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Use of FTIR spectroscopy coupled with ATR for the determination of atmospheric compounds

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Abstract

Attenuated total reflection Fourier transformed infrared spectroscopy (ATR–FTIR) can be successfully used for the quantitative determination of small amounts of pollutants like the organic fraction of aerosols. The relation between sample concentration and reflectance is described by the Kubelka–Munk equation and was found to be linearly proportional to the absorption band of some functional group. Several parameters like the matter of solid matrix, the cleaning of the sampling support, the treatment of reflectance spectra and the base line correction considerably influenced the reflectance spectra and facilitated data interpretations. The feasibility of the ATR–FTIR was evaluated by the monitoring of specific organic *group* bands on filters collected in the French cities of Grenoble and Clermont-Ferrand. We have obtained for hydroxyl group a calibration curve by plotting the relative intensity of reflectance versus the concentration. The linearity was obtained for OH from 1×10^{-1} to 1×10^{0} mol L^{-1} with $r^2 = 0.9959$. We can consider that for a direct measurement of the intensity of reflectance, it is possible to perform quantitative ATR–FTIR organic group analysis.

Keywords: ATR–FTIR; Spectrometry; Organic aerosol; Organic analysis

1. Introduction

Fine particulates have become one of the biggest concerns causing pollution in world cities; the study of their composition is a powerful tool to evaluate the effects on health and identify the pollution sources. Particulate matter (PM) is the term used for a mixture of solid particles and liquid droplets found in the air; PM2.5 refers to particulate matter that is 2.5 μm or smaller in size. However, PM2.5–10 refers to particulate matter having a diameter between 2.5 and 10 μm. The sources of PM2.5 include fuel combustion from automobiles, power plants, wood burning, industrial processes, and diesel-powered vehicles such as buses and trucks. These fine particles are also formed in the atmosphere when gases such as sulfur dioxide, nitrogen oxides, and volatile organic compounds (all of which are also products of fuel combustion) are transformed in the air by chemical reactions. Fine particles are of concern because they are risks to both human health and the environment [1]. These fine particles also have a great affinity for water, thus contributing to acid rain. Acid rain affects all things biological or man made and thus affects the environment. It causes acidification of lakes and streams, damages trees at high elevations, and accelerates the decay of buildings. This problematic cycle has prompted the scientific community to take an initiative to monitor and address the issue of fine particles in the atmosphere [1].

Several analytical techniques are used to measure aerosols. We are enumerating two kinds of analyses: (1) The ex situ analysis known by bulk particle analysis (BPA) enclosing *gas*, liquid, ion and paper chromatography, atomic emission spectroscopy, thermal desorption mass spectrometry; and the

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single particle analysis (SPA) including laser microprobe mass spectrometry, particle-induced X-ray emission (PIXE), X-ray photoelectron spectroscopy and electron microscope techniques. (2) The in situ analysis known by light scattering detection (extinction), differential mobility analyzer (DMA), flame photometric detector (FPD) and semi-continuous ion-chromatographic analysis [2–5].

Since several years, Fourier transformed infrared spectroscopy (FTIR) has become one of the major analytical techniques used for the study of surfaces. It represents an attractive option for quality screening because it is rapid, inexpensive, and non-invasive. Mid-infrared (MIR) spectroscopy, in particular, rapidly provides information on a very large number of analytes, and the absorption bands are sensitive to the physical and chemical states of individual constituents. The high spectral signal-to-noise ratio obtained from modern instrumental analysis allows the detection of constituents present in very low concentrations as well as subtle compositional differences between and among multi constituent specimens. FTIR can be thought of as a molecular “fingerprinting” method. An infrared spectrum contains features arising from vibrations of molecular bonds, and the mid-infrared region (400–4000 cm^{-1}) in particular is highly sensitive to the precise chemical composition of a sample. FTIR can be coupled with accessories like attenuated total reflectance (ATR) allowing the analysis of a wide range of solid or liquid components.

ATR is an analysis technique based on total internal reflection. When a propagating electro-magnetic wave encounters a boundary at which the index of refraction is different from that of the propagating medium, part of that wave may be transmitted and part reflected. This interaction is described by Fresnel equations [6], and the result is a function of the refractive indices of the two materials and the angle of incidence. If the secondary material has a refractive index lower than the initial medium, and the angle of incidence of the wave is greater than the critical angle for the two materials, all the incident energy will be reflected from the interface and will propagate back into the initial medium. This is known as total internal reflection. By controlling the parameters such as crystal material (index of refraction) and angle of incidence, an infrared beam can be directed into a crystal, reflected a controlled number of times within the crystal and redirected out of the crystal and to a detector. What makes this a useful phenomenon for spectroscopic sampling is that at every reflection point in the crystal, a small standing wave known as an evanescent wave is present, extending just outside of the crystal material and into the adjacent medium. If this adjacent medium absorbs infrared energy, the absorbed energy will be missing from the energy that reaches the detector. That is, the adjacent medium produces an absorption spectrum. The absorption that is measured in the final infrared signal is determined by the number of interactions with the sample and the depth of penetration into the sample. The number of reflections is a function of overall optical design. The penetration depth is a function of the angle of incidence and refractive index. The penetration depth multiplied by the number of reflections gives the path length of the infrared beam through the sample. It is given by the equation $d=\lambda/2\pi n_1(\sin^2\theta-n_{21}^2)^{1/2}$, where λ is the wavelength of the electro-magnetic radiation, n_1 the refractive index of the crystal material, n_{21} the ratio of the sample’s refractive index to that of the crystal, and θ the angle of incidence at the sample/crystal interface (Fig. 1). For a given wavelength, sample and ATR crystal the remaining variable within the accessory itself is θ. It should be noted that for a focused infrared beam, the incidence angle for an accessory is an average angle of incidence (the beam is not collimated), and for some crystal designs, the depth of penetration is wavelength-dependent.

