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Application of FTIR Spectroscopy in Environmental Studies

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1. Introduction

FTIR Spectroscopy is a technique based on the determination of the interaction between an IR radiation and a sample that can be solid, liquid or gaseous. It measures the frequencies at which the sample absorbs, and also the intensities of these absorptions. The frequencies are helpful for the identification of the sample's chemical make-up due to the fact that chemical functional groups are responsible for the absorption of radiation at different frequencies. The concentration of component can be determined based on the intensity of the absorption. The spectrum is a two-dimensional plot in which the axes are represented by intensity and frequency of sample absorption.

The infrared region of the electromagnetic spectrum extends from the visible to the microwave (Figure 1).

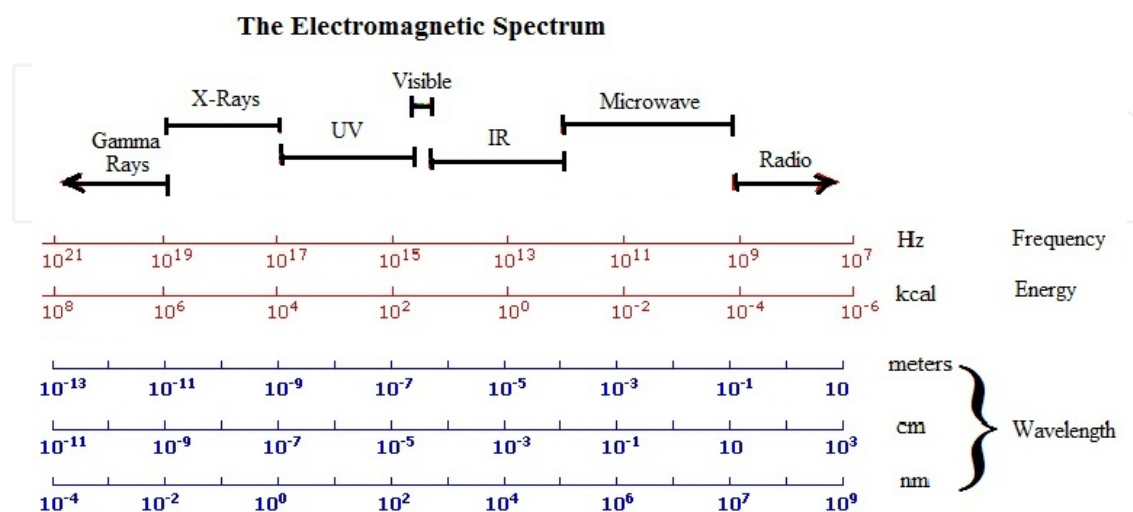


Figure 1. Schematic representation of the electromagnetic spectrum (adapted from <http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/UV-Vis/spectrum/>)

Infrared radiation is divided into:

- near (NIR, $\nu = 10,000 - 4,000 \text{ cm}^{-1}$);
- middle (MIR, $\nu = 4,000 - 200 \text{ cm}^{-1}$) and
- far (FIR, $\nu = 200 - 10 \text{ cm}^{-1}$).

Because all compounds show characteristic absorption/emission in the IR spectral region and based on this property they can be analyzed both quantitatively and qualitatively using FT-IR spectroscopy.

Today FT-IR instruments are digitalized and are faster and more sensitive than the older ones. FT-IR spectrometers can detect over a hundred volatile organic compounds (VOC) emitted from industrial and biogenic sources. Gas concentrations in stratosphere and troposphere were determined using FT-IR spectrometers (Puckrin *et al.*, 1996).

In case of environmental studies FTIR Spectroscopy is used to analyze relevant amount of compositional and structural information concerning environmental samples (Grube *et al.*, 2008). The analysis can be performed also to determine the nature of pollutants, but also to determine the bonding mechanism in case of pollutants removal by sorption processes. Techniques for measuring gas pollutants such as continuous air pollutants analyzer (SO_2 , NO_2 , O_3 , NH_3), on-line gas chromatography (GC) used simple real-time instruments to quantify gas pollutants. They need to use several sensors in order to analyze multiple gas pollutants simultaneously.

FT-IR spectroscopy coupled with other spectroscopic techniques such as AAS (atomic absorption spectroscopy) have been used to assess the impact of industrial and natural activities on air quality (Kumar *et al.*, 2005; Childers *et al.*, 2001).

In addition to the traditional transmission FTIR (T-FTIR) methods (e.g. KBr-pellet or mull techniques), modern reflectance techniques are widely used today in environmental, agricultural, pharmaceuticals, and food studies. These modern techniques are attenuated total reflection FTIR (ATR-FTIR), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The choice of the method to be used depends on many factors such as: the information needed (bulk versus surface analysis), the physical form of the sample, the time required for sample preparation (Majedová *et al.*, 2003).

In the following there will be presented some of the most important research studies related to the involvement of FTIR spectroscopy in environmental studies.

2. Traditional transmission FT-IR (T-FTIR) spectroscopy in environmental studies

Transmission spectroscopy is the oldest and most commonly used method for identifying either organic or inorganic chemicals providing specific information on molecular structure, chemical bonding and molecular environment. It can be applied to study solids, liquids or gaseous samples being a powerful tool for qualitative and quantitative studies.

FTIR instrument's principle of function is the following: IR radiation from the source that hits the beam splitter is partly directed towards the two mirrors arranged as shown in Figure 2. One of the two mirrors is stationary, and the other is moved at a constant velocity during data acquisition. As it can be seen in Figure 2 at first the IR beams are reflected by mirrors, after that are recombined at the beam splitter, and then passed through the sample and reach the detector. This records all wavelengths in the IR range. After the two beams reflected by the mirrors recombine, they will travel different distances, and the recombination will lead to constructive and destructive interference. The result will be an interferogram. After the recombined beam has passed through the sample the detector will record the Fourier transform of the IR spectrum of the sample. The data obtained are then processed by a computer that performs an additional Fourier transform to back-transform the interferogram into an IR spectrum (Smith *et al.*, 2011; Blum and John, 2012).

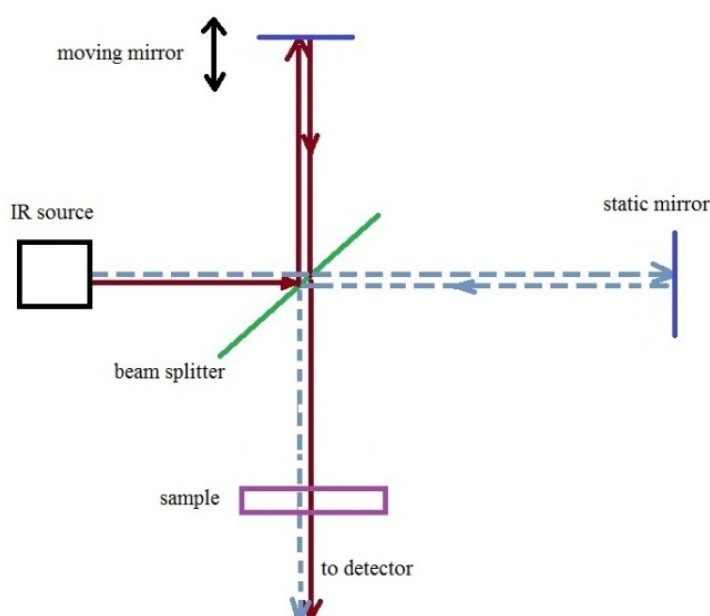


Figure 2. A schematic representation of an interferometer used in FTIR spectrometers (adapted from Blum and John, 2012 with permission (originally published in Drug Test. Analysis, DOI: 10.1002/dta.374))

The potential value of FTIR spectroscopy to a wide range of environmental applications has been demonstrated by numerous research studies. Some of them are presented below.

A review by McKelvy and coworkers containing 132 references at the chapter related to environmental applications of infrared spectroscopy (McKelvy *et al.*, 1998) covers the published literature about relevant applications of infrared spectroscopy for chemical analysis. The literature research was made for the period November 1995 to October 1997. The review contains aspects about infrared accessories and sampling techniques, infrared techniques, applications of infrared spectroscopy in environmental analysis, synthesis chemistry, food and agriculture, biochemistry and also the books and reviews appeared in that period for this subject (McKelvy *et al.*, 1998). An other review concerning the near-infrared and infrared spectroscopy was made by Workman Jr. This review covers the period 1993-1999 and presents the application of the near infrared spectral region to all types of analyses (Workman Jr, 1999).

The basic principle and methods of FTIR spectroscopy of the atmosphere are presented by Bacsik and coworkers in 2004 (Bacsik *et al.*, 2004). The same group of researchers published a review article related to the most significant and frequent applications of FTIR spectroscopy to the study of the atmosphere (Basick *et al.*, 2005). The authors summarized the basic literature in the field of special environmental applications of FTIR spectroscopy, such as power plants, petrochemical and natural gas plants, waste disposals, agricultural, and industrial sites, and the detection of gases produced in flames, in biomass burning, and in flares (Basick *et al.*, 2005).

Applications of FTIR spectroscopy to agricultural soils analysis were presented and discussed by Raphael in the book entitled "Fourier Transforms - New Analytical Approaches and FTIR Strategies" (Raphael, 2011). Chapter 19 of the same book presents the application of FTIR spectroscopy in waste management, and chapter 21 presents the study of trace atmospheric gases using Ground-Based Solar Fourier Transform Infrared Spectroscopy (Smidt *et al.*, 2011; Paton-Wals, 2011).

