ISSN 1063-7850, Technical Physics Letters, 2012, Vol. 38, No. 5, pp. 463–465. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © S.V. Bulovich, A.N. Bazhenov, N.R. Gall, 2012, published in Pis'ma v Zhurnal Tekhnicheskoi Fiziki, 2012, Vol. 38, No. 10, pp. 28–34.

Character of Jet Flows in Mass-Spectrometric Interfaces at Various Pressures and Chamber Lengths

S. V. Bulovich, A. N. Bazhenov, and N. R. Gall*

St. Petersburg State Polytechnical University, St. Petersburg, 195251 Russia
Research Institute for Geology and Mineral Resources of the World Ocean (VNIIOkeangeologiya), St. Petersburg, 190121 Russia
Ioffe Physical Technical Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia
**e-mail: gall@ms.ioffe.ru*

Received 2011

Abstract—Samples—in particular, of bioorganic matter—are usually introduced into a mass spectrometer from atmosphere to high vacuum via a gasdynamic interface that represents a chamber with intermediate pressure or a system of chambers with gradually decreasing pressure. Transformation of the character of an expanding jet flow in a single-chamber interface has been studied as dependent on the chamber length and pressure. Knowledge of this character allows the system parameters to be most effectively used so as to ensure high ion transmission and decrease mass discrimination.

DOI: 10.1134/S1063785012050203

Modern research in biology and biochemistry widely employs mass spectrometry with an ionization technique based on electrospraying liquid samples at atmospheric pressure followed by ion extraction to high vacuum via a gasdynamic interface [1]. Therefore, effort devoted to increasing the sensitivity, precision, and reproducibility of this method is very important. The Nobel Prize in Chemistry 2003 was awarded to the American scientist John B. Fenn for developing the electrospray ionization technique for mass spectrometry. Deeper insight into the character of gas flow at intermediate pressures in the interface chamber provides a basis for the optimum control of ion flows in this region. According to data of the American Society for Mass Spectrometry [2], the number of scientific publications devoted to processes in gasdynamic interfaces exceeded 4000 in the past five years and more than 120 patents were given.

This Letter presents the results of precise numerical calculations that reveal a sharp change in the character of jet flows depending on the interface length and pressure in this chamber. These parameters, especially the latter, belong to the set of instrument design and adjustment parameters. The knowledge of how pressure variations affect the character of ion flows is important for developing and implementing a justified approach to the tuning algorithm and operation of an electrospray-ionization mass spectrometer.

Figure 1 shows a schematic diagram of the model gasdynamic interface representing a classical system of the Kantorowicz–Gray type [3]. A real interface typically also accommodates ion focusing and transporting electrodes, but in this analysis their presence is ignored. Electrode *4* that drives ions to skimmer *2* is only considered as a solid obstacle for the gas flow.

As a rule, a gasdynamic interface operates in a pressure interval of 200–1000 Pa, while ions are introduced via nozzle *1* together with a gas flow from a region with atmospheric pressure P_0. The nozzle can be either very short (diaphragm) or long (capillary), but this circumstance is insignificant in the framework of the present investigation. The nozzle diameter (caliber) D is a natural measure for the chamber length L and all other dimensions of the system. The chamber

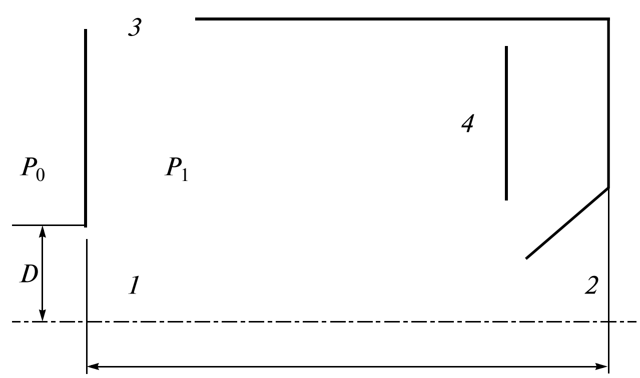

Fig. 1. Schematic diagram of the model gasdynamic interface for an electrospray-ionization mass spectrometer: (*1*) input hole (nozzle), (*2*) output hole (skimmer), (*3*) pumping hole, (*4*) ion focusing diaphragm (wall), (P_0) region of atmospheric pressure, (P_1) static pressure in the interface chamber, (D) input hole diameter, and (L) interface length.

