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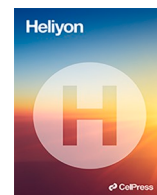
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## Research article

# Validation of an optimised microwave-assisted acid digestion method for trace and ultra-trace elements in indoor PM<sub>2.5</sub> by ICP-MS analysis

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## ABSTRACT

Three microwave-assisted digestion procedures, followed by analysis of digestates employing inductively coupled mass spectrometry (ICP-MS) were evaluated for use in the determination of elements at trace and ultra-trace levels in PM<sub>2.5</sub> samples. Digestion procedure 1 used 2.5 mL HNO<sub>3</sub> (65%) at 200 °C. Procedure 2, consisted of a two-stage digestion step at 200 °C with 2.5 mL HNO<sub>3</sub> (65%) and 3 µL HF (48%) followed by 24 µL H<sub>3</sub>BO<sub>3</sub> (5%). A 10-fold increase in the amounts of HF and H<sub>3</sub>BO<sub>3</sub> was used for procedure 3. The addition of HF/H<sub>3</sub>BO<sub>3</sub> was carried out to aid the dissolution of silicate matrices and refractory compounds. The digestions were carried out using PTFE ultra-trace inserts which increased the sample throughput threefold. The addition of small quantities of HF resulted in the effective solubilisation of Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Cd, Sb and Pb. The optimal method using HNO<sub>3</sub>/HF/H<sub>3</sub>BO<sub>3</sub> digestion as in procedure 3 showed recovery efficiency greater than 70% for all elements. The validated method was applied to quantify the elemental content of indoor and outdoor PM<sub>2.5</sub> (with samples <0.5 mg) at an urban background site in Malta.

## 1. Introduction

The association between different size fractions of particulate matter (PM) and increased morbidity and mortality is well established (Brunekreef and Holgate 2002; Brown et al., 2013; IARC 2015; World Health Organization 2016). The finer PM shows an enhanced penetration efficiency within the respiratory system and subsequent assimilation into the body (Kim et al., 2015). The International Agency for Research on Cancer has classified As, Cr<sup>VI</sup>, Cd, and Ni compounds as carcinogens to humans (group 1), with Pb and Sb compounds classified as possible carcinogens to humans (group 2B) (IARC 2022). Ba causes bronchoconstrictor effects and interferes with the heartbeat (Hicks et al., 1986). Exposure to metal-laden fine PM is a serious concern for human health. Toxic metals

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and their compounds in and on PM are assimilated and end up in vital organs, such as liver and kidneys, resulting in adverse health effects (Zhang et al., 2016). As people spend most of their time indoors [1,2] many studies have been focusing on indoor air quality [3–5] as indoor PM<sub>2.5</sub> can be a major contributor to the personal exposure to fine PM.

Quantifying trace metals in indoor fine fractions, PM<sub>2.5</sub> and PM<sub>1</sub>, poses analytical challenges as small amounts of PM are collected from 24-h samples when operating a low volume sampler. Increasing the sampled volume via high volume samplers is usually not possible as these samplers are not practical for many indoor environments. Indoor PM<sub>2.5</sub> samples typically contain less than 500 µg of PM and are usually associated with low elemental concentrations for most analytes due to lower indoor emissions. These drawbacks could be compensated with longer sampling times, resulting in a lower time resolution. Traditional analytical methods using Energy Dispersive X-ray Fluorescence Spectrometry (ED-XRF) have been used effectively for the elemental composition of PM [6–8]. This technique offers the advantage of little sample manipulation and hence high sample throughput; however, such methods suffer from relatively high detection limits, making them unsuitable for detecting trace or ultra-trace quantities.

ICP-MS coupled with microwave-assisted acid digestions can provide a reliable elemental analysis at trace levels required for environmental samples of PM<sub>2.5</sub> [9–11]. ICP-MS offers the advantage of detection limits in the trace (µg L<sup>-1</sup>) and ultra-trace (ng L<sup>-1</sup>) levels, a wide dynamic range and multi-elemental analysis together with high sample throughput. Most ICP-MS systems are equipped for liquid sample introduction, thus requiring digestion of the PM. A number of digestion techniques are available, including hot acid digestion and microwave-assisted acid digestion. Microwave digestion offers the advantages of a closed system with rapid (20–60 min) digestion cycles at high pressure (16–20 atm) and hence is preferred over longer hot acid digestion at atmospheric pressure. The acid combination used depends on the sample matrix and elements of interest. Mixtures of concentrated mineral and oxidising acids have been used, including HNO<sub>3</sub>, HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>/HCl, HNO<sub>3</sub>/HF and HNO<sub>3</sub>/HF/H<sub>3</sub>BO<sub>3</sub>. The HNO<sub>3</sub>/HF/H<sub>3</sub>BO<sub>3</sub> mixture has been shown to provide near-total digestion of most elements even in the presence of aluminosilicate matrices and refractory compounds [10–12].