In case of air pollution the Fourier transform infrared (FTIR) instrument is used successfully for measuring gas pollutants due to its many advantages such as: multiple gas pollutants will be monitored in real time, the IR spectra of sample can be analyzed and preserved for a long time, can be use to detect and measure directly both criteria and toxic pollutants in ambient air, measures also organic and inorganic compounds, can be also used to characterize and analyze microorganisms and monitor biotechnological processes, is generally installed at one location, but can be also portable and operated using battery for short-term survey, presents sensitivity from very low parts per million to high percent levels, can be applied to the analysis of solids, liquids and gases, no reagent is needed, and data acquisition is faster than with other physico-chemical techniques (Santos *et al.*, 2010).

The basic principle of FT-IR spectroscopy used in air pollutants detection and measuring is that every gas has its own „fingerprint” or absorption spectrum. The entire infrared spectrum will be monitored and FTIR sensor will read the different fingerprints of the gases present in the air sample. In case of determination of gas concentrations from stratosphere, the FT-IR spectrometers have to be designed with a fine resolution (0.01 cm^{-1}) due to the lower atmospheric pressure, and with a lower resolution between 0.05 cm^{-1} and 2 cm^{-1} for tropospheric gases determination. This is due to pressure broadening effects that result in broadened absorption lines. In troposphere water vapor concentrations are higher than those from stratosphere and they have a negative effect on the FT-IR spectrum measurements. The strong interference of water vapor in troposphere is overcome by detecting chemical substances in narrow bands of the IR spectrum where water absorption is very weak.

The total precipitable water vapour (PWV) from air which is responsible for the greenhouse effect being the most important trace gas can be measure using FT-IR spectroscopy. When it was compared with other instruments such as a Multifilter Rotating Shadow-band Radiometer (MFRSR), a Cimel sunphotometer, a Global Positioning System (GPS) receiver, and daily radiosondes (Vaisala RS92) it was estimated that FTIR spectrometer provides very

precise tropospheric water vapour data, but when area-wide coverage and real-time data availability is very important, the GPS and the RS92 data are more appropriate. FTIR spectroscopy can be used also as a reference when assessing the accuracy of the other techniques, but those who use this technique have to be aware of the FTIR's significant clear sky bias (Schneider, 2010).

Animal farms are major sources of air pollution with ammonia and greenhouse gases. Air concentration of these pollutants may be higher or lower depending on the systems used. In addition, these systems have to correspond both in terms of animal welfare, and in terms of environmental protection. If it is considered animal welfare, the straw based systems are considered animal friendly systems, and when it is considered the environmental protection, the slurry based systems are preferred, due to lower ammonia (NH_3) and greenhouse gas (GHG) emissions. For slurry based systems air pollutants emissions were intensively researched, and the specific emission factors for several slurry-based housing systems for pigs are mentioned in the "Guidance document on control techniques for preventing and abating emissions of ammonia" developed by the UN/ECE "Expert Group on Ammonia Abatement" of the "Executive Body for the Convention on Long-Range Transboundary Air Pollution" (EB.AIR/1999/2). The straw based systems have not been extensively studied in terms of emissions of air pollutants. There are few research studies regarding these systems. Thus, high resolution FTIR spectrometry was used in order to determine the emissions of ammonia (NH_3), nitrous oxide (N_2O), methane (CH_4), and volatile organic compounds (VOC) at a commercial pig farm in Upper Austria using a straw flow system by Amon and coworkers (Amon *et al.*, 2007). The straw flow system is an animal friendly housing system for fattening pigs, being often equated with deep litter where there is no separation between the lying and the excretion areas. In deep litter systems most of the pigs welfare requirements are fulfilled. The main disadvantages of these systems are that there is a high straw consumption, the pigs are dirtier and the deep litter are characterized by high levels of NH_3 and greenhouse gases (GHG). Thus the level of NH_3 and greenhouse gases (GHG) has to be monitored in order to control and to avoid air pollution and to take appropriate measures for environment protection. For the pig farm monitored by Amon and coworkers it can be concluded that the straw flow system may combine recommendations of animal welfare and environmental protection (Amon *et al.*, 2007).

Environmental problems are also due to the incorrect application of manure. The main air pollutants associated with manure application are ammonia, and nitrous oxides. In order to develop new environmentally friendly methods for manure applications all aspects have to be investigated. For this purpose Galle and coworkers made some area-integrated measurements of ammonia emissions after spreading of pig slurry on a wheat field, based on gradient measurements using FTIR spectroscopy. They concluded that the gradient method is valuable for measurement of ammonia emissions from wide area, although the detection limits of the system limits its use to the relatively high emissions (Galle *et al.*, 2000).

In another study Jäger and coworkers reported that FTIR spectroscopy is capable of measuring low concentrations of CO₂, CH₄, N₂O and CO as well as isotope ratios (especially that of ¹³CO₂) in gas samples. The concentration levels of these gases are close to them in environmental air (Jäger *et al.* 2011). In the same paper the authors discussed also about the accuracy and stability of the FTIR instrument.

Volcanoes are considered important natural sources of air pollution. The most abundant gas typically released into the atmosphere by volcanoes is water vapor (H₂O), followed by carbon dioxide (CO₂) and sulfur dioxide (SO₂). Other gases such as hydrogen sulfide (H₂S), carbon monoxide (CO), hydrochloric acid (HCl), hydrofluoric acid (HF), hydrogen (H₂), helium (He), silicon tetrafluoride (SiF₄), carbon oxysulfide (COS) are released by volcanoes in small amounts. From the most dangerous to human, animals and agriculture are carbon dioxide, sulfur dioxide and hydrofluoric acid. Therefore it is important to monitor volcanic activities.

The first report about determination of HCl and SO₂ in volcanic gas dates from 1993 when Mori and coworkers used an FT-IR spectrometer during a stage of dome lava extrusion of the Unzen volcano (Mori *et al.*, 1993). Other gases including H₂O, CO₂, CO, COS, SO₂, HF were measured using a remote FT-IR spectral radiometer (Mori and Notsu, 1997; Francis *et al.*, 1996; Love *et al.*, 1998; Burton *et al.*, 2000; Mori and Notsu, 2008).

A telescope-attached FT-IR spectral radiometer was used to study the volcanic gases in seven active volcanoes from Japan. For one of the volcanoes monitored the authors have been used infrared radiation from hot lava domes, for three of them they used infrared radiation of the hot ground surface, and for the other three they used scattered solar light, as infrared sources. The observations over 15 years suggest that HCl/SO₂ and HF/HCl ratios are the most promising parameters reflecting volcanic activity among various parameters observable in remote FI-IR measurements (Notsu and Mori, 2010).

Oppenheimer and coworkers used thermal imaging and spectroscopic (FTIR) techniques to characterize phase-locked cycles of lava lake convection and gas plume composition of the Erebus volcano, Antarctica - a volcano continuously active for decades being now in steady-state. The authors identified a striking, cyclic correspondence between the surface motion of lava lake, and its heat and gas output. They concluded that this can be a reflection of unsteady, bi-directional magma flow in the conduit feeding the lake. It was also determined the ratio between gases emitted by volcanic lake, and the very tight correlation between CO₂ and CO was attributed to the redox equilibrium established in the lava lake. These results have a great contribution to the understanding of the laboratory models for magma convection degassing and volcanic gas geochemistry (Oppenheimer *et al.*, 2009).

FTIR technique offers the potential for the non-destructive, simultaneous, real-time measurement of multiple gas phase compounds in complex mixtures such as cigarette smoke (Bacsik *et al.*, 2007a). Thus, in a study Bacsik and coworkers reported using of FTIR spectroscopy to study the mainstream cigarette smoke from cigarettes of different stated strengths (regular and various light cigarettes with different reported nicotine, tar and CO contents) (Bacsik, 2007b). The cigarette smoke is a very complex mixture that mainly

consists of hydrocarbons and both carbon and nitrogen oxides. The results obtained by the authors reveal the fact that the strength of the cigarettes does not have a significant bearing on the quantity of the observed components obtained (Bacsik, 2007b).

An other anthropic source of air pollution is aircraft flight. The main pollutants released by aircrafts are unburnt hydrocarbons, carbon monoxide, and nitrogen oxides. The level of these pollutants is higher near the airport. For modern aircrafts the level of pollutants emissions is lower due to the using of more efficient turbine engine. Nevertheless the civil aviation authorities require the monitoring emissions from aircraft in airports and in the vicinity of airports. For this a non-intrusive Fourier Transform Infrared (FTIR) spectroscopy has been used to detect hydrocarbons in emissions from gas turbine engines (Arrigone and Hilton, 2005). The advantages of this mentioned techniques reported by Arrigone and Hilton are: it is non-intrusive—no sampling system is required and there is no physical interference with the exhaust plume while measurements are made; is useful for simultaneous monitoring of several species; the equipment is portable and can be simply set up and used outside the laboratory in engine test facilities, airfields (Arrigone and Hilton, 2005).

All these advantages encourage the use of FTIR spectroscopy as a valuable tool in monitoring emissions from aircraft in airports.

Quantitative information about air components and air pollutants is needed to study the impact of pollutants (gaseous, liquids or solids) on human health and atmospheric chemistry. To obtain these information an infrared spectral database was created. This database was completed with spectral information of gases emitted by biomass burning by Johnson and coworkers. The following classes of compounds: singly- and doubly-nitrogen-substituted aromatic, terpenes, hemi-terpenes, retenes and other pyrolysis biomarker compounds, carboxylic acids and dicarboxylic acids were identified in gases from biomass burning (Johnson *et al.*, 2010).

