Morphological and chemical characterization of soot emitted during flaming combustion stage of native-wood species used for cooking process in western Mexico


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1. Introduction

It is estimated that two billion people use biomass fuel (wood, dung and fiber residues) as their primary energy source for domestic needs such as heating and cooking (Bond & Bergstrom, 2005). Biomass fuels account approximately 14% of the worldwide energy consumption, in which only ~3% is used in industrialized countries, but 43% is consumed by developing...
countries (Kozinski & Saade, 1998). Approximately 27 million people in rural areas of Mexico, still use biomass for cooking (Berrueta, Edwards, & Masera, 2008), where fuelwood represents approximately 80% of energy used by rural households and 50% of total energy use in rural communities (Berrueta et al., 2008).

The biomass burning devices used for cooking are known in the literature by various names such as cook stoves, wood-burning cook stoves or biomass cook stoves. People who use these tools on a daily basis for food preparation are exposed to emissions originated by the inefficient combustion, causing serious adverse health effects that mainly affect women and children. In fact, the damage associated with inhaling smoke from open combustion origins acute respiratory infections, which cause nearly 1.2 million premature deaths annually among children less than 5 years of age (Berrueta et al., 2008) and chronic obstructive lung disease among adults (Norbo, Yahya, Bruce, Heady, & Ball, 1990; Boy, Bruce, Smith, & Hernandez, 2000; WHO, 1997; Pope & Dockery, 2006; Popovitscheva et al., 2000; Oberdörster, 2000).

Although work on improving biofuel stoves has been going on for many years, much of the effort has been directed at optimized biomass combustion and reducing fuel consumption mainly for economic and environmental reasons, rather than at reducing exposure levels within the home for health reasons (Boy et al., 2000; Lighty, Veranth, & Sarofim, 2000). However, efforts by the scientific community in Mexico have been made to promote new cook stoves that improve quality of life on rural communities (Berrueta et al., 2008).

It is clear that products of biomass combustion play significant roles in global atmospheric chemistry and the potential for global warming from an enhanced greenhouse gas effect (Seiler & Crutzen, 1980). Soot is an important product of incomplete combustion and comprised of black carbon (BC) and organic carbon (OC). BC absorbs incoming solar radiation (across the visible spectrum) and the OC primarily in the UV portion of the spectrum (Kuhlbusch et al., 1996; Bond & Bergstrom, 2005).

The vast literature on soot formation has been summarized in various reviews and specialized conferences on the subject (Boy et al., 2000). For example, studies on the main parameters that controls primary combustion particle size, morphology, and composition have been reported by Boy et al. (2000), Lighty et al. (2000), Fang, Leavey, and Biswas (2014), Ishiguro, Takatori, and Akihama (1997), Tumolva et al. (2010), Carabali et al. (2012) and Vander Wal, Bryg, and Hays (2011). Despite the above discussion, only few studies characterizing the direct emissions from wood burning cook stoves have been conducted.

The majority of the studies related to wood burning in cook-stoves, have been focused on measuring emission factors (Bhattacharya, Albina, & Salam 2002; Roden et al., 2006) and climate-relevant properties such as absorption and scattering (Martins et al., 1998). None of the studies have reported a physical characterization of soot emitted by cook stoves.

Carbon is a light element with relatively simple electronic structure. The hybridization bonded in soot can be identified by using the X-ray Photoelectron Spectroscopy (XPS) (Kaculis, 2012; Vander Wal et al., 2011). The carbon electronic spectra contain only two main excitations: photoemission line of C 1s and Auger line, which are often called C KVV (so-called X-ray-induced Auger electron spectroscopy, AES). C KVV peaks can also be used to distinguish between different hybridization states of carbon. Several studies use XPS to analyze environmental particulate matter (PM) collected on filters (Song & Peng, 2009; Hutton & Williams, 2000; Zhu, Olson, & Beebe, 2001). It is important to mention that collected particles can be directly analyzed by XPS without further sample preparation, because it is capable to analyze insulating samples (Hutton & Williams, 2000; Gilham, Spencer, Butterfield, Seah, & Quincey, 2008).

