RESEARCH ARTICLE

Numerical Simulation and Experimental Validation of the Three-Dimensional Flow Field and Relative Analyte Concentration Distribution in an Atmospheric Pressure Ion Source

Thorsten Poehler,¹ Robert Kunte,¹ Herwart Hoenen,¹ Peter Jeschke,¹ Walter Wissdorf,² Klaus J. Brockmann,² Thorsten Benter²

¹Institute of Jet Propulsion and Turbomachinery, RWTH Aachen University, Templergraben 55, 52062 Aachen, Germany

²Department of Physical and Theoretical Chemistry, University of Wuppertal, Gauss Straße 20, 42119 Wuppertal, Germany

Abstract

In this study, the validation and analysis of steady state numerical simulations of the gas flows within a multi-purpose ion source (MPIS) are presented. The experimental results were obtained with particle image velocimetry (PIV) measurements in a non-scaled MPIS. Two-dimensional time-averaged velocity and turbulent kinetic energy distributions are presented for two dry gas volume flow rates. The numerical results of the validation simulations are in very good agreement with the experimental data. All significant flow features have been correctly predicted within the accuracy of the experiments. For technical reasons, the experiments were conducted at room temperature. Thus, numerical simulations of ionization conditions at two operating points of the MPIS are also presented. It is clearly shown that the dry gas volume flow rate has the most significant impact on the overall flow pattern within the APLI source; far less critical is the (larger) nebulization gas flow. In addition to the approximate solution of Reynolds-Averaged Navier-Stokes equations, a transport equation for the relative analyte concentration has been solved. The results yield information on the three-dimensional analyte distribution within the source. It becomes evident that for ion transport into the MS ion transfer capillary, electromagnetic forces are at least as important as fluid dynamic forces. However, only the fluid dynamics determines the three-dimensional distribution of analyte gas. Thus, local flow phenomena in close proximity to the spray shield are strongly impacting on the ionization efficiency.

Key words: Computational flow dynamics, CFD, Particle image velocimetry, Atmospheric pressure ionization, API, Simulation

Abbreviations: AN, analyte; AP, atmospheric pressure; APCI, atmospheric pressure chemical ionization; API, atmospheric pressure ionization; APLI, atmospheric pressure laser ionization; DG, dry gas; DIA, distribution of ion acceptance; LC, liquid chromatography; MPIS, multi purpose ion source; MS, mass spectrometry; OP, operating point; PIV, particle image velocimetry; S, volumetric source term; U, velocity vector; u, v, w, velocity vector component

Electronic supplementary material The online version of this article (doi:10.1007/s13361-011-0211-z) contains supplementary material, which is available to authorized users.

Correspondence to: Thorsten Poehler; e-mail: poehler@ist.rwth-aachen.de

Received: 15 March 2011
Revised: 28 June 2011
Accepted: 6 July 2011
Published online: 9 August 2011

in direction of x , y , and z , respectively; x , y , z , Cartesian coordinates; y^+ , dimensionless wall scale; Subscripts: I, ionization; V, validation; x , y , z , vector component in direction of x , y , and z , respectively; Superscripts: $'$, fluctuation; $-$, time-averaged; Greek symbols: μ , dynamic viscosity; ϕ , concentration of analyte per unit mass; ρ , density

Introduction

The introduction of ionization methods operating at atmospheric pressure (AP), such as atmospheric pressure chemical ionization (APCI) [1] and electrospray ionization (ESI) [2], has dramatically changed the application of mass spectrometry (MS) as analytical method. For example, hyphenation of MS with liquid chromatography (LC) became rather simple [3, 4]. Moreover, in the early days of AP ionization and sometimes even today, laboratory or ambient air was used as the bulk gas in the source region [5, 6]. This has tremendously simplified the operation of mass spectrometers as analytical tools; the days of “baking out an electron ion source overnight” seem to be in the past. On the other hand, atmospheric pressure ionization (API) has introduced a hitherto more or less unknown phenomenon in routine mass spectrometric analysis: considerable day-to-day variations of the instrument performance. In other words: lack of analytical stability. This is not observed on the same scale for all API methods, some, e.g., APCI, seem to be rather prone to unexpected performance fluctuations, others are relatively stable. There are myriads of parameters that may severely impact on the performance of any API method; the ion population reaching the detector (and thus the corresponding recorded mass spectrum) has been subject to numerous deeply folded processes following initial ion generation. These processes are physical (non-reactive collisions or fluid dynamical forces, temperature changes, pressure changes, electrodynamic forces) as well as chemical (reactive collisions) in nature. The latter are usually summarized as “ionization mechanism” and are not subject to this work. Physical processes in API are essentially controllable. However, the introduction of pneumatically assisted vaporization (“nebulization”) [7] and dry or curtain gas flows [8], as well as further auxiliary gas flows heated to different temperatures has lead to a complexity in the physical processes that “trial and error” has become the routine approach when optimizing the performance of API MS methods.