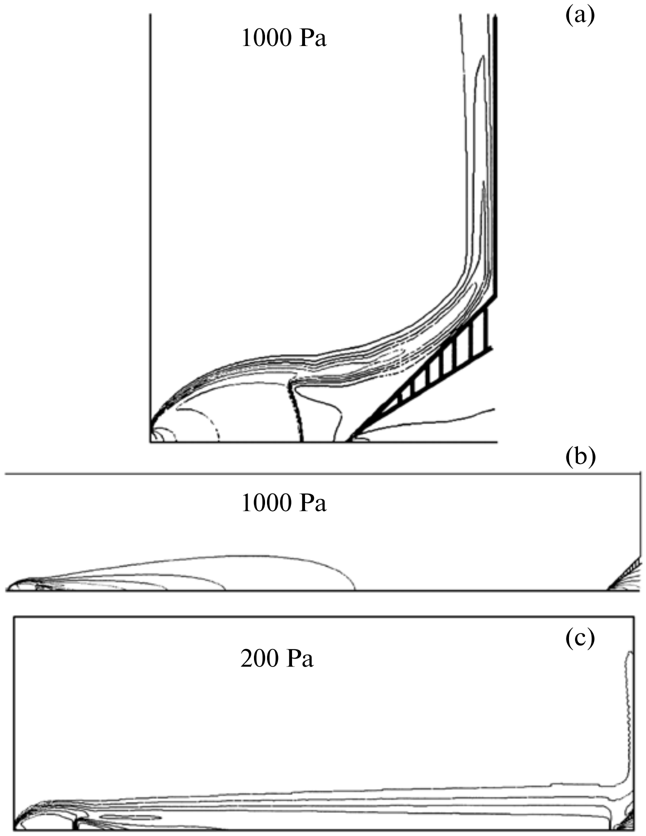

Fig. 2. Calculated patterns of jet flow velocity distribution in gasdynamic interfaces: (a) $L = 7$ mm, $P = 1000$ Pa; (b) $L = 40$ mm, $P = 1000$ Pa; and (c) $L = 40$ mm, $P = 200$ Pa. Velocity isolines are drawn at an interval of 100 m/s.

size in the transverse direction is almost always much greater than its length.

The gas that enters the interface via nozzle *1* is pumped out via hole *3* by a backing pump and partly passes to the next (typically high-vacuum) chamber via hole (skimmer) *2*. Since the skimmer diameter is usually much smaller than that of pumping hole *3*, the gas flux via the skimmer amounts to only a small fraction of the input flux. The term "skimmer" has a definite historical origin and implies cutting of a jet by a sharp edge of an obstacle, although this does not always take place in modern instruments.

Due to a large difference of pressures between the atmosphere and interface, the gas entering via nozzle *1* into the interface chamber forms a characteristic system of shock waves, compression shocks, and both super- and subsonic jet streams [4]. Calculations have been performed in an axisymmetric approximation using the ANSYS FLUENT program package. Details of the computation and verification procedures are described elsewhere [5, 6].

Figure 2 shows three different possible patterns of gas flow in the gasdynamic interface. Figure 2a corresponds to flows in a conditionally "short" chamber with $L = 7$ mm (i.e., 14 nozzle calibers). Figures 2b and 2c correspond to the spatial distribution of flows in a conditionally "long" chamber with $L = 40$ mm (80 nozzle calibers) at different pressures.

Let us analyze changes that take place in the structure of gas flows upon separate variation of one of the key parameters: chamber length and background pressure. First, consider the effect of the chamber length. Figures 2a and 2b compare the gas flow in cases of conditionally "short" and "very long" chambers (these terms will be defined below). In the short chamber, the main effect on the gas flow structure is produced by a rear wall that consists of a skimmer and ion focusing electrode, acting as a solid obstacle to the flowing gas. Immediately behind the nozzle, a Mach barrel is formed with a length (h) approximately given by the following classical formula:

$$h = \frac{2}{3}D(P_0/P_1)^{1/2}$$

(in terms of Fig. 1), which corresponds to ~3 mm in the case under consideration. Past the compression shock, the jet is accelerated and rotated by 90°, after which the main flow passes along the ion focusing electrode and forms vortices of various scales. The flow has an essentially unsteady character, whereby the gas accumulates in front of the obstacle (skimmer) and then the pressure is reset. The nature of observed oscillations in the pressure, temperature, and position of the compression shock, as well as the frequency and amplitude of these oscillations, have been recently determined and described in [6, 7].

