Infrared Spectroscopy in Environmental Analysis

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Infrared (IR) spectroscopy is a universal, versatile analytical technique for the structure elucidation and quantification of a large variety of organic, inorganic and biological samples. The technique is based on the measurement of IR radiation, absorbed or emitted by a sample, as a function of the wavelength in the region 2.5–100 µm, or 4000–100 cm^{-1} in wavenumbers. The absorption or emission of IR radiation is related to discrete vibrational and rotational transitions in a molecule and, therefore, represents structural information. The analytical value of IR spectroscopy is based on the fact that the IR bands occur at more or less localized positions in the spectrum which are correlated to the presence of characteristic structural features of the sample under study. This similarity and transferability of spectral characteristics and the corresponding structural features, makes IR a powerful tool for functional group analysis. On the other hand vibrations, and thus the exact peak positions, are sensitive to the local environment which also makes IR spectra unique molecular fingerprints, highly suited for the unambiguous identification of a sample by comparison with reference spectra. Finally, IR spectroscopy obeys Beer's Law and can thus be used for quantitative purposes too.

The major advantage of IR over other spectroscopic techniques is that practically all compounds show absorption/emission and can thus be analyzed both quantitatively and qualitatively. Besides, IR spectroscopy is nondestructive and admits in situ and remote measurement of almost any sample, irrespective the physical state and without elaborate preparations. A broad variety of advanced accessories and technologies, such as IR microscopy, optical fibers, remote sensing, reflection and emission equipment and the combination with gas chromatography (GC), liquid chromatography (LC) and supercritical fluid chromatography (SFC) sampling and measurement techniques are available to tackle a diversity of problems. The absolute sensitivity is about 50–500 picograms, which is sufficient to solve many problems in trace analysis.

IR spectroscopy is used in a broad range of environmental applications. The technique is a viable tool in remote measurements of gases, liquids and solids and as a fast and reliable method for the characterization and indicative structure classification of a wide variety of samples. Besides, IR is widely applied for identification purposes either to confirm results of other techniques or for reasons of quality assurance (QA).

1 INTRODUCTION

The identification of molecular structures and the determination of their concentration in the sample is an essential part of environmental analysis. Among other selective techniques such as ultraviolet (UV), fluorescence, atomic emission and mass spectrometry, IR spectroscopy has gained wide acceptance as a viable technique for this purpose. The principle of IR spectroscopy is the measurement of the amount of IR radiation absorbed or emitted by a sample as a function of the wavelength. The wavelength of IR ranges from about 0.8 to 100 µm (12 500–100 cm^{-1} in wavenumbers) and is divided into a near-infrared (NIR) (12 000–4000 cm^{-1}) and a mid-IR (mid-infrared) (4000–100 cm^{-1}) part. This

chapter deals with the spectroscopy related to the mid-IR radiation. NIR spectrometry is discussed in the article **Liquid Chromatography/Infrared Spectroscopy** in this encyclopedia.

The absorption or emission of IR photons is related to rotational and vibrational transitions in a molecule and therefore represents structural information. The corresponding IR bands occur at discrete frequencies in the IR spectrum and this relation between the molecular structure of a sample and the IR spectrum is the most important analytical value of IR spectroscopy.

The potential of IR spectroscopy in the elucidation of molecular structures is very high. The number of fundamental vibrations in a molecule of N free-moving atoms is $3N - 6$. In principle, each vibration may give rise to an absorption or emission band but in practice the number is smaller as vibrations may be inactive as result of symmetry and degeneracy. On the other hand, much more than $3N - 6$ absorption bands may be present in the spectra of vapor-phase molecules as result of rotational transitions. Besides, vibrations and rotations are sensitive to a number of physical parameters, such as temperature and pressure, and to intra- and intermolecular interactions. The large number of vibrations and rotations, and the diversity of variables affecting these, make IR spectra unique molecular fingerprints, highly suited for the identification of a sample by comparison with reference spectra.

Valuable structural information can also be derived from the interpretation of spectra, e.g. in case a matching reference spectrum is absent. Contrary to identification, based on the discriminative properties of the spectrum, interpretation relates to the similarity and transferability of spectral characteristics and the corresponding structural features of molecules, i.e. functional groups. For that reason IR spectroscopy is also a useful technique for the characterization and structural classification of samples. However, as result of the large number of variables affecting a spectrum, it is extremely difficult to arrive at a complete molecular structure from a single spectrum without additional knowledge.

Finally, IR spectroscopy is an absorption technique obeying Beer's Law. It can thus be used for quantitative purposes too. A drawback compared to, for instance, UV, visible and fluorescence spectrometry is the small extinction coefficient of IR absorption bands resulting in relatively poor detection limits. Nevertheless, the current absolute limit of detection of about 10–50 picograms, is sufficient to solve many problems in environmental trace analysis.

The major advantage of IR over other techniques is that, apart from homonuclear diatomic molecules such as H_2, N_2 and O_2, all compounds show IR absorbance and can thus be analyzed qualitatively as well as quantitatively. Besides, IR is a nondestructive, non-contact technique, offering the possibilities to perform in situ and remote measurements. From this practical point of view, IR is probably the most versatile of all analytical techniques, as a spectrum can be recorded of almost any sample, irrespective of the physical state and without elaborate preparations within tenths of a second. This versatility has made IR spectroscopy a valuable analytical tool in a variety of environmental applications.

2 HISTORY

Since the development of IR spectroscopy in the early 1940s the instrumentation and environmental applications have developed through a number of stages. The first generation IR spectrometers were single-beam instruments with alkali halide prisms as the dispersive element. The sensitivity and the resolution of these instruments were poor, limiting the applications to functional group analysis and indicative quantification of milligrams of material.

In the 1960s, the instruments became double-beam, and Echelette gratings, combined with optical filters for order separation, replaced the prisms. As a consequence, the optical resolution and the stability and sensitivity of IR spectrometers were considerably enhanced and the detection limits extended to micrograms. A further development, the coupling to chromatographic techniques, via stopped-flow and flow-through cells, led to new applications, particularly in the structure elucidation of constituents in complex matrices.

A further positive impulse was given by the incorporation of computers into the IR spectrometers. Advanced data acquisition and manipulation techniques such as spectrum subtraction, programmes to search in large libraries of digitized spectra, and chemometrical methods were brought to the bench of IR spectroscopists.

Finally, the introduction of the Fourier transform (FT) principle in IR spectrometers in the 1970s dramatically improved the possibilities of IR spectrometry in a wide range of analytical problems. The high scanning speed and sensitivity of Fourier transform/infrared (FT/IR), combined with extended computer facilities for data manipulation and the development of a series of advanced accessories and technologies, such as IR microscopy, high resolution interferometers ($>0.001\,\mathrm{cm^{-1}}$), tunable lasers, specific detectors, reflection and emission equipment and the construction of mobile and portable instruments, have brought IR to its current state of versatility and popularity.

3 SAMPLING AND MEASUREMENT TECHNIQUES

As result of the unique versatility of IR spectrometry a broad variety of sampling and measurement techniques are available to tackle a diversity of problems. The development of several of these methods originate from an environmental demand. An illustrative example is the IR remote sensing technique for the qualitative and quantitative in situ determination of gases.[1] The need to study emissions and chemical processes of greenhouse gases largely contributed to the development of this open-path technique to its current state of maturity. Obviously, the fact that global warming is assumed to be caused by the increasing release of exogenic IR-absorbing gases into the atmosphere, plays a role in this.

The principle of IR remote sensing is shown in Figure 1. In the passive mode, the sun is used as a light source or the spectrometer is operated as a detector to determine the IR radiation emitted by the subject of study. In the active mode the instrument operates as a classical source–detector spectrometer, recording absorption along the beam path to a flat mirror or a retroreflector and back. The IR source and the detector are either incorporated in one instrument or separated into modules.

