

# Applications of Infrared Spectroscopy in Analysis of Organic Aerosols

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## Abstract

This paper reviews the studies of using FTIR to investigate the components of aerosols produced in smog chamber experiments and collected in atmosphere. The fact that aerosols are mixture of small amount of countless individual compounds makes the analysis of aerosol constituents very challenging. Although a number of advanced instruments have been applied to the chemical characterization of aerosol components, the majority of aerosol components, particularly the organics, remain unknown. Being supplemental to the traditional quantitative instruments, FTIR has been recently used either individually or combining with other analytical instruments to characterize the components of aerosol particles. This paper aims to show how FTIR is applied to analysis of organic aerosols in current literature and to summarize the FTIR characteristic peak frequencies that are widely seen in the FTIR measurement of organic aerosols. It will be greatly helpful to researchers whose studies are focused on the analysis of aerosol components.

## Keywords

Organic Aerosol Compositions, FTIR Spectroscopy, Characteristic Peak Frequencies, Heterogeneous Reactions, Source Apportionment

## 1. Introduction

Aerosol contains major fraction of organic compounds. Studies have found that depending on locations, about 10% to 90% of ambient fine particulate matter mass is organic matter [1] [2] [3]. Understanding organic compounds in aerosols is greatly important, since their potential impacts on climate change and human health are strongly associated with their structures and compositions.

Besides that, information on aerosol compositions is critical for identifying and apportioning the major sources of fine aerosols.

However, the current knowledge of organic composition in aerosols is quite limited. Qualification and quantification of organic components in aerosols are very challenging for they contain tens of thousands of various species at trace levels. In recent years, significant research efforts have been carried out towards the application of advanced analytical instruments for chemical characterization of aerosols. Instruments such as AMS, HPLC-MS, GC-MS, NMR, FTIR, etc. either alone or in combination with others, have been widely used to resolve the chemical compositions of aerosols and investigate compound concentrations as well as chemical processes involved in the formation of aerosols. AMS is able to analyze atmospheric aerosol particles within a short time interval and without sample pretreatment. Therefore, it is suitable for the on-line analysis of aerosols and less sensitive to artifact formation than conventional sampling and analytical techniques. AMS instruments usually provide quantitative information of total organic content or specific compounds that are easily identified in mixed spectra. For other individual components of aerosols, they currently give only limited information. Particularly when the ionization technique produces a large number of fragments for a compound, it becomes impossible to track the original compound. In addition to AMS, GC-MS and LC-MS are two common analytical techniques for off-line chemical characterization of aerosol samples. Specific compounds such as carbonyls and carboxylic acid, etc. in aerosols can be identified using GC-MS and LC-MS directly or with different derivatization methods for pretreating samples. To achieve sufficient structural information of specific compounds in complex multicomponent mixtures of aerosols, tandem MS ( $MS^2$ ) combined with GC or LC has been used in a number of studies.

NMR methods have been used for apportioning the aerosol organic carbon into functional groups such as hydroxyls, carbonyls, carboxyls, aromatic and aliphatic groups. The application of  $^1H$  NMR spectroscopy in the chemical characterization of water soluble organic compounds (WSOC) in aerosols is limited for not being able to directly detect organic functional groups carrying no protons or containing acidic protons that exchange with the deuterium of the solvent. To overcome this limitation, chemical derivatization procedures have been developed to convert those functional groups mentioned above to the groups with hydrogen atoms visible to  $^1H$  NMR.  $^{13}C$  NMR spectroscopy is a more suitable tool than  $^1H$  NMR for investigating the distribution of C functional groups in aerosols, for it can demonstrate carbon skeletons of rings and chains directly. A number of recent studies have employed NMR methods to analyze aerosols and their specific compounds, such as biogenic secondary organic aerosol [4], wood burning aerosols [5] [6], and Humic Like Substances (HULIS) [7].

FTIR has many advantages including speed of analysis, simplicity of sample preparation, cost effectiveness, reproducibility of analysis, and no need for extensive operators' expertise in performing the spectra. FTIR is conventionally used for the structural identification of organic compounds, however, with the

development of computer technology and the advance of chemical metrology, FTIR has exhibited its effectiveness in quantitative analysis of organic and inorganic compounds. Up to date, the major FTIR applications to chemical characterization of aerosols are to determine distribution of functional groups and ratios of organic matter to organic carbon in aerosols (OM/OC).

The use of FTIR spectroscopy, compared with other analytical technologies, is relatively novel in quantification analyses of organic compositions of aerosols. In the present and the future when there is no universal technique available for a comprehensive characterization of organic aerosols, appropriate technology combinations must be employed. FTIR could be one of powerful techniques. This review presents a summary of studies reported to date in the literature that have applied FTIR to chemical characterizations of organic aerosols. It focuses on the use of FTIR to investigate the chemical compositions of organic aerosols, with the aim to provide researchers with a database of characteristic peak frequencies of specific functional groups present in organic aerosols, which can be referred to for obtaining useful structural information by simple inspection. The information provided in this review could be of great assistance to researchers interested in exploring FTIR to tackle the problems relevant to organic aerosol compositions.

