customs, airport and battlefield, etc., can be realized. Today, the mature ion sources of commercial MS are almost sealed-in and incompatible with ambient conditions, which results in many disadvantages in applications under ambient conditions. It is necessary to develop a novel kind of mini ambient ion source which can be applied in instruments such as MS, IMS, and FAIMS. Some research groups are working at the development of such ion sources including the dielectric barrier discharge ion source, the desorption electrospray ion source, the atmospheric pressure glow discharge ion source, and the corona discharge ion source with point-to-plane electrodes [2-7].

Radioactive ionization [8-10], ultraviolet light ionization [11,12], and laser multiphoton ionization [13,14] are the common methods to ionize substances under ambient conditions. The workhorse of the radioactive ion source is normally ^{63}Ni foil emitting β particles with a half-life of about 85 years and an average energy of 67 keV. These ionization sources have some advantages (simplicity, stability, noise-free operation, and no need of extra power sources). However, they suffer from some problems. Firstly, the low rate of ion generation with the ^{63}Ni source results in a comparatively weak signal [15]. Secondly, working in the environment of radiation, regular leak tests, special safety regulations, and waste disposal are always required. These limit the applications of radioactive ion sources. Both ultraviolet irradiation ion source and laser desorption ion source can ionize the chemical substances selectively at atmospheric pressure by adjusting the wavelength of the light, but they are very expensive and difficult to miniaturize.

Corona discharge is a good choice for ambient ion

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sources [8,16-22]. If the characteristic dimension of the electrode is much smaller than the interelectrode gap, a strongly non-uniform field, but insufficient for electrical breakdown, can be developed and thus induce a corona discharge [19,23-25]. When the voltage between the electrodes rises up to the corona onset voltage, the current increases suddenly and obscure glow can be observed around the electrode with small curvature radius. Then, the substance between the electrodes is ionized and the ions needed are created. Continuous mode and pulse mode are two types of corona discharge. Continuous corona discharge has enough time to reach self-sustained conditions, while a pulse corona discharge is limited by the pulse width. Therefore, a more stable corona discharge is expected in the continuous mode [3], and that is the reason why a continuous corona discharge method is chosen in this work.

The effective ionization range of the line-cylinder structure is the whole area around the inner electrode, while that of the point-to-plane and line-line is a point and a line respectively. Therefore, the ion quantity produced in the line-cylinder corona discharge is the highest under the same conditions.

If the ion source can be fabricated using micro electrical mechanical system (MEMS) technics, the volume can be reduced significantly. But MEMS technics have some limitations. The classical 3D structure of point-to-plane is hard to realize by bulk silicon process, with the difficulty of fabrication of a smooth cone-shaped tip. Considering the MEMS technics and the electrode structure of corona discharge, line-cylinder electrodes are selected which can be fabricated by deep reactive ion etch (DRIE). DRIE can realize a high aspect ratio of 25:1, and produce a smooth surface with high position accuracy. Thus, a mini line-cylinder ion source with high coaxiality and smooth surface can be achieved. This is helpful to get a stable ionization.

When the electrodes are stuck to glass after being formed by MEMS technics, the surface discharge will follow. Surface discharge is a physical phenomenon which happens in the interface of gas and solid [26]. It is a critical and unstable factor in the ion source. On one hand, because of the asymmetry of voltage distribution, the flashover voltage, the breakdown voltage of the surface discharge, is lower than that of gas discharge under same conditions. It makes the surface discharge always win over gas discharge. On the other hand, as the chemical substances flow into the system, the flashover voltage may change, which is decided by the insulated material characteristic, surface state, structure of electrode, etc. Thus, in order to get a stable ambient ion source, the surface discharge must be prevented.

The design and experimental testing of a negative corona discharge ion source with mini line-cylinder electrodes and a way to prevent surface discharge are proposed in this work. The advantages of the ambient ion source are simplicity of structure, convenience of interface, stability, small volume and compatibility with MEMS process.