The standard method for measuring Pb, Cd, As and Ni in the PM<sub>10</sub> fraction of suspended PM, UNI EN 14902:2005, uses a HNO<sub>3</sub> (70% w/v) and H<sub>2</sub>O<sub>2</sub> (30% w/v) mixture in a 4:1 ratio. Inclusion of hydrogen peroxide increases the oxidative potential of the mixture and reoxidises NO<sub>x</sub> back into nitrate [11]. This reaction has the added benefit of reducing the pressure generated by the digestion of organic matter present in the PM sample, which could be significant in PM<sub>10</sub> samples, thus avoiding overpressure in the digestion vessel. Kulkarni et al. (2007) showed that H<sub>2</sub>O<sub>2</sub> is not essential in the near-total digestion of PM<sub>2.5</sub> and using H<sub>2</sub>O<sub>2</sub> introduces potential contamination from Al, Mg, Zn, Fe, Na present in commercially available 30–50% H<sub>2</sub>O<sub>2</sub> [9], which would increase the detection limit for these elements. Hence, the use of hydrogen peroxide is not desirable in the digestion of indoor PM<sub>2.5</sub> samples.

Certain acids in the digestion matrix could compromise the ICP-MS analysis due to the formation of species with *m/z* ratios that could mask elements of interest. Hydrochloric acid is avoided in ICP-MS analysis due to polyatomic chloride interferences [12]. Whilst modern ICP-MS have collisions/reaction cells to account for these polyatomic spectral interferences, and HNO<sub>3</sub>–HCl mixtures are extremely useful for the digestion and analysis of several metals, these mixtures are not particularly useful for near-total digestion, especially in the presence of aluminosilicates [13]. The use of hydrofluoric acid is therefore required for near-total digestion. HF achieves the decomposition of silicate matrices by converting them into H<sub>2</sub>SiF<sub>6</sub>. Even when used in excess, the loss of volatile fluorides, BF<sub>3</sub>, SiF<sub>4</sub> and SeF<sub>4</sub> is typically unavoidable. High digestion acid concentrations introduce matrix-related interferences and increase the corrosion of ICP-MS parts, most importantly the skimmer cones. Therefore, samples analysed by ICP-MS typically require dilution to keep the concentration of digestion acids as low as possible. High quantities of HF, whilst providing near-total digestion and therefore effective means to quantify elements such as K, Ti, Al, Sb and Cr require specialised HF resistant sample introduction systems. Minimising the amount of HF used in the digestion procedure is desirable as this avoids using specialised equipment.

Elements such as K, Al, Ti and Sb are important for the identification of sources such as Saharan dust events and fireworks in the Central Mediterranean [7,14]. High recovery efficiencies for these elements is therefore required. On the other hand, several source apportionment techniques such as Positive Matrix Factorisation (PMF) require the analysis of hundreds of samples, and fast, reliable digestion techniques with minimal acid use are essential. This study aims to identify a microwave-assisted acid digestion procedure that would give the best elemental extraction from PM<sub>2.5</sub> deposited on PTFE filters whilst maintaining low detection limits. Previous studies [10,15] have shown that nitric acid alone was not suitable for the effective analysis of some metals of interest, including K, Ti, Al and Sb. The aim was to determine the optimal mixture of nitric, hydrofluoric and boric acids that provides near-total digestion at the lowest detection limits.

## 2. Materials and methodology

### 2.1. Reagents, standards and reference materials

Deionised water with a resistivity higher than 18.2 MΩ cm (Elga Purelab system) was used for this work. Concentrated hydrofluoric acid (48% w/v, Honeywell, TraceSELECT), concentrated nitric acid 68% w/v (Honeywell, TraceSELECT) and boric acid (99.9999%, Merck, Suprapur) were used directly without any purification. NIST standard reference material (SRM) 1648a Urban PM [16] was used in this study, and it was handled, stored and used as per instruction in the certificate of analysis. The ICP-MS calibration standard solutions were prepared via dilution of 1 mg L<sup>-1</sup> standards for ICP-MS or 1000 mg L<sup>-1</sup> standards for ICP (Sigma Aldrich, TraceCERT).

### 2.2. Microwave-assisted acid digestion

Microwave-assisted acid digestion of the PTFE filters was carried out using a closed vessel microwave digester (Ethos UP™,

Milestone). The oven is equipped with a 2.45 GHz microwave supply of 0–1.8 kW output, a 15-position rotor for 100 mL PTFE vessels. The acid digestion was carried out in 7 mL PTFE ultra-trace inserts. Each 100 mL PTFE vessel was equipped with a PTFE ultra-trace insert holder capable of carrying three PTFE ultra-trace inserts, increasing the sample throughput threefold. Digestion can be carried out with 2–3 mL of acid in the ultra-trace insert compared to a minimum of 10 mL for the 100 mL vessels. This allows for a fast, reliable digestion method with minimal losses and low detection limits.

