Talanta 85 (2011) 1792–1797

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Atmospheric pressure ion focusing with a vortex stream

Yuri N. Kolomiets*, Viktor V. Pervukhin

Nikolaev Institute of Inorganic Chemistry of SB RAS, Acad. Lavrentieva ave., 3, 630090 Novosibirsk, Russia

ARTICLE INFO

Article history:
Received 24 December 2010
Accepted 5 July 2011
Available online 12 July 2011

Keywords:
Remote ion sampling
Whirled sampling stream
Atmospheric pressure ion focusing

ABSTRACT

For successful operation of ionization analysis techniques an efficient sampling and sample ion transportation into an analytical path are required. This is of particular importance for atmospheric pressure ionization sources like corona discharge, electrospray, MALDI, ionization with radioactive isotopes (^{3}H, ^{63}Ni) that produce nonuniform spatial distribution of sample ions. The available methods of sample ion focusing with electric fields are either efficient at reduced pressure (to 1 Torr) or feature high sample losses. In this paper we suggest to use a highly whirled gas stream for atmospheric pressure ion focusing. We use a ^{63}Ni radioactive source to produce an ionized bipolar sample at atmospheric pressure. It is shown by experiments that compared to an aspiration method a forced highly whirled vortex stream allows one to enhance the efficiency of remote ionized sample collection at distances equal to the vortex sampler diameter by an order of magnitude. With a vortex stream, a sixfold increase in the efficiency of the radial ionized sample collection has been obtained. It may be deduced that with the vortex stream remote sampling obtains a new feature which is characterized by a considerable enhancement of the efficiency of the ionized sample collection and can be called as a “gas-dynamic” ionized sample focusing. Considered is the effect of recombination losses of the ionized sample during the remote sampling thereof with the vortex sampler. Prospects for a practical implementation of the vortex sampler for solving the problems of the customs control over the smuggling of radioactive α and β sources are made based on the research results.

1. Introduction

Sensitivity of ionization analysis methods is much dependent on the efficiency of sampling and sample ion transportation into the analytical path of the analyzers. This is of particular importance for atmospheric pressure ionization sources like corona discharge, electrospray, MALDI, ionization with radioactive isotopes (^{3}H, ^{63}Ni) that produce nonuniform spatial distribution of sample ions. To focus ions and inject them into a mass-spectrometer with electrospray ionization, Shaffer et al. [1–3], Kim et al. [4], Belov et al. [5] used a system of electrodes as a cone to which a combination of high frequency (700 kHz) and static electric fields was applied. This system has shown its efficiency at low pressures (to 1 Torr) allowing to increase an ion signal by an order of magnitude and even more. Colburn et al. [6] successfully used a set of circular electrodes to which a high frequency wave (500 kHz) with a constant phase shift was applied. In these systems gas flow at pressures to 1 Torr did not pay a great part and electric field made a major contribution to the ion focusing and transportation. At pressures close and equal to atmospheric one gas flows become an important factor and should be considered in the processes of ion focusing and transportation. Thus, Guevremont et al. [7,8], Barnett et al. [9] used a gas flow to transport sample ions from the source to the analyzer at atmospheric pressure and a combination of high frequency (180–200 kHz) and constant electric fields transverse to the gas flow to focus ions during transportation. Therewith, a periodic alternating waveform field with a gradient directed along the force field lines was required for ion focusing. This method allows one to reduce ion losses by an order of magnitude and even more, but it can be realized only when an ion channel is made inside the system of electrodes producing a nonuniform electric field. Laiko et al. [10] and Tan et al. [11] suggested another way to increase an amount of ions entering the analyzer. They introduced an additional electrode near the ionization source creating a sweeping field between the source and the inlet of the mass-spectrometer. This allowed an increase in the signal from the sample ions, but the ion losses grew therewith. Kremer et al. [12] suggested to use a conical lens formed by circular electrodes with floating potential for atmospheric pressure ion collimation. Compared to normal sweeping potential, sample ion losses in such a system reduced considerably, and a degree of focusing increased. But a definite time during which considerable sample losses are inevitable is required for an electrostatic lens with floating potential to arrive at operating potential. Besides, such a system can operate with unipolar ion sources like corona discharge, electrospray, etc.

