Evaluation of 213 nm laser as an affordable alternative for the green elemental characterization of particulate matter on quartz fibre filters by laser ablation ICPMS

Monika Ogrizek[a,b], Ana Kroflič[a,c,*], Tomáš Vaculovič[d], Markéta Holá[d,*], and Martin Šala[a,*]

[a]Department of Analytical Chemistry, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

[b]Jožef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia

[c]Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

[d]Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5, 62500 Brno, Czech Republic

*corresponding author. Email: martin.sala@ki.si, ana.kroflic@ki.si, mhola@sci.muni.cz.

ORCID:

Monika Ogrizek: https://orcid.org/0000-0001-5883-4524

Ana Kroflič: https://orcid.org/0000-0003-1722-8397

Tomáš Vaculovič: https://orcid.org/0000-0002-1341-6430

Markéta Holá: https://orcid.org/0000-0002-2665-0832

Martin Šala: https://orcid.org/0000-0001-7845-860X

Acknowledgements Slovenian Environment Agency is gratefully acknowledged for donating PM samples and providing data on PM and elemental concentrations.

Abstract

Airborne particles, denoted as particulate matter (PM), are one of major environmental pollutants. Particles smaller than 10 µm (PM_{10}) penetrate into the human lungs during breathing and exert damage by physical and chemical mechanisms. PM mass concentration in the air as well as major toxicants contained are thus regulated by relevant directives all around the world and their continuous monitoring is prescribed. Elemental composition of PM is one of the most often measured air-quality parameters and the standard method for its determination produces huge amounts of toxic chemical waste. Sustainable alternatives are thus sought for, such as laser ablation inductively coupled plasma mass spectroscopy (LA-ICPMS), which allows for the direct analysis of PM collected on a filter without the microwave-assisted extraction step prior to the analysis with ICPMS. In this work we evaluated the performance of 213 nm Nd:YAG laser system (LA213) compared to the more powerful 193 nm excimer laser (LA193) for this application, in order to facilitate the replacement of the standard method (i.e. MW/ICPMS) with a new, waste-free one. We show that LA213 produces good results when operated under optimized instrument conditions, which were in fact very similar to the LA193 system. Sensitivity for some elements was, however, a bit poorer, but this can be overcome with additional fine-tuning, if necessary. Wrapping-up our thorough evaluation we can conclude that the more affordable LA213 is suitable for air-quality monitoring purposes.

Keywords:

PM, trace elements, metal concentration, sustainable, air quality monitoring, LA-ICPMS

1 Introduction

Particulate matter (PM) is one of the major air pollutants threatening the environment and human population (World Health Organization, WHO). PM is responsible for millions of deaths every year, among others causing pulmonary and cardiovascular diseases, and cancer (Lelieveld et al., 2015; Roy et al., 2016; Zhang et al., 2022). On the other hand, PM contributes to climate change by interfering with sun and Earth radiation pathways (Fuzzi et al., 2015).

The excess of PM which disrupts the natural balance is emitted by anthropogenic activities, such as traffic, industry, and biomass burning (Chatoutsidou et al., 2019; Karagulian et al., 2015; Trippetta et al., 2016; Tsiouri et al., 2015). Although, due to its nanoparticle nature, PM is harmful on its own, different sources produce distinctive particle structures and compositions, which finally determine the level of PM toxicity (Goix et al., 2016; Hu et al., 2012). Typically, PM is composed of inorganic ions, organic carbon, elemental carbon, crustal elements, and trace metals, some of these being known toxicants, such as polycyclic aromatic hydrocarbons (PAH) and particular trace elements. Besides PAH, airborne As, Cd, Ni, and Pb are regulated by the EU Commission (Directive 2004/107/EC and 2008/50/EC) prescribing their limit values and assuring safe living conditions along with limiting their influence on the environment. Moreover, reduction of national emissions of some other trace elements has also been commanded to date (Directive (EU) 2016/2284).

Accordingly, a standard method (microwave digestion (MW) pre-treatment followed by inductively coupled plasma mass spectroscopy (ICPMS) or graphite furnace atomic absorption spectrometry (GF-AAS) analysis) for the element determination in PM is prescribed (EN14902:2005). It is certified for the regulated four elements, although monitoring of Cr, Cu, Se, and Zn has also been ordered in Directive (EU) 2016/2284 due to their adverse effects to human health and the environment (Jaishankar et al., 2014; Tchounwou et al., 2012). The main disadvantage of the standard method is the sample preparation step. Microwave assisted digestion with concentrated nitric acid and hydrogen peroxide does not result in complete digestion of quartz fibre filter and several authors report that accurate multielement determination in various PM matrixes is not guaranteed by this method (Aldabe et al., 2013; Swami et al., 2001). Moreover, MW is an additional step to the analysis, which increases the likelihood of sample contamination and/or loss of volatile elements. It is time consuming and requires high-purity reagents to assure sufficiently low limits of detection (LOD). The required reagents not only raise the cost of analysis but also end up as a toxic waste, which is not negligible if considering every-day monitoring at numerous stations around the world (Bai et al., 2022; Gerboles and Buzica, 2008; Ogrizek et al., 2022; Pant et al., 2019; Rovelli et al., 2018; Wang et al., 1998).

A greener or at least waste-free solution to this problem is to use analytical techniques capable of determining elemental composition directly on the solid PM samples (Gini et al., 2021). Relevant techniques (*i.e.* X-ray fluorescence (XRF) and its variants, instrumental neutron activation analysis (INAA), particle induced X-ray emission (PIXE), and LA-ICPMS) which all have their advantages and drawbacks are described in detail and compared in our recent review paper (Ogrizek et al., 2022), in which energy dispersive XRF (EDXRF) and LA-ICPMS have been recognized as most promising to replace the standard method currently in use. LA-ICPMS generally provides lower LODs than EDXRF and thus allows to detect and quantify more elements especially in low-polluted samples, which is often necessary when performing source apportionment studies. Moreover, LA-ICPMS can be directly applied to quartz fibre filters, the most universal and widely used filter matrix including in environment agencies, since quartz withstands high temperatures needed for complementary organic and elemental carbon analyses.

While the standard MW/ICPMS and the proposed LA-ICPMS method can utilise identical ICPMS instruments, allowing monitoring agencies to keep exploiting the original ICPMS function for liquid environmental samples (*e.g.* ground water samples), save on space and eliminate/limit the need for additional educated personnel, a new LA system is indeed a bigger initial investment compared to a microwave owen. The recently developed method for the elemental determination of PM on quartz fibre filters by Ogrizek et al. (2021) uses a 193 nm excimer LA system (LA193); however, more affordable alternatives also exist on the market, as is 213 nm Nd:YAG (LA213). While method limitations pertaining to the sample itself (e.g. PM inhomogeneity) have already been addressed in our previous paper (Ogrizek et al., 2021) and do not change with the laser wavelength, different LA systems and wavelengths do not couple with material in the same way, which needs to be explored for the case of PM samples.

