

Inter-laboratory comparison of ED-XRF/PIXE analytical techniques in the elemental analysis of filter-deposited multi-elemental certified reference materials representative of ambient particulate matter

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This document is the accepted manuscript version of the following article:
Gini, M., Manousakas, M. I., Kantarelou, V., Karydas, A. G., Chiari, M., Migliori, A., ... Eleftheriadis, K. (2021). Inter-laboratory comparison of ED-XRF/PIXE analytical techniques in the elemental analysis of filter-deposited multi-elemental certified reference materials representative of ambient particulate matter. *Science of the Total Environment*, 780, 146449 (14 pp.). <https://doi.org/10.1016/j.scitotenv.2021.146449>

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Abstract

The quantification of the elemental concentration of ambient particulate matter is a challenging task because the observed elemental loadings are not well above the detection limit for most analytical techniques. Although non-destructive nuclear techniques are widely used for the chemical characterization of ambient aerosol, only one multi-element standard reference filter material that mimics ambient aerosol composition has become recently available in the market. To ensure accuracy, reliability and comparability of instruments performance, multiple reference materials with different elemental mass loadings are necessary. In this study, an intercomparison exercise was performed to evaluate the measurement uncertainty and instruments performance using multi-element dust standard reference samples deposited on PTFE filters. The filter samples, produced by means of dust dispersion, were tested in terms of homogeneity, reproducibility and long-term stability (≈ 80 month). Eight laboratories participated in the exercise. The evaluation of the results reported by the participants was performed by using two sets of reference values: a) the concentrations reported by the Expert Laboratory, b) the robust average concentrations reported by all participants. Most of the reported on the certificate of analysis elements were efficiently detected in the sample loadings prepared as representative for atmospheric samples by the Expert Laboratory. The average absolute relative difference between the reported and the reference values ranged between 0.1 % (Ti) and 33.7 % (Cr) (CRM-2584).

The participants efficiently detected most of the elements except from the elements with atomic number lower than 16 (i.e. P, Al, Mg). The average absolute percentage difference between the participants results and the assigned value as derived by the expert laboratory was 17.5 ± 18.1 % (CRM-2583; Cr, Pb excluded) and 16.7 ± 16.7 % (CRM-2584; Cr, P excluded). The average “relative robust standard deviation” of the results reported by all participants was 25.1 % (CRM-2583) and 22.8 % (CRM-2584).

Keywords Multi-elemental reference material, interlaboratory comparison, PTFE filter, dust dispersion, XRF, PIXE

1. Introduction

Elemental analysis of Particulate Matter (PM) samples collected on filter media is a demanding task that remains challenging. Many factors such as the very low concentrations of the analytes, the non-uniform deposition of the sample on the substrate (especially for PM_{2.5-10} mass fractions), and the reactive species that may lead to positive and/or negative artifact formation contribute to this fact. Analysis of this type of samples is very important not only in environmental monitoring, but also in aerosol chemistry related to transport and transformation processes of atmospheric gases and aerosols (Wätjen et al., 1993).

The resulting elemental concentrations from PM sample analysis are used in many different applications: *identification of the chemical signatures of specific sources, compliance with legal standards for ambient air quality, epidemiological studies to investigate the association between specific PM constituents and health* (Ntziachristos et al., 2007; Saldiva et al., 2002). Considering

the significance of air quality monitoring, it is very important to lower uncertainty and improve quality of analysis. The continuing evaluation of analytical techniques and individual laboratory performances are critical to ensure the high quality of produced chemical composition data. This cannot be achieved without suitable reference material for method validation and calibration.

The standards that are usually used for the calibration of instruments and for method validation regarding PM analysis are commonly liquid solutions suitable for destructive analytical techniques such as Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Mass spectrometry (ICP-MS), or vacuum-deposited metals or salts onto films (i.e. Mylar or polycarbonate) suitable for nuclear techniques, such as Energy Dispersive X-ray fluorescence (ED-XRF or XRF hereafter) and Particle Induced X-ray Emission Spectroscopy (PIXE).

However, these standards do not mimic neither the filters that are typically used for air sampling and PM matrix, nor the very low elemental concentrations the ambient samples have. To our knowledge, there is only one commercially available PM standard on filter substrate, NIST SRM 2783 (PM_{2.5} on polycarbonate filter), which is a multi-elemental standard reference material with loadings that attempt to represent ambient levels, however this standard is currently out of stock and it will take some years before new batches will appear on the market again [NIST Private communication]. Additionally, although such a standard can be used for method validation, for method calibration more than one standard is required if good results are to be achieved.

In order to overcome the limitations of the available standards, testing filter materials with varying aerosol mass concentrations and elemental compositions have been successfully prepared. A method that is commonly used to achieve this goal is the generation of aerosol particles via atomization of liquid solutions containing salts or elements of interest. The generated aerosol particles (droplets) are first dried and then deposited on filters. Although, this

technique was first applied to generate single-compound reference materials (Indresand et al., 2013; Vanhoof et al., 2000; Yarkin et al., 2016a, 2020), it was also used to generate multi-element reference materials. For example, Air Quality Research Center at the University of California Davis (UCD) developed an aerosol generation system (AGS) consisting of an atomizer, diffusive dryer, mixture chamber and sampler to generate multi-element reference materials on filter substrates that mimic typical atmospheric elemental composition, using certified multi-element solutions (Yarkin et al., 2018). Although, these filters do mimic the multi-elemental composition of ambient aerosol, they do not mimic the PM matrix. Another approach is the use of ambient PM filter samples as reference materials; the samples are well-characterized using one or more analytical techniques following a standard analytical procedure (Wätjen, 1990; Wätjen et al., 1993; Wätjen and Cavé, 1996; Traversi et al., 2014; Yarkin et al., 2016b, 2018, 2020). The approach that was utilized in the current study involves the suspension of a suitable NIST reference dust material in a mixing chamber, which is then deposited on a filter substrate. A similar approach has been previously used (Landsberger and Vermette, 1994), but in this case the authors have applied a thin layer of mineral oil in the deposited site to ensure adhesion of the particles.

This study aimed at applying a methodology for reference filter sample preparation and evaluation; Reference samples with different elemental and PM mass loadings representative of atmospheric samples. Specifically, in the framework of the IAEA TC Project RER/1/008 “Supporting Air Quality Management”, a Proficiency Test exercise (PT) of analysis of ambient PM elemental content based on samples prepared from Dust Standard Reference Materials deposited in Polytetrafluoroethylene (PTFE) filters was performed. Two standard Reference Materials were deposited on filters: the 2854 and the 2853 NIST (CRMs). The samples (loaded

filters) that were produced were subsequently checked for the homogeneity and the reproducibility of the deposited mass onto the membrane filters. Loaded samples (2 - CRM 2583 and 2 - CRM 2584) as well as 2 blank filters were selected at random and analyzed by an Expert Laboratory (LABEC ion beam laboratory, INFN, Florence), in order to identify if it is possible to reproduce the deposited elemental bulk mass. Eight laboratories participated in the PT exercise and two non-destructive analytical techniques (XRF and PIXE) were used for the elemental analysis of the samples. The analysis of the reported results was performed in accordance with the ISO 13528:2005 "Statistical methods for use in proficiency testing by inter-laboratory comparisons". The evaluation of the results reported by all the participants was performed using two approaches: a) by using as reference values the analytical results reported by the Expert Laboratory, b) by using as reference values the robust average concentrations reported by all participants. The proposed methodology is suitable for preparation of testing/reference filter materials, representative of the atmospheric samples, that can be used to evaluate the overall performance of the analytical techniques.

2. Materials and Methods

2.1 Sample preparation

For the production of the filter samples, two standard Reference Materials (i.e. NIST CRMs 2584 and 2583 indoor dust) were dispersed and collected on membrane filters. The reference material dust particles became airborne in dry air by using an aerosol generator (220, TOPAS), by means of compressed pure N₂. Although the aerosol generator is used effectively for liquid particle generation, it can be used for dusts as well, with a small effort to ensure continuous uptake of dust material.

The aerosol stream (1.5 lpm) entered a mixing chamber (100 lt) simultaneously with a filtered secondary flow (10 lpm). After that, the mixed and homogeneous stream was drawn through a filter holder at a known flow rate (2 lpm), where the dust particles were collected onto PTFE membrane of desired properties. In Figure 1 the experimental set-up used is presented.

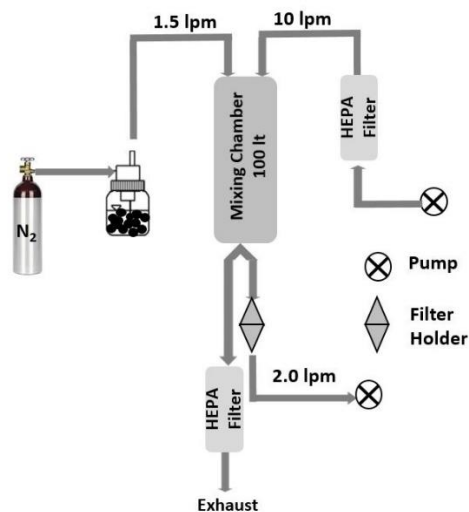


Fig. 1. Experimental set-up for dust aerosol production and collection.