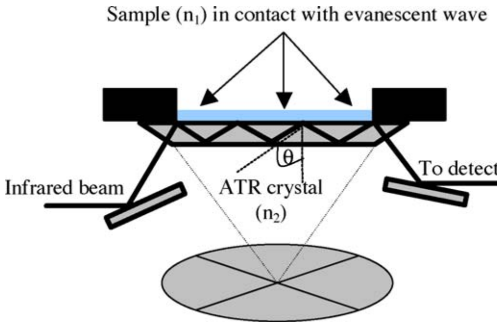

Fig. 1. A multireflexion horizontal ATR system. n_1 and n_2 are the refractive indices of the crystal and the sample, respectively.

Reflectance spectroscopy has been used in a very wide range of applications. Diffuse reflectance in the visible region of the spectrum has been reported by Ghauch et al. [6,7] to quantify cations and metals in water. ATR–FTIR has been shown to be useful for a range of identification and quantification problems in several sectors. (i) Food chemistry: Sedman et al. [8] have determined IV and *trans* content of fats and oils by FTIR employing an ATR accessory. Paradkar and Irudayaraj [9] have obtained a rapid estimation of caffeine content in tea, coffee and soft drinks. (ii) Medicine: Farinas et al. [10] and Hartman et al. [11] have used ATR–FTIR for quantifying drug adsorption and controlled-release delivery systems of therapeutic agents. (iii) Biology: Nadtochenco et al. [12] have studied the *Escherichia coli* photokilling due to TiO_2 under light irradiation in a batch reactor by using of ATR–FTIR. (iv) Material sciences: Darensbourg et al. [13] have reported the integration of the ATR–FTIR technique as a tool of kinetic studies and catalyst design and its successful application to the chromium salen catalyst system for epoxide/CO_2 coupling. (v) Environment: Acha et al. [14] have developed an ATR–FTIR sensor for continuous on-line monitoring of chlorinated aliphatic hydrocarbons in a fixed bed bioreactor. Childers et al. [15] used an open-path Fourier transform infrared (OP/FTIR) spectrometry to measure the concentrations of ammonia, methane, and other atmospheric gases around an integrated industrial swine production facility in eastern North Carolina. FTIR spectrometry has been used successfully to monitor hazardous air pollutants, greenhouse gases, and other emission products at large-area sources, such as coal mines [16], agricultural facilities [17], and industrial sites [18]. Independent studies have shown that the concentrations of target gases reported by Open Path/FTIR methods are comparable to those values determined by more conventional point monitoring methods [19,20]. Shaka' and Saliba [21] investigated the use of ATR–FTIR spectroscopy for the identification of atmosphere particulate matter collected on polytetrafluoroethylene (PTFE) filters. Their work was focused, on the one hand, on inorganic species like sulphate, nitrate, carbonate and silicate and, on the other hand, on organic species like carbonyls, aliphatic carbons, alcohols and water. In the two cases, no quantification was carried out. The authors have only mentioned the presence of some organic species and compared the concentration of PM10–2.5 and PM2.5 with those measured in western Mediterranean cities. The authors found a concentration of PM close to that found in the eastern but higher than that found in the western Mediterranean cities.

The purpose of this paper is to investigate the use of Fourier transformed infrared spectroscopy coupled with an attenuated total reflectance accessory to quantify the organic aerosol part on PTFE filters and to monitor the evolution of organic groups. A sampling methodology, including the choice of filtering media, the flow rate and the time of sampling for best ATR–FTIR analysis, was reported. Qualitative and quantitative characterization of the main functional groups, e.g. phenyl, carbonyl, hydroxyl and alkyl bands present in the aerosol is feasible in addition to a temporal evolution of the ATR–FTIR spectrum.

