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# Risk assessment of trace elements in airborne particulate matter deposited on air filters using solid sampling ETV-ICPOES to measure total concentrations and leaching with simulated saliva, gastric juice and lung fluid to estimate bio-accessibility

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Potentially toxic elements (PTEs) in airborne particulate matter (APM) can cause adverse effects on human health, especially in urban and (current and former) industrial areas. The severity of health effects depends on the availability of the PTEs for absorption into the human body. The bio-accessible fraction of PTEs in APM, *i.e.* released in the gastrointestinal tract and lungs, was estimated in the present study. Polytetrafluoroethylene (PTFE) filters containing previously collected airborne particulate matter were directly analysed by electrothermal vaporisation into inductively coupled plasma optical emission spectrometry (ETV-ICPOES) to obtain the total concentrations of several trace elements (Sb, As, Cd, Cr, Cu, Mn, Ni, Pb, Sr, V and Zn). The results were cross-validated using inductively coupled plasma mass spectrometry (ICPMS) analysis of acid-digested samples. Subsequently, the bio-accessibility of the investigated elements was estimated by leaching the filters with simulated saliva (for 10 min, pH 6.5) and gastric juice (for 2 h, pH < 1). Separate aliquots were also leached with lung fluid (pH 7.4) for 1 h to 56 h. Two leaching groups were identified with saliva: As, Cr, Cu and Sb (2.5% released), and Cr, Sr and Zn (15% released). With gastric juice, 26% of As, Cr, Cu, Ni and Sb, and 77% of Zn, Sr and Pb were released on average. With lung fluid, 56 h leaching was as follows: Sb, 1.1%; As, 2.2%; Cr, 78%; Cu, 9%; Ni, 62%; Pb, 61%; Sr, 46%; V, 32%; and Zn, 89%. The high bio-accessibility of Pb in gastric juice and lung fluid may pose a health risk if such APM is inhaled or swallowed.

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## Introduction

Epidemiological studies have demonstrated an association between potentially toxic elements (PTEs) in airborne particle matter (APM) and human health.<sup>1</sup> Exposure to APM has been associated with a higher rate of morbidity and mortality in urban areas as a consequence of fossil fuels combustion, biomass burning, industrial and construction-related activities. Airborne particulate matter can contain carbonaceous fractions with carbon in organic, elemental and carbonate forms, as well as other components such as crustal elements, trace elements and ionic species.<sup>1</sup> Although multi-element methods allowing

the fast screening of PTEs in APM would be quite valuable, knowing the total concentration of PTEs is usually not enough to assess the potential risk to humans.

Indeed, the health risk depends on the relative abundance of fine and coarse particles. Fine APM can affect respiratory and cardio-vascular systems.<sup>2</sup> The lungs are usually the primary targets of short-term exposure to APM, which can cause asthma and bronchitis, while long-term exposure to high levels of APM can increase the risk of cancer.<sup>2</sup>

The mobility and thus bio-availability (*i.e.*, the amount of element/compound that is actually taken across the cell membrane) may vary for different PTEs in APM. In general, the more soluble the chemical form of the element, the more easily it can become bio-available. Although many studies report the total concentration of PTEs in APM and assume their potential hazard, the toxicity is dependent upon the PTEs' bio-availability, which is usually estimated by *in vitro* bio-accessibility tests.<sup>3</sup> Bio-accessibility is the amount of element/compound that is released from the sample matrix by a simulated body fluid and

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thus becomes available for absorption. *In vitro* bio-accessibility tests consist in leaching procedures using simulated human body fluids, which are usually carried out in batch mode for risk assessment of exposure to PTEs through the gastrointestinal tract and respiratory system. Because bio-accessibility tests are simpler, quicker and easier to conduct than *in vivo* tests, the use of simulated body fluids to mimic natural ones in terms of ionic strength and pH has increased.<sup>3–11</sup> Not only is the use of animal model, enzymes and proteins avoided by using *in vitro* experiments, but a fair estimate of bio-availability can be obtained in an inexpensive manner.<sup>12,13</sup>