---

* Corresponding author. Fax: +7 383 330 94 89.
E-mail addresses: ykolom@niic.nsc.ru, ykolom@ngs.ru (Y.N. Kolomiets).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.07.005

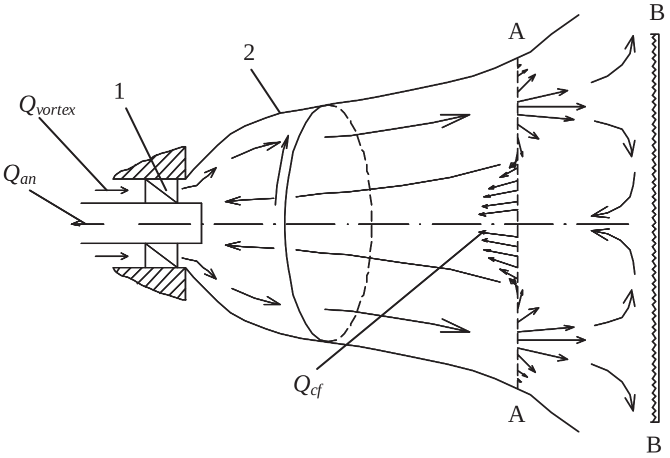

Fig. 1. Ion sampling with a highly whirled stream. 1, swirler; 2, stream boundary; Q_{vortex}, vortex flow; Q_{cf}, counter-flow; Q_{an}, analytical flow.

Fig. 2. The process of a gas dynamic focusing of alcohol vapors by a vortex sampler.

In this paper we propose to use a highly whirled air stream for atmospheric pressure ion focusing. It is suggested to focus ions with specially configured gas flows instead of electric fields as it is in the known methods. The structure of a vortex flow itself serves as prerequisite for this. When the whirl intensity of stream is high, static pressure through the stream volume is below atmospheric one and close to the axis a counter-flow is produced [13]. Sampling procedure involves blowing an object with a vortex flow, so that the entire object or a part of it turns to be in the counter-flow region. Impurity vapors sampled from the surface or forced from the inside of the object by a reduced whirled stream pressure are trapped by the counter-flow and transported to the stream head where an inlet gas analyzer nozzle is positioned. Fig. 1 gives a schematic representation of sampling from the surface. Flow Q_{vortex} passing through swirler 1 produces a highly whirled stream towards the surface B–B with boundaries specified by 2. Arrows at section A–A show the flow velocity distribution equal to a sum of axial and radial components ($V = V_c + V_r$, where V_c is the axial flow velocity, V_r is the radial flow velocity). As Rashidov and Sakaev [14] have proved, the radial component of the flow velocity through the counter-flow region is directed towards the stream axis. Impurity vapors during their motion in the counter-flow are transported towards the axis by the radial flow velocity that is their focusing takes place. We suggest that gas-dynamic ionized sample focusing can be conducted in the same way.

Unlike focusing with electric fields, gas-dynamic focusing with a vortex flow can proceed both with unipolar ionization sources and radioactive ones producing positive as well as negative ions, which expands a field of application for these systems. The use of the vortex flow for ion focusing is unknown in the world practice. At present there are only the simplest models of portable vortex samplers developed for drift spectrometric (MO-2 (“SIBEL”, Russia), Pilot-M (“LAVANDA-U”, Russia)) and gas chromatographic (ECHO-M, ECHO-EW (“MULTICHROM”, Russia)) analyzers. These devices are used to concentrate and deliver neutral sample from an object to an analyzer. In Refs. [15,16] we covered the problems of remote diethylanyline vapor sampling for a mass-spectrometer with atmospheric pressure ionization in tandem with an ion mobility increment spectrometer. Two sampler models with a different stream structure were considered. A sampling stream in model I represents a forced vortex (angular stream velocity is radius independent). The sampling stream in model II represents a composite vortex (near the axis is a vortex nucleus surrounded by a free vortex which angular velocity is inversely related to squared radius). Both models have shown their ability to remove neutral sample from an object and transport it to an analyzer having collected (focused) it towards the axis. An experiment performed with ethyl alcohol vapors cooled by liquid nitrogen clearly demonstrates the process of a gas dynamic focusing of uncharged sample. We injected alcohol vapors into a Dewar’s flask half filled with liquid nitrogen, and covered the flask with a cover provided with two slots 5 mm in width spaced at 50 mm apart. With a vortex sampler with a reflector diameter of 100 mm we sampled aerosol produced by the alcohol vapors at a distance of 50 mm. For the vortex flow visualization we illuminated the flow with a light beam transversely to the sampler axis. Fig. 2 gives a picture of the sampling process. It is clearly seen from the picture that alcohol aerosol drawn from the slots focuses on the sampler axis producing a cone.