Other important physical and chemical information about of soot particles may be collected by ion beam analysis (IBA). This technique uses high-energy proton beams (energies of few MeV) to excite the sample collected on the filters producing γ-rays or scattered characteristic on analyzed particles. These protons have sufficient energy to pass directly through the filter and be measured with detectors placed in different angles. The energy spectra of the interaction products provide information on the sample's elemental composition and the areal density (atoms/cm²) of the carbon deposit (Ferrer et al., 2014; Gurbich, 2014). Among the numerous IBA methods, proton elastic scattering analysis (PESA) and particle-induced gamma emission (PIGE) are governed by rules of nuclear reactions and appropriate kinematic relations (Schmidt & Wetzig, 2013) and are the most common to study atmospheric aerosols (Cohen, Stelcer, Hawas, & Garton, 2004). Both methods are well suited for studying air pollution because they are quick, non-destructive, require little or no sample preparation, and are capable of investigating microscopic samples.

The main goal of this article is to characterize soot particles emitted by wood burning cook stoves. A microstructure and morphology study of soot was carried out with high-resolution transmission electron microscopy (HRTEM) and HRTEM images of soot aggregates to calculate its perimeter fractal dimension (PFD). The chemical composition on surface and carbon bonding is explored with X-ray photoelectron spectra (XPS) of soot samples deposited directly over aluminum foils. Additionally, soot particles deposited onto quartz (SiO₂) filters were analyzed by backscattering elastic protons at 150° and PIGE using deuterons. In the latter case, the carbon useful γ-radiation comes from nuclear reactions.

2. Methodology

2.1. Cook stoves and wood used as fuel

The soot particles analyzed were directly sampled from the chimney of two wood burning cook stoves. Patsari cook stove CS-1 (Fig. 1a) was developed by the Center for Ecosystems Research (CIECO), Universidad Nacional Autónoma de México.
which is an improved design of an older domestic cook stove (Berrueta et al., 2008; Armendáriz-Arnez et al., 2008). Patsari cook stoves tested here were built using brick and cement, with sealed hotplates and a chimney to avoid smoke leaks into the kitchen. It has a ceramic combustion chamber of 20 cm high and hotplates of 52 cm diameter. Further details and complete description of the brick Patsari cook stove is described by Berrueta et al. (2008). Mera-Mera is the other system used (CS-2) shown in Fig. 1b, it is a rocket cook stove adapted with a chimney resulting from a project conducted by the Mexican government to improve older hotplate cook stoves used for cooking. The CS-2 has a stainless steel chimney with end cap and protective fence, a cast iron plate (griddle) of 56 cm diameter and 2 ceramic combustion chambers with refractory metal lining. There is limited literature about rocket-type cook stoves originally invented by Larry Winiarski; however, further information can be found at Bryden et al. (2005) and Sutar et al. (2015).

The wood used in the cooking process was the native white oak (Quercus resinosa) specie of northern Mexico. This is a deciduous tree belonging to Fagaceae family, which is found in the mixed pine-oak forests in Central and Western Mexico (from Nayarit to Michoacán).

The chemical composition of Mexican oak species has been studied by Bautista-Hernández and Honorato-Salazar (2006). The chemical analysis was done in a mixture of sapwood–heartwood taken from Quercus resinosa specie and used to determine contents of cellulose, pentosans, lignin, ethanol–benzene extract, hot water extract, ash and tannin. Bark tannin content was also determined for each species, as well as pH-value of wood. In general, the cellulose content was 52.94%. The amount of pentosans was 20.24%. Lignin content was 21.78%. Extractive content was 3.05% for ethanol–benzene extract and 7.09% for hot water extract. Ash content was 0.74%. Tannin content was 1.10% for wood, and 6.53% for bark. The pH-value was 3.94 for the stirring method and 3.51 for the hot water method.

2.2. Sampling system

Gases and particulate matter emissions during cooking processes were directly conducted to a compact dilution stack sampler (CDS) with a stainless steel duct of 20 cm diameter width and 110 cm length constructed following Hildemann, Cass, and Markowski (1989) and England et al. (2007) designs. A schematic diagram of CDS is shown in Fig. 1c. It consists of four main sections: sampling inlet, diluting/mixing section, residence (aging) chamber, and sampling section. In the sampling inlet section, the combustion products are withdrawn from the cook stove’s chimney using a sampling probe connected to a nozzle and a cyclone with PM2.5 cut point. The nozzle attached to the cyclone is used for isokinetic sampling of particles in the flux mix. The sample enters into the one-step mixing/dilution section where it is diluted and cooled with a large stream of filtered ambient air (air was filtered by using a high-efficiency particulate air (HEPA) filter with a carbon adsorption canister). The sample’s flow rate was 20–25 L/min and the dilution’s flow rates 300–700 L/min were used (the dilution ratio was in the 15:1–40:1 range).

