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Comparison of calculated and experimental flow velocities upstream from the sampling cone of an inductively coupled plasma mass spectrometer

Ross L. Spencer [a], Nicholas Taylor [b], Paul B. Farnsworth [b],*

[a] Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84602, USA
[b] Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602, USA

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ABSTRACT

Experimentally-determined flow velocities in the 6 mm upstream from the sampling cone of an inductively coupled plasma mass spectrometer were compared with velocities determined from a computer simulation of the flow and those calculated from a modified hemispherical sink model. The measured values and those from the simulation agreed within experimental error, but differed from the values calculated from the modified hemispherical sink model by as much as 30%. An empirical alternative to the modified hemispherical sink model is presented that allows for accurate calculation of flow properties upstream from the sampling cone under a range of plasma conditions.

1. Introduction

In a recent paper [1] simulation results were compared with the modified hemispherical sink model of Douglas and French and of Stewart, Hensman, and Olesik [2,3]. This model approximately describes the flow properties near the sampling cone of the first vacuum stage of an inductively coupled plasma mass spectrometer. The simulation was in a relatively small geometry and the experimental velocity data, in the region near the nozzle where the velocity changes most rapidly, were somewhat noisy. Within these limitations it appeared that the modified hemispherical sink model was a fair approximation of the experimental data. Recently, however, we have made a new set of velocity measurements using the cross-correlation of two optical signals from nearby points in the flow and we have also improved our simulation so that it can handle significantly larger geometries. These improvements in both the experimental data and in the simulation allow for a better assessment of the accuracy of the modified hemispherical sink model. We find that the simulation and experimental results match each other quite well, but that the modified hemispherical sink model is only roughly accurate, good to about 30% within about 3 mm of the entrance to the sampling cone. The basic problem is that the modified hemispherical sink model does not have as sharp an increase in velocity near the sampling orifice as do the simulation and the experimental measurements and it doesn't approach constant velocity upstream of the sampler fast enough. An empirically determined formula that is an alternative to the modified hemispherical sink model that fits the data much better is presented in this paper.

The experimental measurements of gas flow velocity will first be discussed, followed by a discussion of the simulation results. The paper concludes with a discussion of the experimental data, the simulation data, the modified hemispherical sink model, and a new formula that describes how the Mach number varies with distance along the axis of the flow between the Mach-1 point inside the sampling nozzle and the torch.

2. Experimental

2.1. Velocity measurements

The method and instrumentation used for the present velocity measurements have been previously described in detail in refs. [4,5] and will only be briefly described here. The experimental setup consisted of two 400 µm diameter optical fibers optically mounted to image the center of the plasma channel, with one fiber sampling upstream emission and one fiber sampling downstream emission. The fibers and optical assembly were mounted onto a one-axis translational stage, which was in turn mounted to the large *x*–*y*–*z* stage that positioned the impedance matching network and torch box relative to the sampling cone. The center-to-center spacing between the two fibers was determined to be 0.826 ± 0.014 mm. The ICP parameters consisted of a plasma flow rate of 12.0 L min^{-1}, an auxiliary flow rate of 0.4 L min^{-1}, a nebulizer flow rate of 1.13 L min^{-1}, and a forward power of 1250 W with less than 5 W of reflected power. A solution of 100 mg L^{-1} calcium was pumped into the spray chamber at a rate of 1 mL min^{-1}. The resulting Ca I 422.7 nm temporal emission signals for both upstream and downstream fibers were acquired on a 500 MHz digital oscilloscope (Wavesurfer, LeCroy, Chestnut Ridge, NY) with a digitization frequency

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* Corresponding author. Tel.: +1 801 422 6502; fax: +1 801 422 0153.
E-mail address: paul_farnsworth@byu.edu (P.B. Farnsworth).

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of 10 MHz. The resulting pair of temporal waveforms was analyzed using Matlab software (The MathWorks, Natick, MD) and gas flow velocities were then calculated using the fiber optic center-to-center distance and temporal interval between the peaks of the cross correlation functions.

2.2. Evaluation of experimental uncertainty

Because of the steepness of the velocity gradient near the sampling cone, positioning of the velocity probe with respect to the sampling cone with sub-millimeter accuracy was important, particularly as we compared experimentally-determined velocities to those derived from the simulation. Several contributions to uncertainty in the determination of the probe position are discussed in the following paragraphs.

For the velocity measurements reported in ref. [4], the location of the probe with respect to the sampling cone was determined at room temperature. In the current experiments we accounted as closely as possible for thermal expansion of the sampling cone and of the stages that supported the optical probe.

Thermal changes in the position of the sampling cone tip were measured as follows. A helium neon laser (Model 1508-1, JDS Uniphase, Milpitas, CA) was mounted to a translational stage above the plasma. The beam was passed through a 0.250 mm pinhole and sent to the sampling tip in a direction orthogonal to the gas flow. With the plasma off, the position of the laser beam was adjusted so that the beam just passed the tip of the sampling cone. The plasma was then ignited and the system was allowed approximately 20 min to reach thermal equilibrium. The position of the helium neon laser was readjusted so that the beam again just passed the tip of the sampling cone. This measurement was repeated five times to yield an expansion of 0.55 ± 0.18 mm.