Along this line, even the design and development of API sources seems to have lost some of the deterministic approaches used before in vacuum (i.e., in essentially collision-free) environments. This seems to be a consequence of the apparent failure of particle tracing software when the motion of ions is electrodynamically driven within viscous flows. Owing to the large number of collisions, fluid dynamical forces may have even larger impact of an ion trajectory than high electrical field strengths. At atmospheric

pressure, each molecule or ion undergoes 10^9 collisions per second [9]. Thus, a directed gas flow may completely reverse the ion motion in an electrical field. This is very well known; ion mobility spectrometry builds on these properties [10]. However, ion trajectory simulation at AP within viscous flows, i.e., within modern API sources, has become a challenging task.

The more recent versions of the widely applied particle tracing software package SIMION [11] offers a user program interface, which allows the direct interaction with the simulation algorithm. In 2005 Dahl et al. [12] introduced an extension to SIMION based on this user program interface, which implements high pressure ion motion simulation in terms of a statistical diffusion simulation (SDS) algorithm. It became thus possible to run trajectory calculations at ambient pressure. Even further, with proper input parameters, i.e., bulk gas velocity vector fields, even simulations within viscous flow became feasible. Very recently, we have investigated the validity of the SDS approach [13]. It was shown that SIMION with SDS and proper fluid dynamical input data reliably models experimental results obtained in a rather simple set-up. It thus appears feasible that ion trajectories within significantly more complex geometries and gas flows, such as prevailing in a multi-purpose ion source (MPIS) [14], may eventually be modeled.

In this paper, we report on the successful modeling of the fluid dynamical properties of an MPIS operated with typical API source settings for LC MS applications (cf. Figure 1). Most importantly, the modeling results are fully validated experimentally. In the near future, these data sets will be used to correctly simulate distributions of ion acceptance (DIA) [15–17], which, in our opinion, would represent a milestone in research towards deterministic AP ion source development.

Experimental Setup

Particle image velocimetry (PIV) measurements were conducted in order to obtain experimental validation data for the simulation runs. PIV is a laser-optical measurement technique which allows gathering 2D velocity flow field data. Seeding oil drops are injected into the flow and illuminated by a laser light sheet in the measurement area. A fast CCD-camera takes two pictures in rapid succession (ns to μ s scale) from whom the flow field is calculated. Details are found in [18, 19].

Figure 1. Cutaway view of the MPIS source. The coordinate system as defined on the bottom right is used throughout this paper

PIV System

A 2D PIV (LaVision, Goettingen, Germany) measurement system was used. A frequency doubled 120 mJ YAG double pulse laser (ESI, Portland, OR, USA) provided a 532 nm green laser beam. A laser beam delivery stage was used to direct the light to the light sheet optics. This optics was able to generate a light sheet of 1 mm thickness with a focal length of 30–200 mm. The seeding generator (Topas, Dresden, Germany) provided a particle concentration greater than 10^8 particles/cm³. The oil DEHS [di(2-ethylhexyl) sebacate] was used as seeding medium. The CCD camera (LaVision) used dual-frame technology for 12 bit digital cross correlation [18] and minimum time between 2 frames of 200 ns. The resolution was 1376×1040 pixels at a pixel size of 6.45 μm .

