

Supplemental Materials for

Household dust: loadings and PM₁₀-bound plasticizers and polycyclic aromatic hydrocarbons

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Analytical technique for quantification of the carbonaceous content of PM₁₀

After gravimetric determination of the PM₁₀ mass, samples were analyzed by a thermo-optical transmission system to obtain the carbonaceous content (organic and elemental content, OC and EC). The thermo-optical system comprises a quartz oven with two distinct heating zones. It also includes a helium-neon laser (632.8 nm) and a detector connected to a transducer. Associated with the laser, there is a chopper whose function is to eliminate interferences that may occur due to the existence of other light sources. To detect the amount of carbon in various stages of heating, the system encompasses a calibrated infrared non-dispersive CO₂ analyzer (LI-COR Environmental, model LI-7000). The temperature program is imposed by a controller. To control the flow of gases (N₂ and O₂) passing through the oven, a mass flow meter is used. A computer terminal makes the data acquisition every second, recording various parameters, such as temperature, flow rate, and CO₂ concentrations. For each filter, two 9 mm diameter punches were used in each analytical run. At least two replicate analytical runs were applied to each filter. To start the analysis, a purge to remove all traces of CO₂ is carried out until zero is read by the non-dispersive infrared analyzer. The data acquisition can be started as soon as the purge is completed. The analysis is done in two stages. In the first phase, the sample is subjected to an anoxic environment with the presence of only nitrogen. Controlled heating in these anoxic conditions is performed to separate OC into two fractions of increasing volatility. The first fraction corresponds to the volatilization at T < 200 °C of lower molecular weight organics. The second fraction is related to the decomposition and oxidation of higher molecular weight species at temperatures ranging from 200 to 600 °C. The last fraction of OC is identified by transmittance and corresponds to pyrolyzed organic carbon (PC) produced in the previous heating steps. The second stage starts by opening a valve that introduces air into the oven. Oxygen will join the existing stream

of nitrogen and will transform the atmosphere of the first heating zone in an oxidizing atmosphere. This factor, coupled with a further increase in temperature, promotes the oxidation and volatilization of EC. The last carbon fraction contains initial EC plus OC that has pyrolyzed during heating under an inert atmosphere. The interference between PC and EC can be controlled by continuous evaluation of the blackening of the filter using a laser beam and a photodetector measuring the filter light transmittance. The split between the PC and EC is assigned when the initial (baseline) value of the filter transmittance is reached. All carbon removed before the split is considered organic, and that removed after the split is considered elemental. The walls of the second heating zone are coated with a catalyst (CuO), which guarantees the conversion of any carbonaceous material to CO₂. Calibration is performed by injecting a known volume of CO₂ standard gas into the sample stream at the beginning and end of each work day to check instrument performance. All integrated peak areas are divided by the calibration peak area and multiplied by an instrument-specific calibration factor to obtain µg carbon per sample punch.

The temperature protocol followed in this study is similar to that of EUSAAR (European Supersites for Atmospheric Aerosol Research). This methodology was previously tested with the NIST (National Institute of Standards and Technology) filter standard and in an intercomparison study with real aerosol samples (Schmid et al., 2001). The results were between those obtained by the NIOSH (National Institute for Occupational Safety and Health) and the IMPROVE (Interagency Monitoring of Protected Visual Environments) protocols, but closer to the latter. The technique was also compared with the EUSAAR II protocol by analyzing samples with distinct characteristics and origins, proving the similarity of results (Almeida, 2009). The accuracy of this method for measuring the total carbon content was regularly ascertained by analyzing a known quantity of potassium hydrogen phthalate applied to blank quartz fiber filters. Relative standard deviations are less than 3%. Precision, measured as a relative standard deviation from replicate analyses of the same samples, fell in the 4–6% range. The uncertainties were estimated from the coefficient of variance for replicate analysis and from the minimum detection limits. Detection limits depend mainly on the variability of filter blanks (adsorption of volatile organic compounds during storage and transport) and the noises of both the laser and the CO₂ analyzer. Based on the variability of blank filter batches, the detection limit of OC (3 times the standard deviation) was found to be of the order of 30–80 ng m⁻³. Evaluation of thermograms shows that masses of carbon lower than 1 µg are difficult to quantify, with the applied methodology, for low filter particle deposits. That corresponds to a detection limit of 30 ng m⁻³ for EC.

Table S1. Standards from Sigma-Aldrich (and product references) used in chromatographic analysis.

Polynuclear Aromatic Hydrocarbons	
Polynuclear Aromatic Hydrocarbons Mix (CRM48905)	Acenaphthene
	Acenaphthylene
	Anthracene
	Benzo[a]anthracene
	Benzo[b]fluoranthene
	Benzo[k]fluoranthene
	Benzo[g,h,i]perylene
	Benzo[a]pyrene
	Chrysene
	Dibenzo[a,h]anthracene
	Fluoranthene
	Fluorene
	Indeno[1,2,3-cd]pyrene
	Naphthalene
Phenanthrene	
Pyrene	
Individual standards	p-Terphenyl (T3203)
	Retene (393959)
	Benzo[e]pyrene (BCR050)
	Perylene (394475)
	Carbazole (442506)
Plasticizers	
EPA 506 Phthalate Esters Mix 1 (48223)	Benzyl butyl phthalate
	Bis(2-ethylhexyl) adipate
	Bis(2-ethylhexyl) phthalate
	Di-n-butyl phthalate
	Diethyl phthalate
	Dimethyl phthalate
Individual phthalates	Di-n-octyl phthalate (31301)
	Diisononyl phthalate (49568)
	Diisodecyl phthalate (80135)

Table S2. Dust loading obtained in the various houses, in both sampling periods, mass percentage of carbonaceous material (TC = OC + EC) and mass fractions of plasticizers and polycyclic aromatic hydrocarbons in PM₁₀.

House	Characteristics	Room	Flooring	µg PM ₁₀ m ⁻²		TC/PM ₁₀ (%)		Σ ₉ Plasticizers (µg g ⁻¹ PM ₁₀)		Σ ₂₀ PAHs (µg g ⁻¹ PM ₁₀)	
				1 st	2 nd	1 st	2 nd	1 st	2 nd	1 st	2 nd
1	Suburban two-story house with well-ventilated kitchen. Two occupants.	Kitchen	Tile	126	67	20	19	3302	1805	3.93	82.2
		Bedroom	Parquet	6032	74	9	45	1947	5094	0.98	116
		Living room	Parquet	670	110	29	21	3949	4580	7.62	2.52
		Living room rug	Cut pile carpet/rug	4742	4932	16	16	574	204	8.82	1.65
		Bedroom rug	Long threads shag rug	59,103	26,695	12	12	1961	1762	14.1	42.9
2	Single story apartment located in the city center. Two occupants.	Kitchen	Tile	107	-	38	-	4901	-	54.4	-
		Bedroom	Parquet	151	63	31	51	17082	1125	47.4	66.7
		Living room	Parquet	86	78	35	48	7712	5663	36.1	59.7
3	Rural two-story house with open fireplace in the living room. Two occupants.	Kitchen	Tile	908	364	11	16	2127	1076	8.24	26.5
		Bedroom	Parquet	3243	737	13	14	2258	58	8.42	5.55
		Living room	Tile	2264	1463	10	12	1805	9410	11.9	2.79
4	Single story apartment with small kitchen open to the living room. One occupant.	Kitchen	Tile	234	271	10	29	5	6662	18.1	59.5
		Bedroom	Tile	181	202	17	18	465	3722	13.7	29.8
		Living room	Tile	152	51	20	28	3330	3168	22.2	12.0

References

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