The internal pressure and temperature were monitored in a control vessel equipped with pressure and temperature sensors. The external temperature of each vessel was monitored via an IR sensor to check any runaway reactions in any of the vessels.

### 2.3. Validation of the digestion method

This study compares three digestion procedures using the Ethos UP™ multiple ultra-trace insert system. This system allows rapid digestion of multiple samples within the standard microwave digestion rotor. The efficiency of tested procedures was evaluated by digesting SRM 1648a. The selected method was applied to 318 PM<sub>2.5</sub> samples. Multiple digestions using the SRM 1648a and the selected method were carried out to confirm the selected method's robustness.

To identify the optimal acid digestion procedure, methods similar to those proposed by Refs. [9,10,15] were optimised for our laboratory equipment and conditions. The use of highly corrosive hydrofluoric acid was minimised to maintain the final concentration of HF to below 0.1% v/v: this enables use of standard quartz ICP torches for the analyses of the digests without significant damage to the equipment. The digestion methods used are described in Table 1. To establish the most suitable method for PM<sub>2.5</sub> samples, SRM 1648a dust was digested with different acid mixtures, and the percentage recoveries for each element were calculated.

Approximately 5 mg of SRM 1648a were weighed on a microbalance (Mettler Toledo, Model XP2U Ultra Micro Balance) using a weighing paper. The powder was then transferred to a 7 mL PTFE ultra-trace insert. Although this sample size is much smaller than 100 mg as recommended by NIST, it has been shown that it provides good analytical reproducibility [10]. The ultra-trace inserts were then transferred to a fume cupboard and 2.5 mL of 69% v/v HNO<sub>3</sub> were added using a pipette. Three different digestion methods were tested. The volume of acid added to each ultra-trace insert, and the digestion cycles are detailed in Table 1. Before digestion, for methods 2 and 3, the corresponding volume of 50% v/v hydrofluoric acid was added to each ultra-trace insert using a pipette. The ultra-trace inserts were capped and a sample holder loaded with three ultra-trace inserts was lowered in the 100 mL PTFE vessel, which was pre-filled with 15 mL of deionised water. Immersion in this “water blanket” ensures a stable and gradual increase in temperature inside the ultra-trace insert. The small volumes of acid used in the ultra-trace insert are prone to develop hotspots. The water blanket around the ultra-trace insert avoids this. The 100 mL PTFE vessels were covered, placed in the protection shields and tightened using a torque wrench. Each vessel was ramped to 200 °C in 20 min and kept at 200 °C and 16 bar for another 20 min.

All vessels were then cooled for a minimum of 45 min to a temperature lower than 50 °C and opened. For methods 2 and 3, the corresponding volume of 5% w/v H<sub>3</sub>BO<sub>3</sub> solution was added to each ultra-trace insert using a pipette. These vessels were re-sealed and ramped again to 200 °C in 20 min and kept at 200 °C and 16 bar for another 20 min. H<sub>3</sub>BO<sub>3</sub> is required to remove excess HF by forming the complex tetrafluoroboric acid, HBF<sub>4</sub>, thereby aiding with the resolubilisation of insoluble fluorides of Mg, Al and Ca. A sample of the microwave digestion profile is shown in Fig. SM 1 in the Supplementary Material (SM).

For each digestion cycle, a reference vessel was used to monitor the temperature and pressure of the digestion process. A reagent blank for each method was added to the reference vessel. This was filled with the same volume of reagents used in the sample vessels.

The contents of each ultra-trace insert were transferred into a 50 mL volumetric flask. The ultra-trace insert were then washed five times with deionised water. Each wash was transferred to the volumetric flask and the volume made up to the mark. The contents of the flask were homogenised and the solution stored in propylene bottles at 4 °C prior to ICP-MS analysis. Each SRM 1648a digestion solution was diluted 5-fold before ICP-MS analysis to bring the elemental concentrations approximately in range to what is expected for the indoor PM<sub>2.5</sub> samples.

### 2.4. ICP-MS analysis

The ICP-MS analysis was carried out at the School of Geography, Earth and Environmental Sciences, University of Birmingham, UK

**Table 1**  
Proposed microwave-assisted digestion methods.

Method	Digestion Solution	Step	Power W	Ramp time	Temp (°C)	Max Pressure (bar)	Hold Time (min)	
1	2.5 mL HNO <sub>3</sub>	1	1200	20	200	16	20	
2 <sup>a</sup>	2.5 mL HNO <sub>3</sub> + 3 µL HF	1	1200	15	200	16	20	
		2	Cooling to < 50 °C (45 min) followed by the opening of the vessels					
		3	1200	20	200	16	20	
3 <sup>b</sup>	2.5 mL HNO <sub>3</sub> + 30 µL HF	1	1200	15	200	16	20	
		2	Cooling to < 50 °C (45 min) followed by the opening of the vessels					
		3	1200	15	200	16	20	
	240 µL 5% m/v H <sub>3</sub> BO <sub>3</sub>							

<sup>a</sup> This method is similar to the procedure used by Ref. [10].