Throughout, latest years, the significance of bioaerosols has been discussed in environmental and occupational hygiene. Identification of microorganisms using cultivation and microscopic examination is time consuming and alone does not provide sufficient information with respect to the evaluation of health hazards in connection with bioaerosol exposure. FT-IR spectroscopy has widely been used for the characterization and identification of bacteria and yeasts, due to the fact that they are hydrophilic microorganisms and can easily be suspended in water for sample preparation (Essendoubi *et al.*, 2005; Duygu *et al.*, 2009). The identification of airborne fungi using FT-IR spectroscopy was described by Fischer and coworkers. They found that the method was suited to reproducibly differentiate *Aspergillus* and *Penicillium* species. The results obtained can serve as a basis for the development of a database for species identification and strain characterization of microfungi (Fischer *et al.*, 2006).

Studies on heavy metals and organic compounds removal from wastewaters using different natural and synthetic materials are many. The important role of FTIR spectroscopy in such studies is either related to the characterization of sorbents, chemical modified sorbents, or to

establish the mechanism involved in sorption processes (Cheng *et al.*, 2012; Chen and Wang, 2012; Xu *et al.*, 2012; Ma *et al.*, 2012a; Wang *et al.*, 2011; Jordan *et al.*, 2011; Bardakçi and Bahçeli, 2010; Pokrovsky *et al.*, 2008; Parolo *et al.*, 2008).

Biosorption is considered as an alternative process for the removal of heavy metals, metalloid species, compounds and particles from aqueous solution by biological materials (Mungasavalli *et al.*, 2007). Biomaterials are adsorbent materials with high heavy metals adsorption capacity. They have many advantages such as reusability, low operating cost, improved selectivity for specific metals of interests, removal of heavy metals found in low concentrations in wastewaters, short operation time, and no production of secondary compounds which can be toxic (Mungasavalli *et al.*, 2007). FTIR spectroscopy can be used for characterization of biomaterials used in depolluting processes, but also to characterize materials obtained after chemical modification of them. Thus we used FTIR spectroscopy to characterize the material obtained after chemical modification of chitosan with glutardialdehyde in order to obtain a product with good sorption properties (Deleanu *et al.*, 2008), but also to characterize the materials obtained after alkaline treatment of bentonite to increase its capacity to retain ammonium ions from synthetic solutions (Simonescu *et al.*, 2005).

FT-IR spectroscopy has been used to identify the nature of possible sorbent (biosorbent) – pollutants (heavy metals, inorganic compounds, organic compounds) interactions.

For copper removal by fungal biomass to determine the characteristic functional groups that are responsible for biosorption of copper ions were made biomass's FTIR spectra before and after the biosorption process took place. The bonding mechanism between copper and biomass (fungal strain, cyanobacteria or other microorganism) (Yee *et al.*, 2004; Burnett *et al.*, 2006) can be determined by interpreting the infrared absorption spectrum.

We used in our studies fungal strains in order to remove heavy metals from synthetic waters which contain also copper in the form of copper sulfide nanoparticles, but also copper in dissolved state. In case of copper biosorption by *Aspergillus oryzae* ATCC 20423 the FTIR spectra registered are presented in Figure 3. The FTIR spectrum for *Aspergillus oryzae* ATCC 20423 before copper biosorption is presented in Figure 3a, the FTIR spectrum of *Aspergillus oryzae* ATCC 20423 after growth in the presence of copper solution with 25 mg copper/L is presented in Figure 3b, the FTIR spectrum of *Aspergillus oryzae* ATCC 20423 after growth in the presence of copper solution with 50 mg copper/L is presented in Figure 3c, the FTIR spectrum of *Aspergillus oryzae* ATCC 20423 after growth in the presence of copper solution with 75 mg copper/L is presented in Figure 3d, and the FTIR spectrum of *Aspergillus oryzae* ATCC 20423 after growth in the presence of copper solution with 100 mg copper/L is presented in Figure 3e.

From the Figure 3 it can be seen that all five FTIR spectra present distinct peaks in the following ranges: 3393 – 3418 cm^{-1} , 2926 – 2968 cm^{-1} , 1629 – 1638 cm^{-1} , 1404 – 1405 cm^{-1} , 1073 – 1077 cm^{-1} , and 529 – 533 cm^{-1} . The broad and strong band situated in the range 3393 – 3418 cm^{-1} can be attributed to overlapping of –OH and –NH stretching. The band from the range 2926 – 2968 cm^{-1} is attributed to the C-H stretching vibrations. The strong peak at 1629 – 1638 cm^{-1}

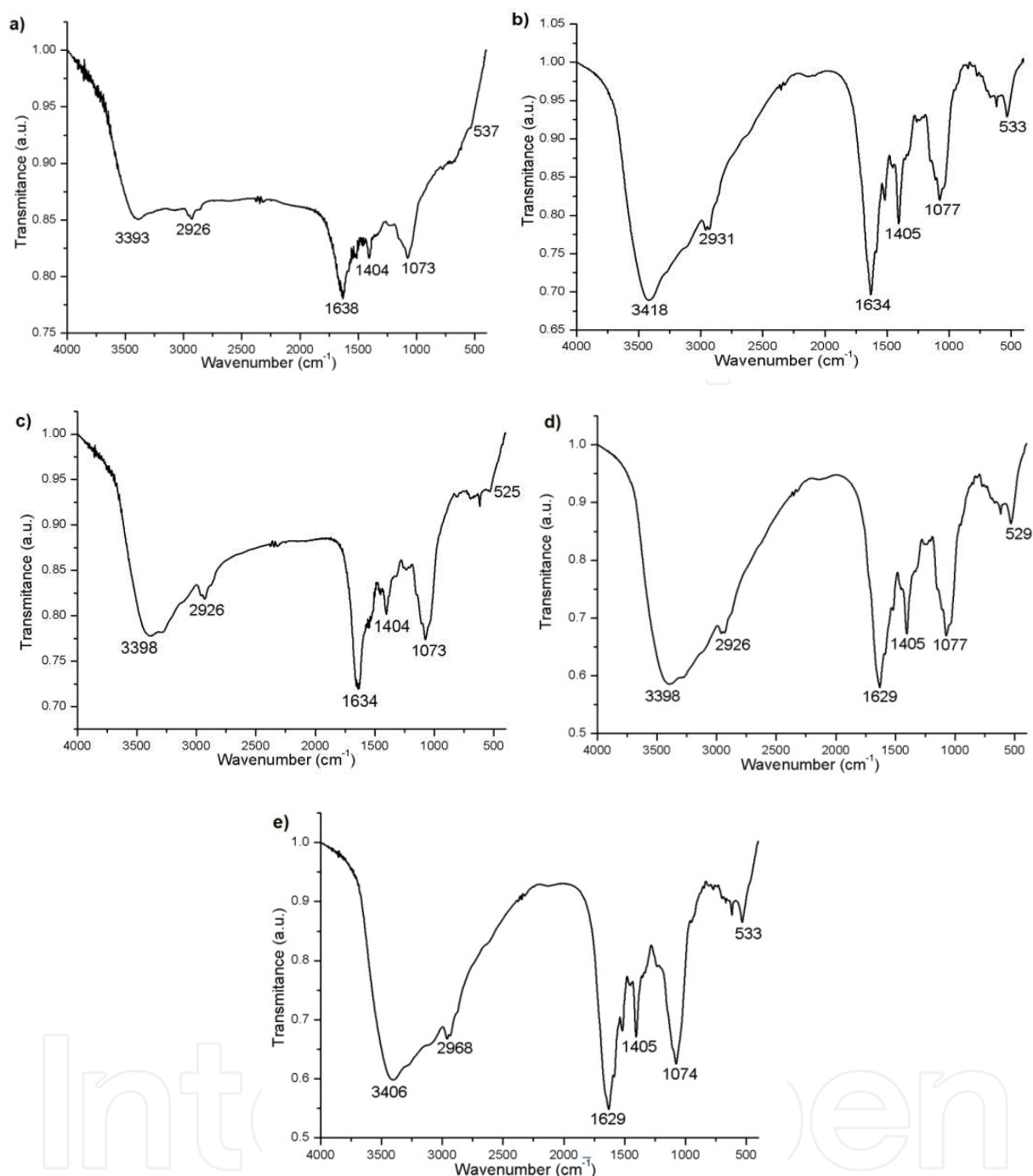


Figure 3. FT-IR spectra of *Aspergillus oryzae* ATCC 20423 unloaded (a) and loaded with Cu(II) ions (b-e)

can be due to a C=O stretching in carboxyl or amide groups. The peak at 1404 – 1405 cm^{-1} is attributed to N-H bending in amine group. The band observed at 1073 - 1077 cm^{-1} was assigned to the CO stretching of alcohols and carboxylic acids. Thus *Aspergillus oryzae* ATCC 20423 biomass contains hydroxyl, carboxyl and amine groups on surface.