## 2. Aerosol Research by FTIR Spectroscopy

Researchers have used FTIR in a variety of organic aerosol studies for understanding the physical and chemical processes involved in heterogeneous reactions, functional group compositions of organic aerosols, OM/OC in aerosols, and source apportionment of aerosol particles. This section summaries some of these studies that would help to extend the application of FTIR in the field of aerosol research.

The study of Jang and Kamens [8] aimed to investigate the potential mechanisms of heterogeneous reactions of aldehydes for the formation of secondary organic aerosols particularly in the presence of acidic seed particles. An FTIR spectrometer was used to analyze functional groups in the aerosol particles generated from aldehydes under darkness in the presence of neutral or acidic seeds. Changes in the spectral features in the O-H stretching of the hydrogen-bonded alcoholic hydroxyl group at 3100 - 3600  $\text{cm}^{-1}$ , the C=O stretching of aldehydes at 1640 - 1780  $\text{cm}^{-1}$  and C-O-C stretching at 1182  $\text{cm}^{-1}$  were studied for group transformation in the aerosol particles as heterogeneous reactions of aldehydes proceeded. In this paper, least-squares curve-fitting was also performed for multicomponent analysis in two spectral regions: one was the carbonyl stretching region (1640 - 1780  $\text{cm}^{-1}$ ) for the free C=O stretching and the hydrogen bonded C=O; the other was OH stretching region (3100 - 3600  $\text{cm}^{-1}$ ) for free O-H, hydrogen bonded O-H and N-H stretching from seed aerosols. The results of FTIR analysis indicated that heterogeneous reactions of aldehydes could produce large molecules such as polymers, hemiacetals/acetals, and aldehyde hydrates (gem-diols) increasing the aerosol mass and showed that hydrogen bonded hy-

droxyl groups were very important intermediates for the heterogeneous reactions to occur.

Similarly, another two studies of Jang *et al.* [9] [10] applied FTIR to directly monitor the transformation of chemical functional groups during the process of aldehyde reactions in the presence of the aqueous  $\text{H}_2\text{SO}_4$  acid catalyst. Octanal and 1-nonanol as well as tiny amounts of aqueous  $\text{H}_2\text{SO}_4$  were added to a ZnSe disc and the FTIR spectra of the mixture were recorded as a function of time. The immediate disappearance of aldehydic C-H stretching at  $2715\text{ cm}^{-1}$  and the gradual decrease in the C=O stretching band at  $1726\text{ cm}^{-1}$  with time were observed. The resulting thin organic layer on the disc remained for a long time. These phenomena indicated that high molecular weight compounds were generated through the reactions of carbonyls.

In the study of Bones *et al.* [11], with the aim to investigate chemical aging of SOA formed from ozonolysis of terpenes in the presence of ammonium sulfate aerosol, FTIR was used to confirm whether the “colored” products, which showed strong visible absorption measured by UV-Vis spectroscopy and fluorescence at UV and visible ranges by three-dimensional fluorescence, could lead to the changes in the chemical compositions of SOA. By comparing FTIR spectra of the fresh SOA to those of the chemically aged SOA, almost no difference was observed, which implied that the “colored” products from the long-term aging chemistry contributed insignificantly to the aged SOA.

Coury and Dillner [12] developed an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopic technique combining with a multivariate calibration method for quantification of ambient aerosol organic functional groups and inorganic compounds. The partial least squares multivariate calibration method established the correlation between changes in absorbance values at each frequency and changes in functional group concentrations using 75 compositions of calibration standard mixtures of 13 organic functional groups (aliphatic and aromatic CH, methylene, methyl, alkene, aldehydes/ketones, carboxylic acids, esters/lactones, acid anhydrides, carbohydrate hydroxyl and ethers, amino acids, and amines) and 2 inorganic compounds (ammonium sulfate and ammonium nitrate) in various concentrations. The sensitivity and accuracy of quantification were improved by the use of the multivariate calibration method in comparison with the univariate calibration. In this study, four regions of the ambient IR spectra of  $3800 - 2600$ ,  $1850 - 1600$ ,  $1600 - 1268$ , and  $1050 - 700\text{ cm}^{-1}$  were used for quantification of 13 organic functional groups and 2 inorganic compounds mentioned above in calibration standards and ambient samples. The results showed that the sum of the mass of all functional groups measured by the ATR-FTIR technique was close to the gravimetric mass of ambient samples, indicating that the FTIR quantification method developed in this study performed well for measurement of aerosol masses.

Coury and Dillner [13] later applied their ATR-FTIR method to quantify organic functional groups and inorganic ions of aerosol samples collected in a rural area near Phoenix, Arizona. The organic functional groups and inorganic

ions investigated in this study were the same as those measured in their previous study of the method development [12]. The compositions of organic aerosols were represented by four classes of functional groups: biogenic functional groups (carbohydrate ether and hydroxyl, amino acids and amines), oxygenated functional groups (aldehyde/ketone, carboxylic acid, ester/lactone, and acid anhydride functional groups), aliphatic hydrocarbon functional groups (aliphatic CH, methylene, methyl and alkene functional groups) and aromatic hydrocarbon functional groups. Such compositional analysis coupling with functional group correlations and back trajectories were used to classify the sampling days into three different air quality events: primary biogenic-influenced event, urban influenced event, or regional background air quality event. This study demonstrated the feasibility of using information about functional groups of organic aerosols obtained by the ATR-FTIR technology for the studies related to source apportionment.

