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Interactive comment on “Quantitative measurement of PM₁₀ by means of X-ray fluorescence spectra” by E. Busetto et al.

E. Busetto et al.

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We want to sincerely thank Referee #4 for his observations, which gave us the opportunity of better highlight details of our experiment.

Firstly, we think it is necessary to stress that it definitely wasn't our intention to build or promote a new commercial instrument, and our effort was more methodological than strictly technological.

We operated in collaboration with our local EPA, into a wider environmental project in which the PM-SMS is just one of the possible (prototype) instruments, but designed fulfilling all the needs of the project, mainly the complete compatibility with the existing methodologies and standards of our partner, and the presence of a customised soft-

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ware able to manage the machine, analyse data and remotely communicate with EPA servers, interfacing the rest of the system and software.

The project give us the opportunity of develop and test a new machine together with an alternative and simple calibration methodology, using self-made preparations, rather than a collection of certified standard samples.

We also not specified enough that we moved not looking for operating parameters giving the best performance possible but strictly into the existing methodologies and standards of our partner. We want also to point out that for an hypothetical commercial use, the machine, being realised with XRF low-cost technologies, should be necessarily upgraded, at least at levels close to the existing commercial devices.

In the following, we tried to answer every raised question.

- 1 However is is not explained how the sampling is done. In the title PM10 is mentioned but in the text the authors only write about PM. It is not explained how the transfer from the sampling position to the measurement position is done, or in general how the instrument operates.**

The transfer of the samples from the sampling position to the measurement position is automatic, trough a specific mechanism inside the machine. Details will be furnished in a revised version of the paper.

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- 2 The use of the microfiber quartz filters is not motivated. It is known that they normally have a high blank and that particles penetrate into the filter, so that the thin film condition is no longer satisfied especially for elements emitting low energy characteristic x-rays.**

Quartz filters are the ones in use by our partner, and we wanted to be completely compliant with their procedures. The pumping system ensure a laminar flux, that cause the particulate to be homogeneously deposited in the filter, mostly on the surface. X-ray absorption effects coming from the filter are negligible, so we can imagine the particulate contributing at the XRF signal as a thin layer.

Our calibration method wanted to reproduce this layer of material, and the results showed that is realistic.

- 3 The excitation conditions of the XRF part of the instrument seems to be rather poor. The spectrum shown in figure 2 shows a very high continuum. The Ar peak from the air is higher than the peak from the element deposited on the filter (Fe). Also the count rate, a few thousand counts per hour, seems extremely low (2000 counts/hour = 0.5 counts per second!).**

We do not stressed out that our instrument is actually a prototype. For example, no vacuum system is equipped inside the instrument, and also the detecting system is a low-cost one. We used the partnership with our regional EPA (A.R.P.A. FVG), in order to develop and test the machine in their standard condition for environmental applications, using the Directive 2008/50/EC of the European Parliament and the European standard EN1234 (for PM10).

The scope of our study was to demonstrate that the machine concept, the calibration methodology, the data analysis could give correct results, and, eventually, determine defects, limits, possible upgrades and applicability to context different to PM10 airborne

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particulate matter monitoring.

The sampling time to achieve enough statistics depends from the concentration of the material and the sensibility at its XRF peak energy. By the way, the sampling and the analysis time are strictly connected with the capability of detecting a peak upon the noise and the minimum amount of material in order to be able to detect it in the chosen sampling time.

Noise has been measured acquiring the XRF spectrum of a clear Quartz filter (“white” spectrum). This spectrum represents what systematically overlap the XRF photons coming from the materials under investigation. The “white” spectrum is composed not only by the background noise, but moreover by the XRF spectrum of the materials already present in the system (i.e. Argon from the air, Silicon from the filter itself).

The root-mean-square deviation calculated on an interval of the “white” spectrum (we used a 50 channels sampling) can furnish an evaluation of the fluctuations coming from the noise only, at different energy values, and a possible evaluation of the threshold of counts (consequently a threshold on the mass) over which it is possible to distinguish an XRF peak coming from a material deposited on the filter, using the following equations:

$$\text{noise}(\text{channel}_i, \text{channel}_f) = \sqrt{\frac{\sum_{k=1}^n (N^{\text{counts}}(\text{channel}_k) - \overline{N_{if}^{\text{counts}}})^2}{f - i}} \quad (1)$$

$$\overline{N_{if}^{\text{counts}}} = \text{averagecountsvalueintherange}(\text{channel}_i, \text{channel}_f) \quad (2)$$

Normalising the number of counts respect to the analysis time, so calculating a frequency, and converting channels in energy, the peak of an element can be considered distinguishable with the following relationship:

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$$\nu_{if}^{noise} = \frac{noise(energy_i, energy_f)}{t_{analysis}} \quad (3)$$

$$\nu_{peak}^{element} > m \cdot \nu_{if}^{noise} \quad (4)$$

where k is an energy value inside the range i and f , and m is a multiplying factor to be determined.

