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Metals, nonmetals and metalloids in cigarette smoke as hazardous compounds for human health

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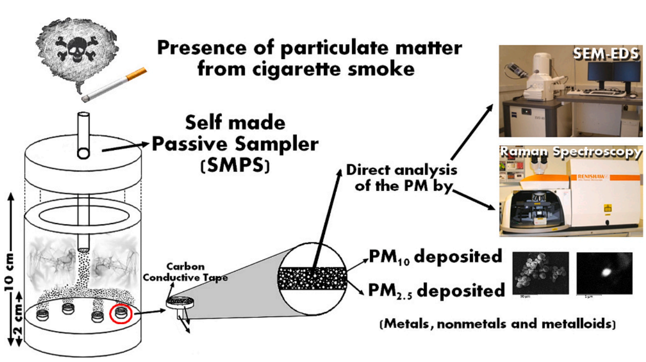
HIGHLIGHTS

- Metals, nonmetals and metalloids as hazardous compounds (HCs) in cigarette smoke
- Innovative self-made passive sampler (SMPS) was tested for the HCs detection.
- SEM-EDS and Raman microscopy were used for the direct study of collected particles.
- Metal oxides, sulfates, silicates, carbonates and phosphates were identified.

GRAPHICAL ABSTRACT



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ABSTRACT

Cigarette smoke contains many chemicals that are harmful to both smokers and non-smokers. Breathing just a little cigarette smoke can be harmful. There are >7000 chemicals in cigarette smoke, at least 250 are known to be harmful and many of them can cause cancer. Currently, many studies reported the types of harmful organic compounds in cigarette smoke; instead, there are almost no works that describe the presence of inorganic compounds. In this work, a cost-effective self-made passive sampler (SMPS) was tested as a tool to collect different types of particulate matter (PM) from cigarette smoke containing metals as hazardous compounds (HCs). To determine the nature of the metals, nonmetals and metalloids as HCs, a direct qualitative analysis of the particulate matter (PM) was conducted without developing any special sample preparation procedure. For that, non-invasive elemental (Scanning Electron Microscope coupled to Energy Dispersive X-ray Spectrometry) and molecular (Raman microscopy) micro-spectroscopic techniques were used. Thanks to this methodology, it was possible to determine in deposited PM, the presence of metals such as Fe, Cr, Ni, Ti, Co, Sn, Zn, Ba, Al, Cu, Zr,

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Ce, Bi, etc. most of them as oxides but also embedded in different clusters with sulfates, aluminosilicates, even phosphates.

1. Introduction

There are about 7000 known chemical products in tobacco and cigarette smoke (Soleimani et al., 2022; Rodgman and Perfetti, 2013), of which at least 250 are known to be harmful, and >70 elements are carcinogenic to humans (IARC, 2004). The smoke of cigarettes in closed spaces is inhaled by all; therefore, both smokers and non-smokers are exposed to its harmful effects (Pagani, 2014). It is estimated that smoking cigarettes kills up to half of its consumers, leading to >8 million deaths per year (Esposito et al., 2022; World Health Organization, 2020), while around 1.2 million are the result of non-smokers being exposed to second-hand smoke being passive smokers (World Health Organization, 2020). In this sense, in 1999 almost half of the children in the world (700 million) were exposed to cigarette smoke and most of this exposure took place at home (World Health Organization, 1999) consequently, almost half of the world's children, breathe air contaminated by tobacco smoke. Second-hand smoke is the cause of serious cardiovascular and respiratory diseases (Erhardt, 2009; Linardatou et al., 2009; Al-Wandaw et al., 2020), including coronary heart disease and lung cancer (Gan et al., 2007; Gottdiener et al., 2022), in adults; of the syndrome of sudden death in the infant (Gemble et al., 2020; Ciccarelli et al., 2021), and of low birth weight in the fetus (Stroud et al., 2022; Correa et al., 2022).

Due to these reasons, it is important to define the sources of these harmful consequences. In this way, cigarette smoke is one of the most important sources of breathable particulate matter (PM) in indoor places (Slezakova et al., 2011; (Yeha et al., 2022). Of course, within these PMs coexist organic and inorganic hazardous compounds (HCs). In the literature, many studies describe the types of harmful organic compounds such as PAHs and aromatic hydrocarbons (Lee et al., 2011; Toriba et al., 2014; Vu et al., 2015; Hearn et al., 2018; Samara et al., 2021), nitrorganic compounds (Verdolotti et al., 2012; Yershova et al., 2016; Zhang et al., 2018; Cui et al., 2020), aromatic amines (Moir et al., 2008; Saha et al., 2009), aliphatic and unsaturated hydrocarbons (Charles et al., 2007; Mola et al., 2008; Marcilla et al., 2012; Oladipupo et al., 2019), carbonyl compounds, aldehydes, and ketones (Chen et al., 2008; Miller et al., 2010; Pang and Lewis, 2011; Ding et al., 2016), alcohol and phenols (Venugopal et al., 2021; King et al., 2021); even heterocyclic compounds (Zhang et al., 2011; Roemer et al., 2016), all of them related to cigarette smoking.

On the contrary, there are very few works that describe inorganic compounds present in cigarette smoke, except some anions and cations were defined (Landsberger and Wu, 1995; Yershova et al., 2016). These inorganic compounds such as metals, nonmetals and metalloids are also present as PM in cigarette smoke and are one of the greatest sources of indoor particles, which have been linked with serious health effects (Matassa et al., 2021). As we have explained above, while the organic components are widely recognized for their harmful effects on human health, the inorganic elements present in cigarette smoke also contribute to various negative health effects. In this way, heavy metals present in cigarette smoke, including cadmium, lead, and arsenic can accumulate in our bodies over time and have been linked to various health problems (Jaishankar et al., 2014). Cadmium, for example, is known to cause chronic damage to the kidneys (Yan and Allen, 2021), while lead can affect the nervous system (Mason et al., 2014) and development in children (Sanders et al., 2009) and arsenic can promote cardiovascular dysfunction and also liver damage (Balali-Mood et al., 2021). Moreover, other inorganic elements such as nickel and chromium are also present in cigarette smoke and can contribute to respiratory issues (Bernhard et al., 2005). Nickel, in particular, has been linked to allergic reactions and asthma (Talio et al., 2011). Thus, Aluminum while not present in large amounts is another inorganic element found in cigarette smoke and it is known that chronic exposure to aluminum has been linked to neurotoxicity and increased risk of Alzheimer's disease (Wang et al., 2016). For this reason, smoking is a major risk factor for a variety of diseases, including cancer and immune-mediated inflammatory diseases and tobacco smoke contains forming reactive oxygen species (ROS) that can cause oxidative stress, leading to cellular damage and inflammation, contributing to various diseases (Caliri et al., 2021). Among these ROSs, iron, and copper, present in cigarette smoke can contribute to the formation of reactive oxygen species during the combustion of tobacco (Valavanidis et al., 2009).

