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The Human Exposome Research Group

ALTERNATIVE METHOD FOR THE ELEMENTAL CHARACTERIZATION OF FINE PARTICULATE MATTER ($PM_{2.5}$) USING HANDHELD X-RAY FLUORESCENCE ON QUARTZ FILTERS: APPLICATIONS IN HEALTH RESEARCH

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USP

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EXPOSOME: CHALLENGES BEYOND UTOPIA
JUNE 24 - 27
PORTO ALEGRE - BRAZIL
UFRGS

UNIVERSIDADE DE SÃO PAULO
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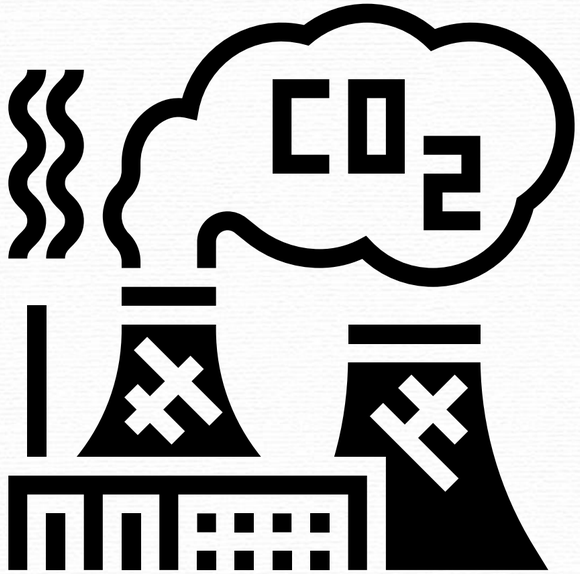
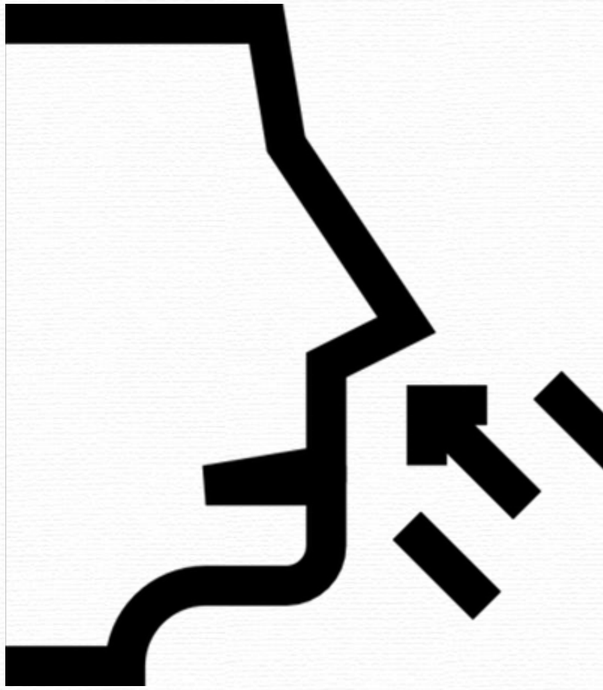
PROBLEM STATEMENT

Air Pollution



- A public health problem associated with adverse health effects, environmental and socio-economic damage (Swiston et al., 2008; Caumo et al., 2022);

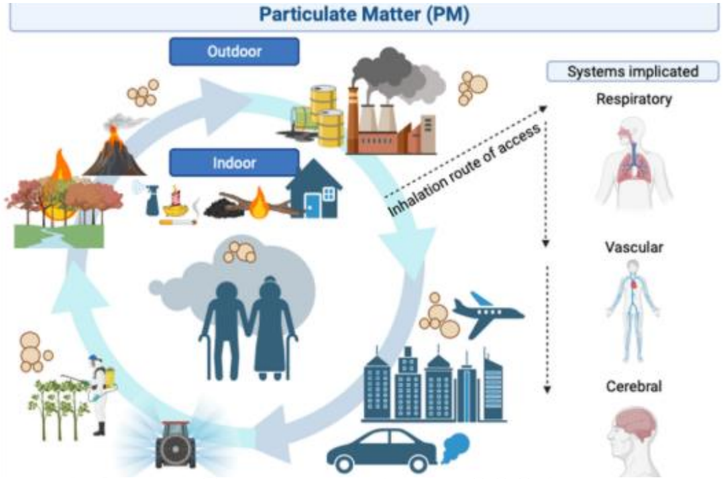
- This is a consequence of anthropogenic activities. Also, it is important to note that exposures are associated with socioeconomic factors (Carvalho et al., 2017).



PROBLEM STATEMENT

PM2.5

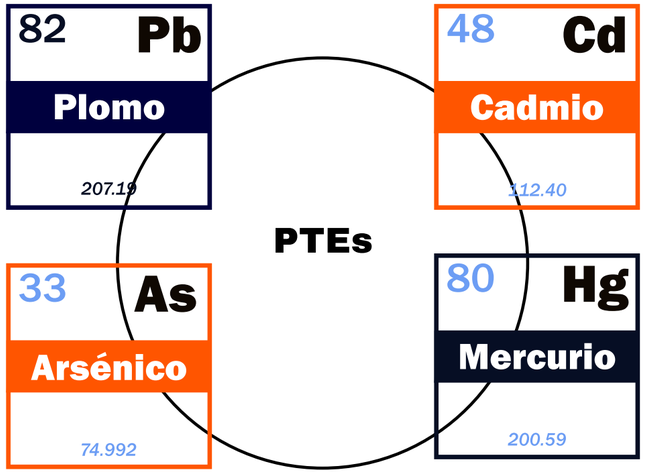
Generated through: combustion processes, atmospheric chemical reactions, wear of tires, brakes, and pavements, and biomass burning, affecting 99% of the world's population (WHO, 2022).



López-Granero et al., 2024

PTEs

Studies from different regions of the globe have identified Potentially Toxic Elements (**PTEs: Pb, As, Cd, Hg, Zn, Ni, and others**) in their composition (Hu et al., 2012; Brito et al., 2013; Li et al., 2017)



Category

Many of these PTEs are classified as **pollutants of environmental concern**, in addition to being **carcinogenic** (ATSDR, 2020; IARC 2012).

ATSDR
AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY

IARC

OBJECTIVE

To evaluate the use of a handheld X-ray fluorescence (XRF) analyzer for the trace elemental analysis of $PM_{2.5}$

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METHODS

AIR SAMPLING

June-October 2024 with a high-volume air sampler (1.13 m³/min, 24 h).

FILTERS

High-purity **quartz** filters (Whatman® QM-A, 8h at 500 ºC).

SAMPLING SITE

High-traffic density avenue in São Paulo.

ELEMENTAL ANALYSIS

Elemental composition was assessed for 13 PTEs (Pb, Cd, Hg, Cu, Fe, Au, Ni, Se, Mo, Cs, Br, K, Cl) using a 6.25 cm^2 section of the filter.

METHODS

Equipment

Niton XL2 700S (Thermo Scientific)

Reference Materials

1) "*Micromatter XRF Calibration Standards Certification Sheet*" for Au, Fe, Ni, Ge, Se, Cu, Te, CaF_2, NdF_3, WO_3, MoO_3, SrF_2, RbI, CsBr, KCl and SiO;

2) "*Tin Check Sample*" 180-606 (batch N) of MBH Analytical for Ag, Cu, Cd and Pb.

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METHOD VALIDATION

Niton XL2 700S

1

REFERENCE MATERIALS

Analyses of the reference materials for calculating the recovery percentage of the PTEs

2

SAMPLE ANALYSES

Triplicate 180-second analyses with mains-powered equipment mounted on a fixed support.

3

LODS DETERMINATION

Following the methodology by ***Chatoutsidou et al (2022)*** for PM analysis on Teflon filters

4

DATA EXTRACTION

Calculation of the integrals of the spectra generated by the NDT software (Thermo Scientific) and interpretation using Spectragryph 1.2

5

PTES CONCENTRATIONS

Using gravimetric values obtained from the differences in filter weights before and after air sampling

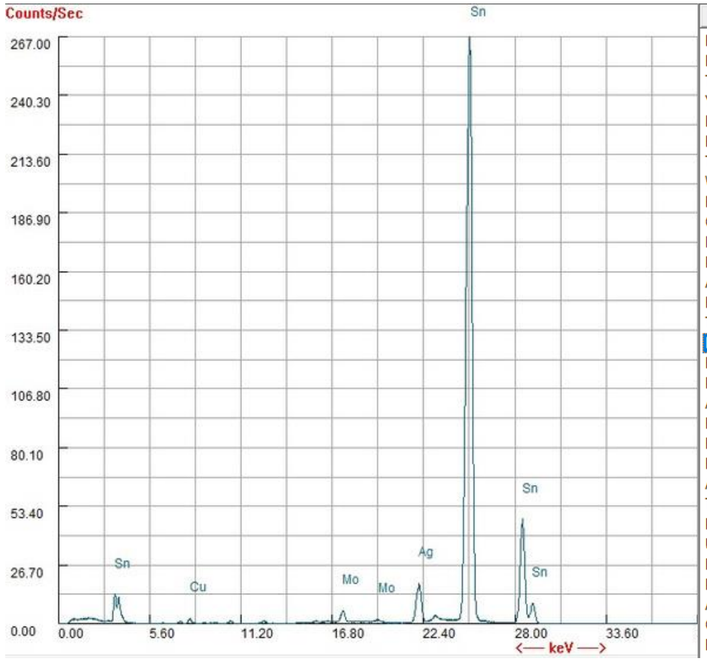
Calculation of LODs

$$(LoD)_a \cong \frac{3\sqrt{B_{ref,a} + N_{bl,a}}}{N_{ref,a} - N_{bl,a}} \cdot C_\alpha$$

Chatoutsidou et al (2022)

$\mathbf{B_{ref,a}}$ = background in the spectrum of the reference sample
$\mathbf{N_{bl,a}}$= Net white counts (blank)
$\mathbf{N_{ref,a}}$ = Net white counts (reference sample)
$\mathbf{C_a}$ = Certified concentration of the element in the reference material

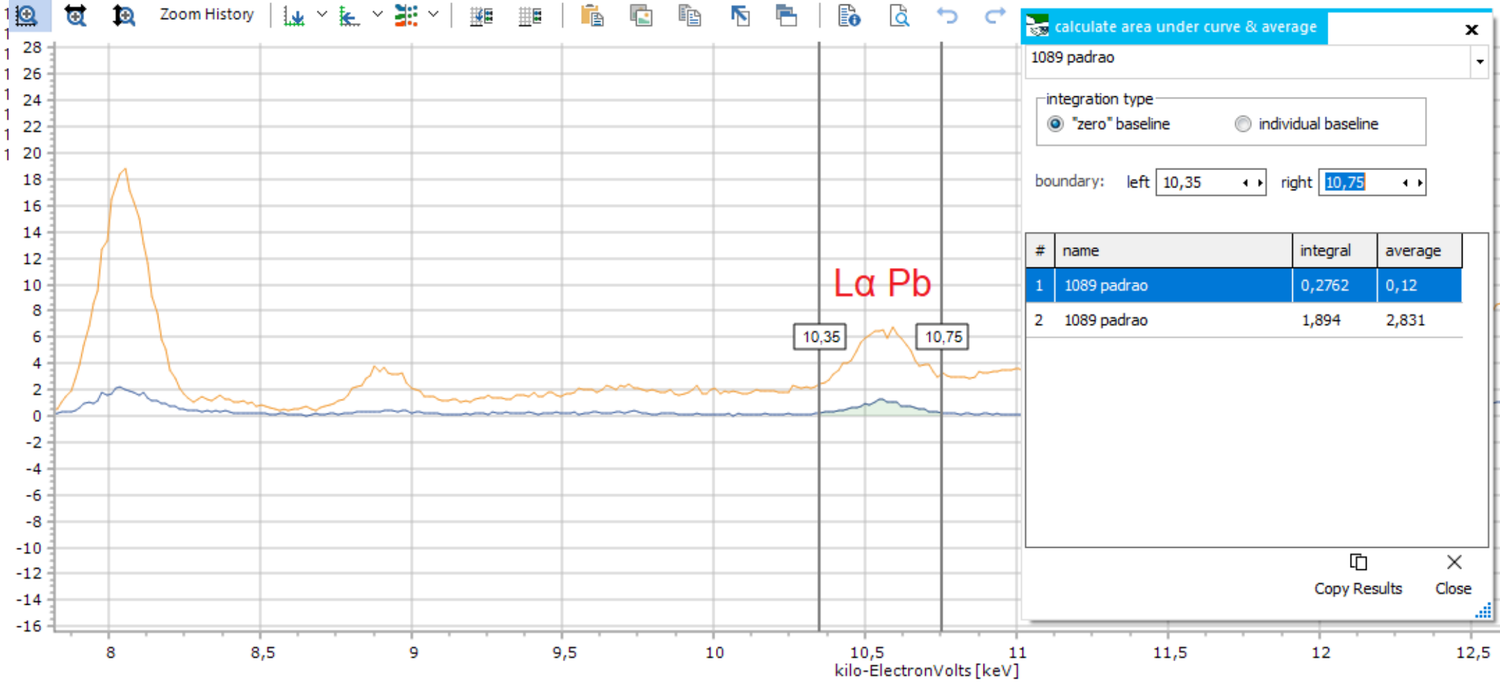
Calculation of LODs



Element	Ka1	Ka2	Kb1	Kb2
Ho	47.547	46.700	53.877	55.293
Er	49.128	48.221	55.681	57.210
Tm	50.742	49.773	57.517	59.090
Yb	52.389	51.354	59.370	60.980
Lu	54.070	52.965	61.283	62.970
Hf	55.790	54.611	63.234	64.980
Ta	57.532	56.277	65.223	66.990
W	59.318	57.982	67.244	69.067
Re	61.140	59.718	69.310	71.232
Os	63.000	61.487	71.413	73.363
Ir	64.896	63.287	73.561	75.575
Pt	66.832	65.112	75.748	77.850
Au	68.804	66.989	77.984	80.150
Hg	70.819	68.895	80.253	82.515
Tl	72.871	70.832	82.576	84.910
Pb	74.969	72.804	84.936	87.320
Bi	77.108	74.815	87.343	89.830
Po	79.290	76.862	89.800	92.387
At	81.520	78.950	92.300	94.973
Rn	83.780	81.070	94.870	97.609
Fr	86.100	83.230	97.470	100.298
Ra	88.470	85.430	100.130	103.039
Ac	90.884	87.670		
Th	93.350	89.953	1	
Pa	95.686	92.287	1	
U	98.439	94.665	1	
Np	101.057	97.067	1	
Pu	103.735	99.525	1	
Am	106.470	102.030	1	
Cm	109.236	104.581	1	
Bk	112.115	107.180	1	

Lα, Lβ, Kα, and Kβ (characteristic X-ray emission lines for the elements) were obtained using the NDT software and confirmed in the relevant literature

The calculations of the peak area integrals and backgrounds were performed using the Spectragryph software



RESULTS

Results from recovery tests with certified reference materials

Recovery % for reference materials

MBH Analytical

PTE	Certified Concentration	Recovery	% Recovery
Pb	0.16 (0.05-0.30)	0.200 ± 0.001	125,00
Cd	0.35 (0.25-0.45)	0.327 ± 0.013	93,43
Cu	0.53 (0.2-0.8)	0.502 ± 0.020	94,72
Ag	3.10 (2.4-3.3)	2.950 ± 0.020	95,18

Micromatter