Russell *et al.* [14] characterized the organic compositions of atmospheric particles by comparisons of measurement results between two techniques (AMS vs. FTIR). Their studies presented the correlations between atmospheric AMS fragment fractions  $m/z$  43 ( $C_3H_7$  and  $C_2H_3O$  fragments), 44 ( $CO_2$  fragments), 57, and 60 ( $C_2H_4O_2$  fragments) and the FTIR carboxylic acid, alcohol, and alkane group fractions for the aerosol samples from eight field projects. With the addition of FTIR interpretation of chemical bonds to the AMS fragmentation measurements, quantification of chemical properties of organic aerosols has been improved greatly.

Schwartz *et al.* [15] used an FTIR spectroscopy along with a high-resolution time-of-flight aerosol mass spectrometry (HR-TOF-AMS) for the measurements of organic masses of submicron biogenic aerosol particles. The results showed that the organic mass concentrations measured by FTIR were higher than those measured by AMS when the aerosol particles contained a remarkable concentration of dust, implying AMS was insufficient for measuring the complete organic mass of the particles with the presence of significant amount of dust. In this study, positive matrix factorization (PMF) was also applied on the FTIR spectra to attribute the fractions of organic functional groups of the ambient particles to the summed biogenic factors. The composition of the summed biogenic factors was compared with the composition of SOA generated in the chamber from oxidation of monoterpenes and isoprene. The great similarity was observed, which, the researchers believed, proved the atmospheric importance of ketone and organic hydroxyl groups rather than aldehyde or organosulfate groups.

Maria *et al.* [16] used FTIR coupled with a four-solvent rinsing procedure to determine the concentrations and solubility of organic functional groups and inorganic ions in submicron aerosol particles collected at three altitude ranges in the atmosphere over Caribbean. The FTIR absorbance of functional groups was used to quantify moles of specific bonds in the aerosol samples based on the prior-known absorption per mole of each bond obtained from the standards. To estimate the hygroscopicity of organic components in aerosols, solvents of

increasing polarity (hexane, dichloromethane, acetone, and water) were used to rinse the aerosol samples sequentially. The resulting FTIR spectra of the samples after each rinsing were compared to determine the fractions of organic components with different solubility. Maria *et al.* [16] also used the measured moles of bonds to estimate the OC and OM mass, which further extended the application of FTIR in the area of organic aerosol analysis. However, only two functional groups, alkane and carbonyl, were considered in that study for OC and OM estimation. This may lead to an underestimation by neglecting the presence of other functional groups containing the bonds between a noncarbon atom and a carbon, such as organonitrates, organosulfates and alcohols, etc. In their later study during the ACE-Asia field campaign [17], estimation accuracy of OM and OC based on measurement of functional groups was improved by including C-OH, C-NH<sub>2</sub> and C-O-S in the calculations. Moreover, it considered C-H bonds not only in alkanes (same as their previous study), but also in alkenes and aromatics. The Equations (1) and (2) (shown below) established in their study, as a prototype for the estimation, have been used and modified by a number of studies. This paper reported that the total OC estimated from FTIR measurements were very close to that obtained from the simultaneous thermal-optical OC measurements (slope = 0.91 and R<sup>2</sup> = 0.93), demonstrating FTIR measured the similar organic components of aerosol particles as the conventional OC measurement. Additionally, FTIR used nearly 100% of the atmospheric OC in its calculation for characterization of OM, unlike some other methods that usually identify less than 20% of the total OC on the basis of the extrapolation from chromatography measurements.

$$\begin{aligned}
 \text{OC} = & \left( 0.5 \times [\text{moles alkane C-H}] \times [12 \text{ g} \cdot \text{mole}^{-1}] \right) \\
 & + \left( [\text{moles alkene C-H}] \times [12 \text{ g} \cdot \text{mole}^{-1}] \right) \\
 & + \left( [\text{moles aromatic C-H}] \times [12 \text{ g} \cdot \text{mole}^{-1}] \right) \\
 & + \left( [\text{moles C=O}] \times [12 \text{ g} \cdot \text{mole}^{-1}] \right) \\
 & + \left( [\text{moles C-OH}] \times [12 \text{ g} \cdot \text{mole}^{-1}] \right) \\
 & + \left( [\text{moles C-NH}_2] \times [12 \text{ g} \cdot \text{mole}^{-1}] \right) \\
 & + \left( [\text{moles C-O-S}] \times [12 \text{ g} \cdot \text{mole}^{-1}] \right)
 \end{aligned} \tag{1}$$

$$\begin{aligned}
 \text{OM} = & \left( 0.5 \times [\text{moles alkane C-H}] \times [14 \text{ g} \cdot \text{mole}^{-1}] \right) \\
 & + \left( [\text{moles alkene C-H}] \times [13 \text{ g} \cdot \text{mole}^{-1}] \right) \\
 & + \left( [\text{moles aromatic C-H}] \times [13 \text{ g} \cdot \text{mole}^{-1}] \right) \\
 & + \left( [\text{moles C=O}] \times [28 \text{ g} \cdot \text{mole}^{-1}] \right) \\
 & + \left( [\text{moles C-OH}] \times [29 \text{ g} \cdot \text{mole}^{-1}] \right) \\
 & + \left( [\text{moles C-NH}_2] \times [28 \text{ g} \cdot \text{mole}^{-1}] \right) \\
 & + \left( [\text{moles C-O-S}] \times [54 \text{ g} \cdot \text{mole}^{-1}] \right)
 \end{aligned} \tag{2}$$