II. PRINCIPLES AND DESIGN

A. Principles and design of the ion source

The experimental setup is show in Fig.1. The main elements of the system are gas discharge cell and traction electrode, powered by DC −5-0 kV and DC −0.5-0 kV respectively. The gas discharge cell is made up of the inner electrode and the outer electrode. The inner electrode is a thin stainless steel cylinder with a diameter of 0.16 mm. The outer electrode is a hollow copper cylinder with an inner diameter of 4 mm. For the injection of samples and traction of ions, four slots are opened in the outer electrode with width of 2 mm. In order to drive the ions out of the discharge chamber, a 2 mm wide slot is opened in the polygonal copper traction electrode.

The line-cylinder corona discharge occurs between the inner and outer electrodes. High coaxiality of inner and outer electrodes is the key to get a stable corona discharge ion source. In order to ensure the coaxiality of the electrodes, a special assembly method is used as shown in Fig.1. The system is made up of a piece of bakelite board, two pieces of epoxy resin board, and several aluminum rods. The mechanical deformations of these materials with temperature and humidity are negligible, which is helpful to maintain the precision of the system, especially the repeatability. The three boards are fixed by interference-fitted screws and sleeve gaskets, and the bakelite board is interference-fitted to the outer electrode through a via hole. The diameter of inner electrode is so small, only 0.16 mm, that it is very difficult to drill such a small via hole in the epoxy resin board. Thus, a groove with depth of 0.11 mm in the retaining plate is designed to fix the inner electrode. The groove is processed by WEDM (wire electrical discharge machine). The inner electrode is put into the groove, and then pressed by the pressure plate. The position of

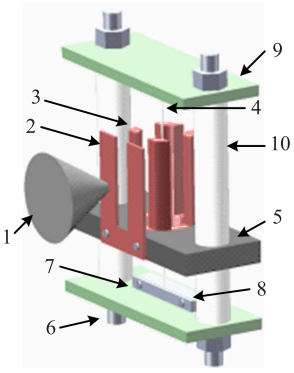

FIG. 1 3D structure schematic of the ion source: 1: MS; 2: Traction electrode; 3: Outer electrode; 4: Inner electrode; 5: Bakelite board; 6: Screw; 7: Pressure plate; 8: Retaining plate; 9: Epoxy resin board; 10: Sleeve gasket.

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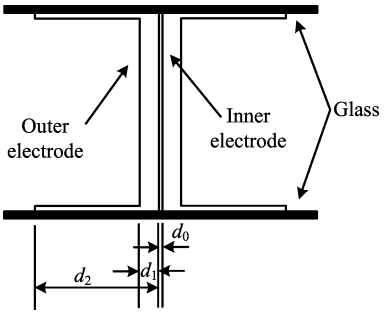

FIG. 2 Improved structure of ion source to prevent surface discharge.

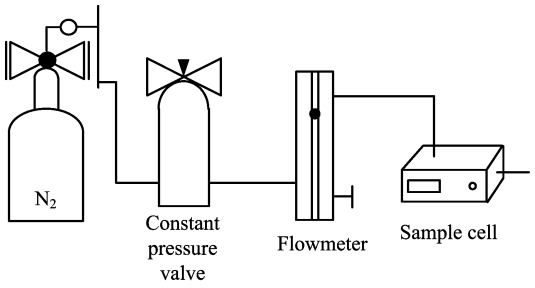

FIG. 3 Injection system of the ion source.

the retaining plate is calculated by the position of outer electrode, and fixed by four interference fitted screws in the epoxy resin board. The traction electrode is fixed in the bakelite board by two interference fitted screws. In this way, the coaxiality of the inner and outer electrode, and the position of the traction electrode can be very accurate.

Because the ion source works under ambient conditions, an ion may have millions of collisions and be annihilated in the process in a very short time. Therefore, ions must be accelerated into the MS to reduce the collision times. Considering the voltage of inner electrode is about –4 kV DC, and the voltage of MS orifice1 is –30 V, the voltages of traction electrode and outer electrode are set at –150 and –200 V respectively.

When the voltage of inner electrode reaches corona onset voltage, the corona discharge initiates, and then substances are ionized. The ions then move towards the outer electrode driven by the electric force. During the process, some ions exude from the slot of the outer electrode, move towards the traction electrode and enter the MS, while others are annihilated.