While excimer LA193 systems are characterized by homogeneous energy distribution inside the laser beam generating evenly flat craters, solid state LA213 systems are known for irregularities in laser energies inside the laser beam, resulting in a more undulating crater base (Gilbert et al., 2014). For this reason, in analytics, LA193 systems are usually preferred. Besides, less fractionation effects are observed in the case of high energy lasers compared to the higher wavelength lasers, which improves analytical accuracy especially when homogeneous, matrix-matched standards are not available for calibration. Another effect arising from the different wavelengths used for laser ablation is distinct size distribution of particles generated during the ablation, which are generally moved towards the smaller size range (< 150 nm) in the case of LA193 compared to the LA wavelengths above 200 nm (particle sizes of up to 1 µm are anticipated; both sizes are related to the ablation of NIST 610 series silicate glasses) (Guillong et al., 2003). Larger particle sizes can be problematic, since they tend to deposit close to the ablation crater and may not get transported to the ICPMS at all. Furthermore, even if these particles enter the plasma, their conversion to ions may be incomplete, which consequently influences the sensitivity of the measurement. It has been further shown that sample characteristics, *i.e.* sample transparency also influence particle size distribution and stability of the signal (Gonzalez et al., 2002; Guillong and Gunther, 2002). While LA193 performed better in the case of more transparent samples (*e.g.* NIST 612 and 614), for more opaque NIST 610 the particle size distribution and signal stability were similar for LA193 and LA213 systems (Guillong et al., 2003).

As PM samples are opaque, beige to dark brown in colour, no differences in fractionation effects due to ablation are expected between LA193 and LA213. Nevertheless, another fractionation effect could be due to different laser irradiances or power densities, which can cause sample heating or melting (Wohlgemuth-Ueberwasser and Jochumb, 2015). The 193 nm excimer and 213 nm Nd:YAG are both nanosecond lasers, where melting was observed in the past compared to the femtosecond lasers (Luo et al., 2020; Wohlgemuth-Ueberwasser and Jochumb, 2015). If similar pulse width (4–5 ns) and laser energy density were used, LA213 produced more melting during the ablation of sulphides compared to LA193 (Wohlgemuth-Ueberwasser and Jochumb, 2015). Notwithstanding, with different pulse width and fluence applied in the ablation of alloy steels (3 ns with fluences 3.5–12.1 J cm^{-2} for LA213 and 15 ns with fluences 5.1–14.5 J cm^{-2} for LA193), the least melting was observed in the case of short pulse width and low fluence with LA213 (Luo et al., 2020). Note, however, that with LA213 systems higher fluence is usually needed for comparable ablation to the LA193 (*e.g.* 4.2 vs 2.7 J cm^{-2} for sulphide analysis (Gilbert et al., 2014), or 15 vs 5 J cm^{-2} for typical reference materials (RM) as are NIST 610, GSE-1G, MACS-3, and STDP5 (Jochum et al., 2014), for LA213 vs LA193, respectively).

In this study we investigate utilisation of the 213 nm Nd:YAG LA-ICPMS for the determination of the elemental composition of PM collected on quartz fibre filters. A new method is developed for this particular application and compared to the already existing 193 nm excimer LA-ICPMS (Ogrizek et al., 2021). The potential of the more affordable LA213 system for air-quality monitoring purposes is specifically addressed, which would facilitate the worldwide transition to a more sustainable analysis in the future. Sensitivity of both methods in respect to different elements is explored and applicability of the new method is discussed, considering also the initial investment in the equipment, which can be critical especially in research, while for environment agencies the return of investment is faster due to circumventing the laborious pre-extraction step (>3 h per sample set) and huge amounts of toxic waste (100 ml per sample).

2 Experimental section

2.1 Samples and standard materials

Ambient PM_{10} samples were donated by the Slovenian Environment Agency (ARSO) and were collected during their routine monitoring according to the current EU legislation (EN12341:2014 and EN14902:2005). Sampling was performed by a high volume sampler (Digitel DHA-80 Aerosol Sampler, Switzerland) for 24 h with a flow rate of 500 L min^{-1} on quartz fibre filters (PALL, USA; filter diameter 150 mm). The samples were collected in Maribor, Slovenia (111,000 inhabitants), representative of an urban environment with traffic and biomass burning as two major pollution sources. Samples from various seasons thus provided different filter loadings and analyte concentrations.

Trace elements in glass SRM 610 and 612 (NIST, USA) were used for testing the intraday stability of the instruments and comparison of sensitivity between LA systems. Pristine quartz fibre filters (PALL, USA) were used as filter blanks.

2.2 LA-ICPMS instruments

LA is a special process used to introduce solid samples to ICPMS for analysis. Since no sample pre-treatment is required, PM_{10} samples were simply cut and mounted to a microscopic glass with a double sided tape (Scotch, USA) and put into a holder for analysis. Two LA systems using different laser generators and wavelengths were compared: (i) 193 nm nanosecond excimer LA system (193 nm ArF*; Analyte G2, Teledyne Photon Machines Inc., Bozeman, MT; later referred as LA193) at the National Institute of Chemistry, Slovenia, and (ii) 213 nm nanosecond solid state LA system (Nd:YAG, LSX 213 G2;

Teledyne Photon Machines Inc., Bozeman, MT; later referred as LA213) at the Masaryk University, Czech Republic. 2-volume ablation cell with He as a carrier gas was used in both cases (HelEx II ablation cell for LA193 and HelEx for LA213). Carrier gas flow rate was 0.5 and 0.6 L min^{-1} for the cup, respectively, and 0.3 L min^{-1} for the cell (in both cases). The same type of a quadrupole ICPMS instrument (Agilent 7900, Agilent Technologies, Santa Clara, CA) was used for detection in both cases, with Ar as a makeup gas (0.8 L min^{-1}). Kinetic energy discrimination (KED) process included in the instrument was used for successful minimization of polyatomic interferences.

Twenty elements (Al, As, Ba, Cd, Co, Cr, Cu, Fe, K, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Ti, Tl, V, and Zn) were measured simultaneously with the total acquisition time of 0.5 s and element specific dwell times as listed in Table S1.

2.2.1 Parameter optimization

Although it is known that each airborne particle is unique, the focus of the current paper is on the analysis of bulk concentrations of trace elements in PM deposited on collection filters, as required by the legislation. Therefore, instrument parameters were optimized to measure large sample area in a short amount of time, and to ablate the majority of the PM deposited on the filter rather than obtaining a perfect LA image. Optimization of LA193 parameters is described in Ogrizek et al. (2021) and LA213 optimization was approached in a similar way.

Based on our previous knowledge, ablation was performed using the adjacent line-scan mode, with the largest beam size LA system is capable to produce, and scan speed calculated to provide square pixels with a minimal smear. Acquisition time was synchronized with the washout time of the used ablation cell and was similar in both LA systems.

Three parameters were optimized experimentally: fluence (0.9–8.6 J cm^{-2}), scan speed and repetition rate that correspond to dosage 2–20 were used with the LA213 (details in Table S2). During fluence optimization, two ablation passes were repeated over the same ablation line to determine the amount of residual PM on a filter. Due to limitations of the maximum repetition rate (20 Hz), dosage optimization had to be performed at two different scan speeds (250 µm s^{-1} for dosages 2–10 and 125 µm s^{-1} for dosages 12–20); therefore, a sum of pixels was used to compare the different dosages instead of an average as used in the fluence optimization. When no signal increase was observed at increasing dosages, we assumed that the relevant PM mass had been ablated from the filter. An area of 3.15 mm^2 was ablated for every tested parameter and experiments were repeated on four different PM samples (two summer and two winter samples) for all twenty elements.