Procedures to estimate bio-accessibility usually follow a sequential extraction to assess the release of PTEs bound to APM.<sup>3</sup> Although saliva is the first fluid of the gastrointestinal process, it is often omitted.<sup>12,13</sup> Simulated gastric juice with pepsin is widely employed to mimic human gastric juice under fasting conditions, with a leaching time ranging from 1 to 4 h, *i.e.*, a reasonable estimation of food digestion in the human gastrointestinal tract. Gamble's solution is the most popular simulated lung fluid.<sup>2</sup> The relative complexity of this fluid,<sup>14,15</sup> owing to its physicochemical characteristics and ionic strength, leads to great variability in the results. Furthermore, most procedures do not take into account the human body temperature (37 °C), thus making comparisons unreliable.<sup>2</sup>

The purposes of this study were: (1) to develop a method for fast screening (direct solid sampling analysis) of PTEs in APM collected on a filter, by using electrothermal vaporisation (ETV) into inductively coupled plasma optical emission spectrometry (ICPOES); and (2) estimate the bio-accessibility of PTEs using batch leaching experiments with simulated saliva, gastric juice and lung fluid.

## Experimental

### Instrumentation

For solid sampling analysis, an ETV 4000c system equipped with an AD30 autosampler (Spectral Systems, Fürstfeldbruck, Germany) was employed along with graphite boats (Meinhard, Golden, CO, USA). The ETV system was connected to the torch through a 1 m long polytetrafluoroethylene (PTFE) tube with 5 mm internal diameter. An ICPOES spectrometer (ARCOS, SPECTRO Analytical Instruments, Kleve, Germany), which allows lateral view of the plasma, was employed as the detector. The obtained data were exported to an Excel spreadsheet for signal processing and peak area integration. Freon-23 (CHF<sub>3</sub>, MEGS Specialty Gases, Ottawa, ON, Canada) was employed as reaction gas to increase the volatility of elements. To improve ETV-ICPOES performance, 0.45 L min<sup>-1</sup> of N<sub>2</sub> (99.99% purity, MEGS Specialty Gases, Ottawa, ON, Canada) was added using a mass flow controller (Model 1259C-01000SV, MKS Instruments) to the Ar plasma flow through a Y connector.

A Varian 820MS ICP mass spectrometry (MS) instrument equipped with a collision–reaction interface (CRI) was employed for analytes determination in leachates and digests of residues. Liquid argon with a purity of 99.996% (MEGS Specialty Gases) was used for ETV-ICPOES, ICPOES and ICMS. For analyses by ICPOES, a T2100 Burgener nebuliser (Burgener

Research, Mississauga, ON, Canada) fitted to a baffled cyclonic spray chamber (SCP Science, Baie d'Urfé, QC, Canada) was employed for introduction of solutions into the ICP. The same nebuliser was employed for ICMS, where it was fitted to a Peltier-cooled Scott double-pass spray chamber maintained at 0 °C. The operating conditions are summarized in Table 1.

### Reagents and solutions

Analytical grade reagents were systematically used. Nitric acid (65% m m<sup>-1</sup>, Fisher Scientific, Ottawa, ON, Canada) and HCl (37% m m<sup>-1</sup>, Fisher Scientific) were purified in a DST-1000 sub-boiling distillation system (Savillex, Minnetonka, MN, USA). Doubly deionized water (DDW) from an Arium Pro UV water purification system (Sartorius Stedim Biotech, Goettingen, Germany) was also used. The simulated saliva with pH 6.5 consisted of 6.8 g of KH<sub>2</sub>PO<sub>4</sub> and 77 mL of 0.2 mol L<sup>-1</sup> NaOH (Bioshop, Burlington, ON, Canada) in 1 L of DDW. Simulated gastric juice was prepared by mixing 2.0 g of NaCl (Bioshop), 3.2 g of pepsin (Sigma-Aldrich, Steinheim, Germany) and 7.0 mL of sub-boiled HCl and diluting to 1 L with DDW. For simulated lung fluid with pH 7.4, 6.020 g of NaCl (Sigma-Aldrich), 256 mg of CaCl<sub>2</sub> (Sigma-Aldrich), 150 mg of Na<sub>2</sub>HPO<sub>4</sub> (Sigma-Aldrich), 2.700 g of NaHCO<sub>3</sub> (Fisher Scientific), 298 mg of KCl (Sigma-Aldrich), 200 mg of MgCl<sub>2</sub> (Fluka, Muskegon, MI, USA), 72 mg Na<sub>2</sub>SO<sub>4</sub> (Fisher Scientific) and 0.4 mL of HCl were mixed and diluted to 500 mL with DDW.