Figure 1S in the Supplementary Information shows a photograph of the mass spectrometer inlet stage comprised of the MPIS, the desolvation unit, and a high vacuum chamber. This system mimics the analyzer inlet stage of the Bruker micrOTOF mass spectrometer series. The ionization chamber with the access for the analyte inflow via pneumatically assisted nebulization is seen in the center. The light sheet optics and the PIV camera were positioned in a 90° angle to the chamber center axis. The optics generated a light sheet of 1 mm thickness with the focus in the measurement plane in front of the spray shield. The light sheet entered the chamber through a glass window. A black paper cylinder between the light sheet optics and the window was used for laser stray light protection.

The optical access for the camera was a glass window at the side of the chamber. The chamber was blackened to avoid laser reflections, which would disturb the particle image capture. For calibration, a plate with a defined pattern was mounted into the measurement plane. The calibration

function and scaling factors were calculated by the system software.

Operating Point Adjustment

The operating point settings were adjusted according to Table 1. Pressurized air was mixed with the seeding flow in order to get a particle concentration for adequate measurement conditions. This mixture supplied the two air flows analyte (AN) and dry gas (DG), which were set by valves and measured by two calibrated volume flow meters (MCC, Dortmund, Germany). Pressure and temperature were measured for calculation of the corresponding mass flows.

Measurement Accuracy

The criteria for an accurate PIV measurement were set according to 0 [18] and [19]. Hence, the temporal separation of the two camera images was adjusted so that the particle spots move 6–10 pixels on the camera chip. The camera objective was adjusted to ensure that the particle image diameter captured 2–3 pixels.

According to 0 [19], sub-pixel accuracy was thus achieved. Further, the light sheet was four times as thick as the average relative particle travel path perpendicular to it. The interrogation window for the vector calculation, as defined by [18], was at least four times as large as the particle movement. As a result, the relative measurement accuracy of the PIV system was calculated to $\pm 2\%$. The volume flow meters had an accuracy of $\pm 2.5\%$. The pressures were measured within $\pm 0.5\%$ and the temperatures within ± 1 K. Taking all errors into account, the estimated absolute accuracy of the results is within $\pm 5\%$.

Numerical Setup

The numerical flow simulations have been conducted with the software package CFX 12.1. (Ansys, Canonsburg, PA, USA). The set of equations solved by the simulation software are the discretized Navier-Stokes equations in their

Table 1. Boundary conditions for validation operating points

	OP _{V1}	OP _{V2}
Inflow analyte:		
Mass flow [g s ⁻¹]	0.04	0.04
Total temperature [C]	20	20
Turbulence intensity [%]	1	1
Analyte concentration [–]	1	1
Inflow dry gas:		
Mass flow [mg s ⁻¹]	4.7	5.7
Total temperature [C]	20	20
Turbulence intensity [%]	5	5
Analyte concentration [–]	0	0
Outflow MS:		
Static pressure [Pa]	93030	93030
Outflow atmosphere:		
Static pressure [Pa]	10^5	10^5

conservation form [20, 21], which describe the processes of momentum, heat, and mass transfer. The iterative solution of these partial differential equations is conducted for each finite volume of a three-dimensional mesh. The entire mesh represents the flow domain of the simulation [20].

In the following sections, the features of the spatial discretization and the settings for the solver are described.

Spatial Discretization

A fundamental part of flow simulations is the discretization for the flow domain in a set of finite volumes, i.e., the numerical mesh. For each of these volumes, the conservation equations are solved.

The numerical mesh has been generated using ICEM CFD 11.0 (Ansys, Canonsburg, Pennsylvania, USA). It consists of about $9.9 \cdot 10^6$ tetrahedron and about $0.6 \cdot 10^6$ prism elements respectively, which represents a rather detailed spatial resolution of the flow field. The boundaries of the computational mesh are depicted in Figure 1.

An example of the discretization is given in Figure 2, which shows the finite volumes of a iso-y (cf. Figure 1) cut through the numerical mesh near the inflow of the capillary.

The usage of 15 layers of prism elements near the walls ensures a sufficiently high resolution of the flow gradients in the boundary layers. This also results in a dimensionless wall scale y^+ of lower than 2, which is important for an adequate turbulence modeling near the walls [21]. Due to the higher numerical effort caused by prism layers [20, 21], only walls with a significant impact on the flow field are covered in by this approach.