2.2.2 Sample Analysis

The set of optimized LA213 parameters was first applied to the ablation of a blank filter, to study the potential influence of impurities to the PM composition determination.

Eight ambient PM_{10} samples with different PM loadings and elemental concentrations (Table S3) were further measured by both LA systems using the optimal sets of parameters to compare instrument performance. Due to the inhomogeneity of PM material deposited on a filter, every time a randomly selected 3 × 12 mm^2 filter area was ablated, which has been previously shown representative of the whole PM filter (Ogrizek et al., 2021). Statistical evaluation of the smallest representative filter area for LA193 is described in detail in the respective paper by Ogrizek et al. (2021) and results in 30 minutes of analysis time per sample.

The samples were quantified based on known elemental concentrations from the standard MW/ICPMS analysis (data received by the Slovenian Environment Agency) with a leave-one-out cross-validation procedure (LOOCV). When heteroscedastic characteristics of the data drastically influenced the determination of low concentration samples, a weighted (x^{-1}) linear model was used (*i.e.* for As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Rb, V, Zn). Reasons for why we used such an approach for calibration are given in our method development paper (Ogrizek et al., 2021).

Differences between LA systems were statistically evaluated with the paired t-test or the paired Wilcoxon test in the case of elements where the assumption of normality was not met (the latter was assessed with the Shapiro-Wilk test). Furthermore, all three determination methods (LA193, LA213, MW/ICPMS) were compared with the repeated measures ANOVA or its appropriate non-parametric alternative (*i.e.* Friedman test). For visual representation of uncalibrated results the data were normalized (1) to allow for the comparison of different scales.

$$x_{normalized} = (x - average)\ stdev^{-1} \qquad (1)$$

Statistical analysis and data handling was performed in software R using raster, data.table, reshape2 (Wickham, 2007), tidyverse (Wickham et al., 2019), caret, and rstatix packages.

The sensitivity of both LA systems was compared by visual assessment of the capability of distinguishing between the ablation signal and the features of gas blank (*i.e.* background noise of the instrument), and graphical comparison of the measured counts. Additionally, NIST glass standards 610 and 612 were used for this purpose (ablation parameters are listed in Table S4). Note, signal intensities (counts) of NIST glasses are more prone to the ablation of different depths as PM samples with the majority of PM material captured in the upper layers of the filter. The ratio between the two LA systems was calculated for every element in order to i) compare ablation volumes and ii) better evaluate method sensitivity.

3 Results and discussion

3.1 LA213 parameters optimization

The LA213 system was first optimized to assure the finest possible sensitivity and repeatability. As already mentioned in the introduction part, how the laser interacts with a sample depends on sample characteristics (*e.g.* transparency, density) and laser wavelength. Usually, LA213 needs more energy (higher fluence) compared to LA193 for similar ablation. For example, NIST 600 glass series RM is optimally ablated using fluence 3–5 J cm^{-2} with LA193, whereas 8–12 J cm^{-2} is needed with LA213. Our samples, however, are much more complex due to their two-component structure (filter matrix and deposited PM), which does not allow to easily draw parallels with RM or other samples from the literature; instrument parameters thus have to be carefully optimized for the specific application.

In PM on a filter samples, particles are mostly deposited in top layers of the filter and are not strongly bound to filter fibres. As PM represents only a small proportion of the sample mass (sample = filter + deposited PM), impurities in the filter matrix strongly interfere with the analysis of trace PM concentrations if large amount of filter matrix is ablated. Since we are only interested in the composition of PM and not in the filter matrix itself, the optimal fluence will be strong enough to allow for the ablation of the deposited PM but low enough to ablate as little quartz fibres as possible at the same time. Therefore, relatively low fluence is preferred for the ablation of PM samples, with the correction to higher dosages (*i.e.* more overlapping shots) in case that PM still remains on the filter after the selected number of overlapping shots.

Table 1 Optimized instrument parameters for the ablation of PM deposited on quartz fibre filters

Parameter	**LA193***	**LA213**
Pre-determined parameters by educated guess		
Laser beam size	128 µm (square mask)	125 µm (square mask)

Scan speed	256 µm s^{-1}	250 µm s^{-1}
Acquisition time	0.5 s	0.5 s
Optimized parameters		
Dosage	10	10
Repetition rate	20 Hz	20 Hz
Fluence	1.5 J cm^{-2} (with 10x demagnification)	1.7 J cm^{-2}
Ablated area	3 × 12 mm^2 (random sampling)	3 × 12 mm^2 (random sampling)

*from Ogrizek et al. (2021)

It turned out that optimal instrument parameters are very similar for both LA systems (Table 1). In the case of LA213, 1.7 J cm^{-2} was chosen as the optimal fluence, because higher fluences did not provide significant increase in the signal intensities (Fig. 1a). The observed increase in the signal intensity with increasing fluence especially in the second ablation pass can be attributed to the ablation of quartz fibre material together with its impurities at higher fluences, which should be avoided. This explanation is additionally confirmed with the lack of signal intensity increase at higher dosages (Fig. 1b). Therefore, we selected dosage 10 as sufficient for winter samples, whereas for summer samples even less dosage would be adequate.