Absorption measurement in a closed gas cell is a good alternative to carry out model studies and in case the analysis has to be performed on previously collected samples. Internal multi-reflection options offer the possibility of enlarging the effective pathlength to 1–100 m within the relatively small dimensions of a 10–30 cm gas cell. This method is particularly attractive in case extremely low detection limits are not crucial. Gas cells are used both separately as an accessory, and fixed, incorporated into a (mobile) spectrometer. An example of the latter is the commercially available mobile FT/IR spectrometer GASMET™ (Temet Instruments Ltd, Finland) as shown in Figure 2.[2]

Remote measurements of gases, liquids and solids can also be carried out with the help of optical fibers.[3] Fibers are used as a transmission wave guide to transfer the IR signal to and from a sensing probe, and as a sensing element itself. The fibers are made of materials such as chalcogenides that combine a certain physical flexibility with a high IR transparency. Optical fibers are particularly useful to carry out in situ measurements and to study compounds with possible toxic or corrosive activity. At present, distances of 5–50 m can be covered, depending on the desired wavenumber region to be scanned.

The advantages of optical fibers and solid-phase micro extraction (SPME) have been combined to a fiber optic
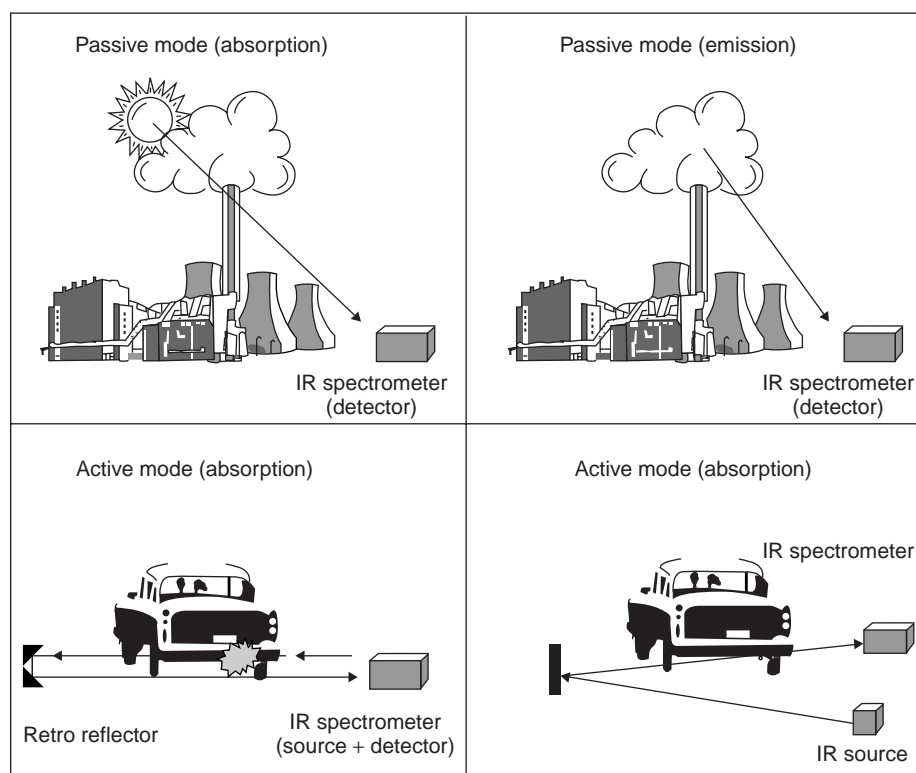

Figure 1 Schematic representation of the principle of active and passive remote sensing IR measurements.
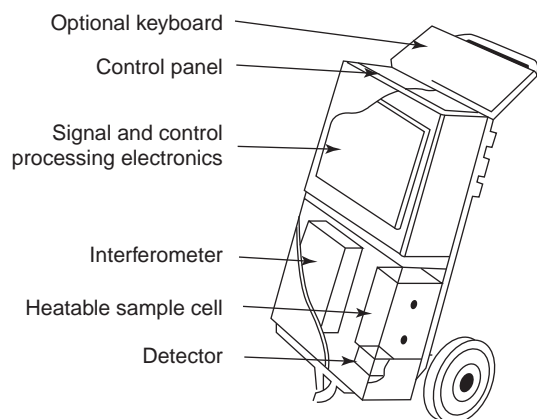
Figure 2 Schematic diagram of a mobile IR gas analyzer (Reproduced by permission of The Royal Society of Chemistry from I. Ahonen, H. Riipinen, A. Roos, 'Portable Fourier Transform Infrared Spectrometer for Use as a Gas Analyzer in Industrial Hygiene', *Analyst*, **121**, 1253–1255 (1996).)
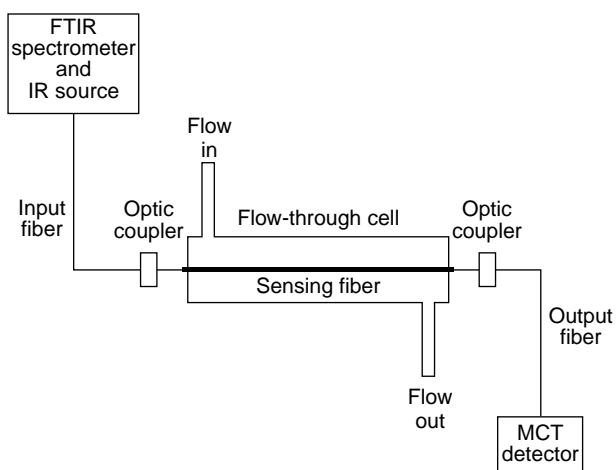
Figure 3 Schematic representation of optical fiber sensing for aqueous samples. (Reproduced by permission of The Royal Society of Chemistry from J.E. Walsh, B.D. MacCraith, M. Meaney, J.G. Vos, F. Regan, A. Lancia, S. Artjushenko, 'Sensing of Chlorinated Hydrocarbons and Pesticides in Water Using Polymer Coated Mid-infrared Optical Fibers', *Analyst*, **121**, 789–792 (1996).)

sensor system for the analysis of microcontaminants in aqueous samples.[4] The experimental set-up of this system is schematically depicted in Figure 3. The actual sensor consists of a silver halide fiber coated with a thin layer of polymer. Similar to SPME, the organic analytes are extracted from the water into the polymer film and scanned with a (portable) IR spectrometer after a certain equilibration time.

Conventional sampling methods such as the liquid cell and the KBr-pelleting technique, as well as more advanced methods such as diffuse reflectance infrared (DRIFT) and attenuated total reflection (ATR), are being used for the characterization and identification of samples in case the available amount is not the limiting factor. For quantitative purposes, liquid cells of variable pathlength, cell volume and window material are available.

IR microscopy is being employed for the analysis of small particles and in combination with the on- and off-line coupling to separation techniques for the determination of trace contaminants. The principle and applications of IR microscopy have been described by Messerschmidt and Harthcock.[5]

The application of IR microscopy as a detector in GC, LC and SFC has largely enhanced the sensitivity of these combined techniques. The current limit of detection is in the (sub)nanogram range which makes these hyphenated techniques useful alternatives or additives to commonly applied detectors such as flame ionization, electron-capture and mass spectrometry.

The interfacing of GC and IR is accomplished in three different ways which are all commercially available. The first one is on-line by means of a heated flow-through cell with an optical pathlength of 10–30 cm. This so called 'light pipe' interface allows continuous monitoring of the GC effluent.

The second one is off-line and comprises the trapping of the GC-separated analytes in an argon matrix on a rotating gold coated cylinder at 4K. After completion of the GC-run, the immobilized chromatogram can be scanned at any desired speed and resolution as long as the cryogenic conditions are maintained. This technique is called matrix isolation gas chromatography/infrared (GC/IR).

The third one is also a cryogenic sample storage technique and is called cryotrapping or direct deposition GC/IR. The analytes are crystallized directly on a moving IR transparent window at liquid nitrogen temperature (77K). Scanning can be carried out both on-line, a few seconds after deposition, or post-run, after completion of the GC separation.