The produced test samples were weighed in the Standard Conditions Weighing room (SCW), operated by the Environmental Radioactivity Laboratory/NCSR "Demokritos", where the temperature and the relative humidity is maintained at 20 ± 1 °C and $50 \pm 5\%$, respectively. Prior to weighing, all the filters were placed for at least 24 hr in the SCW room, according to the standard operating procedure EN1234:1998. All the filters, before and after the deposition of the reference dust, were weighted twice on a Sartorius microbalance; The microbalance was calibrated on a daily basis by its internal calibration system. Additional weighing was conducted in case the difference in the mass between repeated measurements was more than 30 µg. The detection limit of the microbalance was 20 µg, therefore the targeted mass of the deposited dust on each test filter was defined to be higher than 3*DL (60 µg). A Po-210 (alpha emitter)

electrostatic charge eliminator was used to eliminate the static charge accumulated on the filters before each weighing.

Two standard Reference Materials were used in this exercise; the 2854 and the 2853 NIST CRMs, which were intended for use in the evaluation of methods and for the calibration of apparatus used to determine lead and other trace elements in dust. The certified weight fractions (mg/kg) for five elements (i.e. As, Cd, Cr, Pb and Hg) were reported on the certificate of analysis for both reference materials (2584 and 2583), while the reference values for 10 additional elements (i.e. Al, Ca, Fe, K, La, Mg, Na, P, Ti, Zn) were reported on the certificate of analysis for the standard reference material 2584.

According to the producer of the CRMs, the minimum sample mass for the certified values to be valid should be 100 mg. However, taking into account that a maximum ambient PM mass concentration of about $100 \mu\text{g}/\text{m}^3$ and a minimum of about $10 \mu\text{g}/\text{m}^3$ is a reasonable approximation for atmospheric samples, the targeted deposited mass on the test filters was defined in this range. After filter production, it was verified by weighing the test samples (CRM) produced that the deposited mass on each sample ranged between 0.41 mg and 5.52 mg, corresponding to $8 \mu\text{g}/\text{m}^3$ and $100 \mu\text{g}/\text{m}^3$ respectively, assuming a nominal flow rate of $2.3 \text{ m}^3/\text{h}$ and 24h sampling usually applicable for low volume samplers. It was therefore considered that the masses of the test samples prepared for the inter-comparison were representative of atmospheric particulate matter mass concentration levels.

The minimum (calculated) elemental mass deposits were derived by calculation from the certified and reference mass values provided on the certificates of analysis. This was done in order to evaluate whether the elemental loadings are within the range of the observed ambient

elemental concentrations. The results are presented in Tables 1 and 2. The results presented in Table 2 showed that the minimum calculated concentrations, although found to be close to the lower limits of the measured weight fractions, still remain within the range of the observed elemental concentrations in ambient particulate matter (Limbeck et al., 2009; Manousakas et al., 2014, 2013; Terzi et al., 2010; Vasilatou et al., 2017). Thus, we can conclude that the prepared samples can be considered representative of ambient particulate matter.

Furthermore, it should be mentioned that the system used for the production of the test filters was tested for contamination. Two “field” blank filters (exposed only to filtered air and N₂) were produced using the same experimental set-up as the one described above. The unexposed blank filters were analyzed by XRF analysis Institute of Nuclear and Particle Physics, “NCSR” Demokritos), but no contamination was detected for the elements of interest.

Table 1. Minimum calculated concentrations and calculated area mass deposit (i.e. for minimum loading mass: 0.41 mg for NIST CRM2584 and 0.72 mg for NIST CRM2583, loaded filter area: 10.75 cm², and volume of sampled air: 55 m³)

Element	Min Calculated	Min Calculated	Min Calculated	Min Calculated
	Conc. ng/m ³	Mass ng/cm ²	Conc. ng/m ³	Mass ng/cm ²
	CRM 2584	CRM 2584	CRM 2583	CRM 2583
As	0.13±0.03	0.66±0.16	0.09±0.02	0.47±0.11
Cd	0.07±0.01	0.38±0.04	0.10±0.05	0.49±0.25
Cr	1.01±0.07	5.2±0.4	1.05±0.18	5.4±1.5
Pb	72.8±0.5	372.2±2.6	1.12±0.09	5.8±0.5
Hg	0.039±0.002	0.20±0.01	0.020±0.002	0.10±0.01

Table 2. Reference concentrations and minimum calculated area mass deposit (i.e. for minimum loading mass: 0.41 mg for NIST CRM 2584, loaded filter area: 10.75 cm², and volume of sampled air: 55 m³)

Element	Min Calculated Concentration ng/m ³ CRM 2584	Min Calculated Mass ng/cm ² CRM 2584
Al	173.0±4.5	884.7±22.9
Ca	471.9±22.4	2413.8±114.4
Fe	122.3±9.2	625.4±45.8
K	70.8±10.4	362.3±53.4
La	0.14±0.01	0.72±0.08
Mg	118.5±2.2	606.3±11.4
Na	206.5±9.0	1056.3±45.8
P	14.9±0.9	76.3±4.6
Ti	31.3±2.2	160.2±11.4
Zn	19.2±1.1	98.4±5.7

2.2 Sample homogeneity testing

An important aspect when preparing filter samples is to ensure the homogeneity of the testing material. To this end, six test samples were prepared through the methodology described in section 2.1; Three of the samples were prepared onto PTFE membrane filters (coded as W) and three onto PTFE membrane filters with support ring (coded as T). Both certified materials, CRMs 2584 and 2583, were tested. The samples were further analyzed by means of a portable milli-probe XRF spectrometer at the XRF laboratory of the Institute of Nuclear and Particle Physics at the “NCSR” Demokritos. The portable milli-XRF spectrometer has been developed in

201 NCSR “Demokritos” laboratory and consists of a Rh anode tube (spot size with a diameter of
202 about 3mm, max 50 kV, max 1 mA, 50W maximum power consumption, Be window 0.125 mm
203 thickness), a Si-Pin detector (XR-100CR, Amptek Inc.) with a 500 μm nominal thickness (165
204 eV FWHM at 5.894keV), a digital signal processor (PX4, Amptek Inc.) and two lasers for the
205 correct placement of the sample. For the aerosol sample measurements an operational high
206 voltage equal to 20 kV was used with an unfiltered excitation mode.

207 Five different points on each filter were measured by the milli-probe XRF spectrometer. The
208 points were selected at the periphery (4 points) and at the centre of the sample (1 point). All
209 spots were measured at 20 kV and 300 μA , while the samples were measured for 3000s. The
210 interpretation of the X-ray spectra and the determination of the net peak areas were performed
211 using the AXIL-QXAS software.

212 Overall, the deposited mass of CRM on the test samples ranged between 0.7 mg and 4.5 mg,
213 which correspond to a 24h mass concentration of 13 $\mu\text{g}/\text{m}^3$ and 85 $\mu\text{g}/\text{m}^3$, respectively. The
214 average counts, the standard deviation (SD) and relative standard deviation (RSD) from the five
215 points of measurement for each sample and detected element (Table 1) are listed in Table 3.
216 Moreover, the standard error (SE) and the relative standard error (RSE) of the mean were
217 calculated, as indicators of the reliability of the mean value. Generally, areal inhomogeneity had
218 little effect on the overall good reproducibility observed for both T- and W-membrane filters, for
219 the majority of the detected elements, despite low statistics for few elements; It was observed
220 that the RSDs ranged between 0.7% (Zn, CRM 2584) and 20.9% (K, CRM 2583).

221

222 Table 3. Mean value, Standard Deviation (SD) and Relative Standard Deviation (RSD, %),

223 Standard Error of the mean (SE) and Relative Standard Error (RSE, %) of the counts

Elements	K	Ca	Ti	Fe	Zn	Pb
W1 (CRM2584)						
Average (n=5)	3368	38282	3180	14424	1776	789
SD	165	796	181	455	83	103
RSD (%)	4.9	2.1	5.7	3.2	4.7	13.1
SE	74	356	81	203	37	46
RSE (%)	2.2	0.9	2.5	1.4	2.1	5.9
W2 (CRM2584)						
Average	9004	106453	7934	38723	4288	1984
SD	1101	8267	722	2934	565	237
RSD (%)	12.2	7.8	9.1	7.6	13.2	11.9
SE	492	3697	323	1312	253	106
RSE (%)	5.5	3.5	4.1	3.4	5.9	5.3
W3 (CRM2583)						
Average	3738	11091	418	1878	198	ND
SD	374	858	37.7	147.3	20.9	
RSD (%)	10.0	7.7	9.0	7.8	10.5	
SE	167.3	383.5	16.8	65.9	9.4	
RSE (%)	4.5	3.5	4.0	3.5	4.7	
T1 (CRM2584)						
Average	6373	79710	5798	27088	3155	1412
SD	256	1176	424	297	22	81
RSD (%)	4.0	1.5	7.3	1.1	0.7	5.7
SE	114	526	190	133	10	36
RSE (%)	1.8	0.7	3.3	0.5	0.3	2.6
T2 (CRM2584)						
Average	13575	150599	11443	51178	5755	2443
SD	953	6993	519	2606	474	169
RSD (%)	7.0	4.6	4.5	5.1	8.2	6.9
SE	426	3127	232	1165	212	75
RSE (%)	3.1	2.1	2.0	2.3	3.7	3.1
T3 (CRM2583)						
Average	666	3514	117	743	58	ND
SD	139	139	12.2	25.9	10.2	
RSD (%)	20.9	4.0	10.4	3.5	17.5	
SE	62	62	5	12	5	
RSE (%)	9.3	1.8	4.7	1.6	7.8	

224 ND – non detected

225

Moreover, in Table 4 the z-score values for the data in Table 3 are listed. The z-score is a measure of the distance between each data point and the mean value of the data set for each element and filter sample, in standard deviation units. The z-score was calculated as:

$$z = \frac{x - \bar{x}}{\sigma} \quad (1)$$

Where, x is the number of counts at each point (spot) and σ and \bar{x} are the standard deviation and the mean value of the data set (number of counts) for each element and filter sample, respectively. z-score values between (2.0, 3.0) or (-3.0, -2.0) shall be considered to give a “warning” signal, while z-score values above 3.0 or below -3.0 shall be considered to give an “action” signal. As shown in table 4, the z-score values were found between -2 and 2 in all cases, indicating that “warning” signals or “outliers” do not exist.