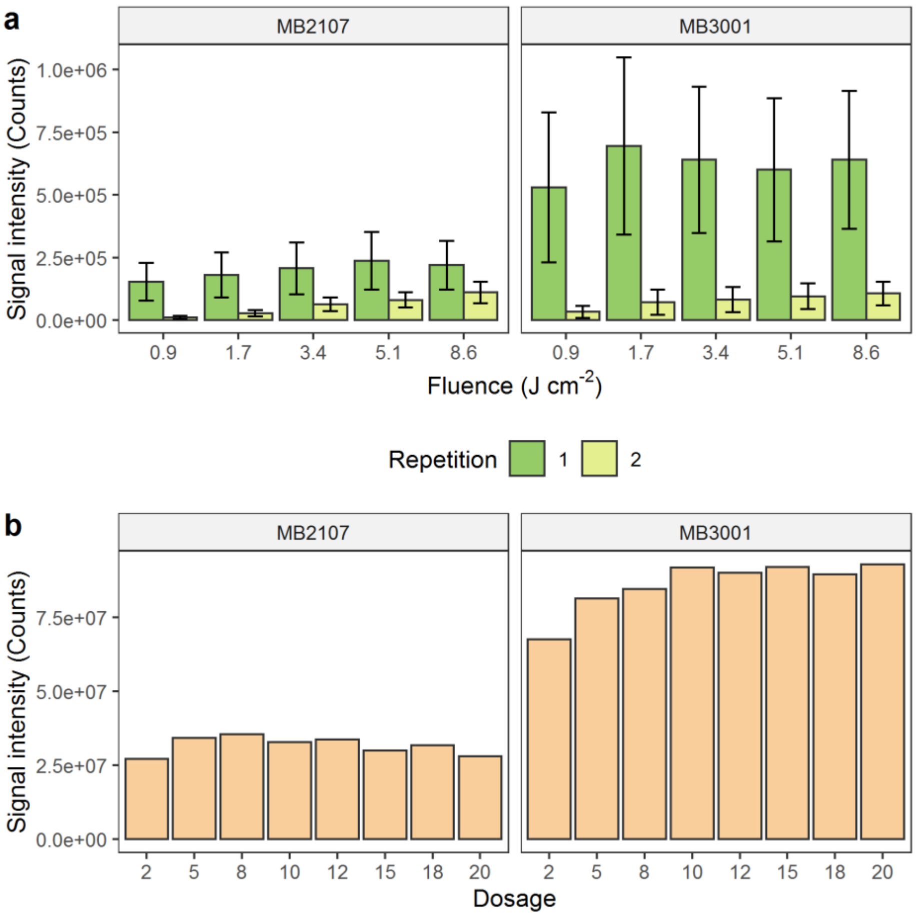

Fig. 1 Optimization of LA213 parameters: example for Cr. One highly loaded sample (MB3001) and one sample with a low PM mass-load (MB2107) are shown. In the optimization of fluence, dosage was fixed at 10, and for the optimization of dosage, fluence 1.7 J cm^{-2} was used. Error bars in A represent variability between the pixels (standard deviation). In B, the sum of pixels is shown instead of an average, not allowing us to calculate the standard deviation

We should mention at this point that instrument parameters are optimized for typical ambient PM concentration levels in Europe (PM_{10} mass concentration < 50 µg m^{-3}). However, if samples are collected in much more polluted areas with significantly higher mass loadings, the dosage needs to be adjusted, keeping the fluence at the determined level (*vide supra*). From this perspective, LA213 has some limitations, since the maximum repetition rate is 20 Hz, compared to LA193 where 300 Hz or even 1000 Hz can be used (Šala et al., 2020). For instance, with the maximum repetition rate of 20 Hz, scan speed has to be adjusted for dosages above 10, resulting in a prolonged measurement time.

3.2 Blank filter ablation

Although ablation parameters were optimized to ablate as little filter matrix as possible, in the upper layers of the filter quartz fibres and PM are intertwined together so that ablation of some fibres cannot be completely avoided. Along with the fibres, some impurities from the filter are always sampled as well. Whenever the impurities of blank filter differ significantly from the background noise (*i.e.* gas blank), their contribution needs to be accounted for during PM analysis. Therefore, filter blanks were analysed with both LA systems using the set of optimized instrument parameters and compared (Fig. 2).

The most pronounced interferences originating from blank filters that were detected with both LA systems are Al, Cr, and Mo (Fig. S1). Aluminium impurities are not problematic, since Al is one of the Earth crust elements that are naturally present in PM in relatively high concentrations even in low-polluted areas. On the other hand, Cr and Mo are less abundant in PM and in low-polluted samples non-negligible blank signals can substantially affect their determination.

Overall, with use of the optimised set of parameters, LA213 seems to ablate more blank filter material and consequently more impurities than LA193 (observe the differences between gas blanks and filter blanks in Fig. S1). With LA213, Ni was clearly detected in blank filters and some barely noticeable differences between gas and filter blanks were also found for Fe, K, Mn, Ti, and Zn. On the other hand, LA193 barely detected Ni, Sb, and Ba impurities, whereas the latter two elements were not detected with LA213 at all, indicating higher detection limits.

Among the listed elements, special attention should be paid to Cr, Ni, and Mo when using LA213 (filter blanks accounted for up to 20, 20, and 45% of low-concentration samples, respectfully), and to Cr when using LA193 (filter blank accounted for 8% of the low-concentration sample). All other impurities were low enough compared to sample concentrations to avoid an influence on the final quantification (impurities in blanks contributed <3% to the lowest sample signal in both LA systems).

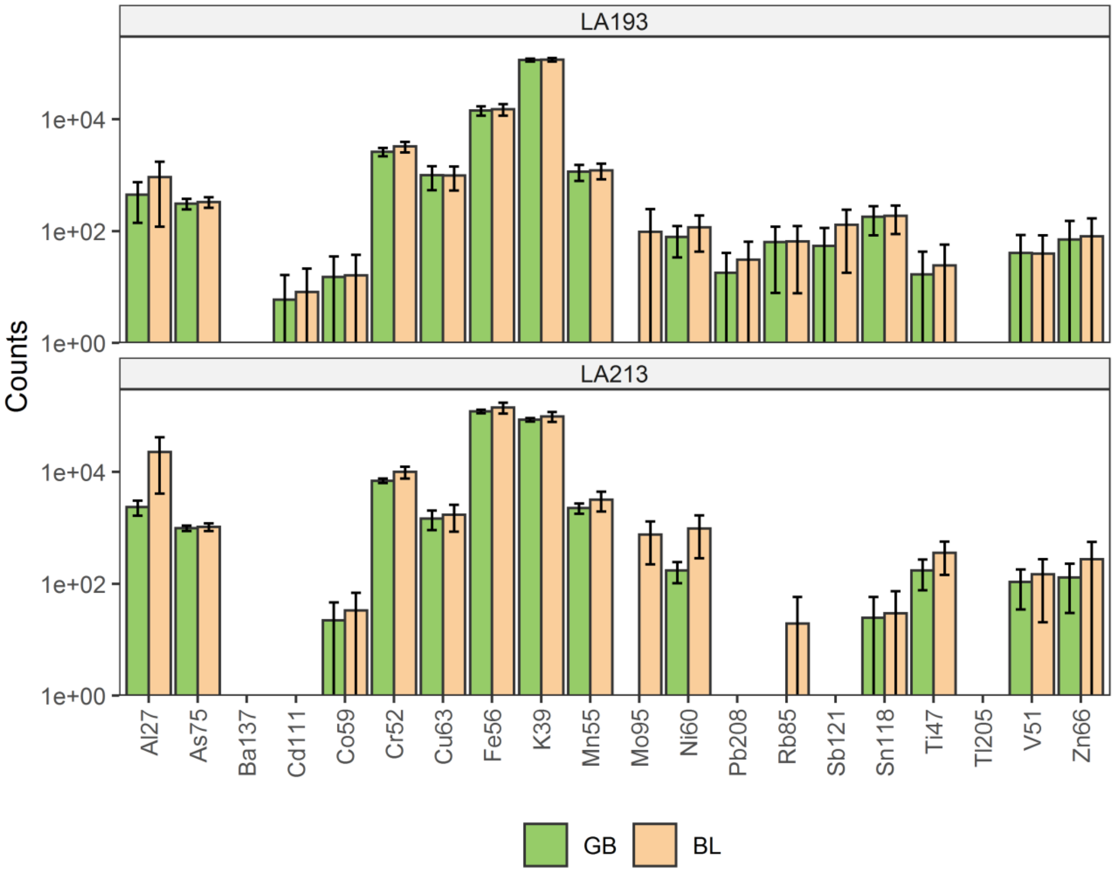

Fig. 2 Gas blank (GB) vs. filter blank (BL): Comparison of signals from the background noise (*i.e.* GB) with the impurities in blank filters (*i.e.* BL). The plotted error bars are standard deviations between the pixels, representing their scattering

3.3 PM sample ablation: comparison of LA213 with LA193

It has already been explained that laser interaction with the ablated material is wavelength specific and can lead to distinctive elemental fractionation effects. The ablation of PM samples is performed in a line-scan mode and since the majority of PM mass is deposited in the upper layers of the sample, an in-depth fractionation effect is not likely to be observed. Moreover, potential fractionation effects are expected to be corrected for by calibration with matrix-matched standards. However, calibration still remains an issue in LA-ICPMS.