### Procedure

For total analysis by ETV-ICPOES, APM on air filters samples (obtained from an apartment building in Kingston, ON, Canada) were cut into 8–12 mg pieces so as to fit into graphite boats. The air filter pieces were weighted using a balance (GR Series, A&D Company, Mississauga, ON, Canada) with 0.01 mg precision. An intact new filter, which served as blank, as well as two high-porosity and two low-porosity air filters with APM collected over two months of continuously filtering the air from the apartment were analysed.

Leaching experiments were carried out in triplicate in batch mode using 0.30 g (10 cm<sup>2</sup>) pieces of air filter. First, 6 mL of simulated saliva (37 °C) were added to the sample in a graduated polypropylene flask and the mixture was mechanically shaken for 10 min. Subsequently, the supernatant was collected for analysis and 24 mL of synthetic gastric juice were then added. The new mixture was shaken for 2 h and the supernatant removed for analysis. The residue was placed in 1 mL of HNO<sub>3</sub> and allowed to stand for 24 h before dilution to 20 mL with DDW and centrifugation prior to elemental analysis. This decomposition procedure was also employed for total element determination in APM on air filters samples.

Separate experiments were conducted with simulated lung fluid using 0.30 g (10 cm<sup>2</sup>) pieces of air filter. The latter were placed in 10 mL aliquots of the fluid and mechanically mixed for 1, 2, 4, 8, 12, 24, 48 or 56 h. In each case, the supernatant was collected for analysis and the remaining residue treated as described above.

Table 1 Instrumental conditions

Parameter	ETV-ICPOES	ICPOES	ICPMS
Plasma gas flow rate (L min <sup>-1</sup> )	14.5	12.0	18.0
Auxiliary gas flow rate (L min <sup>-1</sup> )	1.5	1.0	1.75
Sample uptake rate (mL min <sup>-1</sup> )	—	1.0	1.0
RF power (kW)	1.7	1.4	1.45
Ar sheathing gas flow rate (L min <sup>-1</sup> )	—	—	0.04
Nebuliser gas flow rate (L min <sup>-1</sup> )	—	0.70	1.1
Carrier gas flow rate (L min <sup>-1</sup> )	0.1	—	—
By-pass gas flow rate (L min <sup>-1</sup> )	0.2	—	—
Flow rate of N <sub>2</sub> in the plasma gas (L min <sup>-1</sup> )	0.45	—	—
Sampling frequency (Hz)	10	—	—
Integration time (ms)	10	28 000	—
Dwell time (ms)	—	—	10
CHF <sub>3</sub> flow rate (mL min <sup>-1</sup> )	7	—	—
Skimmer cone CRI H <sub>2</sub> flow rate (mL min <sup>-1</sup> )	—	—	65
Observation height above the load coil (mm)	10	10	—
Sampling position (mm)	—	—	6.4
Nuclides ( <i>m/z</i> ) or emission lines (nm) monitored	As I 189.042, Cd II 226.502, Cr II 267.716, Cu I 324.754, Mn II 260.569, Ni II 221.648, Pb II 220.353, Sb I 206.833, Sr II 407.771, V II 311.071, Zn I 213.856	—	<sup>51</sup> V <sup>+</sup> , <sup>52,53</sup> Cr <sup>+</sup> , <sup>55</sup> Mn <sup>+</sup> , <sup>60</sup> Ni <sup>+</sup> , <sup>65</sup> Cu <sup>+</sup> , <sup>66,68</sup> Zn <sup>+</sup> , <sup>75</sup> As <sup>+</sup> , <sup>77,78</sup> Se <sup>+</sup> , <sup>88</sup> Sr <sup>+</sup> , <sup>111,112,114</sup> Cd <sup>+</sup> , <sup>121</sup> Sb <sup>+</sup> , <sup>206,207,208</sup> Pb <sup>+</sup>

<sup>a</sup> Indicates instantaneous heating or cooling to the selected temperature.

