

Response to comments of Referee #1

We would like to thank Referee #1 for his valuable and thoughtful comments, which helped us to improve the content and quality of our manuscript. In the following we have addressed all the comments of the Referee #1 and incorporated changes in the manuscript as follows:

Blue: Comments of the Referee

Black: Answers of Authors

Black, italic, "": "Changes in the manuscript"

General:

1. Does the paper address relevant scientific questions within the scope of AMT? Yes
2. Does the paper present novel concepts, ideas, tools, or data? Yes
3. Are substantial conclusions reached? Partly, see major points of criticism.
4. Are the scientific methods and assumptions valid and clearly outlined? Partly, see major points of criticism.
5. Are the results sufficient to support the interpretations and conclusions? Partly, see major points of criticism.
6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? Partly, see major points of criticism.
7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution? Yes
8. Does the title clearly reflect the contents of the paper? Yes
9. Does the abstract provide a concise and complete summary? Yes
10. Is the overall presentation well-structured and clear? Yes
11. Is the language fluent and precise? Yes
12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? Overall, yes
13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? Some parts need clarification and additional detail information. See below.
14. Are the number and quality of references appropriate? Yes
15. Is the amount and quality of supplementary material appropriate? Yes

Thank you very much for this assessment.

- 1.1. Line 55 to 59 describes the technical challenge to which the paper is dedicated: Increasing the detection efficiency of TXRF by complete excitation of the deposit and complete detection of the fluorescence response. The authors present a solution by shrinking the lateral diameters of centric deposit patterns on cascade substrates (carriers) to less than 5 mm and describe an appropriate cascade impactor design. To

the reader the 5 mm criterion seems to be an arbitrary choice and a justification is lacking. A justification could e. g. be derived from an excitation beam profile analysis along with a description of the detector's aperture and lateral efficiency distribution. Both would, e. g. for the used Bruker TStar spectrometer, clearly reveal that other than the authors implicitly assume even within the "5 mm area" the excitation and detection would have radial dependencies, i.e., decrease with distance to the center.

In the TXRF spectrometer used in this study, the excitation beam covers a rectangular area on the sample carrier with a width of 6 mm and a length of 30 mm. This means that the excitation beam covers the area of the sample carrier completely in which the new impactor deposits the particles, namely the centric circle with a diameter of less than 5 mm. This information was added to the revised manuscript in section 3.3, lines 274 to 277 of the revised manuscript, to justify the targeted size of the deposition pattern ("less than 5 mm") and to make it more comprehensible:

„A circular area with a diameter of approximately 5 mm in the centre of the sample carrier is the effective analysis area, which results from the superposition of the area excited by the X-ray beam, namely a rectangular area with a width of 6 mm and a length of 30 mm, and the field of view of the detector.“

The authors agree with the referee that both excitation and detection are not homogeneous over the entire surface of the deposited particles.

These inhomogeneities of the TXRF spectrometer are specific for the model and/or manufacturer of the TXRF spectrometer applied for analysis, and therefore these inhomogeneities are not compensated by the design of the new impactor.

A corresponding statement was added to the revised manuscript in section 3.3, line 277 to 279 of the revised manuscript for clarification:

„Both excitation and detection are not homogeneous over the entire surface of the deposited particles. These inhomogeneities of the TXRF spectrometer are specific for the model of the TXRF spectrometer applied for analysis, and therefore these inhomogeneities are not compensated by the design of the new impactor.“

Last but not least, we would like to reiterate as pointed out in the manuscript that the optimisation of the new impactor is not only in a simple shrinking of the pattern of the deposited particles, but also, for example, in an optimised lateral arrangement of the nozzles in order to enable an optimised cross-flow out of the impaction area. In addition, the impactor was designed for a comparatively low flow rate of 5 l/min in order to reduce the requirements for the pump and its power source; this significantly improves the possibilities for mobile and portable use of the new impactor.