The most important advantage of the sample storage methods is the sensitivity which is about two orders of magnitude better than that of a light-pipe instrument as result of the application of IR microscopy and the possibility of long-time signal averaging.[6]

A series of papers on the environmental applications of GC/IR have been published by Gurka et al.[7] The analytical value of multidimensional gas chromatography/infrared/mass spectrometry (GC/IR/MS) for the investigation of environmental samples has been summarized by Krock and Wilkins,[8] while the synergetic value of GC/IR in combination with other spectrometric techniques has been reviewed by Ragunathan et al.[9]

IR detection in LC and SFC is accomplished on-line by passing the effluent through a liquid flow-through cell, or off-line by elimination of the solvent prior

to detection of the deposited analytes. Flow cells for any type of mobile phase, including supercritical fluids, and solvent elimination liquid chromatography/infrared (LC/IR) interfaces can be purchased from several companies. Off-line detection is highly favorable since important parts of the spectral region may be obscured by absorption bands of the eluents. Particularly in reversed phase, the strong absorption of water is a major limiting factor not only in terms of poor spectral information but also in sensitivity as a feasible pathlength should not exceed 10–20 microns. An extensive review of the merits and limitations of on- and off-line coupled LC/IR has been reviewed by Somsen et al.[10]

4 ENVIRONMENTAL APPLICATIONS

Numerous papers on the application of IR spectrometry in environmental analysis have been published in analytical, environmental and spectroscopic journals. State-of-the-art surveys are frequently published of which the comprehensive biannual reviews of *Analytical Chemistry* on IR spectroscopy[11] and environmental analysis[12] are recommended as good starting points.

Papers on specific IR sampling and detection techniques also contain valuable information on environmental applications. Representative examples are the previously mentioned reviews on IR microscopy,[5] GC/IR[7–9] and LC/IR.[10]

The diversity in applications is extremely large. The analytes vary from organic and bio-organic molecules to polymers, inorganics and even microorganisms. Next to air, soil and water, IR analysis is employed in all sorts of matrices at concentration levels between bulk and trace. Real-time and in situ measurements are performed for dynamic studies while various on- and off-line methods are being used for characterization, classification, structure elucidation and quantitative analysis. A summary of the IR spectroscopic applications is presented in Table 1. A selection of the most relevant and illustrative applications is described into more detail in the following sections.

4.1 Indoor Air

The concern for good quality of indoor air has urged the development of techniques that are able to monitor the presence and release of harmful gases. Not only in the laboratory and industrial environment but also in, for instance cleaning and printing shops and during painting, relatively high concentrations of volatile organic compounds (VOCs) may be released. In principle, IR spectrometry is an attractive technique for the screening and monitoring of VOCs in the gas phase.

All compounds show IR absorption and can thus be determined, while measurements can be performed remotely and continuously without any sampling. The sensitivity of IR is in the low ppm range, which is relatively low compared to some other techniques but sufficiently high for many applications. Therefore, several systems to monitor emissions of VOCs are based on IR detection.

Three types of IR–gas measurement systems can be distinguished:

1. low cost non-scanning detectors that are specifically used to determine the presence of one or two target-components;
2. portable instruments with filters or an interferometer for wavelength selection;[2]
3. remote open-path IR spectrometers.[13]

An instrument, specially designed to monitor indoor air concentrations, is the Infrared Gas Cloud (IGC) scanner developed by ter Kuile et al.[14] This apparatus is used for the selective analysis of gases in the ppm range to visualize the spatial distribution of the analyte in the workplace. Specific applications are the testing of ventilation systems and the remote detection of gas leaks.

Dispersive IR analysis of gases, released by the smoking of cigarettes, proves to be a better method for quantification than most other spectrometric techniques. The yield for carbon monoxide, hydrogen cyanide and nitric oxide turns out to be about 45% higher when detected with IR.[15]

In case direct IR measurement is hampered, for instance as result of weak absorbing properties of the analyte, indirect detection after conversion into a stronger absorbing compound is a good alternative. An example is the analysis of H_2S and O_2 which can be detected at much lower concentrations after oxidation to SO_2 and ozone respectively, by UV irradiation over a certain period of time.[16]

Preconcentration techniques, occasionally combined with a derivatization or modification, are used as well. Fillipi[17] for instance, developed a purge and trap method combined with a chemical reduction step prior to GC/IR and atomic absorption spectrometry (AAS) to determine methyl and dimethyl mercury in air at a 50 pg level.

4.2 Atmosphere and Stratosphere

The detection of exogenic and endogenic gases in the outdoor atmosphere relies to a large extent on the same methods as used for the analysis of indoor air. Similar specific single-compound detectors are used for continuous monitoring or occasional field measurements to determine and quantify a selection of predefined harmful gases and VOCs at, for example, industrial

Table 1 Applications of infrared spectroscopy in environmental analysis

Matrix type	Aim	Methods	Analytes
Ambient atmosphere	Structure elucidation, quantification, monitoring, screening, mapping, gas release	Nonscanning IR sensors, gas cells, active remote sensing, portable instruments	CFCs, VOCs, BTEX, PAHs, nitro-PAHs CO_x, NO_x, HCN, H_2S, O_2, Hg-alkanes
Stratosphere	Structure elucidation, quantification, monitoring, local and global environment, greenhouse effects, volcanic emission studies, biomass burning	Active and passive remote sensing, multipass gas cells, GC/IR mobile and airborne spectrometers	CFCs, VOCs, BTEX, PAHs, CO_x, NO_x, HCN, H_2S, O_3, ClO_x, SO_x, HCl, HF, SiF_4, $ClNO_x$, H_2O, hydrocarbons, etc.
Aerosols	Structure elucidation, quantification, combustion products and processes, photooxidation, air particulate matter	Active and passive remote sensing, multipass gas cells, GC/IR, LC/IR	(Metabolites of) terpenes, pheromones, PAHs, nitro-PAHs, nitro-cresols, phenols photodissociation and oxidation products
Smoke and exhausts	Structure analysis, quantification, monitoring, motor cars, aircraft, incinerators, power plants	Active and passive remote sensing, GC/IR mobile spectrometers, multipass gas cells	PAHs, hydrocarbons, H_2O, CO_x, NO_x, SO_x, HCN, H_2S, O_2
Water	Structure elucidation, quantification, confirmation, trace analysis	SPE, SPME, LLE/GC/IR and LC/IR, SFE/IR, sparging-IR, optical fibers	CFCs, pesticides, industrial contaminants, pharmaceuticals, oils, greases, VOCs, PAHs, biomolecules (microorganisms)
Soil	Soil characterization, trace analysis, structure elucidation, quantification	Films and pellets, DRIFT, PAS, GC/IR, LC/IR, SFE/IR, optical fibers	HA and FA fractions, pesticides, inorganics, nitrates, silicates (asbestos), oils and greases, VOCs, CFCs, PAHs
Sediments	Structure elucidation, quantification, trace analysis, confirmation	GC/IR, LC/IR, thermal desorption IR, multipass gas cells, SPME/IR	Pesticides, PAHs, oils and greases
Reference materials	QC, identity control geometrical characterization	KBr, liquid film, solutions, DRIFT, reflection, GC/IR, LC/IR	Pesticides, PAHs, PCBs, PCDFs, PCDDs
Waste	Characterization, structure analysis, quantification, recycling purposes, polymer sorting	Active remote reflection, ATR, PAS	Industrial and domestic contaminants, oil, polymers, plasticizers, detergents

PAS, photo-acoustic spectrometry; QC, quality control.

sites and waste incinerators. Multi-pass gas cells and open-path equipment are applied for the detection of other, non-target analytes.[18]

Remote sensing open-path IR spectrometry has substantial advantages over the other methods. It can be used to measure absorption as well as emission and the technique is capable of covering almost infinite distances. This offers the possibility of detecting fluxes of trace gases over a much wider area than can be achieved by any other technique. For that reason, active and passive remote sensing IR are the methods of choice for monitoring gases and gaseous emissions, not only in the lower atmosphere but at any altitude and even in space.