<sup>b</sup> In this method higher quantities of HF and H<sub>3</sub>BO<sub>3</sub> are used to test if higher extraction efficiencies are obtained with the 10-fold increase in HF quantity adopted.

on a PerkinElmer Nexion 300x ICP-MS equipped with a glass sea spray nebuliser and glass cyclonic spray chamber. The elements were analysed using the parameters listed in Table 2. The helium kinetic energy discrimination (KED) mode was used, in order to reduce polyatomic interferences derived from the plasma via a collision cell.

Internal standardisation was carried out using the internal standard stock solution of Li-6 and Rh-103, which was added automatically by the system to account for instrument drift and physical interferences. The same amount of internal standard solution that was added to the samples was also added to the reagent blank. Calibration was carried out for the following elements Na-23, Mg-24, Al-27, K-39, Ca-43, V-51, Cr-52, Mn-55, Fe-57, Ni-60, Cu-63, Zn-66, As-75, Sr-88, Cd-111, Sb-121, Ba-138 and Pb-208. Table SM 1 lists the concentrations used for the calibration curves.

## 2.5. Limits of detection (LOD)

The limits of detection for each analyte for the three digestion procedures were calculated from reagent blanks that were digested using identical amounts of reagents used in each digestion procedure. The LOD was calculated from the reagent blanks of each digestion procedure set at three times the standard deviation of a reagent blank and was calculated from the calibration plot using equation (1).

$$MDL = \frac{I_o \cdot 3\sigma}{m_c} \quad \text{Eq. 1}$$

where  $I_o$  is the net intensity of the reagent blank (cps),  $m_c$  is the gradient of the calibration curve, and  $\sigma$  is the standard deviation based on 11 measurements of the blank with the confidence factor set at 3.

## 2.6. Selection of the optimised digestion method

The different methods were assessed for their recovery efficiency and detection limits. The best method would provide the highest recovery efficiency across the selected elements but still maintain low detection limits, as would enable quantification of elemental content in daily indoor PM<sub>2.5</sub> samples using low volume air samplers. The chosen, validated method was then used for the analysis of PM<sub>2.5</sub> samples collected at an urban background site.

## 2.7. Quality and contamination control

Maintaining low and stable blank concentrations and limits of detection is essential in the analysis of trace and ultra-trace metals. The concentration of the elements in the blanks is affected by the quality of reagents used, laboratory procedures used for digestion and dilution and most importantly cleaning procedures. To obtain consistent low MDLs and blank concentrations, after each digestion, the ultra-trace inserts and the 100 mL PTFE vessels were rinsed three times with DI water and transferred to a 10% HNO<sub>3</sub> bath for 48 h. All vessels were then rinsed three times with DI water and allowed to air dry.

For the analyses of the PM<sub>2.5</sub> samples, a calibration standard was run with every 20 samples to ensure that the instrument remained within the calibration parameters. If any of the analytes' concentration varied by more than ±15% from the true concentration of the calibration standard, the standard was re-tested. If the concentration was again outside the ±15% limit, the instrument was recalibrated. Reagent blanks, method blanks and field blanks were analysed for each digestion run as part of the quality control procedure. The blank concentrations were monitored to ensure the concentrations were below the detection limits.

# 3. Results and discussion

## 3.1. Method validation

The standard digestion method for analysis of Pb, Cd, As and Ni in PM<sub>10</sub> (EN 14902:2005) uses a digestion mixture of 80% HNO<sub>3</sub> (68% v/v) and 20% H<sub>2</sub>O<sub>2</sub> (30% v/v). However, if a total dissolution of several trace elements, including Na, Al, K, Ti, Cr and Sb is required, digestion in the presence of HF is required [10]. This was confirmed in this study as the recovery efficiencies for Na, Al, K, Ti, Cr and Sb increased significantly with a digestion mixture of HNO<sub>3</sub>/HF/H<sub>3</sub>BO<sub>3</sub> as shown in Table 3. The correct contribution of these elements from crustal, fireworks and vehicular sources cannot be determined accurately without near-total digestion.

**Table 2**  
ICP-MS setup.

Parameter	Values
Sample flow rate into the nebuliser	0.3 mL min <sup>-1</sup>
Nebuliser gas flow rate	0.94 mL min <sup>-1</sup>
Plasma auxiliary gas flow rate	1.2 mL min <sup>-1</sup>
Plasma gas flow rate	18 mL min <sup>-1</sup>
ICP RF power	16,000 W
Helium Collision cell flow rate	4 mL min <sup>-1</sup>

The use of HF is required for complete solubilisation of samples containing inorganic silicates. The complexation property of HF acid explains the increased recoveries of Sb when compared to HNO<sub>3</sub> digestions [10]. H<sub>3</sub>BO<sub>3</sub> is typically added to the digestion mixture after HNO<sub>3</sub>/HF digestion to complex unreacted HF and re-solubilise insoluble fluorides such as CaF<sub>2</sub> and MgF<sub>2</sub>. However, this increases the digestion cycle duration and detection limits as additional reagents are used. HF also brings about significant complications to the digestion and analytical procedures. High concentrations of HF preclude the use of glass equipment due to the leaching of the borosilicate/quartz components such as the nebuliser and ICP torch.

The presence of small amounts of hydrofluoric acid can have a significant impact on the extraction of these elements. The mean percentage recoveries, shown in Table 3 show that adding HF to the digestion procedure in method 2 increased the recovery efficiency for Al, Sb, Cr, Ni, K and Na by approximately 30% over method 1. With a tenfold increase in quantity of HF used in method 3, all elements recorded a recovery efficiency greater than 70%. Compared to similar studies, slightly lower percentage recoveries were reported for Sb, Ni, Cr and Ti for both methods 2 and 3 compared to similar digestion methods as reported by Refs. [9,10] as shown in Table 3. Therefore, for near-total digestion, method 2 or method 3 is needed even though digestions with HF increased the detection limit for most elements when compared to HNO<sub>3</sub> digestions.

Si cannot be determined in digestions using HF since gaseous SiF<sub>4</sub> formed in the reaction is lost during the digestion cycle. Adding HF also increases the reagent blank concentrations for Si, as acidic attack on the borosilicate volumetric glassware becomes significant. The reagent blank values for Si for method 3 were more than 200 µg/L. Analysis of Si was, therefore, not performed for methods involving HF acid.

The LODs given in Table 4, for digestion methods 2 and 3 were slightly higher than the values reported for method 1, which included only HNO<sub>3</sub> acid in the digestion procedure. Nonetheless, the LODs for both methods 2 and 3 are sufficiently low for elemental analysis of PM<sub>2.5</sub> from outdoor and indoor environments. Table 4 shows that the LODs for methods 2 and 3 are very similar to, and for some elements lower than LODs reported for a digestion procedure very similar to method 2 by Ref. [10].

Based on the elemental recoveries and LODs, method 3 was chosen as the preferred digestion method for near-total digestion of PM<sub>2.5</sub>. It offers significantly better percentage recoveries for most elements than digestion with HNO<sub>3</sub>, especially for Sb, Cr, Ni, K and Na. It also offers better percentage recoveries than method 2 for Ti and Sb. Even though method 3 shows a marginal increase of the LOD for some elements (Mg, Al, Ti, Fe, Ni, Zn, Sr and Ba) when compared to method 2, the LODs of method 3 are still reasonably low and in fact lower for most elements when compared to the extraction method employed by Refs. [9,10]. Given that the quantity of aluminosilicates in PM<sub>2.5</sub> varies significantly, and is especially important during Saharan dust events as occur in the central Mediterranean region, method 3 provides for better near total digestion given the tenfold abundance of HF when compared with method 2.

Table 5 gives the mean percentage recoveries of the twelve-quality control SRM digests that were carried out with method 3 during the sampling campaign. Except for Cr, all elements had acceptable recovery efficiencies of between 80% and 120%. This data also show marginally better recoveries for Ni, Ti and Sb for method 3 when compared to data from Table 3. The results in Table 5 were obtained from a larger sample, which could explain the slightly higher recoveries.

**Table 3**

Percentage elemental recoveries of SRM 1648a by ICP-MS after microwave-assisted acid digestion and their respective standard deviations shown in brackets for each digestion method carried out in this study and similar other studies.

Element	Method 1		Method 2		Method 3		Celo et al., 2010	Celo et al., 2010	Kulkarni et al., 2007
	2.5 mL HNO <sub>3</sub>		2.5 mL HNO <sub>3</sub> , 3 µL HF, 24 µL H <sub>3</sub> BO <sub>3</sub>		2.5 mL HNO <sub>3</sub> , 30 µL HF, 240 µL H <sub>3</sub> BO <sub>3</sub>		Conc HNO <sub>3</sub>	1.5 mL HNO <sub>3</sub> , 3 µL HF, 24 µL H <sub>3</sub> BO <sub>3</sub>	3 mL HNO <sub>3</sub> , 300 µL HF, 2.4 mL H <sub>3</sub> BO <sub>3</sub>
Na	56.2	(1.7)	116.1	(12.3)	109.9	(5.4)			88 (7)
Mg	101.1	(2.8)	90.5	(0.7)	89.0	(2.1)			101 (4)
Al	60.8	(0.1)	88.8	(3.7)	91.4	(1.6)	26 (8)	86 (10)	104 (8)
Si	13.9	(24.5)	27.1	(66.6)	2.5	(37.8)			
K	39.4	(0.5)	72.5	(0.6)	74.3	(0.8)			95 (5)
Ca	107.8	(0.5)	106.3	(4.7)	106.0	(0.5)			
Ti	35.7	(3.1)	53.2	(8.7)	78.4	(1.1)	17 (15)	73 (10)	107 (4)
V	87.3	(0.4)	93.9	(0.6)	96.2	(0.6)	70 (2)		101 (6)
Cr	44.1	(11.4)	70.7	(8.9)	73.0	(3.9)	23 (1)	56 (14)	81 (8)
Mn	92.8	(0.5)	98.6	(1)	101.2	(1.3)	84 (2)	99 (7)	96 (5)
Fe	85.1	(1.2)	93.3	(0.4)	92.4	(0.7)	72 (1)	92 (10)	98 (4)
Ni	66.5	(7.7)	75.9	(10.9)	77.2	(18.8)	76 (2)	93 (10)	99 (4)
Cu	89.8	(1)	88.1	(2.5)	91.0	(2.7)	83 (1)	91 (5)	91 (7)
Zn	90.7	(4.5)	85.5	(8.4)	77.0	(2.4)	94 (2)	94 (4)	101 (9)
As	86.0	(3.4)	83.8	(0.9)	82.8	(0.3)	91 (1)	102 (4)	109 (7)
Sr	122.3	(5.9)	101.0	(4.7)	99.0	(4.1)			
Cd	82.7	(0.5)	84.3	(0.1)	83.2	(0.7)	91 (1)	99 (5)	112 (4)
Sb	42.6	(8)	70.7	(11)	79.0	(0.7)	16 (11)	101 (9)	86 (3)
Pb	90.0	(0.9)	87.6	(1.7)	83.8	(0.1)	94 (1)	98 (4)	108 (5)

**Table 4**  
Limits of Detection (LODs) calculated from the reagent blank for each method.

Element	LOD for Method			LOD (HNO <sub>3</sub> HF, H <sub>3</sub> BO <sub>3</sub> ) [10] <sup>a</sup>	LOD (HNO <sub>3</sub> HF, H <sub>3</sub> BO <sub>3</sub> ) [9]
	1	2	3		
	(µg L <sup>-1</sup> )			(µg L <sup>-1</sup> )	(µg L <sup>-1</sup> )
Na	0.004	0.118	0.096		0.921
Mg	0.070	0.408	2.539		0.398
Al	1.144	1.440	7.420	7.6	4.025
Si	2.556	28.86	51.93		
K	1.924	2.606	1.689		
Ca	17.77	40.06	23.47		
Ti	0.622	0.559	1.322	1.1	4.056
V	0.008	0.027	0.014	0.11	0.051
Cr	0.033	0.032	0.016	1.1	0.363
Mn	0.015	0.028	0.027	0.22	0.021
Fe	0.857	2.121	2.644	10.8	3.246
Ni	0.047	0.022	0.132	0.86	0.124
Cu	0.025	0.020	0.021	2.2	0.062
Zn	0.313	0.356	0.495	9.7	1.026
As	0.028	0.113	0.074	0.11	0.019
Sr	0.027	0.018	0.113	0.22	
Cd	0.011	0.022	0.010	0	0.035
Sb	0.014	2.201	0.858	0.43	0.026
Ba	0.010	0.012	0.018	0.22	0.436
Pb	0.027	0.236	0.196	0.65	0.086

<sup>a</sup> The LODs in this study were reported for filter blanks and hence would be expected to be marginally higher than LODs from reagent blanks.

**Table 5**  
Percentage Recovery efficiencies for quality control SRM digests.

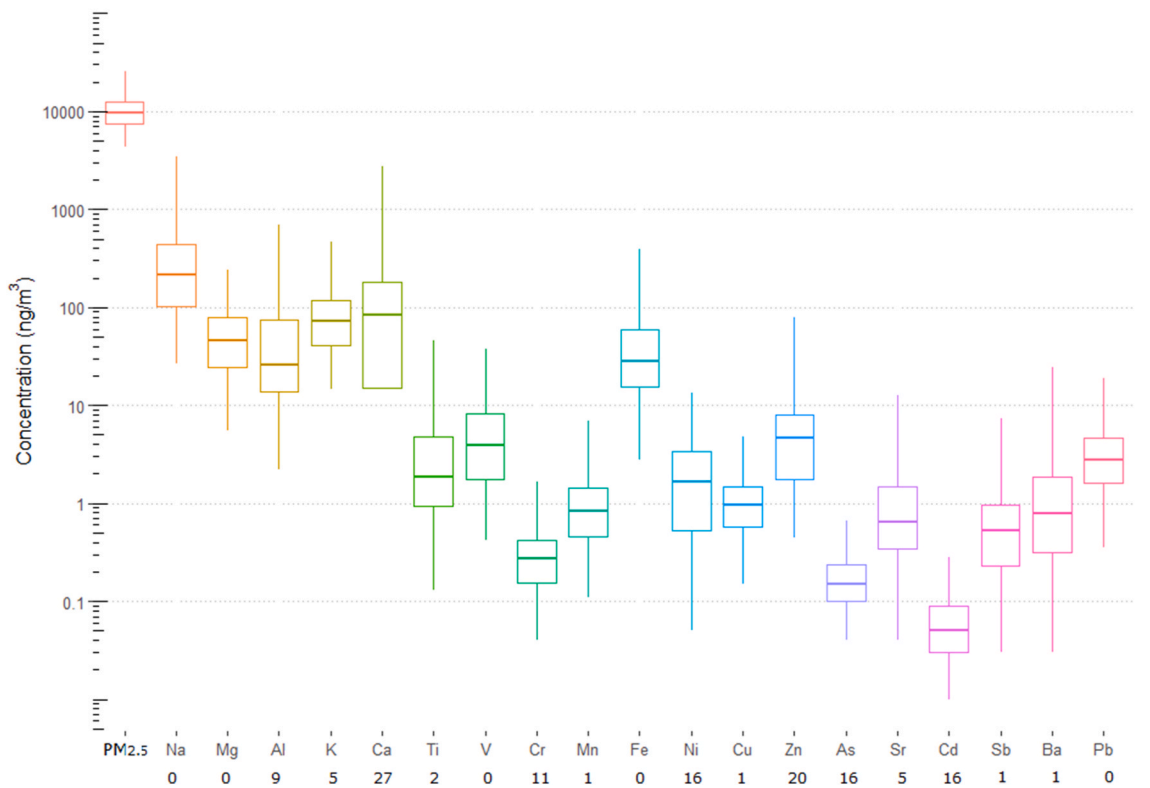
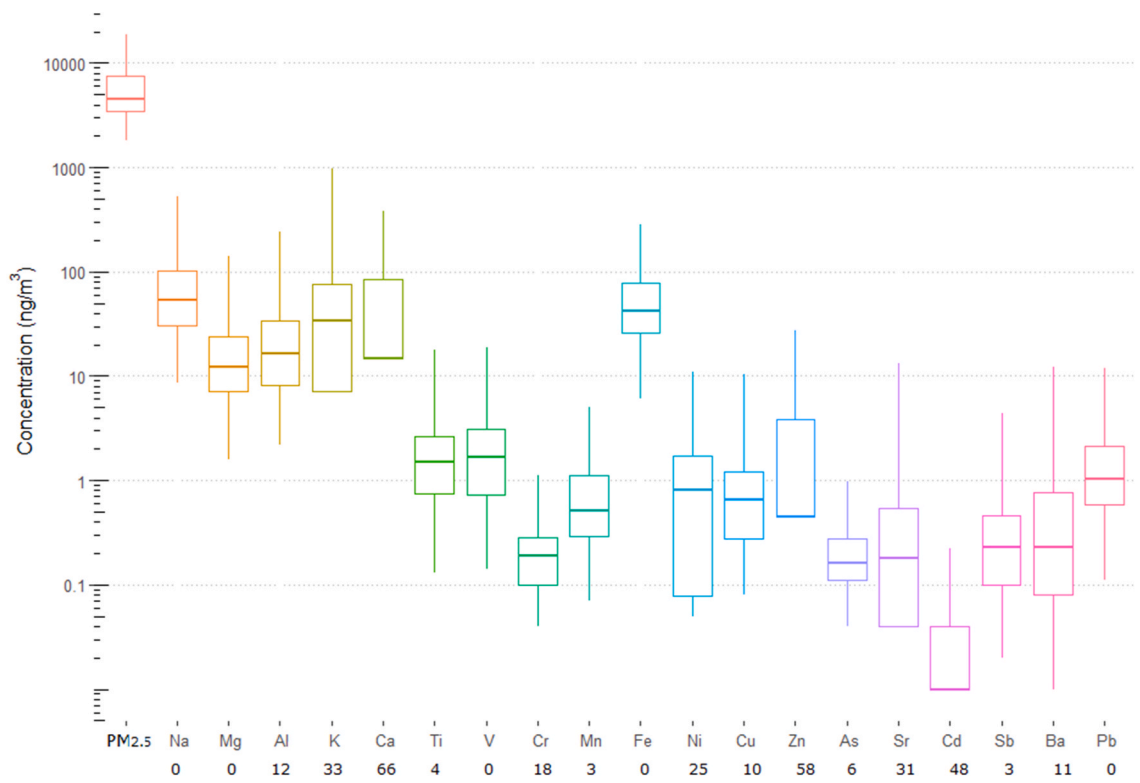
N = 12	SRM digests carried out during Filter analysis	
Element	Mean	(SD)
Na	100.9	(12.4)
Mg	97.0	(11.2)
Al	101.5	(4.2)
K	92.6	(11.2)
Ca	98.5	(9.4)
Ti	85.3	(5.6)
V	102.8	(7.2)
<sup>a</sup> Cr	63.2	(4.6)
Mn	99.4	(6.9)
Fe	100.8	(5.6)
<sup>a</sup> Ni	92.2	(20.9)
Cu	95.0	(9.9)
Zn	97.9	(8.1)
As	107.3	(7.3)
Sr	91.1	(8.3)
Cd	100.4	(5.1)
Sb	98.9	(5.3)
Pb	99.8	(4.0)