Table 4. z-score values

	Point1	Point2	Point3	Point4	Point5		Point1	Point2	Point3	Point4	Point5
K						Fe					
W1	1.1	-1.0	-1.1	0.6	0.5	W1	0.1	-0.6	-1.2	0.2	1.5
W2	-1.4	0.6	0.3	1.1	-0.6	W2	-1.1	-0.9	1.3	0.5	0.3
W3	-0.5	0.5	1.5	-1.1	-0.4	W3	-0.5	0.7	1.4	-0.9	-0.7
T1	-1.4	0.6	0.3	1.1	-0.6	T1	-1.1	-0.9	1.3	0.5	0.3
T2	-0.3	0.0	1.4	0.2	-1.3	T2	-1.0	-0.1	1.4	0.5	-0.9
T3	1.4	-1.1	0.6	-0.4	-0.4	T3	-0.4	1.2	1.0	-0.9	-0.8
Ca						Zn					
W1	0.8	0.2	-0.9	-1.2	1.0	W1	-0.9	-0.9	-0.4	1.2	0.9
W2	-1.7	0.8	0.2	0.5	0.3	W2	-1.1	1.5	0.4	-0.3	-0.4
W3	-0.7	0.6	1.5	-0.8	-0.6	W3	-1.0	-0.4	1.6	0.1	-0.3
T1	-1.7	0.8	0.2	0.5	0.3	T1	-1.1	1.5	0.4	-0.3	-0.4
T2	-0.7	0.0	1.5	0.4	-1.1	T2	-0.8	-0.6	1.5	0.5	-0.7
T3	1.2	-1.0	0.9	-0.3	-0.9	T3	-1.2	0.1	1.5	0.0	-0.5
Ti						Pb					
W1	0.1	-0.4	-1.4	1.3	0.4	W1	-1.6	-0.2	0.7	0.9	0.2
W2	-0.6	-0.1	-0.3	1.7	-0.7	W2	-0.8	-0.1	1.3	-1.0	0.6
W3	-0.6	0.5	1.5	-0.6	-0.8	W3					
T1	-0.6	-0.1	-0.3	1.7	-0.7	T1	-0.8	-0.1	1.3	-1.0	0.6
T2	-0.5	0.9	0.7	0.3	-1.5	T2	-1.0	0.7	1.1	0.3	-1.1
T3	-1.0	-0.1	1.6	-0.7	0.1	T3					

2.3 Stability of the deposited material

In the present study, no adhesive materials were used during the preparation of the reference filter materials to avoid contamination and loss of volatile material that might influence the accuracy of the overall measurement (weighing and analytical) procedure. That fact might lead to the creation of standards that are more susceptible to losing surface deposited material. To evaluate the mechanical stability of the produced standards, one of them was selected to be periodically analyzed by XRF for a long period of time (2014-2018), thus collecting a high number of measurements. In the Figure 2, the results of the XRF determination of calcium in cps/mA are presented along with the $\pm 2\sigma$ limit. Ca was selected because it is the element with the lower relative standard deviation (RSD, Table 3) on the sample homogeneity test. Additionally, it is expected that the loss of surface material, if any, would affect more the elements that have higher concentrations. It is apparent that Ca mass remains within the $\pm 2\sigma$ limit and no loss of material was observed despite the high number of measurements and the time that has passed since the production of the test filter.

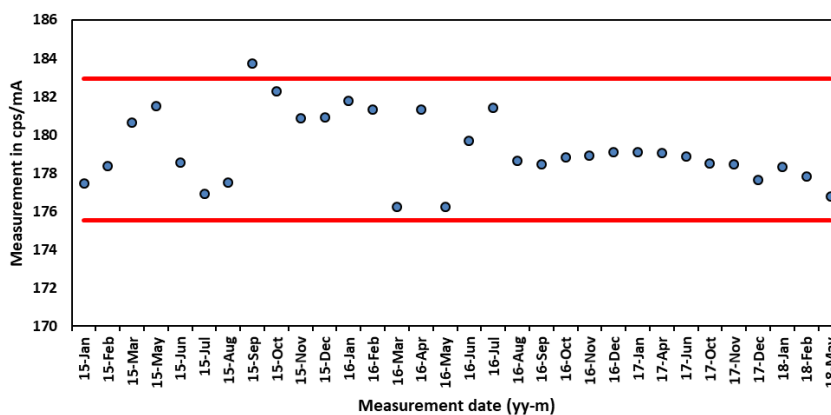


Fig. 2. XRF determination of calcium in cps/mA for the time period Jan-15 to Feb-18. The red lines represent the $\pm 2\sigma$ limit

2.4 Evaluation of the participants' results

Each participant received 2 samples of each material and two blanks (CRM 2583 and CRM 2584) and reported the results along with their expanded uncertainties. Then, different criteria were used to evaluate the results reported by the participants. In order to further evaluate the participants' results, we omitted to consider as "assigned values" the values derived by calculation from the elemental weight fractions reported on the certification of each CRM, because, according to the producer of the CRMs, the minimum sample mass for the certified values to be valid should be 100 mg. It has to be noted that evaluation criteria, such as the ζ -score numbers, that require knowledge of the measurement standard uncertainty to be reported by each participant were not taken into account in the present analysis given that the participants did not report the uncertainties in a uniform way.

2.4.1 Consensus values obtained from expert laboratory

In order to evaluate the results reported by all participants, the assigned value (X_{Lab}) and standard uncertainty of the assigned value reported by an expert lab (i.e. LABEC ion beam analysis laboratory, INFN) for both CRM materials (CRM 2583 (2 samples) and CRM 2584 (2 samples)) was used. LABEC has a long tradition of participation to many aerosol monitoring campaigns, performed in urban and remote areas, both daily and with high time resolution (hourly samples), as well as with size selection (Lucarelli et al., 2018; Calzolari et al., 2015). At LABEC, the combined use of PIXE with Particle Induced Gamma-ray emission (PIGE) technique and other complementary (non-nuclear) techniques provides high quality analytical results for a wide range of elements. The measurements were performed in an external beam PIXE set-up. Na, Mg, Al, P, K and Ca were detected with a 30 mm² Silicon Drift Detector with He gas flow (2.5 l/min).

277 Heavier elements were detected with an 80 mm² Silicon Drift Detector, filtered with 450 µm
 278 Mylar. A 3 MeV proton beam (on target energy) was used; beam currents were in the 45-65 nA
 279 range and the measurements lasted 300 sec. All elements were quantified by the K lines, except
 280 for La, Hg and Pb where L lines were considered. Other elements were detected and quantified
 281 above the minimum detection limit, apart those requested, namely: Si, S, Cl, Cr, Mn, Ni, Cu, Rb,
 282 Sr, Zr. Quantitative results were obtained by comparison with thin MicroMatter elemental
 283 standards (mono- or bi-elemental) of known composition and with the afore mentioned NIST
 284 standard SRM2783 (Air Particulate on Filter Media).

285 The relative difference between the assigned value provided by the expert laboratory and
 286 “values” derived by calculation (X_c) from the elemental weight fractions reported on the
 287 certificate of analysis was obtained as follows:

$$288 \quad Dc(\%) = \frac{(X_{Lab} - X_c)}{X_c} * 100 \quad (2)$$

289 The z'-score values were used to evaluate participants' performance, although $u_{X_{Lab}} \leq 3 * \sigma$,
 290 using the following equation:

$$291 \quad z' = \frac{\chi - X_{Lab}}{\sqrt{\sigma^2 + u_{X_{Lab}}^2}} \quad (3)$$

292 Where, (χ) is the participant result (i.e. average value of all their measurements on the test
 293 material) and (σ) is the standard deviation for proficiency assessment. The standard deviation for
 294 proficiency assessment was calculated in accordance with the ISO 13528:2005 (algorithm A). By
 295 taking into account the reported uncertainties in such a case, could increase the risk that some

laboratories will receive action or warning signal due to the inaccuracy in the determination of the uncertainty rather than the reported results.