This relationship has been used to identify the sensitivity of our measurement of the quantity of mass of the elements present on the filter.

In order to understand how to evaluate this sensitivity, i.e. how to choose the factor m , we compared real spectra, using samples where we put a known quantity of mass of a single material, with different analysing time, verifying which one could be considered a good compromise between visibility of the XRF peaks and duration of the measurement.

As an example, in figure 1 is shown a study on peak of Manganese coming from few micrograms of material, with analysing time from 1200s to 7200s. In the while, we analysed also the factor m , which actually define the threshold on the counts for the detectability of a peak, and consequently the threshold on the mass of the material, verifying, for every material and analysing time, the visibility of the peak with $m=1$, 2, and 3. In figure 2 is possible to see such a study.

At the end of our investigation, with all the materials, we decided that 3600s of analysing time and a $m=2$ was that compromise, which allowed us to reject not existing peaks without reducing significantly the sensitivity, which is summarised in the following table, where the limit mass is obtained with the following equation:

$$m_{limit}^{element} = \frac{2\nu^{noise}}{slope_{calibration}} \quad (5)$$

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| Element | Peak Energy (KeV) | Limit Mass (μg) |
|---------|-------------------|------------------------------|
| K | 3.314 | 6.5 ± 0.2 |
| Ca | 3.690 | 0.9 ± 0.1 |
| Cs | 4.286 | 7.2 ± 0.1 |
| Ba | 4.465 | 6.5 ± 0.1 |
| V | 4.949 | 1.3 ± 0.1 |
| Mn | 5.895 | 2.1 ± 0.1 |
| Fe | 6.400 | 1.0 ± 0.1 |
| Co | 6.925 | 1.4 ± 0.1 |
| Ni | 7.472 | 3.7 ± 0.1 |
| Cu | 8.041 | 1.7 ± 0.1 |
| Zn | 8.631 | 0.9 ± 0.1 |
| Hg | 9.987 | 16.7 ± 1.0 |
| Pb | 10.550 | 19.6 ± 1.1 |
| Br | 11.907 | 7.2 ± 0.2 |

Even if the sampling time in situ should strictly depends on this sensitivity, and should be determined in a similar way, we adopted as the typical sampling time, the one adopted by our EPA: 24 hours.

4 In the quantitative comparison of this instrument with other techniques (ICP-AES in table 1 and figure 4) only Ca and Fe are shown. Detection limits are not mentioned. This gives the impression that the instrument is not sensitive enough for real environmental monitoring. This impression is further supported by the fact that sampling periods of 48 hours are used.

We presented Ca and Fe as to be considered an example of the method application and results, being the ones more frequently present on the filters. Of course, also

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the other cited elements where present on the filter, and have been measured and compared as well. In a revised version of the paper we will show the other results.

Referring to the table 1, and we can show the detection limits for 1 hour sampling time and 24 hour sampling time.

| Element | 1 hour minimum detection limit ($\mu\text{g}/\text{m}^3$) | 24 hour minimum detection limit ($\mu\text{g}/\text{m}^3$) |
|---------|-------------------------------------------------------------|--------------------------------------------------------------|
| K | 2.83 | 0.12 |
| Ca | 0.39 | 0.02 |
| Cs | 3.13 | 0.13 |
| Ba | 2.83 | 0.12 |
| V | 0.57 | 0.02 |
| Mn | 0.91 | 0.04 |
| Fe | 0.43 | 0.02 |
| Co | 0.61 | 0.03 |
| Ni | 1.61 | 0.07 |
| Cu | 0.74 | 0.03 |
| Zn | 0.39 | 0.02 |
| Hg | 7.26 | 0.30 |
| Pb | 8.52 | 0.36 |
| Br | 3.13 | 0.13 |

Finally, we should better specify that the first campaign of measurement was done not in the EPA areas, but was just a test of both the machine and the procedure.

For this reason even if the machine operated following the realistic condition we decided to pump material with many different sampling time, in order to verify also the behaviour of the filters and stress the machine (we also sampled for 72 and 96 hour).

For this first test we adopted 48 hour because we wanted to collect significant amount of particulate considering that the Elettra Park is on the top of an hill, with a good quality

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of the air. In fact, successively, comparing daily XRF spectra coming from the machine in the Elettra park and the ones coming from the machines downtown, we found them very similar but with the intensity reduced of more than half.

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