CONSTRUCTION AND PERFORMANCE TESTING OF AN AEROSOL GENERATION SYSTEM FOR QUANTITATIVE CALIBRATION OF IN-SITU LASER INDUCED BREAKDOWN SPECTROSCOPIC MEASUREMENTS

Howard Johnsen and David Ottesen
Analytical Materials Science Department
Sandia National Laboratories
Livermore, CA 94550

ABSTRACT

An aerosol generation system has been constructed and tested in cooperation with Corning, Inc. under the DOE Office of Industrial Technologies GPLUS program. This system will be used primarily to calibrate Laser Induced Breakdown Spectroscopy (LIBS) measurements for elemental species of interest to the glass industry. Where the environment of in-situ measurements can be simulated in the generated aerosol flow, the calibration will be quantitative. In other process environments (typically either high temperature or containing toxic or reactive species) the system serves as a developmental environment for designing optimum LIBS measurement parameters. In this case, the in-situ optical emission data are calibrated by independent off-line methods for process characterization and control.

In this report we describe an aerosol generation system that enables the production of precise mass flow streams of well characterized, submicron sized aerosol particles. The construction and testing of this system has been carried out in cooperation with Corning, Inc. under the DOE Office of Industrial Technologies GPLUS program. Particle characterization, including detection of low-concentration contaminants, and new on-line process monitoring technologies may serve as important enabling technologies. These and other application needs served as the motivation for development of an aerosol generation system for calibrating in-situ laser diagnostic measurements.

A pneumatic-type nebulizer is used to produce an aqueous aerosol of dissolved metals. The liquid aerosol is subsequently dried in a gaseous co-flow, producing a stream of fine solid particles with a known mass concentration. We used the aerosol generator as a calibration source of aerosol particles for laser-induced breakdown spectroscopy (LIBS) [Cremers and Radziemski, 1987; Adrain and Watson, 1984] and produced linear calibration curves for several elemental species of interest to the glass industry (Na, Ca, Si, Al, B, K, Mg)

Laser-induced breakdown spectroscopy, also referred to as laser-induced plasma spectroscopy, dates to the 1960s. The LIBS technique utilizes a small (typically <1 mm diameter) laser-induced plasma to dissociate all molecules and fine particles within the highly energetic plasma volume. Continuum emission (bremsstrahlung and electron-ion recombination) and atomic line emission are observed from the ensuing plasma emission The atomic emission lines may be resolved both spectrally and temporarily, enabling identification and quantification of the elements present. The LIBS technique has been applied to the analysis of solids, liquids, and gases, and a number of literature reviews are available that cover a wide range of LIBS-based analysis [Cremers and Radziemski, 1987; Adrain and Watson, 1984].

The aerosol generation system is shown schematically in Figure 1. The primary components are a pneumatic-type medical nebulizer (Hudson model 1724), a tapered mixing/drying section, and a sample analysis section. The nebulizer is press fit (hand tight) into a Teflon annular ring mounted at the base of the aerosol generator. A compressed gas (typically dry nitrogen or dry air) is used to drive the nebulizer flow, and the nebulizer aerosol droplets exit directly into the mixing/drying section. The nebulizer gas flow is regulated with a laminar-flow-element controller, and is directed through the center hole of a stainless steel, porous plate 12.5-cm in diameter. O-rings seal the porous plate along the perimeter and at the center hole. A gaseous co-flow is introduced below the porous plate. The gaseous co-flow functions to provide bulk flow through the aerosol generator, both drying the liquid aerosol droplets and transporting the resulting solid particles to the sample analysis section. The co-flow gas is metered by a thermal-type mass flow controller at 70 lpm. All co-flow gases can include various combinations of air, dry nitrogen, carbon dioxide, carbon monoxide or other gases relevant to the calibration environment.

The mixing/drying section consists of a 17.5-cm length of micropolished stainless steel. The inner diameter of the mixing/drying vessel is 12.5 cm at the porous plate, and the

vessel tapers to an inner diameter of 2.5 cm over a linear distance of 12.5 cm. A final 80-cm long, 2.5-cm constant diameter section connects the mixing/drying section to the sample analysis chamber. A photograph of the assembled aerosol generation and mixing/drying section is shown in Figure 2.

Aerosols were generated using NIST-traceable aqueous solutions of dissolved metals (SPEX CertiPrep). Nominal concentrations of 10,000 μg/ml of selected species in 5% nitric acid were used as supplied, or were subsequently diluted with ultra-pure deionized water.

The nebulizer is used to introduce a well-controlled flow of aqueous solution containing the desired analyte into the gaseous co-flow stream as a mist of nominally submicron-sized droplets. As the droplets enter the co-flow in the mixing/drying section, the droplets subsequently dry via evaporation and usually form oxides. The nebulizer is characterized by the mass flow rate of nebulized liquid as a function of gas flow rate into the nebulizer. A high degree of precision in the nebulizer mass flow is desirable.