The relative bias (percentage difference) between participants' results (from non-destructive techniques) and the results (X_{Lab}) reported by the "expert" laboratory, were calculated using the following expression:

$$D(\%) = \frac{(x - X_{Lab})}{X_{Lab}} * 100 \quad (4)$$

2.4.2. Consensus values obtained from the results reported by all participants

The z-scores of the participants results (i.e. standardized measure of laboratory bias) were calculated using as assigned value of the elemental weight fractions the robust average (ISO 13528:2005, algorithm A) of the results reported by all the participating laboratories as:

$$z^* = \frac{x - X^*}{\hat{\sigma}} \quad (5)$$

Where, (X^*) is the assigned value (robust average) and $\hat{\sigma}$ is the standard deviation for proficiency assessment (s^*).

The relative biases between participants' results and the robust averages (X^*) were also calculated using the following expression:

$$D^*(\%) = \frac{(x - X^*) * 100}{X^*} \quad (6)$$

Additionally, the mean values (\bar{X}), standard error (SE), repeatability standard deviation ($\sigma(r)$), reproducibility ($\sigma(R)$) standard deviation and between-laboratory standard deviation (σ_L) were calculated for both CRMs (ISO 5725:1994).

3. Results and Discussion

3.1 Expert laboratory sample analysis

In order to identify if it is possible to adequately reproduce the deposited elemental bulk mass on filter samples, the data reported by the expert laboratory were compared to the “values” derived by calculation from the elemental weight fractions reported on the certificate of analysis which accompanied each reference material. Figure 3a, shows the relative difference between the elemental mass concentrations reported by the expert laboratory (X_{Lab}) and the elemental weight fractions reported on the certificate of analysis for both reference materials (CRM 2583 and CRM 2584). Whereas, figure 3b shows the ratio of the reported by the expert laboratory elemental loadings over the reference (calculated) values reported on the certificate of analysis. The expert laboratory was able to effectively detect the majority of the elements reported in the certificate for both materials. The elemental concentrations were in the ranges of values found in ambient atmosphere for the majority of the detected elements. Overall, it was observed that the expert laboratory could adequately reproduce the deposited elemental bulk mass for the majority of trace and major elements (CRM 2584); the ratios of the reported over the reference values ranged between 0.51 (As) and 1.34 (Cr), while the absolute value of relative difference between the assigned and calculated values ranged between 0.1 % (Ti) and 21.3 % (Pb) for the major and trace elements, except for: As (48.7 %), Cr (33.7 %) and Na (43.1 %) where higher discrepancies were detected. For the CRM 2583, the ratios of the reported by the expert lab over the reference values ranged between 1.28 and 1.66. The absolute value of relative difference was 28.0 % (As), 65.7 % (Cr) and Na 27.5 % (Na), while no values were reported by the expert laboratory for Cd and Hg. Taking into account that, according to the producer, a minimum mass of 100mg (much higher than the one used to produce the testing filter materials) is needed for the

certified/reference values to be considered as valid, we can conclude that the expert lab reported reasonable results, within the range of uncertainty, at least for specific major and trace elements, namely: Al, Ca, Fe, K, Mg, P, Ti, Pb and Zn. The absolute concentrations reported by the expert, converted in mg/kg, are presented in Figure 6 (CRM 2583) and Figure 7 (CRM 2584).

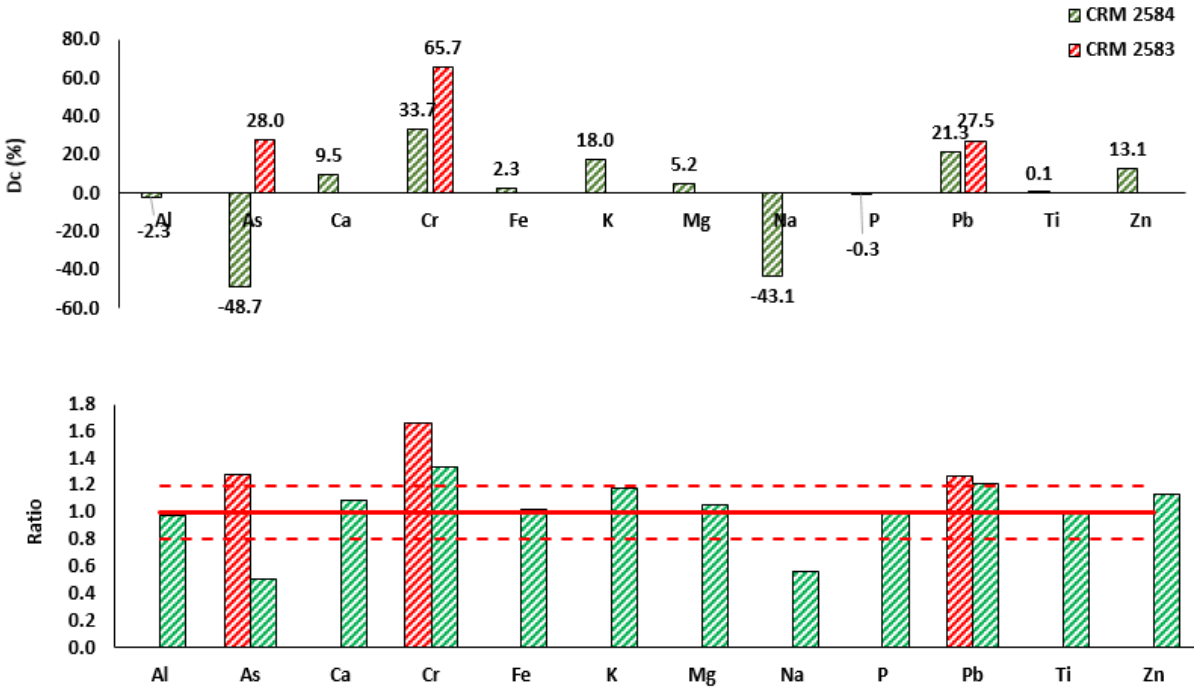


Fig. 3. a) Percentage difference (D_c , %) between the measured by the expert laboratory elemental weight fractions and the certified/reference values, derived by calculation from the elemental weight fractions reported on the certificate of analysis, for both CRMs (2583-red and 2584-green) and b) ratio of the reported by the expert laboratory loadings over the reference values reported on the certificate on analysis.

3.2 Evaluation of participants results

As mentioned before, according to the producer the minimum sample mass, for the certified values to be valid, should be 100 mg. However, for the specific PT exercise the deposited CRM

mass on each sample ranged between 0.41 mg and 5.52 mg, so as to be in the range of atmospheric particulate matter mass concentration levels. Therefore, the assigned (reference) value in order for the participants results to be evaluated was obtained either from the results reported by the expert laboratory or as the robust average calculated from the results reported by all the participants through the algorithm A (robust analysis), ISO 13528:2005. It has to be noted that a unique identifier (i.e. C_{no}) was used for each participant, to ensure confidentiality.

3.2.1 Assigned value delivered from expert laboratory

Figures 6 and 7 present the results reported by all the participants for CRM 2583 and CRM 2584, respectively. The result reported by each participant was considered as an average of the replicate measurements obtained by the participant for each sample, while the assigned value for each element corresponds to the value reported by the expert laboratory. The elements Ca, Fe, Pb, K, Ti and Zn were reported by the majority of the participants, while not all the participants reported results for the elements of lower atomic numbers (i.e. Al, Mg and P).

In order for the results reported by the participants to be evaluated, the percentage difference between the reported values by all participants and the assigned value reported by the expert was investigated (Eq. 4). The results are presented in Figure 4 (CRM 2583) and Figure 5 (CRM 2584). In the case of CRM 2583, the average absolute percentage difference was 19.6 % (Ca), 8.0 % (Fe), 27.6 % (K), 15.6 % (Ti) and 9.4 % (Zn). Instead, the average absolute percentage difference was 21.6 % (Ca), 11.8 % (Fe), 26.0 % (K), 15.1 % (Ti) and 9.9 % (Zn) for CRM 2584. Pb was also effectively detected by the majority of the participants (only one outlier was detected, C4) in the case of CRM 2584; the percentage difference ranged between -14.4 % and 14.4 % (C4: 86.6 %). Higher percentage differences were instead found for CRM 2583, ranging

between 5 and 253%, while three of the participants did not report any result. This could be attributed to the fact that Pb concentrations collected on the CRM 2583 samples were close to the lower limit of detection. As far as for the case of Cr, although most of the participants effectively detected the assigned Cr concentration for both materials, three of the participants either they did not report any result or the absolute percentage difference between the reported values and the reference value was higher than 50 %. While for the rest of the detected elements of lower atomic number ($Z < 16$), a limited number of participants managed to efficiently detect these elements (Al, P and Mg).

Then, the z' -scores were used to identify possible warning signals and outliers. The z' -scores were calculated as described in section 2.4.1. The standard deviation for proficiency assessment was derived from the results reported by all participants (i.e. robust standard deviation), using algorithm A (robust analysis). The results are summarized in Table 5. Overall, it was observed that 6.6 % (CRM 2583) and 4.7 % (CRM 2584) of the reported results triggered an “action” signals and were therefore considered as outliers.