In the same year, one of the coauthors of the two studies mentioned above, Dr. Russell [18] published another paper, which emphasized the importance and necessity of the actual measurements of ratios of OM to OC in aerosol samples instead of employing the values between 1.4 - 1.7 that have been conventionally taken for estimation of the OM mass based on the measured OC mass, by showing the large variability of measured OM to OC ratios of all aerosol samples collected from Caribbean and northeastern Asia. It concluded that the application of FTIR can improve the current aerosol measurements by reducing the uncertainties to a great degree. This paper also presented a detailed estimation process of errors in the measurement of OM to OC ratios based on FTIR spectra of functional groups.

With reference to the studies of Maria *et al.* [16] [17], Gilardoni *et al.* [19] [20] conducted two studies to estimate functional group compositions of ambient aerosols at various platforms during different sampling campaigns by FTIR. The organic functional groups, such as non-acid organic hydroxyl C-OH group, aromatic C=CH group, aliphatic unsaturated C=C-H group, aliphatic saturated C-C-H group, non-acid carbonyl C=O group, carboxylic acid COOH group, and amine NH<sub>2</sub> group, were identified in their studies. The standard aerosol samples used for the calibration coefficients of the organic functional groups contained 1-docosanol, anthracene, sodium benzoate, 1-docosene, alanine, citric acid, and adipic acid. With the calibration coefficients, the molar concentrations of the functional groups were obtained based on the FTIR spectra of the ambient aerosol samples. The value of OC was calculated by multiplying functional group molar concentrations with 6 for saturated carbon chains and 12 for unsaturated ones. OM was the sum of contributions from different functional groups that were obtained by multiplying molar concentrations of the functional groups with the corresponding group molecular weights. For the samples collected at two selected locations, Gilardoni *et al.* [19] [20] also used Thermo-Optical Analysis (TOA) and AMS to measure the OC and the OM respectively, which were then compared to those obtained by FTIR. Their results showed that these techniques seemed to correspond fairly well, but the linearity of the correlations between them varied greatly.

Russell *et al.* [21] utilized FTIR to determine the organic functional group compositions of atmospheric aerosol particles collected on a ship traveling around Houston, TX. In this work, a series of mathematical treatments was applied to analyses of FTIR spectra. Baselineing and spectral smoothing were processed using a third-order polynomial. Spectral interferences from CO<sub>2</sub> and H<sub>2</sub>O were eliminated with an interpolated spline and wavelet denoising methods respectively. The measured functional groups in their study mainly included alkane, alkene, aromatic, alcohol, carboxylic acid, nonacidic carbonyl, primary amine, and organosulfate groups. To resolve the broad O-H stretching band in carboxyl groups that was superimposed on the peaks of interest (such as C-H stretching bands) between 3100 and 2400 cm<sup>-1</sup>, Russell *et al.* [21] performed PMF analysis on a set of FTIR spectra, obtained from the NIST Chemistry

Webbook, of carboxylic acids containing different numbers of aliphatic C-H and COOH groups (adipic, glutaric, malonic, azelaic, decanoic, stearic, and succinic acids) for a two-factor solution. The Gaussian peaks for COOH groups were defined when the resulting spectra matched the adipic acid reference spectra obtained in their laboratory and showed the great similarity in absorptivities of saturated aliphatic C-H observed in noncarboxylic acid species. All spectra were pretreated by deducting spectra of carboxylic C-OH and ammonium for better accuracy. The remaining peaks were then assigned to specific functional groups with box constraints obtained from reference spectra [19]. The quantification of carboxylic group was determined based on the difference degree between moles of C=O and C-OH as follows: When the two values were close, the mole of carboxylic group equaled the average of the moles of C=O and C-OH; when they were considerably different, the mole of carboxylic group took the smaller value of the moles of C=O or C-OH. The sum of the concentrations of the functional groups was equivalent to the OM of the aerosol samples. The results showed that the FTIR OM was generally in good agreement with the AMS OM except at low concentrations where FTIR OM was usually higher than AMS OM. In this study, PMF was also used to apportion the functional groups to sources contributing the OM. In order to distinguish the fractions of primary components (defined in their study as that emitted from a single source) from those of secondary components (defined as that relying on other pollutants probably from multiple sources and atmospheric conditions) in aerosol particles, Russell *et al.* [21] proposed an approach based on a statistical correlation of functional group compositions of PMF factors with concentrations of source-specific nonvolatile metal tracers measured by XRF. That is, mild and strong correlations implied OM from primary sources, while weak correlations indicated atmospheric processes mainly responsible for organic aerosols. The method of Russell *et al.* [21] has been applied to determination of the mass concentrations of organic functional groups in ambient aerosol samples [22] [23]. Takahama *et al.* [24] evaluated the algorithm of Russell *et al.* [21] for characterization and quantification of carbonyl and hydroxyl bonds in carboxylic COOH functional groups, carbonyl C=O (aldehydes and ketones) functional groups and alcohol COH functional groups separately. Their study enhanced the accuracy and consistency of FTIR spectra interpretation among different users and thus promoted applications of FTIR to analyzing complex aerosol samples, especially multifunctional compounds and mixtures.