A possibility to focus an ionized sample with a highly whirled stream as a forced vortex is studied experimentally in this paper. A ^{63}Ni radioactive source was used as an ionization source. We registered ions with an electrometric amplifier on a collector positioned in the analytical channel. To determine the efficiency of ion collimation and transportation we studied the relationship between the registered signal and the variation in the position between the source and the swirler both in axial and radial directions.

2. Experimental

To conduct an experiment we used a vortex sampler like the one described in Ref. [16] producing a sampling stream as a forced vortex. Table 1 gives the sampler parameters. Fig. 3 gives a scheme of the experiment. Vortex forming flow Q_{vortex} is fed by a centrifugal pump (not shown) to fixed impeller (1) with an angle of blade of 45° and creates a fan vortex stream that spreads over the inside surface of reflector (2) producing a volumetric whirled stream with an axial counter-flow. The boundaries of direct and counter flows are given by solid (3) and dashed (4) lines.

For an object we used metal screen (5) 18 cm × 25 cm in size in the centre of which a ^{63}Ni source (Izotop, Saint-Petersburg, Russia) with an activity of 10 mCi (6) was positioned. The source represented a cylinder 10 mm in diameter closed from the sampler with a cover with an opening 2 mm in diameter. Laboratory air (temperature, 20–23 °C, relative humidity, 40–60%) was subject to

Table 1
Main parameters of a vortex sampler.

Reflector diameter, D_R (mm)	44
Diameter of fixed vortex impeller (mm)	25
Width of fixed vortex impeller (mm)	3
Diameter of analytical channel (mm)	9
Range of vortex flow rate through fixed impeller, Q_{vortex} (cm^3/s)	0–640
Analytical flow, Q_{an} (cm^3/s)	50