The expansion of the torch and load coil assembly was estimated next, based on the size of the apparatus and the thermal expansion of aluminum. After ignition of the plasma, the temperature inside the torch box that housed the torch and load coil assembly rose by 14.6 °C. Outside of the torch box, where the aluminum translational stage was positioned, the temperature rose by 3.2 °C. Using the coefficient of linear expansion, $\alpha = 23 \times 10^{-6}$ $(°\mathrm{C})^{-1}$ for aluminum at 25 °C [6], and the lengths along the axis of the aluminum supports inside and outside the torch box of 34.3 cm and 58.4 cm, respectively, an overall expansion of the support was estimated at 0.16 mm. Since the torch and the load coil were independent of the sampling cone interface assembly, the result was a small migration of the torch and load coil towards the sampling cone, reducing the torch-to-cone sampling depth. It should be emphasized here that due to the complexity of the current experimental setup and large thermal gradients that exist, this value of 0.16 mm is a rough estimate, with an uncertainty of at least ± 0.1 mm.

There was additional uncertainty in the measurement of the torch to sampling cone distance (± 0.1 mm) and in the initial positioning of the fiber optic probes with respect to the load coil (± 0.1 mm). Propagating these known uncertainties gives an overall uncertainty in the position of the load coil with respect to the sampling cone and of the position of the optical probes with respect to the sampling cone of at least ± 0.25 mm.

3. Theoretical

3.1. Simulation

The simulation used in this study is a modification of the Direct Simulation Monte Carlo simulation described in ref. [1]. It has been modified to run on the Fulton Supercomputing Laboratory's cluster of processors at Brigham Young University. The results reported here were obtained by running simultaneously on 200 processors, which made it possible to use 700 million simulation particles. The simulation geometry is a cylinder 4 mm in radius and 9 mm in length extending from 6 mm upstream from the entrance to the sampling nozzle to 2.5 mm downstream from the exit point of the nozzle. The geometry is shown in Fig. 1 where the velocity streamlines of the flow calculated by the simulation are displayed. The upstream temperature of this simulation was 5000 K and the upstream pressure was atmospheric pressure at sea level. To compare this simulation to the experimental results reported in this paper we use the fact that along the central axis the flow obeys the equations of ideal fluid dynamics [1], which means that the velocity is a function of Mach number and upstream temperature (see Eq. (1) below). This property, coupled with the fact that the spatial variation of the Mach number is very nearly independent of upstream conditions, means that one simulation can describe many different experiments.

3.2. Modified hemispherical sink model

The modified hemispherical sink model relies on the ideal fluid relation between Mach number and velocity [7]

$$V = M\sqrt{\frac{\gamma k_B T_0}{m}}\left(1 + \frac{\gamma - 1}{2}M^2\right)^{-1/2}, \tag{1}$$

on the ideal fluid connection between cross-sectional area (of a duct) and the Mach number [7]

$$\frac{A}{A^*} = \frac{1}{M}\left[\frac{2}{\gamma + 1}\left(1 + \left(\frac{\gamma - 1}{2}\right)M^2\right)\right]^{(\gamma+1)/2(\gamma-1)}, \tag{2}$$

where A^* is the area of the duct at the point where the Mach number is unity; and on the following approximate relation between duct area and radial distance R from the Mach-1 point in the nozzle [2]:

$$A = A^* + 2\pi R^2. \tag{3}$$

In these equations γ is the ratio of specific heats (5/3 for argon), k_B is Boltzmann's constant, m is the molecular mass, M is the local Mach number, i.e., the ratio of the gas velocity to the local speed of sound, and T_0 is the upstream stagnation temperature along the central axis. Solving these three equations simultaneously determines $V(R)$ the velocity as a function of distance from the Mach-1 point in the nozzle.

This model predicts zero velocity far away from the nozzle, which is unphysical, so it was modified by Stewart, Hensman, and Olesik [3] by adding a constant velocity correction to model the speed at which gas flows from the torch [2,3]. The predictions of this modified hemispherical sink model are compared to experimental and simulation results in the next section.

4. Results and discussion

Fig. 2 shows the comparison between the experimental velocity measurements and the simulation velocity measurements. In order to obtain the good agreement indicated in this figure between the simulation and the experimental results the experimental points had to be uniformly shifted to the right in the figure by 0.3 mm, a distance

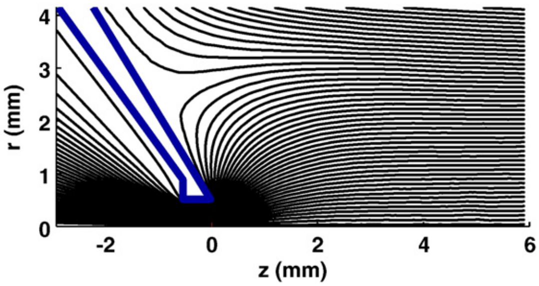

Fig. 1. Flow streamlines in the large simulation geometry are shown. This simulation used 200 processors and 700 million simulation particles.