2. Experimental

2.1. Instrumentation

All spectra were collected on a Perkin-Elmer *spectrum one* (Shelton, USA) FTIR spectrometer operating in the infrared (350–7800 cm^{-1}) region. The instrument was fitted with a sealed and desiccated interferometer with a deuterated triglycine sulfate (DTGS) detector and a He–Ne laser. The FTIR apparatus was equipped with an ATR accessory, comprising transfer optics within the chamber through which the infrared radiation was directed to a detachable ATR crystal. The diamond crystal was a parallel sided plate typically 5 cm × 1 cm with the upper surface exposed. The number of reflections at each surface of the crystal was usually between 5 and 10 depending on the length and thickness of the crystal and the angle of incidence. The crystal geometry was a 45° parallelogram with mirrored angled faces with nominal 10 internal reflections. The depth of penetration that gave a measure of the intensity of the resulting spectrum was extended between 0.5 and 5 μm. All spectral measurements were made at 4 cm^{-1} resolution. The background spectrum was recorded using the atmospheric vapor correction (AVC). This features an advanced filtration system designed to eliminate CO_2 and H_2O vapor in real-time. AVC eliminates errors, allowing us to achieve accurate results in less time. In addition, all recorded spectra are subjected to the absolute virtual instrument (AVI) that allows the same standardization used on individual measurements to be applied to measurements collected over time. AVI's internal, traceable protocol allows data to be transferred quickly and accurately between instruments. In addition, the ATR module allows the possibility to control on-screen the force applied to a filter, ensuring sampling reproducibility. In our case, the force was fixed to 100 N. Single-beam ATR spectra were collected from each sample and transformed to absorbance units using a background spectrum of blank filter. The surface of the solid matrix irradiated by the IR beam was about 1 mm in diameter (Fig. 2). The ATR crystal was carefully cleaned between analyses with water and dried with nitrogen gas. The cleaned crystal was checked spectrally to ensure that no residue from the previous sample was retained on the crystal surface. Four scans were realized for each sample during all experiments.

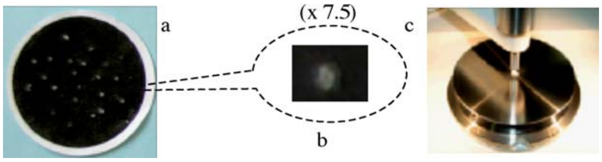

Fig. 2. (a) Picture of the PTFE filter (48 h of sampling at 1.25 m^3/h) showing the homogeneity of aerosols distribution. The white spots correspond to the surface of the solid matrix directly irradiated by the IR beam for several analyses. (b) Picture representing one of the real diameter irradiated by the IR beam ($d = 1$ mm). (c) The plate (sample holder) and the corresponding arm of the ATR module.

2.2. Reagents

All the chemicals were of analytical-reagent grade and used without further purification. Methanol, tetra chloromethane, methyl acetate, propanol, acetic acid and toluene were purchased from Across (Belgium). Nucleopore (0.22 μm pore size, cellulose acetate membrane), quartz and PTFE (0.45 μm pore size), filters (25 mm in diameter) were acquired from Arelco (France). Deionised water was used throughout all experiments.

2.3. Procedure

The sampling equipment used for the collection of particulate matter consisted of an air-sampling pump, model DOA-p101-BN, and a Gas meter, FLONIDAN Gallus 2000 G1.6. The filters were connected within their filter holder (placed 2 m above the ground) to the Gallus counter via 1.5 m, i.d. 0.46 cm PTFE tubing. They have been washed in a class 10,000 clean room for three times with ultra pure methanol, desiccated under a class 100 laminar flow hoods and stocked in Petri dishes at −20 °C in a refrigerator until their use at the sampling site. This treatment is required in order to avoid artifacts depositing on the surface of blank filters. The sampling was done over 4, 12, 16, 24, 48 or 100 h period with a total flow rate of 20.83 L min^{-1} (1.25 m^3 h^{-1}). We have chosen these durations for sampling to perform some tests that allow us to define the sensibility of the ATR–FTIR technique. The sampling time for quantitative analysis was hold up for 12 h. This duration is found to be enough for this kind of sampling and sufficient to have a good resolution of bands that correspond to organic species.

3. Results and discussion

3.1. Filter material

After the above-cited preparations, preliminary studies have been engaged to choose the best filter materials that can be used in this work. Parameters like pore size and thickness of the filters have not been studied to know if some influence on the aerosol collection will be observed. The work was focused on the aerosols collected on the surface of the filters. The diameter of aerosols is certainly higher than 0.5 μm due to the diameter of filtering media which is about 0.22 μm for nucleopore filters and 0.45 μm for PTFE filters. Results have revealed that PTFE is more adapted to ATR–FTIR analyses than Nucleopore and quartz. The blank Nucleopore filter presents absorption bands higher than the sampled one. This phenomenon is mainly due to the acetate absorption band of the nucleopore filter. Aerosols collected on the filter masked the nucleopore material filter and generally resulted in the decreasing of the signal after 4 h of sampling (see Fig. 3(A)). However, insignificant difference of signal was shown between blank filter and sampled quartz filter (Fig. 3(B)) in the 3900–1400 cm^{-1} region of the spectrum which represents the band with the most absorbency of organic aerosols. On the other hand, Fig. 3(C) shows vibrational frequencies of organic groups for the sampled PTFE filter. The obtained spectrum matched with the blank spectrum only around absorbance band of the carbon–fluor (C–F) bond of PTFE. This region of the spectrum is less important than the region situated between 3900 and 1400 cm^{-1}. If the ATR spectra of the sampled filters have shown difference with different filters, this may be due to differences of the deposited layers on different filters, i.e. the filters have somehow collected samples little different from the aerosol.

One can notice the presence of hydroxyl group around 3400 cm^{-1}, carbonyls in the region of 1700–1745 cm^{-1} and alkyls close to 2860–2930 cm^{-1}. This result has encouraged us to carry out all the following experiments on PTFE filters. ATR was shown to be better than FTIR transmission for this kind of analysis. A test has been carried out on a PTFE filter sampled during 48 h. The spectrum obtained with the same filter by ATR analysis was clear, sensitive and more easy to discuss than the spectrum acquired with transmission analysis. As a result, the relative intensities for ATR and transmission spectra for the same sample were different; however, the absorption frequencies remain unchanged (see Fig. 4). All the assigned organic bands and their references are listed in Table 1. Specific organic molecules are difficult to confirm, but organic functional groups were assigned.