A review on atmospheric and stratospheric research is given by Farmer.[19] Most studies focus on the detection and the quantification of a large variety of trace gases in order to monitor possible compositional changes as a result of human activities and to get insight into the underlying physical and chemical processes. Subjects of research are the fluxes and effects of fertilizers, pesticides, industrial waste contamination, energy production, etc. Analogous studies are performed on environmental burdening by compounds emitted from natural sources, such as plants, animals, volcanic activity and biomass burning. As noted before, special interest is given to the greenhouse effect and the depletion of the stratospheric ozone layer over the Arctic and Antarctic areas.

The IR spectra of gases in space and in the stratosphere exhibit extremely narrow vibrational and rotational bands as result of the very low temperature at site. In order to extract maximum information from the spectra, high-resolution facilities are essential and for that reason, measurements are preferably carried out with instruments with a data point resolution of 0.05 to 0.002 cm^{-1}. As
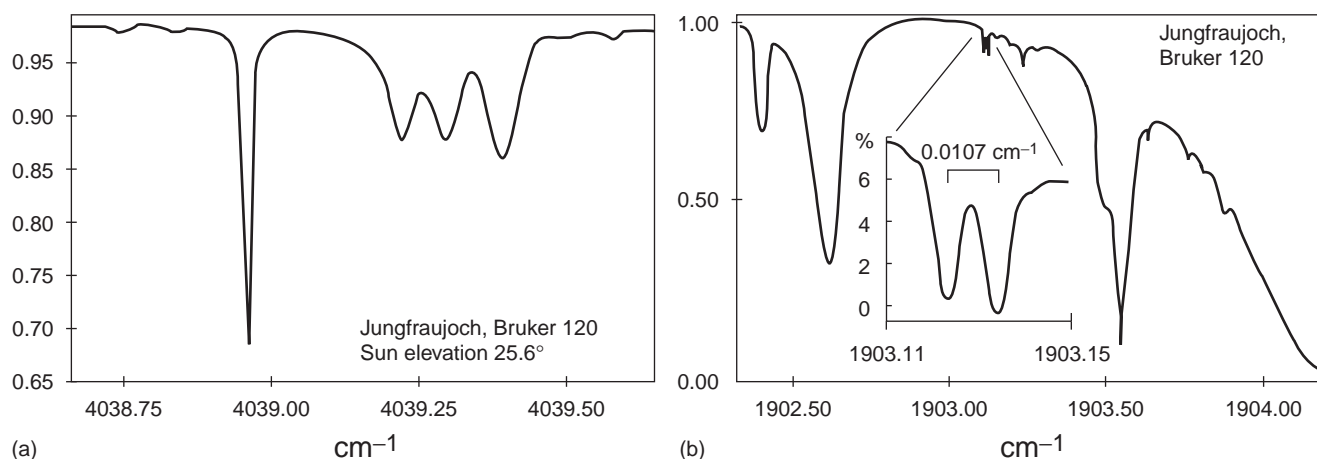
Figure 4 High-resolution IR spectra recorded at the Jungfraujoch observatory; (a) the HF line at 4038.9625 cm^{-1} and (b) the NO doublet around 1903 cm^{-1}. (Reproduced by permission of The Society of Photo-optical Instrumentation Engineers from L. Delbouille, 'The Role of Very High Resolution FTS in Recent Determinations of the Quantitative Composition of the Stratosphere', *Proc. SPIE-Int. Soc. Opt. Eng.*, **2089**, 32–37 (1993).)

well as molecules involved in the photodissociation of chlorofluorocarbons (CFCs), a diversity of other minor constituents such as CO, CH$_4$, HF, HCl, HCN, O$_3$, NO$_2$, NO, SF$_6$, N$_2$O, N$_2$O$_5$, H$_2$O$_2$, OCS and ClONO$_2$ can be determined with this type of IR-spectrometric technique.

Measurements are performed:

1. directly by air-borne spectrometers in space and aircraft or in balloons;
2. directly by ground-based remote sensing techniques;
3. indirectly by laboratory analysis of samples collected by aircraft or balloon.

In addition to these techniques, kinetic laboratory studies are undertaken to mimic atmospheric and stratospheric conditions and processes. For this type of research, pressure- and temperature-controlled gas cells are used.

Air-borne instruments are in general of special design such as the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument that is used in Space Shuttle flights. Measurements from aircraft are usually preferred to observations from balloons, since the latter are relatively expensive and limited to balloon-accessible altitudes of about 45 km. Yet it is a viable and frequently used method for direct analysis and for the validation of data obtained from other techniques.[20]

Examples of ground-based measurements are the observations at the Jungfraujoch mountain station in the Swiss Alps, where IR spectra of the global atmosphere and stratosphere have been acquired over a period of almost five decades,[21] and the measurements in the Arctic area where the column densities of several atmospheric gases have been determined during summer and winter seasons.[22] In these observations, the sun is used as the IR light source, either directly at daytime or indirectly by reflection via the moon at night. Long-term scanning is required to get sufficient signal-to-noise ratio which implies that a tracker is necessary to follow the course of the emitting object. Examples of the information obtained from such high-resolution data are depicted in Figure 4 showing the extremely narrow absorption lines of HF and NO recorded at the Jungfraujoch observatory.

4.3 Smoke Stacks and Exhaust Gases

Many studies have been dedicated to the on- and off-line measurement of smoke stacks, and flue gases released from traffic and power plants.[23] The popularity of the remote methods is rapidly growing due to the fact that it is a noncontact real-time technique. Besides, it enables the performance of multicomponent analysis in seconds.

A remote-sensing IR method to determine the constituents of the exhaust gas of a coal-fired power plant has been developed by E. Lindermeir.[24] The principle of this method is the measurement of the emission lines of released gases at medium resolution (0.5 cm^{-1}). Accurate concentrations of H$_2$O, CO$_2$, CO, NO and SO$_2$ in smoke stacks at heights up to 200 m were calculated from the IR spectra using special algorithms to compensate for background fluctuations.

A commercial remote sensing FT/IR instrument RSD 1000, (Remote Sensing Technologies Inc. Maryland, USA) is used by Sjödin[25] to determine the instantaneous concentrations of CO and hydrocarbons in the exhaust of motor cars. The measurements are used to select major polluters for subsequent roadside inspection. It has proven to be a useful tool to increase the efficiency of

roadside inspections to detect cars violating governmental idle test standards.

Roadside and laboratory inspections can be readily performed by flow-through and sampled gas cells as well. The portable mobile IR spectrometer GASMET™ for instance, equipped with a 1.8 m multipass gas cell, can detect a variety of exhaust gases at levels of 0.2–20 ppm.[2]

Specific spectrometers have been developed for FT/IR emission measurements of aircraft engine exhausts under active conditions. It enables the determination of emission rates of gases like NO, CO, CO_2 and H_2O with a resolution of $0.2 \, cm^{-1}$ during the flight at cruising altitudes up to 25 000 ft.[26]

A mobile air pollution search system has been developed by the Kayser–Threde Company (Munich, Germany). The system is based on a K300 double pendulum spectrometer that operates at a spectral resolution of $0.08 \, cm^{-1}$. In the passive emission mode, the instrument can determine gas concentrations of CO, CO_2, N_2O, NO, SO_2 and HCl in smoke-stack effluents of power plants and municipal incinerators with high accuracy.[27]

4.4 Terpenes and Biogenic Aerosols

Environmental risk-assessment studies generally comprise the release of compounds of anthropogenic origin. From the viewpoint of health care, however, the emission of molecules from natural sources are of almost equal interest. The release of gases from a single volcanic eruption, for instance, can be in the order of billions of tons. Other sources that are known to have large impacts on the local or global environment are bush fires, aqueous microorganisms and emissions from terrestrial plants (terpenes) and animals (pheromones).