From the Figures 3b-e it can be seen that the stretching vibration of OH group was shifted from 3393 cm^{-1} to 3418 cm^{-1} (3b), to 3398 cm^{-1} (3d), 3406 cm^{-1} (3e). These results revealed that chemical interactions between the copper ions and the hydroxyl groups occurred on the

biomass surface. The carboxyl peak observed for unloaded biomass at 1638 cm^{-1} is shifted to 1634 cm^{-1} or 1629 cm^{-1} . This decrease in the wave number of the peak characteristic for C=O group from carboxylic acid revealed that interacts with carbonyl functional group are present between biomass and copper ions. These results indicated that the free carboxyl groups changed into carboxylate, which occurred during the reaction of the metal ions and carboxyl groups of the biosorbent.

No frequency changes were observed in the C-H and $-\text{NH}_2$ groups of biomass after copper biosorption. In addition, all FTIR spectrum of *Aspergillus oryzae* ATCC 20423 loaded with copper ions contain bands at $533, 529, 525\text{ cm}^{-1}$ which can be attributed to Cu-O stretching modes (Simonescu and Ferdes, *in press*).

The similar FT-IR results were reported for the biosorption Pb(II), Cd(II) and Cu(II) onto *Botrytis cinerea* fungal biomass (Akar *et al.*, 2005) and Pb(II) and Cd(II) from aqueous solution by macrofungus (*Lactarius scrobiculatus*) biomass (Anayurt *et al.*, 2009).

In our work we used also FT-IR spectroscopy in order to determine the characteristic functional groups which are responsible for biosorption of copper ions by *Polyporus squamosus*, *Aspergillus oryzae* NRRL 1989 (USA), *Aspergillus oryzae* 22343 (Simonescu *et al.*, 2012).

In case of biological degradation of pollutants a significant role can be attributed to biodegradation pathway due to the fact that different biodegradation pathways lead to different biodegradation products. Thus it is important to determine biodegradation pathways. For this purpose FTIR spectroscopy is a relevant tool for rapid determination of the resulting biotransformation product or mixtures. With this respect, Huang and coworkers investigated the ability of FT-IR to distinguish two different m-cresol metabolic pathways in *Pseudomonas putida* NCIMB 9869 after growth on 3,5-xyleneol or m-cresol. From this study, it can be concluded that FT-IR spectral fingerprints were shown to differentiate metabolic pathways of m-cresol within the same bacterial strain and thus FTIR spectroscopy might provide a rapid, non-destructive, cost-effective approach for assessing of products resulted in biological degradation of pollutants (Huang *et al.*, 2006).

The main directions of use of FTIR spectroscopy in waste management are about getting information regarding the stage of organic matter for process and product control, and for monitoring of landfill remediation. For this purpose, Smidt and Meissl used FTIR spectroscopy to assess the stage of organic matter decomposition in waste materials (Smidt and Meissl, 2007). The results obtained confirm that FTIR spectroscopy represents an appropriate tool for process and quality control, for the assessment of abandoned landfills and for monitoring and checking of the successful landfill remediation (Smidt and Meissl, 2007).

The structural changing in biodegradation processes can be determined by FTIR analysis. Thus Tomšič and coworkers studied structural changes of cellulose fabric modified by imidazolidinone biodegradation after different period using electron microscopic and spectroscopic analyses (Tomšič *et al.*, 2007). Also FT-IR spectroscopy is a quick and useful method to monitor the composting process (Grube *et al.*, 2006). The aim of them study was

to elucidate the typical IR absorption bands and correlation of band growth rates with the compost maturity or degradation degree. The results of this study revealed that IR spectroscopy is a simple, quick and informative method that can be used instead of several time consuming chemical methods for monitoring of routine composting processes.

Soil is a complex medium with important ecological functions. Its functions depend on its characteristics. FTIR spectroscopy can be used to describe soil characteristics in the form of complex multivariate data sets. Thus FTIR spectroscopy has been used by Elliott and coworkers to investigate soils at different stages of recovery from degradation following opencast mining and from undisturbed land (Elliott *et al.*, 2007). When a FT-IR spectrometer was used to determine gases from soils and rock formations no other gases than CO₂ have been detected except CO in the open-path compartment dedicated to atmosphere analysis (Pironon *et al.*, 2009).

The use of living organisms to manage or remediate polluted soils named bioremediation represents an emerging technology. This technology is defined as the elimination, attenuation or transformation of polluting or contaminating substances by the use of biological processes. The results *in situ* bioremediation depend by microbial strains from contaminated site. The biodegradation process can be monitored by FTIR spectroscopy. For this purpose Bhat and coworkers performed a study about remediation of hydrocarbon contaminated soil through microbial degradation. The bacterial strains involved in bioremediation process were collected to be isolated from contaminated soil. FTIR spectra of untreated and treated soil samples revealed that the isolated bacterial strains have a substantial potential to remediate the hydrocarbon contaminated soils (Bhat *et al.*, 2011).

Biom mineralization has an important role for pollutants removal from environment. It has been known the mechanism involved in such processes to establish the nature of intermediates and final compound formed. FTIR spectroscopy is well-suited for such investigations, because it provides simultaneously molecular-scale information on both organic and inorganic constituents of a sample. Consequently FTIR spectroscopy was used in several complementary sample introduction modes as transmission (T-FTIR), attenuated total reflectance (ATR-FTIR), diffuse reflectance (DRIFTS) to analyze the processes of cell adhesion, biofilm growth, and biological Mn-oxidation by *Pseudomonas putida* strain GB-1 by Parikh and Chorover (Parikh and Chorover, 2005).

Fourier Transform Infrared (FT-IR) and Attenuated Total Reflectance (ATR) spectroscopy in the mid infrared (MIR) wavelength range (2500 – 16,000 nm) have been also developed for contaminant detection in water (Gowen *et al.*, 2011a). The authors tested the near infrared spectroscopy (NIRS) for the detection and quantification of pesticides including Alachlor and Atrazine in aqueous solution. Calibration models were built to predict pesticide concentration using PLS regression (PLSR). The proposed method shows potential for direct measurement of low concentrations of pesticides in aqueous solution. The research was performed in the laboratory conditions, and it is well known that the NIR spectrum of aqueous samples is susceptible to changes in the environment (e.g. temperature, humidity) and sample (e.g. pH, turbidity). Thus further experiments are necessary to test the effect of such perturbations on predictive ability (Gowen *et al.*, 2011b).

By joining FTIR spectroscopy with two dimensional correlation analysis (2DCORR) there will be obtained a device with improved performance in the study of complex environmental systems (Noda and Ozaki, 2005). The two dimensional correlation analysis (2DCORR) is a method to visualize the dynamic relationship between the variables in multivariate data set with application of the complex cross-correlation function. With the help of this analysis there will be identified the spectral features which change in phase (i.e. linearly correlated among them) and out of phase (partially or not at all correlated among them) (Mecozzi *et al.*, 2009). This technique can be applied to study the evolution of environmental complex systems. Mecozzi and coworkers applied FTIR spectroscopy joined with two dimensional correlation analysis (2DCORR) to identify the aggregation pathways of extractable humic substance from marine sediments, and to compare the molecular modifications determined by the actions of different pollutants on the marine algae *Dunaliella tertiolecta* that is a biomarker of environmental quality (Mecozzi *et al.*, 2009). From this study it can be concluded that FTIR spectroscopy joined with 2DCORR analysis can be an important tool for evaluating toxic effects on the marine life.

3. Attenuated Total Reflection – Fourier Transform Infrared (ATR-FTIR) spectroscopy in environmental studies

Attenuated Total Reflection – Fourier Transform Infrared (ATR-FTIR) Spectroscopy was introduced in 1960s (Harrick, 1967), and now is widely used in many areas.

The principle of this is FTIR technique is that light introduced into a suitable prism at an angle exceeding the critical angle for internal reflection develops an evanescent wave (a special type of electromagnetic radiation) at the reflecting surface. Interaction of this evanescent wave with the sample determines ATR spectrum recording. The main characteristic of this techniques is the fact that particle samples are deposited on the surface of a horizontal ATR crystal for spectroscopic analysis (Figure 4). Zinc selenide (ZnSe) or Ge crystals are the most commonly used in ATR-FTIR spectroscopy.

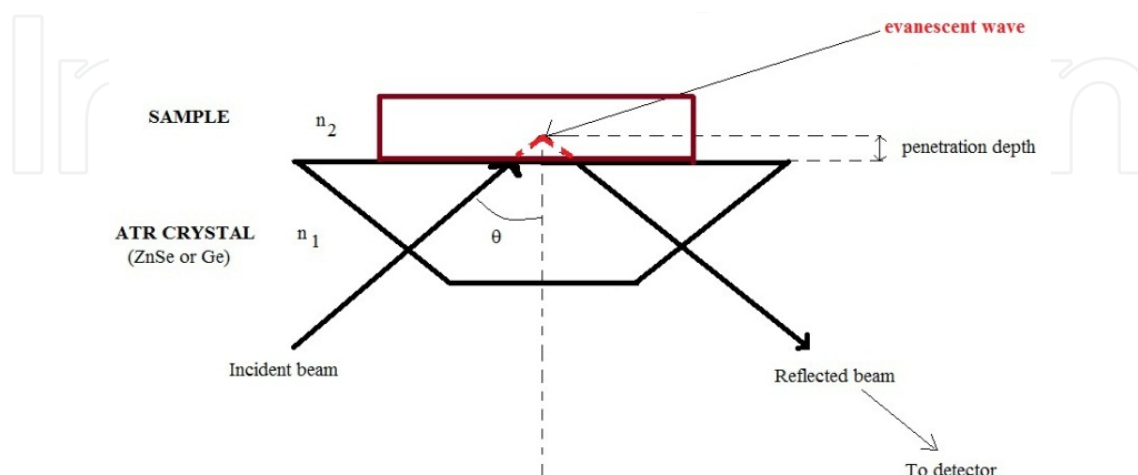


Figure 4. The principle of ATR-FTIR where n_1 and n_2 are the refractive indices of the crystal and the sample, respectively.