B. Surface-discharge proof structure

In order to fabricate a MEMS-compatible and surface-discharge proof ion source, the theory of surface discharge is studied. If the relative humidity of the gas is lower than 40%, the influence of moisture on the flashover voltage can be neglected [26]. But if the ion source works under severe ambient conditions, the relative humidity of the gas may exceed 40%, leading to an obvious drop in the flashover voltage. In addition, easily-moistened materials such as chinaware and glass are more vulnerable to such an effect than the hard-moistened materials such as olefin. Under the ambient conditions, the influence of moisture on surface discharge must be considered because the insulating material of the ion source in MEMS structure is an easily-moistened material, glass. If the glass surface is covered by a layer of moist contaminations, the layer turns into a conductor. Furthermore, the water on the surface can be evaporated by the heat of the leakage current, and then some parts of the surface become anhydrous. Due to the change of resistivity, the current intensity becomes non-uniform and the voltage distribution along the surface changes. The voltage on the anhydrous parts is higher than other parts. When it exceeds the breakdown voltage of the gas, surface discharge initiates in the anhydrous parts. The discharge types may be spark, light blue or yellow filamentary discharge, or local arc spanning the anhydrous parts, which are decided by the pollution and humidity level. It is very unstable with random discharge points. If the local arc is created in the anhydrous parts, it can develop into surface flashover throughout the electrodes under proper conditions. This is how the pollution flashover occurs. It is a special kind of surface discharge, with the breakdown voltage lower than that of the gas discharge. The pollution flashover is one of the most unstable factors of ionization.

These factors of surface discharge discussed above exist in the ion source. In order to prevent the surface discharge, an improved structure shown in Fig.2 is proposed. The flashover voltage is proportional to the distance between the electrodes along the surface, while the breakdown voltage of gas discharge is proportional to the interelectrode distance. If d_2 (the radius of bottom surface shown in Fig.2) is sufficiently larger than d_1 (the radius of outer electrode shown in Fig.2), the surface discharge can be prevented. The smaller the contact area of cathode and glass is, the higher the flashover voltage along surface. With a very small d_0 (the radius of inner electrode serving as cathode), the structure of the electrodes inhibits surface discharge. The proper ratio of d_2 to d_1 is determined by many factors such as the property and state of the glass and the structure of the electrode. Considering all the influences, the ratio of d_2 to d_1 is set as 4 to ensure the prevention of the surface discharge. In this design, d_0=0.08 mm, d_1=1 mm and d_2=4 mm.

III. EXPERIMENTS AND DISCUSSION

A. Experiments of the ion source

In order to test the ion source, an injection system shown in Fig.3 is designed to make the chemical sub-

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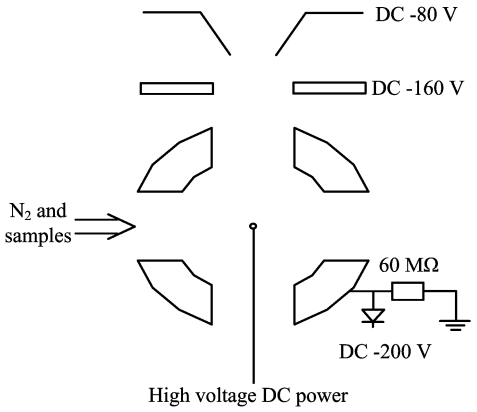

FIG. 4 Electric sketch of the system.

stances flow into the ion source. The injection system is made up of a gas cylinder, a constant pressure valve, a flowmeter and a sample cell. To understand the design, the saturated vapor pressure should be introduced first. It is a property of chemical substance, which describes the vapor pressure on the surface of the chemical substance. It is the function of temperature and can reflect the volatility of the chemical substance. In the sample cell, with an electric heater and a temperature control device, the temperature can be set [27] according to the properties of the chemical substances, which means the concentration is also controlled with the carrier gas N_2. Besides, the heating technique enables the chemical substances to flow into the ion source easily, even if they are difficult to volatile. Thus, the temperature and the carrier gas flow must be regulated for quantitative experiments.