3.2.2 Assigned value obtained as a consensus of the results of all participants

Robust analysis was performed to calculate the assigned value along with its standard uncertainty as described in section 2.4.2. The results are summarized in Figures 6 and 7, where the robust average, the standard deviation and the relative standard deviation for each element and CRM material are presented. Additionally, in Figure 8 and 9, the percentage difference between the results reported by the participants and the assigned value (robust average) is presented for both CRMs 2583 and 2584, respectively. Overall, in the case of CRM 2583, the average absolute percentage difference was 17.6 % (Ca), 4.2 % (Fe), 28.4 % (K), 15.7 % (Ti)

and 9.1 % (Zn). Instead, the average absolute percentage difference was 16.9 % (Ca), 5.1 % (Fe), 26.8 % (K), 13.9 % (Ti) and 7.9 % (Zn) for CRM 2584. As far as for Cr, the average percentage difference was 37.5 % (CRM 2583) and 21.8 % (CRM 2584) excluding the outliers and warning signals (Table 6). Only three of the participants reported values for the light elements (i.e. Al, P and Mg); the average absolute percentage difference (for both CRMs) was 12.2 % (Al), 7.8 % (Mg) and 47.1 % (P).

The relative standard deviation (RSD) was also calculated as a measure of the robust deviation around the robust mean (Figure 6 and 7). Overall, in the case of CRM 2583, the RSD was 27 % (Ca), 13 % (Fe), 31 % (K), 25 % (Ti), 13 % (Zn), 61 % (Cr) and 36 % (Pb). While, the RSD was 22 % (Ca), 5 % (Fe), 37 % (K), 19 % (Ti), 9 % (Zn), 33 % (Cr) and 18 % (Pb) for CRM 2584. Overall, the average “relative robust standard deviation” of the results reported by all participants was 25.1 % and 22.8 % for CRM 2583 and CRM 2584, respectively.

Afterwards, the z^* -scores were calculated taking into account the results reported from all the participants, as described in section 2.4.2. The results are summarised in table 6 for both materials. In the case of CRM 2583, only one of the reported results was considered as outlier, while 4 of the reported results were identified as outliers for CRM 2584.

Additional statistical parameters were calculated and summarized in Table 7 to assess the accuracy of the results reported by all participants for both CRMs and estimate the overall between-laboratory measurement uncertainty. On average, the reproducibility standard deviation was 2.1 times the repeatability standard deviation. The average repeatability relative standard deviation $R\sigma_r$ was 20.4 % and 10.8 % (Cr excluded) for CRM2583 and CRM2584, respectively. While the average reproducibility relative standard deviation $R\sigma_r$ was 29.3 % (CRM2583) and

27.4 % (CRM2584) (Cr excluded). Then, the between-laboratory relative standard deviation $R\sigma_L$ was calculated; It was found that the average $R\sigma_L$ was 17.2 % (CRM2583) and 24.1 % (CRM2584), which seems to be reasonable for such low elemental concentration levels that push the measurement techniques to their limits.

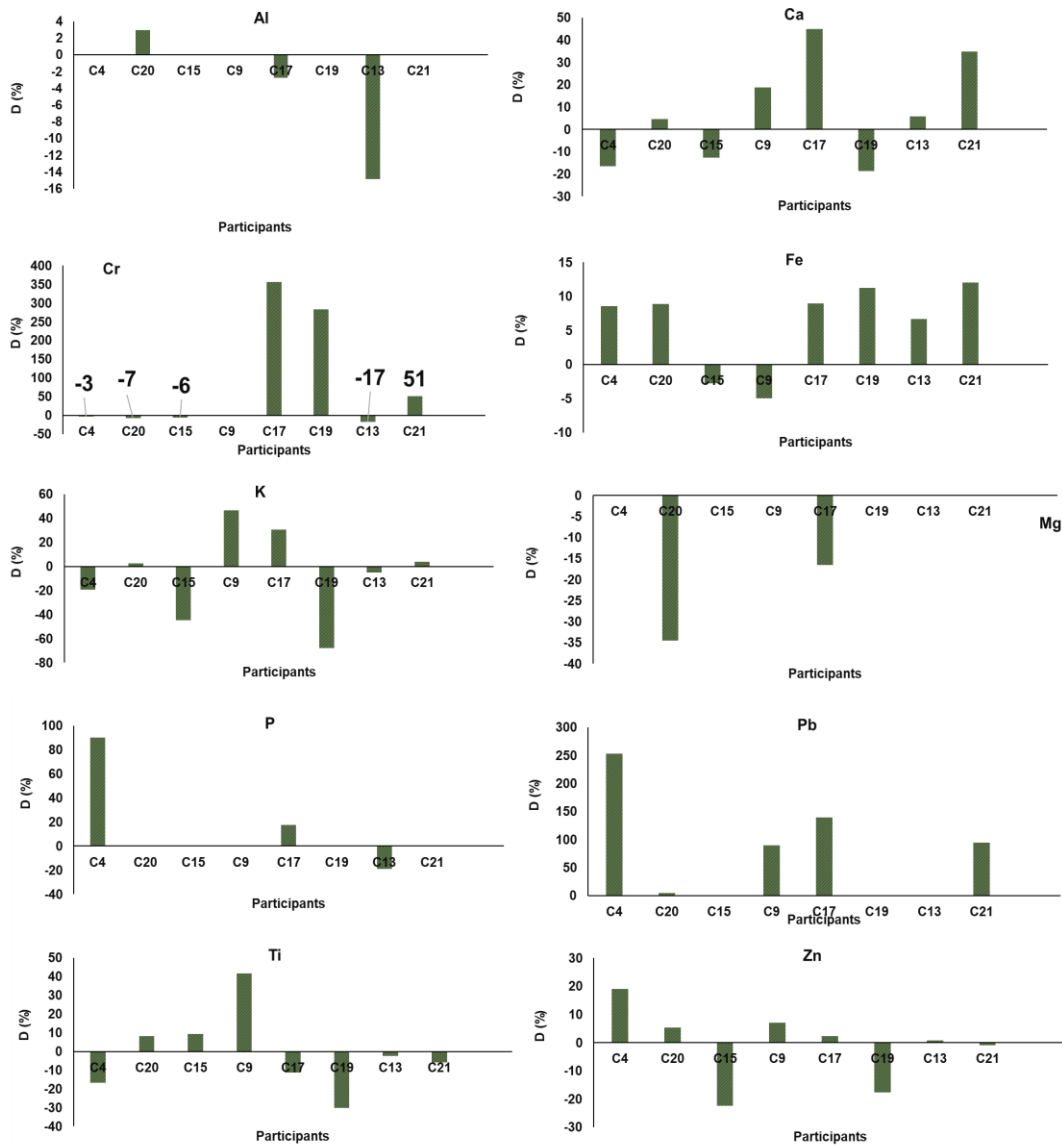


Fig. 4. Relative percentage difference between the reported results by all participants and the assigned values reported by the expert laboratory for CRM 2583.