Chhabra *et al.* [25] investigated the evolution of functional groups in the process of chamber SOA formation and aging with a high-resolution AMS and FTIR. They applied FTIR to determine not only the mass concentrations of functional groups but also elemental ratios of H/C and O/C in secondary organic aerosols generated from oxidation of  $\alpha$ -pinene and guaiacol. The functional groups investigated include alkane, carboxylic acid, hydroxyl, amine, non-acid carbonyl, organonitrate, alkene, and aromatic functional groups. For quantification of those functional groups, the algorithms and standards reported by the

previous studies [14] [18] [21] were employed. The ratios of O/C and H/C were determined by estimating the moles of oxygen, carbon, and hydrogen atoms contained in each measured functional group based on its spectral absorbance.

Liu *et al.* [26] used agglomerative hierarchical clustering technique with the Ward algorithm to group the FTIR spectra of the particle samples collected at different sites into seven clusters. According to the similarities (two to ten branches), individual FTIR spectrum was merged into the same clusters gradually. The similarities shown in the spectra from various sites indicated that the regional pollution might influence the sources for these aerosol particle samples or those sites could possess the common sources, while the three clusters that contained the spectra of the samples solely from one platform (NCAR C130 aircraft) suggested a wide range of different sources for the samples collected by the C130 aircraft. In their studies, PMF was also applied to the FTIR spectra from the three platforms jointly or from each location separately, in order to attribute the functional groups to the general sources (three to six factors). They found that functional groups such as alkane, carboxylic acid, amine, and alcohol were mostly from combustion related sources, while non-acid carbonyl groups from biomass burning events. Moreover, combustion sources contributed the majority of OM and OC of the particle samples collected from the three platforms. With the introduction of clustering analysis and PMF, the use of FTIR was further explored for the insight into the compositions and sources of organic aerosols.

Day *et al.* [27] also used FTIR with the similar method to quantify organic functional group concentrations for the submicron ambient particles collected in coastal southern California. The OM masses of the particles were equivalent to the total mass contributed from all organic functional groups detected by FTIR including saturated aliphatic (alkane [CH]) groups), alcohol [COH] groups, carboxylic acid [COOH] groups, non-acidic carbonyl [CO] groups, primary amine [NH<sub>2</sub>] groups, organosulfate [COSO<sub>3</sub>] groups, unsaturated aliphatic (alkene [CH] groups) and aromatic [CH] groups. The masses assigned to each mole of the absorbing bonds were the same as those used in the study of Gilar-doni *et al.* [19] [20]. The main focus of Day *et al.*'s [27] research was to investigate the contents of organonitrate groups in the ambient particles using the FTIR absorptivities at 860 cm<sup>-1</sup> based on a calibration curve with 2-ethylhexyl nitrate as the calibration standard. Although three strong organonitrate absorption peaks were observed at around 1629.6, 1278.6, and 860.9 cm<sup>-1</sup>, to avoid the interference of the amine absorbance near 1630 cm<sup>-1</sup> and of the Teflon filter absorbance near 1280 cm<sup>-1</sup>, only the peak at 860 cm<sup>-1</sup> was chosen in their study for the purpose of the quantification. In addition, the algorithm for baselining and peak-fitting the three organonitrate peaks that was tested and employed in this study was also addressed in details. Based on previous studies [28]-[30] most of which aimed at qualification, Day *et al.* [27] further developed a promising quantification method for organonitrate groups in ambient aerosol particles using FTIR. This method was later applied by other researchers to the investigations

into the organonitrate groups in aerosol particles [31] [32].

On the basis of the previous studies of Maria *et al.* [16] [17] and Gilardoni *et al.* [19] [20], Day *et al.* [33] introduced an automated algorithm to do the baselining, peak fitting, integration and calibrations for the FTIR measurements of functional groups. In their aerosol samples collected from an aircraft platform over the eastern Pacific and western North America, the concentrations of alkene, aromatic, amine, and organosulfate groups were found under the detection limit. Thus, only alkane, alcohol and carboxylic acid groups were considered for OM quantification. In addition, the agglomerative hierarchical clustering with the Ward algorithm was used for the comparison among the FTIR spectra, in order to investigate the similarities and differences of organic compositions, sources and processing of aerosol samples from different locations.

Russell *et al.* [34] used FTIR to quantify the functional groups of the aerosol particles collected in 21 campaigns in North America, Asia, South America, and Europe. The functional groups that they looked into included mainly alkane, carboxylic, carbonyl, hydroxyl groups. Besides that, amine, organosulfate, and organonitrate groups were also considered. A great number of FTIR spectra (over 1000) were analyzed by application of agglomerative hierarchical clustering technique with the Ward algorithm and PMF, yielding functional group compositions of fuel combustion, terrestrial biogenic and burning vegetation, and marine biogenic sources. In addition, they compared the chemical similarities between the functional group compositions of atmospheric particles and those of secondary organic aerosols generated from the chamber experiments, in the purpose of evaluating the feasibility of using the findings of chamber studies to predict the formation of atmospheric secondary organic aerosols.