Soot particles were collected in an 8-stage Micro Orifice Uniform Deposit Impactor (MOUDI, Model 100, MSP Corp.) over 47 mm aluminum foil substrates. Additionally, particles were collected onto 200 Gilder mesh grids from Ted Pella (TEM-grids, LF-200-Cu) coated with a thin film of collodion polymer (Carabali et al., 2012). TEM-grids were fixed on the aluminum foil by using a double-sided adhesive carbon tape and finally were placed in the last MOUDI stage (d_{50}=0.18 μm). The MOUDI inlet flow was calibrated to 30 L/min. Also 30 min sampling times were settled to ensure the formation of a homogeneous carbonaceous thin film onto aluminum foils.
In addition, soot particles from each stove were collected in quartz filter \((20.3 \times 25.4 \text{ cm}^2)\) supplied by Whatman, preheated at 900 °C for 24 h before being used. Sampling was performed with a high-volume sampler (HiVol 3000, Ecotech) operating at 1.13 m³ min⁻¹, which was connected directly to the dilution chamber outlet. The wood burning in both stoves was performed by keeping the same conditions during the combustion process (amount and type of wood). By placing the HiVol sampler, three quartz filters with soot samples (S1, S2 and S3) were obtained. Sample S1 are particles emitted from Patsari stove (CS-1), while S2 and S3 contains particles from Mera-Mera stove (CS-2). All these filters were analyzed with IBA techniques to determine the areal density (atoms/cm²).

2.3. HRTEM and morphological analysis

We obtained the HRTEM micrographs with a JEOL HRTEM 4000EX microscope of 0.17 nm point-to-point resolution, operated at 400 KV. In order to calculate the perimeter fractal dimension (PFD), HRTEM digital images were processed using Scion Image software for image optimization and extraction of particle coordinates \((x, y)\) (Carabali et al., 2012). The program additionally provides the particle’s area and perimeter length in pixels. The particle border-based (perimeter) fractal dimension is then calculated by a FORTRAN code developed by Mamani-Paco and Heble (2007) with the following Eq. (1), which is well described by Kindratenko, Van Espen, Treiger, and Van Grieken (1994).

\[
L(\lambda) = K\lambda^{(1-D_f)}
\]

where \(L\) is the particle perimeter, \(\lambda\) is the particle’s boundary step size (the length by which the perimeter is cut in smaller pieces), \(K\) is a positive constant factor, and \(D_f\) is the fractal dimension (Kindratenko et al., 1994; Kaye, 1994).

2.4. XPS technique

X-ray photoelectron spectroscopy (XPS) used un-monochromatized Al Kα line at 1486.6 eV for analyses of samples. The energy scale was calibrated using thick films of copper and silver, with lines at 932.67 eV for Cu2p3/2 and 368.26 eV for Ag3d5/2. The high-resolution XPS scans were completed at 0.2 eV energy steps and pass energy of 5.16 eV (constant pass energy mode). Then, survey scans were accomplished for every film in the 1400–0 eV energy interval at 1 eV per step. The system is equipped with an electron energy analyzer model Phoibos 150, an electron gun and a dual anode X-ray source from SPECS.

2.5. PESA, NRA and PIGE techniques

The analysis using particle-induced gamma emission (PIGE), nuclear reaction analysis (NRA), proton elastic scattering analysis (PESA) techniques were performed at the Tandem Accelerator Laboratory of the Mexican Institute for Nuclear Research (ININ), which is provided with an EN Model tandem accelerator, HV Eng. Corp. (USA), and its associated beam lines, scattering chambers and equipment for experimental nuclear physics applications and basic research (Policroniades et al., 2014). The sputtering of the samples was carried out in a vacuum chamber shown in Fig. 2. The chamber geometry allows the simultaneous detection of charged particles, gamma radiation and characteristic X-rays generated by exposure of the samples (targets) to the ion beam. To measure γ-rays data, a hyper-pure germanium detector (HPGe) of 13% efficiency was

Fig. 2. Scheme of the vacuum chamber used for the PIGE analysis.
placed 120°. A silicon surface-barrier detector (SSBD’s) of 1000 μm placed to 150° was used to measure charged particles generated after proton and deuteron sputtering.