The electric sketch of the MS experiment is shown in Fig.4. The sample of the first experiment is formic acid. When the voltage on the inner electrode reaches –3.8 kV, the corona discharge initiates between the inner and outer electrode. Since the electric field is the highest near the inner electrode, the ionization occurs mainly around this area. Once the negative ions are generated, they move towards the outer electrode due to the effect of the electric field. Some exude from the slot of the outer electrode, move towards the traction electrode, and then enter the MS under the effect of the traction electrode.

The mass spectrogram shown in Fig.5(a) is the formic acid ionization result of the line-cylinder ion source. According to theory of APCI, $[M\text{-}H]^-$ (m/z: 45) is generated during the ionization, making the highest peak shown in Fig.5(a). Another peak (m/z: 46) exceeds 2.2% of that of formic acid ion, which means there are other ions whose m/z is also 46. The peak (m/z: 62) can not be found in experiments of formic acid by commercial ion source of MS.

The other mass spectrogram shown in Fig.5(b) is the ionization result of gas with the sample of acetic acid. The highest peak $[M\text{-}H]^-$ (m/z: 59) is the ionization

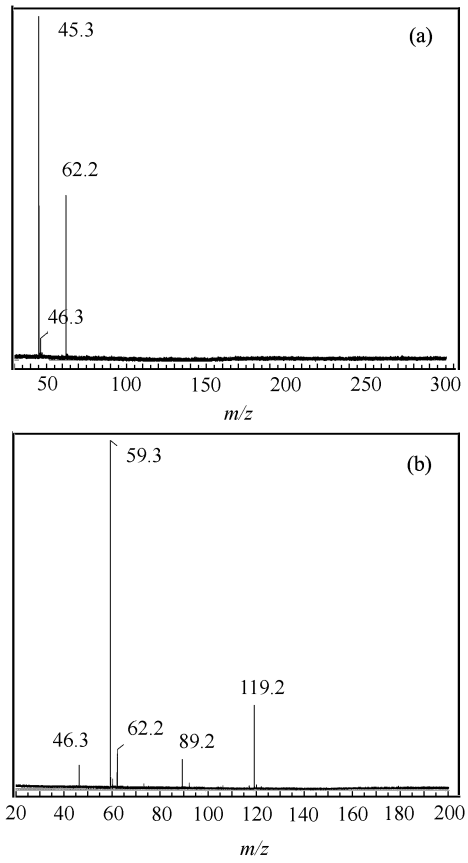

FIG. 5 (a) The mass spectrogram of formic acid. (b) The mass spectrogram of acetic acid.

result of acetic acid. The combination of the molecule M with $[M\text{-}H]^-$ generates the dimer $[M+M\text{-}H]^-$ (m/z: 119), making another peak. The peaks of 46 and 62 also appear in this experiment. According to the results, these peaks may be NO_2^- (m/z: 46) and NO_3^- (m/z: 62) generated by N_2 and O_2 during the gas discharge in the air.

B. The corona onset voltage in the experiments

It is necessary to know the corona onset voltage which is the threshold of ionization. The corona onset voltage of line-cylinder electrodes can be calculated from the following formulas:

$$E_x = V\left(x\ln\frac{R}{r}\right)^{-1} \quad (1)$$

$$(E_r)_s = E_0 m\delta\left(1+\frac{K}{\sqrt{\delta r}}\right) \quad (2)$$

where E_0=3.1 MV/m, m is a constant to describe the surface state of the electrode ($0.6<m<1$). δ is the relative density of air:

$$\delta = \frac{2.94\times10^{-3}P}{273+T} \quad (3)$$

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If P=101.325 kPa, T= 25 °C, then δ=1. K= 3.08×10^{-2} $m^{1/2}$. r and R are the radii of the inner and outer electrode respectively.

The corona onset voltage can be derived from Eqs.(1) and (2),

$$V_s = (E_r)_s r \ln \frac{R}{r} \tag{4}$$

where $(E_r)_s$ is the threshold electric field intensity of the corona discharge, and V_s is the voltage difference of the inner and outer electrodes.

