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Atmospheric Measurement Techniques Discussions

Interactive comment on "Quantification of toxic metallic elements using machine learning techniques and spark emission spectroscopy" *by* Seyyed Ali Davari and Anthony S. Wexler

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1. My major concern is that quantification of deposited samples on the electrode should be difficult. The accurate known amount of deposited mass will guarantee the improvement of quantitative performance of the spark system. How to control the mass of deposited elements on a 1 mm diameter tungsten ground electrode of the spark system for emission analysis? The use of a micropipette was sufficient to control the mass of certain element on the electrode?

Authors' Response: First of all, the authors would like to thank the reviewers for their time and effort in evaluating the manuscript. As the reviewer accurately mentioned,

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Discussion paper

the amount of deposited material would change the spark-induced plasma response. In our experiments, we used a 10μL pipet and added the solution with known concentration in small increments. This would assist us to control the deposition process in order to minimize solution loss to electrode's wall. The choice of 10μL pipet was not obvious. Many experiments were performed with many pipette configurations before settling on this choice. Using large pipets make the deposition control difficult, and hence introduces errors in the amount of deposited mass.

2. Is this spark system applicable for the ambient PM samples, which should be their target in the future as stated in introduction? The airborne particle deposition on the electrode would be totally different from current configuration where the solution was deposited with the use of micropipette.

Authors' Response: The authors agree with reviewer. At this stage, our focus was to develop a low-cost core of an instrument that can be used to detect and quantify toxic metals in atmosphere. The current set-up can be employed to characterize ambient PM by adding a nozzle to deposit particles onto the electrode. Previous studies have shown the feasibility of such a design (Diwakar and Kulkarni 2012). Compared to those studies, we aimed to illustrate the possibility of setting-up similar systems at low-cost. We accomplished this goal by designing and prototyping the expensive components such as spark generation, delay generator, and controlling unit.

3. Most of contents in this paper were related to machine learning process for analysis of emission spectra, not much about aerosol measurement systems. In my view, it might be more appropriate to submit this study to machine learning or AI journals.

Authors' Response: The main reason that we incorporated two machine learning (ML) algorithms in our study was to address issues related to low-cost components and improve the system performance. Indeed, here our main objective is to introduce a low-cost system that can detect and quantify toxic metals in air in an affordable fashion. However, we want to illustrate the potentials that these ML techniques have for the

community. With the progresses in cloud-based platforms and AI, it is essential to adopt these technologies in fields where they can be beneficial. In the work presented here, we have not developed new ML algorithms. Instead, we have employed standard algorithms on the data generated by this system in order to predict concentrations.

More detailed schematics for experimental setup should be useful. Figures 1 and 3 would be moved to supplementary materials.

Authors' Response: The main reason that we provided those figures was to show the low-cost perspective of the paper and the possibility of designing a low-cost set-up for such a measurement.

"For each element, 0.1, 1, 10 and 100 ng of mass were deposited on the ground electrode. For each concentration, 10 spectra were collected using 2 μg delay between the observed and recorded emissions." How to obtain the mass here ? More explanation is required here. The delay time unit would be μs, not μg.

Authors' Response: The authors would like to thank the reviewer for correcting our error. This has been addressed in the revised manuscript at Pg. 6, Line 126: "For each element, 0.1, 1, 10 and 100 ng of mass were deposited on the ground electrode. For each concentration, 10 spectra were collected using 2 μs delay between the observed and recorded emissions." We purchased standard samples with known concentrations and then diluted them to known concentrations. By taking specific volume out of the diluted solution, we were able to calculate the mass that was deposited on the ground electrode. In order to address the reviewer comment, we have added the following at Pg. 5, Line 112: "The total mass can be calculated from the deposited volume and solution concentration."

Any effect of delay time control on the emission spectra?

Authors' Response: Previous studies including the authors' (Davari, Hu et al. 2017, Davari, Hu et al. 2017, Davari, Masjedi et al. 2017) have shown that by increasing the

delay time, the continuum emission decreases. At the same time the plasma species emissions also decreases, but for some species it is possible that the continuum decreases more quickly than the signal and hence improves the signal-to-noise ratios. In this study, we have chosen 2μs for all measurements. Since the optimum delay varies based on the element of interest, it would not be practical to change the delay time especially if we do not know the type of element in advance. Our main purpose was to have a system with performance that is independent of the delay, independent of knowing the type of elements of interest in advance. Having a short delay will suppress the elements signal, and a long delay will lose information and intensity level. Moreover, it has been shown that usually after 1μs the local thermodynamic equilibrium is established, which assists us to diagnose the plasma characteristics.

More explanation on the spark energy? Can you guess plasma temperature? How stable the spark energy ? You may discuss this with laser induced plasma system.

Authors' Response: From Lochte-Holtegreven (Lochte-Holtgreven 1968) and based on the Boltzmann distribution, the emission from an energy level k is equal to:

$$I_{em} = h\nu_{ki} N_k A_{ki} \tag{1}$$

$$N_k = N \frac{g_k e^{-\frac{E_k}{k_B T_{exc}}}}{U(T_{exc})} \tag{2}$$

Replacing Nk from equation (2) into (1) gives:

$$I_{em} = \frac{hcN}{U(T_{exc})} \frac{g_k A_{ki}}{\lambda_{ki}} e^{-\frac{E_k}{k_B T_{exc}}} \tag{3}$$

Therefore, taking the logarithm of both sides, we obtain:

$$ln(\frac{I_{em}\lambda_{ki}}{g_k A_{ki}}) = -\frac{E_k}{k_B T_{exc}} + ln(\frac{hcN}{U(T_{exc})}) \tag{4}$$

Considering various transition of a species, one can plot $ln(\frac{I_{em}\lambda_{ki}}{g_k A_{ki}})$ as a function of normalized upper energy level $\frac{E_k}{k_B}$. Based on equation (4), the slope of the linear fit to the Boltzmann plot (a) indicates $\frac{-1}{k_B T_{exc}}$. Therefore, the plasma excitation temperature is obtained as:

$$T_{exc} = -\frac{1}{a} \tag{5}$$

Following the procedure using the Tungsten lines: