**Atmospheric
Measurement
Techniques**
Discussions

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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 #3 for taking time in reviewing our paper. We will take into account his observations in a further review of it.
In the following, we tried to answer every raised question.

1 The authors design a new XRF instrument or the modified a commercial one? Technical details must be given.

The project give us the opportunity of fully 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, together with a customised software able to manage the machine, analyse data and remotely communicate with our local EPA servers, interfacing the rest of the system and software. 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 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.

2 p.4 line 22: how are the samples produced? Are they standard samples? They must be better defined

They are self-made samples, consisting in a salt deposited on a polymeric (kapton) film. See also section 10.

3   In the pattern of FIG.1 all the metals are present. Then, have been used five samples or just one for the calibration? How exactly has the calibration been performed?

The calibrator is a special sample containing all the metals inside. The spectrum is collected in Counts vs. (MCA) Channels, then, after fitting the position in channels of every peak (which energy is known), it is possible to plot the following relationship:

$$E(channel) = E_0 + Gain \cdot channel \tag{1}$$

veryfing, also, the linearity of the MCA response.

4   TABLE 1:why only two elements have been considered?

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.

5   p.4 line 29: the mathematical term deconvolution is not properly used.

It is not clear to what the referee is referring to. By the way, see also section 6.

C1855

6   p.5 line 16: errors must be given

ok.

7   p. 5 line 17: what salts have been used? The sample preparation procedure is missed.

The list of the salts is:

Element	Salt	Name
Al		
Cl	$(AlCl_3, 6H_2O)$	Aluminium (III) Chloride
K	CH_3COOK	Potassium Acetate
Ca	$(C_4H_6CaO_4, H_2O)$	Calcium Diacetate Hydrate
V	NH_4VO_3	Ammonium Metavanadate
Mn	$(MnCl_2, 4H_2O)$	Manganese Chloride Tetrahydrate
Fe	$(FeCl_3, 6H_2O)$	Ferric Chloride Hexahydrate
Co	$(CoSO_4, 7H_2O)$	Cobalt Sulfate Heptahydrate
Ni	$(NiCl_2, 6H_2O)$	Nickel Chloride Hexahydrate
Cu	$(Cu(NO_3)_2, 3H_2O)$	Copper (II) Nitrate trihydrate
Zn	$(ZnSO_4, H_2O)$	Zinc Sulfate Hydrate
Br	$NaBr$	Sodium Bromide
Ag	(CH_3CO_2)	Silver Acetate
Cd	$(2CdCl_2, 5H_2O)$	Cadmium Chloride Pentahydrate
Sn	$(SnCl_2, 2H_2O)$	Stannous Chloride
Cs	$ClCs$	Cesium Chloride
Ba	$(BaCl_2, 2H_2O)$	Barium Chloride Dihydrate
Hg	$HgCl_2$	Mercury Chloride
Pb	$PbCl_2$	Lead Dichloride

Not all the element where calibrated, as visible from the published tables, because of a timing issue. See also section 10.

8   FIG.2 The presence of contaminants in the polymeric film is relevant. Wasn't other option?

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 $\pm$ 1 μg, Cu = 5 $\pm$ 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.

9   p.6 line 23: what are the standard sampling rules? A reference must be given. What means "we randomly selected a part . . ."?

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).
We used TCR TECORA PM10 inlet which is the one commonly in use by the A.R.P.A. instrumentation.   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 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; 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.

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:

$$noise(channel_i, channel_f) = \sqrt{\frac{\sum_{k=1}^{n}(N^{counts}(channel_k) - \overline{N_{if}^{counts}})}{f - i}} \tag{2}$$

$$\overline{N_{if}^{counts}} = average\,counts\,value\,in\,the\,range(channel_i, channel_f) \tag{3}$$

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:

C1859

$$\nu_{if}^{noise} = \frac{noise(energy_i, energy_f)}{t_{analysis}} \tag{4}$$

$$\nu_{peak}^{element} > m \cdot \nu_{if}^{noise} \tag{5}$$

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:

$$m_{limit}^{element} = \frac{2\nu^{noise}}{slope_{calibration}} \tag{6}$$

C1860

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.

10 How have the concentration errors been calculated? - Figure 3a and 3b: Have the straight lines y-intercept equals to zero? - Figure 4: This results is quite surprising. How have the experimental errors for XRF values been calculated?

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:

$$\nu_{peak}^{element}(Energy) = \frac{N_{Counts}^{Fit}(Energy) - N_{Counts}^{Continuum}(Energy)}{t_{analysis}} \qquad (7)$$

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:

$$m^{element} = \frac{\nu_{peak}^{element} - intercept_{calibration}^{element}}{slope_{calibration}^{element}} \tag{8}$$

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