The main advantages of ATR-FTIR spectroscopy are: can be applied to a large variety of materials such as: powders, liquids, gels, pastes, pellets, slurries, fibers, soft solid materials, surface layers, polymer films, samples after evaporation of a solvent being a versatile and non-destructive technique; is useful for surface characterization, opaque samples; faster sampling being a non-destructive technique; is considered an extremely robust and reliable technique for quantitative studies involving liquids; excellent sample-to-sample reproducibility.

All these advantages make that ATR-FTIR spectroscopy to be used for: analysis of processes at surfaces (Freger and Ben-David, 2005), surface modification (Lehocký et al. 2003; Janorkar et al., 2004), surface degradation (Bokria et al., 2002), study of enzymatic degradation of a substrate film attached to a solid surface (Snabe et al. 2002), study of sunscreens on human skin (Rintoul et al., 1998), research of cereal, food and wood systems (D'Amico et al. 2012), detection of microbial metabolic products on carbonate mineral surfaces (Bullen et al., 2008), self-assembled thin films (Gershevit et al. 2004), grafted polymer layers (Granville et al. 2004), adsorption processes (Sethuraman et Belfort 2005; Al-Hosney et Grassian 2005) of biological (Jiang et al. 2005; Mangoni et al. 2004) and synthetic (Freger et al. 2002) materials.

The followings are some examples of *in situ* ATR-FTIR spectroscopy's application in environmental studies.

In recent years adsorptive removal of heavy metals from aqueous effluents have received much attention because numerous materials such as: clays, zeolites, activated carbon can be used as adsorbents. The adsorption of inorganic ions on metal oxides and hydroxides was resolved using *in situ* ATR-FTIR spectroscopy. In a review Lefèvre describes and discusses *in situ* ATR-FTIR used in order to obtain information on the sorption mechanism of sulfate, carbonate, phosphate, perchlorate on hematite, goetite, alumina, silica, TiO₂ (Lefèvre, 2004). This is due to the fact that FTIR technique allows to analyze the sorption/desorption phenomena *in situ* being helpful in determining of the speciation of sorbed inorganic anions or ternary inorganic complexes formed. In addition this technique offers the possibility to distinguish outer-sphere and inner-sphere complexes. In this regard Yoon and coworkers used *in situ* ATR-FTIR spectroscopy and quantum chemical methods to determine the types and structures of the adsorption complexes formed by oxalate at boehmite (γ -AlOOH)/water and corundum (α -Al₂O₃)/water interfaces (Yoon *et al.*, 2004). They found that the adsorption mechanism of a aqueous HO_x⁻ species involves loss of protons from this species during the ligand-exchange reaction. The results obtained are useful in establishing the transport model of toxic species in natural waters, and remediation of liquid wastes.

Contamination of soils and groundwater by radioactive wastes containing uranium and other actinides is a significant problem. The fate and transport of these kind of pollutants in aquifers, design of cost-effective remediation techniques for radioactive-contaminated soils, and developing of materials proper for encapsulation and disposal of nuclear waste require knowledge of mechanism of radioactive pollutants – sorbent interactions. For radioactive waste depositories one of the most important factors which has to be considered is the long-term safety of them. For this, natural or anthropogenic barriers for sorption of radionuclides around

the depositories are placed. Sorption data at the laboratory scale are useful to predict the behaviour of real systems. For this purpose Lefèvre and coworkers used ATR-IR spectroscopy to study the sorption of uranyl ions onto titanium oxide (mixture of rutile and anatase) and hematite. They found that the uranyl sorption on titanium oxide in the pH range 4-7 occurs by formation of one surface complex with uranium atoms bounded by two different chemical environments (Lefèvre *et al.*, 2008), and in case of sorption on hematite they concluded that the same surface species is responsible for the uranyl sorption in the pH range 5-8 (Lefèvre *et al.*, 2006). Due to the fact that experiments were reversible the authors concluded that reaction of hematite deposit with uranyl ions is the same with the reaction of it in dispersed suspensions (Lefèvre *et al.*, 2006). The sorption of U(V) on different forms of titanium dioxide was also studied using ATR-IR spectroscopy by Comarmond and coworkers. They showed the effect of different sources of sorbent and its surface properties on radionuclide sorption (Comarmond *et al.*, 2011). On the same subject Müller and coworkers used the high sensitivity of the *in situ* ATR-FTIR spectroscopy to establish the mechanism of sorption processes of U(VI) onto TiO₂ even at concentrations down to the low micromolar range. The Mid-IR spectra of U(VI) aqueous solutions and of U(VI) sorption onto different TiO₂ samples is presented in Figure 5.

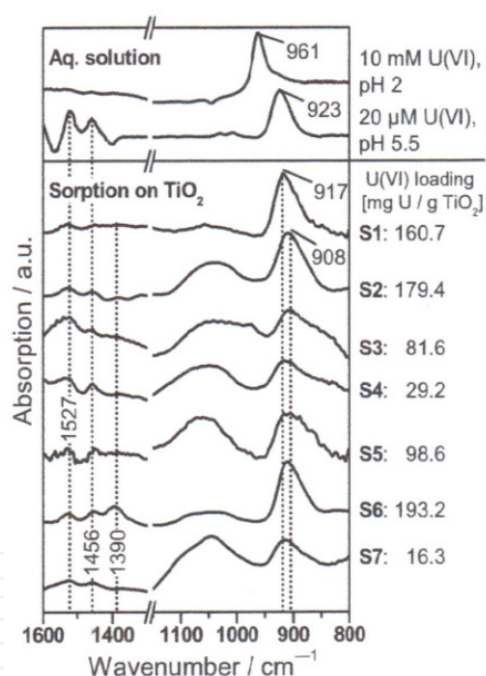


Figure 5. Mid-IR spectra of U(VI) aqueous solutions and of U(VI) sorption onto different TiO₂ samples (the values on the IR spectra are in cm⁻¹) (S1-S7 are different titania samples with different content of anatase and rutil, different particle size, and different origins) (from Müller *et al.*, 2012 used with permission (originally published in *Geochimica et Cosmochimica Acta*, <http://dx.doi.org/10.1016/j.gca.2011.10.004>))

By comparing the spectrum of the aqueous species spectra with the spectra of samples obtained after U(VI) sorption on TiO₂ it can be seen that the frequencies of the $\nu_3(\text{UO}_2)$ modes presented at 961 cm⁻¹ for the aqueous species are significantly shifted (with 53-44 cm⁻¹) which suggests that uranyl surface complexes are formed at all titania samples.

This study is one complex due to the fact that authors performed researches to establish the influence of: stages of *in situ* sorption experiments (conditioning, sorption, and flushing), the contact time of U(VI) with the mineral, the initial U(VI) concentration, pH values, the origin and manufacturing procedure of TiO₂ samples and the absence of atmospheric-derived carbonate on the species formed in sorption processes of U(VI) on TiO₂. The results obtained by authors are relevant to the most environmental scenarios (Müller *et al.*, 2012).

Sorption of Np(V) onto TiO₂, SiO₂ and ZnO was investigated using ATR-FTIR spectroscopy. The results showed obtaining structurally similar bidentate surface complexes for all sorbents used (Müller *et al.*, 2009).

ATR-FTIR spectra confirmed formation of actinyl-carbonato complexes from interaction of actinide with hematite at a specific pH value. This can control the actinide transport in numerous subsurface receptors due to the abundance of carbonate in aquifers (Bargar *et al.*, 1999).

The influence of dissolved CO₂ on UO₂²⁺ sorption process was determined by Foerstendorf and Heim using ATR-FT-IR spectroscopy. They obtained a similar surface complex of the uranyl ion at the ferrihydrite-phase irrespective of the presence of atmospheric CO₂. Sorption of actinide ion on mineral phase determines a change of the carbonate ion from a monodentate to a bidentate ligand (Foerstendorf and Heim, 2008).

ATR-FTIR and FT-IR spectroscopy together with other techniques were used to determine the fate and transport of radionuclides in natural environments. The main mechanisms that are responsible for these are: sorption on organic (living matter and humic materials), sorption on inorganic materials (soil media and minerals), precipitation of them under oxic conditions, reduction in presence of microorganisms, and structural incorporation in different mineral host phases (Duff *et al.*, 2002).

Citric acid being a naturally-occurring acid commonly found in soils, and also a strong complexant of UO₂ is often found as a component of radioactive waste. Advantages such as: its biodegradability and complexing efficiency make from it a good candidate for remediation of uranium contaminated soils (Kantar and Honeyman, 2006). Factors with influence on the uranyl adsorption process to oxide minerals in presence of citric acid were determined by Logue and coworkers. Redden and coworkers have proposed formation of a ternary uranyl-citrate complexes on goethite (Redden *et al.*, 2001). Establishing the interactions between UO₂, citrate and mineral surfaces on a molecular level represents a key factor for modeling adsorption phenomena affecting transport in soils. For this purpose Pasilis and Pemberton used ATR-FTIR to elucidate the mechanism of UO₂ adsorption on aluminium oxide in the presence of citrate. They found that there is an enhanced citrate adsorption to Al₂O₃ in the presence of uranyl. This result suggests that uranyl may be the central link between two citrate ligands, and the uranyl is associated with the surface through a bridging citrate ligand. One other observation is that uranyl citrate complexes interact with citrate adsorbed to Al₂O₃ through outer sphere interactions (Pasilis and Pemberton, 2008).