Since PM material on quartz fibre filter is a very specific sample in its structure, none of the commonly used RM (*e.g.* glass or gelatine standards, pressed pellets, spiked filter matrix, ...) is suitable for its calibration (Brown et al., 2013; Miliszkiewicz et al., 2015; Šala et al., 2017). Matrix-matched RM of PM on quartz fibre filter with certified elemental composition is also not yet commercially available. Although the use of ambient PM samples previously characterized with MW/ICPMS as standards for the calibration is not an ideal practice, since erroneous determination due to the MW pre-treatment step can lead to inaccurate LA-ICPMS analysis, it is a matrix-matched material and fits the purpose of our research.

The constructed calibration curves were not ideal (note that MW/ICPMS used for their standardization is not certified for all elements); but still, LOOCV analysis showed they were comparable for LA193 and LA213 (Fig. S2). Both LA systems exhibited high R^2, low root mean squared errors (RMSE), and low mean absolute errors (MAE) for Al, As, Co, Cu, Fe, Mn, Mo, Sb (Fig. S2). Somehow poorer performance was obtained for Cd, Rb, and Zn, with both instruments. Furthermore, we can see that LOOCV calibration curves, which are presented in Fig. S3 for the case of As, show substantial deviation from the rest of the curves only when the highest concentration measured is omitted (as part of statistical procedure). This may lead to biases in the quantification of analytes with concentrations in the upper part of each calibration curve, while confidence of the determination of low-concentration samples should not be compromised.

In Fig. S4 we compare the results of sample analyses with all three methods. Samples determined with both LA systems and MW/ICPMS do not reveal any credible evidence for the difference for any of the elements, which was also confirmed by statistical testing (Table S5). Note that MW/ICPMS results were used as calibration standards, masking eventual systemic biases due to incomplete digestion in the respective method. Airborne concentrations of all elements as determined by LA193 and LA213 are further compared in Fig. 3, Table S6, and Table S7. Higher deviations (although randomly distributed) between the LA systems are observed in the samples with the highest element concentrations, which is in line with the nature of the constructed calibration curves as explained in the previous paragraph. Moreover, the highest concentrations measured felt outside of the calibration range, which resulted in even poorer confidence of their determination. Consequently, high absolute differences between the two LA systems are observed at the highest concentrations measured. Note that according to Directive 2004/107/EC, accuracy of determination of As, Cd, and Ni in PM is reported within 40 % by MW/ICPMS. From all this we may conclude that the performance of LA213 is comparable to LA193.

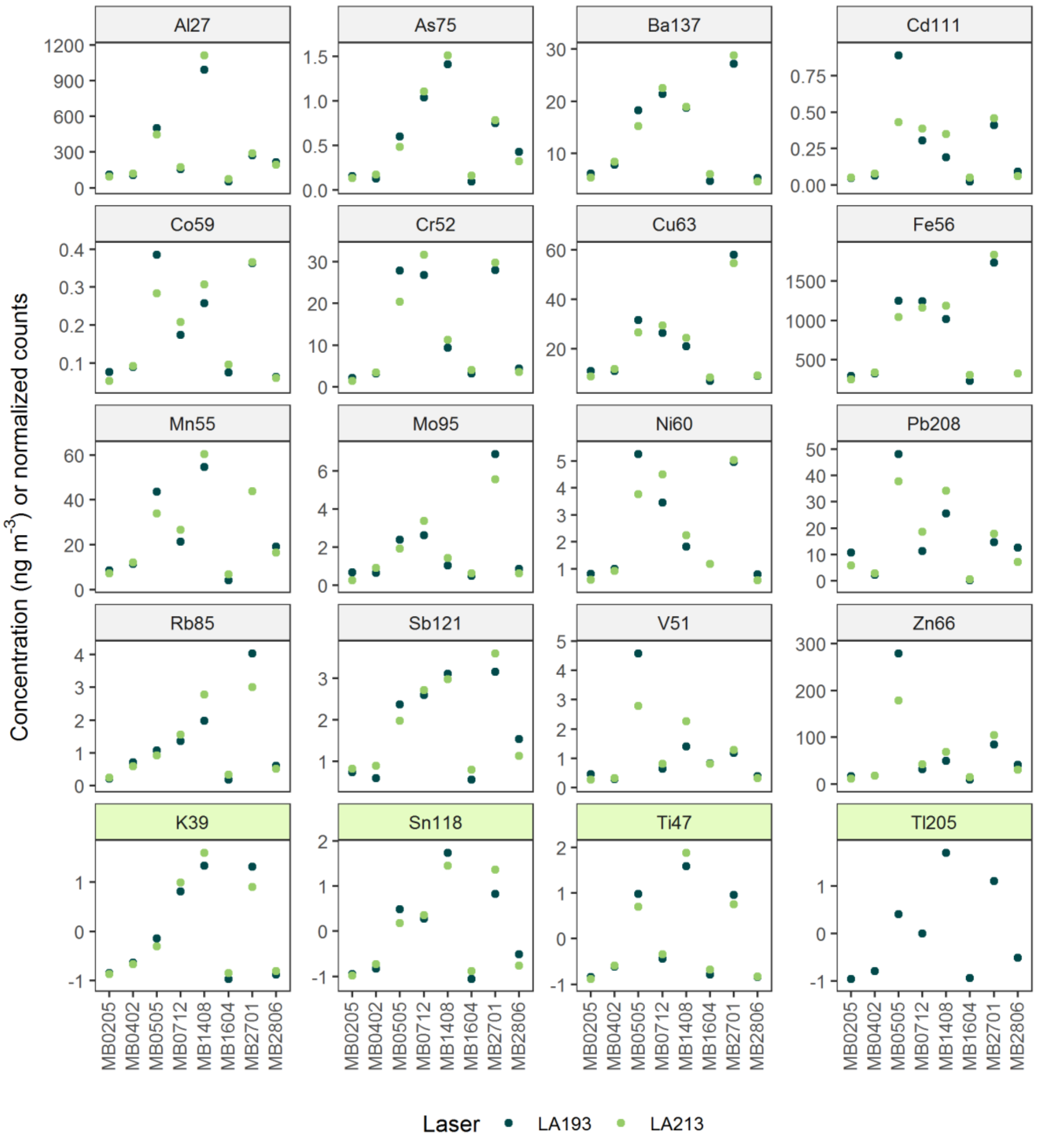

Fig. 3 LA193 vs LA213: Comparison of ambient sample element concentrations. The top 4 rows (grey) present calibrated elements with concentration on y-axis, and the bottom row (green) are non-calibrated elements with normalized counts on y-axis, since the 4 elements (*i.e.* K, Sn, Ti, and Tl) were not measured with MW/ICPMS. Tl could only be detected with LA193

Although we showed that both LA systems perform comparably well in terms of accuracy, different sensitivity was observed for some elements. LA213 turned out to be less sensitive for Ba, Cd, Pb, Sb, Sn and Tl in PM samples (Fig. S5) as well as NIST glass standards (Fig. S6). Sb and Sn are not considered problematic, since they are usually present in PM in fairly high concentrations. On the contrast, in low-concentration samples, Ba, Cd, and Pb were at the edge of LOD in LA213 measurements, which was not the case with LA193 (refer here also to Fig. S7). We were also unable to determine Tl with LA213 in either the PM samples or NIST glass standards. Among the referenced elements in NIST 610, Tl has the lowest reported concentration (approximately 7-times lower than the other elements of interest), which points to the poor sensitivity of the method for this particular element. Besides, Tl is also volatile and could be lost during the ablation, especially with LA213. Note, however, that when particular elements are of specific interest, high LODs and/or low sensitivities can be overcome by additional optimization and introducing more material for their analysis (*e.g.* bigger beam size or longer acquisition times; the latter consequently means measuring fewer elements at a time) (van Elteren et al., 2019).