- 1.2. In line 120 authors describe a Reynolds number of ~3000 in the nozzles as a design criterion. This is in my understanding for cylindrical pipes the transition regime between turbulent (>3000) and laminar (<=2300) flow. In line 125 to 130 authors describe that the flow profile in the nozzles should be "plug-shaped", i. e. turbulent, rather than "parabolic" aka laminar. This is in contradiction to line 137, where a Reynolds number of < 3000 is described as desirable. The relation between number and diameter of nozzles and mean velocity could be described more precisely and as a

design challenge. It is desirable to have the finally applied ratios of nozzle lengths to diameters presented as a result of theoretical calculations or CFD modelling.

Both (a) an upper limit $Re_{\max} = 3000$ for the Reynolds number Re and (b) a laminar rather than a turbulent nozzle flow are design criteria in full accordance with VDI Guideline 2066, Part 10, which specifies (in point 4.2.c) that the Reynolds number for the nozzle flow in the impactor should be within a range of laminar flow between 100 and 3000.

At the same time, a plug-shaped flow profile at the end of the nozzles is preferable over a parabolic flow profile, as the differences between the flow velocity in the centre of the nozzle and the flow velocity at the edge of the nozzle are smaller with a plug-shaped flow profile, which is advantageous for steep separation characteristics. Since a parabolic flow profile is formed in a pipe in laminar flow conditions only after some distance from the pipe inlet, the length l_n of the cylindrical section of the nozzles was chosen to be small compared to the diameter d_n of the cylindrical section of the nozzles in order to avoid the complete formation of a parabolic flow profile and maintain a plug-shaped flow profile. A corresponding statement was added to the revised manuscript in section 2.2, line 133 to 136 of the revised manuscript for clarification:

„Since a parabolic flow profile is formed in a pipe in laminar flow conditions only after some distance from the pipe inlet, long classifying nozzles favour the development of a parabolic, pipe-like flow profile, resulting in a less steep separation curve. Therefore, the cylindrical throat length of the classifying nozzles l_n was kept short in order to facilitate the formation of a plug-shaped flow profile.“

The finally applied ratios l_n/d_n are between 0.5 and 1.5, as described in line 130 of the preprint manuscript.

The relations between the separation diameter d_{ae50} , the number N_n and diameter d_n of the nozzles, the mean velocity v_0 , and the volumetric flow rate Q , which are the relevant parameters for the design of the impactor nozzles, are given by equations 1, 2, and 3 in chapter 2.2, lines 106 to 125 of the preprint manuscript. The applied values are summarized in Table 1, line 135 of the preprint manuscript.

- 1.3. Attrition (section 3.3.1). To me, sample contamination by metallic attrition appears a bit far-fetched. This section could possibly be eliminated. Authors could e. g. have made a point in discussing attrition by solid, abrasive particles. The authors also did not consider the possible contamination of a quartz disc by unintended mechanical contact with metallic parts (e. g. impactor structure, tweezers...) or other materials which have had mechanical contact to metals. This seems to me a more likely possible source of contamination. The presentation of related results in section 4, Table 2 has some deficiencies as will be discussed below.

The authors respect the referee's doubts about the relevance of metallic attrition, but respectfully prefer to keep this section in the manuscript.

In a previous study, Klockenkämper et al. (1995) determined blank values of 40 % on average for stainless steel impactors in relation to the actual measured values, and explicitly attributed these high blank values to abrasion of metallic particles from the impactor. As a result, Klockenkämper et al. (1995) recommend avoiding stainless steel as a material for an impactor. Since we did not find any literature that refuted this contamination potential, we considered it necessary to carry out corresponding investigations ourselves.

We agree with the referee that the possible contamination of the sample carrier by unintended mechanical contact with metallic parts is a relevant potential source of contamination. However, this potential source is not due to the impactor material or design but rather due to the handling of samples.

In view of referee's comment, we introduced a corresponding explicit advice in section 3.1.1, line 203 to 205 of the revised manuscript:

„...of the above-mentioned composition. In addition, non-metallic tweezers were used to manipulate the sample carriers, and even beyond that, undesirable metallic contamination of the sample carriers was avoided by careful handling. To determine the...”

