



## FOURIER TRANSFORM INFRARED SPECTROSCOPIC CHARACTERIZATION FOR DETECTING SOIL MINERALS AND TOXICOLOGICAL EFFECTS OF SELECTED MINERALS IN SOILS

RACHNA GARG\*

MIET, AMBALA (Haryana) INDIA

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### ABSTRACT

Infrared (IR) spectrometry is the study of the interaction of infrared light with matter. Infrared spectroscopy is also useful in measuring the degree of polymerization in polymer manufacture. Changes in the character or quantity of a particular bond are assessed by measuring at a specific frequency over time. Modern research instruments can take infrared measurements across the range of interest as frequently as 32 times a second. This can be done whilst simultaneous measurements are made using other techniques. A number of mathematical equations are employed to understand the kinetics of potassium release from soils<sup>1</sup>. The present study is therefore, undertaken to investigate retention behavior of mineralogically different soils of India, with particular emphasis on the effect of minor minerals.

**Key words:** Infrared spectroscopy, Fourier transform infrared (FTIR) spectrometer, Vibrational modes, Kaolinization, Pulse Sequence.

### INTRODUCTION

#### Infrared spectroscopy

Infrared spectroscopy<sup>2</sup> (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The higher-energy near-IR, approximately 14000–4000 cm<sup>-1</sup> (0.8–2.5 μm wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately 4000–400 cm<sup>-1</sup> (2.5–25 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately 400–10 cm<sup>-1</sup> (25–1000 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The names and classifications of these sub regions are conventions, and are only loosely based on the relative molecular or electromagnetic properties.

## Concept

Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. The energies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling.

In particular, in the Born–Oppenheimer and harmonic approximations, i.e. when the molecular Hamiltonian corresponding to the electronic ground state can be approximated by a harmonic oscillator in the neighborhood of the equilibrium molecular geometry, the resonant frequencies are determined by the normal modes corresponding to the molecular electronic ground state potential energy surface. Nevertheless, the resonant frequencies can be in a first approach related to the strength of the bond, and the mass of the atoms at either end of it. Thus, the frequency of the vibrations can be associated with a particular bond type.

## Number of vibrational modes

In order for a vibrational mode in a molecule to be "IR active," it must be associated with changes in the dipole. A permanent dipole is not necessary, as the rule requires only a change in dipole moment.

A molecule can vibrate in many ways, and each way is called a vibrational mode. For molecules with  $N$  atoms in them, linear molecules have  $3N - 5$  degrees of vibrational modes, whereas nonlinear molecules have  $3N - 6$  degrees of vibrational modes (also called vibrational degrees of freedom). As an example  $H_2O$ , a non-linear molecule, will have  $3 \times 3 - 6 = 3$  degrees of vibrational freedom, or modes.

Simple diatomic molecules have only one bond and only one vibrational band. If the molecule is symmetrical, e.g.  $N_2$ , the band is not observed in the IR spectrum, but only in the Raman spectrum. Asymmetrical diatomic molecules, e.g.  $CO$ , absorb in the IR spectrum. More complex molecules have many bonds, and their vibrational spectra are correspondingly more complex, i.e. big molecules have many peaks in their IR spectra.

The atoms in a  $CH_2$  group, commonly found in organic compounds, can vibrate in six different ways: symmetric and anti symmetric stretching, scissoring, rocking, wagging and twisting.

## Literature review

Recent assessments of the ecosystem service functions of soils and their importance for global sustainability underscore the importance of sustainable management of soil resources for present and future societal welfare<sup>3</sup>. However, a fundamental challenge to managing soils, especially in Africa, is the lack of appropriate approaches and tools for reliable case definition of poor or degraded soils that would permit diagnostic screening for spatially explicit targeting of management interventions. The dynamics of soil quality change is well documented. It is observed that agricultural land continues to lose carbon at successively lower rates with time, approximating a low steady state after 30 to 50 years conceptualizing a nonlinear trajectory for changes in ecosystem carbon stocks after disturbance or degradation. It is illustrated that changes in exchangeable K over time when no amendments are applied can be depicted theoretically as a nonlinear decline trajectory<sup>4</sup>. At the landscape level, the existence of multiple soil condition states (fertility gradients) present a great opportunity for the development of spatially explicit case definitions for poor soils. Using multiple soil condition states as a basis for case definition to define degraded and non-degraded soils is contingent upon portable testing and large area diagnostic screening methods that are sensitive to