Although we observed a similar pattern in sensitivity towards different elements for real samples and NIST standards, we should not neglect the fact that with the different lasers we indeed ablated different volumes of the material due to different beam sizes (256 µm for LA193 and 125 µm for LA213), but also due to differences in the used fluence and laser wavelengths, influencing intensity of the signal (*i.e.* counts). As already mentioned, ablation volume is especially important in the case of NIST standards. Therefore, in order to understand differences between both ablations, we further examined the ratios between the elements measured with the LA systems in both RM, which are shown in Table S8.

Based on the ratios of most elements (*i.e.* Al, As, Co, Cr, Cu, Fe, K, Mn, Ni, Ti, V, and Zn), larger volumes seem to be ablated with LA213 compared to LA193. If this is true, LA213 indeed exhibits much lower sensitivity for the above-mentioned elements. Furthermore, when comparing the ratios for NIST 610 and 612, more abnormalities were found in the case of NIST 612 (see Table S8), which implies more fractionation effects in the case of NIST 612. Similar observations were reported by Guillong et al. (2003), where fractionation indexes of LA193 and LA213 were different in the case of NIST 612, but still very similar in the case of NIST 610.

Ba, Cd, Pb, Sb, Sn, and Tl are normally produced by anthropogenic activities (*e.g.* traffic, industry) and usually exhibit lower airborne concentrations than elements originating from natural sources (*e.g.* Al, Fe, K). In source apportionment studies, those 6 elements are usually associated with traffic or traffic-related emission factors as are break and tyre wear (*e.g.* Ba, Cd, Pb, Sb, Sn), biomass burning (*e.g.* Cd, Tl), or industrial emission factors as are metallurgical emissions (*e.g.* Pb, Tl) (Almeida et al., 2020; Belis et al., 2013; Ferreira et al., 2016; Landis et al., 2017; Massimi et al., 2020). Our samples were collected in an urban environment, close to a road with heavy traffic where anthropogenic emissions are relatively constant regardless of the seasons. Nevertheless, with LA213 we could barely detect some of these elements in summer samples, which may be generally problematic when studying samples collected in warmer parts of the year or in rural areas with less traffic and industrial emission sources. From this perspective, LA193 is a preferential choice of use in source apportionment studies conducted in low-polluted areas or where Tl is the targeted element of interest (*e.g.* determination of the influence of specific industry on air pollution), unless LA213 method parameters are further optimized for these elements (Karbowska, 2016).

Even though the sensitivity of LA213 is poorer than of LA193 for some elements, it is still sufficient to meet the current legislation (limit values are 6, 5, 20, and 500 ng m^{-3} for As, Cd, Ni, and Pb, respectfully; EU Directive 2004/107/EC and 2008/50/EC), and to compete with the current standard method (low limit of working range is set at 0.5, 0.1, 2, and 1 ng m^{-3} for As, Cd, Ni, and Pb, respectfully). In our work, airborne concentrations were in the range of 0.09–1.5 ng m^{-3} for As, 0.02–0.9 ng m^{-3} for Cd, 0.6–5.3 ng m^{-3} for Ni, and 0.3–50 ng m^{-3} for Pb as shown in Fig. 3; we were able to determine them all, although some concentrations fall below the certified LOD of MW/ICPMS. Multi-element determination and other pros of the method can be exploited as comparable with MW/ICPMS, without concerning about the problems connected with MW digestion in the case of LA-ICPMS. Therefore, we can conclude that LA213 performs suitably well for monitoring of elemental concentrations in PM according to the current legislation and is a valid alternative to the more expensive LA193 system.

4 Conclusions and outlook

Striving for sustainability has become an important part of our everyday life. Analytical techniques often produce large quantity of toxic chemical waste and to achieve sustainable future, green analytical methods have to be promoted even in research laboratories. Air quality monitoring is one of the continuous processes where green analytical methods are especially appreciated. The intention of detecting pollution for the purpose of its mitigation and at the same time producing toxic waste and polluting the environment seems somehow contradictory. Moreover, monitoring network is expected to continuously grow and extend even to the less developed countries, which will multiply the number of analyses and consequently their effect on the environment. Waste-free analytical methods with a minimal burden to the environment should thus replace the old methods, whenever possible.

One such example is the proposed LA-ICPMS for the elemental characterization of PM instead of the standardized MW/ICPMS method. While LA-ICPMS certainly circumvents the production of toxic waste (approx. 140 ml 16 % nitric acid pH <1) and minimizes manual work (by 4-times), one may question the consumption of gases and power due to the longer operation time during the analysis (about 10-times longer compared to solution ICPMS). Although a detailed Life cycle analysis is out of scope of this manuscript, we still want to argue in favour of the method we promote also from this point of view. By comparing the cost of consumables, which somehow resembles their production costs including energy consumption, LA-ICPMS turns out 2-times cheaper than MW/ICPMS. If we further account for MW digestion, the difference in power consumption between LA-ICPMS and MW/ICPMS is only left at 2-3 times and is still expected to decrease, because modern LA instruments tend to be more eco-friendly. While the development of LA systems is currently on the rise, no drastic improvements are expected in the field of ICPMS, although N_2 plasmas are on the horizon and will positively affect both MW/ICPMS and LA-ICPMS analyses. Moreover, there is already 20 % difference in power consumption between the two instruments used, in favour of the LA213, and ICPMS usually uses more energy when working in solution mode compared with LA (Fietzke and Frische, 2016). Considering also necessary requirements for the specific application (*i.e.* large laser beams, moderate laser energy), we believe that power consumption of LA systems can be still substantially improved.

Many different LA systems are currently available on the market, varying in performance and price availability. We show that the 193 nm excimer LA system enables low-limit determination of all 20 elements of interest and is presented as a preferable choice in source apportionment studies, where multi-element quantification is especially appreciated. On the other hand, 213 nm solid state LA system exhibits slightly higher LODs for some elements, which can be critical in low-polluted samples. Nevertheless, LA213 is still shown satisfactory for use in the elemental determination of PM according to the current legislation (*i.e.* meets prescribed limit values) and it can be further fine-tuned for specific target analytes or extremely low-concentration samples while retaining the benefits over other surface techniques (*e.g.* low LOD, direct measurement on fibrous filters). Therefore, we assess the cheaper LA213 system adequate for air-quality monitoring purposes, which lowers the initial investment needed for the transition to the greener analytical alternative.