Consequently, there is a widespread interest in analyzing cigarette smoke related to indoor particulate matter (PM) (Slezakova et al., 2011). Therefore, more studies about PMs present in cigarette smoke must be required and chemical characterization of individual particles must be provided.

In this work, a cost-effective self-made passive sampler (SMPS) was tested as a tool to collect different types of PM from cigarette smoke containing metals, nonmetals and metalloids as hazardous compounds (HCs). To determine the nature of the metals, nonmetals and metalloids as HCs, direct analysis of the PM was conducted without developing any special sample preparation procedure. For that, non-invasive elemental (Scanning Electron Microscope coupled to Energy Dispersive X-ray Spectrometry) and molecular (Raman microscopy) micro-spectroscopic techniques were used.

2. Materials and methods

2.1. Self-made passive sampler (SMPS)

The objective of the design of the SMPS was the construction of an instrument able to reproduce in a simple and low-cost way the emission of cigarette smoke and the risk of inhaling this type of smoke indoors by second-hand smokers. This passive sampler consists of a cylindrical polystyrene box, with an opening to introduce a small polystyrene tube through which to exhale cigarette smoke. Logically, the collaboration of cigarette smokers is needed. Moreover, inside the cylindrical box, several pin stubs covered with carbon tape were inserted (see Fig. 1). One of the advantages of this self-made device is that the particulate matter is spontaneously trapped (without artificially pumping the air), in a carbon tape fixed on the surface of a typical SEM pin stub used to fix samples during SEM-EDS measurements (see Fig. 1). It should be noted that for each pin stub a procedural blank was made on each carbon fixed tape always obtaining only the signal of C element. The content of the "pin stubs", mainly particulate matter ($PM_{2.5}$ and PM_{10}) adhered to it, can be characterized directly without any further pretreatment in the laboratory, which can be considered the second advantage of this sampler, compared to other systems of particulate matter sampling.

In the used-passive sampler, four pin stubs with carbon tape were inserted at the bottom of the cylindrical box (see Fig. 1). To carry out this study, a voluntary regular smoker exhaled cigarette smoke in the SMPS for four weeks to collect the highest amount of particulate matter and consequently extract more information. To do this, all the PMs that adhered to the pins were the result of smoking 100 blond cigarettes in that period. To carry out this study, blond cigarettes from one popular brand produced by Philip Morris International Products S.A. in Spain were selected. Finally, to validate the presence of the presented compounds, only those that have been repeated at least ten times in the analyses have been reported.

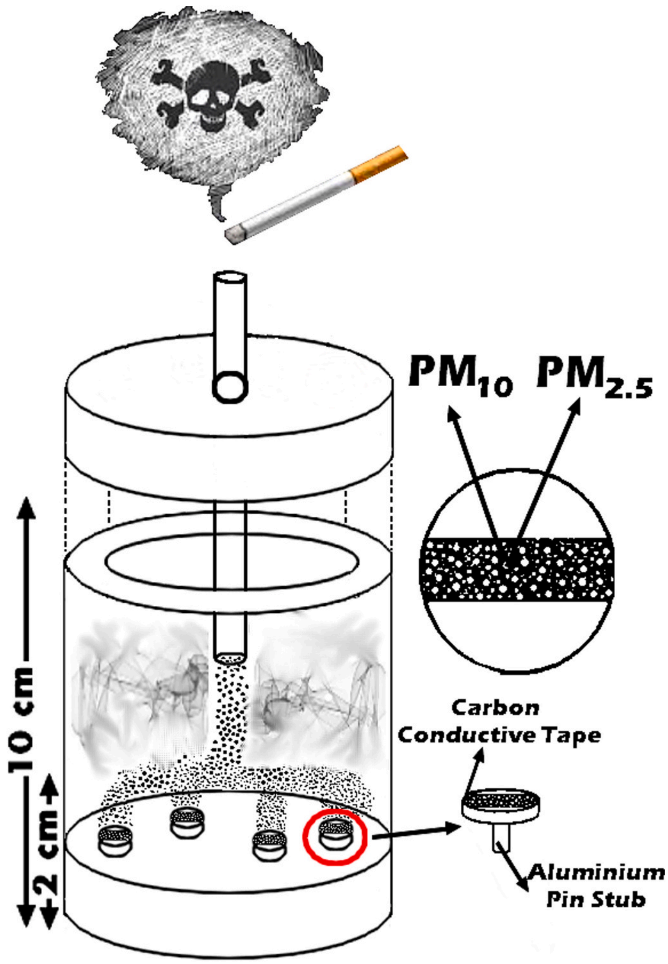

Fig. 1. Design of the SMPS to reproduce the emission of cigarette smoke and direct analyses of PMs.

2.2. Instrumentation

The SEM-EDS analyses were carried out using an EVO®40 Scanning Electron Microscope (Carl Zeiss NTS GmbH, Germany) coupled to an X-Max Energy-Dispersive X-ray spectrometer (Oxford Instruments, Abingdon, Oxfordshire, United Kingdom) for electron image acquisitions and elemental analysis (punctual and imaging). Although sometimes, deposited particles alone were not conductive, it was possible to obtain optimal results without coating the samples. SEM images were obtained at a high vacuum employing an acceleration voltage of 30 kV and a 10 to 400 μm working distance. Different magnifications (reaching up to ×6800) were used for secondary electron images and an integration time of 50 s was employed to improve the signal-to-noise ratio. The EDS spectra were acquired and treated using the INCA suite software (version 4.13) (Oxford Instruments, Abingdon, Oxfordshire, United Kingdom). Furthermore, a map acquisition of specific microscopic areas in the samples was also performed, allowing the evaluation of the distribution of these elements throughout the sample.