In recent years it ATR-FTIR spectroscopy has been used to investigate the atmospheric heterogeneous reactions. Thus Al-Hosney and Grassian (2005) used this technique to investigate water adsorption on the surface of CaCO_3 . They further used T-FTIR in order to investigate the role of surface adsorbed water in adsorption reactions of SO_2 and HNO_3 (Zhao and Chen, 2010). In other study Schuttlefield and coworkers (2007a) used ATR-FTIR spectroscopy to provide detailed information about water uptake and phase transitions for atmospherically relevant particles. To determine the factors involved in water uptake on the large fraction of dust present in the Earth's atmosphere, Schuttlefield and coworkers (2007b) used a variety of techniques, including ATR-FTIR. They concluded that water uptake on the clay minerals depends on the type and the source of the clay. These results are important because mineral dust aerosol provides a reactive surface in troposphere being involved in reactions for atmosphere. The role of halogens in the aging process of organic aerosols was determined by Ofner and coworkers (2012) using long-path FTIR spectroscopy (LP-FTIR), attenuated-total reflection FTIR (ATR-FTIR), UV/VIS spectroscopy, and ultrahigh resolution mass spectroscopy (ICR-FT/MS). They concluded that the aerosol-halogen interaction might strongly contribute to the influence of organic aerosols on the climate system (Ofner *et al.*, 2012).

Khalizov and coworkers (2010) investigated the heterogeneous reaction of nitrogen dioxide (NO_2) on fresh and coated soot surfaces to assess its role in night-time formation of nitrous acid (HONO) in the atmosphere using ATR-FTIR (Khalizov *et al.*, 2010).

Segal-Rosenheimer and Dubowski (2007) combined two setups of FTIR for the parallel analysis of both condensed and gas phases of products resulted at the oxidation of cypermethrin (a synthetic pyrethroid being one of the most important insecticides in wide-scale use both indoors and outdoors) by gaseous ozone (Segal-Rosenheimer and Dubowski, 2007).

ATR-FTIR and T-FTIR methods provide detailed information on the composition of PM (particulate matter) samples. Both techniques can be used for qualitative and quantitative studies of particulate samples. Thus Veres (2005) used both methods to analyse particulate matter collected on Teflon Filters in Columbus – Ohio. He mentioned that ATR spectroscopy has limited applications in quantitative studies since it has a penetration depth of only a few microns, and this method can be replaced by transmission spectroscopy which penetrates into the bulk of substance (Veres, 2005).

Several groups of researchers used ATR-FTIR to particulate matter analysis. Thus Shaka and Saliba (2004) used ATR-FTIR spectroscopy in order to determine the concentration and the chemical composition of particulate matter at a coastal site in Beirut, Lebanon. Kouyoumdjian and Saliba (2006) determined the levels of the coarse ($\text{PM}_{10-2.5}$) and fine ($\text{PM}_{2.5}$) particles in the city of Beirut using ATR-FTIR spectroscopy. They also showed that nitrate, sulfate, carbonate and chloride were the main anionic constituents of the coarse particles, whereas sulfate was mostly predominant in the fine particles in the form of $(\text{NH}_4)_2\text{SO}_4$. Ghauch and coworkers (2006) used the same technique for the determination of small amounts of pollutants like the organic fraction of aerosols in the French cities of Grenoble and Clermont-Ferrand.

The applications of ATR-FTIR cover a wide range of subjects such as estimating of soil composition and fate of some soil components.

Monitoring of nitrate in soil is very important for managing fertilizer application and controlling nitrate leaching. This monitoring help to adjust nitrate level in soils in order to maintain the soil fertility, or to detect soil pollution. Due to the technological limitations, *in situ* or near real-time monitoring of soil nitrate is currently not feasible. In this purpose can be used the following methods: nitrate selective electrodes (Sibley, 2010), ion sensitive field effect transistor (Birrell and Hummel, 2001), mid-infrared spectroscopy, and more particularly attenuated total reflectance (ATR) with Fourier transform infrared (FTIR) spectroscopy. Thus Raphael Linker submitted a report to the Grand Water Research Institute about simultaneous determination of $^{15}\text{NO}_3\text{-N}$ and $^{14}\text{NO}_3\text{-N}$ in aqueous solutions, soil extracts and soil pastes. The results obtained show that a combination of ATR-FTIR analysis with appropriate chemometrics can be successfully used to monitor $^{15}\text{NO}_3\text{-N}$ and $^{14}\text{NO}_3\text{-N}$ concentrations in soil during an incubation experiment (Linker, 2010). From the studies performed about measurement of nitrate concentration in soil pastes it can be concluded that ATR-FTIR appears to be a promising tool for direct and close to real-time determination of nitrate concentration in soils, with minimal treatment of the soil samples (Linker *et al.*, 2004; Linker *et al.* 2005; Linker *et al.*, 2006; Linker *et al.*, 2010). The same technique was used by Du and coworkers in order to evaluate net nitrification rate in *Terra Rosa* soil (Du *et al.*, 2009). ATR-FTIR spectroscopy was the technique preferred to mass spectrometry due to reduced cost, it is not time consuming, and doesn't require long and laborious preparation procedures. The results obtained have made major contributions for the estimation of the contribution of applied nitrogen and mineralized nitrogen to net nitrification rates ((Du *et al.*, 2009).

Soil paste was used by Choe and coworkers in order to improve the contact between sample and ATR crystal in case of using of the ATR-FTIR spectroscopy to determine the level of nitrate in soils. By comparing the nitrate peak intensity of soil pastes and their supernatant, it was shown that the nitrate dissolved in soil solution of the paste mainly responded to the FTIR signal. The results obtained are useful for the monitoring of nutrients in soils (Choe *et al.* 2010).

4. Diffuse Reflectance Infrared Fourier Transform (DRIFTS) spectroscopy in environmental studies

DRIFTS spectroscopy is considered a technique more sensitive to surface species than transmission measurements and is an excellent *in situ* technique. The principle is simple one: when incident light strikes a surface, the light that penetrates is reflected in all directions. This reflection is called diffuse reflectance. If the light that leaves the surface will pass through a thin layer of the reflecting materials, its wavelength content will have been modified by the optical properties of the matrix. The wavelength and intensity distribution of the reflected light will contain structural information on the substrate (Analytical Spectroscopy available at: <http://www.analyticalspectroscopy.net/ap3-11.htm>) (Figure 6).

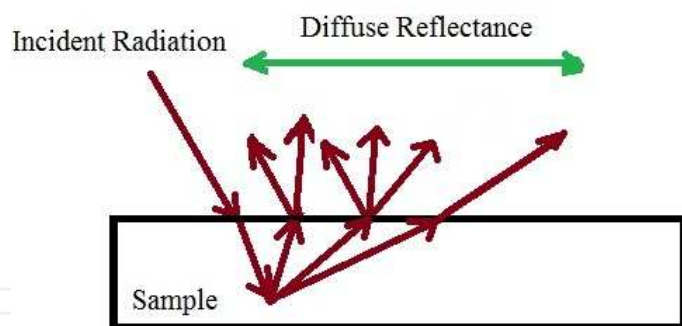


Figure 6. The principle of Diffuse Reflectance Infrared Fourier Transform Spectroscopy (adapted from Analytical Spectroscopy available at: <http://www.analyticalspectroscopy.net/ap3-11.htm>)

The main advantages of DRIFTS spectroscopy are: fast measurement of powdered samples, minimal or no sample preparation, ability to detect minor components, ability to analyze solid, liquid or gaseous samples, is one of the most suitable method for the examination of rough and opaque samples, high sensitivity, high versatility, capability of performing the measurements under real life conditions.

In the environmental studies diffuse reflectance Fourier transform infrared (DRIFTS) spectroscopy is considered an alternative methodology for the quantitative analysis of nitrate in environmental samples (Verma and Deb, 2007a). It is considered a new, rapid and precise analytical method for the determination of the submicrogram levels of nitrate (NO_3^-) in environmental samples like soil, dry deposit samples, and coarse and fine aerosol particles. The DRIFTS method is a feasible nondestructive and time saving method for quantitative analyses of nitrate in soil, dry deposit and aerosol samples.