Second, as far as the impactor structure is concerned, numerous design measures were described in the manuscript to prevent metallic contamination of the sample carrier. For example, the sample carrier is fixed in the impactor by means of a (non-metallic) “elastic mounting ring made from laser sintered polyamide”, see lines 90 and 91 of the preprint manuscript, in order to avoid contact between the surface of the sample carrier examined by TXRF analysis and metallic parts.

In view of referee's comment, we added a clarification to the caption of Figure 1 in line 100/101 of the revised manuscript:

“...accommodating the nozzle module (red and green), a non-metallic mounting ring (olive) for fixing the sample carrier, and a lower body (light grey) accommodating...”

1.4. Line 265: The statement on the “effective area” is vague.

As already indicated in item 1.1, the authors have amended the manuscript to clarify why a circular area with a diameter of approximately 5 mm in the centre of the sample carrier is regarded as “the effective analysis area, which results from the superposition of the area excited by the X-ray beam, namely a rectangular area with a width of 6 mm and a length of 30 mm, and the field of view of the detector of the TXRF spectrometer used in this study.”

As pointed out above, the efficiency will most probably have a radial dependency. Authors do not present an argument why this could be ignored.

It is not the intention of the authors to evoke the impression that radial

inhomogeneities of the excitation beam and/or the detection of fluorescence of the TXRF spectrometer should be ignored in the TXRF analysis. However, when developing the new impactor, the aim was to ensure that the aerosol particles are deposited on the sample carrier in an area that is, on the one hand, completely covered by the excitation beam and, on the other hand, completely covered by the field of view of the detector. It is true, as the referee points out, those radial inhomogeneities in the TXRF analysis affect the result. Therefore, as already mentioned in item 1.1 above, a corresponding statement has been added to the revised manuscript in section 3.3, line 274 to 277 for clarification.

Line 269: "Calibration samples as external standards". This is a crucial point in quantitative TXRF analysis, and the paper is much too vague here. The authors should explain the calibration samples in detail. I assume that these were prepared by drying a small drop of an aqueous solution with known element quantity (probably Yttrium?) in the center of the carrier.

The authors have amended the manuscript in section 3.3, line 281 to 284 of the revised manuscript to provide more clarity to the calibration process:

"... mass was calibrated for each element. For this purpose, the ratio (counts per mass unit) of fluorescence intensity (TXRF measurement) and mass was first determined for reference samples of which the mass per element was known. Subsequently, the samples with the impacted aerosol particles were quantified with the ratio determined in this way."

I have the impression that the authors implicitly assume for the whole deposition pattern area the same detection efficiency as for a punctiform central deposition of an internal standard and they should give a proper justification for this assumption. As the commercial Bruker software for the TStar offers several options for quantification the chosen method (internal fundamental parameters, internal standard...) should be mentioned.

The authors don't want to give the impression described by the referee. Indeed, it can make a difference for TXRF analysis whether the sample to be analysed is presented in a single closed surface, preferably still centred on the sample carrier, or as a multi-point deposition pattern, as is the case when using an impactor. This is discussed, among others, in the reference Prost et al. (2017) cited in the original manuscript. It is beyond the scope of the manuscript to develop a TXRF calibration strategy for impaction deposition patterns. The objective is the development of a new impactor that achieves improved results with the TXRF spectrometers available on the market, in particular through the detection of not only a part but of all aerosol particles impacted on the sample carrier.

- 1.5. Chapter 4, Table 2: "...mean blank values of impactor stages 1 to 5 ...": I guess that this are the means over repeated measurements. Lines 291 to 295. I would expect a proper measure of variance, at least an estimation of the uncertainty. Each single

measurement should come with an uncertainty provided by the analyzing software. The absolute lower detection limits (LLOD) should be quantified. Line 299 to 301: The significance of the statement should be reevaluated considering realistic uncertainties in the measurements. I am reluctant to accept conclusions without proper consideration of uncertainties, the more so as the data are close to the LLOD.