#### ETV program

Step	Temperature (°C)	Ramp (s)	Time (s)
Pyrolysis	400	0 <sup>a</sup>	20
Cool down	20	0	15
Vaporisation	2200	0	30
Cooling	20	0	20

Matrix-matched external calibration was systematically carried out. For the analysis of leachates by ICPMS or ICPOES, calibration solutions (up to 0.2 and 1.0 mg L<sup>-1</sup> for ICPMS and ICPOES, respectively) were prepared in leaching reagents by serial dilution of mono-elemental 10 000 mg L<sup>-1</sup> standards (SCP Science). Calibration solutions in 5% (v/v) HNO<sub>3</sub> were used for the analysis of digests. For ETV-ICPOES calibration curves, 0.5 to 6 mg aliquots of NIST 1648a urban particle matter certified reference material (CRM) (National Institute of Standards and Technology, Gaithersburg, MD, USA) were weighed into graphite boats and heated according to the temperature program in Table 1.

## Results and discussion

### Optimisation of ETV-ICPOES for the determination of total PTEs concentrations

Direct solid sampling analysis of pieces of air filter with APM by ETV-ICPOES was optimised. The effect of the pyrolysis temperature was studied for two elements with different volatilities: Cr (boiling point 2671 °C) and Sb (boiling point 1587 °C).<sup>16,17</sup> Representative transient signals for these elements are shown in Fig. 1, where Cr is not prematurely vaporised before the vaporisation step (starting at 35 s) at pyrolysis temperatures lower than 800 °C while premature vaporisation of Sb leads to

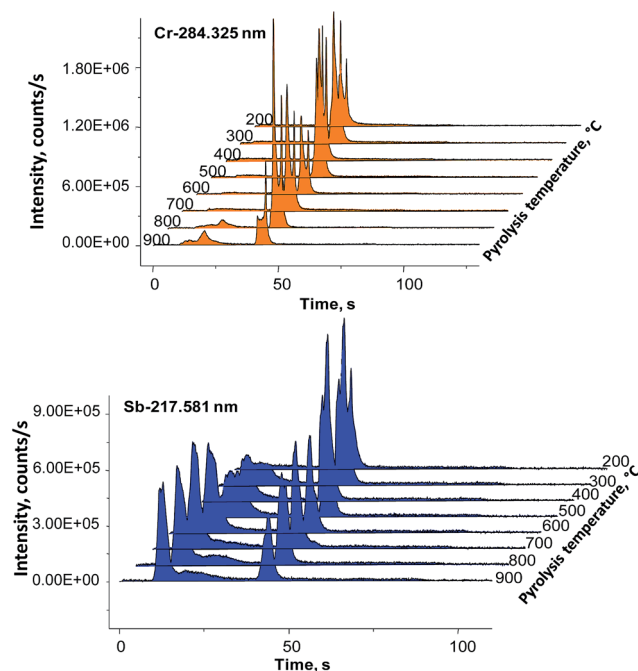


Fig. 1 Transient signals for Cr and Sb during the analysis of APM on air filter by ETV-ICPOES as a function of pyrolysis temperature (200–900 °C), with the vaporisation temperature fixed at 2200 °C.

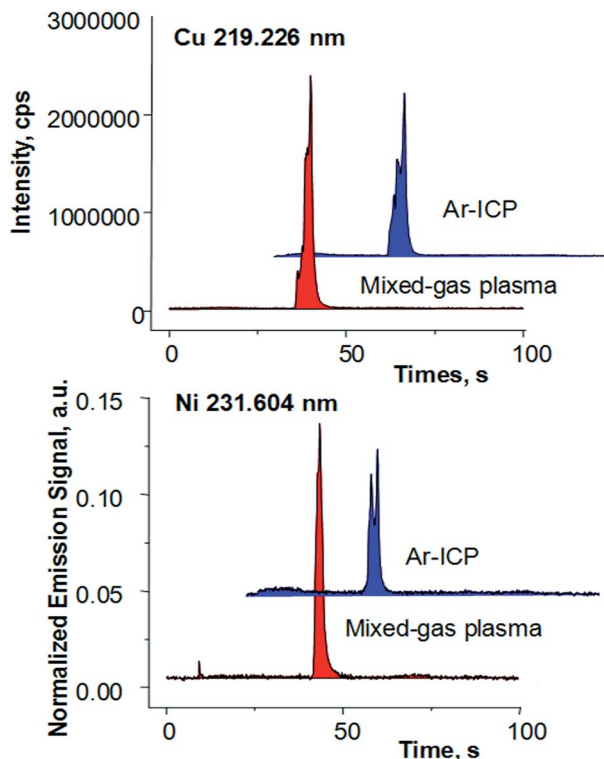


Fig. 2 Transient ETV-ICPOES signals observed with an Ar plasma and an Ar-N<sub>2</sub> plasma for Cu (without normalization to Ar) and Ni (with point-by-point normalization to Ar 763.511 nm as internal standard) from APM on air filter.