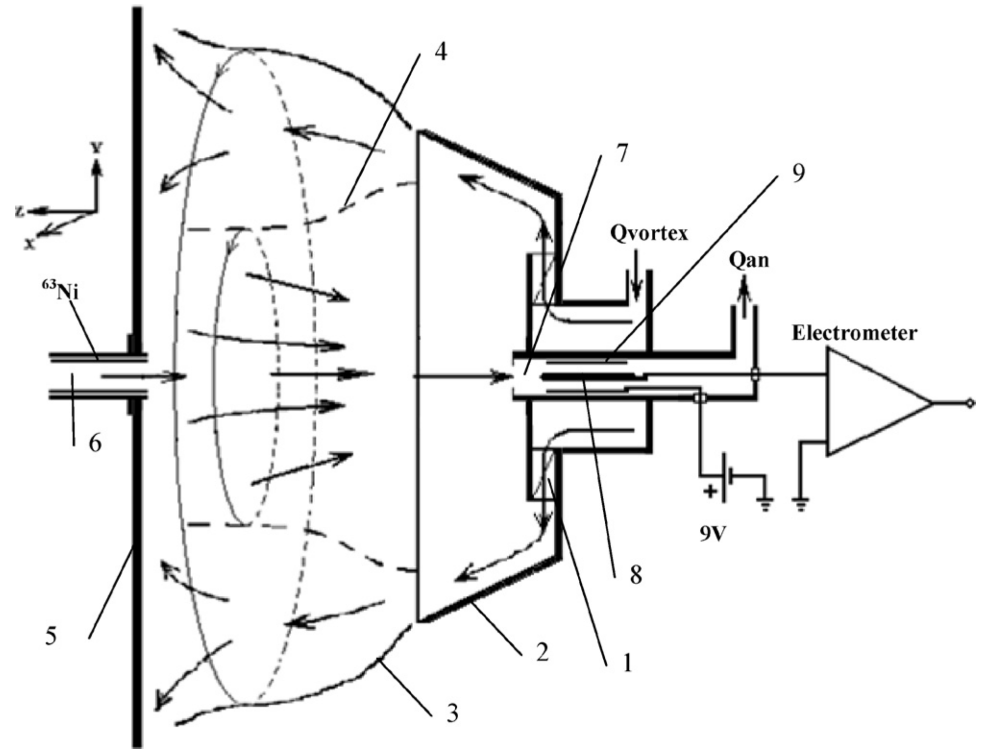

Fig. 3. Scheme of the experiment. Q_{vortex}, vortex flow; Q_{an}, analytical flow; 1, fixed impeller; 2, reflector; 3, external stream boundary; 4, counter-flow boundary; 5, screen; 6, ion source; 7, analytical channel; 8, collector; 9, deflection electrode.

ionization. Plasma produced thereby contained mostly background ion-reactants [17]: positive $(H_2O)_nNH_4^+$, $(H_2O)_nNO^+$, $(H_2O)_nH^+$ and negative $(H_2O)_nO_2^-$, $(H_2O)_n$ $(CO_2)_mO_2^-$ ions. We registered signal from positive ions with collector (8) in the analytical channel. To do this, we applied a potential of +9 V to additional electrode (9) ensuring collection of all positive ions entering the analytical channel. We measured current with a relative error of ±0.3% with an electrometer U5-11 (Russia). The ratio of a minimal registered signal to a background value was $I/I_{background} \geq 10^2$. We determined the relationship between the registered signal and the ion source position to evaluate the efficiency of ion focusing. For this purpose provision is made for coordinate displacement of the screen in X, Y, Z directions (X, Y are directions in the screen plane; Z is a direction along the stream axis at right angle to the screen plane).

We used an aspiration sampler “Model 822” (Saint-Petersburg, Research and production association “Krasnogvardeets”(not shown) to deliver ions from the vortex stream into analytical channel (7). Analytical flow was $Q_{an} = 50\ cm^3/s$ in all experiments.

We measured tangential and axial velocities of the vortex sampling flow with an accuracy of ±0.02 m/s by the DISA 55M System Constant-temperature Anemometer of Disa Elektronik A/S, Denmark.

3. Results and discussion

One can define three parts in the experimental research into the remote sampling and focusing of an ionized sample with the whirled air stream.

The first part deals with a choice of an operating value of vortex flow Q_{vortex} that was used in subsequent experiments. Maximum, $\max(I(Q_{vortex}))$, reached in the relationship between registered signal I and the value of vortex flow Q_{vortex} was used as a criterion.

The second part is devoted to the research into the remote vortex stream efficiency upon ionized sample collection. For this purpose we determined the relationship between registered signal I and distance L between the sampler and the ionized sample source. Based on the research results, we determined operating distances for studying the efficiency of ionized sample collection with the vortex stream.

The third part deals with the research into the efficiency of ionized sample collection with the vortex stream. For this purpose we determined the dependence of the registered signal on the value of the ionization source displacement from the sampler axis.