management-induced differences in soil attributes. Soil testing using conventional laboratory methods carry prohibitive costs (both time and effort) and hence not suitable for rapid testing and diagnostic screening at large spatial scales. Furthermore, soil is a complex, multivariate assemblage of correlated and interacting constituents that is simultaneously exposed to degradation. Effective management of soil resources is therefore unlikely to be successful if based on individual soil property dynamics studied using conventional laboratory analytical methods<sup>5-6</sup>. There is need for novel analytical methods that recognize that soil is a system comprised of correlated constituents whose dynamics must be monitored simultaneously. Recent advances in soil analysis demonstrate that diffuse reflectance spectroscopy is a robust analytical technique suited for rapid and simultaneous analysis of biological, chemical and physical attributes of soil. Using wavelength ranges in the visible (VIS, 0.4–0.7  $\mu\text{m}$ ), the near infrared (NIR, 0.7–2.5  $\mu\text{m}$ ) and the mid infrared (MIR, 2.5–25  $\mu\text{m}$ ) researchers have successfully predicted several soil fertility parameters including organic carbon (SOC), inorganic carbon, total nitrogen (TN), cation exchange capacity (CEC), pH, potassium (K), magnesium (Mg), calcium (Ca), zinc (Zn), iron (Fe), and manganese (Mn) with various levels of prediction accuracy<sup>7</sup>. The potential of diffuse reflectance spectroscopy as a robust technique for rapid and simultaneous prediction of a suit of soil properties is clear. However, the challenge is to move the application of spectroscopy toward a diagnostic screening tool that can aid the development of reliable spectral case definition to characterize soil health for agricultural and environmental management at the farm and landscape level. This pointed to the potential of soil spectroscopy for risk based assessment of the effects of land use and land management on soil condition<sup>8</sup>. A spectral screening test was used to “harden” a case definition of soil erosion status in Kenya based on subjective visual field assessments<sup>9</sup>. The spectral fertility index and used it to investigate effects of land use and time since forest conversion on soil condition in Madagascar<sup>10</sup>. Such approaches need validation more widely, especially to test the application of reflectance spectroscopy for detection of management-induced changes in soil condition and for case definition of poor or degraded soils. In this study we apply a proportional odds logistic regression model to uncover the inherent spectral structure of soils drawn from a tropical forest-cropland chronosequence in Kenya. Discriminant analysis was used to compute linear mathematical functions to classify new, unclassified data, into the respective soil condition classes<sup>11-12</sup>. This paper proposes a framework for the use of infrared spectroscopy as a tool for:

(i) Building spectrally based soil condition classes; (ii) Spectral case definition of poor soils, leading to case classification of unknown samples; and (iii) Estimating the probability of a soil sample belonging in a soil condition class (corresponding to the decision nodes illustrated in Fig. 1). The objectives of this study were to: (i) Evaluate the ability of near infrared spectroscopy to detect changes in soil properties across a forest-cropland chronosequence; and (ii) Develop a heuristic scheme for the application of infrared spectroscopy as a tool for case definition and diagnostic screening of soil condition for agricultural and environmental management.

### **Need of the study**

Infrared spectroscopy is a simple and reliable technique widely used in both organic and inorganic chemistry, in research and industry. It is used in quality control, dynamic measurement, and monitoring applications such as the long-term unattended measurement of CO<sub>2</sub> concentrations in greenhouses and growth chambers by infrared gas analyzers.

It is also used in forensic analysis in both criminal and civil cases, for example in identifying polymer degradation. It can be used in detecting how much alcohol is in the blood of a suspected drunk driver measured as 1/10,000 g/mL = 100  $\mu\text{g/mL}$ .