The authors agree with the referee that the blank values measured and summarized in Table 2 of section 4.1 are very small and very close to the absolute lower detection limits given in line 293 of the preprint manuscript. This is ultimately due to the fact that the sample carriers were not contaminated in the course of the experiment. The mean values are calculated from five measurements, respectively. The maximal standard deviation was 0.0033 ng for Fe, 0.0016 ng for Cr, and 0.0008 ng for Ni. A corresponding statement has been added in section 4.1, line 307 to 309 of the revised manuscript:

“...of the blank value experiments. The mean values are calculated from five measurements, respectively. The maximal standard deviation was 0.0033 ng for Fe, 0.0016 ng for Cr, and 0.0008 ng for Ni. With the TXRF spectrometer applied...”

Therefore, the statement in lines 299 to 301 of the preprint manuscript concerning the observed increase of the mass of Fe from 0.004 ng to 0.010 ng over the course of the experiment seems to be reasonable, whereas for the elements Cr and Ni the measured variations remain within the standard deviation.

- 1.6. Chapter 4 from line 345 on and Figure 5 and Supplement Table S.2: “Figure 5 shows the mass concentrations of the trace metals Zn, Cu, Mn, Pb and Ni collected during these three sampling periods in three size fractions, i. e. PM1 (top of blue bar), PM2.5 (top of green bar) and PM10 (top of red bar).”. Authors should describe how they calculated the PMx mass fractions from the masses determined by TXRF on the five cascade impactor stages.

The authors are pleased to follow up on this recommendation and amended line 366 to 368 of the revised manuscript as follows:

“...periods in three size fractions, i.e. PM1 (top of blue bar, i.e. sum of masses of impactor stages 4 and 5), PM2.5 (top of green bar, i.e. sum of masses of impactor stages 3, 4, and 5) and PM10 (top of red bar, i.e. sum of masses of impactor stages 2, 3, 4 and 5).”

Were for the 0.11 to 1 μm fraction the masses from stages 3 to 5 just summed up, and accordingly for the other PM fractions in Figure 5?

Stage 3 has a separation diameter of 0.915 μm (or approximately 1 μm). This means that – in an idealised view – particles with an aerodynamic diameter of 1 μm are impacted on stage 3 with 50 % efficiency and larger particles more efficiently. Therefore, the mass of the particles impacted on stage 3 must not be attributed to the PM1 fraction, but the fraction of PM1 is to be calculated by summing the masses of the particles impacted on stages 4 and 5. Other PM fractions in Figure 5

were determined accordingly, which is now clarified in the revised manuscript.

If the coarse (10 μm) stage was included into the calculations at least all values labeled as PM10 (top of red bar) do contain a priori unknown quantities of particles larger than 10 μm as no preseparator was reportedly used and the separation curve steepness according to DIN 481 or US EPA was not determined. However, the photo (Fig. 3) probably shows an inlet separator which is not described at all.

Stage 1 has a separation diameter of 9.96 μm (or approximately 10 μm). This means that – in an idealised view – particles with an aerodynamic diameter of 10 μm are impacted on stage 1 with 50 % efficiency and larger particles more efficiently. Thus, stage 1 acts as a pre-separator for particles larger than 10 μm . Accordingly, the mass of the particles impacted on stage 1 must not be attributed to the PM10 fraction, but the fraction PM10 is to be calculated by summing the masses of the particles impacted on stages 2, 3, 4 and 5.

As stated above, the calculation scheme is now explicitly stated in the amended manuscript in order to avoid misunderstandings.

1.7. Conclusions and Outlook seems not well-balanced: One half of the text can be considered merely as outlook.

The first part comprising 13 lines (lines 373 to 386 of the preprint manuscript) summarises what has been achieved with the newly developed impactor. The second part, comprising 9 lines (lines 387 to 396 of the preprint manuscript), gives some concrete recommendations as to which measures (e.g. laser drilling of the nozzles) can be used to achieve further improvements or extensions (e.g. even smaller separation diameters), or which problems have to be avoided (no particle overload of the sample carriers). We consider both parts relevant and would prefer to keep this section as is.

The following three points can in essence be regarded original results from this work:

1. “Due to the compact arrangement of the impactor 375 nozzles, the high detection sensitivity of the TXRF analysis method can be fully exploited.” A convincing proof of this statement is however lacking. The statement in lines 375 to 379 is valid.
2. The statement on the “new spin-coating method” is valid.
3. No contamination issues during mounting/dismounting of carriers.