For the micro-Raman analyses, the inVia Renishaw confocal Raman micro-spectrometer (Renishaw, Gloucestershire, UK) coupled to a DMLM Leica microscope with 5×, 20×, 50×, and 100× long working distance lens was used. Excitation laser (514 nm; nominal laser power 350 mW and 50 mW, respectively) and different magnification lenses (50× and 100×, mainly) were used to perform the measurements. The spectrometer was daily calibrated by using the 520 cm^{-1} Raman band of a silicon chip. Lasers were set at low power (not >1 mW at the sample) to avoid sample decomposition. Data acquisition was carried out using the Wire 3.2 software package (Renishaw). Spectra were acquired between 100 and 3000 cm^{-1} and several scans (between 10 and 40 scans) were accumulated for each spectrum to improve the signal-to-noise ratio. The interpretation of all the Raman results was performed by comparison of the acquired Raman spectra with the Raman spectra of pure standard compounds collected in the e-VISNICH dispersive Raman database (Maguregui et al., 2010). Additionally, free Raman databases (e.g. RRUFF (Downs and Hall-Wallace, 2002)) were also considered for the assignation of Raman bands.

3. Results and discussion

3.1. Elemental and molecular characterization of metals, nonmetals and metalloids as PM

As mentioned above, to determine the nature of the different metals, nonmetals and metalloids as PMs being HCs from cigarette smoke, collected particles were analyzed directly without applying any sample treatment and using a non-invasive strategy based on the combined use of SEM-EDS and Raman microscopy. To consider a specific particle containing HCs as a representative particle in the carbon tapes of the SMPS, at least ten particles of the same elemental and molecular nature should be identified during the SEM-EDS and micro-Raman screening.

3.2. SEM-EDS analyses

The results obtained by SEM-EDS indicated a wide heterogeneity in the elemental composition of the different particles trapped from cigarette smoke in the carbon tapes fixed in the “pin stubs” inserted in the SMPS. Most of the particles were observed as single ones, but there were also examples of others embedded in a bigger one forming a cluster particle.

In Fig. 2A, an aggregation/cluster particle of 50 μm of carbon and oxygen mixture, was presented. This cluster could surely be related to the presence of some unknown hydrocarbon compound. In Fig. 2B, an irregular particle with an equivalent size of 2.5–3 μm (or less) mainly composed of Cu and O was presented. This compound could be related to the presence of CuO. This compound is related to the use of these particles to improve the degree of conversion of CO to CO_2 (Li and Hajaligol (2003a, 2003b). Moreover, in Fig. 2C, an unusual irregular 20 μm cluster formed by Fe-Cr-Ni-Cu was observed. These elements together can be considered as very harmful cluster particles and are related to the use of them to improve catalytic activities for volatile organic compounds (VOCs) (Zang et al., 2019). Additionally, these metals are related to respiratory diseases, including lung cancer (Martín-Ruiz et al., 2004). In Fig. 2D, a cubic 10 μm cluster particle could be observed. The elemental analyses reported the presence of many elements related to the probable presence of silicates with other minor elements such as Mg, Fe, P, S, K, Ca, Mn even Ti. In this case, it was very common in the presence of silicates such as kaolin ($Al_2Si_2O_5(OH)_4$). The silicon element is taken up from the soil by tobacco plants in the available silicate form, generally in the form of kaolin (Pappas, 2011). Moreover, in Fig. 2E, an irregular 2 μm rolled particle could be observed. The elemental analyses revealed the presence of Sn together with Co (minor proportion). Sn particles such as SnO_2 are used as catalysts for the oxidation of aromatic compounds (Begum et al., 2016). In Fig. 2F, an additional 1 μm rolled particle was detected. This particle analysis revealed the presence of Ba, S, and O, which could be related to the presence of some sulfate, such as barite ($BaSO_4$). This particle among others, such as the present in Fig. 2G (an irregular 2 μm acicular particle) with the elemental composition of Zr and O, was probably related to the presence of zirconia and the one present in Fig. 2H (a rodlike 5 μm acicular particle) with the presence of Ti and O, which could be related with the presence of Titanium oxide (TiO_2); all of them (particles of Fig. 2F, G, and H) are related with the presence of additives and adsorbents in cigarette filters (Taniguchi, 2012).

