Carbonaceous contamination on glass exposed to atmospheric pollution in Paris

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Float glass samples were exposed to the atmosphere, sheltered and unsheltered from the rain, in the centre of Paris, and withdrawn after 1, 2, 6 and 12 months. Before and after exposure the following analyses were performed: ASEM, XPS, Carbon Coulometric Titration, Light Microscopy and IRRS; contact angle with water and optical properties. The results show that glass surfaces are subject to a soiling process by submicron atmospheric particles (C-rich soots). Carbon contents increase with time especially for sheltered samples. For unsheltered samples the increase is slower due to a balance between deposition and rain washing; the contact angles measured on these surfaces reveal an increasing water repellency. On the contrary, contact angles are constant on sheltered samples because of the accumulation of inorganic deposits, lowering the contact angle. IRRS analysis shows that the spatial distribution of the organic fraction is strongly heterogeneous. Finally optical measurements show that the glass surface loses transparency with time due to the deposited light absorbing soot particles.

Introduction

The last decades have recorded an increasing use of glass as building material. Indeed, if at the beginning of 20th Century the utilisation was limited, nowadays glass is widely used in private and office buildings, sometimes occupying most of the building surface. This growing utilisation is due to the main properties of glass: transparency and durability. Nevertheless, when exposed to urban polluted atmosphere, glass undergoes a soiling process[1,2], accompanied by a weak leaching. Soiling implies the deposition of atmospheric particles on the glass surface, leading to transparency loss. Atmospheric carbonaceous soots seem to play a very important role in this mechanism[3]. These atmospheric particles emitted by incomplete combustion processes (light oil, gasoline, kerosene, natural gas, biomass...), consist of a graphitic core (referred to as Black Carbon or Elemental Carbon, EC) onto which a thin layer of organic compounds (Organic Carbon, OC) is deposited by condensation or adsorption processes[4]. The total Carbon content (TC) is the sum of EC and OC fractions. The aim of this paper is to determine and quantify the carbonaceous contamination on the surface of a float glass exposed in urban polluted atmosphere.

Materials and Methods

The samples (1.8 x 1.8 x 0.2 cm) of both the "atmosphere" and the "tin bath" side of a float glass were exposed for up to one year at the top of Saint-Eustache Church (45 meters high) in the centre of Paris. According to the exposure protocol of UN-ICP Material[5], sheltered samples were exposed vertically in a box naturally ventilated, while unsheltered

samples were positioned on a rack, inclined of 45° and facing South. Glass samples were withdrawn after 1, 2, 6 and 12 months. The exposure began on August 1st, 2000. The glass chosen for the experiment is a soda-lime float glass produced by Saint Gobain Vitrage (SiO_2 71.7; Na_2O 13.1; CaO 9.6; MgO 4.1; K_2O 0.35; Al_2O_3 0.7; Fe_2O_3 0.1; results in mass percentage).

The samples were analysed before and after exposure by different analytical methods:

- *Analytical Scanning Electron Microscopy* (ASEM) (Jeol JSM 6301-F): particles deposited in a randomly chosen area were characterised by their morphology, size, chemistry and number. The surface percentage covered by deposited particles (%cs) was estimated by an image processing system linked to the SEM;
- *Optical measurements* (VIS Spectrometer, Lamba 9, Perkin-Elmer): total and diffuse light transmittance and reflectance. The percent (direct) transmittance loss (%LT), according to Sharples et al. modified[6], and light absorptance were calculated;
- *X-Ray Photoelectron Spectrometry* (XPS) (XSAM 800 SAC KRATOS): determination of the chemical composition of a thin surface layer (5 nm) including both deposited particles and the underlying glass surface;
- *Carbon Coulometric Titration* (Carbon Analyser, Ströhlein Coulomat 702C): absolute TC content (mass in μg) deposited on the glass surface was quantified. Glass samples were introduced in a furnace linked to the Carbon Analyser. At 1200° C, under oxygen flow, the carbon deposited on the samples was totally oxidised to CO_2, whose amount is proportional to the original carbon content. In addition, on samples exposed 12 months OC and EC were also measured. In this case the samples are divided into two portions, one of which undergoes a thermal pre-treatment at 340° C (for 2 hours, under oxygen) [7].
- *Wettability*: the contact angle with water on the glass surface was determined using a light microscope equipped with a goniometer (model 113 G77, Marcel Auber)[8]. An evaluation of the water repellency allows to estimate the extent of organic contamination.
- *Fourier Transform Infra Red Spectroscopy* (FTIR): provides a qualitative and semi-quantitative evaluation of the organic carbonaceous contamination[9]. The glass surface was analysed by microIRRS under a light microscope (AUTOIMAGE) linked to the IR Spectrophotometer (GXI Perkin-Elmer). Spectra were obtained between 3100 and 2700 cm^{-1}, with a diaphragm of 0.1x0.1 mm^2. The height of C-H bands present in the range 3000 and 2800 cm^{-1} is proportional to organic contamination[9]. Furthermore, the deposit on the glass surface was extracted by solvent and analysed by IR transmittance[8]. After the extraction the contact angle with water was re-measured.

