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Atmospheric Measurement Techniques
Discussions

Interactive comment on "Quantitative measurement of PM_{10} by means of X-ray fluorescence spectra" *by* E. Busetto et al.

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We want to sincerely thank Referee #1 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-

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 pag. 4314, line 4: elements like Al, Si, S, Cl which are relevant for aerosol studies are missed; the authors should give a comment about this

We do not stressed out that our instrument is actually a prototype. 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.
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 particulate matter monitoring.
For this reason, because of a time limit, even if the machine is actually capable of detecting XRF signals from elements with atomic number from 13, we limited our study on a list of elements indicated by our partner as the ones on which they usually focus their attention.
Thus, we did the full calibration of just one of the three machines realised (the one

installed in the Elettra park), limiting to such a list the other two, gone downtown for the in-situ test, and then we showed the calibration data as starting from Potassium.

2 the authors use quartz filters: why did they make this choice? quartz filters often present worse blank levels respect to other kind of filters

Quartz filters are the ones in use by our partner, and we wanted to be completely compliant with their procedures.

3 §2: most of the relevant technical parameters are not given in the article, only a qualitative description is given, which is not appropriate for a scientific publication.

3.1 pag 4317, lines 14-22: which kind of inlet is used (PM10, PM2.5..)? is it possible to change it?

We used TCR TECORA PM10 inlet which is the one commonly in use by the A.R.P.A. instrumentation. The head could be replaced with a PM5, PM2.5 as well.

3.2 Which is the air flux?

The air flux is regulated by a pumping system, together with a set of vacuometers, which allows the system to monitor the flux and eventually tuning the pumping speed in order to keep the flux constant.
Again we used the configuration adopted by the A.R.P.A and the flux is set to 38.33 L/min. The air pumping system is also equipped with a set of thermocouples and

hygrometer, allowing to monitor and calculate also the air density, in order to properly calculate the concentration of the materials deposited on the filter.

3.3 Which are the dimension of the filter? Since the areal density of the deposit is an important parameter to obtain a good sensitivity this is a relevant information.

The filters we used are the standard 47mm quartz filters used by A.R.P.A. PM10 instruments (i.e. TCR TECORA AD99-007-0008CR, or Munktell Micro-Glass fiber filters). The area of the particulate spot is a 20 mm diameter disc. The area exposed to X-ray is a 25 mm diameter disc.

3.4 Was any comparison made with a certified sampler at least to compare the total aerosol mass?

We do not measure and compare the total mass of PM10 with a certified laboratory, considering it out of our scope, because our instrument is not able to measure it. We compared our results giving the collected filters to two different certified laboratories, as explained in the paper, in order to independently measure the mass of the elements present on the filters with a different technique (ICP-AES and ICP-MS).

3.5 Which is the typical sampling time to obtain sufficient statistics for the most relevant elements? Which is the minimum analysis time to obtain sufficient statistics for the most relevant elements?

The sampling time to achieve enough statistics depends from the concentration of the material and the sensibility at is 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:

$$noise(channel_i, channel_f) = \sqrt{\frac{\sum_{k=1}^{n}(N^{counts}(channel_k) - \overline{N_{if}^{counts}})}{f-i}} \tag{1}$$

$$\overline{N_{if}^{counts}} = averagecountsvalueintherange(channel_i, channel_f) \tag{2}$$

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:

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

$$\nu_{peak}^{element} > m \cdot \nu_{if}^{noise} \tag{4}$$

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:

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

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.

3.6 Which are the dimensions of the detector and which is the distance from the sample?

The detector is a Si-Pin diode by Amptek Inc., with a sensible area of 6 mm^2 and thickness of 500 μm. Its resolution at 5.9 keV is 165 eV. The distance from the sample is 35.1 mm.

3.7 Why a Mo target was chosen?

A Mo target has been chosen because we wanted to stimulate the XRF of heavy metals up to the Pb L$_\alpha$. Of course even a Ag target could have been used.

4 Fig. 1 could be removed

ok.

5 Fig. 2: at which concentrations in air correspond the Ca and Cu contaminations due to the filter holder?

The support has been made originally in Delrin, but considering the effect contamination it will be replaced with a different material. By the way at the time of our study the contamination corresponded to approximately: Ca = 12 ± 1 μg, Cu = 5 ± 1 μg. We remember that the calculation consider the presence of the “white” spectrum, which has been measured accurately in order to be subtracted without introducing a significant error. Moreover, for every calibration we verify that the intercept of the linear fit of the “Counting Frequency vs. Mas” plot, which correspond to the 0 mass value, is a value compatible within the errors, with the corresponding counting frequency in the “white” spectrum at the energy of the peak.

6 pag 4318: A basic information are the minimum detection limits (in micrograms/cubic meter) which are obtained by the system. Without these information the performances of the system may be not evaluated.

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 (μg/m^3)**	**24 hour minimum detection limit (μg/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

7 §3: pag. 4319, lines 12-14: Which is the advantage respect to the use of certified standards produced by some companies for XRF calibration?