A useful way of analyzing solid samples without the need for cutting samples uses ATR or attenuated total reflectance spectroscopy. Using this approach, samples are pressed against the face of a single crystal. The infrared radiation passes through the crystal and only interacts with the sample at the interface between the two materials.

With increasing technology in computer filtering and manipulation of the results, samples in solution can now be measured accurately (water produces a broad absorbance across the range of interest, and thus renders the spectra unreadable without this computer treatment).

Some instruments will also automatically tell you what substance is being measured from a store of thousands of reference spectra held in storage.

Infrared spectroscopy is also useful in measuring the degree of polymerization in polymer manufacture. Changes in the character or quantity of a particular bond are assessed by measuring at a specific frequency over time. Modern research instruments can take infrared measurements across the range of interest as frequently as 32 times a second. This can be done whilst simultaneous measurements are made using other techniques. This makes the observations of chemical reactions and processes quicker and more accurate.

### **Two-dimensional IR**

Two-dimensional infrared correlation spectroscopy analysis is the application of 2D correlation analysis on infrared spectra. By extending the spectral information of a perturbed sample, spectral analysis is simplified and resolution is enhanced. The 2D synchronous and 2D asynchronous spectra represent a graphical overview of the spectral changes due to a perturbation (such as a changing concentration or changing temperature) as well as the relationship between the spectral changes at two different wave numbers.

Pulse Sequence used to obtain a two-dimensional Fourier transform infrared spectrum. The time period  $\tau_1$  is usually referred to as the coherence time and the second time period  $\tau_2$  is known as the waiting time. The excitation frequency is obtained by Fourier transforming along the  $\tau_1$  axis.

Nonlinear two-dimensional infrared spectroscopy is the infrared version of correlation spectroscopy. Nonlinear two-dimensional infrared spectroscopy is a technique that has become available with the development of femtosecond infrared laser pulses. In this experiment, first a set of pump pulses are applied to the sample. This is followed by a waiting time, wherein the system is allowed to relax. The typical waiting time lasts from zero to several picoseconds, and the duration can be controlled with a resolution of tens of femtoseconds. A probe pulse is then applied resulting in the emission of a signal from the sample. The nonlinear two-dimensional infrared spectrum is a two-dimensional correlation plot of the frequency  $\omega_1$  that was excited by the initial pump pulses and the frequency  $\omega_3$  excited by the probe pulse after the waiting time. This allows the observation of coupling between different vibrational modes; because of its extremely high time resolution, it can be used to monitor molecular dynamics on a picosecond timescale. It is still a largely unexplored technique and is becoming increasingly popular for fundamental research.