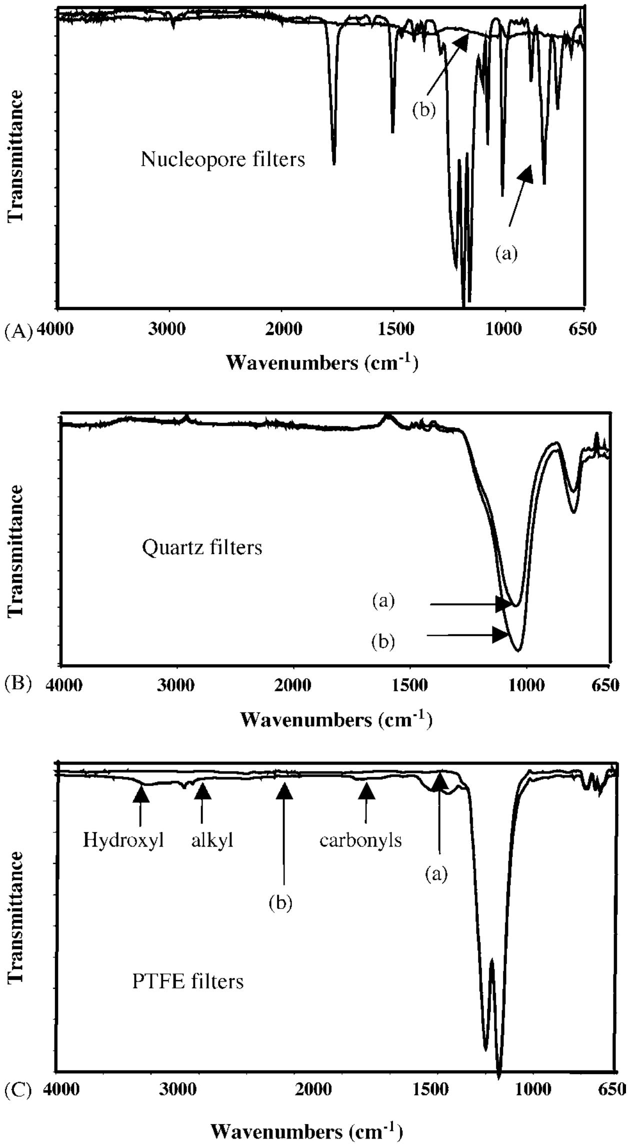

Fig. 3. ATR spectra of blank and sampled filters done over a 4-h period with a total flow rate of 20.83 L min^{-1} in Grenoble city: (A) nucleopore filters; (B) quartz filters and (C) PTFE filters. The sampled PTFE filter represents (from left to right) hydroxyl O—H (3325 cm^{-1}), C—H (2921 cm^{-1}), C—H (2851 cm^{-1}) and C═O (1722 cm^{-1}): (a) blank filters; (b) sampled filters.

3.2. Analytical curves characteristic and data treatment

3.2.1. Absorption frequencies

As it can be seen in Table 2, the lower the wave numbers are, the higher the standard deviation is. The two strong peaks observed between 1250 and 1100 cm^{-1} are due to the carbon–fluor bonds. The difference in absorbance intensities between the spectra of different blank filters especially in this region of the spectrum is probably due to the artefacts present on the surface of the PTFE filter. Indeed, the procedure of

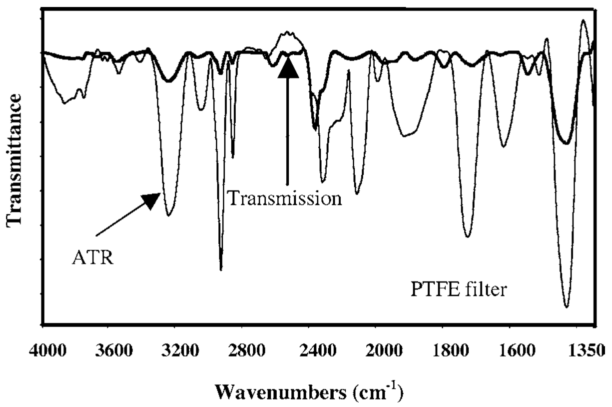

Fig. 4. FTIR spectra of aerosols collected on PTFE filter after 48 h of sampling at 20.83 L min^{-1} (urban area at Grenoble city). ATR spectrum presents more intense bands than transmission spectrum recorded through the filter. The absorption frequencies of the spectra have not shifted.

Table 1
Absorption frequencies and vibrational mode of observed organic species on PM[a] PTFE filters [15]

Species	Wavenumbers (cm^{-1})	Vibrational mode[b,c]
Alcohols	3200–3600	ν(O–H)
Water	3400	ν(O–H)
	1620	δ(H–O–H)
Carbonyls	1745, 1700	ν(C=O)
Aliphatic carbons	2925, 2855	ν_3, ν_1

[a] Particulate matter.

[b] Symmetric stretching (ν_1), asymmetric stretching (ν_2) and bending (ν_3).

