===== **ARTICLES** =====

Investigation of Electrospray Stability with Dynamic Liquid Flow Splitter

A. N. Arseniev, N. V. Krasnov, and M. Z. Muradymov

Institute for Analytical Instrumentation, Russian Academy of Sciences, Rizhskii pr. 26, St. Petersburg, 190103 Russia,
E-mail: krasnov@alpha-ms.com
Received @@

Abstract—The article gives the results of research of electrospray stability with the use of a dynamic splitting of a flow in the spray area under normal conditions. An acidified water—acetonitrile solution (1 : 1) was used as an eluant. Experimental results for the used configuration of electrospray junction with a coaxial selection of fluid excess as a steam—gas mixture taken out of the dispersion area (meniscus fluid on the butt-end of a capillary) in the compass of a fluid flow along the capillary from 50 up to 200 µL/min showed more stable relation of an atomized solution flow in comparison with a mode without use of a dynamic splitting of an atomized fluid flow.

Keywords: liquid electrospray, dynamic splitting of fluid flow, eluate

INTRODUCTION

Since the development of an atmospheric pressure electrospray ionization method for the mass-spectrometric analysis of the solutions of labile substances [1, 2], it became obvious that the stability of the electrospray process, in particular, at test solution flow rates of about 50–500 µL/min characteristic of HPLC, is a problem of considerable current interest. At a solution flow rate of several tens of microliters per minute (with the forced pumping of liquid by a pump), the electrospray process becomes unstable due to a disagreement between the supplied and sprayed liquid volumes. An increase in the electric field intensity in the region of spraying does not lead to an agreement between flows, but it only changes the structure and shape of a meniscus and a jet (torch) of sprayed solution. The single-jet axial spraying mode is changed to the multijet mode and then to the single-jet spraying at an angle of about 60° to the capillary axis with its circular rotation. In this case, the amount of ions obtained upon this spraying becomes vanishingly small and undetectable after the nozzle (diaphragm) at first stage of the differential evacuation of the electro-gas-dynamic interface of a mass spectrometer.

Several types of electrospray units have been currently developed and introduced into the analytical practice in order to solve the problem of stabilizing the spraying process. The Agilent ion source [3], in which cold spray gas and hot desolvation gas flows in the direction of spraying and the heating of the desolvation region between the sprayer and the nozzle are used, is a recent modification.

For solving the problem of the adjustment of liquid flows supplied to the electrospray region and for spray analysis, Samokish et al. [4] proposed a flow chart for arranging supplied and sprayed liquids and removing unsprayed liquid residues from the meniscus (spray) region with the aid of a gas counterflow arranged at the capillary end. They also demonstrated the mobility spectra and the mass spectra of a solution of reserpine with the use of the dynamic split mode in the spray process. After the demonstration of the possibility of the dynamic splitting of a liquid flow to be sprayed, the question arises of whether spraying in this configuration is stable. This work was dedicated to an experimental study of the stability of electrospray with the dynamic splitting of a fluid flow at different solution supply flow rates.

EXPERIMENTAL

The stability of the electrospray of analyzed liquid with the use of dynamic flow split was experimentally studied using a setup schematically shown in Fig. 1. The eluant flow rate was adjusted with a MAI 70-2208 single-plunger micropump (Harvard Apparatus) in a range from 50 to 200 µL/min; the air evacuation rate was 0–5.5 L/min with the use of a Thomas G12/045 air pump (with a desiccant) powered with an adjustable direct current source of 0–12 V. The spray voltage between a stainless steel capillary and a counter electrode was supplied from a Stanford Research Systems PS350 high-voltage source of 0–5000 V. The spray current passed through the counter electrode was measured with an electrometric amplifier with a mea-
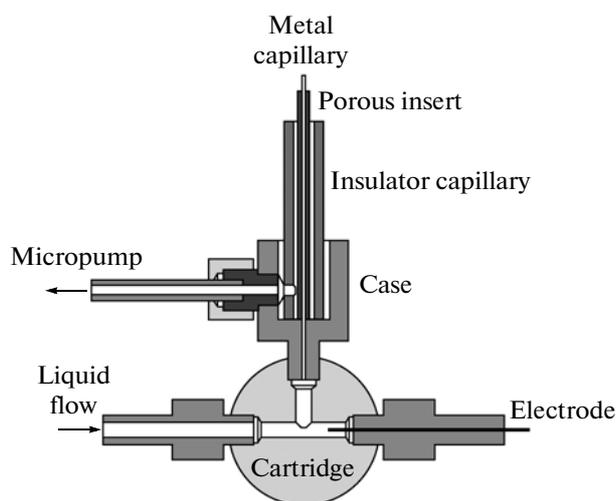
Fig. 1. Schematic diagram of the setup with the dynamic splitting of a liquid flow.

