

31-January-2017

AMT-2016-323 - Calibration of a photoacoustic spectrometer cell using light absorbing aerosols.  
A technical note.

Dear Herrmann:

We would like to thank the Editor and the Reviewers for the thoughtful and helpful remarks. We are convinced that these comments helped us to improve the manuscript. Following the reviews, we modified and explained more clearly issues suggested by the reviewers. As you can see below, we have addressed all comments made by the referees.

Reviewers' suggestions and remarks:

**A. Petzold (Referee#3):**

The presented work tackles the important experimental question of how to calibrate photoacoustic aerosol instruments for wavelength regimes where no reference gases are available. The authors suggest the use of light absorbing aerosols generated from nebulized light absorbing organic materials which were preselected in size before measurement by means of an electrostatic classifier. The reference absorption coefficient for the calibration is calculated from the size of the aerosol by using Mie theory. The required complex refractive index for the material is determined experimentally by means of spectroscopic ellipsometry. The presented work builds on carefully conducted experimental studies and deserves publication in AMT after consideration of one major concern which is discussed below.

**Replay: We thank Dr. Petzold for the time and thoughtful comments to the manuscript.**

**SPECIFIC REMARKS**

1. My major concern refers to the calibration procedure. The method of generating particles of given size and spherical shape, and calculating the absorption coefficient from measured number concentrations by Mie theory is justified and works well for

calibrating optical instruments. Here, the additional complexity arises from the fact that the complex index of refraction for the used materials has to be determined separately. The authors demonstrate the robustness of their approach by comparing calibrations with three different materials. They found similar instrument responses for all materials, which is shown in their Figure 5.

On the other hand, they applied the accepted methodology of using ozone as a light absorbing gas at the selected wavelength of 404 nm. The ozone calibration however produces an instrument response two times higher than the values found for particulate calibration material.

To me, it has to be discussed in more detail which process can cause the differences between the calibration using light absorbing gases or particles.

**Replay:** We appreciate this comment and have done our best to trace the source of the differences. We describe the study and all the steps we conducted in order to understand this and we welcome following work by our colleagues who use same instrumentation.

It would be highly beneficial to show simultaneous measurements of light extinction and scattering coefficients and apply the difference method.

**Replay:** Unfortunately, we do not have a nephelometer at 404 nm so the extinction minus scattering validation of the absorption coefficient could not be applied here.

A separate proof of the robustness of the calibration by particulate matter combined with Mie theory would be a convincing argument which is not yet given.

**Replay:** We show for three different light absorbing organic materials that O<sub>3</sub> calibration of the PA-CRD-S system results in significant over estimation of their absorption coefficient. While aerosol calibration adds technical complexity and uncertainty compared with gas phase calibration we are certain that sufficient evidence was presented

to show that significant bias in light absorption properties may be avoided using the proposed methodology.

2. A full theoretical description of photoacoustic signal generation is provided by Petzold and Niessner (1996), however for an azimuthal resonator. Together with the description of a longitudinal photoacoustic resonator given by Arnott et al. (1999), the authors may investigate potential sources of this discrepancy between the calibration approaches also on a theoretical basis.

Replay: The proposed papers were considered and are cited in the main text. However, non of them described results which may be related to what we results described in our manuscript.

#### MINOR COMMENTS

1. Line 45: The correct reference is Müller et al. (2011).

Replay: Corrected

2. Line 49: correct: “: : : to measure : : :”

Replay: Corrected

3. Line 82: correct: “: : : photolyses : : :”

Replay: Corrected

4. Line 203: I assume the later used acronym SE refers to spectroscopic ellipsometry. If this is the case, it should be introduced here.

Replay: The acronym SE was introduced in this line

5. Line 285: correct "PAS instrument".

Replay: Was corrected

6. Figure 5: It should be noted in the y-axis title that the absorption coefficient is obtained from Mie theory.

Replay: The following line was added to the figure caption: "Absorption coefficient for the nigrosin, SRFA and PPFA were calculated using Mie theory routine."