[c] Deformation (δ).

cleaning the filters may be responsible for this phenomenon. However, our study is focused on the 4000–1400 cm^{-1} region and should not be troubled by this occurrence as we can observe in Table 2.

Table 2
Reproducibility of ATR-absorption frequencies of blank PTFE filters[a]

High (cm^{-1})[b]	S.D.%[d]	Low (cm^{-1})[c]	S.D.%
4000	0.13	1250	0.240
3750	0.08	1200	0.570
3500	0.04	1150	4.36
3250	0.007	1100	4.98
3000	0.02	1050	1.55
2750	0.02	1000	0.31
2500	0.007	950	0.13
2250	0.007	900	0.10
2000	0.04	850	0.14
1750	0.10	800	0.19
1500	0.12	750	0.30
1300	0.24	700	0.52
R.S.D.%[e]	0.05	R.S.D.%	1.25

[a] The data were obtained by using treated PTFE filter as solid substrate previously soaked and washed three times with ultra pure methanol in a clean room and desiccated before analyses.

[b] The region of the spectrum situated between 4000 and 1300 cm^{-1}.

[c] The region of the spectrum situated between 1250 and 700 cm^{-1}.

[d] Standard deviation ($n = 7$).

[e] Relative standard deviation.

3.2.2. *Analytical protocol and optimization process*

In order to have a good spectral acquisition and to locate organic absorption bands, we have defined a protocol that we have used throughout this work. This protocol consists of three tasks included in the software of the Perkin-Elmer FTIR apparatus so as to optimize the analytical signal and to detect information hidden in the signal. First, the baseline correction that minimizes the interferences between the IR beam and the sample. Second, the spectra smoothing tool used to eliminate the noise related to instrument environmental conditions. Third, the standardization device restoring the baseline of the spectra to an original common baseline and enhancing the absorption bands by increasing their intensity.

3.2.3. *Temporal evolution of organic groups*

After the above-cited protocol, we have carried out four consecutive samplings for a duration of 6 h. Each spectrum (Fig. 5.1) is a result of three analyzed spots on the filter making sure the homogeneity of the aerosols distribution on the surface of the PTFE filter. As we can see, the ATR–FTIR technique is able to monitor the evolution of some characteristic bands of the organic aerosols. In addition, tests are carried out to observe if the intensity of absorption grows with the increase in sampling duration. Results for 16, 48 and 100 h of sampling (not presented here) have revealed that the whole of the aerosol was analyzed on a measured surface and not a simple surface layer due to the deep penetration of the incident IR beam. Fig. 5.2 shows histograms of the temporal evolution of the target organic groups during the day on 27 March 2003. The intensity of hydroxyl group presents a decline until 18:00 h followed by a little increase in intensity around 24:00 h. This phenomenon was observed for phenyl and alkyl groups. However, the intensity of alkyl band between 12:00 h and 18:00 h has decreased more quickly than phenyl. It can be explained by the dominant photo oxidation of alkyls under sunlight irradiation during afternoon. On the other hand, an accumulation of phenyl and alkyl compounds rises after 18:00 h due to the absence of sunlight irradiation. The evolution of carbonyl compounds (C=O) is less significant. However, one can notice that their intensity is higher than hydroxyl, phenyl and alkyl compounds.

3.2.4. *First test for semi-quantitative measurements*

In order to explore the possibility to quantify the organic matter in the aerosol fraction, we performed the spot tests of pure organic solvent on the surface of the PTFE filter. ATR–FTIR spectra have shown absorbencies similar than those made from liquid solutions through a transmission cell especially for characteristic vibrational bands (Fig. 6). This result was expected because insignificant bathochromic and hypsochromic shifts were noticed when FTIR analyses were made of on PTFE. The chemicals used were propane-2-ol (OH), acetone (C=O), toluene (phenyl ring), methyl acetate (C=O and C–O–R) and acetic acid (C=O and C–O–H).

Meanwhile, tests were carried out to evaluate the reproducibility of measurements on three filters having the same