It is well known that soil can act as sinks as well as sources of carbon. A major fraction of carbon in soils is contained in the soil organic matter (SOM). It contributes to plant growth through its effect on the physical, chemical, and biological properties of the soil. Characterization of soil organic matter (SOM) is important for determining the overall quality of soils. For this DRIFTS spectroscopy can be used. This method only takes a few minutes, and is much faster than fractionating of soil samples using chemical and physical methods and determining the carbon contents of the fractions (Zimmermann *et al.*, 2007). In another study, Rumpel and coworkers tested diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy in combination with multivariate data analysis [partial least squares (PLS)] as a rapid and inexpensive means of quantifying the lignite contribution to the total organic carbon (TOC) content of soil samples (Rumpel *et al.*, 2001). DRIFTS spectroscopy is also considered to be one of the most sensitive infrared technique to analyze humic substances (Ding *et al.*, 2000). Studies by Ding and coworkers demonstrate that both DRIFT and ^{13}C NMR are suitable for examining the effect of tillage on the distribution of light fraction in soil profile (Ding *et al.*, 2002). More recently Ding and coworkers examined the effect of cover crops on the chemical and structural composition of SOM using chemical and DRIFT spectroscopic analysis. From this study it was concluded that both organic carbon (OC) and light fraction (LF) contents were higher in soils under cover crop treatments with and without fertilizer N than soils with no cover crop. Thus cover crops had a profound

influence on the SOM and LF characteristics (Ding *et al.*, 2006). In other study Janik and coworkers (1995) showed that the use of diffuse reflectance infrared Fourier-transformed Spectroscopy (DRIFT) in combination with partial least squares algorithm (PLS) is a fast and low-cost method to predict carbon content and other soil properties such as clay content and pH. Zimmermann and coworkers evaluated the possibility of using of DRIFT-spectroscopy to estimate the soil organic matter content in soil samples from sites across Switzerland (Zimmermann *et al.*, 2004). It was concluded that DRIFT spectroscopy is a tool to predict changes in soil organic matter contents in agricultural soils resulting from changes in soil management. In other study Nault and coworkers used DRIFT spectroscopy to compare changes in organic chemistry of 10 species of foliar litter undergoing *in situ* decomposition for 1 to 12 years at four forested sites representing a range of climates in Canada (Nault *et al.*, 2009). This study demonstrated that DRIFT spectroscopy is a fast and simple analysis method for analyzing large numbers of samples to give good estimates of litter chemistry. Thus DRIFTS spectroscopy is considered a more faster technique to analyse the composition and the dynamics of organic matter in solis compared with FTIR spectroscopy (Tremblay and Gagné, 2002; Spaccini *et al.*, 2001).

Earth's atmosphere contains aerosols of various types and concentrations divided in: anthropogenic products, natural organic and inorganic products. The negative effects of these components refers to interaction with Earth's radiation budget and climate. In direct way aerosols scatter sunlight directly back into space, and indirect aerosols in the lower atmosphere can modify the size of cloud particles, and consequently changing the way in which clouds reflect and absorb sunlight. Aerosols act also as sites for chemical reactions to take place. As an exemple of these kind of reactions can be mentioned destruction of stratospheric ozone. The inorganic component of aerosols consist of inorganic salts (e.g. sulfate, nitrate, and ammonium). The most used method for analyzing these salts is ion chromatography (IC) (Chen *et al.*, 2003). The main disadvantages of this method are: time required for sample preparation and analysis that is up to 1 week, and the fact that this method is a destructive method of analysis. IR spectroscopy offers a simple and rapid alternative to IC for aerosols analysing, but it is imprecise and therefore only semi-quantitative. Advances in optics and detectors have allowed the development of more precise IR spectroscopy methods such as FTIR and DRIFT spectroscopy. FTIR spectroscopy was employed to determine on-site chemical composition of aerosol samples and to investigate the relationship between particle compositions and diameters (Tsai and Kuo, 2006). DRIFTS spectroscopy was used for quantitative analysis of atmospheric aerosols (Tsai and Kuo, 2006). The components of aerosols determined quantitative in area investigated were SO_4^{2-} , NO_3^- and NH_4^+ . Compared with IC method, the DRIFT spectroscopy is a non-destructive, and quantitative method for aerosols analyzing.

Nitrogen dioxide, one of the key participants in atmospheric chemistry has been determined using DRIFT spectroscopy. Compared with other methods for nitrogen dioxide determination such as chemiluminiscence and fluorescence method that are multi-reagent procedure with the increased possibility of the experimental errors, the DRIFTS spectroscopy involves using NaOH-sodium arsenite solution as an absorbing reagent.

Another advantage of DRIFTS spectroscopy is that it can determine ambient nitrogen dioxide, in terms of nitrite, at submicrogram level (Verma *et al.*, 2008).

The feasibility of employing diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy as a sensitive tool in the submicrogram level determination of sulphate (SO_4^{2-}) was checked by Verma and Deb in a study performed in 2007. The level of sulphate in environmental samples analysed like coarse and fine aerosol particles, dry deposits and soil was in range of ppb. The DRS-FTIR absorption spectrum of these real samples are presented in Figure 7.

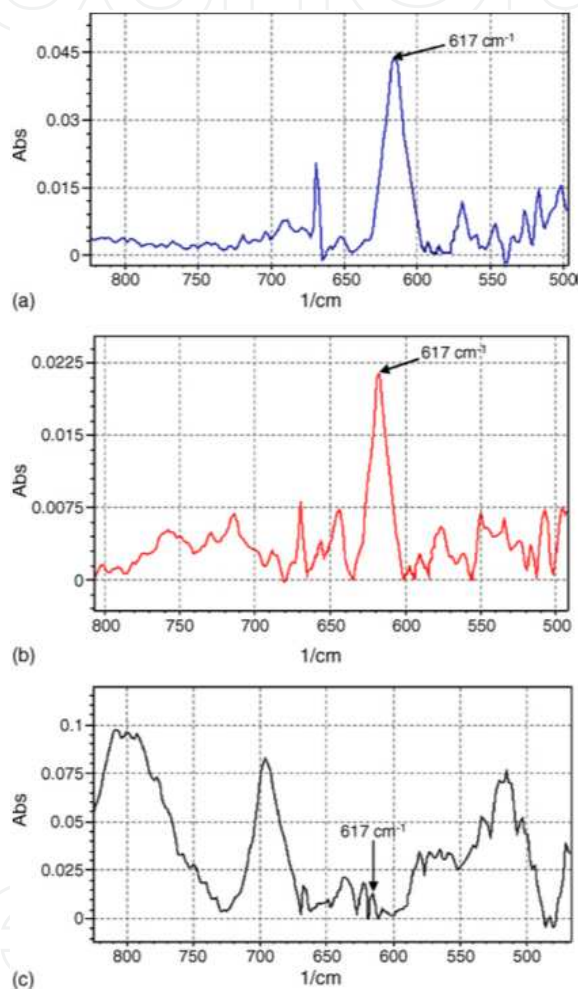


Figure 7. DRS-FTIR absorption spectrum of: (a) aerosol samples; (b) dry deposition sample; (c) soil sample (from Verma and Deb, 2007b used with permission (originally published in Talanta, doi:10.1016/j.talanta.2006.07.056))

For all real samples analyzed two-point baseline corrections were performed to obtain the quantitative absorption peak for sulphate at around 617 cm^{-1} (Verma and Deb, 2007b). The DRIFT method involved in this study did not require pretreatment of samples being reagent less, nondestructive, very fast, repeatable, and accurate and has high sample throughput value (Verma and Deb, 2007b). On the same topic Ma and coworkers have published paper entitled, "A case study of Asian dust storm particles: Chemical composition, reactivity to

SO₂ and hygroscopic properties". This paper presents a study about characterization of Asian dust storm particles using multiple analysis methods such as SEM-EDS, XPS, FT-IR, BET, TPD/mass and Knudsen cell/mass. The atmospheric dust particles are responsible by absorption and scattering of solar radiation and indirect acting as cloud condensation nucleus. The composition, source and size distribution of dust storm are important in predicting their impacts on climate and atmospheric environment. The dust particles can react with gaseous components or pollutants from the atmosphere such as sulfur dioxide. Thus numerous studies were performed to determine the role of dust in SO₂ chemistry (Prince *et al.*, 2007; Ullerstam *et al.*, 2002, 2003; Zhang *et al.*, 2006; Ma *et al.*, 2012b). The morphology, elemental fraction, source distribution, true uptake coefficient for SO₂ and hygroscopic behavior were studied. The major components of Asian dust storm particles were aluminosilicate, SiO₂ and CaCO₃ mixed with some organic and nitrate compounds. The particles analyzed by Ma and coworkers are coming from anthropogenic sources and local sources after long transportation. Between SO₂ uptake coefficient and mass was established a linear dependence. Consequently DRIFTS and FTIR spectroscopy combined with other analytical methods will provide important information about the effects of dust storm particle on the atmosphere (Ma *et al.*, 2012b).

One of the most important application of DRIFTS spectroscopy is to investigate sorption-uptake processes on different materials in order to reduce the impact of pollutants. Thus Valyon and coworkers studied N₂ and O₂ sorption on synthetic and natural mordenites, and on molecular sieves 4A, 5A and 13X using DRIFT spectroscopy (Valyon *et al.*, 2003). Kazansky and coworkers used DRIFTS spectroscopy to study sorption of N₂, both pure and in mixtures with oxygen, O₂, by zeolites NaLSX and NaZSM-5 (Kazansky *et al.*, 2004). Llewellyn and Theocharis studied carbon dioxide adsorption on silicate using DRIFTS spectroscopy (Llewellyn and Theocharis, 1991). Heterogeneous oxidation of gas-phase SO₂ on different iron oxides was investigated *in situ* using a White cell coupled with Fourier transform infrared spectroscopy (FTIR) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) by Fu and coworkers (Fu *et al.*, 2007). From this study it can be concluded that adsorbed SO₂ could be oxidized on the surface of most iron oxides to form a surface sulfate species at ambient temperature, and the surface hydroxyl species on the iron oxides was the key reactant for the heterogeneous oxidation (Fu *et al.*, 2007). Heterogeneous reaction of NO₂ with carbonaceous materials (commercial carbon black, spark generator soot, Diesel soot from passenger car and high-purity graphite) at elevated temperature (400°C) was studied using DRIFT spectroscopy. Different infrared signals appear when NO₂ is adsorbed either on aliphatic or graphitic domains of soot (Muckenhuber and Grothe, 2007).