3.1. Determination of an operating value of the vortex sampler flow

As is shown in Ref. [16], the formation of a stable vortex stream for the sampler used begins with flow $Q_{vortex} \geq 210$ ml/s when linear stream velocity becomes ≥1 m/s and prevents convective destruction of the sampling flow structure. When $Q_{vortex} = 210$ ml/s, the value of the counter-flow is $Q_{cf} = 250$ ml/s (Ref. [16]) and with analytical flow $Q_{an} = 50$ ml/s the entire region of the sampling vortex flow represents a forced whirl with a constant angular velocity for all values of $Q_{vortex} \geq 210$ ml/s. We determined the operating value of the vortex flow by a maximum in the relationship between the registered signal and the vortex flow value, $I(Q_{vortex})$. We placed the ionization source along the sampler axis at distance $L = 22$ mm, which corresponded to a half of the reflector diameter. Relationship $I(Q_{vortex})$ is shown in Fig. 4(1). One can see from Fig. 4 that with increasing Q_{vortex} a significant rise in the signal (by an order of magnitude) smoothly transforms to its saturation when $Q_{vortex} > 300$ ml/s. The nature of the signal variations is determined by the processes of the sample growth and losses caused by different reasons. The growth of the sample is conditioned by an increase in the sample volume entering the counter-flow from the source as the vortex flow increases. As for the sample losses the situation is more complicated. Negative and positive ions are characteristic features of an ionized sample produced by a ^{63}Ni radioactive source. When taking such a sample with the vortex

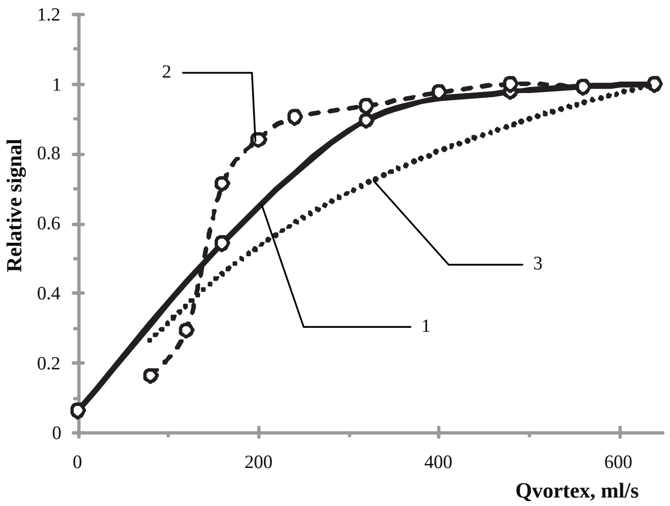

Fig. 4. Registered signal versus vortex flow Q_{vortex}. 1, ^{63}Ni source; 2, diethylanyline (sampling of non-ionized DEA vapors with a vortex sampler); 3, variation in the ion concentration due to recombination during vortex sampling.

flow, one should expect losses caused by recombination processes beside the gas dynamic ones that reveal when a non-ionized sample is taken and are associated with the peculiarities of the whirled stream structure. For comparison, relationship $I(Q_{\text{vortex}})$ obtained for the non-ionized DEA vapor sample [16] taken with the same sampler under the conditions described in this paper is shown by a dashed line in Fig. 4(2). It is evident that at the initial portion in the region of $Q_{\text{vortex}} < 300$ ml/s relationship $I(Q_{\text{vortex}})$ features a higher increase for the neutral sample than it is for the ionized one. We think this to be due to the differences in the processes defining sample losses. As for the neutral sample, this region is associated with a stable stream formation [16], which produces a sharp decrease in the sample losses and a signal growth, respectively. We think that recombination is a mechanism defining ionized sample losses with $Q_{\text{vortex}} < 300$ ml/s. We made evaluation with the Thomson theory by which the rate of a decrease in the concentration of n ions upon recombination is described by a square law [18]:

$$\frac{dn}{dt} = -\alpha n^2 \tag{1}$$

where α is a recombination coefficient.

Keeping with (1), the time dependence of the relative concentration n/n_0 is expressed by:

$$\frac{n}{n_0} = \frac{1}{1 + \alpha n_0 t(Q_{\text{vortex}})} \tag{2}$$

where n_0 is initial ion concentration, t is the time of a sample travel from the source to the sampler.