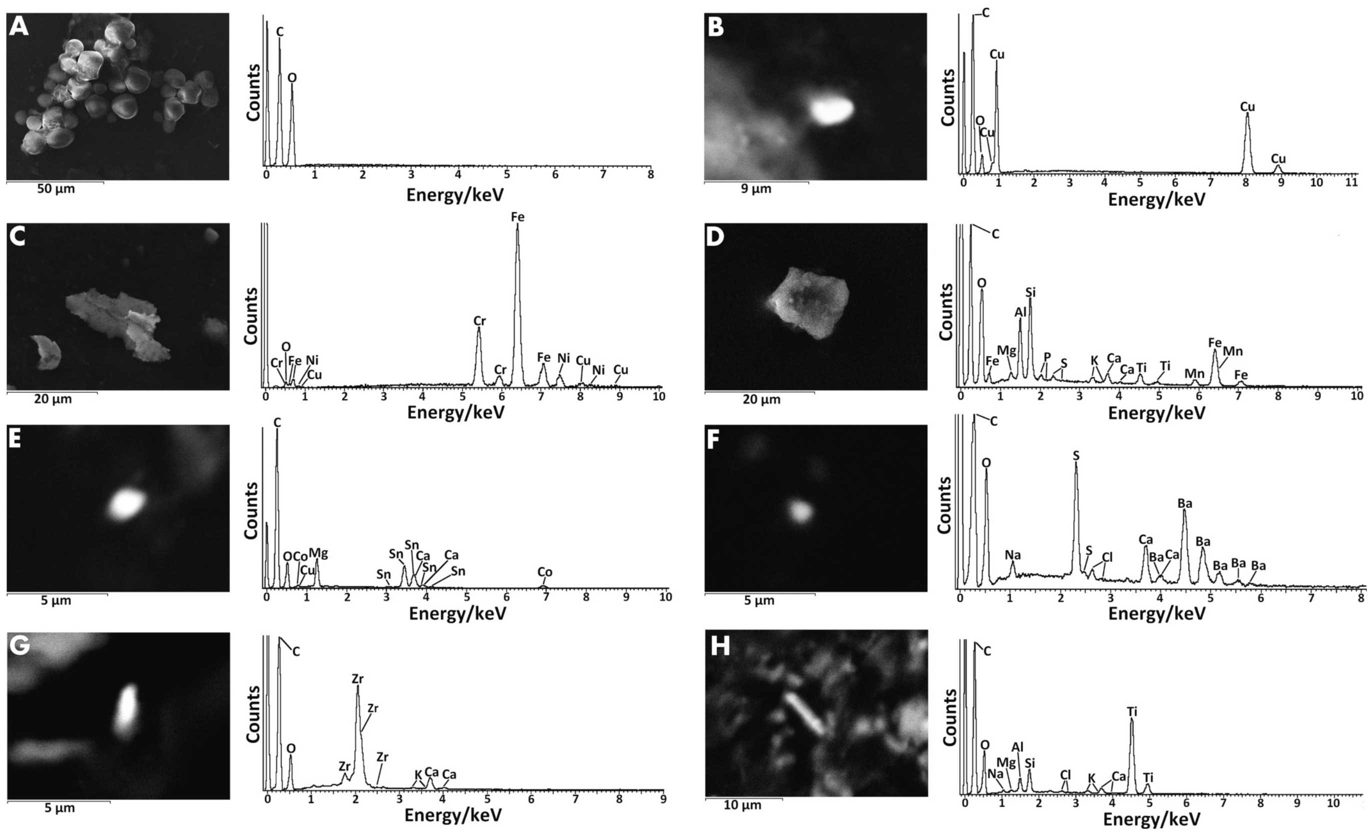

Fig. 2. Single point SEM-EDS analyses showing the presence of A) 50 μm aggregation/cluster particle composed by C and O, B) 2.5–3 μm irregular particle composed by Cu and O, C) 20 μm irregular cluster formed by Fe-Cr-Ni-Cu, D) cubic 10 μm cluster particle composed by Mg, Fe, P, S, K, Ca, Mn and Ti, E) irregular 2 μm rolled particle composed by Sn and Co, F) 1 μm rolled particle composed by Ba, S and O, G) irregular 2 μm acicular particle composed by Zr and O and H) rodlike 5 μm acicular particle mainly composed by Ti and O.

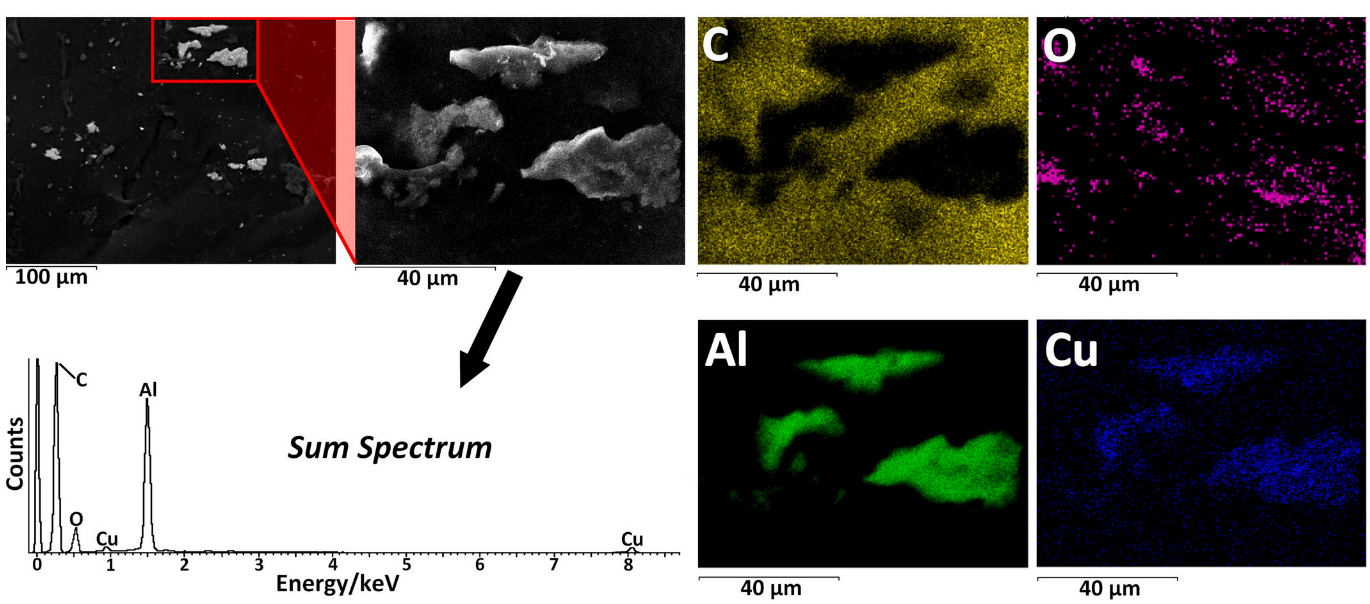

Fig. 3. SEM-EDS mapping of the irregular particles observing the metal aggregation of Al—Cu particle.

To obtain more information about the elemental composition of metals, nonmetals and metalloids present in cigarette smoke as particulate matter, in Fig. 3, a mapping of three different 40 μm irregular particles is presented. According to the elemental distribution maps (see Fig. 3) the three particles were composed of an Al—Cu particle (see blue and green distribution maps). The presence of Aluminum and Copper cigarette smoking can promote different diseases and is directly related to dialysis encephalopathy, microcytic anemia, osteomalacia even Alzheimer's diseases (Forster et al., 1995; Becaria et al., 2003; Bernhard et al., 2005).

Moreover, in Fig. 4A, and Fig. S1 from Supplementary Material, an irregular $PM_{2.5}$ particle formed by Bi and Cl could be observed and