In the case of a long chamber (Figs. 2b and 2c), the obstacle is far from the nozzle and does not influence the main flow structure. The gas efflux from the atmosphere via the nozzle into the interface is accompanied by the formation of a classical Mach structure, subsequent acceleration of the jet, and its deceleration as a result of the diffusion smearing and gas leak to the periphery. The gas flow has a laminar character, which is especially pronounced at a pressure of 200 Pa. The longer the chamber, the closer the flow to a free regime and the higher the self-similar character of this flow. A self-similar flow is characterized by a decrease in the jet flow velocity according to a power law that depends on the flow mode: x^{-1} for turbulent jets and $x^{-1/3}$ for laminar jets, where x is the distance from the "source" to the current point downstream.

It can probably be expected that, in chambers of intermediate lengths, a regime is possible in which there are already no oscillations caused by flow reflection from the rear wall, while the chamber is still not long enough to ensure the development of a self-similar flow.

In the case of long chambers, the flow is laminar over most of its length, but turbulence still arises about 40 calibers downstream from the nozzle output. This turbulence takes place over a region of about

10–15 calibers long and is characterized by a turbulent viscosity coefficient that reaches 20 at the maximum.

Now let us consider the effect of pressure on the gas flow in long chambers by comparing the flow patterns presented in Figs. 2b and 2c. As can be seen, the main features of the flow structure are retained, with the Mach barrel formed immediately behind the nozzle, followed by the self-similar flow region and gas spreading along the rear wall. On the other hand, characteristics of the flow at 200 Pa differ rather significantly from those at 1000 Pa: (i) the Mach barrel length and width are about five times greater, (ii) the jet is broad and weakly divergent, and (iii) the jet remains laminar over the entire length.

The situation described above is a partial case of transformation of the pattern of jet flows depending on the background pressure in the interface chamber. As the pressure is increased, the region of supersonic flow decreases and the tendency toward self-similar retardation increases, which corresponds to an increase in the effective length of the interface. On the contrary, a decrease in the pressure leads to an increase in the transverse size of the jet, while the region of self-similarity decreases. This is equivalent to an effective reduction in the chamber length. In addition, decreasing pressure leads to an increase in the role of diffusion and a decrease in the level of turbulence of the flow.

Thus, in choosing the interface geometry and selecting the working pressure, one should take into account the following trends. An increase in the chamber length and background pressure leads to a more predictable character of the jet flow that is close to the self-similar mode. The jet is rather narrow behind the nozzle and exhibits rapid expansion. A decrease in the background pressure leads to an increase in the initial jet width at a relatively lower expansion. In a very short interface with a length comparable to that of the Mach barrel, the flow is substantially unsteady and the mass transfer becomes perpendicular to the initial flow direction almost immediately behind the compression jump. This behavior should be taken into account in adjusting pressure in the presence of ion-focusing electrodes in interfaces [8].

Acknowledgments. The authors are grateful to Shimadzu Co. (Japan) for support of this investigation.

REFERENCES

1. J. B. Fenn, V. V. Mann, C. K. Meng, S. F. Wong, and C. M. Whitehouse, Science **246**, 64 (1989).
2. www.asms.org/whaisms/p16.html.
3. M. Yamashita and J. B. Fenn, J. Chem. Phys. **88** (20), 4451 (1984).
4. A. Entwistle, A. Andreyeva, S. Bulovich, M. Lapushkin, A. Bazhenov, R. Giles, and N. Gall, *Abstracts of Papers. Conf. of American Society for Mass Spectrometry (ASMS-2011, June 2–6, Denver, USA)*, p. 1633.
5. S. V. Bulovich, V. E. Vikolainen, and R. L. Petrov, Tech. Phys. Lett. **33**, 1025 (2007).
6. S. V. Bulovich, A. N. Bazhenov, and R. L. Petrov, Tech. Phys. **54**, 1814 (2009).
7. A. N. Bazhenov, S. V. Bulovich, L. N. Gall', and N. R. Gall', Mass-Spektrometriya **8** (1), 27 (2011).
8. R. T. Kelly, A. V. Tolmachev, J. S. Page, K. Tang, and R. D. Smith, Mass Spectrom. Rev. **28**, 56 (2009).

Translated by P. Pozdeev