<sup>a</sup> Mean value obtained from 10 samples due to outlier values in 2 samples.

### 3.2. Application of the validated digestion method to PM<sub>2.5</sub> samples

Indoor PM<sub>2.5</sub> concentrations ranged from 1.8 to 18.6 µg m<sup>-3</sup>, with outdoor PM<sub>2.5</sub> ranging from 3.2 to 47.6 µg m<sup>-3</sup> (Fig. 1a and b). Fig. 1 shows the elemental composition of 19 elements detected in 159 indoor and outdoor PM<sub>2.5</sub> samples from an urban background site in Malta. On average, outdoor concentrations were 5.1 µg m<sup>-3</sup> higher than indoor concentrations. The highest indoor and outdoor elemental concentrations were recorded for the crustal elements Na, Mg, Ca, K, Al, and Fe. All elements, except for As, recorded a higher outdoor daily mean concentration. The remaining outdoor elemental concentrations were higher, primarily due to the higher amount of PM<sub>2.5</sub> sampled from the ambient environment. This suggests that indoor PM<sub>2.5</sub> concentrations at the sampling site are mainly dependent on outdoor sources and indoor PM<sub>2.5</sub> concentrations are lower due to low infiltration of outdoor PM<sub>2.5</sub>.

Due to the high detection limit of Ca and low indoor PM<sub>2.5</sub> concentrations, 61% of the indoor samples were below the MDL for Ca. The number of indoor samples below the MDL was also high for Ni, Zn and Cd. This was mainly due to very low indoor PM<sub>2.5</sub> concentrations during the colder months and the absence of indoor emissions for these elements. The newly developed method was able to detect elements at ultra-trace levels (pg m<sup>-3</sup>) for an air volume of 55.2 m<sup>3</sup>. Elements of crustal origin (Al, Fe and Ti), elements



(caption on next page)



**Fig. 1.** Elemental composition of 159 (a) indoor and (b) outdoor samples from an urban background site in Malta. The box includes the 25th and 75th percentiles and the whiskers are determined by the 5th and 95th percentiles with the horizontal line inside the box showing the median. The percentage number of samples below the MDL for each element is given underneath each element's symbol. For these plots, elemental values below the MDL are given as half the MDL.

associated with vehicular activities (As, Fe, Cu, Sb and Ba), elements associated with shipping emissions (V and Ni) and fireworks-related elements (Cu, Ba and Sb) were quantified in at least 75% of indoor samples. Method 3 was shown as a suitable method for the detection of these elements in indoor PM<sub>2.5</sub> sampled using low volume samplers. It also provides rapid near-total digestion with high throughput that can be used in source apportionment studies.

#### 4. Conclusion

SRM 1648a has been effectively used to validate a two-stage microwave-assisted acid digestion procedure using HNO<sub>3</sub>/HF in the first stage, followed by H<sub>3</sub>BO<sub>3</sub> in the second stage, followed by ICP-MS analysis. This method was used successfully for the ultra-trace analysis of elements related to fireworks (Cu, Sr, Ba and Sb) and crustal geological matter (Na, Mg, Ca, K, Al, and Fe) in indoor PM<sub>2.5</sub> with samples containing <0.5 mg of fine dust. Microwave digestion was successfully carried out using ultra-trace inserts which have the advantage of lowering the detection limit whilst increasing the throughput of the analytical method. This method is better at quantifying a wider range of elements at trace and ultra-trace levels and is, therefore, more suited for the quantification and source identification of elements in indoor PM<sub>2.5</sub>. The method also has the major advantage of minimising the use of HF, hence allowing safe use of standard ICP-MS equipment.

#### CRediT taxonomy

Renato Camilleri: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper. Noel J. Aquilina, Roy M. Harrison, Alfred J. Vella: Wrote the paper. Christopher Stark: Performed the experiments; Contributed reagents, materials, analysis tools or data.

#### Declaration of competing interest

No potential competing interest was reported by the authors.

#### Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article and/or its supplementary materials.

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This publication is part of a PhD thesis at the University of Malta. The authors declare that any opinions expressed in this article are their own and do not necessarily represent the opinions of the institutions to which they are affiliated.

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.heliyon.2023.e12844>.

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