Response to referee comments

Manuscript Number: amt-2024-134

Performance evaluation of an online monitor based on X-ray fluorescence for detecting elemental concentrations in ambient particulate matter
by I. Trebs et al.

Anonymous Referee #2

Reviewer–8¿The manuscript describes the use and evaluation of an online energy-dispersive X-ray fluorescence (EDXRF) detector, the Horiba PX-375, for elemental analysis of ambient particulate matter. The team characterized the performance of the detector, including its limit of detection and measurement uncertainties, and compared the field measurements.

This online EDXRF technique offers advantages for non-destructive, near-real-time, and continues measurements, as well as source apportionment. A comprehensive study and understanding of the detector's performance is highly desired. I would recommend accepting the manuscript with minor edits.

Reply to Reviewer #2: We would like to thank the referee for the positive evaluation of our manuscript. The proposed revisions will substantially improve the quality of the paper. Please find our detailed responses below:

Line 160-171: Equations (1) and (2) need clarification. In particular, is the standard deviation term the average of three standard deviations? Also, how is the calibration curve derived?

Reply: The details for these equations are described in the text, line 167: "The σ_b is calculated from the average of the standard deviation of each measurement (n = 10)". The reviewer is correct, the standard deviation is the average of three σ_{bi}. We will add some more details in the text.

The calibration curve is derived by plotting the blanks and concentrations of the UCD standards (ME-233, ME-234) with the instrument response (intensity x0) for each standard. This results in scatter plots with three data points and linear regression analysis is used to obtain the equation to derive the mass of the samples (normalized by the sampled air volume). An example is shown in Figure 3. The convention is to plot the instrument response data on the y-axis and the values for the standards on the x-axis. This is due to the assumption that the errors in the instrument response values (due to random variation) are greater than those in the values assigned to the standards. However, we reversed this plotting scheme as this is not the case for our data because the standard uncertainty of the ME-233, ME-234 (10-20%) is larger than the precision (random variation) of the instrument. We will add some more details in the text.

Line 175-177: Is the standard uncertainty calculated from the mean of a series of observations, or from the standard deviation of the observations, or from several means of several series of observations?

Reply: In lines 152-154 it is stated that the **"**Type A evaluation of uncertainty was conducted by a check standard procedure including three sequential measurement series (each with n = 10) of both ME-RMs from UCD and deriving the standard deviation (precision) and bias for each element." We will add some more information in the text directly related to this calculation.

Line 198-199: Are 50 kV and 15 kV the energies of the incident photons radiating the samples? Or are they the incident beams hitting some targets, generating photons that then excite the samples. My understanding from the manuscript (Line 137) is that they are the incident photon energies directed at the sample. However, in that case, I am not sure why 50 kV is used instead of 15 kV for Fe. Fe is excited with 15 kV and has a higher cross section at 15 keV than 50 keV. In fact, many elements listed in the 50 keV section of Table 2 should be excited with 15 keV incident photons. It may be helpful to include more instrument details.

Reply: Yes, they are the incident photon energies directed at the sample. We clarify this in the manuscript. When the tube voltage is 15 kV, the maximum energy of the X-rays irradiated to the sample is 15 keV, and the intensity of the X-rays (7.11 keV or higher) that can excite Fe is weak, so Fe cannot be excited efficiently. A tube voltage of 50 kV results in better excitation efficiency.

Line 240: Does "self-absorption" here refer only to the signal absorption by the particles themselves, or does it include more general signal absorption, such as by the air path, detector window, etc.? Corrections for the air path and window thickness should be implemented in the data quantification. The impart of particle absorption can be estimated by the size of the particles.

Reply: It refers only to signal absorption by the particles. This, however, cannot be quantified at the exact size of the individual particles is unknown. Elements are quantified considering the conditions of the detector and its surroundings (air path and window thickness). We will add some more details about this in the revised manuscript.

Lastly, I suggest adding a description of the spectrum analysis, including, for example, spectrum fitting and peak identification.

Reply: When the energy is assigned to the horizontal axis and the pulse counts to the vertical axis, the values obtained by the multi-channel analyzer are shown as a spectrum on the LCD. The constituent elements are identified by the peak positions on the spectrum and quantitatively analyzed by the peak height. We will add some more details about this in the revised manuscript.

Technical corrections:

Line 82, should be "several months"

Reply: This typo will be corrected.