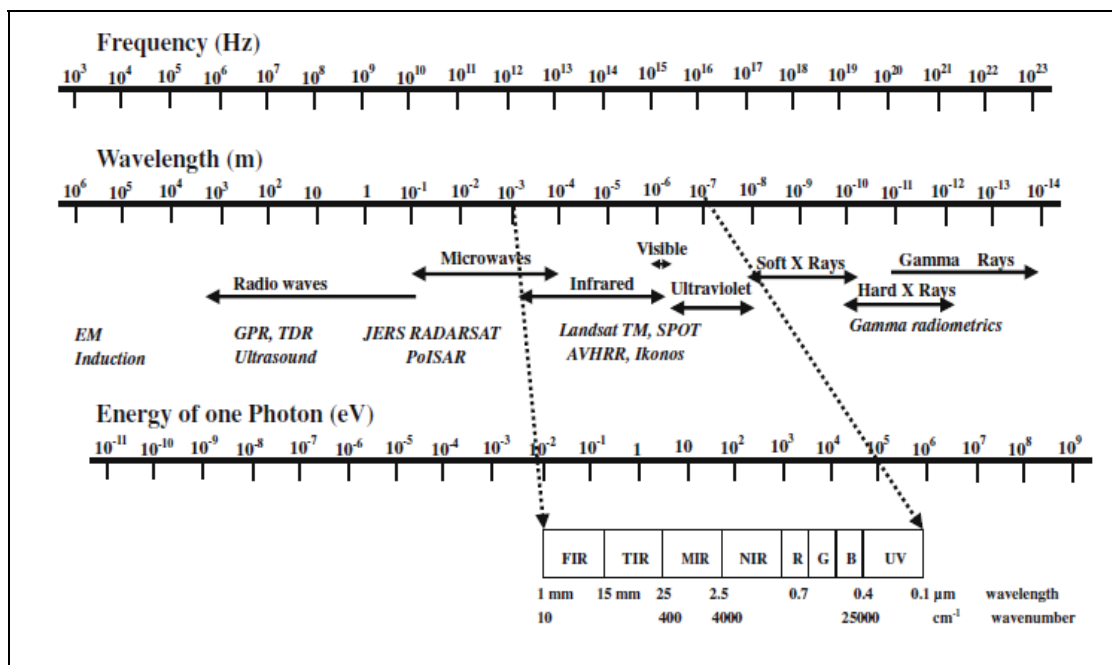
As with two-dimensional nuclear magnetic resonance (2 DNMR) spectroscopy, this technique spreads the spectrum in two dimensions and allows for the observation of cross peaks that contain information on the coupling between different modes. In contrast to 2 DNMR, nonlinear two-dimensional infrared spectroscopy also involves the excitation to overtones. These excitations result in excited state absorption peaks located below the diagonal and cross peaks. In 2 DNMR, two distinct techniques, COSY and NOESY, are frequently used. The cross peaks in the first are related to the scalar coupling, while in the

latter they are related to the spin transfer between different nuclei. In nonlinear two-dimensional infrared spectroscopy, analogs have been drawn to these 2 DNMR techniques. Nonlinear two-dimensional infrared spectroscopy with zero waiting time corresponds to COSY, and nonlinear two-dimensional infrared spectroscopy with finite waiting time allowing vibrational population transfer corresponds to NOESY. The COSY variant of nonlinear two-dimensional infrared spectroscopy has been used for determination of the secondary structure content proteins.

### Scope of the study

#### Mid-infrared techniques commonly used for soil analysis

Infrared (IR) spectroscopy is based on the interaction of molecules with electromagnetic energy in the infrared spectral region, which is in the wavelength range of 0.8-1000  $\mu\text{m}$ . This IR range is commonly divided into four regions, labeled near-, mid-, thermal- and far infrared, respectively (Figure 1). The particularity of the mid-infrared range is that it includes the so-called fundamental vibrations of the molecules. When a molecule absorbs IR radiation at frequencies matching that of its own molecular vibrations, it results in an increase of the amplitude of the vibrations at these frequencies. Since each frequency corresponds to a given amount of energy and a specific molecular motion (e.g. stretching, bending or contracting of chemical bonds), the mid-IR spectrum can reveal the kind of molecular motions and bonds (functional groups) that are present in the molecule and hence can serve as a unique fingerprint of a specific compound. Furthermore, most functional groups have characteristic IR absorption bands that do not change much from one compound to another. By comparison, the near-infrared range is dominated by overtone and combinations of these fundamental vibrations, which makes the interpretation of the NIR spectra much more difficult.



**Fig. 1: The electromagnetic spectrum with emphasis on the ultra-violet – infrared range  
Reproduced from Viscarra Rossel et al. (2006)**