In this paper we present state-of-the-art capabilities of LA-ICPMS systems for the analysis of ambient PM samples and identify their potential benefits in air quality monitoring. However, just as standard MW/ICPMS has many drawbacks (*e.g.* incomplete digestion, limited RM), LA-ICPMS also has some limitations. We want to encourage relevant manufacturers to direct their development to the production of standards/parts specific for this application enabling proper method validation and better automatization. The field of LA-ICPMS is continuously improving and actively developing in the direction of having more and more commercially available certified matrix matched standards for various calibration purposes, and autosamplers customized for specific samples. This is necessary for assuring the required traceability in regulatory agencies and facilitating the analysis of large number of samples. We believe LA-ICPMS is the green analytical method on the rise, that can contribute with a small step towards achieving the desired sustainable future even within air-quality monitoring.

Declarations

Ethics approval and consent to participate Not applicable. No human or animal subject were involved in the study.

Consent for publication Not applicable.

Availability of data and material The datasets generated during and/or analysed during the current study are available from corresponding author on reasonable request.

Competing interests The authors have no relevant financial or non-financial interests to disclose.

Funding This study was financially supported by Slovenian Research Agency (research core funding Nos. P1-0034 and P2-0152) and Czech Science Foundation (project No. 20-02203S). The authors acknowledge the project Impacts of PM Pollution on Cultural Heritage (J1-1707) financially supported by the Slovenian Research Agency. M.O. further thanks the Slovenian Research Agency for funding her PhD research.

Author Contributions Monika Ogrizek: Investigation, Formal analysis, Writing – Original Draft, Visualization. Ana Kroflič: Conceptualization, Writing – Review & Editing, Supervision, Funding acquisition. Markéta Holá: Investigation, Writing – Review & Editing. Tomáš Vaculovič: Investigation, Writing – Review & Editing. Martin Šala: Conceptualization, Methodology, Writing – Original Draft, Supervision, Funding acquisition.

References

Aldabe, J., Santamaria, C., Elustondo, D., Lasheras, E., Santamaria, J.M., 2013. Application of microwave digestion and ICP-MS to simultaneous analysis of major and trace elements in aerosol samples collected on quartz filters. Anal. Methods 5(2), 554-559.

Almeida, S.M., Manousakas, M., Diapouli, E., Kertesz, Z., Samek, L., Hristova, E., Šega, K., Alvarez, R.P., Belis, C.A., Eleftheriadis, K., Albania, Civici, N., Radic, R., Vukic, L., Hristova, E., Veleva, B., Šega, K., Bešlic, I., Davila, S., Godec, R., Manousakas, M., Diapouli, E., Vratolis, S., Eleftheriadis, K., Kertesz, Z., Belis, C.A., Bernatonis, M., Djukanovic, G., Jancic, D., Samek, L., Furman, L., Stegowski, Z., Almeida, S.M., Galinha, C., Balan, V., Nikolovska, L., Stefanovska, A., Radenkovic, M., Kneževic, J., Banu Oztas, N., Cantay, E., Turchenko, D.V., Abdullaev, S., Padilla Alvarez, R., Karydas, A.G., The, I.E.R.S.G., 2020. Ambient particulate matter source apportionment using receptor modelling in European and Central Asia urban areas. Environ. Pollut. 266.

Bai, H.M., Yan, R.S., Gao, W.K., Wei, J., Seong, M., 2022. Spatial representativeness of PM2.5 monitoring stations and its implication for health assessment. Air Qual. Atmos. Health 15(9), 1571-1581.

Belis, C.A., Karagulian, F., Larsen, B.R., Hopke, P.K., 2013. Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe. Atmos. Environ. 69, 94-108.

Brown, R.J.C., Jarvis, K.E., Disch, B.A., Goddard, S.L., 2013. An investigation of calibration materials for the measurement of metals in ambient particulate matter on filters by LA-ICP-MS. Int. J. Environ. Anal. Chem. 93(3), 335-348.

Chatoutsidou, S.E., Kopanakis, I., Lagouvardos, K., Mihalopoulos, N., Torseth, K., Lazaridis, M., 2019. PM10 levels at urban, suburban, and background locations in the eastern Mediterranean: local versus regional sources with emphasis on African dust. Air Qual. Atmos. Health 12(11), 1359-1371.

Ferreira, A.J.D., Soares, D., Serrano, L.M.V., Walsh, R.P.D., Dias-Ferreira, C., Ferreira, C.S.S., 2016. Roads as sources of heavy metals in urban areas. The Covões catchment experiment, Coimbra, Portugal. Journal of Soils and Sediments 16(11), 2622-2639.

Fietzke, J., Frische, M., 2016. Experimental evaluation of elemental behavior during LA-ICP-MS: influences of plasma conditions and limits of plasma robustness. J. Anal. At. Spectrom. 31(1), 234-244.

Fuzzi, S., Baltensperger, U., Carslaw, K., Decesari, S., Denier van der Gon, H., Facchini, M.C., Fowler, D., Koren, I., Langford, B., Lohmann, U., Nemitz, E., Pandis, S., Riipinen, I., Rudich, Y., Schaap, M., Slowik, J.G., Spracklen, D.V., Vignati, E., Wild, M., Williams, M., Gilardoni, S., 2015. Particulate matter, air quality and climate: lessons learned and future needs. Atmos. Chem. Phys. 15(14), 8217-8299.

Gerboles, M., Buzica, D., 2008. Intercomparison exercise for heavy metals in PM10, EUR 23219 EN. Office for Official Publications of the European Communities, Luxembourg.

Gilbert, S.E., Danyushevsky, L.V., Goemann, K., Death, D., 2014. Fractionation of sulphur relative to iron during laser ablation-ICP-MS analyses of sulphide minerals: implications for quantification. J. Anal. At. Spectrom. 29(6), 1024-1033.

Gini, M., Manousakas, M.-I., Kantarelou, V., Karydas, A.-G., Chiari, M., Migliori, A., Civici, N., Veleva, B., Šega, K., Samek, L., Samara, C., Kertesz, Z., Osan, J., 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.

Goix, S., Uzu, G., Oliva, P., Barraza, F., Calas, A., Castet, S., Point, D., Masbou, J., Duprey, J.L., Huayta, C., Chincheros, J., Gardon, J., 2016. Metal concentration and bioaccessibility in different particle sizes of dust and aerosols to refine metal exposure assessment. J. Hazard. Mater. 317, 552-562.

Gonzalez, J., Mao, X.L., Roy, J., Mao, S.S., Russo, R.E., 2002. Comparison of 193, 213 and 266 nm laser ablation ICP-MS. J. Anal. At. Spectrom. 17(9), 1108-1113.

Guillong, M., Gunther, D., 2002. Effect of particle size distribution on ICP-induced elemental fractionation in laser ablation-inductively coupled plasma-mass spectrometry. J. Anal. At. Spectrom. 17(8), 831-837.

Guillong, M., Horn, I., Gunther, D., 2003. A comparison of 266 nm, 213 nm and 193 nm produced from a single solid state Nd : YAG laser for laser ablation ICP-MS. J. Anal. At. Spectrom. 18(10), 1224-1230.