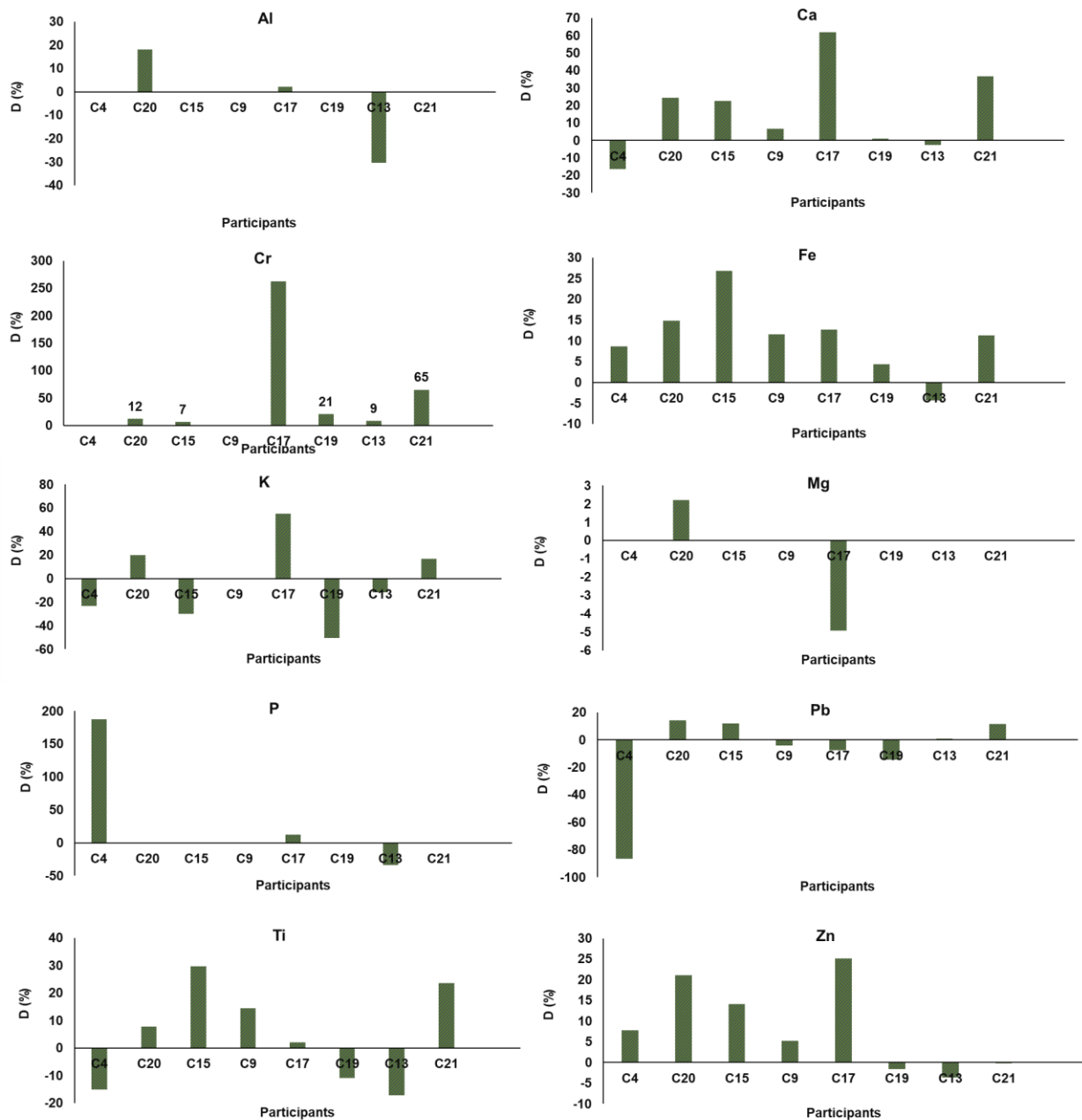


Fig. 5. Relative percentage difference between the reported results by all participants and the assigned values reported by the expert laboratory for CRM 2584.

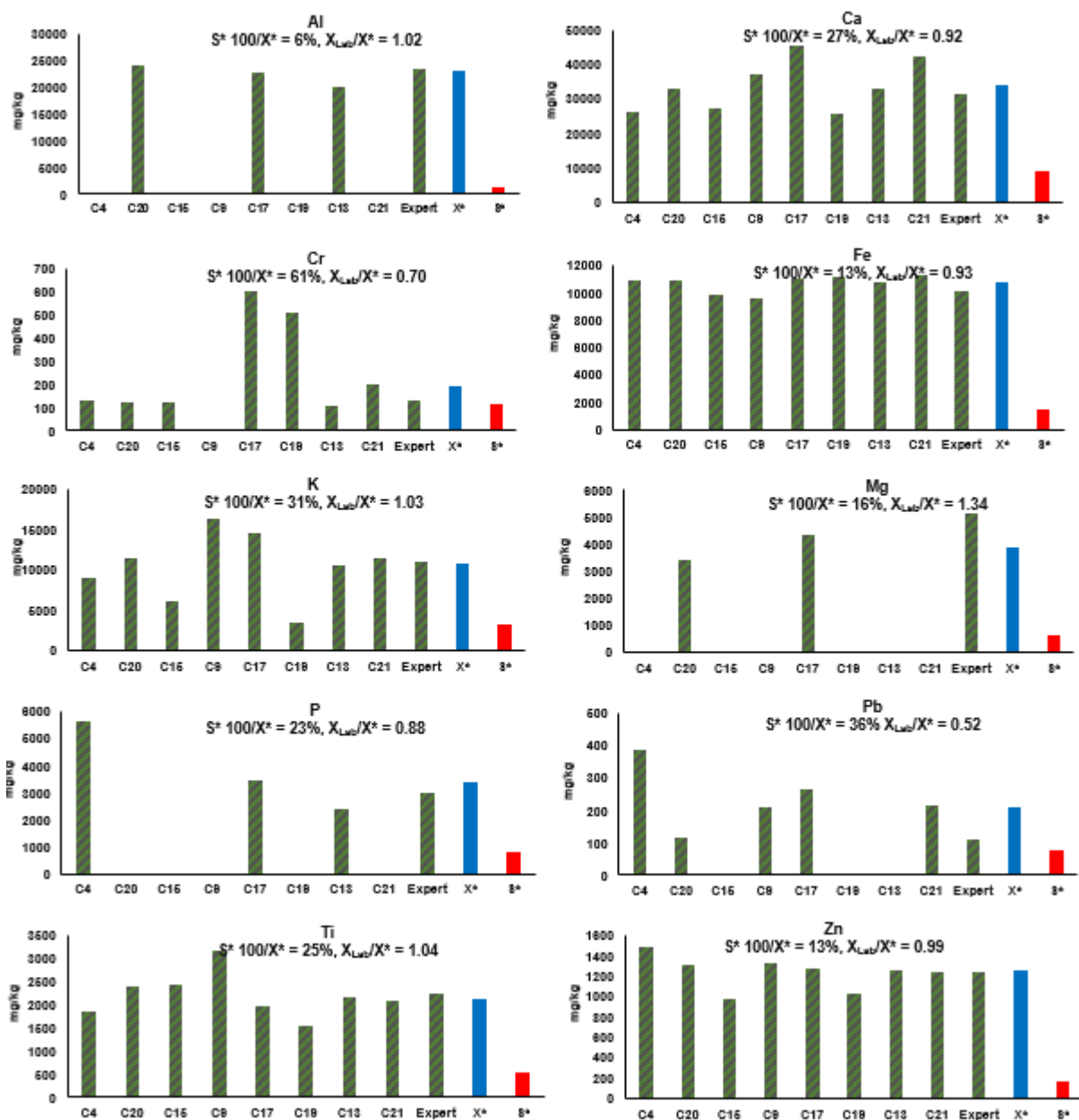


Fig. 6. Results reported by all participants and expert laboratory along with the robust average and standard deviation (CRM 2583)

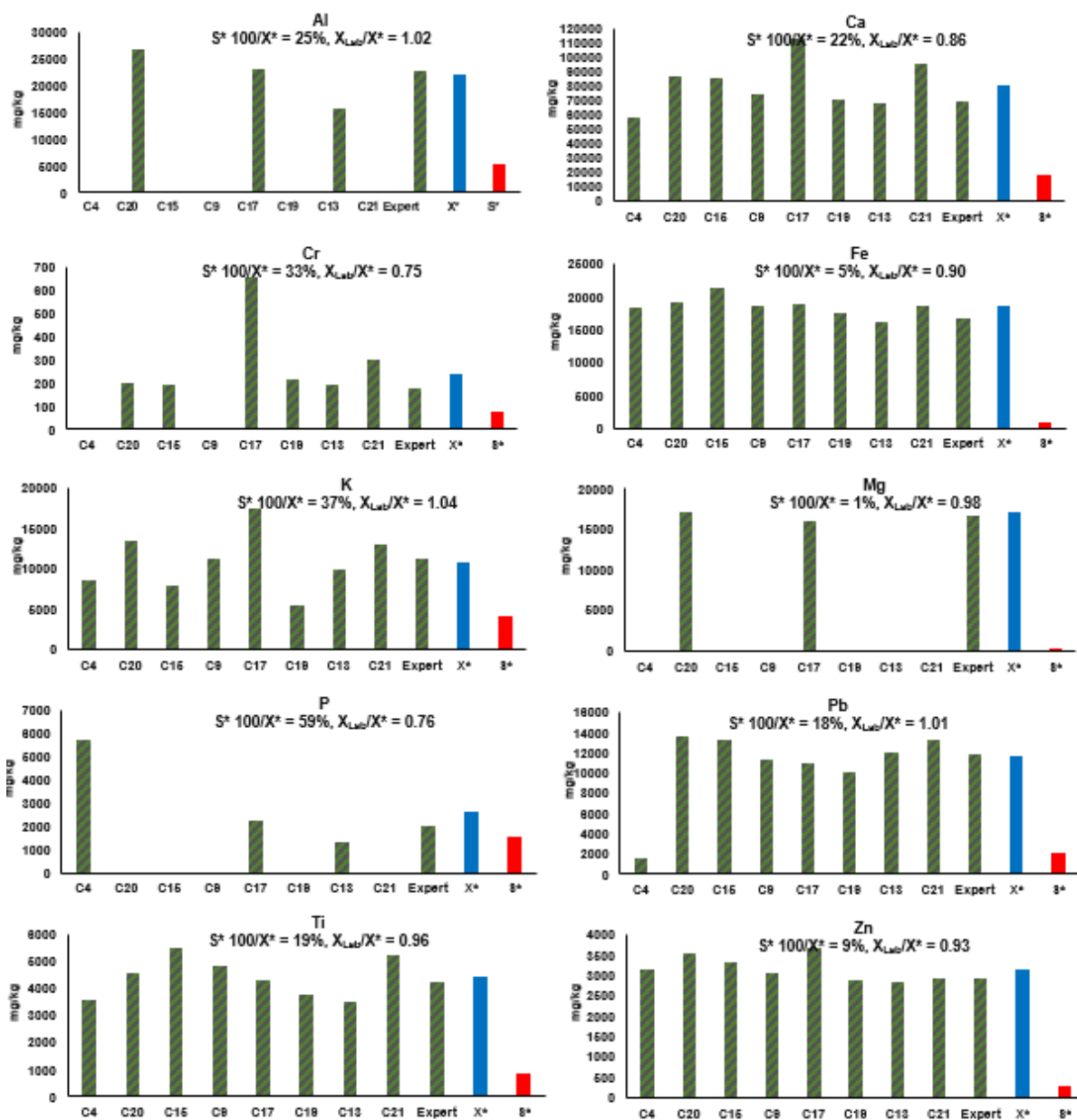


Fig. 7. Results reported by all participants and expert laboratory along with the robust average and standard deviation (CRM 2584)