Knowledge of the nebulizer rate, the analyte mass concentration, and the co-flow rates enables the calculation of the resulting analyte mass concentration produced in the LIBS sample chamber. The analyte concentration C (mass of analyte per volume gas) is given by the following equation:

$$C = (NR * SS) / (Q_{co\text{-}flow} + Q_{nebulizer})$$

where the nebulizer rate (NR) is determined experimentally. By calculating the weight loss of the analyte in the nebulizer over time, NR was found to be 0.09ml/min for a nebulizer gas flow of 5 lpm. SS is the analyte solution concentration (μg/ml) in the nebulizer, $Q_{co\text{-}flow}$ is the flow rate of the co-flow gas (70 lpm) and $Q_{nebulizer}$ is the nebulizing gas flow rate (5 lpm).

LIBS measurements were performed directly in an aerosol sample chamber (Figure 3) utilizing metal concentrations from zero to 11,666 $\mu g/m^3$ (a view of the laser-induced plasma in the ambient air above the aerosol generator is shown in Figure 4). Signal integration of the plasma emission for several atomic species (Ca, Si, Al, K) was performed using a delay of 50-μs with respect to the incident laser pulse and a corresponding integration time of 150-μs. For other species of interest (Mg, B), a 10-μs delay with respect to the incident laser pulse, and an integration time of 4-μs were used. All spectra were ensemble averaged using a minimum of 3000 laser shots. Final average spectra were processed using the integrated analyte atomic emission line intensity normalized by the off-line continuum baseline intensity for each atomic species of interest.

LIBS spectra were recorded for Ca, Si, Al, K, Mg, and B. A representative spectrum, corresponding to the average of 1000 laser pulses at different concentrations for boron is shown in Figure 5. The calibration curve for these data is shown in Figure 6. A linear least-squares regression analysis of these data yields a correlation coefficient of 0.999.

Similar calibration curves were calculated for calcium, silicon, aluminum, potassium magnesium and boron.

The nebulization of aqueous solutions enables the generation of a reasonably large range of overall mass concentrations. This aerosol generator system is well suited for the development, assessment and calibration of LIBS (as well as other laser-based diagnostic techniques) for a variety of in-situ process measurements.

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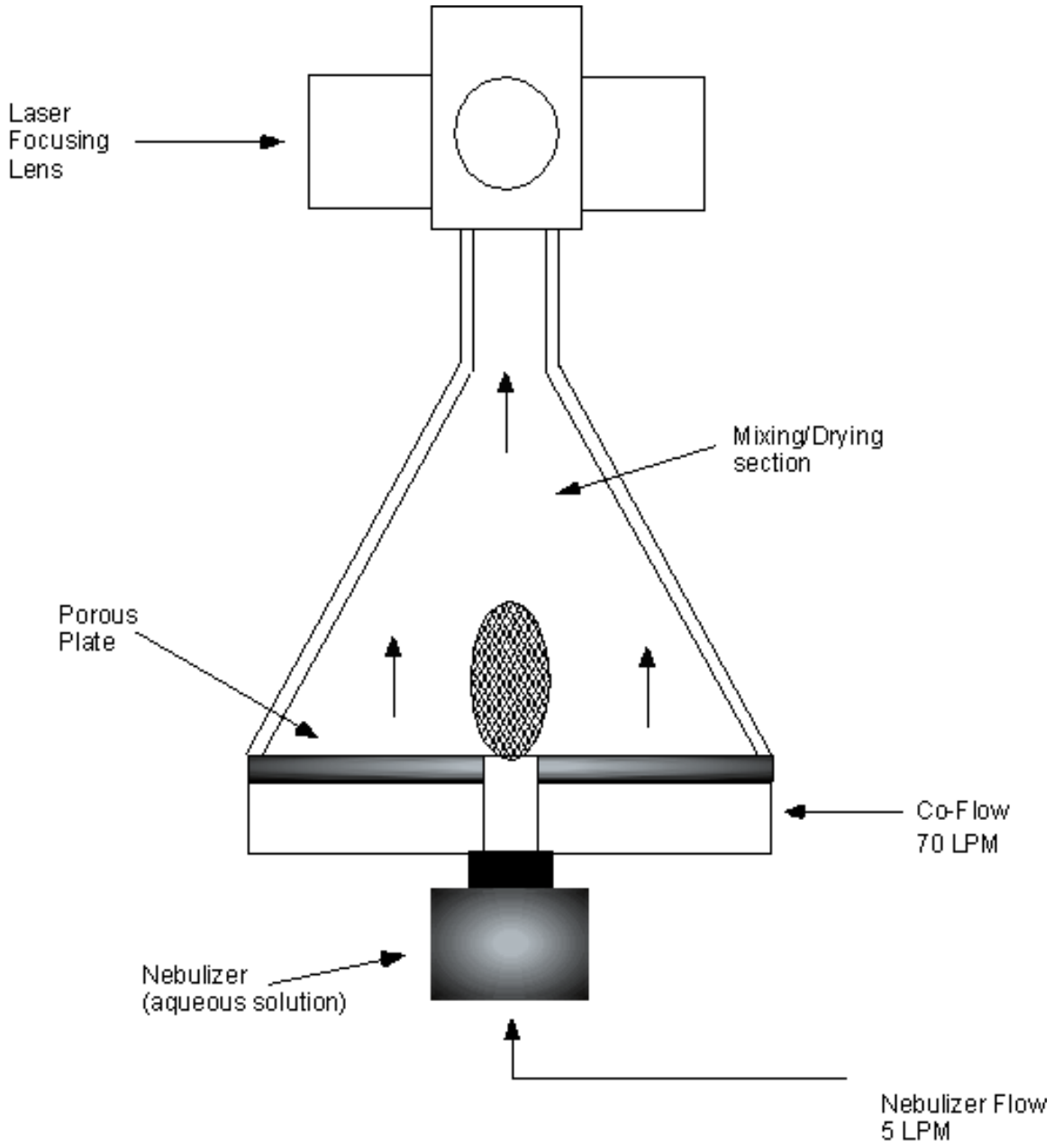