We obtained relationship $t(Q_{\text{vortex}})$ from the ratio $t = L/(U_c(Q_{\text{vortex}}))$, where U_c is an axial counter-flow velocity, L is a distance between the ionization source and the sampler. Relationship $U_c(Q_{\text{vortex}})$ was determined experimentally by a Disa anemometer. When deriving dependence (2), we take recombination coefficient $\alpha = 2.2 \times 10^{-6}$ cm^3/s (coefficient of three-body recombination at pressure of 1 atm [18]), initial ion concentration $n_0 = 1.24 \times 10^7$ cm^{-3} (which corresponds to current 1×10^{-10} A with analytical flow value $Q_{an} = 50$ cm^3/s, $Q_{\text{vortex}} = 0$, $L = 0$). Relationship $n/n_0(Q_{\text{vortex}})$ is given by dots in Fig. 4(3). As is evident from Fig. 4 the nature of variations in the recombination dependence (Fig. 4(3)) at the initial portion is closely related to that in the registered signal dependence (Fig. 4(1)). With a further increase in the vortex flow to $Q_{\text{vortex}} > 300$ ml/s the nature of the signal dependence for neutral (Fig. 4(2)) and ionized (Fig. 4(1)) samples almost coincides, which suggests that gas dynamic sample losses prevail in the region. As stated in Ref. [16], two processes affect the signal value in this region. On the one hand, the volume of the sample entering counter-flow from the source increases with the vortex flow, on the other hand, sample dilution reducing a portion thereof introduced into the analytical channel increases with Q_{vortex} and counter-flow. With $Q_{\text{vortex}} > 480$ ml/s a balance between two processes takes place and the signal becomes saturated. We take the value of $Q_{\text{vortex}} = 480$ ml/s for an operating vortex flow.

3.2. Research on the remote vortex stream efficiency upon ionized sample collection

To evaluate the remote vortex stream efficiency we determined the dependence of the registered signal on the distance between the sampler and the ionized sample source with $Q_{\text{vortex}} = 0$ ml/s and $Q_{\text{vortex}} = 480$ ml/s. We placed the sample source along the sampler axis. Fig. 5 gives the results of measurements in relative units. Considering relationships 1 and 2, one should first mention an order of magnitude increase of the signal registered by the collector with the vortex sampler on, which suggests that the efficiency of the remote ionized sample collection is enhanced compared to aspiration sampling. The distance dependence of the registered IMIS-MS signal upon remote vortex sampling of non-ionized DEA vapors is given in Fig. 5(4) for comparison. As is evident from Fig. 5(4), the nature of these dependences differs greatly. When a non-ionized sample is taken (line 4), the signal remains almost unchanged to distances equal to the reflector diameter (44 mm). On the contrary, a sharp signal decrease, almost by an order of magnitude, is observed within the same distance range when an ionized sample is taken (line 2). It is evident that additional ion loss mechanisms are available for an ionized sample. First of all, these are recombination processes typical of bipolar plasma formed by a ^{63}Ni radioactive source. We used the Thomson theory [18] to evaluate recombination losses (line 3, Fig. 5). To do this, we preliminary determined the L distance dependence of the axial counter-flow velocity and defined the time of ion transportation from the source to the sampler. As is evident from Fig. 5, relationship $n/n_0(L)$ (line 3) turns to be more flattened and does not explain a sharp decrease in the registered signal. It possible to assume that there are other mechanisms of ion losses besides recombination, like a space-charge effect, that have a profound effect on the registered signal value resulting in an additional signal drop.

The L-dependence of on the signal ratio I/I_0 is given in the insert of Fig. 5 (I – with $Q_{\text{vortex}} = 480$ ml/s, I_0 – with $Q_{vortex} = 0$). As is evident from Fig. 5, the value $I/I_0 \geq 10$ is almost for all the distances corresponding to the reflector diameter (44 mm), that is a rather high efficiency of remote vortex sampling is preserved compared to the aspiration one. Therewith, the efficiency grows with the distance in spite of a considerable decrease of the registered signal.