The pressure in the chamber at the downstream end of the capillary of 3 mbar results in an overcritical pressure ratio over the entire capillary. Therefore, at the exit of the capillary, where the velocity reaches its maximum value due to the increased boundary layers, the local Mach number becomes 1. Since the flow state at this point is known and

the pressure loss in the capillary can be well estimated, it is possible to determine the aerodynamic state in the upstream entry region of the capillary. Therefore, it is not necessary to extend the mesh throughout the entire capillary (cf. Figure 1) because the outlet boundary conditions can be specified for every cross section of the capillary.

Solver Settings

The numerical solution of the Navier-Stokes equations requires initial and boundary values and some specifications for the solver. Since the software evaluates an initial solution of the flow field, only the boundary conditions and the solver specifications are described in this section.

In addition to the Navier-Stokes equations the equation of state and the turbulence model have to be specified. Since the static pressure is approximately 10^5 Pa, the ideal gas equation with the properties of air is chosen to determine the fluid state. For turbulence modeling the Shear-Stress-Transport model [22], which provides accurate results in the boundary layer as well as in the free stream, is used to simulate the impact of turbulence on the mean flow.

In order to differentiate the analyte and the dry gas flow, an additional scalar variable has been defined, which is considered as a mass concentration of analyte gas. The three-dimensional distribution of the additional variable is solved via an additional transport equation (Equation 1):

$$\frac{\partial(\rho\varphi)}{\partial t} + \nabla \cdot (\rho U \varphi) = \nabla \cdot (\rho D \nabla \varphi) + S \quad (1)$$

(Note: All variables and terms used in this paper are listed in the *Abbreviations* section). Since only steady state simulations are considered and no sources of analyte exist, the first and the last term of the equation become zero. The molecular diffusivity D is set to $7 \cdot 10^{-6} \text{ m}^2\text{s}^{-1}$ and the density and the velocity vector are results of the solution of the Navier-Stokes equations.

An overview of the boundary conditions for the validation simulations is given in Table 1, while the values for the ionization operating conditions are given in Table 2. In all cases all walls are considered to be isothermal at 348.15 K. The total temperature is the sum of the (static) temperature and a dynamic part, which can be defined as mass-specific kinetic energy of the flow divided by the heat capacity at constant pressure. Due to the low flow velocities, the total temperature equals approximately the static temperature. The analyte inflow Reynolds Number of approximately 430 indicates a laminar flow state. Therefore, the analyte inlet volume flow has been specified in terms of a quadratic velocity profile and the turbulence intensity has been estimated to be 1%.

Figure 2. Numerical mesh near capillary inflow

Table 2. Boundary conditions for ionization operating points

	OP ₁₁	OP ₁₂
Inflow analyte:		
Mass flow [g s ⁻¹]	0.0237	0.0237
Total temperature [C]	183	183
Turbulence intensity [%]	1	1
Analyte concentration [–]	1	1
Inflow dry gas:		
Mass flow [mg s ⁻¹]	3.337	5.269
Total temperature [C]	131	131
Turbulence intensity [%]	5	5
Analyte concentration [–]	0	0
Outflow MS:		
Static pressure [Pa]	93030	93030
Outflow Atmosphere:		
Static pressure [Pa]	10 ⁵	10 ⁵

Validation of the Flow Simulations

Numerical solutions of fluid flow are naturally only approximations of the real flow. Several kinds of errors are included in numerical flow approximations (modeling errors, discretization errors, and iteration errors) [20, 21, 23]. In the literature, several approaches have been presented to evaluate discretization and iteration errors [20, 23]. However, evaluating the modeling error is not possible at acceptable costs if no analytical solution exists, which is always the case for complex flows. Therefore, experimental data are required to validate the numerical model. In the following sections, the comparison of experimental and numerical velocity and turbulence data will be presented. The consideration focuses on the flow field in close proximity of the spray shield, where the analyte gas jet and the dry gas jet interact (cf. Figure 1).

