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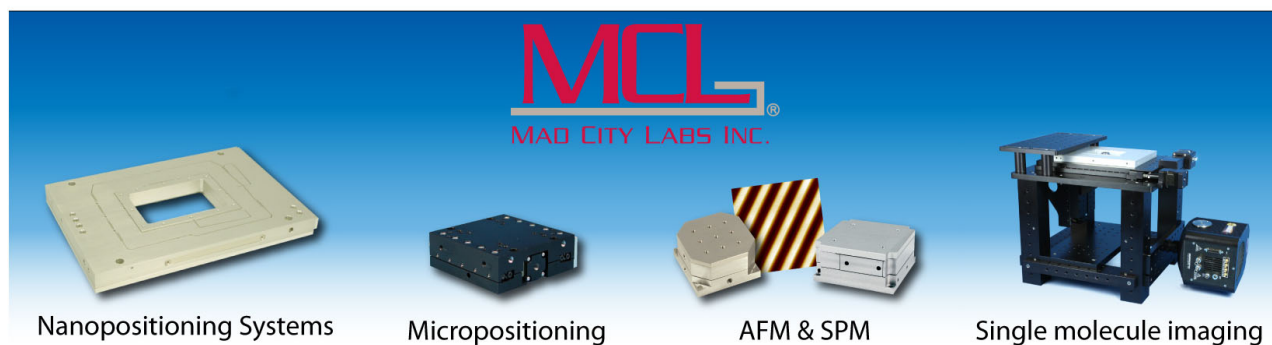
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Note: A portable laser induced breakdown spectroscopy instrument for rapid sampling and analysis of silicon-containing aerosols

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A portable instrument has been developed for measuring silicon-containing aerosols in near real-time using laser-induced breakdown spectroscopy (LIBS). The instrument uses a vacuum system to collect and deposit airborne particulate matter onto a translatable reel of filter tape. LIBS is used to analyze the deposited material, determining the amount of silicon-containing compounds present. In laboratory testing with pure silica (SiO₂), the correlation between LIBS intensity for a characteristic silicon emission and the concentration of silica in a model aerosol was determined for a range of concentrations, demonstrating the instrument's plausibility for identifying hazardous levels of silicon-containing compounds. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4949506>]

Inhalation of airborne particulate matter containing respirable, crystalline silica (silicon dioxide, SiO₂) can lead to a lung disease known as silicosis, a potentially fatal condition involving scarring of lung tissue and inflammation of the upper airways.¹ Globally, silicosis has been identified as the most common work-related lung disease.² Mining work, in particular, where drilling, grinding, crushing, breaking, and cutting of rock in enclosed spaces are commonplace in order to access ores and minerals, produces dust that can contain dangerous levels of respirable silica. Over 1×10^6 U.S. workers are routinely exposed to silica and, in 2010, over 100 U.S. workers died with silicosis as a contributing or underlying factor.^{3,4}

Given the long span (10–30 yr) between initial exposures and manifestation of silicosis (as identified through radiography measurements and/or autopsy reports), regulation and the monitoring of exposure are the key components to maintain a safer environment.⁵ The standard analysis technique for respirable silica in coal mine dust described by the Mine Safety and Health Administration (MSHA) involves field collection of air samples followed by external laboratory evaluation, with response times on the order of 1–2 weeks.⁶ Advances in portable infrared (IR) spectroscopic instrumentation suggest that this response time can be greatly reduced by providing end-of-shift (EOS) analysis, allowing more timely feedback to workers.³ However, environmental conditions can change rapidly and dramatically for miners in active mine operations, suggesting that an instrument with near real-time response would more closely match their safety needs.

Laser induced breakdown spectroscopy (LIBS) has previously been used as a method for characterizing airborne particulate matter, including filter-trapped samples^{7,8} and near real-time measurements.^{9,10} Laboratory studies have also demonstrated that LIBS emission intensities collected from prepared filter samples of silica (Min-U-SIL®, US Silica) and silica containing coal dust (Pittsburgh-4, Illinois-6) could

be used to determine the amount of deposited silicates.¹¹ This note describes a portable, rapid analysis instrument for aerosolized silicon containing materials using the LIBS technique.

A schematic of the prototype instrument developed for this study is shown in Figure 1. The entire system, except for the vacuum pump, is sealed within a 35 cm × 35 cm × 51 cm enclosure. In the sampling stage, a depositing head lowers and forms an airtight seal around the filter tape (Kimoto PTFE Membrane) using a large silicone rubber gasket. A vacuum pump pulls ambient aerosol through a cyclone (BGI GK4) and then through the filter tape for a fixed amount of time (adjustable depending on the application), producing a deposition area of about 1 cm in diameter on the tape. The deposition system was set to collect aerosol samples at 10 l/min using a vacuum pump (Gilian AirCon 2) located external to the primary instrument enclosure, but operated via the instrument's microcontroller (in future iterations, the pump will be housed within the instrument enclosure).