The advantage is the full control of the quantity of material on the filter, giving the capability of checking the linearity of the response, measuring the conversion factor from counting frequency to absolute mass.
We wanted to calibrate the system material by material, having under control the mass quantity deposited on the filter, the shape and the thickness of the material layer.
This because we needed to verify the linearity of the relationship “Counting Frequency vs. Mass” in our system, measuring with several different (known) quantity of material deposited on the filter. Moreover, matrix effects were to be verified and demonstrated to be irrelevant for our system.
NIST SRM (SRM 1648 or 2783) contains just a single, fixed (certified) quantity of several materials, all together. Of course, a calibrated machine can be “certified” measuring a SRM sample or one of the NIST-traceable standards produced by some companies (Cooper. . .).

8 pag. 4319, line 17: the particulates penetrate into the quartz fiber filter, therefore the standard does not represent the real particulate deposited on the filter. The authors should make a comment.

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.

9 I do not understand the advantage of the use of the new calibration method described by the authors. More comments should be given (see also comment to pag. 4319, lines 12-14)

The main advantage is the capability of checking the response of the machine for several and arbitrary concentrations of materials, without buying customised prepared filters, self producing the samples in an easy way.

10 pag 4320 lines 1-5: I do not understand what the authors say; if the spot of the beam is the same both for the standard and the sample analysis, the determination of the area illuminated by the X-ray source is not critical at all, if it is smaller than the deposit size, like is done in all the XRF commercial devices.

If the spot is smaller than the area of the material deposited on the filter you must be sure of the homogeneity of the material and/or the mass value illuminated by the spot (if someone is interested in measuring the absolute mass). Having a x-ray spot size bigger than the dimension of the area covered by the material ensures that the entire amount of it contributes to the fluorescence and there is no need to take care about homogeneity.
By the way, as the referee correctly says, if the deposit is uniform and homogeneous, concentrations are independent from the dimension of the x-ray spot.

11 pag. 4320 line 17: if such an alteration is not observed, simple certified standards could be used without any problem.

Yes, for sure, but this is a result after verifying the linearity of the response and that the matrix effects is negligible.

12 §4: pag. 4320, line 19: What does it mean “standard operating conditions”? Some numbers are necessary

See also previously. Summarizing:
- Sampling time: 24 hours
- Analysing time: 1 hour
- Air flux 38.33 l/min.

13 pag. 4320, line 22: why 48 hours if the standard sampling period is 24 hours?

Effectively 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 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.

14 No discussion on the procedure which has been used to calculate the experimental error is presented. Which are the uncertainties considered to determine the values reported in the table? Without such a discussion, what the authors say at pag 4321 has no sense

The experimental error must be treated considering the two phases of calibration and in-situ measurement.
The calibration phase is based on the knowledge of the absolute mass of the element deposited on the sample. The mass value is evaluated through the solubility of the salt used for the saturated solution, and the dilution of the saturated solution. The mass value is successively correlated to the intensity of the peak of the corresponding element in the XRF spectrum.
Random errors on the solubility come from the dependency of the solubility with the temperature, and were maintained negligible keeping under control the experimental and environmental conditions during the preparation of the samples.
The knowledge of the mass value of the water used for the dilution is another source of errors, which have been obtained by characterising every instrumentation (i.e. pipettes) used, through repeated measures of the weight of withdrawn liquid with a precision balance. Propagating all the errors, the global error on the mass value ranged from 1% to 15%. This error has been taken into account during the fitting phase of the calibration data, using an error weighted fit.
The value of the peak intensity in the XRF spectrum is using the Savistsky-Golay fit procedure, giving a line fitting the spectrum and the evaluation of the “continuum” as visible in figure 3. The estimation of the peak intensity is given by the following:

$$\nu_{peak}^{element}(Energy) = \frac{N_{Counts}^{Fit}(Energy) - N_{Counts}^{Continuum}(Energy)}{t_{analysis}} \tag{6}$$

Considering negligible the error on the time, the error on the measure of that frequency contains the following contribution:

- statistic error (Poisson distribution)
- error on the determination of the continuum value
- repeatability of the measure

From our analysis the only significant contribution comes from the statistic error.
The calibration parameter (intercept and slope of the linear fit), used for the determination of the absolute mass, are associated to the standard errors calculated by the weighted fit. The absolute value of the mass deposited on a sample measured in-situ, is obtained using these calibration parameters and the measure of the peak intensity on the spectrum (which has the same kind of error already discussed), with the following:

$$m^{element} = \frac{\nu_{peak}^{element} - intercept_{calibration}^{element}}{slope_{calibration}^{element}} \tag{7}$$

The error on the absolute mass is obtained propagating the errors from the calibration parameters and the peak intensity.

15 pag 4320,line 11-13: Why did the authors not analyze one of the aerosol standards produced by NIST which are typical for testing the accuracy of the analytical systems? Furthermore, only results for two elements (Fe and Ca) are reported; no comments about other relevant elements like K, Ni, Cu, Zn, Pb .... are done

The machine has been developed in collaboration with our EPA, which was designed as the “official” referee for every comparison. We remember that we wanted just to verify the validity of the method and not develop a commercial machine. For sure a test of accuracy with a NIST or NIST-traceable standard sample could give an added value. 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 the other cited elements where present on the filter, and have been measured and compared as well.