a substantial decrease in the vaporisation peak area and a corresponding increase in the peak observed during pyrolysis (at 10–25 s), when the pyrolysis temperature is 550 °C. The use of CHF<sub>3</sub> reaction gas to produce more volatile analyte species evidently leads to some release of Sb during the pyrolysis step. The pyrolysis temperature was thus set to 400 °C, and 80 s signal integration time was adopted to encompass analyte release during both the pyrolysis and vaporisation steps. The vaporisation temperature was fixed at 2200 °C, because sharp peaks

were obtained with little or no analyte condensation in the transfer line.

Addition of 0.45 L min<sup>-1</sup> N<sub>2</sub> to the plasma gas was also investigated. The CHF<sub>3</sub>, carrier gas and by-pass gas flow rates were then re-optimised in a multivariate way (yielding the conditions in Table 1). The enhanced sample-plasma interaction, promoted by the higher plasma temperature and power density in the mixed-gas plasma, assists particle decomposition, resulting in improved sensitivity (Fig. 2), precision and detection limit (Table 2). In fact, the mixed-gas plasma is so robust that no internal standardization with an Ar emission line, as usually required with an Ar ICP for sample aliquots greater than 1 mg,<sup>18–21</sup> was necessary (Fig. 2).

The optimized ETV temperature program is actually identical to that previously used for the accurate analysis of austenitic steel<sup>18</sup> and magnesium alloy<sup>21</sup> by ETV-ICPOES using external calibration with NIST 1648a urban particle matter CRM, despite the significantly different matrix. This indicates that, using CHF<sub>3</sub>, analytes are effectively released from the matrix, which eliminates the requirement for closely matching the CRM used for calibration to the sample in terms of matrix. The calibration is further simplified with the mixed-gas plasma, as it also eliminates the internal standardization step.

The analysis results for APM on air filters obtained by ETV-ICPOES are compared to those obtained by ICPOES with regular nebulisation following HNO<sub>3</sub> digestion in Table 2. Considering that 8–12 mg aliquots were analysed by ETV-ICPOES whereas 300 mg aliquots were digested before analysis by ICPOES, fair agreement was obtained, which suggests a reasonable accuracy. As expected, precision was worse for solid sampling ETV-ICPOES. Some significant differences between the results of the two methods can be explained by the fact that, due to the small aliquot size, the ETV-ICPOES method is more susceptible to small variation in composition of APM over the surface of the air filter. This is the most logical explanation for the As results by the two methods agreeing (according to a student's *t* test at the 95% confidence level) for the high-porosity filter but not for the low-porosity filter, the Cr results agreeing for the low-porosity filter but not the high-porosity

Table 2 Detection limits in mg kg<sup>-1</sup> by ETV-ICPOES and total concentration in mg kg<sup>-1</sup> (±standard deviation; relative standard deviation in brackets) measured directly in APM on air filters by ETV-ICPOES (*n* = 9) or by ICPOES following acid digestion (*n* = 8)

Analyte emission line (nm)	High-porosity filter		Low-porosity filter		ETV-ICPOES detection limit		
	ICPOES	ETV-ICPOES	ICPOES	ETV-ICPOES	Ar ICP (A)	Ar-N <sub>2</sub> ICP (B)	(A)/(B)
Sb 206.833	3.8 ± 0.2 (5.8)	4.1 ± 0.9 (21)	15.1 ± 0.7 (4.3)	13.5 ± 0.9 (6.3)	0.09	0.01	9
As 189.042	9.4 ± 0.2 (2.1)	9 ± 1 (12)	4.9 ± 0.2 (3.1)	7.4 ± 0.9 (12)	2	0.4	5
Cd 226.502	0.64 ± 0.08 (1.2)	0.6 ± 0.1 (19)	0.6 ± 0.1 (10)	0.60 ± 0.08 (11)	0.5	0.2	2.5
Cr 267.716	0.80 ± 0.03 (4.0)	1.5 ± 0.2 (13)	1.7 ± 0.3 (17)	1.8 ± 0.2 (11)	20	1	20
Cu 324.754	—	—	8.5 ± 0.2 (1.7)	8 ± 1 (14)	40	2	20
Mn 260.569	51 ± 3 (5.8)	46 ± 4 (8.7)	60 ± 10 (18)	52 ± 6 (12)	8	0.8	10
Ni 221.648	12 ± 1 (8.7)	15 ± 2 (13)	6.4 ± 0.8 (13)	8 ± 1 (12)	8	2	4
Pb 220.353	10.6 ± 0.2 (1.9)	15 ± 1 (6.6)	6.8 ± 0.2 (3.2)	4.8 ± 0.6 (13)	2	0.4	5
Sr 407.771	10.3 ± 0.9 (8.7)	10 ± 2 (15)	5.3 ± 0.2 (4.5)	5.7 ± 0.8 (13)	10	5	2
V 311.071	8.1 ± 0.3 (3.7)	8.9 ± 0.9 (10)	10 ± 1 (9.6)	9 ± 1 (13)	4	1	4
Zn 213.856	280 ± 40 (14)	320 ± 40 (12)	380 ± 20 (5.3)	330 ± 40 (12)	3	0.07	43