PTE	Certified Concentration	Recovery	% Recovery
Cu	49.6 ± 5%	47.1 ± 4.0	95,03
Fe	48.5 ± 5%	42.4 ± 3.8	97,40
Ni	49.6 ± 5%	47.1 ± 4.0	95,03
Au	50.0 ± 5%	31.7 ± 0.8	62,00

PTES RESULTS IN AIR SAMPLES

30 samples were analyzed, and the technique proved to be feasible for the quantification of the elements Pb, Cd, Hg, Cu, Fe, Au, and Ni.

Cadmium
Median: 2.21 $ng.m^{-3}$
Min-Max: 0.25-4.38 $ng.m^{-3}$
LOD: 95.8 $\mu g.g^{-1}$

Cupper
Median: 0.62 $ng.m^{-3}$
Min-Max: 0.22-50 $ng.m^{-3}$
LOD: 25.44 $\mu g.g^{-1}$

Gold
Median: 1.42 $ng.m^{-3}$
Min-Max: 0.13-34 $ng.m^{-3}$
LOD: 74.5 $\mu g.g^{-1}$

Lead
Median: 0.24 $ng.m^{-3}$
Min-Max: 0.05-4.00 $ng.m^{-3}$
LOD: 10.06 $\mu g.g^{-1}$

Mercury
Median: 0.98 $ng.m^{-3}$
Min-Max: 0.0004-24.00 $ng.m^{-3}$
LOD: 52.31 $\mu g.g^{-1}$

Iron
Median: 29.27 $ng.m^{-3}$
Min-Max: 3.0-1100 $ng.m^{-3}$
LOD: 76.70 $\mu g.g^{-1}$

Nickel
Median: 0.70 $ng.m^{-3}$
Min-Max: 0.03-30.0 $ng.m^{-3}$
LOD: 40.3 $\mu g.g^{-1}$

The data are comparable to those reported by Samek et al. (2015) in Poland and Chatoutsidou et al. (2022) in Greece, both of which analyzed Teflon filters

CONCLUSIONS

1.

QUARTZ FILTERS

To the best of our knowledge, this is the first study to optimize a handheld X-ray device for determining the elemental composition of particulate matter collected on this type of filter.

2.

THE METHOD

It proved to be reliable, as well as more cost-effective and faster than conventional techniques such as ICP-MS, for Pb, Cd, Fe, Ni , Au and Cu.

3.

PUBLIC HEALTH POLICIES

In light of the exposome concept, assessing the concentrations of these air pollutants in major metropolises like São Paulo is crucial for safeguarding public health, particularly among socially vulnerable groups.

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THANK YOU!

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