438 Table 5. z' - score values for CRM 2583 and CRM 2584

z'-score	C4	C20	C15	C9	C17	C19	C13	C21
CRM 2583								
Al		0.37			-0.34		-1.84	
Ca	-0.56	0.15	-0.42	0.63	1.51	-0.62	0.19	1.17
Cr	-0.03	-0.08	-0.06		4.07*	3.24*	-0.19	0.59
Fe	0.58	0.60	-0.19	-0.34	0.61	0.76	0.46	0.82
K	-0.63	0.08	-1.46	1.54	1.00	-2.23	-0.17	0.13
Mg		-2.37			-1.13			
P	3.34*				0.65		-0.70	
Pb	3.17*	0.06		1.12	1.75	-1.25		1.19
Ti	-0.67	0.32	0.38	1.68	-0.45	-1.22	-0.09	-0.23
Zn	1.31	0.36	-1.54	0.48	0.16	-1.21	0.06	-0.06
CRM 2584								
Al		0.73			0.08		-1.23	
Ca	-0.62	0.93	0.86	0.26	2.35	0.04	-0.10	1.39
Cr	-2.16	0.26	0.14	-2.16	5.66*	0.46	0.19	1.41
Fe	1.19	2.06	3.71*	1.60	1.76	0.61	-0.60	1.56
K	-0.64	0.54	-0.82	-0.02	1.52	-1.39	-0.32	0.46
Mg		0.27			-0.60			
P	2.40				0.16		-0.43	
Pb	-4.67*	0.77	0.65	-0.21	-0.41	-0.77	0.05	0.62
Ti	-0.72	0.37	1.42	0.69	0.09	-0.52	-0.82	1.13
Zn	0.73	1.97	1.32	0.49	2.34	-0.15	-0.34	-0.02

439 * Red values: outliers

440 Table 6. z*-score values for each participant and element for CRM 2583 and CRM 2584;
 441 Assigned values and standard deviations were calculated via robust statistical analysis.

z*-score	C4	C20	C15	C9	C17	C17	C13	C21
CRM 2583								
Al		0.88			-0.17		-2.41	
Ca	-0.85	-0.13	-0.72	0.36	1.25	-0.92	-0.09	0.90
Cr	-0.52	-0.57	-0.56		3.63*	2.79	-0.69	0.10
Fe	0.09	0.11	-0.74	-0.90	0.12	0.28	-0.05	0.34
K	-0.54	0.19	-1.38	1.67	1.12	-2.16	-0.07	0.23
Mg		-0.75			0.75			
P	2.91				0.16		-1.22	
Pb	2.32	-1.27		-0.05	0.68			0.03
Ti	-0.53	0.50	0.55	1.89	-0.30	-1.09	0.07	-0.08
Zn	1.30	0.29	-1.75	0.41	0.08	-1.40	-0.04	-0.16
CRM 2584								
Al		0.84			0.18		-1.17	
Ca	-1.25	0.33	0.27	-0.35	1.79	-0.58	-0.72	0.80
Cr		-0.48	-0.61		5.17*	-0.28	-0.56	0.72
Fe	-0.58	0.64	2.99	-0.01	0.22	-1.41	-3.13*	-0.05
K	-0.55	0.65	-0.73	0.08	1.63	-1.31	-0.22	0.56
Mg		0.68			-10.03*			
P	2.00				-0.24		-0.83	
Pb	-4.79*	0.87	0.74	-0.16	-0.36	-0.74	0.12	0.71
Ti	-0.98	0.15	1.25	0.49	-0.13	-0.78	-1.08	0.95
Zn	0.02	1.43	0.69	-0.25	1.86	-0.98	-1.20	-0.84

* Red values: outliers

442

443 Table 7. Statistical parameters calculated based on the participants reported results for both
 444 certified reference materials CRM2583 and CRM2584.

CRM2583	Al	Ca	Cr	Fe	K	Mg	P	Pb	Ti	Zn
n	6	16	12	16	16	4	6	9	16	16
X	22250	33685	273	10677	10329	3838	3842	220	2203	1236
σ	2739	8559	257	1800	4309	546	1991	85	626	252
SE	1118	2140	74	450	1077	273	813	28	157	63
σ_r	2537	6384	213	2313	2215	131	1729	31	579	267
σ_R	2787	8694	260	2313	4421	662	2052	89	629	267
σ_L	1154	5902	149	0	3825	649	1105	84	246	0
RSE (%)	5.0	6.4	27.2	4.2	10.4	7.1	21.2	12.8	7.1	5.1
$R\sigma_r$ (%)	11.4	19.0	78.2	21.7	21.4	3.4	45.0	13.9	26.3	21.6
$R\sigma_R$ (%)	12.5	25.8	95.4	21.7	42.8	17.2	53.4	40.5	28.6	21.6
$R\sigma_L$ (%)	5.2	17.5	54.7	0.0	37.0	16.9	28.7	38.1	11.2	0.0
X*	22972	33923	189	10808	10721	3838	3359	211	2136	1263
S*	1270	9166	115	1388	3317	619	785	76	535	169
RSE* (%)	2.3	6.8	17.5	3.2	7.7	8.1	9.5	12.0	6.3	3.3
CRM2584										
n	6	16	12	16	16	4	6	15	16	16
X	21877	80962	294	18576	10864	16501	3102	10791	4383	3167
σ	5312	17312	180	1759	3668	1129	2174	3956	768	423
SE	2169	4328	52	440	917	564	888	1021	192	106
σ_r	2284	6272	70	1388	898	1094	812	975	366	406
σ_R	5828	17841	187	1783	3789	1146	2396	4087	789	425
σ_L	5362	16703	174	1119	3681	342	2255	3969	699	124
RSE (%)	9.9	5.3	17.7	2.4	8.4	3.4	28.6	9.5	4.4	3.3
$R\sigma_r$ (%)	10.4	7.7	23.8	7.5	8.3	6.6	26.2	9.0	8.4	12.8
$R\sigma_R$ (%)	26.6	22.0	63.8	9.6	34.9	6.9	77.3	37.9	18.0	13.4
$R\sigma_L$ (%)	24.5	20.6	59.2	6.0	33.9	2.1	72.7	36.8	16.0	3.9
X*	22152	80329	241	18717	10805	17023	2622	11700	4396	3142
S*	5449	17858	80	852	4034	112	1555	2112	843	274
RSE* (%)	10.0	5.6	9.6	1.1	9.3	0.3	24.2	4.7	4.8	2.2

445 *: refers to values calculated through robust statistics, n: number of the reported values

