



A Novel Approach to Measurement of Atmospheric Fine Siliceous Particulate Matter

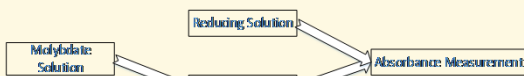
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Motivation

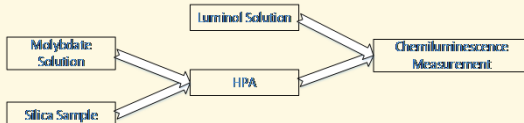
Due to the harmful health effects of respirable crystalline silica, the National Institute of Occupational Safety and Health (NIOSH) has recently updated the personal exposure limit to an 8-hour average of 0.05 mg SiO₂/m³. The EPA regulates PM 2.5 and PM 10, but has not established a standard for particulate silica. Hydrofracturing for petroleum extraction has increased the production and use of industrial sand, leading to concerns of increased exposure hazards. Current analysis techniques require *ex situ* analysis using involved preparation steps and expensive equipment, while our proposed method is inexpensive and enables *in situ* measurements on a relatively quick timescale. In this work, we tested the well-established^{1,2} heteropoly blue method alongside a novel chemiluminescence-based measurement.

Heteropoly Blue Method



- A silica-containing sample and a molybdate solution were combined to form a heteropoly acid (HPA).
- The HPA is reduced with 1-amino-2-naphthol-4-sulfonic acid, which converts the HPA to heteropoly blue complex.
- The absorbance of the solution is measured at 820 nm.

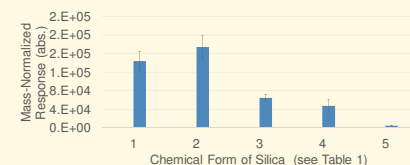
Chemiluminescence Method



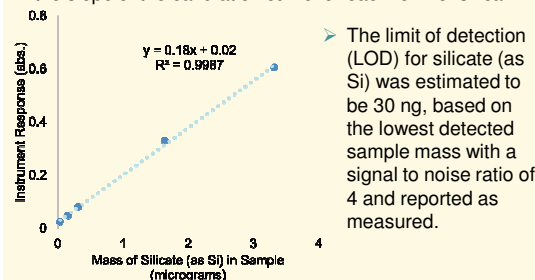
- Several forms of silica were tested; see table 1.
- This method is the same as the above, except the HPA solution is reacted with a luminol solution^{3,4}, which produces a quantitative amount of light at 445 nm.
- Chemiluminescence (CL) measurements are generally highly sensitive due to low background levels.

Table 1	Chemical Form of Silica
1	Sodium Silicate (aqueous)
2	Colloidal Silica (0.05 microns)
3	Silica Gel (60-80 mesh)
4	Silica Gel (<40 μm particles)
5	Amorphous silica (0.5-10 microns) suspended in 0.8 M sulfuric acid with 1.5 ppm NaF added

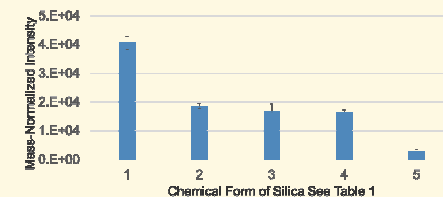
Heteropoly Blue Results



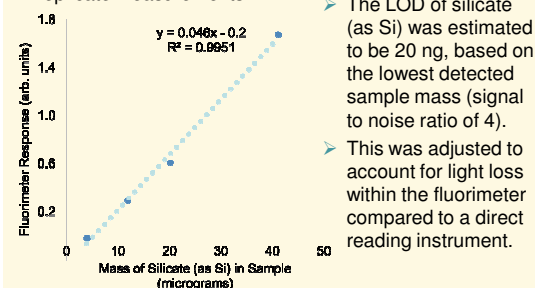
- Mass-normalized values are calculated as the instrument absorbance divided by the mass of Si the analyte.
- Uncertainties are reported as the standard deviation of the slope of the calibration curve for each form of silica.



Chemiluminescence Results



- Measurements were normalized to mass of Si in sample and also corrected using a standardized CL reference reaction to account for day-to-day instrumental variability.
- Uncertainties are reported as one standard deviation of replicate measurements.

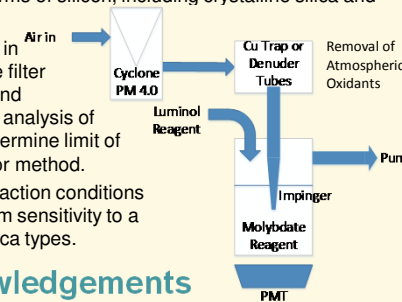


Conclusions

- Chemiluminescence is detected and absorbance is measured for several different forms of silica.
- But there is a wide range of sensitivities depending on the chemical form of silica analyzed.
- Species that were more solvated by water tended to give higher responses using both methods.
- This is most likely due to reduced reactivity of more stable forms of silica, leading to incomplete conversion to HPA – we need to continue to optimize the chemistry.
- The improved sensitivity of CL relative to absorbance measurements is now estimated from instrument design parameters, but the fluorimeter has low light transmission and poor reproducibility – to establish these explicitly, a direct-read instrument must be designed and built.
- A sample volume of only 10 liters of air is estimated to reach the NIOSH personal exposure limit (PEL) using the proposed CL technique, the LOD for silicate (as Si), and instrument design (below), using conservative estimates of light capture efficiency and throughput. Given the reduced reactivity currently observed for SiO₂ compared to silicate, this would still enable silica measurement at the PEL in less than 1 hour of sampling at 5 liters per minute airflow.

Future Work

- Continue research on analysis sensitivity of different chemical forms of silicon, including crystalline silica and “frac” sand.
- Test design in the lab; use filter collection and gravimetric analysis of silica to determine limit of detection for method.
- Optimize reaction conditions for maximum sensitivity to a range of silica types.



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References

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