As described in the manuscript, the deposition pattern of impactors available so far, especially in the impactor stages for the sub- μm particles, have such large lateral dimensions that a substantial part of the impacted particles is deposited outside the area covered by the excitation beam and/or that the fluorescence of a substantial part of the impacted particles could not be captured by the detector. All these not-excited or not-detectable particles were a priori lost to TXRF analysis. As a result, the high potential of TXRF analysis, especially in terms of small sample air flows (-> small pumps, low energy consumption, low weight, mobile application, no local

particle overload, etc.) and short sampling time (-> high temporal resolution, thus possibility of identification of particle sources), cannot be fully exploited.

Due to the compact arrangement of the nozzles of the newly developed impactor any deposition of particles outside the excitation beam and outside the detectable area is omitted. No particle gets lost for the TXRF analysis. Instead, all particles impacted on the sample carrier are covered by the excitation beam, and the fluorescence of all particles impacted on the sample carrier is captured by the detector.

Three particle collections in outdoor air were conducted with the new impactor, each for 30 minutes within a total of only 96 minutes, with fully mobile equipment including battery powered pumps. The subsequent TXRF analysis reveals metal concentrations very close to the values published by governmental measuring agencies.

In view of referee's comment the authors have amended section 5, line 393 to 395 of the revised manuscript in order to clarify the contribution of the compact arrangement of the impact nozzles to the detection sensitivity of the TXRF analysis:

...Due to the compact arrangement of the impactor nozzles, the entire sample interacts with the TXRF excitation beam and contributes to the TXRF analysis signal, thereby supporting the high detection sensitivity of the TXRF analysis method can be fully exploited.

Minor points / editorial suggestions:

Line 76 to 77: The citation refers to rather broad outdoor aerosol size distributions, e. g. accumulation or coarse mode. There might be outdoor scenarios where the Aitken mode is interesting to observe even with high time resolution, or indoor scenarios where the < 0.1 μm fraction is dominant. Authors should comment on that.

The authors thank the referee for this advice and have amended lines 77 to 84 of the revised manuscript as follows:

“Previous TXRF analysis results of impactor samples (e.g. Seeger et al., 2021) suggest that particles of 0.1 μm diameter or less make only a minor contribution to particulate mass assuming a typical outdoor aerosol size distribution with significant contributions of the accumulation mode and coarse modes. Therefore, a fourth stage with a separation diameter of approximately 0.1 μm can be used to collect almost the entire PM1 fraction. In the present study, we apply a fourth stage with a nominal separation diameter of 0.13 μm , and a fifth stage with a nominal separation diameter of 0.095 μm for experimental purposes. In special circumstances it might be important to collect ultrafine particles, e.g. with an additional impactor stage with a separation diameter of e.g. 0.02 or 0.01 μm , as outlined in section 5 of the manuscript, or alternatively a final filter stage.”

Line 82: “slm” (standard litre per minute) refers to us-american nomenclature with standard

conditions 0 deg Celsius (32 deg F) and 1.0125 bar (14.69 psia). European nomenclature uses subscript “_s” for standard flow at 20 C and 1.0125 bar, e.g., m³_s/h. Standard flow at 0 C and 1.0125 bar is in Europe expressed as e.g., m³_n / h with subscript “_n”

For reasons of clarity, the authors prefer to keep the unit "slm" for the mass flow rate: The unit “slm” is defined in the manuscript as "standard litres per minute"; the referenced standard conditions (1.013 hPa and 20 °C) are also explicitly specified in the manuscript, see section 2.1, line 82 of the preprint manuscript. The unit “slm” is therefore clearly defined in the present manuscript.

Line 165: “in the low single-digit percentage range” ?? “few percent relative deviation” sounds better.

The authors thank the referee for this advice and have amended line 172 of the revised manuscript accordingly:

“...resulted in relative deviations of only a few percent in relation to ~~from~~ the respective nominal diameters ~~in the low single-digit percentage range...~~”