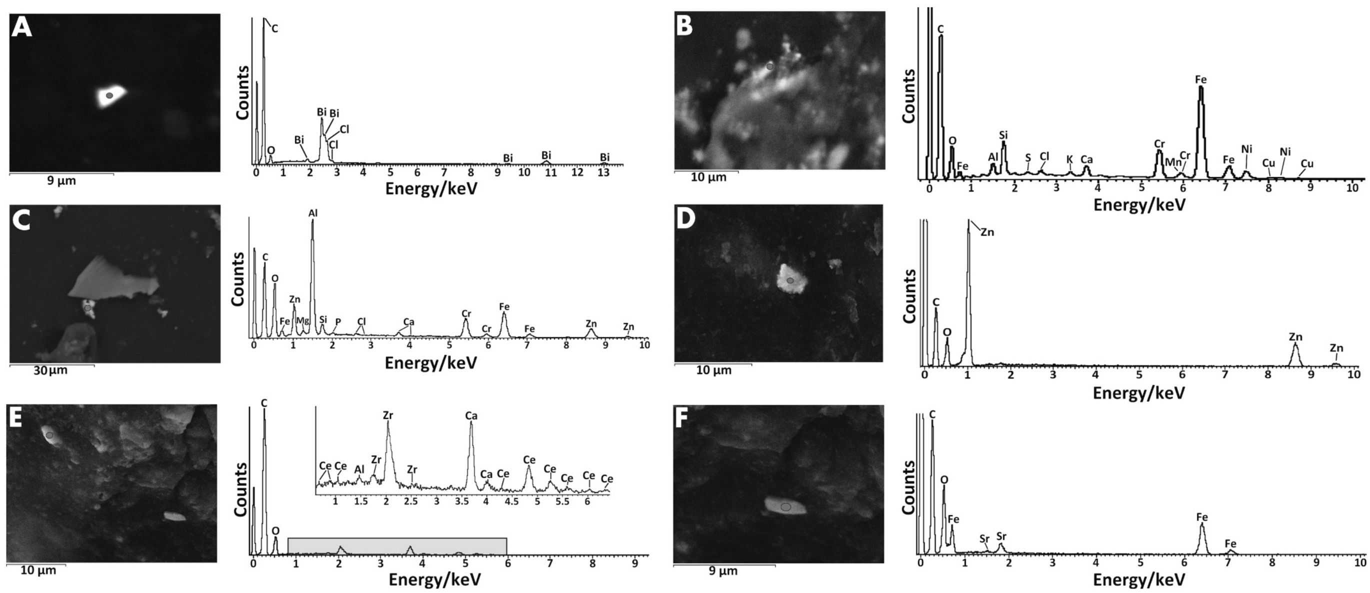

Fig. 4. Single point SEM-EDS analyses showing the presence of A) A) 4 μm irregular particle composed by Bi and Cl, B) 5 μm irregular particle composed mainly by aluminosilicates and presence of Fe-Ni-Cr-Cu, C) 7 μm irregular particle composed mainly by aluminosilicates and presence of Fe-Cr-Zn, D) 3–4 μm irregular particle composed by Zn and O, E) 4 μm irregular particle composed mainly by Zr and Ca (both majority) and other elements such as Ce and Al and F) 3–4 μm acicular particle composed by Fe (majority) and Sr.

predicted the presence of BiOCl compound. Additionally, the same kind of particles was repeatedly observed many times during the EDS analyses as can be seen in Fig. S1 from Supplementary Material. The use of this compound is related to its oxidant properties as a catalyst for volatile organic compounds, even phenolic compounds present in cigarette smoke (Wu et al., 2020). In this way, small bismuth-containing compounds are preferred due to the enhanced reactivity of bismuth with specific compounds, like phenolic compounds in mainstream smoke, when the compound itself is compact. One such compound is BiOCl, featuring bismuth with a substantial reactive surface area available for interaction. The extensive reactive surface of bismuth facilitates its increased availability for reacting with targeted constituents, leading to more effective removal of such elements from smoke. (Xue and Chan, 2008). Therefore, treatment of tobacco material with this bismuth oxychloride helps to reduce the content of phenolic compounds, such as phenol, cresols, hydroquinone, and resorcinol, and polycyclic aromatic hydrocarbons (PAHs), such as naphthalene, fluorine, anthracene, pyrene, and/or benzo[*a*]pyrene, in the particulate phase of the main smoke. Moreover, as observed in Fig. 4B and 4C, 5 and 7 μm irregular particles were presented. For the case of Fig. 4B and Fig. 4C elements such as Si, Al, Ca, K, Mg, S, and Cl could be identified. These elements are related to the presence of silica, some aluminum silicates, and even calcium compounds, which, are reported on the surfaces of tobacco leaves (Halstead et al., 2015; Pappas et al., 2016). Additionally, phytolithic

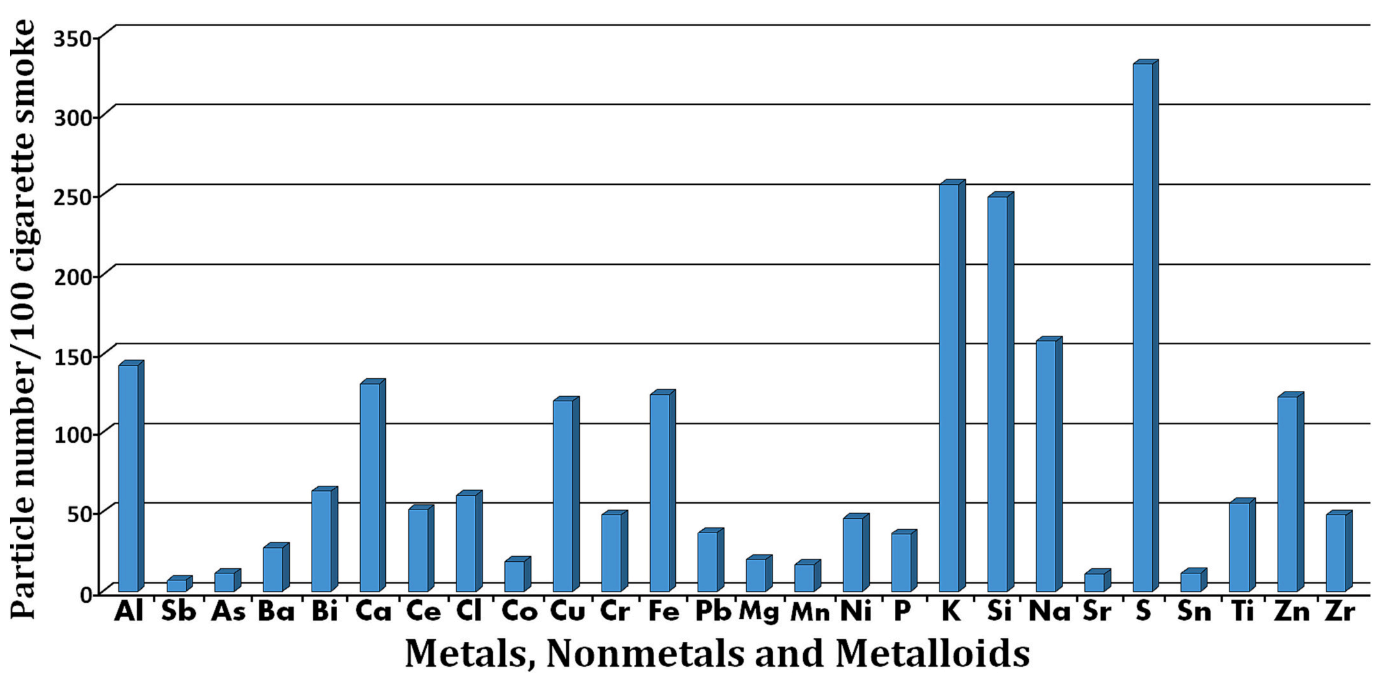

Fig. 5. Variability of presence of metals, nonmetals and metalloids present as PMs per 100 cigarette smoke.