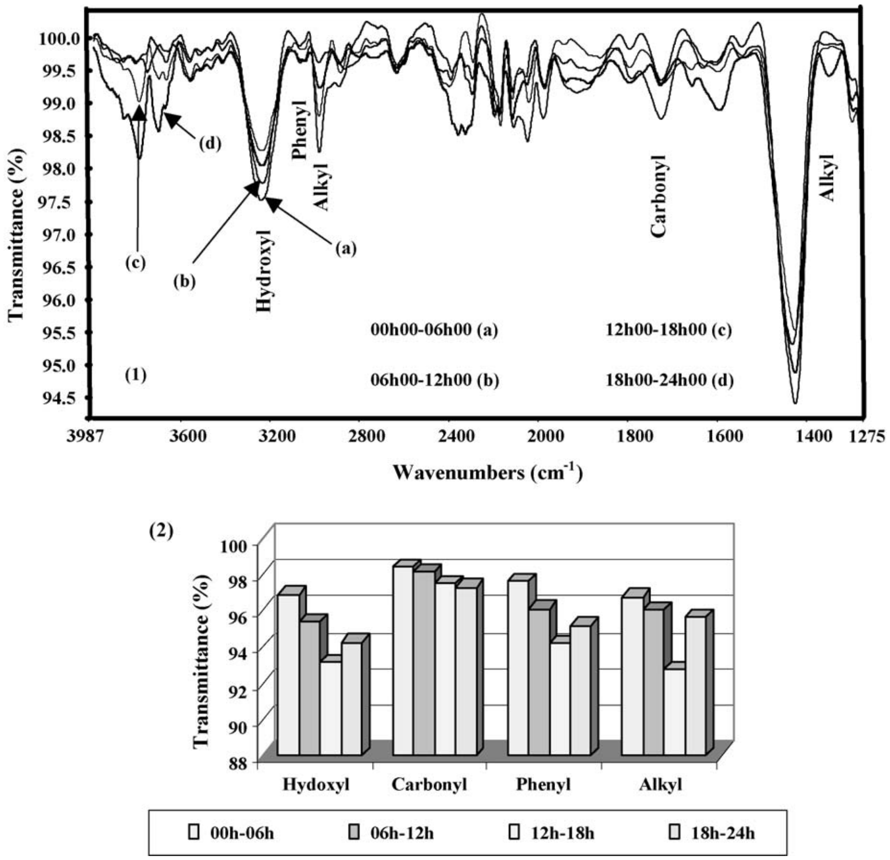

Fig. 5. (1) Optimized ATR spectra of aerosols (urban area of Clermont-Ferrand city) collected on Teflon filters over a 6-h period with a total flow rate of 20.83 L min^{-1} showing the evolution of different absorbance bands of organic functions: (a) spectrum of a filter sampled from 00:00 to 06:00 h; (b) spectrum of a filter sampled from 06:00 to 12:00 h; (c) spectrum of a filter sampled from 12:00 to 18:00 h; (d) spectrum of a filter sampled from 18:00 to 24:00 h. (2) Comparison of organic ATR–FTIR bands as function of time on 27 March 2003 in Clermont-Ferrand urban sector. Histograms represent the height of hydroxyl bands (3108–3360 cm^{-1}), phenyl bands (2984–3108 cm^{-1}), alkyl bands (2784–2984 cm^{-1}) and carbonyl bands (1664–1784 cm^{-1}).

sampling duration (2 h) and on a fourth filter having a total of 6 h sampling duration. These measurements were carried out for hydroxyl peaks at 3400 cm^{-1}. Six analyses have been made of on each filter. Results obtained have shown a very good reproducibility with a relative standard deviation less than 6%. However, a relative error about 1.44% can be noticed between the ATR intensities of hydroxyl peak corresponding to the fourth filter and the three filters cumulated (Table 3).

Table 3
Reproducibility of ATR–FTIR measurements of hydroxyl band on PTFE filters

PTFE filters (no.)	Time of sampling (h)	ATR intensity[b] ($\times 10^{-2}$) (a.u.)	R.S.D.%[c]
1	2	3.17	5.85
2	2	5.02	6.15
3	2	4.77	4.28
4	6	13.15	3.20
1 + 2 + 3[a]	6	12.96	–

[a] Sum of the three hydroxyl intensity bands showing the concordance of this value with that obtained for a sampling of 6 h (relative error = 1.44%).

[b] Values are determined by measuring the height of each hydroxyl band at the wave number 3400 cm^{-1}.

[c] Relative standard deviation ($n = 6$).

These results encouraged us to consider that quantitative analysis can be done with a simple procedure directly *of* the surface of the PTFE filter and without any treatment.

3.2.5. *Hydroxyl group calibration curve*

The quantification of hydroxyl group requests the preparation of standards. A stock propane 2-ol solution was diluted with acetone several times in order to create a calibration curve (1×10^{-1}, 2×10^{-1}, 2.5×10^{-1}, 5×10^{-1}, 10×10^{-1} mol L^{-1}). We have used acetone because its absorbance band (1745, 1700 cm^{-1}) will not interfere with OH band situated at 3200–3600 cm^{-1}. A blank PTFE Filter was also used in the same conditions in order to subtract its signal *from* all standards. These two organics have different polarities which minimize bathochromic and hypsochromic spectral effects. The Perkin-Elmer software made automatically the correction of the baseline in the studied interval and plotted the concentration of OH group (mol L^{-1}) versus calculated height of each peak. The calibration curve obtained (Fig. 7) presents a linear dynamic range from 1×10^{-1} to 10×10^{-1} mol L^{-1} and a correlation coefficient about 0.9959.