Table 3 Concentrations in  $\text{mg kg}^{-1}$  (average  $\pm$  standard deviation,  $n = 3$ ) released from APM on air filters by simulated saliva, gastric juice and lung fluid

Analyte	Saliva			Gastric juice			Residue			Total		
	ICPOES	ICPMS	Released (%)	ICPOES	ICPMS	Released (%)	ICPOES	ICPMS	Released (%)	ICPOES	ICPMS	Released (%)
As	$0.07 \pm 0.02$	$0.05 \pm 0.01$	1.7	$0.2 \pm 0.1$	$0.21 \pm 0.09$	7.2	$2.4 \pm 0.7$	$2.8 \pm 0.6$	$3 \pm 1$	$2.9 \pm 0.8$		
Cd	$<0.10$	$<0.01$	—	$<0.50$	$<0.05$	—	$<0.20$	$<0.10$	$<0.20$	$<0.20$		
Cr	$0.08 \pm 0.01$	$0.09 \pm 0.03$	15	$0.18 \pm 0.08$	$0.14 \pm 0.03$	24	$<0.54$	$0.27 \pm 0.07$	$<0.54$	$0.6 \pm 0.2$		
Cu	$0.6 \pm 0.1$	$0.40 \pm 0.10$	1.6	$9.0 \pm 0.9$	$8.5 \pm 0.8$	36	$12 \pm 1$	$12 \pm 2$	$25 \pm 2$	$24 \pm 4$		
Ni	$<0.15$	$0.14 \pm 0.04$	12	$0.5 \pm 0.2$	$0.38 \pm 0.08$	32	$0.4 \pm 0.2$	$0.4 \pm 0.1$	$1.4 \pm 0.2$	$1.2 \pm 0.3$		
Pb	$<0.20$	$0.013 \pm 0.003$	5.2	$0.3 \pm 0.2$	$0.12 \pm 0.03$	48	$<0.20$	$0.18 \pm 0.03$	$0.35 \pm 0.06$	$0.25 \pm 0.02$		
Sb	$0.15 \pm 0.04$	$0.17 \pm 0.03$	4.0	$1.0 \pm 0.2$	$1.05 \pm 0.02$	25	$3 \pm 1$	$3.03 \pm 0.09$	$5 \pm 1$	$4.2 \pm 0.5$		
Sr	$1.25 \pm 0.08$	$1.10 \pm 0.03$	20	$4.5 \pm 0.5$	$4.0 \pm 0.3$	71	$1.4 \pm 0.2$	$1.20 \pm 0.08$	$6.4 \pm 0.4$	$5.6 \pm 0.6$		
V	$<0.10$	$<0.03$	—	$<0.10$	$0.15 \pm 0.02$	45	$<0.50$	$0.13 \pm 0.02$	$<0.50$	$0.33 \pm 0.02$		
Zn	$1.3 \pm 0.3$	$1.0 \pm 0.1$	13	$7 \pm 1$	$7 \pm 1$	97	$1.4 \pm 0.5$	$1.8 \pm 0.4$	$10 \pm 1$	$7 \pm 2$		
Lung fluid												
ICPMS												
Analyte	1 h	2 h	4 h	8 h	12 h	24 h	48 h	56 h	ICPMS	ICPOES	Released (%)	
As	$0.060 \pm 0.001$	$0.062 \pm 0.003$	$0.064 \pm 0.001$	$0.065 \pm 0.001$	$0.065 \pm 0.001$	$0.065 \pm 0.001$	$0.063 \pm 0.002$	$0.062 \pm 0.001$	$0.062 \pm 0.001$	$0.07 \pm 0.01$	2.2	
