Review of

"Performance evaluation of an online monitor based on X-ray fluorescence for detecting elemental concentrations in ambient particulate matter"

Summary

The authors describe the use of an online XRF instruments to detect metallic constituents of particulate matter. The instrument is evaluated in controlled, laboratory settings as well as at field sites in Luxembourg with varying anthropogenic influences. Online XRF is a relatively new method, and this work helps fill in gaps of evaluation and near-real time observations. There are a few areas that could be improved prior to publication.

Scientific Questions/Issues

Line 32 – It was surprising for OC and EC to be listed first in the description of PM. First, because they are generally not the dominant components by mass, nor are they chemically defined. The EC and OC parameters are operationally defined depending on the method of analysis. I would recommend moving these after SNA at least.

Line 59 – "difficulties in the analysis of trends" should be elaborated, since several large networks have been deducing atmospheric trends using discontinuous collection on filters for decades.

Lines 83-84 – I recommend including the latest census population estimate with "moderately inhabited rural area", as this can mean very different populations internationally.

Line 130 and subsequent – The ordering of the elements is not conventional. I am guessing that this was done purposely to highlight elements analyzed at the two different energy levels. You may choose to order your elements by atomic number, which aids interpretation of the results and figures.

Line 131 – The US EPA does not manufacture or specify a manufacturer for PM10 inlets. I recommend listing the actual manufacturer for clarity.

Line 167 – Based on the description, it sounds like $\sigma_b$ is calculated from three standard deviations (n=3), one from each set of 10 blank analyses. If that is not correct, maybe more clarity is required here.

Section 2.5 – Are there any uncertainty estimates or potential for stretching of the PTFE membrane? If not, this should be stated.

Table 2 – This table would benefit from an additional column showing LoD estimates from an applicable air monitoring program, such as EMEP or Eurotrac-2.

Line 229 – Many readers will find fault with the use of "perfect" in an experimental result. I suggest replacing with a different adjective (e.g., strong) validated with the metric you used to evaluate it (e.g., $r^2 = 0.99$).

Lines 241-243 – XRF sensitivity to light elements decreases only under insufficient atmospheric control. LoD for light elements can be similar to other elements when using vacuum (< 1mTorr) or even with

helium purge. The choice of detector also matters; Ge and CdTe detectors have inherently low sensitivity to light elements while Si and Si-vortex can have better sensitivity.

Figure 4 – While this view of the precision results is sufficient, it may be better represented with mass loading on the x-axis and viewed as a scatterplot. This may help explain the observed differences.

Line 276 – How was the 20 % Type B uncertainty determined?

Table 4 – The Remich and Vianden instrument comparisons are both close to 10 % while Belvaux is ~ 50 %. This should be discussed or noted for further investigation.

Lines 381-384 and Table 6 – This is not a valid argument or presentation of the data. Trace elements are so called because they contribute little to total mass under normal circumstances. Chronic exposure to elevated levels of toxic metals can induce health effects, in spite of its percent contribution to total PM10 loading. For example, Ni may be three times the EU limit of 20 ng/m$^3$ and only contribute 0.15 % to an acceptable level of PM10 (< 40 µg/m$^3$).

A better comparison would be to calculate relative differences or enrichment with regard to either local geology or the most rural site.


Technical Corrections

Line 65 – "… breakdown spectroscopy determine allow for a …"; maybe just "determine"

Line 137 – The "X" in "X-ray" should be capitalized.

Line 152 – The citation for GUM should be capitalized.

Lines 161 and 164 – The citations for IUPAC should be capitalized.

Figure 2 – There is an excessive amount of space below -15 % and error bars would be useful.

Line 274 – "… achieved due to the carful filter tape …"; maybe "… due to careful filter …"