Results and discussion

Nature and quantification of carbonaceous compounds: ASEM observations show that carbonaceous soots are the prevailing particle category deposited onto the glass surface (90-99 % in number for unsheltered and 77-97 % for sheltered samples). Other C-containing particles, e.g. carbonates or biogenic particles, are negligible. Furthermore, salts, essentially sulphates, are abundant on sheltered samples. Sulphates and Nitrates were also detected by XPS. *%cs* occupied by fine particles (Φ<1μm) increases with time for both sheltered and unsheltered glass. In the same way, the carbon content measured by XPS increases with time more rapidly for sheltered than for unsheltered surfaces. Carbon is the major constituent of the deposit on the glass surface. Even though carbonaceous particles are the most abundant deposit in number, their mass corresponds to about 10% of the total mass deposited (evaluation for 12 months exposure). The absolute quantification of TC performed by

Coulometric Titration (figure 1a) agrees with XPS and ASEM: at 1 and 2 months exposure carbon contents are similar for sheltered and unsheltered samples. After two months the TC increases more rapidily for sheltered samples.
For sheltered samples a more or less steady particle accumulation takes place. The slope increase observed between 6 and 12 months can be attributed to the influence of the particles already deposited. For unsheltered glass the carbon gain rates are moderate in the first two months and just perceptible between 2 and 12 months, due to the competing mechanisms of accumulation and rain removal. Figure 1a shows that the "Sn bath side" exposed sheltered from the rain is more contaminated than the "atmosphere side", as confirmed below by contact angle measurements. The TC contents are in good agreement with the percentage of surface covered by fine particles (Figure 1b). This result confirms that submicronic particles (soots) are the majority of the C-rich deposit.

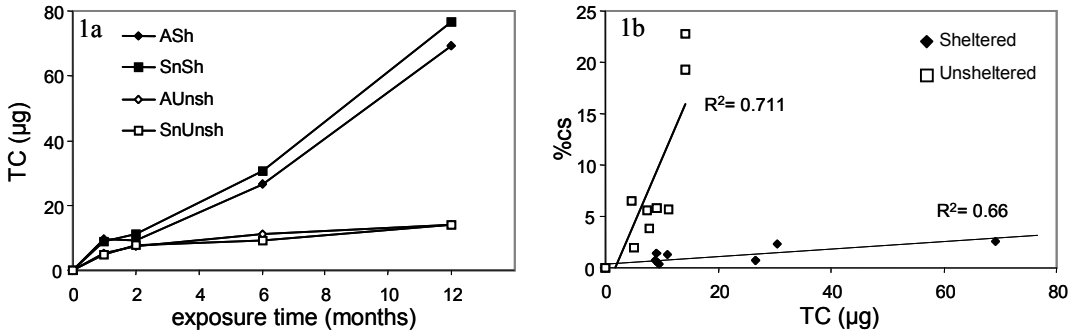

Figure 1: TC (µg deposited on one glass sample) vs exposure time (1a) and %cs vs TC (1b); (A: atmosphere side, Sn: Tin bath side, Sh: Sheltered, Unsh: Unsheltered)

Organic Compounds: due to the quite similar values of bond energies (384,5 eV for graphite and 384,6 eV for C-H groups) it is not possible to evaluate the organic fraction by XPS. This separation was possible by Carbon Coulometric Titration. On glass samples exposed for 1 year OC and EC were quantified separately. OC represents about 50-60% of TC, without any significant differences between sheltered and unsheltered samples. This result is in good agreement with atmospheric measurements of TC, OC and EC made in the Paris area in 1997[10]. The contact angles with water (table 1) show a marked difference between sheltered and unsheltered samples. In fact for unsheltered samples contact angle measurements reveal an increasing organic contamination on the "Sn side". In spite of a more pronounced TC increase, there is no contact angle evolution for sheltered glass: this behaviour is probably due to the presence of inorganic particles (salts observed by ASEM, XPS and IRRS), which lower the contact angle and compensate the tendency of organic deposits to increase the water repellency of the glass surface. It is also important to remark that the contact angle values of unexposed surfaces were higher than expected for freshly produced and thoroughly cleaned float glass[8].
A given degree of residual pre-contamination before exposure is not excluded. Observations of the glass surface made by light microscopy linked to micro-IRRS confirm that the sheltered samples are more contaminated than unsheltered ones. Moreover, it was shown that the spatial distribution of the organic deposits is strongly heterogeneous. In fact when the surface is analysed by IRRS a significant signal (C-H bands at 2920-2850 cm^{-1}) is recorded only near particles, between particles the signal is below the detection limit[9]. An