Table 1
Summary of the characteristic Raman bands and the corresponding inorganic compounds identified in the cigarette smoke.

Analyzed particles	Mineral name	Raman bands ν (cm^{-1})
α-FeOOH	Goethite	245 w , 297 s, 390 s, 480 w, 551 w
Fe_3O_4	Magnetite	305 m, 539 m, 667 vs
α-Fe_2O_3	Hematite	226 s, 292 vs, 410 w, 497 m, 613 m
NH_4HCO_3	Ammonium bicarbonate	223 w, 444 vw, 703 m, 811 m, 842 m, 1044 vs, 1086 s, 1262 w, 1452 w
$Na_2CO_3·10H_2O$	Natron	1068 vs
$CaCO_3$	Calcite	281 m, 711 m, 1086 vs, 1435 w
α-SiO_2	Quartz	207 vw, 261 m, 354 m, 394 m, 465 vs, 694m, 805 m, 1159 m
$Al_2Si_2O_5(OH)_4$	Kaolinite	248 w, 276 w, 338 m, 397 w, 431 w, 474 m, 513 w, 638 vs, 709 w, 751 w, 790 w, 914 m, 1121 w
$(NH_4)H_2PO_4$	Diammonium phosphate (BisPhosphammite)	340 w, 400 w, 478 w, 546 w , 925 vs, 1439 w, 1662 w, 1702 w
$BaSO_4$	Barite	460 s, 618 m, 648 m, 987 vs, 990 vs, 1084 m, 1104 m, 1141 w, 1167 m.
Na_2SO_4	Thenardite	451 w, 466 w, 621 m, 632 m, 648 m, 992 vs, 1101 m, 1132 m, 1152 m.
α-TiO_2	Rutile	145 s, 437 vs, 610 vs
Al_2O_3	Corundum	378 m, 415 vs, 449 m, 575m, 748 vw
As_2O_3	Arsenolite	147 m, 216 s, 298 vs, 327 w, 376 vs, 409 w, 424 vw, 434 m, 449 vs, 470 w, 567 w, 656 vs
Sb_2O_3	Valentinite	142 s , 190 vw , 217 m, 296 vs , 502 vw, 596 w , 682 w, 783 w
CuO	Tenorite	145 vs, 147 vs, 170 vs, 177 vs, 184 vs, 189 vs, 198 w, 212 w, 217 w, 422 w, 485 w, 635 w
ZnO	Zincite	330 vw, 437 s, 521 vs, 562 w, 1089 vw.
NiO	Bunsenite	544 w, 734 w, 1093 vs, 1483 vs
PbO	Litharge	147 vs, 339 m
Cr_2O_3	Eskolaite	292 m, 347 m, 550 vs, 612 m, 649 w, 689 w

s: strong; m: medium; w: weak; v: very.

silica, a biogenic mineral that is commonly produced in plants was also observed in the inner parts of tobacco leaves (Huitu et al., 2014; Sivanesan and Park, 2014). Thus, in the spectra from Fig. 4B and Fig. 4C elements such as Fe, Cr, Ni, Cu, and Zn are also able to be observed. As mentioned in Fig. 2C the presence of this type of particle is related to oxidizing properties in the catalyzing processes for some VOCs (Zang et al., 2019) and directly related to respiratory disorders (Martín-Ruiz et al., 2004). As can be seen, almost all particles were isolated metal particles. For example, the particle of 3–4 μm only composed of Zn and O could be mentioned (see Fig. 4D). The major presence of Zn and O was determined by the EDS technique suggesting a possible presence of zinc oxide, probably zincite (ZnO). This compound could be related to a direct influence on the possible testicular toxicity induced by nicotine-promoting testicular dysfunction (Mahmoud and Shalaby, 2019). Additionally, in Fig. 4E, an irregular 4 μm particle could be observed. This particle was mainly composed of Zr and Ca (both majority) and other elements such as Ce and Al. Recently, some studies (Li and Hajaligol, 2003a, 2003b) have described the use of Fe_2O_3, CuO, TiO_2, CeO_2, Ce_2O_3, and Al_2O_3 among other nanoparticles, mainly doped with Zr, Mn_2O_3, or with Pb, as well as mixtures of these compounds for increase the degree of conversion of CO to CO_2. This last observation matches with the one presented in Fig. 3. Finally, in Fig. 4F, a 3–4 μm acicular particle was presented. In this case, this irregular particle was composed of Fe (majority) and Sr. In this way, it must be highlighted that some studies in tobacco smoke report micro and nanoparticles of iron oxides identifying as active compounds for CO catalyst, as a CO oxidant, and in its reduced forms as a NO catalyst (Li et al., 2004). Fe_2O_3 (hematite) and FeOOH (goethite) are the common iron oxides that act as catalytic oxidators for CO removal (Li et al., 2003).

As the summary of the observed particles, in Fig. 5, different metals, nonmetals and metalloids present in 100 cigarette smoke could be observed. As can be seen, S > K > Si were the most predominant metals, nonmetals and metalloid particles and Al, Ca, Cu, Fe, and Zn were the following metals that appeared approximately in the same magnitude. As a curiosity, Bi and Cl also appeared in the same magnitude. The last observation matched with the ones observed by SEM-EDS, in which many particles of BiOCl were observed. Additionally, other metals, nonmetals and metalloids could be observed but presented with a minority. Many of them, using SEM-EDS or Raman spectroscopy were observed in their respective molecular form as oxides, sulfates, phosphates even carbonates.