3.3. Research into the efficiency of ionized sample collection with the vortex stream

To study the efficiency of ionized sample collection with the vortex stream we determined the dependence of registered signal I on the value of the ionization source displacement from the sampler axis. As mentioned above, it is the properties of the highly whirled stream structure that involve directing radial velocity in the counter-flow region towards the stream axis allow one to use the vortex flow for gas dynamic ionized sample focusing. In the process of sample transportation from the source to the analyzer the radial vortex flow component removes the sample from the entire counter-flow volume towards the stream axis, thus executing its focusing. Relationship between the registered signal and the radial

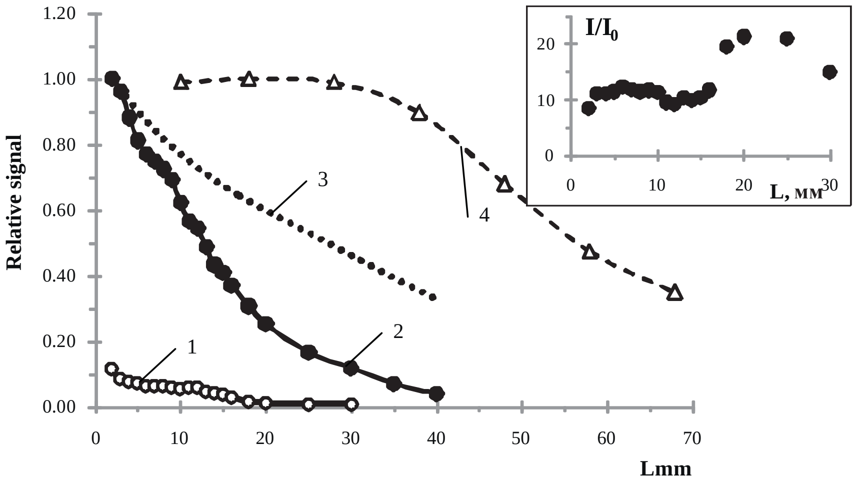

Fig. 5. Curves of registered signal versus the distance between the sampler and ionized sample source. 1, $Q_{vortex} = 0$ (I_0); 2, $Q_{vortex} = 480$ ml/s (I); 3, n/n_0 (recombination sample losses); 4, non-ionized sample (DEA).

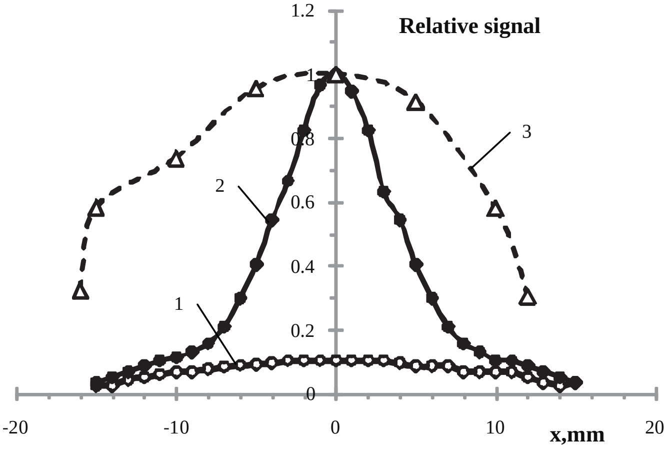

Fig. 6. Registered signal versus radial displacement of the ionization source relative the stream axis. 1, $Q_{vortex} = 0$; 2, $Q_{vortex} = 480$ ml/s; 3, non-ionized sample (DEA).

source displacement relative to the stream axis is an efficiency factor of such a “gas dynamic” sample focusing.

In Fig. 6 the curves of the registered signal versus displacement X of the ionized sample source relative to the axis with $Q_{vortex} = 0$ ml/s (line 1) and $Q_{vortex} = 480$ ml/s (line 2) are given. We placed the sample source at a distance of 15 mm from the reflector.

As is evident from Fig. 6, the behavior of the signal dependences for $Q_{vortex} = 0$ ml/s (line 1) and $Q_{vortex} = 480$ ml/s (line 2) over the measured interval of displacements X differs greatly. When no vortex is found within the range of X variations from −10 mm to +10 mm, the registered signal changes 1.5 times. When the vortex stream is found within the same range of displacements X, the signal changes 9.5 times. Such a difference in the signal behavior suggests that with the vortex stream remote sampling obtains a new feature characterized by a considerable increase in the efficiency of ionized sample collection that can be called a “gas dynamic” ionized sample focusing. It should be mentioned that unlike the neutral sample (line 3) [16] the ionized one features a sharper signal drop due to recombination and a space-charge effects. Considering the dependencies represented as peaks, one can evaluate their width at half height. Peak width at half height makes up 25 mm for the neutral sample and 9 mm – for the ionized one. Thus, the availability of ion-ion interaction narrows peak 3 times. Therewith, the region of efficient ionized sample collection narrows. An assessment of peak width at half height for the ionized sample upon aspiration sampling gives a value of 24 mm (line 1), which almost coincides with peak width at half height of the neutral sample. We think that with no vortex stream such a peak tailing is associated with a long time of ionized sample transportation and a profound effect of ion-ion interaction processes.