Terpenes, released from plants and trees, are known to be important in the formation of photochemical oxidants and secondary organic aerosols. To determine the qualitative and quantitative composition of terpene emissions and its oxidation products in the related aerosols, an IR spectroscopic method in addition to gas chromatography/mass spectrometry (GC/MS), has been developed by Schrader et al.[28] It is demonstrated that cryotrapping GC/IR supplies important complementary information for the structure elucidation of mono- and sesquiterpenes as well as other ethereal compounds, at the high picogram level.

Biogenic aerosols from photooxidation of terpenes have been analyzed by Palen et al.[29] too, using IR microscopy. The quantitative possibilities of this method are limited but valuable information can be obtained concerning the presence of compounds with oxygen-containing functional groups such as hydroxyls,

ethers, ketones, aldehydes, carboxylic acids, lactones and esters.

Finally, IR spectrometry is also used to determine and characterize waterborne microorganisms in drinking water.[30]

4.5 Volcanic Emissions

Passive and active open-path IR spectrometry are the principal methods of monitoring emissions from active volcanoes. The IR spectra are primarily used to determine the identity and flux of gases released during eruption. Other information that is extracted from the IR data deals with the eruptive history of volcanoes and the effects of vulcanism on the local and global climate. A case study on this subject is given by Chaffin et al.[31] Measurements over pathlengths of 500 m to nearly 2 km have been carried out with a mobile spectrometer operating at a resolution of $0.5 \, cm^{-1}$. Large amounts of CO_2 and SO_2 in the volcanic plume hamper the identification of compounds that absorb in the same regions as these two components; however, several other constituents such as HCl, SO_2 and SiF_4 can be determined at ppm level in very short measurement times (less than one minute is typical). As an example of the performance of these measurements, the field-recorded spectrum of HCl and the vapor-phase reference spectrum of this compound, are depicted in Figure 5.

4.6 Biomass Burning

According to Griffith,[32] the burning of biomass is a highly underestimated source of air pollution. The annual release of carbon into the atmosphere as result of wild fires and the prescribed combustion of bush, forest, savanna and agricultural waste is about 3–6 gigaton which is of the same order as the annual combustion of fossil fuels. FT/IR studies are used to determine the composition of the smoke gases in order to distinguish between the different types of biomass burning and to assess the impact of this type of process on the atmosphere. The IR analysis is performed both directly by field measurements using long-open-path spectrometers, and by laboratory studies of smoke samples that have been taken by cold trapping in canisters at the ground and at higher altitudes using light aircraft. The in situ measurements are carried out at high resolution ($0.05 \, cm^{-1}$) with a typical pathlength of 20–200 m. The samples are analyzed by matrix isolation FT/IR.

Next to the well known carbon, sulfur and nitrogen oxides, tens of other trace gases including CS_2, CSO, HCN, CH_3CN, and hydrocarbons have been identified and quantified. A spectrum, typical for a smoke sample, is shown in Figure 6.
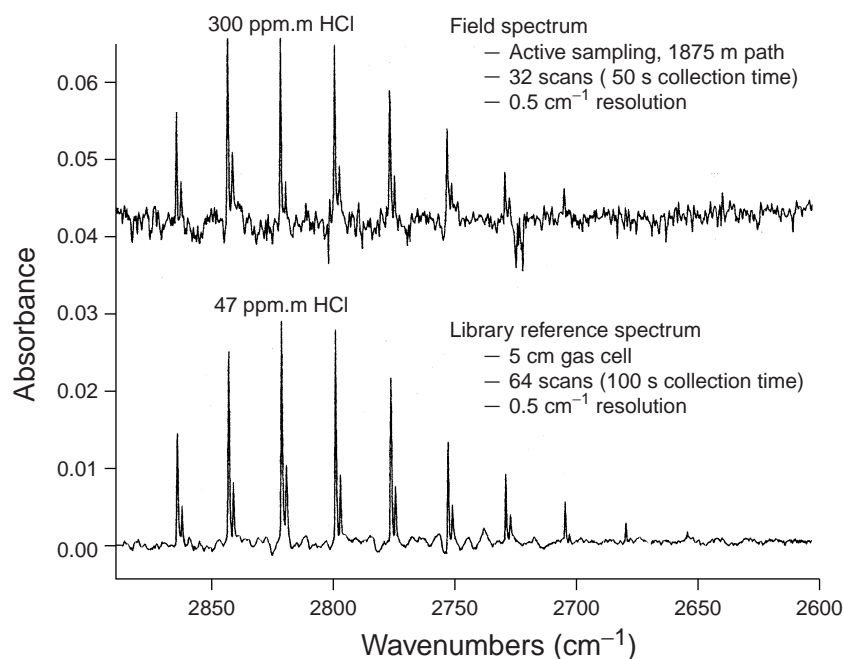
Figure 5 Reference IR spectrum and active field spectrum of HCl from a volcanic plume. Pathlength 1875 m, resolution $0.5\,\text{cm}^{-1}$, scanning time 50 s. (Reproduced by permission of Wiley-VCH from C.T. Chaffin, T.L. Marshall, W.G. Fateley, R.M. Hamaker, 'IR Analysis of Volcanic Plumes: A Case Study in the Application of Open Path FT/IR Monitoring Techniques', *Spectrosc. Eur.*, **7**, 20–24 (1995).)
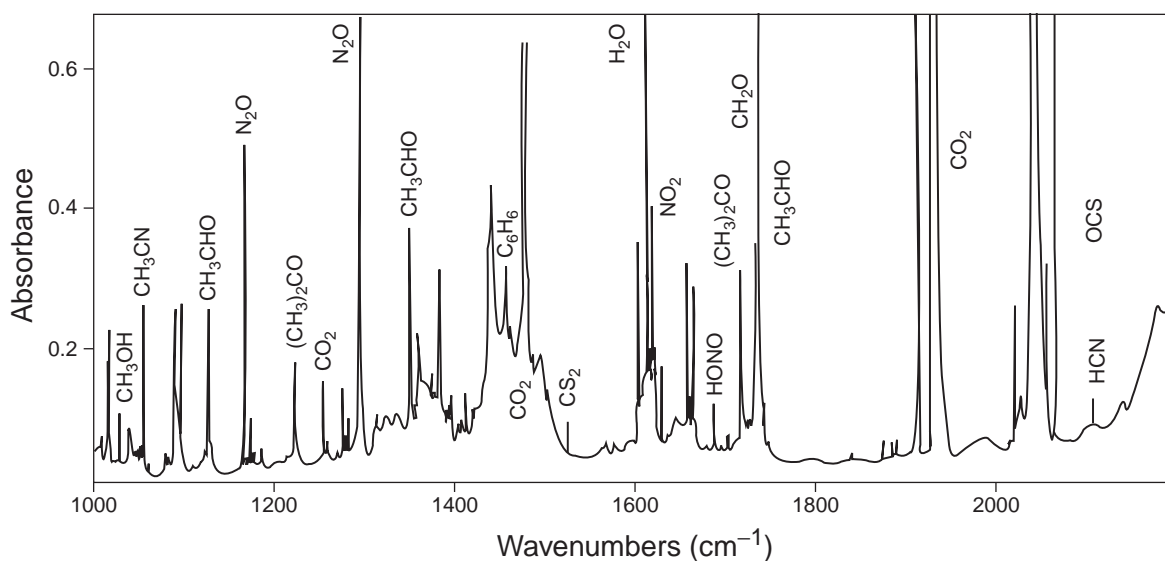

Figure 6 Matrix isolation FT/IR spectrum of a smoke sample from burning savanna grassland. (Reproduced by permission of The Society of Photo-optical Instrumentation Engineers from D.W.T. Griffith, 'FT/IR, Bushfires and Atmospheric Chemistry', *Proc. SPIE-Int. Soc. Opt. Eng.*, **1575**, 59–69 (1991).)

4.7 Volatile Organic Compounds

The relevance of the determination of VOCs in the indoor and outdoor atmosphere, and the IR spectroscopic techniques that can be used for this purpose, have already been described in sections 4.1 and 4.2. Obviously,

the analysis of VOCs in other matrices is of similar importance. A rapid screening method to determine and quantify VOCs in soil has been developed by Clapper et al.[33] The principle of this method is the thermal desorption of the analytes from the soil sample with subsequent analysis of the vapor in a multipass gas cell

with a pathlength of 13.2 m. The sensitivity is at microgram level.