3. Results

3.1. HRTEM images and morphological analysis

The morphology and microstructure of soot particles emitted by both stoves were studied by HRTEM. The micrographs in Figs. 3 and 4 show soot particulates emitted by Patsari (CS-1) and Mera-Mera (CS-2), respectively. Both figures also show chain-like agglomerated structures of nano-sized primary spherical particles, a typical structure present in soot or carbonaceous material originated in combustion processes (Popovitcheva et al., 2000; Vander Wal et al., 2011). Soot aggregates had clearly irregular shapes and non-uniform sizes; however, agglomerates built up from spheres have sizes ranging from nanometers to micrometers. Comparing shapes of particles emitted by both stoves, it is possible to see some morphological differences at first glance. Particles emitted by CS-1 cook stove tend to aggregate in a more compact shape, while those emitted by CS-2 show chain-like structures. Those differences could be associated to the combustion-chamber design of each cook-stove. CS-1 soot aggregates spend more time in the cook-stove combustion chamber and chimney allowing the collision process, leading to the formation of more compact particles and with different sizes and shapes. The formation of particles with chain structure is due to the size and geometry of CS-2 combustion chamber.

We used perimeter fractal dimension (PFD) to quantify particle morphologies. The fractal dimension parameter ($D_f$) is a dimensionless quantity used to characterize morphologies. A scale of PFD has been constructed by Dye, Rhead, and Trier (2000) to better understand the relationship between $D_f$ and particular shapes. In general as $D_f$ tends toward two, this indicates a more rugged boundary, while $D_f$ values close to 1 indicated particles with round boundary. The $D_f$ parameter of soot particles emitted by CS-1 and CS-2 were calculated for 30 individual particles. Histograms of fractal dimension (Carabali et al., 2012; Mamani-Paco & Heble, 2007) for fresh particles released by both stoves are shown in Fig. 5. Average values of $D_f$ found were $\sim 1.77 \pm 0.04$ and $\sim 1.80 \pm 0.03$ for CS-1 and CS-2, respectively. Values of $D_f$ above 1.8 imply soot particles with complex morphologies are formed by collisions between primary nano-sized particles. As the particle agglomeration takes place, there are collisions between clusters leading to the formation of soot aggregates (Lee et al., 2002).
Fig. 4. HRTEM images of soot particles sampled from Mera-Mera wood burning cook-stove (CS-2).

Fig. 5. Fractal dimension histograms to soot particles aggregates emitted by Patsari (CS-1) and Mera-Mera (CS-2).
Fig. 6. HRTEM images of nano-sized primary soot particles. In order to show the structure of closed shells, the magnification of the microscope is increased through the images a–c. Figures d–f correspond to different magnifications of a nanosized primary particle.

Fig. 7. Survey XPS scan of soot particles emitted by botch wood-burning stoves: CS-1 (top) and CS-2 (bottom).
Although some morphological differences are observed in TEM images (particles in Fig. 3 are more compact that those shown in Fig. 4), the dimension fractal ($D_f$) values have almost no difference. This small difference is because the particles are generated under the same combustion process conditions (amount and type of wood). Other important reason for that little difference is the methodology used to calculate the fractal dimension. In this work a border-based fractal dimension calculation was used, which only analyzes the perimeter of the particles and does not provide further information on internal details of the particle structure. However the values that we reported in this work are in agreement with those ($\sim 1.80$) reported by Lee et al. (2002). Both values are characteristic of soot aggregate particles and suggest that soot emitted from wood-burning process in cook stoves are formed by cluster–cluster aggregation mechanism (Lee et al., 2000).