Cd	$<0.08$	$<0.08$	$<0.08$	$<0.08$	$<0.08$	$<0.08$	$<0.08$	$<0.08$	$<0.08$	$<0.30$	—	
Cr	$0.44 \pm 0.01$	$0.65 \pm 0.06$	$0.68 \pm 0.07$	$0.73 \pm 0.05$	$0.70 \pm 0.04$	$0.65 \pm 0.05$	$0.83 \pm 0.04$	$1.10 \pm 0.02$	$1.10 \pm 0.02$	$0.90 \pm 0.06$	79	
Cu	$0.40 \pm 0.05$	$0.41 \pm 0.03$	$0.45 \pm 0.02$	$0.50 \pm 0.02$	$0.48 \pm 0.02$	$0.54 \pm 0.02$	$0.76 \pm 0.03$	$0.82 \pm 0.02$	$0.82 \pm 0.02$	$0.72 \pm 0.02$	10	
Ni	$0.90 \pm 0.02$	$1.00 \pm 0.07$	$1.00 \pm 0.05$	$1.00 \pm 0.10$	$1.04 \pm 0.08$	$0.99 \pm 0.08$	$1.01 \pm 0.06$	$1.09 \pm 0.03$	$1.09 \pm 0.03$	$1.2 \pm 0.1$	62	
Pb	$0.58 \pm 0.08$	$0.9 \pm 0.2$	$0.9 \pm 0.1$	$0.95 \pm 0.07$	$1.0 \pm 0.1$	$0.9 \pm 0.2$	$0.97 \pm 0.08$	$1.0 \pm 0.1$	$1.0 \pm 0.1$	$1.17 \pm 0.09$	61	
Sb	$0.07 \pm 0.01$	$0.11 \pm 0.01$	$0.10 \pm 0.02$	$0.09 \pm 0.01$	$0.11 \pm 0.02$	$0.13 \pm 0.03$	$0.14 \pm 0.02$	$0.14 \pm 0.01$	$0.14 \pm 0.01$	$0.15 \pm 0.01$	1.1	
Sr	$2.00 \pm 0.05$	$2.2 \pm 0.1$	$2.20 \pm 0.08$	$2.5 \pm 0.1$	$2.6 \pm 0.1$	$3.10 \pm 0.08$	$3.1 \pm 0.1$	$3.10 \pm 0.09$	$3.10 \pm 0.09$	$2.7 \pm 0.2$	46	
V	$0.24 \pm 0.02$	$0.24 \pm 0.02$	$0.25 \pm 0.03$	$0.22 \pm 0.02$	$0.22 \pm 0.01$	$0.24 \pm 0.01$	$0.24 \pm 0.02$	$0.24 \pm 0.01$	$0.24 \pm 0.01$	$<0.12$	32	
Zn	$8 \pm 2$	$9 \pm 2$	$9 \pm 1$	$7 \pm 1$	$8 \pm 1$	$7 \pm 1$	$8 \pm 1$	$8.0 \pm 0.4$	$8.0 \pm 0.4$	$8.5 \pm 0.7$	89	

one, *etc.* Nonetheless, the results are close enough that ETV-ICPOES is sufficient for screening purposes: to quickly identify APM samples that may pose a health risk if PTEs are fully bio-accessible. These samples should then be submitted to bio-accessibility studies to determine the fraction of PTEs that may actually pose a threat.