Nowadays, Fourier Transform Infrared (FTIR) is the preferred method for mid-IR spectroscopy as it provides quantitative information in a rapid and accurate fashion. A typical FTIR spectrometer obtains an infrared spectrum by collecting the interferogram of a sample signal, which contains all the infrared

frequencies, applies the Fourier transform to the digitized signal, and outputs the spectrum. Such a FTIR spectrometer relies on an interferometer, which splits to radiation beam into two beams that are recombined after a path difference has been introduced<sup>13</sup>. The most common interferometer is the so-called Michelson interferometer, which consists of a beam splitter located between two perpendicular mirrors, one of which can move along an axis perpendicular to its plane. At the beam splitter, the radiation beam from the infrared source is partially reflected to the fixed mirror and partially transmitted to the moveable mirror. The moveable mirror is moved in a highly controlled fashion to create the path difference between the two beams. After the beams return to the beam splitter, they interfere and are again partially transmitted and partially reflected to the detector. Due to the effect of the interference, the intensity of each beam passing to the detector and returning to the source depends on the path-length difference between the two beams. The two beams can undergo constructive interference, destructive interference or a combination of both, depending on the path-length difference. Constructive interference, which yields a maximum detector signal, occurs when the optical path difference is an integer multiple of the wavelength. The variation in the energy that reaches the detector as a function of the path difference yields the interferogram, which is the integral of all interference patterns produced by each wavelength. The detected interferogram can not be interpreted directly, but has to be "decoded" using the well-known Fourier Transformation (Griffiths&de Haseth1986). Fourier transform is typically thought of as decomposing a signal into its component frequencies and their amplitudes. The Fourier transform is an integral transform that re expresses a function in terms of sinusoidal basis functions, i.e. as a sum or integral of sinusoidal functions multiplied by some coefficients ("amplitudes"). The general idea is that a multiplication of the input waveform of unknown amplitude and frequency (interferogram signals) by a known reference frequency of unity amplitude (the analyzing wave) can give us the unknown amplitude and original frequency. Thus, by using a frequency-adjustable analyzing wave, each digitized point of the interferogram can be transformed from the time (or optical retardation) domain to the frequency domain, which results in the IR spectrum. When a single interferogram is thus Fourier-transformed, a so called single-beam spectrum is generated, which is the raw detector response versus the wavelength. In order to produce the absorption spectrum of a sample, the sample single beam spectrum must be normalized against a background spectrum taken with no sample in the beam path. The absorption spectrum can be presented equivalently as a transmittance ( $T = I/I_0$ ) or absorbance ( $A = \log_{10} I_0/I$ ) spectrum, where  $I$  is the intensity measured with the sample in the beam and  $I_0$  is the intensity measured from the background spectrum. Direct transmittance is the oldest and most straightforward spectroscopic technique, which is based on the absorption of the IR radiation as it passes through the sample. Clearly, this technique is applicable only to samples that do not absorb all the incoming IR energy and are sufficiently transparent in this spectral range. For highly absorbent samples, such as soils, it is necessary to prepare a pellet that embeds the soil sample in a transparent matrix, most usually KBr. The pellet preparation involves grounding 2-3 mg of soil with ~1 g of KBr using a mortar and pestle and using a hydraulic press and die to create a thin, IR transparent disk. The main advantage of this technique is that it yields very clear and information-rich signals. Its main disadvantages are the lengthy preparation required to prepare the pellets and the fact that it is difficult to obtain quantitative results. Also, since only a few mg of soils are used for the preparation of each pellet, the resulting spectrum may not be representative of the bulk soil. For these reasons, transmittance measurements are rather rarely used in soil analysis and the reflectance and photoacoustic methods are preferred.

### **Physical and chemical properties of selected minerals**

#### **Bentonite**

Bentonite feels greasy and soap-like to the touch<sup>14</sup>. Freshly exposed bentonite is white to pale green or blue and, with exposure, darkens in time to yellow, red, or brown. The special properties of bentonite are an ability to form thixotropic gels with water, an ability to absorb large quantities of water with an accompanying increase in volume of as much as 12–15 times its dry bulk, and a high cation exchange