attempt to identify the nature of the organic contamination was performed by solvent extraction followed by identification with *FTIR*. Due to the complex nature of the deposits it was only possible to identify the main class of compounds: saturated hydrocarbons, also containing ester groups. The ester/hydrocarbon ratio varied between 0.2-0.3 (after 6 months) and 0.7-1.4 for the 12 months samples. The efficiency of extraction was less than 100% [8]. The glass surfaces retained a given fraction of their organic coverage, for this reason the contact angles measured after solvent extraction were always above 10°. It is reasonable to think that if organic contaminants resist to solvent extraction they are also resistant to rain washing in unsheltered position. It is also quite probable that particles stick on the surface due to some chemical interaction with the glass structure[11]. The interaction of organic materials with the surfaces of float glass was recently discussed by Hayashi et al.[12].

exposure time	A Sh		Sn Sh		A Unsh		Sn Unsh	
	before	after	before	after	before	after	before	after
month 0	25-35		20-30		25-35		20-30	
month 1	20-25		20-30		20-30		30-40	
month 2	20-30		20-30		25-30		30-40	
month 6	20-30	10-20	20-30	10-20	30-40	20-30	40-50	20-30
month 12	20-30	20-30	20-30	20-30	30-40	20-35	40-50	30-40

Table 1: Contact angle with water measured on the glass surface before and after solvent extraction (for symbols see the caption of figure 1)

Optical properties: %LT (responding to light scattering caused by surface particles) increases with time for both sheltered and unsheltered surfaces. The absolute values (7.5% maximum) are consistent with literature data. %LT shows a good correlation with TC (Figure 2a).

A good correlation with TC is also recorded for the light absorptance (figure 2b). This is reasonable since the soot particles are the main agent responsible for light absorption on the glass surface. The higher slope observed for unsheltered samples (with smaller TC contents) is puzzling. Possibly for sheltered samples the effective absorption is attenuated by the light scattering effects of salts. Similar results were obtained when studying light absorption by airborne particles in urban polluted atmospheres[13].

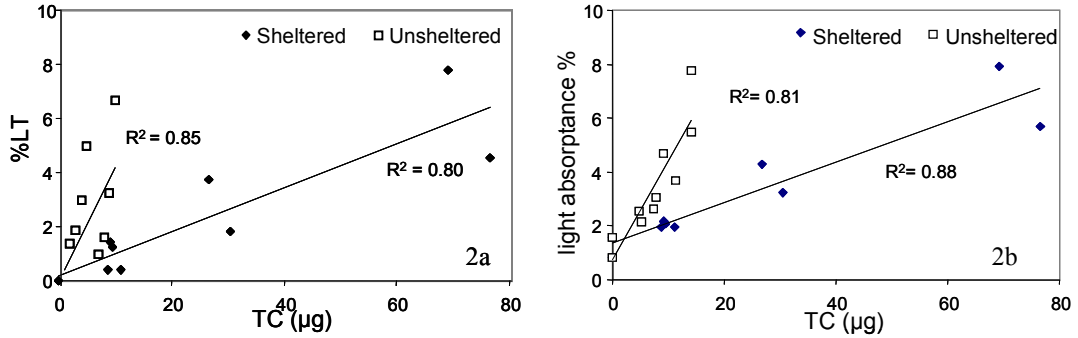

Figure 2: %LT vs TC (a) and light absorptance vs TC (µg deposited on each glass sample) (b)

Conclusion

While the weathering processes are moderate (the leached layer measured by TOF-SIMS has a depth of up to 50 nm, results not reported here) soiling is non negligible, especially for glass placed in urban polluted environment. Accumulation of particles leads principally to transparency loss, that is to say soiling impairs the glass characteristics.
Carbonaceous atmospheric compounds (OC and BC) are the main agents of this process. The analysis shows that the carbon contamination increases with time for all samples. With regard to the exposure mode, sheltered samples are more contaminated that unsheltered ones. Rain washing removes salts and some soot particles, while hydrocarbons compounds firmly adhere and continue to accumulate on the glass surface. Concerning the different float sides, the "Sn side" shows a stronger tendency to fix organic carbon than the "atmosphere side"[14]. To know the extent and nature of deposits is crucial to successfully perform glass cleaning and to develop new products, e.g. self-cleaning glass.

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