Morphological features of soot particles emitted by cook stoves have been examined by electron microscopy at high-magnifications, shown in Fig. 6. High-resolution transmission micrographs of nano-sized primary soot particles show the structural arrangement of carbon atoms. Particles exhibit a high degree of disorder composed of curved graphitic lamellae within their internal structure. In Fig. 6a–c a nano-sized primary particle with a structure of completely closed shells is shown, while Fig. 6d–f exhibit a disordered structure consisting of short, disconnected, and randomly oriented graphene segments. All structures in Fig. 6 were observed randomly in soot particles emitted by both cook stoves. The nature of the wood fuel strongly influences the composition and therefore the morphology of the soot particles emitted (Pitman, 2006). The HRTEM images obtained in this study show that the process of burning wood in cook stoves generates soot particles mainly composed of amorphous carbon.

3.2. XPS analysis

XPS experiments were carried out in order to get information on the chemical composition of particles surface. The XPS survey spectra are shown in Fig. 7. The survey scan covers a very broad energy range (0–1400 eV) and each peak over the energy binding scale identifies the elemental composition on the particle surface. The spectra show a predominant graphitic C-1s peak at 284 eV, an O-1s peak at 532 eV, and a small signal of silicon. Other peaks arising from secondary Auger electrons (from oxygen) are labeled in standard KL format. The silicon traces observed in soot particles come from soils, which are trapped in low-levels in the wood bark during harvesting process (Pitman, 2006). Biswas and Wu (1998) describe the transformation pathways (volatilization, chemistry at high-temperatures and aerosol growth dynamic) of inorganic material or metallic species that lead to the inclusion of inorganic material in aerosol particles.

![Fig. 8. C 1s XPS spectra of soot particles emitted by Patsari (CS-1) and Mera-Mera (CS-2) cook-stoves. Peaks in the spectra were fitted with Lorentz functions. The three important features observed were: peak at 284.3 eV of sp² hybridization (C–C bonding), peak located at 285.0 eV to sp³ hybridization (C–O bonding) and a low-intensity peak with at 286.1 eV associated to C–O bonding.](image-url)
One of the major components observed in XPS survey spectra is the oxygen. The C/O ratio measured were 2.0 for CS-1 and 1.5 for CS-2. Those values are in agreement with C/O ratios ranged from 1.1 to 2.1 of biomass burning soot particles measured by high-resolution X-ray techniques. The oxygen content in biomass burning soot can be observed as oxygenated compounds mainly from phenolic and ketone functional groups, and a variety of phenolic compounds, including guaiacols and catechols known to form during the combustion of biomass, mainly from lignin pyrolysis (Hopkins, Tivanski, Marten, & Gilles, 2007; Fine, Cass, & Simoneit, 2001; Rogge, Hildemann, Mazurek, Cass, & Simoneit, 1998).

Figure 8 corresponds to XPS C 1s spectra of soot particles sampled directly from both cook stoves chimneys. Particles with an aerodynamic diameter of 0.18 μm were collected on aluminum foil substrates. To avoid any effects caused by uneven filter coverage during XPS analysis, the sampling time in MOUDI was set to favor the formation of a thin carbon film on the surface of aluminum foils. Because the XPS technique has the advantage of analyzing insulating samples, the thin carbon films were directly analyzed by XPS without further sample preparation (Hutton & Williams, 2000). To identify the center and width of the different peaks in the spectra, a convolution with Lorentz functions was done.

The spectra show three important features: an asymmetry with the highest intensity peak at 284.3 eV that corresponds to sp² hybridization (C=C bonding) (Nuzzo & Jackson, 1995; Mérel, Tabbal, Chaker, Moisa, & Margot, 1998; Kaciulis, 2012; Atzei et al., 2014; Diaz, Paolicelli, Ferrer, & Comin, 1996). The peak located at 285.0 eV that corresponds to sp³ hybridization (C–C bonding) and a broad peak with low intensity at 286.1 eV associated to C–O bonding (Gardner, Singamsetty, Booth, & He, 1995; Ferro, Dal Colle, & De Battisti, 2005; Kaciulis, 2012). This latter peak accounts the low surface concentration of oxygen bonded species present on these samples.

The difference between bonding energies of the sp³ and sp² peaks in both spectra is 0.7 eV, which is lower than values reported of synthesized samples on amorphous carbon (Häerle, Riedo, Pasquarello, & Baldereschi, 2001). According to similar results, many authors (Arezzo, Zacchetti, & Zhu, 1994; Häerle et al., 2001) have affirmed that energy shift between sp² and sp³ carbon atoms are definitively larger than 0.2–0.3 eV. This energy shift may depend on surface effect, although the origin of this discrepancy is unclear.