Gas sensors are playing an important role in the detection of toxic pollutants such as CO, H₂S, NO_x, SO₂, and inflammable gases such as hydrocarbons, H₂, CH₄. Diffuse Reflectance Infrared (DRIFT) spectroscopy has been used to characterize them. Thus, the studies performed by Harbeck in his Dissertation have shown that thick film sensors can easily be characterized in different working conditions (at elevated temperatures, in the presence of humidity) using Diffuse Reflectance Infrared (DRIFT) spectroscopy. He characterized un-

doped and Pd-doped SnO₂ sensor surfaces at different temperatures using two different methods in parallel: DRIFT spectroscopy and electrical measurements. Simultaneous recording of the DRIFT spectra and the sensor resistance helped him to clarify the role of the individual surface species in the sensing mechanism. The results of his work show that several reactions take place in the presence of CO depending both on temperature and humidity. It was found that all surface species are involved in the reactions and it is supposed that parallel and consecutive CO reactions take place on the surface (Harbeck, 2005).

DRIFT spectroscopy is also suitable for application to studies of surface phenomena and large specific surface materials such as the sensing layers. In this purpose Bârsan and Weimar investigated the effect of water vapour in CO sensing by using Pd doped SnO₂ sensors obtained using thick film technology as an example of the basic understanding of sensing mechanisms applied to sensors. The results obtained show that all parts of the sensor (sensing layer, electrodes, substrate) have influence to the gas detection and their role has to be taken into consideration when one attempts to understand how a sensor works (Bârsan and Weimar, 2003).

All the examples mentioned above show the importance of DRIFT spectroscopy in analyzing of environmental samples either liquid, solid or gaseous.

5. Open Path FT-IR spectroscopy in environmental studies

The open-path FT-IR Spectroscopy is conventionally used for monitoring gaseous air pollutants, but can also be used for monitoring both the gaseous or particulate air pollutants. The principle of function is the same with classical FTIR Spectroscopy, except the cell into the sample will be injected which it is extended to open atmosphere (Minnich and Scotto, 1999). In this technique the infrared light sources can be either natural solar light, or light coming from a heated filament situated behind the target gas. The infrared signal passes through a sample and chemical vapors present in sample will absorb the infrared energy at different wavelengths. All compounds in the vapor will give unique fingerprints of absorbance features which will be compared to a library of spectra on the computer. This comparison will be useful to identify and quatify in real time.

The advantages of open-path FT-IR Spectroscopy include: no sample collection, handling ar preparation is necessary; good sensivity for certain species; real time data collection and reporting; ability to simultaneously and continuously analyze many compounds; remote, long-path measurements; *in situ* application; stored data can be used and re-analyzed for a divers range of volatile or non-volatile compounds; cost effectiveness (Marshall *et al.*, 1994).

The main disadvantage of OP-FTIR is considered to be the fact that it can be applied only to the cases with high concentrations of gases such as stack measurement, landfill measurement, and fence-line monitoring (Hong *et al.*, 2004). Thus Perry *et al.* (1995) and Tso and Chang applied OP-FTIR to determine the VOC and ammonia concentrations in industrial areas, the concentration of pollutants being in this area in the level of 0.1 ppm

(Perry *et al.*, 1995; Tso and Chang, 1996). Childers *et al.* applied OP-FTIR spectroscopy for the measurement of ammonia, methane, carbon dioxide, and nitrous oxide in a concentrated swine production facility. The pollutants concentration was in the ranges 0.1 – 100 ppm. The results have led authors to conclude that the confinement barns was the significant source of ammonia emission, and the waste treatment lagoon was the major source of methane (Childers *et al.*, 2001). A similar research was performed by Hedge *et al.* in order to monitor methane and carbon dioxide emitted from a landfill in northern of Taiwan (Hedge *et al.*, 2003), and Thorn *et al.* used OP-FTIR to measure phosphine concentrations in the air surrounding the large fumigated structures of a tobacco warehouse (Thorn *et al.*, 2001). OP-FTIR was used by Harris and coworkers to monitor ammonia and methane emissions from animal housing and waste lagoons due to the ability to detect multiple compounds simultaneously (Harris *et al.*, 2007).

Levine and Russwurm described in an article the use of the open-path FT-IR Spectroscopy in remote sensing of airborne gas and vapor contaminants (Levine and Russwurm, 1994). Applying open-path Fourier transform spectroscopy for measuring aerosols was described by Wu and coworkers (Wu *et al.*, 2007).

Air monitoring during site remediation using open-path FTIR Spectroscopy was reported by Minnich and Scotto (Minnich and Scotto, 1999), and monitoring trace gases from aircraft emissions using the same technique was reported by Haschberger (Haschberger, 1994).

The use of OP-FTIR spectroscopy for identification of fugitive organic compound (VOC) emission sources and to estimate emission rates at an Air Force base in United States was described by Hall (Hall, 2004). Galle *et al.* have demonstrated advantages of FTIR over traditional point-measurement methods by providing detection over large sampling areas (Galle *et al.*, 2001).

OP-FTIR was successfully applied by Walter *et al.*, and Kagann *et al.* for the measurements of air quality criteria pollutants such as ozone, carbon dioxide, sulfur dioxide, and nitrogen dioxide in ambient air (Walter *et al.*, 1999; Kagan *et al.*, 1999). Grutter and coworkers used OP-FTIR spectroscopy to measure trace gases over Mexico City. This was the first report on the concentration profiles of acetylene, ethylene, ethane, propane, and methane in this region. Specific correlation between the profiles and wind direction were made in order to determine the main sources that contribute to these profiles (Grutter *et al.*, 2003).

A comparison between different analysis techniques applied to ozone and carbon monoxide detection was made by Briz and coworkers. They compared classical least-squares (CLS) procedures with line-by-line method (SFIT) to analyze OP-FTIR spectra and concluded that discrepancies observed in CLS-based methods were induced by the experimental background reference spectrum, and SFIT results agreement well with the standard extractive methods (Briz *et al.*, 2007). The same author together with other coworkers proposed a new method for calculating emission rates from livestock buildings applying Open-Path FTIR spectroscopy (Briz *et al.*, 2009). The method was applied in a cow shed in the surroundings of La Laguna, Tenerife Island (Spain), and results obtained revealed that the

livestock building behaves such as an accumulation chamber, and methane emission factor was lower than the proposed by Emission Inventory (Briz *et al.*, 2009).

As was described by Lin and coworkers an open-path Fourier transform infrared spectroscopy system can be used for monitoring of VOCs in industrial medium. They used this system to monitor VOCs emissions from a paint manufacturing plant, and they determined seven VOCs in ambient environment. The same system was also used to determine the VOCs in a petrochemical complex. The results obtained were correlated with meteorological data and were effective in the depiction of spatial variations in identifying sources of VOC emissions. They also mentioned another important advantage of OP-FTIR spectroscopy such as the ability to obtain more comprehensive data than by using the traditional multiple, single-point monitoring methods. It can be concluded that OP-FTIR can be useful in both industrial hygiene and environmental air pollutant regulatory enforcement (Lin *et al.*, 2008).

Ammonia, CO, methane, ethane, ethylene, acetylene, propylene, cyclohexane, and O-xylene were identified as major emissions in a coke processing area from Taiwan using OP-FTIR system by Lin and coworkers (Lin *et al.*, 2007). Main gaseous byproducts (CO, CO₂, CH₄ and NH₃) of thermal degradation (pyrolysis) of biomass in forest fires were determined accurately using OP-FTIR. The results obtained in this study can help to improve the modelling of the pyrolysis processes in physical-based models for predicting forest fire behaviour (de Castro *et al.*, 2007). An other research in this field was performed by Burling and coworkers who measured trace gas emissions from biomass burning of fuel types from the southeastern and southwestern United States (Burling *et al.*, 2010) with the help of OP-FTIR. The authors detected and quantified 19 gas-phase species in these fires: CO₂, CO, CH₄, C₂H₂, C₂H₄, C₃H₆, HCHO, HCOOH, CH₃OH, CH₃COOH, furan, H₂O, NO, NO₂, HONO, NH₃, HCN, HCl, and SO₂. The emission factors depend on the fuel composition and fuel types.

All the advantages of OP-FTIR spectroscopy and all the studies mentioned above demonstrate the utility of OP-FTIR in measuring and monitoring of atmospheric gases. This technique has increasingly been accepted by different environmental agencies as a tool in the measurement and the monitoring of the atmospheric gases (Russwurm and Childers, 1996; Russwurm, 1999).

6. Conclusion

All these presented above show the importance of FTIR spectroscopy in environmental studies. The major advantages of this technique are: real time data collection and reporting, excellent sample-to-sample reproducibility, enhanced frequency accuracy, high signal-to-noise ratios, superior sensitivity, analytical performance. In addition, the measurement is very rapid so that a large number of samples can be analyzed. Consequently FTIR spectroscopy coupled with other techniques is widely used to determine the nature of pollutants (gaseous, liquid or solid), to monitor environment, to assess the impact of pollution on health and environment, to determine the level of decontamination processes.

The modern techniques such as attenuated total reflection FTIR (ATR-FTIR), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), but also traditional transmission FTIR can be used for such studies according to the information needed, the physical form of the sample, and the time required for the sample preparation.

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