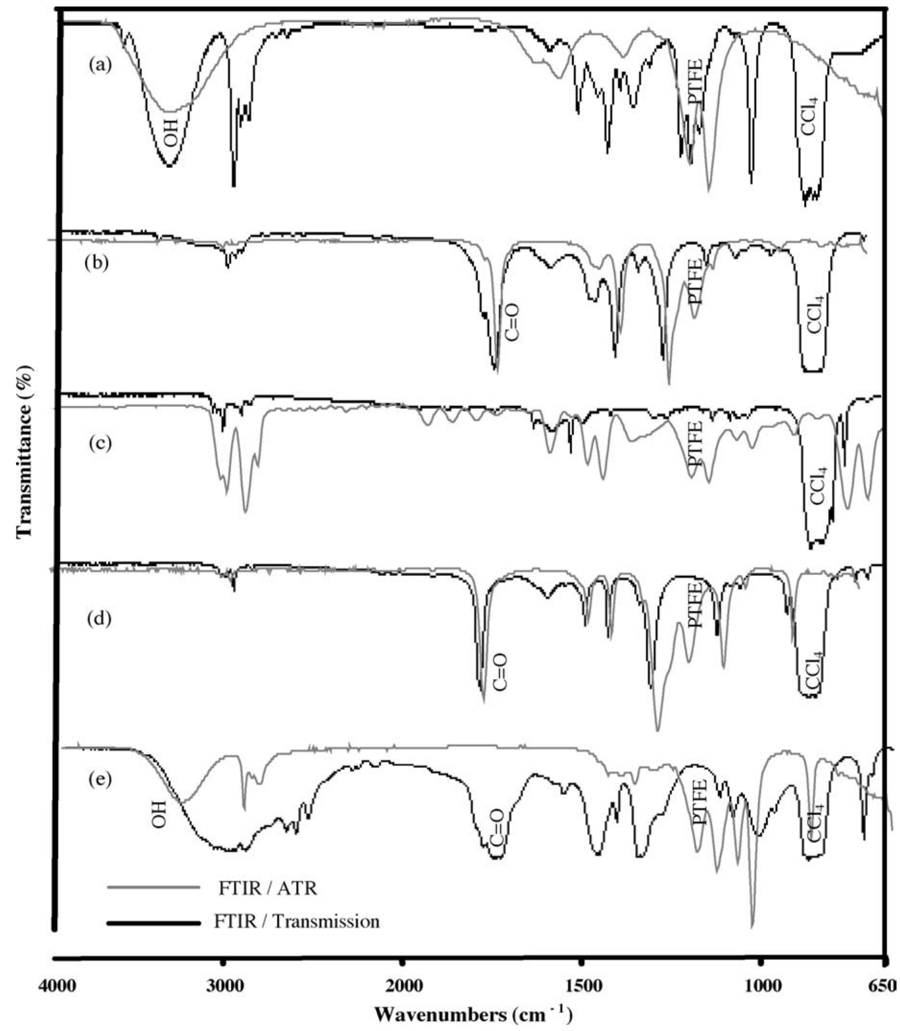

Fig. 6. Optimized FTIR–ATR spectra of pure solutions spotted on the surface of the Teflon filter paper (gray color). Optimized FTIR transmission spectra of 10% CCl_4 diluted pure solutions through a transmission cell (black color): (a) propane-2-ol (OH); (b) acetone (C═O); (c) toluene (phenyl ring); (d) methyl acetate (C═O and C─O─R); (e) acetic acid (C═O and C─O─H).

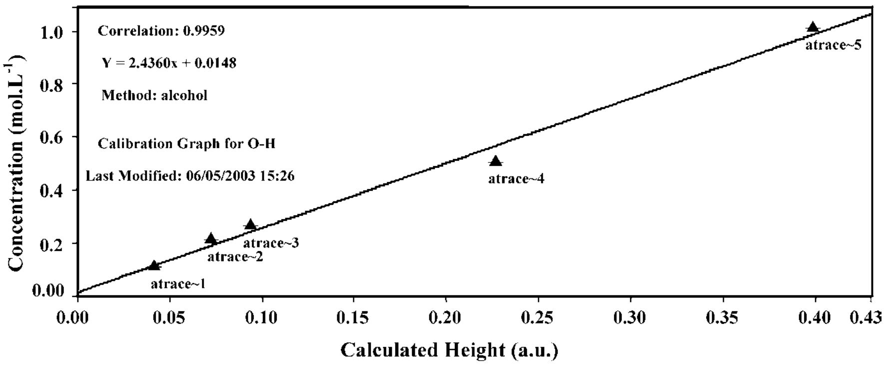

Fig. 7. Calibration curve for hydroxyl group (OH). The deposition of the standards were made by spot tests on the surface of the PTFE Filter. The Perkin-Elmer software has automatically plotted the concentration (mol L^{-1}) vs. calculated height of each peak. The maximum ATR intensity was taken in the defined wave numbers interval (3200–3700 cm^{-1}) that corresponded to the O─H vibrational frequency. After the baseline correction, the interval was changed to 3126–3620 cm^{-1}. The bars represent the standard deviations. The correlation coefficient is $r^2 = 0.9959$.

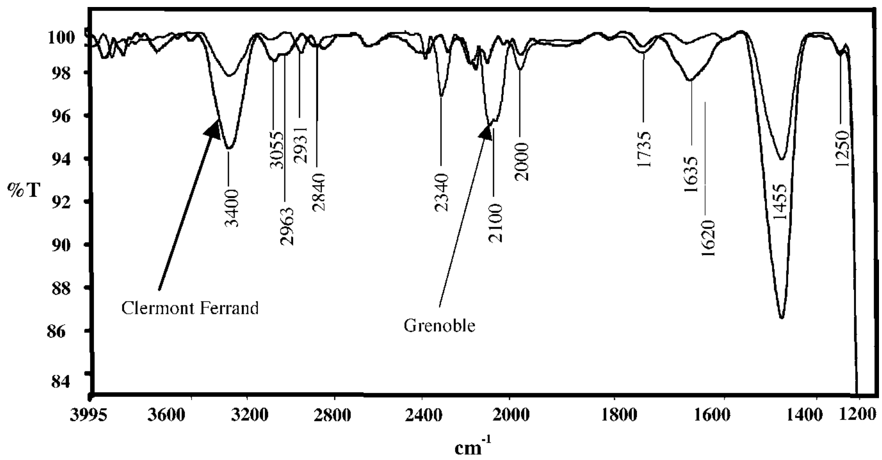

Fig. 8. ATR spectra of PM collected on 27 March 2003 in Clermont-Ferrand and Grenoble urban areas. Samplings are done over a 12 h period with a total flow rate of 20.83 L min^{-1} on PTFE filters.