In this experiment, the radii of inner and outer electrodes are 0.08 and 2 mm respectively, m=1 and δ=1. Then the threshold electric field intensity and threshold voltage of the corona discharge are 13.828 MV/m and 3.56 kV respectively, derived from Eqs.(2) and (4). Normally, the voltage of the outer electrode is set to zero. Because –200 V is applied to the outer electrode to drive ions into MS in the experiments, the corona discharge will initiate when the voltage of the inner electrode reaches –3.76 kV according to the calculation result. In the experiments, when the voltage of the inner electrode reached –3.8 kV, ions were detected by MS, which matches the calculated value perfectly.

C. Experiment of the surface discharge

In order to test whether the improved structure can prevent surface discharge, an experiment was designed. A photograph of the experiment apparatus is shown in Fig.6(a). The outer electrode is stuck to the glass by hot sol, and the inner electrode is stuck by super glue. The hot sol is a viscous liquid after heating, and solidifies quickly when the temperature goes down, which keeps the gap between the electrode and the glass clear. The organic glass cylinder shown in the Fig.6(a) makes the outer electrode and inner electrode coaxial. The electric sketch of the experiment is shown in Fig.6(b). In the experiment, the discharge point should be examined carefully. If the discharge point is along the surface, it means surface discharge happens. Otherwise, the surface discharge is prevented. In order to observe the discharge point, a higher voltage is given to stimulate light-emission. In other words, whether the surface discharge occurs is judged by the observation of light-emitting points. If they are not along the surface, then the surface discharge is prevented. When the voltage of the inner electrode reaches –2.8 kV, a streamer corona is developed, which can be judged from the discharge voltage waveform shown in Fig.6(c). Blue-violet light can be observed only between the inner and outer electrodes but not along the glass. This means the structure with d_2=4d_1 can prevent surface discharge while initiating stable corona discharge.

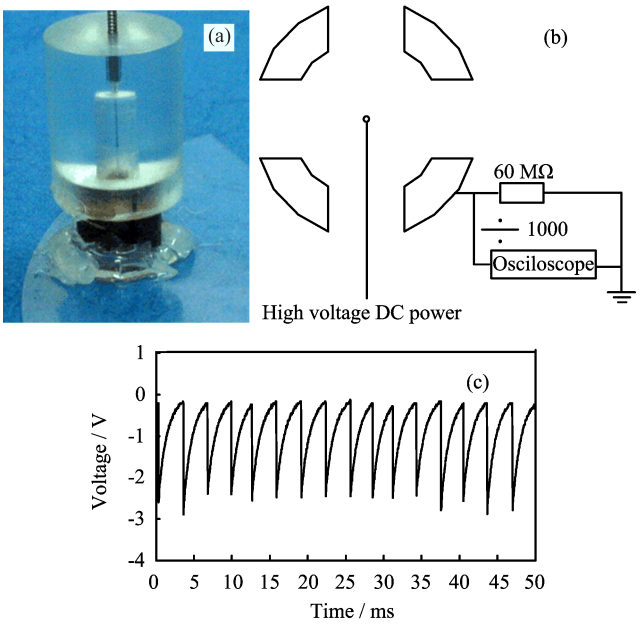

FIG. 6 (a) Photo of the improved electrodes; (b) Electric sketch of the experiment; (c) Discharge waveform.

IV. CONCLUSION

A negative corona discharge ion source with mini line-cylinder electrode was developed. Experiments show that formic acid and acetic acid are ionized and driven into MS under ambient conditions. But, there are some confusing peaks in the mass spectrogram. They may be NO_2^- and NO_3^- generated by N_2 and O_2 during the gas discharge in the air. For confirmation, further research will be done. However, these peaks do not affect the analysis of chemical substances. The ion source can be used in detection of drugs, explosives, and environmental contamination. In order to reduce the volume and fabricate a hand-held instrument, a MEMS technic is introduced, but the result has a surface discharge problem. An improved structure with d_2=4d_1 is put forward to solve the problem. In experiments on the surface discharge, blue-phosphor light can be observed only between the inner and outer electrode, not along the glass, which means the surface discharge is prevented in the improved structure. The simplicity of the interface of the ion source makes it suitable for MS, MMS (micro MS), IMS, and FAIMS applications. It can be used as a foundation for hand-held instruments for rapid detection in complicated environments such as airport, customs and battlefield.