Two-Dimensional Turbulence

Turbulence can be considered as a fluctuation of a flow quantity around a mean value. The local flow velocity can therefore be written as the sum of mean and fluctuation value (Equation 2):

$$U = \bar{U} + U' \quad (2)$$

The mass-specific kinetic energy of the turbulence is then defined as (Equation 3)

$$TKE = \frac{1}{2} (u'^2 + v'^2 + w'^2) \quad (3)$$

Due to the measurement technique only two dimensions of the turbulence have been resolved. The numerical solutions have been conducted with an isotropic turbulence model, therefore the two-dimensional turbulent kinetic

energy is 2/3 of the corresponding value of a three-dimensional turbulence.

In order to evaluate the validity of the assumption of isotropic turbulence, Figure 3 shows the turbulence components in the two Cartesian directions for OP_{V1}. The main part of the turbulence is produced by turbulent fluctuations in x-direction at the edge of the analyte gas jet, which is due to the strong impact of the intensive shear stresses on turbulence generation. In stream-wise (z-) direction the normal stresses increase because of the decelerating jet, which stimulates the turbulence in z-direction. However, the anisotropy of the turbulence locally achieves a factor of 3 in different directions and thus the isotropic turbulence model could overpredict the impact of the normal stresses.

Figure 3. Turbulent velocity components for the x- (top) and z-direction (bottom). Cf. Figure 1 for the orientation of the coordinate system

In Figure 2S in the Supplementary Information the turbulent kinetic energy distribution is presented for both operating points. Operating at OP_{V1} the overall turbulent kinetic energy is very low. An increase of TKE can be detected in the region where both components of turbulent fluctuations are of a significant magnitude. In the numerical results an additional spot of higher TKE at $(x; z) = -0.087; 0.007$ occurs. This turbulent spot is also present in both numerical and experimental results for OP_{V2} , but is more intensive in the numerical result. This turbulent spot is

produced by a vortex, which will be discussed in the following section.

Mean Flow Field

Contour plots and streamlines of the velocity are presented in Figure 4. In terms of the overall velocity vector field, numerical and experimental results are in very good agreement at both operating points. However, there are some

Figure 4. Comparison of experimental (left) and numerical (right) results of the velocity field at OP_{V1} (top) and OP_{V2} (bottom). Cf. Figure 1 for the orientation of the coordinate system

subtle differences in the flow field, which are discussed in the following sections.

Considering the analyte gas jet, the main difference is found in the width of the jet. The analyte jet is significantly wider in the numerical results. The discretization error resulting from a coarse grid in this region elevates an artificial (numerical) diffusion. The strong gradients at the edge of the jet cannot be resolved by the large finite volumes in this region, which then leads to a numerical diffusion.

Another feature of the flow pattern is the deflection of the analyte gas jet in OP_{V2}. It is present in both the numerical and the experimental results and the agreement is good.

At both operating points, the flow angle of the dry gas jet differs, which is due to a different mass flow distribution in the dry gas connector. The reasons for the non-uniform flow in the dry gas connector are as follows. A lower back-pressure at the numerical capillary outflow in the CFD simulations could improve the conformity to the experimental results concerning the velocity level and the flow angle of the jet.

In the interaction zone of the two jets a vortex is generated in the numerical results for both operating points. This is a well known effect, which, e.g., can be observed at smoke ring generators. The torus shape of the vortex ring is broken into a horseshoe shape by the analyte gas jet. Therefore, the second vortex core is not present at the bottom of the dry gas jet.

The experimental results show two vortices in the same region. Due to the fact that in the experimental results there also is only one turbulent spot in OP_{V2}, and there is no physical reason for the existence of two vortices, it is assumed that the second vortex is a misinterpretation of the PIV postprocessor. It is possible, that the vortex core position is changing in time.

Therefore, time-averaged post-processing could lead to a depiction of two vortices.

Conclusions of the Validation

Keeping in mind that the interaction of two jets is a very complex flow situation the agreement between numerical and experimental results is very good. All significant flow features have been resolved accurately. A reduction of the remaining differences between the numerical and the experimental results could be achieved by usage of a more accurate turbulence model, e.g., a Reynolds stress model [24] to resolve the anisotropy of the turbulence, a more detailed discretization, time-resolved simulations, and an adaptation of the back-pressure capillary outflow, since it based on estimations of pressure losses occurring in the capillary.