Takahama *et al.* [35] analyzed organic functional group compositions of atmospheric particles collected in the Southeast region of Tijuana, Mexico using FTIR. The resulting concentrations of functional groups such as alkane, carboxylic acid, organic hydroxyl, primary amine, and carbonyl groups were used to estimate the OM of the aerosol particles based on the calculations similar to the study of Russell [18]. The carbonyl groups in their study referred to ketonic carbonyl only due to the absence of the aldehydic hydrogen absorption in the range of  $2700\text{ cm}^{-1}$  and  $2860\text{ cm}^{-1}$ . FTIR spectra of the atmospheric particles were also analyzed by PMF for source apportionment. Four source factors (two factors for fossil-fuel combustion with the difference on their correlated elemental tracers and the ratios of O/C; one factor for marine source; one for biomass burning) were investigated. In combination with the statistical analysis methods, the measurement results of BC and VOC, the elemental tracer analyses, and the back trajectory analyses, FTIR exhibited the effectiveness for tracking the sources of OM in aerosol particles.

### 3. FTIR Spectral Interpretations for Characteristic Groups in Organic Aerosol Particles

A comprehensive interpretation of FTIR spectra has been tabulated in **Table 1**,

**Table 1.** IR frequencies and assignments for functional groups in organic aerosols.

Wavenumber (cm <sup>-1</sup> )	Band Assignment	Ref.
3750 - 3500	Alcohols -OH	[29] [36] [37] [38]
3650 - 3500	Hydrogen bonding free	[8]
3650 - 3250, 1450 - 1400, 1050 - 1000	Hydroxyl (-OH)	[39]
3600 - 3100	OH stretching	[9] [40] [41] [42]
3500 - 3420, 3420 - 3340, 1650 - 1580, 850 - 750	Amino acids/Amines (NH <sub>2</sub> )	[12]
3500 - 3400	O-H stretching region	[7] [24] [43]
3500 - 3300	Secondary and primary amines N-H stretch	[44]
3500 - 3300 1650 - 1550 900 - 660	Amino	[39]
3500 - 3100	Alcohol (C-OH)	[17] [20]
3500 - 2500, 1440 - 1395, 960 - 900	Aliphatic carboxylic acids (OH) and Amino acids/Amines (OH)	[12]
3500 - 2500	Carbohydrates (C-OH)	[12]
3500 - 3100	Organic hydroxyl (C-OH)	[19]
3440 - 3400	Hydroxyl (-OH)	[30]
3400 - 2500	Carboxylic acid (OH)	[45]
3400-2400	Carboxylic acid (OH stretch)	[24] [44]
3400, 1440 - 1220, 1260 - 1000	Alcohol and phenol	[44]
3400, 1625	Amine (NH <sub>2</sub> )	[19] [20]
3400	OH stretching of phenol hydroxyl and carboxyl	[5]
3382 - 3323	Alcohol (OH)	[45]
3380	H-bonding of hydroxyl	[46]
3350, 1350, 650 ± 50	Alcohols/Phenols (OH)	[12]
3350 - 3205	Alcohol COH	[24]
3350, 3180	Primary amide N-H stretch	[44]
3300 - 3150	Alcohol groups	[33]
3300 - 2900	C-H stretching in alkane, alkene, alkyne, aromatic	[44]
3300	Secondary amide N-H stretch	[44]
3300	Hydrogen bonded	[8]
3200 - 3000, 1290 - 1000	Aromatic carbon (Arom-H)	[38]

## Continued

3200 - 3000	Aromatic C-H	[37] [41]
3200 - 2400	H-bonding of organic acids	[41] [47]
3200 - 3000	Aromatic carbons (Arom-H)	[36]
3130 - 3030, 900 - 670	Aromatic (C=C-H)	[48]
3100 - 3070	Carboxylic acid (COOH)	[30]
3100 - 3000	Aromatic (C-H)	[42]
3100 - 2900	Unsaturated aliphatic (C=C-H)	[17] [19] [20]
3100 - 3000	Alkene (C-H)	[38]
3100 - 3000	Aromatic (C=C-H)	[17] [19] [20]
3100 - 3000	Unsaturated aliphatic (C=C-H)	[48]
3100 - 3000	Unsaturated and aromatic (C-H)	[12]
3100	H-bonding of organic acid	[46]
3100 - 2900	Alkane groups	[33]
3090 - 3075, 3050 - 3000, 990 - 815	Aliphatic Hydrocarbons (C-H)	[12]
3050	Aromatic (C-H)	[24] [49]
3040, 2920, 2860	Aromatic (C-H)	[28]
3006	=CH stretch	[50]
>3000, 860 - 710	Nitro-polyaromatic hydrocarbons (PAH) aromatic (C-H)	[12]
>3000, 860 - 710	Aromatic polycarboxylic acids aromatic (C-H)	[12]
3000 - 2880	Aliphatic (C-H)	[49]
3000 - 2850, 1480 - 1370	Aliphatic carbon (C-H)	[38]
3000 - 2850, 1410	Aliphatic carbons (-CH <sub>2</sub> )	[39]
3000 - 2850	Aliphatic (C-H)	[5] [12]
3000 - 2800, 1452 - 5	Aliphatic carbons (C-H)	[17] [29] [36] [37]
3000 - 2800, 1450	Saturated aliphatic (C-C-H)	[19] [20]
3000 - 2800	Aliphatic (C-H)	[1] [24] [30] [41] [42] [46]
2980 - 2835	Alkane absorption (C-H)	[51]
2980	Alkene (C-H)	[24]
2970 - 2930	Aliphatic (C-H)	[7]
2970 - 2845, 1485 - 1445, 1395 - 1385, 750 - 720	Saturated aliphatic (C-C-H)	[48]
2970 - 2830	CH stretching in-CH <sub>2</sub> , and-CH <sub>3</sub> groups	[8]
2962, 2872, 1460, 1375 ± 10	Aliphatic hydrocarbons CH <sub>3</sub>	[12]