V. ACKNOWLEDGMENTS

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[1] E. V. Krylov, Tech. Phys. **45**, 1496 (2000).
[2] B. L. Chua, Z. Li, D. T. McCormick, W. P. Shih, N. C. Tien, A. S. Wexler, D. A. Niemeier, and B. Holmen, *17th IEEE International Conference on MEMS*, Netherlands: Maastricht, 261 (2004).
[3] T. Khayamian, M. Tabrizchi, and M. T. Jafari, Talanta. **69**, 795 (2006).
[4] N. Na, M. X. Zhao, S. C. Zhang, C. D. Yang, and X. R. Zhang, J. Mass. Spec. **18**, 1859 (2007).
[5] C. Ismael, T. Zoltan, T. Nari, H. W. Chen, and C. R. Graham, Anal. Chem. **77**, 6755 (2005).
[6] R. G. Lonwigtz, Ph.D. Dissertation, Switzerland: Swiss Federal Institute of Technology, Lausanne (2004).
[7] R. G. Longwitz, H. V. Lintel, and P. Renaud, J. Vac. Sci. Technol. B **21**, 1570 (2003).
[8] H. H. Hill and G. Simpson, Field Anal. Chem. Technol. **1**, 119 (1997).
[9] H. H. Hill, W. F. Siems, R. H. Louis, and D. G. St. McMinn, Anal. Chem. **62**, 1201 (1990).
[10] H. Borsdorf, E. G. Nazarov, and G. A. Eiceman, J. Am. Soc. Mass. Spectrom. **13**, 1078 (2002).
[11] M. A. Baim, R. L. Eatherton, and H. H. Hill, Anal. Chem. **55**, 1761 (1983).
[12] C. S. Leasure, M. E. Fleischer, G. K. Anderson, and G. A. Eiceman, Anal. Chem. **58**, 2142 (1986).
[13] D. M. Lubman and M. N. Kronick, Anal. Chem. **54**, 1546 (1982).
[14] E. G. Nazarov, R. A. Miller, G. A. Eiceman, and J. A. Stone Anal. Chem. **78**, 4553 (2006).
[15] M. Tabrizchi, T. Khayamian, and N. Taj, Rev. Sci. Instr. **71**, 2321 (2000).
[16] I. M. Lazar, M. L. Lee, and E. D. Lee, Anal. Chem. **68**, 1924 (1996).
[17] T. Khayamian, M. Tabrizchi, N. Taj, and J. Fresenius, Anal. Chem. **370**, 1114 (2001).
[18] M. Tabrizchi and A. Abedi, Int. J. Mass Spectrom. **218**, 75 (2002).
[19] T. Khayamian, M. Tabrizchi, and M. T. Jafari, Talanta **59**, 327 (2003).
[20] H. Borsdorf, E. G. Nazarov, and R. A. Miller, Anal. Chim. Acta **575**, 76 (2006).
[21] M. Tabrizchia and F. Rouholahnejad, Rev. Sci. Instrum **75**, 4656 (2004).
[22] M. T. Jafari, T. Khayamian, V. Shaer, and N. Zarei, Anal. Chim. Acta **581**, 147 (2007).
[23] X. J. Xu and D. C. Chu, *Gas discharge physics*, *1st edn.*, Shanghai: Fudan Press, 243 (1996).
[24] Z. Q. Hu, H. S. Zhen, and Y. N. Shi, *Gas Electronics 1st Edn.*, Shanghai: Electronic Industry Press, 124 (1985).
[25] J. S Chang, F. Pontiga, P. Atten, and A. Castellanos, *3rd Industry Applications Society Annual Meeting*, Toronto, Can, 1887 (1993).
[26] X. D. Liang, Y. C. Chen, and Y. X. Zhou, *High Voltage Engineering*, 1st Edn., Beijing: Tsinghua Press, (2003).
[27] J. P. Davies, S. G. Davis, L. D. Goodrich, and R. A. Larson, Anal. Chem. **65**, 3004 (1993).

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