4. Conclusion

Studies performed have shown a possibility of focusing ionized bipolar samples with a highly whirled vortex stream. It is possible to state based on the results obtained that despite of a significant recombination and a space-charge effects a highly whirled vortex stream allows an efficient remote collection of the ionized bipolar sample. This in its turn offers prospects for a practical implementation of the vortex samplers for solving the problems of the customs control over the smuggling of radioactive α and β – sources via ionized sample detection. One knows that it is difficult to detect such sources with available devices under the customs control conditions.

Acknowledgement

The work is supported by the Presidium RAS, Program 8, project 5, 2009–2011, and RFBR Project # 11-08-00329-a, Russia.

References

[1] S.A. Shaffer, D.C. Prior, G.A. Anderson, H.R. Udseth, R.D. Smith, Anal. Chem. 70 (1998) 4111.
[2] S.A. Shaffer, K. Tan, G.A. Anderson, D.C. Prior, H.R. Udseth, R.D. Smith, Rapid Commun. Mass Spectrom. 11 (1997) 1813.
[3] S.A. Shaffer, A.V. Tolmachev, D.C. Prior, G.A. Anderson, H.R. Udseth, R.D. Smith, Anal. Chem. 71 (1999) 2957.
[4] T. Kim, A.V. Tolmachev, R. Harkewicz, D.C. Prior, G.A. Anderson, H.R. Udseth, R.D. Smith, T.H. Bailey, S. Rakov, J.H. Futrell, Anal. Chem. 72 (2000) 2247.
[5] M.E. Belov, et al., J. Am. Soc. Mass Spectrom. 15 (2004) 212.
[6] A.W. Colburn, A.E. Giannakopulos, P.J. Derrick, Eur. J. Mass Spectrom. 10 (2004) 149.
[7] R. Guevremont, R.W. Purves, Rev. Sci. Instrum. 70 (1999) 1370.
[8] R. Guevremont, L. Ding, B. Ells, D.A. Barnett, R.W. Purves, J. Am. Soc. Mass Spectrom. 12 (2001) 1320.
[9] D.A. Barnett, B. Ells, R. Guevremont, R.W. Purves, J. Am. Soc. Mass Spectrom. 13 (2002) 1282.
[10] V.V. Laiko, M.A. Baldwin, A.L. Burlingame, Anal. Chem. 72 (2000) 652.
[11] P.V. Tan, V.V. Laiko, V.M. Doroshenko, Anal. Chem. 76 (2004) 2462.
[12] E.P. Kremer, G.J. Evans, R.E. Jervis, J. Phys. D: Appl. Phys. 39 (2006) 5008.
[13] R.B. Akhmedov, T.B. Balagula, F.K. Rashidov, A.Y. Sakaev, in R.B. Akhmedov (Ed.), Energy, Moscow, 1977, p. 18 (in Russian).

[14] F.K. Rashidov, A.K. Sakaev, Proceedings of the IV Republican Scientific and Technical Energy Workshop, Tashkent, September, 1973, pp.108–109.
[15] Y.N. Kolomiets, V.V. Pervukhin, Tech. Phys. Lett. 35 (17) (2009) 18–25.
[16] Y.N. Kolomiets, V.V. Pervukhin, Talanta 81 (1–2) (2010) 294–300.
[17] H.H. Hill Jr., W.F. Siems, R.H. St. Louis, D.G. McMinn, Anal. Chem. 62 (1990) 1201A–1209A.
[18] H. Massey, Negative Ions, 3rd edn., Cambridge University Press, Cambridge, 1976.