During sampling, particles larger than approximately 4 μm are removed in the cyclone. The smaller particles that pass through the cyclone and are deposited onto the PTFE filter tape fit the accepted conventions for respirable particle size.^{12,13} Once the aerosol has been sampled, the depositing head is lifted, and the filter tape advances using a stepper motor attached to the take-up reel until the deposited area is beneath the laser. The distance the filter tape advances is measured using an idler wheel and encoder located on the opposite end of the length of tape. The motor controller uses information from the encoder to ensure that the deposited mass is positioned under the laser before analysis. The filter tape is supplied on a 30-m spool, sufficient for approximately 2300 measurements.

During the analysis stage, a laser ablates the mass deposited on the filter tape and the resulting emission spectrum is analyzed. The LIBS system uses a Q-switched, Nd:YAG

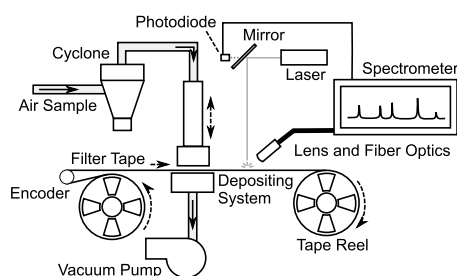


FIG. 1. Schematic of the portable LIBS instrument.

laser (Kigre, MK-367), with an average output of 44 mJ ($s = 0.96$ mJ, $N = 20$) as measured using an EnergyMax power meter (Coherent, Inc.). The laser is directed toward the filter tape using a turning mirror and an adjustable 40 mm focal length lens. The turning mirror allows approximately 5% of the laser energy to pass to a photodiode used to trigger a single channel Aventes spectrometer (AvaSpec-2048-USB2). The spectrometer has a measurement range of 200 nm–450 nm with 0.1 nm resolution and a 16-bit converter. Emission from the plasma is transmitted through a fiber optic cable to the spectrometer. Custom software identifies emission peaks of interest and reports on the magnitude of these peaks. The results of the analysis are displayed on a LCD screen in the front of the instrument.

The entire system is controlled using a compact PC (the-BookPC, DE2700) running Windows 7 OS. A microcontroller (PIC32MX460F512L, 80Mz) handles the low level control including triggering the laser, monitoring the encoder, and controlling the vacuum pump, and the depositing system's linear actuator and the stepper motor. The instrument is capable of running autonomously or in manual mode. In autonomous operation, the instrument automatically samples, analyzes, and displays results at preset intervals. Spectral data collected during the analysis are also stored in the instrument's hard drive for retrieval and further detailed analysis if desired.

The instrument was tested by collecting and measuring an aerosol with a known concentration of SiO_2 . The arrangement for these tests, shown in Figure 2, includes a six channel particle counter/sizer (MET One 237) and a sealed mixing chamber with a volume of approximately 80 l that houses a mixing fan and a nebulizer. Makeup air for the aerosol chamber was provided through a HEPA filter to prevent contamination. Prior to testing, the chamber was flushed with filtered air until the particle counter measured below 100 particles/l on all channels. Silicon dioxide powder (Alfa Aesar) with mean particle size of 1.5 ± 0.1 μm was mixed with deionized water and nebulized into the chamber, continuing until the

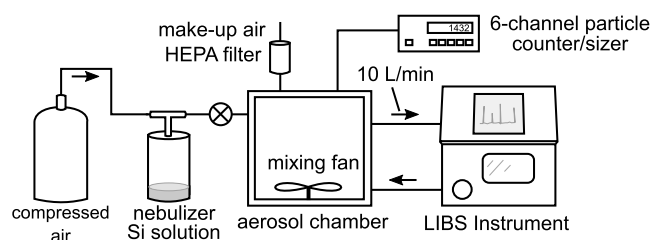


FIG. 2. Schematic of the pure silica aerosol test setup.

particle counter indicated approximately 80 000 particles/l on the counter channels for 1 μm and 2 μm diameter particles. The instrument then sampled aerosol from the chamber for 60 s, advanced the tape, fired the laser, and measured the emission spectrum. The concentration of SiO_2 in the chamber was measured every 30 s during testing using the particle counter. Tests were continued until the concentration in the chamber was less than 5000 particles/l on the 1 μm and 2 μm channels. The chamber was then refilled with silica aerosol and the test sequence repeated. In total, 54 samples were collected and analyzed.