capacity. Substitutions of silicon by cations produce an excess of negative charges in the lattice, which is balanced by cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) in the interlayer space. These cations are exchangeable due to their loose binding and, together with broken bonds (approximately 20% of exchange capacity), give montmorillonite a rather high (about 100 meq/100 g) cation exchange capacity, which is little affected by particle size. This cation exchange capacity allows the mineral to bind not only inorganic cations such as caesium but also organic cations such as the herbicides diquat, paraquat<sup>15-16</sup>, and even bio-organic particles such as rheoviruses and proteins<sup>17-18</sup>, which appear to act as cations. Variation in exchangeable cations affects the maximum amount of water uptake and swelling. These are greatest with sodium and least with potassium and magnesium. Interstitial water held in the clay mineral lattice is an additional major factor controlling the plastic, bonding, compaction, suspension, and other properties of montmorillonite group clay minerals. Within each crystal, the water layer appears to be an integral number of molecules in thickness. Physical characteristics of bentonite are affected by whether the montmorillonite composing it has water layers of uniform thickness or whether it is a mixture of hydrates with water layers of more than one thickness. Loss of absorbed water from between the silicate sheets takes place at relatively low temperatures (100–200°C). Loss of structural water (i.e., the hydroxyls) begins at 450–500°C and is complete at 600–750°C. Further heating to 800–900°C disintegrates the crystal lattice and produces a variety of phases, such as mullite, cristobalite, and cordierite, depending on initial composition and structure. The ability of montmorillonite to rapidly take up water and expand is lost after heating to a critical temperature, which ranges from 105 to 390°C, depending on the composition of the exchangeable cations. The ability to take up water affects the utilization and commercial value of bentonite. Montmorillonite clay minerals occur as minute particles, which, under electron microscopy, appear as aggregates of irregular or hexagonal flakes or, less commonly, of thin laths<sup>19</sup>. Differences in substitution affect and in some cases control morphology

### **Kaolin**

Kaolinite, the main constituent of kaolin, is formed by rock weathering. It is white, greyish-white, or slightly colored. It is made up of tiny, thin, pseudo hexagonal, flexible sheets of triclinic crystal with a diameter of 0.2–12  $\mu\text{m}$ . It has a density of 2.1–2.6  $\text{g}/\text{cm}^3$ . The cation exchange capacity of kaolinite is considerably less than that of montmorillonite, in the order of 2–10 meq/100 g, depending on the particle size, but the rate of the exchange reaction is rapid, almost instantaneous. Kaolinite adsorbs small molecular substances such as lecithin, quinoline, paraquat, and diquat, but also proteins, poly acrylonitrile, bacteria, and viruses<sup>20</sup>. The adsorbed material can be easily removed from the particles because adsorption is limited to the surface of the particles (planes, edges), unlike the case with montmorillonite, where the adsorbed molecules are also bound between the layers (Weber et al., 1965). Upon heating, kaolinite starts to lose water at approximately 400°C, and the dehydration approaches completeness at approximately 525°C (Grim, 1968). The dehydration depends on the particle size and crystallinity.

### **Sources of human and environmental exposure**

#### **Natural occurrence**

**Bentonite:** Bentonite derived from ash falls tends to be in beds of uniform thickness (from a few millimetres to 15 m) and extensive over large areas. Bentonite from ash falls and other sources occurs worldwide in strata spanning a broad range of ages, but is most abundant in Cretaceous or younger rocks. Bentonite is a widely distributed material. Accordingly, its major component, montmorillonite, occurs abundantly as dust at and near surface deposits of bentonite and is dispersed widely by air and moving water. Montmorillonite is thus ubiquitous in low concentrations worldwide in soil, in the sediment load of natural waters, and in airborne dust. Biodegradation appears minimal, if it occurs at all, and there is no evidence of or reason to suspect accumulation in the foodchain. Abiotic degradation of bentonite into other minerals takes place only on a geological time scale.

## Kaolin

Kaolin and the clay mineral kaolinite are natural components of the soil and occur widely in ambient air as floating dust. Kaolinite is formed mainly by decomposition of feldspars (potassium feldspars), granite, and aluminium silicates. It is also not uncommon to find kaolin deposited together with other minerals (illite, bentonite). The process of kaolin formation is called kaolinization. Kaolinite formation occurs in three ways:

- Crumbling and transformation of rocks due to the effects of climatic factors (Zettlitz type);
- Transformation of rocks due to hydrothermal effects (Cornwall type); and
- Formation by climatic and hydrothermal effects (mixed type).