Fiber-optic analysis is a useful alternative when direct analysis of high concentrations of organic solvents in soil is required. As shown by Ewing et al.,[34] this technique is very selective for the identification of benzene, toluene, ethylbenzenes and xylenes (BTEX) as well as for the remote detection of high concentrations of trichloroethylene.[35]

Optical-fiber sensing is also used for the analysis of chlorinated hydrocarbons in water samples. The sensitivity of the sensor is increased by application of a polymer coating on the fiber surface. This type of analyte enrichment is analogous to the principle of SPME and enables the detection of chlorinated solvents such as tetrachloroethylene at a concentration level of 300 ppb.[36]

SPME has also been used for direct detection of VOCs in water by extraction of the organic compounds into a 130 µm thick parafilm.[37] After a certain equilibration time, the film is measured by IR transmission spectroscopy. Reproducible extraction and detection is achieved for VOCs such as benzene, toluene and chlorotoluene at concentration levels of 0.1–1 ppb.

Another technique for the determination of volatile pollutants in surface and wastewater is sparging-IR. This technique is based on the favorable partitioning of volatile and semivolatile organic molecules for the vapor phase over the liquid aqueous phase. Contaminants are forced into the vapor phase by a stream of nitrogen bubbles passing through the sample. Subsequently, the vapor is directed into a multipass gas cell for measurement of the target components. Sparging-IR is a multicomponent method with detection limits at the ppb level.[38]

4.8 Industrial Contaminants

Industrial processes and their products are a major source of environmental burdening. Production processes are generally accompanied by the emission of considerable amounts of waste chemicals, solvents and by-products. Indeed, the final products, especially chemical ones such as pesticides, pharmaceuticals, dyes, oils, plastics and paints, are obvious potential polluters. Finally, several of these compounds may give rise to the formation of metabolites and oxidation and degradation products.

Notorious examples of hazardous waste compounds are the polychlorinated benzenes (PCBs), dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) because of their high toxicity and persistency. Other well-known industrial contaminants are VOCs, polyaromatic hydrocarbons (PAHs), phenols and (metabolites of) pesticides.

Many IR spectroscopic methods are available for the analysis of this large variety of compounds. The determination of VOCs has been discussed in the previous section. A selection of the most important other compound classes is presented in the following sections.

4.9 Pesticides

Several IR spectroscopic methods have been developed for the determination of pesticides and their metabolites in aqueous matrices. Because of the limited sensitivity of IR in relation to the required limits of detection (0.1 to $1 \mu g \, L^{-1}$ typical), the methods usually comprise a pretreatment such as liquid–liquid extraction (LLE), solid-phase extraction (SPE), thermal desorption and derivatization.

The potentials of GC/IR for the determination of pesticides have been summarized by Kalasinsky.[39] Recent work on the combined GC/IR and GC/MS analysis of pesticides in surface and groundwaters from different locations in Lithuania has been carried out by Ellington et al.[40] Organic constituents were extracted from the water samples by SPE on cartridges. Subsequently, the cartridges were transported to the laboratory, eluted by an organic solvent and injected on the GC. As well as triazines and Alachlor, several chlorinated and aromatic carboxylic acids were determined.

A similar method for the analysis of microcontaminants in tap and surface water has been developed by Hankemeier et al.[41] After SPE extraction of 20 mL samples of water at site, the SPE cartridges are dried and brought to the lab. Next, the cartridges are desorbed on-line into the GC with 100 µL of ethylacetate using on-column large-volume injection interfacing. The IR detection is performed with a cryogenic sample storage GC/IR instrument. As can be seen from Figure 7(a), the Gram–Schmidt GC/IR chromatogram, reflecting the total IR absorption in the range $4000–6000 \, cm^{-1}$ as a function of time, permits detection and identification of all eluting components. Functional group GC/IR chromatograms (Figure 7b), show elution of compounds that absorb in a preselected wavenumber region and can be used to monitor the presence of compounds with a specific structural element.

A variety of pollutants have been identified at 0.1 to 1 ppb level, the current alert and alarm levels for micropollutants. As an example of the performance of this system, the IR spectra of the pesticides Sulfotep and Diazinon, extracted from the chromatograms recorded from 1 ppb in Figure 7, are shown in Figure 8.

The utility of solvent elimination LC/IR for the determination of pesticides in aqueous matrices has been studied extensively by Somsen et al.[42–44] Three different methods have been investigated for application to reversed-phase separations. The first method is an on-line post-column extraction of the analytes
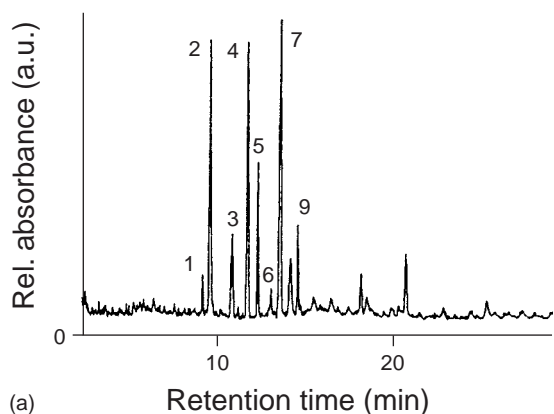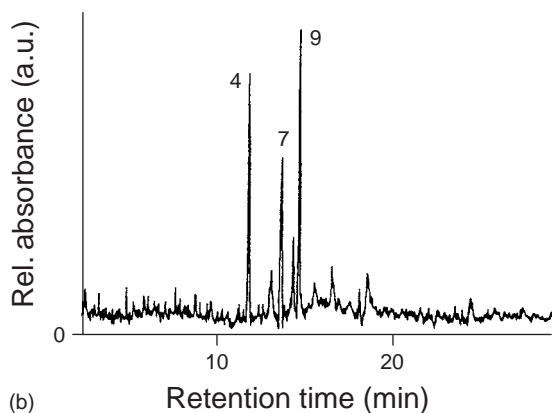
Figure 7 Gram–Schmidt GC/IR chromatogram (a) and functional group chromatogram of the region $1580-1520\,cm^{-1}$ (b) obtained from on-line desorption of an SPE cartridge sampled with 20 mL tap water spiked at $1\,\mu g\,L^{-1}$. Peak 4: Atrazine, peak 7: Simetryn, peak 9: Metolachlor. (Reproduced from *J. Mol. Struct.*, **408/409**, T. Visser, M.J. Vredenbregt, A.P.J.M. de Jong, G.W. Somsen, Th. Hankemeier, N.H. Velthorst, U.A.Th. Brinkman, 'Recent Improvements in Environmental Trace Analysis by GC/IR and LC/IR', 97–103 (1997) by permission of Elsevier Science Ltd.)