## Continued

2960 - 2800	Alkane (C-H)	[45]
2956 - 2870	C-H stretching in-CH <sub>3</sub> groups	[40]
2950 - 2850	Aliphatic C-H,-CH <sub>2</sub> , -CH <sub>3</sub> stretching	[52]
2929 - 2860	C-H stretching in-CH <sub>2</sub> groups	[40]
2926, 2855, 1455, 720 ± 10	Aliphatic hydrocarbons CH <sub>2</sub>	[12]
2925	-CH <sub>2</sub> antisymmetric stretching	[50]
2925, 2882, 2852, 2800	Alkane	[24]
2920 - 2850	Aliphatic (C-H)	[16]
2915	-CH <sub>2</sub> asymmetric stretching	[53]
2860 - 2800, 2760 - 1200	Aldehyde C-H stretch	[44]
2860 - 2700	Aldehydic hydrogen stretching	[54]
2854	-CH <sub>2</sub> symmetric stretching	[50]
2850 - 2700	Aldehydic (C-H)	[12]
2847	-CH <sub>2</sub> symmetric stretching	[53]
2815, 2715	CH stretching of aldehyde group	[8]
2715	Aldehydic stretching (C-H)	[9]
2150	Alkyne (C≡C)	[44]
1870 - 1720	Acid anhydrides (C=O)	[12]
1850 - 1775	C=O stretch in acid chloride	[44]
1850 - 1650 (1640)	Carbonyl (C=O)	[16] [17] [19] [39] [53]
1850 - 1640	Non-acid carbonyl (C=O)	[29] [36]-[38]
1850 - 1640	Carboxylic acid (COOH)	[20]
1850 - 1600	Carbonyl functional group (C=O)	[12]
1830 - 1800	C=O stretch in anhydride	[44]
1800 - 1670	Carbonyl (C=O)	[30] [42]
1775 - 1740	C-O stretch in anhydride	[44]
1762	C=O in carboxylic acids and esters	[55]
1750 - 1735	Esters/Lactones (C=O)	[12]
1750 - 1700	C=O stretching in aldehyde, ketone, ester	[44]
1750 - 1680	Carbonyl (C=O)	[48]
1748 - 1693	Carbonyl (C=O)	[45]
1743	Ester C=O stretching	[50]
1738	Carbonyl (C=O)	[1]

## Continued

1730 - 1700	Aliphatic carboxylic acids(C=O)	[12] [44]
1730 - 1650	Carbonyl stretching (C=O)	[10]
1730 - 1640	Aldehydes/Ketones C=O	[12]
1728 - 1694	Carbonyl (C=O)	[46]
1727 - 1720	Carbonyl (C=O)	[41]
1726 - 1724	Carbonyl (C=O)	[40]
1726	Carbonyl (C=O)	[9]
1726 - 1715	Hydrogen bonding free	[8]
1720	Carboxyl (C=O)	[5] [7] [28]
1720 - 1714	Carbonyl (C=O)	[24]
1713	Carbonyl (C=O)	[47]
1710	Carbonyl (C=O)	[27] [50]
1710 - 1680	Aromatic polycarboxylic acids (C=O)	[12]
1706	C=O in aldehydes and ketones	[55]
1700	Carbonyl (C=O)	[54]
1690 - 1680	Hydrogen bonded (O-H)	[8]
1680 - 1665, 1660 - 1630	Aliphatic hydrocarbons (C=C)	[12]
1680 - 1630	C=O stretch in amide	[44]
1680 - 1620	Unsaturated aliphatic (C=C)	[48]
1650 - 1620	Alkenyl double bond stretch (C=C)	[10]
1650 - 1590	Amino (C-NH <sub>2</sub> )	[48]
1644, 1281, 849	O-N groups	[31]
1640 - 1560	N-H bend in primary amines	[44]
1640 - 1550	Primary and secondary amide N-H bend	[44]
1640 - 1550	C=O stretching in cyclic and acyclic compounds, ketones and quinones	[52]
~1640	Asymmetric-NO <sub>2</sub> stretch	[32]
1631, 1278, 856	Organonitrates (CONO <sub>2</sub> )	[29] [37] [38]
1630 - 1620	Amine (C-NH <sub>2</sub> )	[24]
1630	Amines (C-NH <sub>2</sub> )	[17]
1630	Organic (NO <sub>3</sub> )	[28]
1630, 1280 - 1260, 860	Organonitrates (R-ONO <sub>2</sub> )	[36] [37]
1630 - 1620, 1280 - 1260, 860 - 855	Organonitrates	[27]

