

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

Antoine Ghauch^{a,*}, Pierre-Alexandre Deveau^b, Véronique Jacob^b, Patrick Baussand^b

^a National Council for Scientific Research, Lebanese Atomic Energy Commission, Environmental and Atmospheric Research Chemistry Team (ERECA), P.O. Box 11-8281, Beirut, Lebanon

^b Grenoble University Institute of Technology, Department of Chemistry, Environmental and Atmospheric Research Chemistry Group (GRECA), 39-41 Boulevard Gambetta, 38000 Grenoble, France

Received 16 March 2005; received in revised form 22 June 2005; accepted 20 July 2005

Available online 24 August 2005

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.

© 2005 Elsevier B.V. All rights reserved.

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; PM_{2.5} refers to particulate matter that is 2.5 μm or smaller in size. However, PM_{2.5–10} refers to particulate matter having a diameter between 2.5 and 10 μm. The sources of PM_{2.5} 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

* Corresponding author. Tel.: +961 1 450 811; fax: +961 1 450 810.
E-mail address: aghauch@cnrs.edu.lb (A. Ghauch).

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 ($400\text{--}4000\text{ cm}^{-1}$) 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 inci-

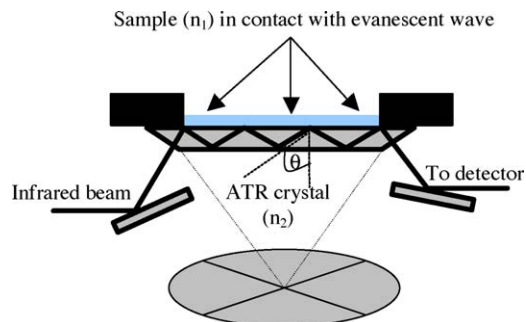


Fig. 1. A multireflexion horizontal ATR system. n_1 and n_2 are the refractive indices of the crystal and the sample, respectively.

dence 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.

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: Nadochenko 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

Download English Version:

<https://daneshyari.com/en/article/1246419>

Download Persian Version:

<https://daneshyari.com/article/1246419>

[Daneshyari.com](https://daneshyari.com)