However, particularly the first three approaches would increase the numerical effort significantly. Since the numerical results are already mostly within the experimental accuracy, the numerical setup is thus considered to be valid.

Results and Discussion

Numerical results for operating conditions of a multi-purpose ion source (MPIS) are presented in this section. As has been mentioned previously, two operating points were simulated, which differ in the dry gas volume flow.

Overall Flow Pattern

The overall analyte gas distribution for both operating points is presented in Figure 5 in terms of a mid surface contour plot of analyte concentration and surface stream lines.

Figure 5. Relative analyte distribution in the MPIS source at OP₁₁ (left) and OP₁₂ (right). Note the dramatic change of the distribution in close proximity to the spray shield

Operating at OP_{11} the analyte gas jet dominates the flow pattern. The flow direction of the jet is nearly undisturbed and impinges on the opposite wall of the MPIS. The deflection at this wall leads to a large vortex on the left side of the jet, while on the right side the fluid directly flows towards the atmospheric outlet.

Therefore, already at operating point conditions with low dry gas mass flow, there is no direct flow of analyte gas into the spray shield. It thus has to be concluded that electromagnetic forces have to be at least of the same magnitude as the fluid dynamic forces in order to facilitate efficient transport of ions into the mass spectrometer.

The increase of the dry gas mass flow in OP_{12} changes the flow pattern entirely. Under these conditions, the dry gas jet dominates the flow field. The flow pattern is characterized by two large vortices with opposite sense of rotation. Again, the vortices are produced by the impingement of the jet on the MPIS wall. The vortices support an immediate and homogeneous distribution of analyte gas. However, the presence of analyte gas in front of the spray shield is lower than in case of OP_{11} .

Jet Interaction

As has been mentioned previously, the flow angle of the dry gas jet is a result of a non-uniform mass-flow distribution in the dry gas connector. Figure 3S in the Supplementary Information shows schematically a section of the desolvation unit used for the present experiments and simulations. It is strongly emphasized that this unit, particularly the connector region shown, represents an early prototype design. Current series production units differ considerably from this design and thus behave differently. Figure 3S shows the distribution of velocity in x-direction in the channels of the dry gas connector. Negative values represent flow into the spray shield, while positive values represent reversed flow. Behind the inflow of the dry gas, the flow is split into two legs around the torus. The impingement of these legs at the bottom of the torus deflects the flow towards the bottom channel. Since there is no natural deflection in front of the other channels, the sharp deflection at the inlet of these channels causes flow separations. This leads to reversed flow regions, which tighten the effective throat size. The displacement of the mass flow towards the bottom channel results in a stronger momentum of the flow in the bottom of the spray shield, which consequently leads to an inclined jet through the spray shield, cf. Figure 5.

The inclination of the dry gas jet supports the generation of the horseshoe-shaped vortex, which was also discernible in the validation results. Figure 6 shows the three dimensional shape of this vortex in terms of an isosurface of $\lambda_2 = -80 \text{ s}^{-2}$. Negative values of λ_2 characterize closed vortical regions with a pressure minimum in the vortex core. Details of the definition of λ_2 are found in [25].

The contour demonstrates the mixing of dry gas and analyte gas enforced by this vortex. With an initial analyte

concentration of 0 in the torus center, which is coherent with the core of the dry gas jet, the analyte concentration increases due to diffusion processes and is transported towards the spray shield by the vortical motion. Thus, the vortex considerably changes the concentration of analyte gas in front of the spray shield. This is the region, though, where primary ionization often occurs (e.g., APCI, APPI, APLI).

Conclusions

Accurate CFD data sets are required for high-level ion trajectory calculations at viscous flow conditions. This work has demonstrated that the presently chosen modeling approach, including the applied turbulence model, yielded appropriate CFD data sets that were fully validated experimentally.