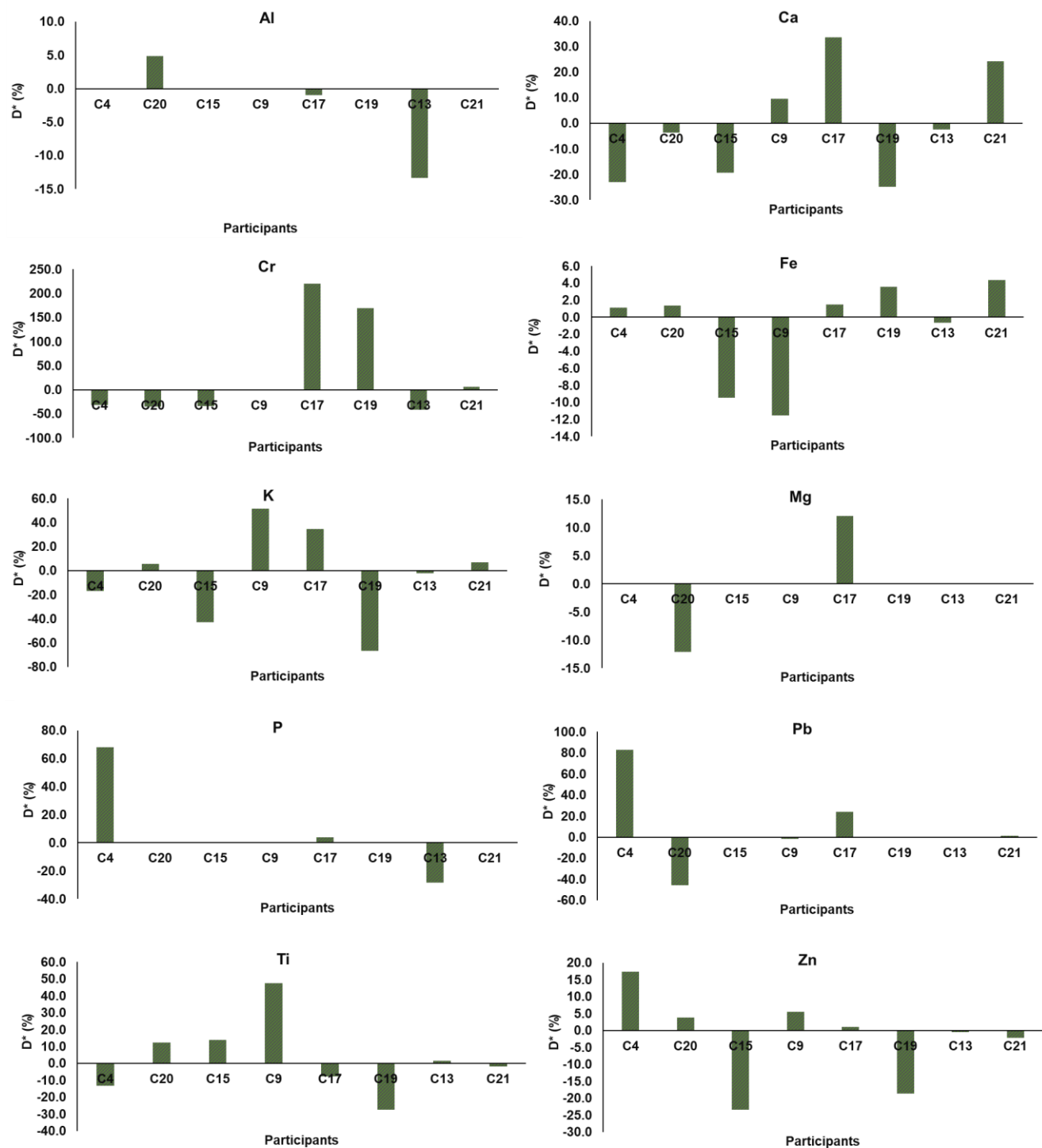
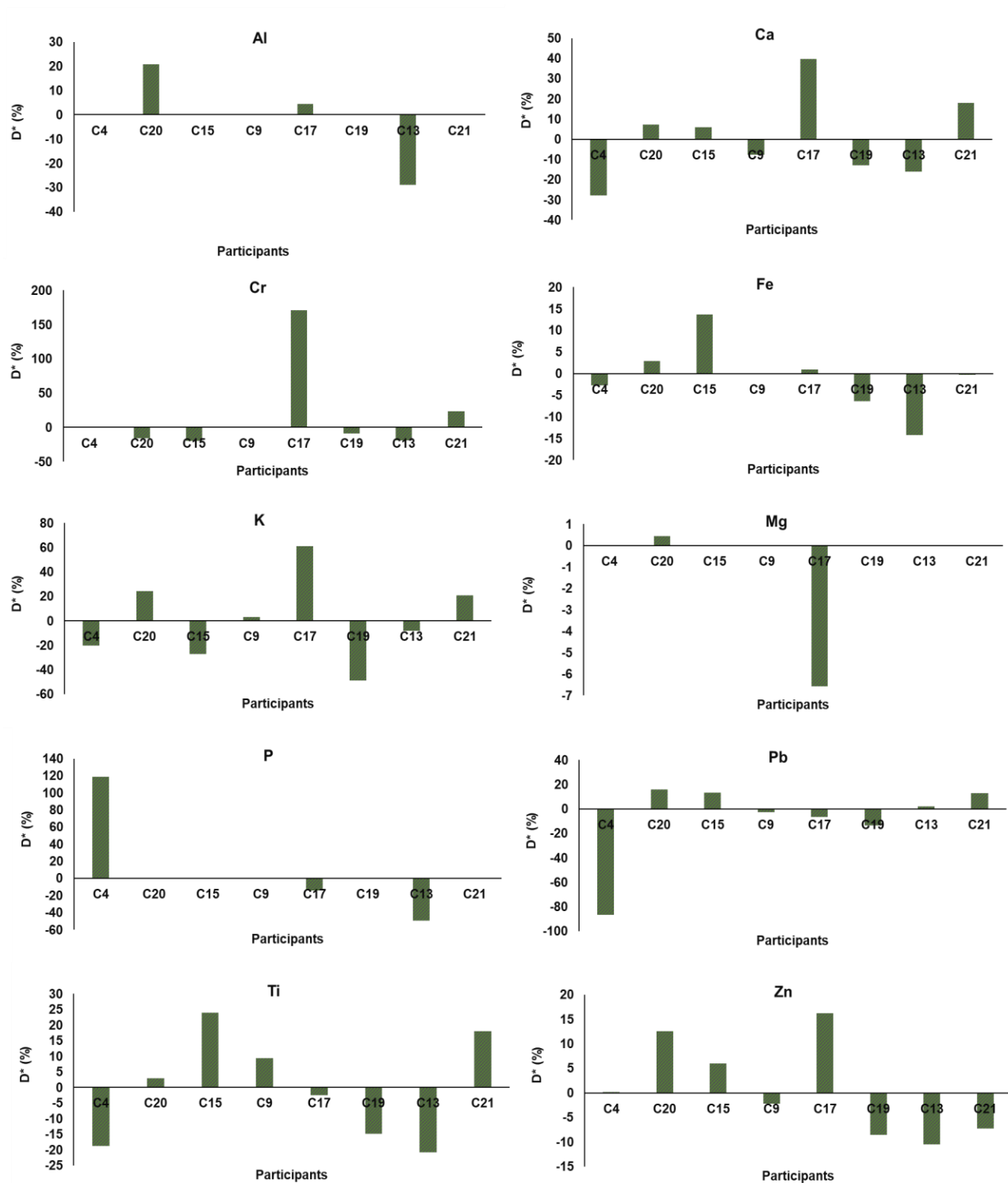


Fig. 8. Relative percentage difference between the reported results by all participants and the assigned values (robust average) for CRM 2583.



449

450 Fig. 9. Relative percentage difference between the reported results by all participants and the
 451 assigned values (robust average) for CRM 2584.

4. Conclusions

The inter-laboratory comparison of filter standards generated by two certified reference materials (CRM2583 and CRM2584) was a challenging exercise with respect to the selection of representative elements like the ones typically found in the atmospheric environment that will be contained in weight fractions per unit of reference dust mass well above their respective XRF and PIXE detection limits. However, in the absence of reference materials representative of the ambient particulate matter, the inter-comparison exercise was conducted with filter-samples produced via dispersion of dust-materials (indoor dust certified reference material) in a mixing chamber and subsequent gravimetric collection on PTFE filters.

The absolute relative percentage difference (aRD, %) between the reference values and the values reported by the Expert Laboratory ranged between 0.1 % (Ti) and 21.3 % (Pb) for most of the referred elements (i.e. Al, Ca, Fe, K, Mg, Na, P, Ti, Zn, Pb), while higher aRD values were found for As (28.0 %- 48.7%), Cr (33.7 % - 65.7 %) and Na (43.1%) (CRM2584). The majority of the participants also efficiently detected most of the elements (i.e. Ca, Fe, K, Ti, Zn, Cr, Pb), but only three participants reported values for light elements of atomic numbers lower than 16 (i.e. P, Mg and Al); light elements are difficult to identify because of the low X-ray fluorescence cross sections and therefore must be analyzed with special care. The average relative difference between the participants results and the assigned value as derived by the expert laboratory was 17.5 ± 18.1 % (CRM2583; Cr and Pb excluded) and 16.7 ± 16.7 % (CRM2584; Cr and P excluded). While, the average “relative robust standard deviation” of the results reported by all participants was 25.1 % and 22.8 % for CRM 2583 and CRM 2584, respectively. Finally, the average “between-laboratory relative standard deviation, $R\sigma L$ ” was found equal to 17.2 % (CRM2583) and 24.1 % (CRM2584) (Cr excluded). It has to be noted that very low quantity of

the standard materials was used to produce the testing samples, which is much lower than the one suggested by the manufacturer. In such a case, it is hard to achieve a real homogeneity, which is more pronounced in the case of elements with relative low concentrations (e.g. Cr).

Furthermore, in the framework of the present study, the mechanical stability of the produced standards was evaluated, for a long period of time and a high number of measurements. The results showed that the prepared sample was stable over a long time period (≈ 80 months) and no loss of material occurred, although no adhesive material was used for the sample preparation. The above conclusions provide a strong indication that the proposed versatile and cost-effective methodology can be considered as appropriate to the preparation of representative of atmospheric samples testing/reference filter materials and evaluation of the overall performance of the analytical techniques.

Acknowledgements

The intercomparison exercise was supported by the IAEA within the framework of TC Project RER/1/008 “Supporting Air Quality Management”, and partially supported by CALIBRA/EYIE” (MIS 5002799) implemented under the Action “Reinforcement of the Research and Innovation Infrastructure”, funded by the Operational Programme “Competitiveness, Entrepreneurship and Innovation” (NSRF 2014–2020) and co-financed by Greece and the European Union (European Regional Development Fund).

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Author Contributions: Conceptualization, K. E., M. G; methodology, K. E., M. G., A. G. K., M. C.; writing—original draft preparation, M. G. and M. I. M.; formal analysis, M. G., V. K.; investigation, all authors; writing - review & editing, K. E., A. G. K., M. C., A. M.; supervision, K.E. All authors have read and agreed to the published version of the manuscript.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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