Fig. 2. The time dependence of the current of solution spraying at the flow rate of the sprayed solution of 50 μL/min and a counter-electrode voltage of 4700 V with dynamic splitting produced by an air micropump with a pumping rate of 1.5 L/min.

Fig. 3. The time dependence of the current of solution spraying at the flow rate of the sprayed solution of 100 μL/min and a counter-electrode voltage of 4700 V with dynamic splitting produced by an air micropump with a pumping rate of 1.5 L/min.

Fig. 4. The time dependence of the current of solution spraying at the flow rate of the sprayed solution of 200 μL/min and a counter-electrode voltage of 4000 V with dynamic splitting produced by an air micropump with a pumping rate of 2.0 L/min.

suring resistor resistance of 10^7 Ω. The amplifier output voltage was measured with an Agilent 34401A multimeter connected to a computer; the data were recorded using the Excel software. The rate of measurements was 3 measurements per second. A microscope was used for the visual observation of a meniscus and spray torch.

A water–acetonitrile solution (1 : 1) acidified with a 0.1% solution of acetic acid was used as an eluant, which meets the requirements imposed on eluants used in HPLC with electrospray ionization.

It was experimentally found that, with the use of a spraying unit whose configuration was given in Fig. 1 in [4], the effective sampling of the resulting excess of solution from the meniscus of liquid at the end of a metallic capillary on its outer side occurred at an air flow rate of 1–2.5 L/min under normal conditions. At lower airflow rates, the excess liquid was taken incompletely from the spray region, and unsteady-state conditions appeared with the periodic formation of large drops, which were responsible for the instability of the current dependence and distortions in the spectra of ionic mobility [4]. Another disturbance in the process of spraying—the almost complete disappearance of the meniscus of liquid at the capillary end and the absence of spraying—occurred at too high airflow rates.

RESULTS AND DISCUSSION

Figures 2–5 show the time dependence of the spray current of solution at different liquid space velocities and air pumping rates with dynamic splitting and in the splitless mode (without pumping air from the spray region).