The analysis of the three-dimensional flow within a multi-purpose ion source at two operating points is presented. The numerical data have been generated by an iterative solution of the Reynolds-Averaged Navier-Stokes equations with a commercial software package. The implementation of an additional transport equation enabled resolution of the distribution of analyte relative mixing ratios within the MPIS. The numerical setup has been validated by particle image velocimetry measurements.

The flow pattern is analyzed with a focus on the flow features in close proximity of the spray shield. The reasons for the analyte concentration distribution are demonstrated. It is also shown that, since no analyte flows directly into the capillary towards the mass analyzer, electromagnetic forces have to be at least of the same magnitude as the fluid dynamic forces in order to enable the transport of ions.

Very recently, Wissdorf et al. [13] have shown that CFD simulation results of simple flow patterns at essentially laminar conditions yield accurate, experimentally verified

Figure 6. Horseshoe-shaped vortex in front of the spray shield

ion trajectory calculation results using single particle tracings with the SIMION program package and the statistical diffusion simulation module installed along with appropriate custom software. Since the present complex flow simulations were experimentally verified, it is envisioned that the present results are valid input parameters for ion trajectory calculations. At this time, we are using the present data set for ion trajectory calculations in the MPIS. First results are very promising, since there exist very detailed experimental data on the distribution of ion acceptance in an MPIS [15–17] and on spatially resolved ion arrival times [26]. Given the quality of the results presented here, it is speculated that DIA data are very useful for a validation of such calculations. This is currently a work in progress, and preliminary results were very recently shown [27]. It thus appears that a new set of simulation tools becomes available soon, which allows a rather accurate calculation of ion trajectories at complex viscous flow conditions. A number of applications comes to mind, particularly the computer aided design of ion optical elements operating at elevated pressure (e.g., ion funnels), or AP ion sources (e.g., high-flow applications), among many others.

Acknowledgments

The authors express their gratitude to the Deutsche Forschungsgemeinschaft (DFG) for funding this joint interdisciplinary research project (BE 2124/6-1).