## Continued

1615 - 1580	Aromatic (C=C)	[48]
1600, 1475	Aromatic (C=C)	[44]
1570 - 1500, 1370 - 1300	Aromatic-NO <sub>2</sub>	[48]
1550 - 1500, 1390 - 1330, 890 - 835	Nitro-polyaromatic hydrocarbons (PAH) (NO <sub>2</sub> )	[12]
1530	Nitroaromatics	[41]
1535 - 25	Nitroaromatics (Armo-NO <sub>2</sub> )	[36] [37] [38]
1518	Stretching vibrations of aromatic C=C bonds	[5]
1500	Secondary amines N-H bend	[44]
1470 - 1420	C-H deformation of aliphatic	[52]
1465	Bend in (CH <sub>2</sub> ) of alkane	[44]
1465, 1412	-CH <sub>2</sub> bending	[50]
1450, 1375	Bend in (CH <sub>3</sub> ) of alkane	[44]
1450 - 1280	Deformation of C-O-H, -CH <sub>2</sub> -, and -CH <sub>3</sub> groups	[8]
1442	CH <sub>3</sub> , CH <sub>2</sub> aliphatic bending	[53]
1440 - 1220	Alcohol and phenol (C-O-H bend)	[44]
1400 - 1390	C-H deformation of CH <sub>3</sub> groups	[52]
1400	OH in carbohydrates	[12]
1400	C-H in carbohydrates	[12]
1350 - 1340	Nitro-aromatic (NO <sub>2</sub> )	[42]
1350 - 1000	C-N stretch in amines	[44]
1340 - 1250	Aromatic (C-N)	[48]
1320 - 1210	Aliphatic carboxylic acids (CO)	[12]
1320 - 1210	Amino acids/Amines (CO)	[12]
1300 - 1100	Ketone C (C=O)C bend	[44]
1300-1000	C-O stretch in ether, ester	[44]
1298 - 1200	Organonitrates	[46]
1286, 1249, 1222	-CH <sub>2</sub> wagging	[50]
1280	Organonitrate	[41]
1280 - 1278, 1631	Organonitrate	[53]
1280 - 1270	Organonitrate (ONO <sub>2</sub> )	[42]
1280 - 1210	Esters/ethers/phenols (C-O)	[7]
1280 - 1137	C-O stretching of esters, ethers and phenols	[52]
1280	Symmetric NO <sub>2</sub> stretch in organonitrate	[44]

## Continued

1278	Organonitrate	[1]
1260 - 1000	Alcohols/Phenols (C-O)	[12] [44]
1260 - 700	Alkane skeletal vibration (C-C)	[38]
1220	C-O stretching and O-H bending vibrations of COOH	[5]
1210 - 1160, 1100 - 1030	Esters/Lactones (C-C-O)	[12]
1200 - 900	Carbohydrates (C-O-C)	[12]
1182	C-O-C stretching	[8]
1170	C-O-C stretch of polymers	[10]
1122	C-O-C from esters, or from the oligomers that were formed from dihydration of hydrated glyoxa	[47]
1080 - 1030	C-O stretching for primary alcohols	[8]
1080, 1050	C-C-OH of alcohols	[47]
1060 - 1035, 960 - 880	Acid anhydrides (C-O)	[12]
1052	C-C-O asymmetric stretch of alcohols	[10]
1040	C-O from organic groups, carbohydrates and acid anhydrides	[12]
940	OH from aliphatic and aromatic carboxylic acids	[11]
900 - 690	Aromatic C-H out-of-plane bend	[44]
890	C-C-O symmetric stretch of polymers; symmetric stretch of alcohols	[10]
880 - 750	OH stretching vibration of carboxylic groups	[52]
876	Organosulfate (C-O-S)	[17] [19] [33] [37] [44] [54]
860 - 750	OH stretching vibration of carboxylic groups	[7]
800	Secondary and primary amines N-H out of plane bend	[44]
785 - 540	Alkyl chlorides	[23]
730 - 550	C-Cl stretch in acid chloride	[23] [44]
720	Alkene C-H bend, rocking	[44]
650 - 100	Alkene C-H out-of-plane bend	[44]
578	-OH out of plane or C-C-O deformation	[10]

which offers a detailed description of spectral frequencies of the organic functional groups in aerosols reported to date in the literature.

## 4. Summary

With the advancement in mathematical and computer technologies as well as chemical metrologies, FTIR that was initially developed as a qualification tool for functional group analysis has become one of powerful techniques to determine the chemical compositions of aerosols and investigate compound concentrations as well as chemical processes involved in the formation of aerosols. It is believed that an increasing number of studies would prefer the FTIR quantification methods for the organic aerosols, once well established, since the advantages of affordable price, rapid analytical speed, simple sample preparation, low requirement for operators' skill and so on. By showing how studies used FTIR to investigate the physical and chemical processes involved in heterogeneous reactions, functional group compositions of organic aerosols, OM/OC, and source apportionment of aerosol particle etc. and summarizing the characteristic peak frequencies of functional groups present in organic aerosols reported in current literatures, this review would be helpful to those who are interested in applying FTIR to gain insight for complex and tiny organic aerosol particles.

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