Figure 8 Cryotrapped GC/IR spectra of the insecticides (a) Sulfotep and (b) Diazinon obtained from SPE-large volume cryotrapping GC/IR of 20 mL of tap water spiked at $1\,\mu g\,L^{-1}$. (Reproduced from *J. Mol. Struct.*, **408/409**, T. Visser, M.J. Vredenbregt, A.P.J.M. de Jong, G.W. Somsen, Th. Hankemeier, N.H. Velthorst, U.A.Th. Brinkman, 'Recent Improvements in Environmental Trace Analysis by GC/IR and LC/IR', 97–103 (1997) by permission of Elsevier Science Ltd.)

from the buffered aqueous mobile phase into the more volatile dichloromethane to improve the performance of the spray-jet LC/IR interface.[42] This technique allows identification of phenylureas and quinones at a level of $50\,\mu g\,L^{-1}$. Improvement has been achieved by incorporation of a trace enrichment step using on-line SPE. With this method triazines and phenylurea herbicides can be identified at the alert level of $1\,\mu g\,L^{-1}$. The quality of the spectra obtained from the LC/IR analysis of a 100 mL sample of river Meuse water, spiked at $2\,\mu g\,L^{-1}$, is shown in Figure 9. For 20 mL injections, the analyte recovery is about 90% which indicates that this method can be used not only qualitatively but also for quantitative purposes.[43]

On-line trace enrichment combined with capillary column switching LC has proven to be a useful
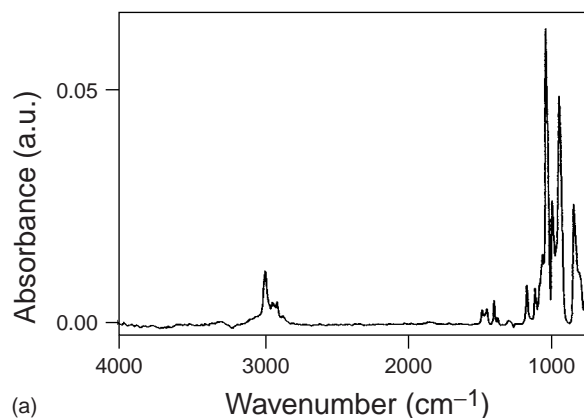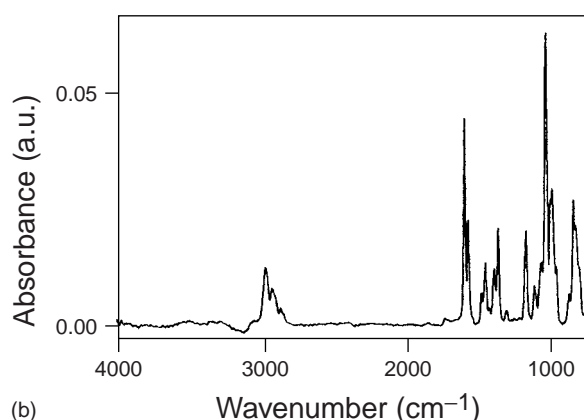
alternative for reversed-phase LC/IR when gradient elution separation is required. Post-column extraction cannot be applied because of the continuously changing composition of the mobile phase. However, these fluctuations are masked by addition of an excess of a volatile make-up liquid. The limit of identification of this method is about $20\,\mu g\,L^{-1}$ for triazines.[44]

Optical-fiber sensing is suited to the analysis of high concentrations of chlorinated hydrocarbons and pesticides in water samples. Analogous to SPME, analyte enrichment is accomplished by a thin polymer film on the fiber surface. The detection limit is about 2 ppm for the pesticides Alachlor and Atrazine.[45]

Finally, the same method of thermal desorption with subsequent measurement of the vapor phase, as applied for the determination of VOCs in soil, is applied for the determination of (semi)volatile pesticides when present in high concentrations.[33]
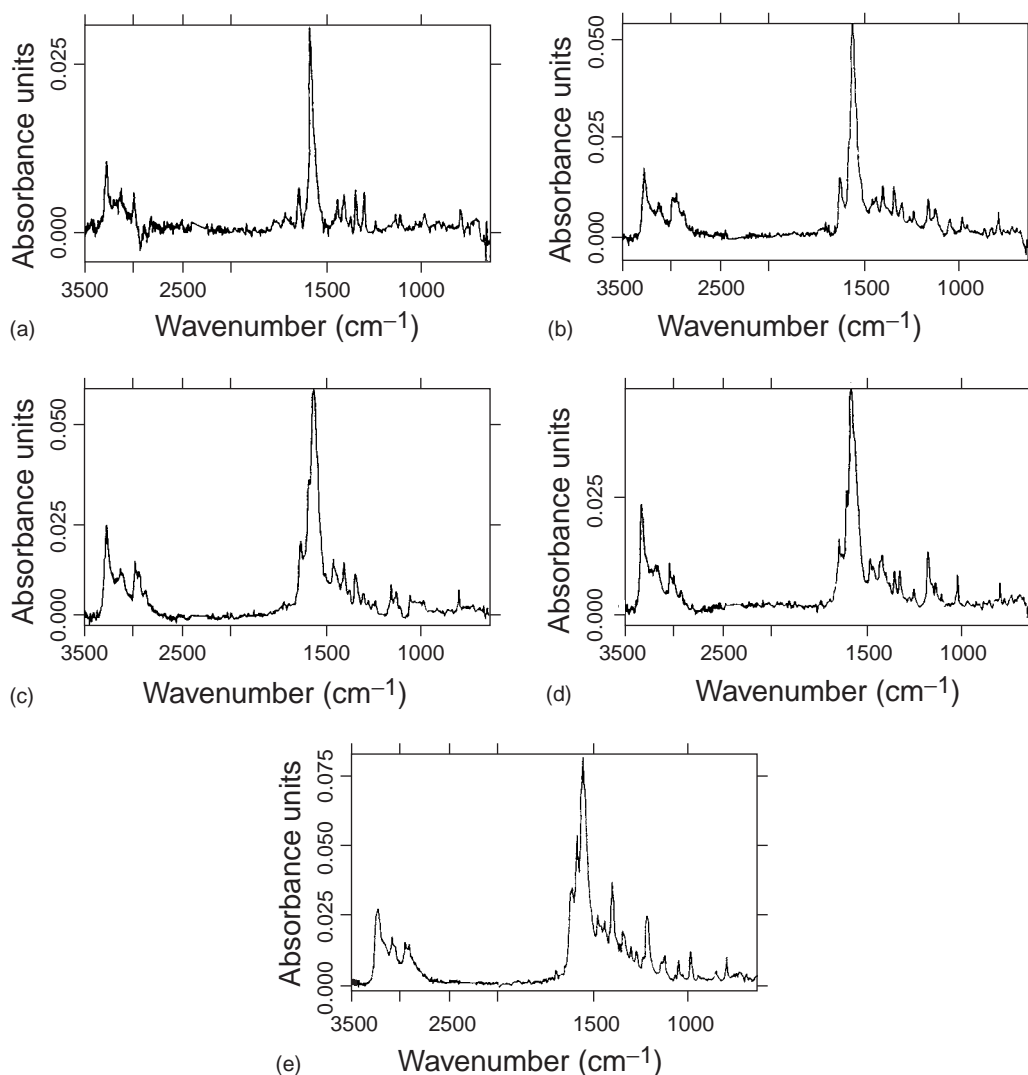
Figure 9 IR spectra of the triazines (a) Simazine, (b) Atrazine, (c) Sebutylazine, (d) Propazine and (e) Terbutylazine detected in river water by SPE on-line trace enrichment LC/IR analysis. Water sample: 100 mL, concentration level $2 \mu g \, L^{-1}$. (Reproduced from *J. Chromatogr. A*, **756**, G.W. Somsen, I. Jagt, C. Gooijer, N.H. Velthorst, U.A.Th. Brinkman, T. Visser, 'Identification of Herbicides in River Water Using On-line Trace Enrichment Combined with Column Liquid Chromatography-Fourier-transform Infrared Spectroscopy', 145–157 (1996) by permission of Elsevier Science Ltd.)

4.10 Phenols

Phenols and, particularly, nitrated and chlorinated phenols are an important class of contaminants in aqueous matrices. The compounds are released by the chemical industry as by-products, but are also formed as result of degradation of insecticides and herbicides. As result of exposure to UV radiation from the sun, oxidation and isomerization of phenols easily occurs which implies that a large number of nitro- and chlorophenol isomers is found in air, particulate matter, aerosols, wastewater effluents, surface water and groundwater. Several of these phenols are considered as high-priority pollutants and for that reason unequivocal identification is demanded.

Since IR spectroscopy is extremely powerful in the differentiation between isomers, IR spectroscopic methods have been used for this purpose on several occasions. Vredenbregt et al.,[46] for example, applied cryotrapping GC/IR in addition to GC/MS, to distinguish between the ten molecular isomers of chloronitrophenol in surface water. Despite the absence of several reference standards, all isomers have been identified by interpretation of the complementary IR and MS data. The same sample storage GC/IR technique combined with GC/MS was used by Rodriguez et al.[47] to identify structural isomers of (poly)chlorinated phenol. After acetylation and preconcentration on graphitized carbon cartridges, 17 isomers have been identified.