References

- Moini, M.: Atmospheric pressure chemical ionization: principles, instrumentation, and applications. In: Gross, M.L., Caprioli, R.N. (eds.) *The Encyclopedia of Mass Spectrometry*, Vol. 6, Ionization Methods, 1st edn. Elsevier, Oxford, U.K (2007)
- Bruins, A.P., Cook, K.D.: Electrospray ionization: principles and instrumentation. In: Gross, M.L., Caprioli, R.N. (eds.) *The Encyclopedia of Mass Spectrometry*, Vol. 6, Ionization Methods, 1st edn. Elsevier, Oxford, U.K (2007)
- Niessen, W.M.A.: *Liquid chromatography-mass spectrometry*, 3rd ed. Chromatographic Science Series, Vol. 97, CRC Press Taylor and Francis, Boca Raton, FL (2006)
- Maurer, H.H.: Hyphenated mass spectrometric techniques – indispensable tools in clinical and forensic toxicology and in doping control. *J. Mass Spectrom.* **41**, 1399–1413 (2006)
- Carroll, D.I., Dzidic, I., Horning, E.C., Stillwell, R.N.: Atmospheric pressure ionization mass spectrometry. *Appl. Spectrosc. Rev.* **17**, 337–406 (1981)
- Badjagbo, K., Picard, P., Moore, S., Sauve, S.: Direct atmospheric pressure chemical ionization-tandem mass spectrometry for the continuous real-time trace analysis of benzene, toluene, ethylbenzene, and xylenes in ambient air. *J. Am. Soc. Mass Spectrom.* **20**, 829–836 (2009)
- Jong, R.: Pneumatically assisted electrospray ionization. In: Gross, M.L., Caprioli, R.N. (eds.) *The Encyclopedia of Mass Spectrometry*, Vol. 6, Ionization Methods, 1st edn. Elsevier, Oxford, U.K (2007)
- Bruins, A.P.: Mass spectrometry with ion sources operating at atmospheric pressure. *Mass Spectrom. Rev.* **10**, 53–77 (1991)
- Sone, Y.: *Molecular Gas Dynamics*, 8th edn. Boston, New York, Birkhäuser (2007)
- Creaser, C.S., Griffiths, J.R., Bramwell, C.J., Noreen, S., Hill, C.A., Thomas, C.L.P.: Ion mobility spectrometry: a review. Part 1. Structural analysis by mobility measurement. *Analyst* **129**, 984–994 (2004)
- Scientific Instrument Services Inc., SIMION ver. 8.0, Ringoes, NJ, USA
- Appelhans, A.D., Dahl, D.A.: SIMION ion optics simulations at atmospheric pressure. *Int. J. Mass Spectrom.* **244**, 1–14 (2005)
- Wissdorf, W., Pohler, L., Klee, S., Müller, D., Benter, Th.: Simulation of Ion Motion at Atmospheric Pressure: Particle Tracing vs. Electrokinetic Flow. Paper submitted for publication in *J. Am. Soc. Mass Spectrom.* (2011)
- Schiewek, R., Lorenz, M., Brockmann, K.J., Benter, Th., Gäb, S., Schmitz, O.J.: Development of a multimode ion-source for LC- and GC-MS. *Anal. Bioanal. Chem.* **392**, 87–96 (2008)
- Lorenz, M., Schiewek, R., Brockmann, K.J., Schmitz, O.J., Gäb, S., Benter, Th.: The distribution of ion acceptance in atmospheric pressure ion sources: spatially resolved APLI measurements. *J. Am. Soc. Mass Spectrom.* **19**, 400–410 (2008)
- Lorenz, M., Wißdorf, W., Klee, S., Kersten, H., Brockmann, K.-J., Benter, Th.: Spatially and Temporally Resolved Atmospheric Pressure Laser Ionization as a Powerful Tool for the Characterization of Ion Sources: An overview. *Proceedings of the 58th ASMS Conference on Mass Spectrometry and Allied Topics*; Salt Lake City, UT (2010)
- Klee, S., Kersten, H., Lorenz, M., Wißdorf, W., Brockmann, K.-J., Benter, Th.: A Comparison of the Performance of Diode Pumped Solid State Lasers and Excimer Lasers in LC- and GC-APLI MS. *Proceedings of the 58th ASMS Conference on Mass Spectrometry and Allied Topics*; Salt Lake City, UT, 2010. Paper accepted for publication in *J. Am. Soc. Mass Spectrom.* (2011)
- Raffel, M., Willert, C.E., Wereley, S.T., Kompenhans, J.: *Particle Image Velocimetry. A Practical Guide*, 2nd edn. Springer, New York (2007)
- Westerweel, J.: Fundamentals of digital particle image velocimetry. *J. Measurement Sci. Technol.* **8**, 1379–1392 (1997)
- Ferziger, J.H., Peric, M.: *Computational Methods for Fluid Dynamics*, 3rd edn. Springer, New York (2002)
- Casey, M., Wintergerste, T.: ERCOFTAC special interest group on quality and trust in industrial CFD: best practice guidelines, V.1. European Research Community on Flow, Turbulence, and Combustion (2000)
- Menter, F.R.: Two-equation eddy-viscosity turbulence models for engineering applications. *AIAA J.* **32**, 1598–1605 (1994)
- Roache, P.J.: Quantification of uncertainty in computational fluid mechanics. *Ann. Rev. Fluid Mech.* **29**, 123–160 (1997)
- Hadžić, I.: Second Moment Closure Modelling of Transitional and Unsteady Turbulent Flows. Ph.D. Thesis, Delft University of Technology, Delft, The Netherlands (1999)
- Jeong, J., Hussain, F.: On the identification of a vortex. *J. Fluid Mech.* **285**, 69–94 (1995)
- Wißdorf, W., Lorenz, M., Kersten, H., Klee, S., Brockmann, K.-J., Benter, Th.: Systematic DIA Measurements for APLI Method Development. *Proceedings of the 57th ASMS Conference on Mass Spectrometry and Allied Topics*; Philadelphia, PA (2009)
- Wißdorf, W., Lorenz, M., Benter, Th.: Numerical Simulation of the Distribution of Ion Acceptance (DIA) in a Commercial API Source. *Proceedings of the 59th ASMS Conference on Mass Spectrometry and Allied Topics*; Denver, CO (2011)