### Determination of bio-accessibility

Another set of APM on air filters were analysed for this part of the work. Simulated saliva, gastric juice and lung fluids were added to 10 cm<sup>2</sup> squares of the filters samples to obtain the bio-accessibility of PTEs and assess the worst-case scenario (when all that is bio-accessible becomes bio-available) for risk assessment. The PTEs concentrations in the leachates were determined by ICPOES and ICPMS for cross validation. The ICPMS instrument was operated in CRI mode, where H<sub>2</sub> was introduced through the skimmer cone to overcome interference by polyatomic ions, mainly <sup>35</sup>Cl<sup>16</sup>O<sup>+</sup> on <sup>51</sup>V<sup>+</sup>, <sup>40</sup>Ar<sup>12</sup>C<sup>+</sup> on <sup>52</sup>Cr<sup>+</sup>, <sup>40</sup>Ar<sup>13</sup>C<sup>+</sup> on <sup>53</sup>Cr<sup>+</sup>, and <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup> on <sup>75</sup>As<sup>+</sup>. Although sensitivity was in general reduced, the CRI mode made it possible to obtain accurate results. One exception is monoisotopic Mn, which was subject to interference by too many polyatomic ions (<sup>40</sup>Ar<sup>14</sup>N<sup>1</sup>H<sup>+</sup>, <sup>39</sup>K<sup>16</sup>O<sup>+</sup>, <sup>37</sup>Cl<sup>18</sup>O<sup>+</sup>, <sup>40</sup>Ar<sup>15</sup>N<sup>+</sup>, <sup>38</sup>Ar<sup>17</sup>O<sup>+</sup>, <sup>36</sup>Ar<sup>18</sup>O<sup>1</sup>H<sup>+</sup>, <sup>38</sup>Ar<sup>16</sup>O<sup>1</sup>H<sup>+</sup>, <sup>37</sup>Cl<sup>17</sup>O<sup>1</sup>H<sup>+</sup>, <sup>23</sup>Na<sup>32</sup>S<sup>+</sup>, *etc.*) and was thus omitted. The operating conditions of the ICPMS instrument were selected while aspirating a digest of APM on air filter sample.

The leaching yields for simulated saliva, gastric juice and lung fluid are given in Table 3. When APM is inhaled through the mouth, saliva is the starting leaching agent. However, the percentage of PTEs released is low due to the almost neutral pH and short exposure time. In any case, PTEs can be sub-divided into two groups, with average released percentages of 3 ± 1% (for As, Cu, Pb and Sb) and 15 ± 4% (for Cr, Ni, Sr and Zn). More significant release occurred in gastric juice, where 43 ± 27% of analytes (with the exception of As) was released on average. This is commensurate with the 2 h leaching time at low pH, which suggests that carbonates are the main components of the retained APM. The results obtained by ICPMS and ICPOES for analytes determined in the residue after acid digestion were in good agreement. Mass balance was also verified (not shown). Comparison to already published results is difficult given that variations in particle size, emission sources, atmospheric conditions, collection site, extraction medium and temperature occur from one study to another.

With respect to leaching with simulated lung fluid, ideally, the leaching time should be representative of the residence time of APM in the lungs. Particles stay in the lungs for about 24 h if they take the tracheobronchial route and longer if they reach the alveolar region.<sup>14</sup> However, Table 3 reveals that As, Ni, V and Zn are released within 1 h, with negligible additional release over an extended contact time with lung fluid. Similarly, Pb and Sb, are mostly released within 2 h whereas Cr, Cu and Sr continue to be released over up to 56 h. These results highlight the importance of estimating the bio-accessibility of PTEs. For example, most of Sb and As in the studied APM are not bio-accessible.

Julien *et al.*<sup>22</sup> investigated the bio-accessibility of toxic elements in certified APM by means of water and Gamble's solution. They observed a rapid increase in dissolution during the first 30 min to 5 h and an asymptotic response approaching equilibrium between 24 h and 48 h. Generally, the bio-accessibility at 24 h ranged from 86% to 102%, the maximum bio-accessibility being measured at 72 h. Thus, the simulated lung fluid leaching behaviour observed in Table 3 is in reasonable agreement with that previously reported. Differences likely arise because real samples instead of certified reference material were analysed in the present study.

## Conclusions

A quick screening method for the determination PTEs in APM on air filters was developed using ETV-ICPOES where the advantage is direct analysis of the solid. Sensitivity of ETV-ICPOES was enhanced by adding N<sub>2</sub> to the plasma gas flow and performing multivariate optimization of the reaction, carrier and bypass gases, which improved detection limits. Bio-accessibility tests are important to assess the potential risk caused by these elements. The lowest bio-accessibility was observed for simulated saliva, due to the shortest leaching time and almost neutral pH. Leaching with simulated lung fluids and gastric juice revealed the bio-accessible fraction of PTEs that can be inhaled or swallowed from the air. While Cd is not bio-accessible and only 2–9% of the As is released by lung fluid or gastrointestinal fluids, 53–61% of Pb is concurrently released by the same fluids.

## Conflicts of interest

There are no conflicts to declare.

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