Hu, X., Zhang, Y., Ding, Z.H., Wang, T.J., Lian, H.Z., Sun, Y.Y., Wu, J.C., 2012. Bioaccessibility and health risk of arsenic and heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn and Mn) in TSP and PM2.5 in Nanjing, China. Atmos. Environ. 57, 146-152.

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B., Beeregowda, K.N., 2014. Toxicity, mechanism and health effects of some heavy metals. Interdisciplinary Toxicology 7(2), 60-72.

Jochum, K.P., Stoll, B., Weis, U., Jacob, D.E., Mertz-Kraus, R., Andreae, M.O., 2014. Non-Matrix-Matched Calibration for the Multi-Element Analysis of Geological and Environmental Samples Using 200 nm Femtosecond LA-ICP-MS: A Comparison with Nanosecond Lasers. Geostand. Geoanal. Res. 38(3), 265-292.

Karagulian, F., Belis, C.A., Dora, C.F.C., Prüss-Ustün, A.M., Bonjour, S., Adair-Rohani, H., Amann, M., 2015. Contributions to cities' ambient particulate matter (PM): A systematic review of local source contributions at global level. Atmos. Environ. 120, 475-483.

Karbowska, B., 2016. Presence of thallium in the environment: sources of contaminations, distribution and monitoring methods. Environmental Monitoring and Assessment 188(11), 640.

Landis, M.S., Pancras, J.P., Graney, J.R., White, E.M., Edgerton, E.S., Legge, A., Percy, K.E., 2017. Source apportionment of ambient fine and coarse particulate matter at the Fort McKay community site, in the Athabasca Oil Sands Region, Alberta, Canada. Science of The Total Environment 584-585, 105-117.

Lelieveld, J., Evans, J.S., Fnais, M., Giannadaki, D., Pozzer, A., 2015. The contribution of outdoor air pollution sources to premature mortality on a global scale. Nature 525(7569), 367-371.

Luo, T., Wang, Y., Li, M., Zhang, W., Chen, H.H., Hu, Z.C., 2020. Determination of Major and Trace Elements in Alloy Steels by Nanosecond and Femtosecond Laser Ablation ICP-MS with Non-matrix-matched Calibration. Atom. Spectrosc. 41(1), 11-19.

Massimi, L., Ristorini, M., Astolfi, M.L., Perrino, C., Canepari, S., 2020. High resolution spatial mapping of element concentrations in PM10: A powerful tool for localization of emission sources. Atmos. Res. 244, 11.

Miliszkiewicz, N., Walas, S., Tobiasz, A., 2015. Current approaches to calibration of LA-ICP-MS analysis. J. Anal. At. Spectrom. 30(2), 327-338.

Ogrizek, M., Jaćimović, R., Šala, M., Kroflič, A., 2021. No more waste at the elemental analysis of airborne particulate matter on quartz fibre filters. Talanta 226, 122110.

Ogrizek, M., Kroflič, A., Šala, M., 2022. Critical review on the development of analytical techniques for the elemental analysis of airborne particulate matter. Trends in Environmental Analytical Chemistry 33, e00155.

Pant, P., Lal, R.M., Guttikunda, S.K., Russell, A.G., Nagpure, A.S., Ramaswami, A., Peltier, R.E., 2019. Monitoring particulate matter in India: recent trends and future outlook. Air Qual. Atmos. Health 12(1), 45-58.

Rovelli, S., Nischkauer, W., Cavallo, D.M., Limbeck, A., 2018. Multi-element analysis of size-segregated fine and ultrafine particulate via Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry. Anal. Chim. Acta 1043, 11-19.

Roy, R., Jan, R., Yadav, S., Vasave, M.H., Satsangi, P.G., 2016. Study of metals in radical-mediated toxicity of particulate matter in indoor environments of Pune, India. Air Qual. Atmos. Health 9(6), 669-680.

Swami, K., Judd, C.D., Orsini, J., Yang, K.X., Husain, L., 2001. Microwave assisted digestion of atmospheric aerosol samples followed by inductively coupled plasma mass spectrometry determination of trace elements. Fresenius J. Anal. Chem. 369(1), 63-70.

Šala, M., Šelih, V.S., Stremtan, C.C., van Elteren, J.T., 2020. Analytical performance of a high-repetition rate laser head (500 Hz) for HR LA-ICP-QMS imaging. J. Anal. At. Spectrom. 35(9), 1827-1831.

Šala, M., Šelih, V.S., van Elteren, J.T., 2017. Gelatin gels as multi-element calibration standards in LA-ICP-MS bioimaging: fabrication of homogeneous standards and microhomogeneity testing. Analyst 142(18), 3356-3359.

Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K., Sutton, D.J., 2012. Heavy Metal Toxicity and the Environment, in: Luch, A. (Ed.) Molecular, Clinical and Environmental Toxicology: Volume 3: Environmental Toxicology. Springer Basel, Basel, pp. 133-164.

Trippetta, S., Sabia, S., Caggiano, R., 2016. Fine aerosol particles (PM1): natural and anthropogenic contributions and health risk assessment. Air Qual. Atmos. Health 9(6), 621-629.

Tsiouri, V., Kakosimos, K.E., Kumar, P., 2015. Concentrations, sources and exposure risks associated with particulate matter in the Middle East Area-a review. Air Qual. Atmos. Health 8(1), 67-80.

van Elteren, J.T., Šelih, V.S., Šala, M., 2019. Insights into the selection of 2D LA-ICP-MS (multi)elemental mapping conditions. J. Anal. At. Spectrom. 34(9), 1919-1931.

Wang, C.F., Jeng, S.L., Lin, C.C., Chiang, P.C., 1998. Preparation of airborne particulate standards on PTFE-membrane filter for laser ablation inductively coupled plasma mass spectrometry. Anal. Chim. Acta 368(1-2), 11-19.

Wickham, H., 2007. Reshaping Data with the reshape Package. Journal of Statistical Software 21(12), 1 - 20.

Wickham, H., Averick, M., Bryan, J., Chang, W., D'Agostino McGowan, L., François, R., Grolemund, G., Hayes, A., Henry, L., Hester, J., Kuhn, M., Pedersen, T.L., Miller, E., Bache, S.M., Müller, K., Ooms, J., Robinson, D., Seidel, D.P., Spinu, V., Takahashi, K., Vaughan, D., Wilke, C., Woo, K., Yutani, H., 2019. Welcome to the tidyverse. Jurnal of Open Source Software 4(43), 1686.

Wohlgemuth-Ueberwasser, C.C., Jochumb, K.P., 2015. Capability of fs-LA-ICP-MS for sulfide analysis in comparison to ns-LA-ICP-MS: reduction of laser induced matrix effects? J. Anal. At. Spectrom. 30(12), 2469-2480.

Zhang, T.F., Mao, W.H., Gao, J.H., Song, X.Q., Li, L.F., Sun, X.B., Ding, X.F., Li, J.B., Zhai, Y.K., Ma, W., Zhao, J., 2022. The effects of PM2.5 on lung cancer-related mortality in different regions and races: A systematic review and meta-analysis of cohort studies. Air Qual. Atmos. Health 15(9), 1523-1532.