The type of clay mineral formed during the decay of rocks containing aluminium silicates is influenced by the climate, the aluminium/silicon ratio, and pH. Conditions conducive for kaolinite formation are strong dissolution of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^{+}$  ions and the presence of  $\text{H}^{+}$  ions (pH 4–5).

Kaolinite quarries can be categorized according to the geo historical age of the parent rock:

- Precambrian (Ukraine, Spain, Czech and Slovak republics)
- Postcambrian (Cornwall, England, and Ural Mountains, Russia)
- Palaeovolcanite (Meissen, Germany)
- Neovolcanite (Tokaj Mountain, Hungary).

Kaolinite can also be categorized according to whether it remained at the place of formation or was transported<sup>21</sup>:

- *Primary*: lateritic types formed mainly under tropical climatic conditions (South America, Africa, Australia); and
- *Secondary*: transported by different forces, water, wind (Georgia, USA).

Owing to the different ways in which kaolin can form, several kinds of minerals may occur in natural kaolins. For example, the kaolin of Cornwall, England, contains 10–40% kaolinite; the rest is made of quartz, mica, and feldspar. The kaolin of Georgia, USA, contains 85–95% kaolinite, as well as quartz, muscovite, and feldspar<sup>22</sup>.

## Objectives of the study

### Fourier transform infrared spectroscopy.

Fourier transform infrared (FTIR) spectroscopy is a measurement technique that allows one to record infrared spectra. Infrared light is guided through an interferometer and then through the sample (or vice versa). A moving mirror inside the apparatus alters the distribution of infrared light that passes through the interferometer. The signal directly recorded, called an "interferogram", represents light output as a function of mirror position. A data-processing technique called Fourier transform turns this raw data into the desired result (the sample's spectrum): Light output as a function of infrared wavelength (or equivalently, wave number). As described above, the sample's spectrum is always compared to a reference.



There is an alternate method for taking spectra (the "dispersive" or "scanning monochromator" method), where one wavelength at a time passes through the sample. The dispersive method is more common in UV-Vis spectroscopy, but is less practical in the infrared than the FTIR method. One reason that FTIR is favored is called " Fellgett's advantage"<sup>23</sup> or the "multiplex advantage": The information at all frequencies is collected simultaneously, improving both speed and signal-to-noise ratio. Another is called "Jacquinot's Throughput Advantage": A dispersive measurement requires detecting much lower light levels than an FTIR measurement<sup>3</sup>. There are other advantages, as well as some disadvantages, but virtually all modern infrared spectrometers are FTIR<sup>24-25</sup> instruments.

## **Research methodology**

### **Special effects**

The simplest and most important IR bands arise from the "normal modes," the simplest distortions of the molecule. In some cases, "overtone bands" are observed. These bands arise from the absorption of a photon that leads to a doubly excited vibrational state. Such bands appear at approximately twice the energy of the normal mode. Some vibrations, so-called 'combination modes,' involve more than one normal mode. The phenomenon of Fermi resonance can arise when two modes are similar in energy; Fermi resonance results in an unexpected shift in energy and intensity of the bands.

### **Practical IR spectroscopy**

The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. When the frequency of the IR is the same as the vibrational frequency of a bond, absorption occurs. Examination of the transmitted light reveals how much energy was absorbed at each frequency (or wavelength). This can be achieved by scanning the wavelength range using a monochromator. Alternatively, the whole wavelength range is measured at once using a Fourier transform instrument and then a transmittance or absorbance spectrum is generated using a dedicated procedure. Analysis of the position, shape and intensity of peaks in this spectrum reveals details about the molecular structure of the sample<sup>26</sup>.

This technique works almost exclusively on samples with covalent bonds. Simple spectra are obtained from samples with few IR active bonds and high levels of purity. More complex molecular structures lead to more absorption bands and more complex spectra. The technique has been used for the characterization of very complex mixtures. Spectra issues with Infrared Fluorescence are rare.