Since the area of each peak is directly related to the concentration of the corresponding phase, the sp²/sp³ ratio was estimated from its relative intensities (Muller, Su, Wild, & Schlögl, 2007). The sp²/sp³ ratio found to soot particles emitted by both cook stoves are 1.5 and 1.8 for top and bottom spectra, respectively. Hybridization ratios of 1.9 and 3.3 have been measured on soot emitted by diesel engines and industrial furnaces (Müller et al., 2007).

X-ray photoelectron spectroscopy is a suitable technique to study carbon bonds, although it could be difficult to differentiate soot from different sources by analyzing solely the XPS spectra. This occurs due to the small difference in the binding energies position of C 1s peak. However, there are substantial differences in the spectral shape which appeared as a shoulder or additional features observed in the higher and lower binding energy region of the C 1s peak, as shown in Fig. 9. The graphite C 1s XPS spectra reported by Blyth et al. (2000) show intense peaks, without presenting shoulders and other important features, observed in the XPS spectra of soot from wood burning (reported here), and urban soot particles reported by Cheng, Weng, Lau, Chan, and Chan (2013) and Vander Wal et al. (2011).

The acquisition of C KVV spectra and parameter D determinations are other suitable and practical methods used to evaluate carbon hybridization in samples. This method denominated the Lascovich analysis (Rau et al., 2010., Lascovich, Giorgi, & Scaglione, 1991) where the D-value represents the binding energy separation in eV between the most positive

![Graphite and Urban aerosol XPS spectra](image-url)
maximum and the most negative minimum in the first derivative of AES spectra. For carbon species the energy separation indicates whether it is involved in sp$^2$ or sp$^3$ bonding. Carbon with sp$^2$ bonding gives around 20 eV of energy separation meanwhile sp$^3$ bonding yields a narrower energy separation of about 14 eV (Rau et al., 2010). For our samples, D-values were 39.5 and 25.5 eV for CS-1 (Fig. 10a) and CS-2 (Fig. 10b) stoves, respectively. Higher values of $D$ are associated to surface effects and the increasing number of sp$^2$ bond in the film (Rau et al., 2010).

Fig. 10. The first derivative of C KLL AES spectra of soot samples obtained from (a) Patsari (CS-1) and (b) Mera-Mera (CS-2) cook-stoves.

Fig. 11. Proton elastic scattering analysis (PESA) of the blank filter (without sample) and sampled filter (with soot samples).
3.3. Sample's analysis by PESA, NRA and PIGE techniques

In this section is presented the analysis of the soot samples by using Ion Beam Analysis (IBA) techniques. These techniques are multi-elemental, fast, sensitive, nondestructive and providing a distinctive profile (the relative composition of the detected elements) of the sample. In order to determine the elements present in soot particles and estimate the areal density of carbon, the characterization is obtained from a combination of PESA, NRA and PIGE analysis.

Figure 11 shows an elastic proton-scattering energy spectrum of a quartz filter without any deposit (blank-filter), superimposed with an analogous energy spectrum of a sample with soot deposit (sampled-filter). These spectra were taken at 4.2 MeV proton energy and detected with a silicon surface barrier detector sited at 150° in relation to the beam direction and the samples position. As it can be appreciated, the blank filter spectrum does not present any carbon events, whereas the soot sample shows a very intense peak. This spectrum shows that the main elements that compose the soot samples are C, O and Si.

In Fig. 12, PIGE spectra of a soot sample deposited onto a quartz fiber substrate are shown. These spectra were obtained by exposing the sample to deuteron (DIGE) and proton (PIGE) beams with energies of 2.0 and 4.2 MeV, respectively, and by detecting the gamma radiation with a hyper-pure germanium detector (HPGe) fixed just outside the scattering chamber at 120°. The labels shown in DIGE spectrum indicate the emission lines of interest for the analysis, given in keV, which correspond to carbon, oxygen and silicon. The most important emission line for the purposes of this study is the very intense
peak observed at 3088 keV, which is assigned to the (first) $^{13}$C excitation energy. This excitation line is generated by means of the $^{12}$C (d, $p_0$) $^{13}$C reaction, that is the nuclear transition most used in PIGE analysis for carbon determination. This excitation line has a high cross section in a wide energy range, which allows estimating the carbon areal density over a large depth.