Figure 1. Schematic layout of nebulizer calibration system for in-situ laser diagnostic measurements.

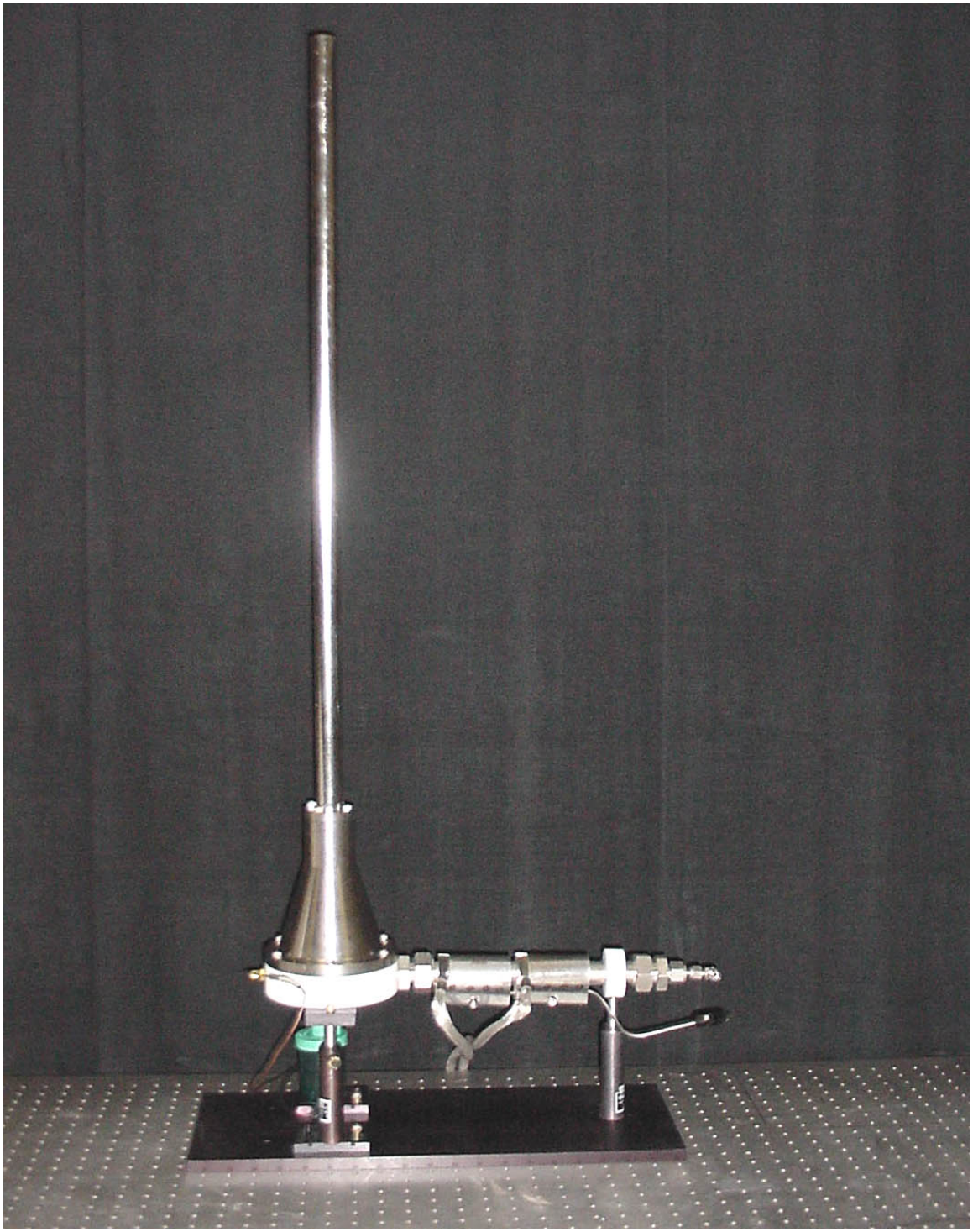

Figure 2. Photograph of nebulizer calibration system for in-situ laser diagnostic measurements.