3.3. Micro-Raman spectroscopic analyses

To define the molecular composition of the PM deposited on the SMPS, Raman microscopy was used. The following presented spectra observation matched with many of them observed by SEM-EDS and results came totally in agreement. According to the obtained results, a high content of mainly different clusters was observed in the cigarette smoke. Table 1 shows a summary of the molecular composition of the characterized particles. The obtained results indicated a high content of oxides and mixed oxides, mainly related to its presence in catalytic processes. In this way, according to the spectra obtained directly on the pin stubs, in Fig. 6, different iron oxides could be observed. Concretely iron(III) oxyhydroxide, goethite (α-FeOOH, Raman bands at 245, 297, 390, 480 and 550 cm^{-1}) (see Fig. 6A), magnetite (Fe_3O_4, Raman bands at 305, 539 and 667 cm^{-1}) (see Fig. 6B) and iron (III) oxide (Fe_2O_3) in form of hematite (Raman bands at 226, 292, 410, 497 and 613 cm^{-1}) (see Fig. 6C) were observed. These iron compounds are closely related to oxidation catalysts for CO as mentioned earlier. Moreover, another kind of compound such as carbonates could be detected. Compounds such as ammonium bicarbonate (NH_4HCO_3, Raman bands at 223, 443, 704, 810, 842, 1044, 1085, 1262 and 1451 cm^{-1}) (see Fig. 6D); natron ($Na_2CO_3·10H_2O$, main Raman band at 1068 cm^{-1}) (see Fig. 6E) and calcite ($CaCO_3$, Raman bands at 281, 711, 1086 and 1435 cm^{-1}) (see Fig. 6F) were presented. These carbonates for instant ammonium bicarbonate are used to enhance nicotine absorption for provoking smoke addiction (Mitra, 2016) or in the case of calcite, are used as a component in cigarette filters or as pigment added to cigarette paper, to ensure the creation of an attractive ash of cigarette (Browne, 1990). Additionally, some silicates and phosphates were also detected; some silicates such as quartz (α-SiO_2, Raman bands at 207, 261, 354, 394, 465, 694, 805 and 1159 cm^{-1}) (see Fig. 6G); kaolinite ($Al_2Si_2O_5(OH)_4$, Raman bands at 248, 276, 338, 397, 431, 474, 513, 638, 709, 751, 790, 914 and 1121 cm^{-1}) (see Fig. 6H); and phosphate as diammonium phosphate (DAP) ($(NH_4)H_2PO_4$, Raman bands at 340, 400, 478, 546, 925, 1439, 1662 and 1702 cm^{-1}) (see Fig. 6I). Quartz and kaolinite are well-known compounds that are used in cigarette filters (Taniguchi, 2012). For the case of DAP, is usually used as a retardant in cigarettes. In this sense, due to the addition of ammonia to cigarettes, smokers are exposed to higher internal nicotine doses and become more addicted to the product, due to the nicotine enhancer effect. The base ammonia, as well as ammonia-forming compounds such, as DAP or Phosphammite, ammonium hydroxide, and urea, have been routinely added to the tobacco used in cigarettes (Coggins et al., 2011; Stavanja et al., 2008).

According to the presence of sulfates as compound emissions, two kinds of sulfates were observed. On the one hand, barium sulfate or barite ($BaSO_4$, Raman bands at 460, 618, 648, 987, 990, 1084, 1104, 1141 and 1167 cm^{-1}) (see Fig. 6J) and on the other hand, sodium sulfate or thenardite (Na_2SO_4, Raman bands at 451, 466, 621, 632, 648, 992, 1101, 1132 and 1152 cm^{-1}) (see Fig. 6K). Both are closely related with

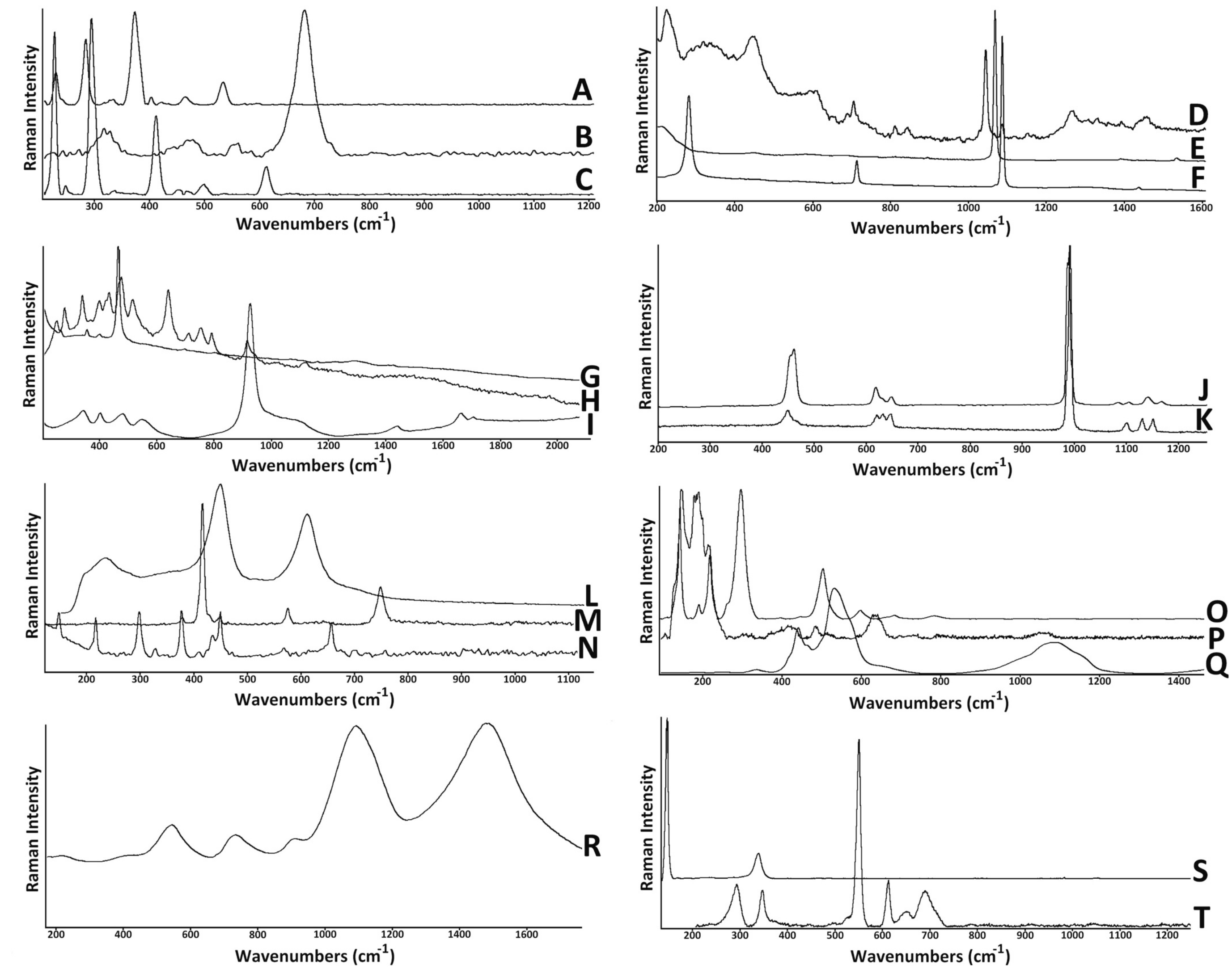

Fig. 6. Examples of Raman spectra of different compounds detected in the PM retained in the SMPS showing the presence of A) goethite (α-FeOOH), B) magnetite (Fe_3O_4), C) hematite (α-Fe_2O_3), D) ammonium bicarbonate (NH_4HCO_3), E) natron ($Na_2CO_3 \cdot 10H_2O$), F) calcite ($CaCO_3$), G) quartz (α-SiO_2), H) kaolinite ($Al_2Si_2O_5(OH)_4$), I) diammonium phosphate (DAP) ($(NH_4)H_2PO_4$), J) barite ($BaSO_4$), K) thenardite (Na_2SO_4), L) rutile (α-TiO_2), M) aluminum oxide (Al_2O_3), N) arsenolite (As_2O_3), O) valentinite (Sb_2O_3), P) tenorite (CuO), Q) zincite (ZnO), R) bunsenite (NiO), S) litharge (PbO) and T) eskolaite (Cr_2O_3).