As a complement, the exposure of the soot samples to deuteron beams with 2.0 MeV, allows obtaining an isolated $^{12}$C (d, $p_0$) $^{13}$C proton peak which is shown in Fig. 13. This $^{12}$C (d, $p_0$) $^{13}$C peak and the lower energy events due to O and Si were fitted with SIMRA code (Mayer, 1999; Policroniades et al., 2014). The continuous line accompanying the experimental data in Fig. 13, is the simulated spectrum with SIMRA. The area of this carbon peak and the PIGE data were used to assure the thickness of the soot film deposits.

In Table 1, we present the results obtained by these ion beam analysis techniques, where a combination of charged particles and gamma induced emission data are combined to assure the characteristics of the soot targets analyzed. The blank quartz filters (without soot sample), not shown in the table, did not show up any significant quantity of carbon, nor any other measurable contaminant. The difference in the areal density values shown in Table 1 may be due to the amount of particles emitted by each cook-stove analyzed. According to the results, it can be interpreted that CS-1 emitted more soot particles than CS-2 stove.

4. Conclusions

This paper presents a physical and chemical characterization of wood-soot particles emitted by designed cook-burning wood-stoves. The application of compact dilution stack sampler (CDS) offers an opportunity to make a comprehensive study of the chemical composition and microstructure of fine soot particles emitted by stationary sources.

Soot particles emitted by cook stoves were collected by placing TEM grid into a MOUDI stage and analyzed by using high-resolution microscopy and image processing. With this methodology was successfully studied the particles morphology applying the Mandelbrot equation (Kindratenko et al., 1994). Fractal dimension ($D_f$) values found for selected soot particles were 1.77 (Patsari stove) and 1.80 (Mera Mera-stove); these values are similar to $D_f$ values reported for soot generated in other combustion processes (Lee et al., 2000). This result suggests that soot emitted by wood-burning stoves could be formed by cluster–cluster aggregation process. Although the calculation of $D_f$ not show sufficient resolution to differentiate particles emitted from the stoves studied here, this methodology can be a useful tool to characterize the shape of the particles emitted from different sources.

XPS analysis shows that the samples studied exhibit differences in amount of surface functional groups, which is revealed by differences in the O/C rate. XPS spectra of soot emitted by both stoves display a similar bonding behavior, where dominates the sp² hybridization (C=C bonding). The analysis of C 1s line carried out for soot, demonstrated that the BE values for all investigated samples, are practically identical, i.e. they are always located around 284.3 eV.

Through the analysis of simultaneous IBA techniques, namely PIGE and PESA, it was possible to characterize filters with soot particles. IBA methods are particularly well suited to these types of samples with carbonaceous material because they produced accurate measurements of the areal density (atoms/cm²) in a few minutes of machine running. The main characteristic of this method is that γ-rays are not attenuated by the material in which the deuteron beam penetrates. Thus, the measurements are not influenced by surface irregularities. Finally, it was possible to determine the bulk density of carbon by making the correct choice of the deuteron energy. All this was possible using the simulation program (SIMRA) to determine the cross sections of γ-rays from the (d,p) reactions of $^{12}$C. Our intent is to apply this technique in future works to the determination of carbon from other combustion sources.

In this study it was observed that soot from different sources presents structural variations and more research is needed in order to learn more about its structure, bonding and potential health risks. The stoves analyzed in this work, are being distributed in rural of Mexico to improve the quality of life of users who used them. The stove performance should continue to be evaluated from multiple physical parameters (thermal efficiency, size distribution, etc).

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### Table 1

<table>
<thead>
<tr>
<th>Cook-stove</th>
<th>Sample</th>
<th>Charge (μC)</th>
<th>Counts</th>
<th>Thick (μg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS-1</td>
<td>S1</td>
<td>5.80</td>
<td>3749</td>
<td>47.6</td>
</tr>
<tr>
<td>CS-2</td>
<td>S2</td>
<td>4.31</td>
<td>1894</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>3.76</td>
<td>2220</td>
<td>28.5</td>
</tr>
</tbody>
</table>

Main results of the soot film thickness (μg/cm²). Values were obtained by using ion beam analysis techniques on samples S1 (for CS-1), S2 and S3 (for CS-2).
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