A representative spectrum from a test is shown in Figure 3 with the peaks for silicon and carbon emissions identified. After each test, the whole spectrum was normalized with respect to an emission peak of carbon (247.3–248.6 nm). Normalizing the signal in this way ideally helps to mitigate shot-to-shot variations associated with the LIBS technique.¹¹ Carbon was chosen because it is present in the filter tape at a nearly uniform level, but is not present in the aerosol being measured in this experiment.

Following normalization, the area under an emission peak corresponding to Si (287.26–288.67 nm) was calculated. The results obtained for all 54 tests are shown in Figure 4. Mass concentration of SiO_2 was estimated using particle concentrations measured by the counter/sizer for 1 μm and 2 μm particles, assuming spherical SiO_2 particles and a density of 2.65 g/cm³. Figure 4 shows the linear regression line with $R^2 = 0.78$. For comparison, the same calculations for non-normalized data yield $R^2 = 0.71$, suggesting normalizing has a positive, but minimal, impact on this particular data set.

It is important to note here that normalizing with respect to carbon is effective when the filter tape is the only source of carbon; however, if carbon containing species are present in the aerosol sample, this technique is likely not reliable. A potential alternative is normalizing with respect to the fluorine (from the PTFE tape) emission at 623 nm, an avenue to be explored in future studies. Figure 4 also illustrates the corresponding 95% confidence interval and the 95% prediction interval for the normalized data, as well as the 95% confidence interval on the mean for 20 samples. This latter interval was determined using

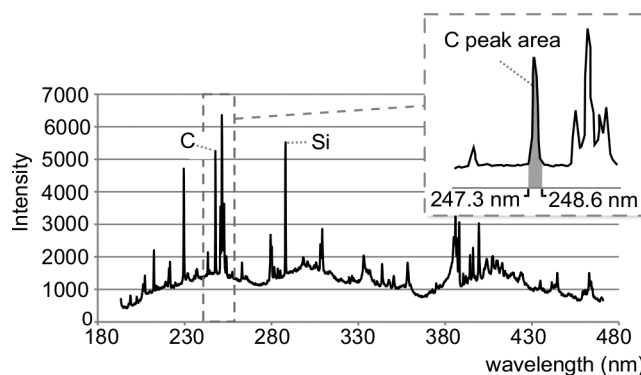


FIG. 3. Representative LIBS emission spectrum of pure silica collected on PTFE filter tape, identifying the emission lines used for analysis. The inset illustrates the carbon peak area used for normalization. Additional strong lines at 229 nm and 251 nm correspond to other carbon and silicon emissions, respectively.

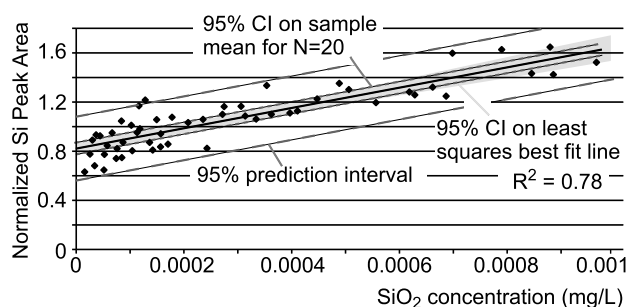


FIG. 4. Normalized LIBS data from pure silica aerosols are shown.

the standard error of the data set and represents the expected bounds ($\pm 6.8 \times 10^{-5}$ mg/l) on an average of 20 samples.

The limit of detection (LOD) for the instrument, determined as three standard deviations of the noise divided by the slope of the least-squares fit in Figure 4, is estimated to be 2.3×10^{-5} mg/l. The noise level for this calculation was found by identifying a frequency range in the emission spectrum with no perceptible peaks and calculating the standard deviation of the signal over that frequency range ($N = 72$). The corresponding limit of quantization (LOQ), defined as the LOD multiplied by 3.3, is estimated to be 6.8×10^{-5} mg/l. NIOSH considers airborne silica to be a health risk at concentrations above 5.0×10^{-5} mg/l.¹ While this value is near the LOQ with 60 s sampling time, the instrument can be operated at longer sampling intervals to increase the signal without greatly reducing response time. It is important to note as well that LIBS measures total silicon (Si), not silica (SiO₂) exclusively. To account for other silicon containing minerals (e.g., kaolinite) potentially present in field samples, a correction scheme can be applied to more accurately represent the amount of respirable silica.¹¹

The prototype LIBS instrument described here has shown promise in rapidly monitoring the concentration of airborne

silicon containing compounds at a concentration level defined by NIOSH as harmful, suggesting that it can provide faster identification of potentially hazardous conditions than is currently utilized. In addition, the instrument can, in principle, be adapted to a wide range of concentrations by altering the sampling time, and potentially used for other airborne particulates due to the general applicability of LIBS.

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