their presence as additives in cigarette filters (Taniguchi, 2012).

Apart from these compounds, many different metal oxides were also identified. In this way, titanium oxide or rutile (α-TiO_2, Raman bands at 145, 437, and 610 cm^{-1}) (see Fig. 6L); Corundum or Aluminum oxide (Al_2O_3, Raman bands at 378, 415, 449, 575 and 748 cm^{-1}) (see Fig. 6M) and Arsenolite (As_2O_3, Raman bands at 147, 216, 298, 327, 376, 409, 424, 434, 449, 470, 567 and 656 cm^{-1}) (see Fig. 6N). In the case of TiO_2, toxicity studies have also shown that TiO_2 may induce lung injury of the lung (Wang and Fan, 2014). Moreover, there are works in which it is shown that Al_2O_3 particles serve to capture other types of compounds and be expelled through mainstream cigarette smoke (Fresquez et al., 2021). Thus, As_2O_3 is not only a toxic oxide but also a carcinogenic metalloid (Liu et al., 2021; De, 2005).

Moreover, other kinds of metal oxides were observed; the presence of valentinite was also detected (Sb_2O_3, Raman bands at 142, 190, 217, 296, 502, 596, 682, and 783 cm^{-1} (see Fig. 6O). This type of oxide is widely used as an additive for the flame retardant material used in many industries (Wagner et al., 2013; Niu et al., 2018); tenorite (CuO, Raman bands at 145, 147, 170, 177, 184, 189, 198, 212, 217, 422, 485 and 635 cm^{-1}) (see Fig. 6P). This copper oxide is usually used to increase the degree of conversion of CO to CO_2 in smoking (Li and Hajaligol, 2003a, 2003b) and zincite (ZnO, Raman bands at 330, 437, 521, 562 and 1089 cm^{-1}) (see Fig. 6Q). These ZnO particles can be considered as HE's particle is highly related with the human liver cells accumulating and resulting in a very negative influence in the human health (Sharma et al., 2012). Thus, another harmful oxide such as Bunsenite (NiO, Raman bands at 544, 734, 1093, and 1483 cm^{-1}) (see Fig. 6R) was also observed. NiO has a long retention half-time in the lungs; and it persisted there for >3 months (Benson et al., 1994; English et al., 1981) and can be considered as a human carcinogen (Sunderman et al., 1987).

Finally, Pb and Chromium oxides in the form of Litharge (PbO, Raman bands at 147 and 339 cm^{-1}) (see Fig. 6S) and Eskolaite (Cr_2O_3, Raman bands at 292, 347, 550, 612, 649 and 689 cm^{-1}) (see Fig. 6T) were observed. In this case, Pb is closely related to affections in the central nervous system and the kidneys (Tona et al., 2013; Rathanavel and Thillai, 2013) and for the case of Chromium oxide, it must highlight firstly that Cr (VI) is more toxic and has a higher solubility in water than Cr (III) such as Cr_2O_3. In both cases, one of the most common routes for Cr exposure is through inhalation (smoking) and is associated with liver, lung, and kidney damage, widespread dermatitis, GI tract damage, human lung cancer, cardiomyopathies, cardiovascular disease, and even promote Alzheimer's disease (Wallin et al., 2017).

4. Conclusions

The use of conventional SEM pin stubs together with the adhesive carbon tape was revealed as a good alternative tool for the direct characterization (without applying any sample treatment) of metallic (metal, nonmetal and metalloid) particles as HCs present in the PMs from cigarette smoke. Thanks to the multi-analytical methodology applied in this work, using SEM-EDS (single point and imaging) and single point Raman microscopy, it was possible to determine the presence of a wide variety of heavy metals and their related molecular forms from cigarette smoke. Therefore, the SMPS used in this work can be proposed as a cost-efficient sampling system to detect the presence of metallic HCs in the PM from cigarette smoke, as an alternative to other expensive devices.

Regarding the particle composition, and thanks to SEM-EDS application, it was possible to observe different sizes of emitted metal particles from cigarette smoke (from 20 μm to 2 μm, or smaller) indicating the different elemental composition of metals alone or even as small clusters, for instances, Fe, Cr, Ni, Al, Zr, Ti, Ba, Cu, Co, Bi, Sn, Zn, Sr, etc. Thanks to the use of SEM-EDS, we could comprehend how in some cases, metal particles with very fine size ($PM_{2.5}$ or less) are embedded in others with greater size (PM_{10}).

Moreover, the use of Raman microscopy has been revealed as a perfect analytical tool to complement the SEM-EDS information and accomplish the interpretation of the molecular forms present in the PMs. In this way, different carbonates, such as DAP and others, apart from silicates, phosphates, and sulfates were observed. Thus, and according to the results obtained, Ti, Al, As, Sb, Cu, Zn, Ni, Pb, and Cr oxides were also observed. To the best of the author's knowledge, this is the pioneer discovery of which these metals, nonmetals and metalloids (in many cases aggregates or clusters) have been detected directly without any preparative method from cigarette smoke.

Finally, it should be noted that this first approach can be considered very important in the context of research on the effects of cigarette smoke on human health and can contribute to the general understanding of the composition of the metallic particles present in it. Furthermore, this study can relate the health of smokers to non-smokers and provide an answer to the associated risks of these HCs in cigarette smoke particles. The presented results could even help in the development of health policies and prevention strategies or even regulatory measures.

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CRediT authorship contribution statement

Héctor Morillas: Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Euler Gallego-Cartagena:** Writing – review & editing, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Settakorn Upasen:** Writing – review & editing, Software, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Data availability

The authors do not have permission to share data.

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