### **Sample preparation**

Gaseous samples require a sample cell with a long path length to compensate for the diluteness. The path length of the sample cell depends on the concentration of the compound of the interest. A simple glass tube with length of 5 to 10 cm equipped with infrared windows at the both ends of the tube can be used for concentrations down to several hundred ppm. Sample gas concentrations well below ppm can be measured with a White's cell in which the infrared light is guided with mirrors to travel through the gas. White's cells are available with optical path length starting from 0.5 m up to hundred meters.

Liquid samples can be sandwiched between two plates of a salt (commonly sodium chloride, or common salt, although a number of other salts such as potassium bromide or calcium fluoride are also used). The plates are transparent to the infrared light and do not introduce any lines onto the spectra.

Solid samples can be prepared in a variety of ways. One common method is to crush the sample with an oily mulling agent (usually Nujol) in a marble or agate mortar, with a pestle. A thin film of the mull is

smearred onto salt plates and measured. The second method is to grind a quantity of the sample with a specially purified salt<sup>27</sup> (usually potassium bromide) finely (to remove scattering effects from large crystals). This powder mixture is then pressed in a mechanical press to form a translucent pellet through which the beam of the spectrometer can pass. A third technique is the "cast film" technique, which is used mainly for polymeric materials. The sample is first dissolved in a suitable, non hygroscopic solvent. A drop of this solution is deposited on surface of KBr or NaCl cell. The solution is then evaporated to dryness and the film formed on the cell is analysed directly. Care is important to ensure that the film is not too thick otherwise light cannot pass through. This technique is suitable for qualitative analysis. The final method is to use microtomy to cut a thin (20–100  $\mu\text{m}$ ) film from a solid sample. This is one of the most important ways of analysing failed plastic products for example because the integrity of the solid is preserved.

In photoacoustic spectroscopy the need for sample treatment is minimal. The sample, liquid or solid, is placed into the sample cup which is inserted into the photoacoustic cell which is then sealed for the measurement. The sample may be one solid piece, powder or basically in any form for the measurement. For example, a piece of rock can be inserted into the sample cup and the spectrum measured from it.

It is important to note that spectra obtained from different sample preparation methods will look slightly different from each other due to differences in the samples' physical states.

### **Comparing to a reference**

A beam of infrared light is produced, passed through an interferometer and then split into two separate beams. One is passed through the sample, the other passed through a reference. The beams are both reflected back towards a detector, however first they pass through a splitter, which quickly alternates which of the two beams enters the detector. The two signals are then compared and a printout is obtained. This "two-beam" setup gives accurate spectra even if the intensity of the light source drifts over time.

To take the infrared spectrum of a sample, it is necessary to measure both the sample and a "reference" (or "control")<sup>28</sup>. This is because each measurement is affected by not only the light-absorption properties of the sample, but also the properties of the instrument (for example, what light source is used, what infrared detector is used, etc.). The reference measurement makes it possible to eliminate the instrument influence. Mathematically, the sample transmission spectrum is divided by the reference transmission spectrum.

The appropriate "reference" depends on the measurement and its goal. The simplest reference measurement is to simply remove the sample (replacing it by air). However, sometimes a different reference is more useful. For example, if the sample is a dilute solute dissolved in water in a beaker, then a good reference measurement might be to measure pure water in the same beaker. Then the reference measurement would cancel out not only all the instrumental properties (like what light source is used), but also the light-absorbing and light-reflecting properties of the water and beaker, and the final result would just show the properties of the solute (at least approximately).

A common way to compare to a reference is sequentially: first measure the reference, then replace the reference by the sample and measure the sample. This technique is not perfectly reliable; if the infrared lamp is a bit brighter during the reference measurement, then a bit dimmer during the sample measurement, the measurement will be distorted. More elaborate methods, such as a "two-beam" setup can correct for these types of effects to give very accurate results. The Standard addition method can be used to statistically cancel these errors.

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