3.2.6. Identification of all organic species and quantification of hydroxyl groups

The feasibility of ATR–FTIR spectroscopy for monitoring organic group in the environment was evaluated by using a PTFE filter sampled during 12 h with a total flow rate of 20.83 L min^{-1} (1.25 m^3 h^{-1}) in Clermont-Ferrand and Grenoble urban areas. Six direct measurements have been carried out so as to improve the homogeneity of the distribution of organic species on the surface of each PTFE filter. As shown in Fig. 8, FTIR vibrational modes due to organonitrates in ambient aerosols were identified around 1635 cm^{-1} [22,23]. No absorbed nitrogen oxides were depicted since peaks in the 1500 cm^{-1} region were not shown [24]. Furthermore, aromatic nitro groups, which absorb strongly between 1540 and 1500 cm^{-1} [25] were not identified in the studied spectra. Peak around 1735 cm^{-1} is attributed to carbonyl groups (carboxylic acids) which are reported to absorb over the broad range of 1640–1850 cm^{-1} [22]. As well as the carbonyl peak, the OH stretching frequency around 3400 cm^{-1} suggested the presence of carboxylic acid compounds in the PM. However, water absorption was confirmed by a broad peak around 3400 cm^{-1} and a peak at 1620 cm^{-1} [21]. Aliphatic carbon absorbances in aerosols are depicted by the broad band in the range between 2800 and 3000 cm^{-1} peaking at 2931 and 2963 cm^{-1}. The stretching frequency at 2963 cm^{-1} is assigned to CH_3 aliphatic carbon stretching absorptions, while 2931 cm^{-1} is due to CH_2 bonds. A higher absorption band at 1455 cm^{-1} includes the contributions from CH_3 and CH_2 bending aliphatic carbon bonds. Peaks at 2000 cm^{-1} and 2100 cm^{-1} are assigned to stretching vibrations of the alkenes and alkynes, respectively. Nevertheless, peak at 2340 cm^{-1} can be attributed to Si–H bond. This hypothesis is confirmed by the absorption peak at 1250 cm^{-1} that corresponds to Si–CH_3 bond. Moreover, the spectra of the two different sites bear a resemblance to each other. However, one can note that these two spectra present dissimilarities in some peaks. This can be explained by bathochromic and/or hypsochromic shifts which are due to the nature of the typical aerosol of the sampled site (polarity of adsorbed compounds on the surface of the PM). On the other hand, hyperchromic and hypochromic phenomena are observed especially for alkyl and hydroxyl bands.

ATR spectra show that Clermont-Ferrand was more polluted than Grenoble on the same day of March 2003. This statement is based on the study of more than one organic group such as hydroxyls (O–H). If we look for example at the 1455 cm^{-1} band, we can observe a significant increase in the ATR signal of alkyl groups for Clermont-Ferrand spectrum.

Using standard calibration data, the concentration of hydroxyl groups in the PM was estimated to be 8.21×10^{-2} and 3.28×10^{-2} mol L^{-1} for Clermont-Ferrand's and Grenoble's samples, respectively. If we consider that these concentrations are present in the sampling volume, we can find approximately 5.47×10^{-6} mol L^{-1} for Clemont ferrand and 2.18×10^{-6} mol L^{-1} for Grenoble. These values are obtained by dividing the whole sampling volume ($V_L = \text{time}_{(\text{min})} \times \text{flow}_{(\text{L min}^{-1})}$) with the concentrations acquired via the calibration curve. They should certainly include water present in the liquid form on the PTFE filter and water in the adsorbed form on the surface of PM.

4. Conclusion

The objective of this research was to study the feasibility of ATR–FTIR analytic technique for the identification and/or quantification of organic groups on aerosols collected on PTFE filters. The results show that the appropriate use of the ATR–FTIR spectrometry leads to satisfying quantitative measurements. ATR–FTIR at solid surfaces is of particular interest because of the simplicity of substrate preparation and the very good reproducibility. To ensure satisfactory results, some conditions must be respected, such as pretreatment of the PTFE filter, uniform spot measurement, repeatability in the positioning of the pressure gauge on the diamond and mathematical (software) treatment of ATR–FTIR spectra (correction of the baseline, smoothing property, standardization, etc.). A prompt comparison between several polluted areas is now possible after the collection of PM on a PTFE filter. Quantification of hydroxyl group was realized after carrying out calibration curve using standards (alcohol). However, in order to more optimize the quantification protocol, one should develop a software that include Beer's law for reflectance measurements by estimating the penetration depth of the evanescent IR wave. This software facilitates for the users the quantification of specific organic groups like acids, esters, and ketones. Development should take into consideration the bathochrome and hypsochrome shifts due to the complexity of the media in addition of possible aerosol surface reactions. We are currently working to analyze the major organic group adsorbed on aerosols in order to be able to quantify the whole of organic substances that consist of the major part of atmospheric organic pollutant.

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