The results of the measurements of the time dependence of the current of sprayed solution under normal conditions clearly indicate that the use of the dynamic
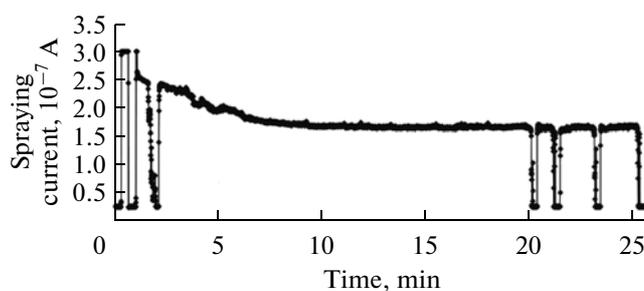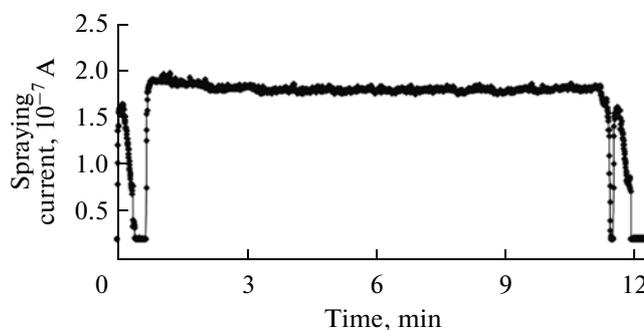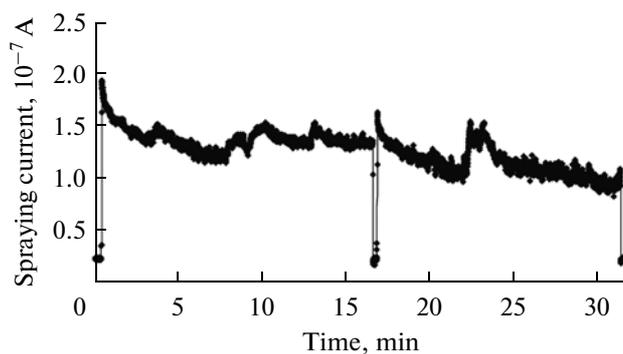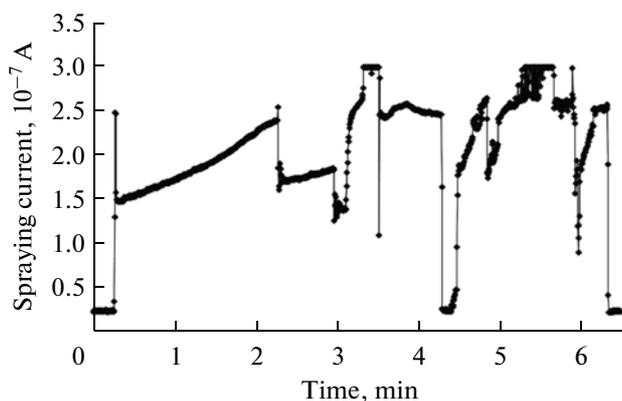
Fig. 5. The time dependence of the current of solution spraying at the flow rate of the sprayed solution of 50 μL/min and a counter-electrode voltage of 4000 V without dynamic splitting; air was not pumped by a micropump at the capillary end.

splitting of a sprayed liquid flow makes it possible to obtain a more stable spray (Figs. 2–4) than that in the splitless mode (Fig. 5). The most stable spray for the used geometry of a spraying unit was obtained under conditions when the solution flow rate was 100 μL/min, the counter-electrode voltage was 4700 V, and the air-flow rate was 1.5 L/min for the used spraying unit geometry. It is likely that this regime was most consistent in terms of a ratio between the flow rates of removed and sprayed liquid. Furthermore, note that this regime is suitable for the implementation of time-of-flight HPLC/MS in the electrospray ionization mode.

The experimental results (Fig. 4) obtained at a liquid flow rate of 200 μL/min are completely acceptable, especially, in comparison with the results obtained using the splitless mode at a liquid flow rate of 50 μL/min (Fig. 5), where the stable electrospray was observed only in the very narrow time domains. This was caused by the accumulation of excess liquid in the meniscus, a change in its shape, and, as a consequence of this, the stripping of large drops from its apex.

of dispersion without the application of dynamic division of fluid flow in 1 min^{-1} about it is possible to speak

CONCLUSIONS

The experimental results on the study of the stability of electrospray, and, correspondingly, the stability of ion current with the dynamic splitting of the analyzed solution make possible to consider a new stage in the development of electrospray ionization, which has been actively applied for longer than 25 years.

ACKNOWLEDGMENTS

REFERENCES

1. Aleksandrov, M.L., Gall', L.N., Krasnov, N.V., Nikolaev, V.I., Pavlenko, V.A., and Shkurov, V.A., *Dokl.* 1 *Akad. Nauk SSSR*, 1984, vol. 277, no. 2, p. 379.

2. Yamashita, M. and Fenn, J.B., *J. Phys. Chem.*, 1984, vol. 88, no. 20, p. 4451.

3. http://www.agilent.com. Accessed October, 18, 2013.

4. Samokish, V.A., Krasnov, N.V., and Muradymov, M.Z., *Rapid Commun. Mass Spectrom.*, 2013, vol. 27, no. 8, p. 904.

Translated by V. Makhlyarchuk

SPELL: 1. Shkurov