Childers et al.[48] employed matrix isolation GC/IR for the characterization of nitrocresols in air sample extracts. These products are formed by photooxidation of NO_x and toluene in the atmosphere. A number of specific isomers have been identified by comparison with the GC/IR spectra of nitrocresol standards.

4.11 Polyaromatic Hydrocarbons

PAHs and their nitro derivatives are well established environmental contaminants which are invariably generated during combustion processes of fossil fuels. Unambiguous identification of PAHs and nitro-PAHs is important as the mutagenity and carcinogenity among these molecules may differ considerably. The identification and structure elucidation relies primarily on GC/MS. However, especially in the absence of reference compounds, MS is insufficiently specific to distinguish between the relatively large number of isomers. GC/IR is a useful method to discriminate between PAH congeners that are difficult to distinguish by other methods. The relevance of such analysis has been demonstrated by Childers et al.[49] and Kalasinsky et al.[50] in methods for detecting and identifying PAHs and nitro-PAHs in urban air particulate matter.

Other applications of GC/IR for the analysis of PAHs are the characterization of aromatic isomers in marine sediments from mildly polluted sites in the Arabian Gulf area[51] to endorse and confirm the results from GC/MS analysis and the confirmational analysis of PAHs in soil extracts in addition to a standard high-pressure liquid chromatography/ultraviolet (HPLC/UV)/fluorescence procedure.[52]

Raynor et al.[53] demonstrated that PAHs can also be determined adequately by capillary supercritical fluid extraction (SFE) combined with off-line FT/IR microspectrometry. Several PAHs have been identified in coal tar pitch samples after evaporation of the supercritical eluent and deposition of the separated analytes on a KBr disc.

Among the PAHs, the nonalterant cyclopentafused PAHs represent a unique class, being responsible for most of the genotoxicity of PAHs exhausts. Hence, their identification and the elucidation of their build-up mechanism is of major relevance. GC/IR has been used in addition to GC/MS for the identification of these PAHs and their intermediate PAHs. A cryogenic sample storage GC/IR interface has been applied to obtain sufficient sensitivity for subnanogram detection. Experiments have been carried out on standard compounds and on samples generated by in situ pyrolysis (T = 600–1100 °C) of ethynyl PAHs as model compounds for mimicking combustion processes. Conclusions from GC/MS have

been confirmed and, additionally, the molecular structures of previously unidentified components have been elucidated.[54]

4.12 Dioxins, Dibenzofurans and Polychlorinated Biphenyls

PCDDs, PCDFs and PCBs are subject to considerable environmental interest due to the combination of their high toxicity and persistency. The three compound classes count 75, 135 and 209 congeners respectively, differing over six orders of magnitude in toxicity. It follows that highly sensitive univocal identification is required for these substances. For that reason, high-resolution GC/MS is the method of choice for this type of analysis.

Occasionally, however, additional IR spectrometric information is necessary to distinguish between the large number of possible molecular isomers, either for confirmational purposes in addition to GC/MS analysis, or for the identification of compounds that are to be used as analytical standards. As a consequence, many IR studies have been dedicated to the analysis of PCDDs, PCDFs and PCBs. Also, IR data are used to obtain information on the relationship between the toxicity and the geometrical structure of the molecules. Grainger and co-workers,[55,56] for instance, demonstrated that the IR vapor-phase spectra point to a near planar geometry for the highly toxic laterally substituted isomers, and a more tetrahedral type of geometry for the less toxic isomers in which the aromatic rings have lower electron withdrawing capacity. These conclusions are consistent with the data obtained from X-ray crystallography.

The importance of the identity conformation of standard materials for reference purposes has also been commonly acknowledged. Examples are the characterization of PCBs[57,58] and chlorinated and brominated dibenzodioxins and dibenzofuranes,[59] by matrix-isolation GC/IR, and the recording of the GC/IR reference spectra of all 209 individual PCB congeners.[60] The discriminative properties of IR spectrometry for this type of analyte are well illustrated by the spectra of 5 congeners of chlorinated and brominated dibenzodioxins in Figure 10.

Applications of IR spectrometry to the analysis of PCDDs, PCDFs and PCBs in real-life samples are scarce and restricted to samples with high concentrations. A recently published example is the GC/IR analysis of extracts of fly ash from a municipal waste incinerator to confirm the results from GC/MS.[61] PCDD- and PCDF-congeners have been identified unambiguously at high picogram level as result of the complementary information from both techniques.
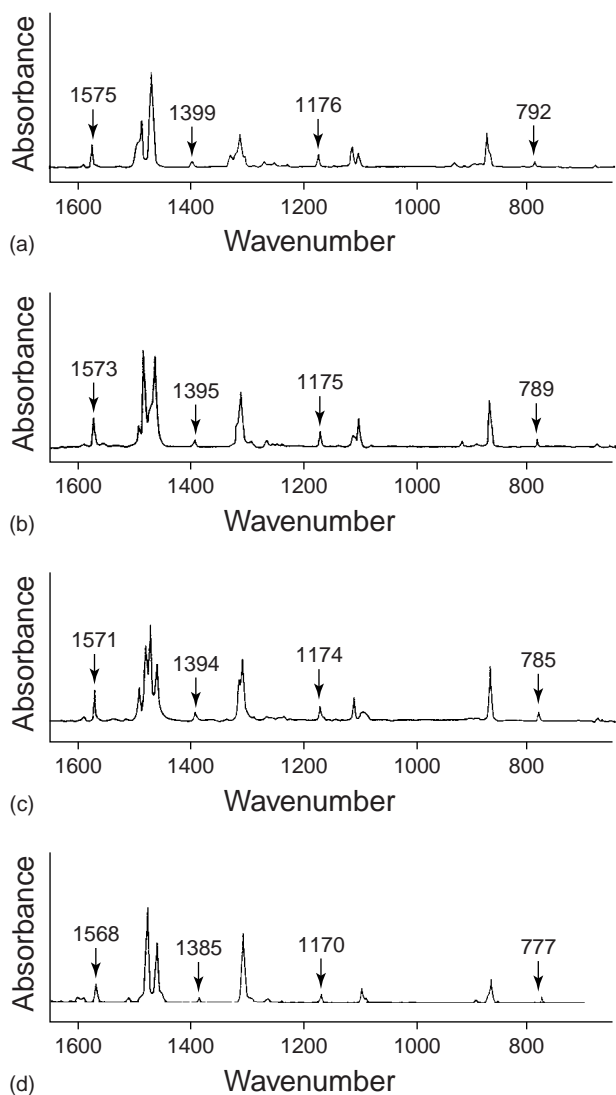
Figure 10 Matrix isolation GC/IR spectra of 2,3,7,8-substituted dibenzo-*p*-dioxins. (a) 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin, (b) 2-bromo-3,7,8-trichloro-dibenzo-*p*-dioxin, (c) 2,3-dibromo-7,8-dichloro-dibenzo-*p*-dioxin and (d) 2,3,7,8-tetrabromo-dibenzo-*p*-dioxin. (Reproduced from *Chemosphere*, **25**, J.W. Childers, N.K. Wilson, R.L. Harless, R.K. Barbour, 'Characterization of Brominated and Bromo/chloro Dibenzo-*p*-dioxins and Dibenzofurans by Gas Chromatography/Matrix Isolation-Infrared Spectrometry', 1285–1290 (1992) by permission of Elsevier Science Ltd.)

4.13 Oils and Greases

For many years, the quantitative determination of mineral oil in water, soil and sediment samples by IR spectrometry has been a widely applied standard protocol for environmental and QC. The methods are based on the extraction of the hydrocarbons by an apolar solvent, followed by elimination of possibly co-extracted polar substances by means of Florisil, and subsequent measurement of the absorption maxima of the C−H
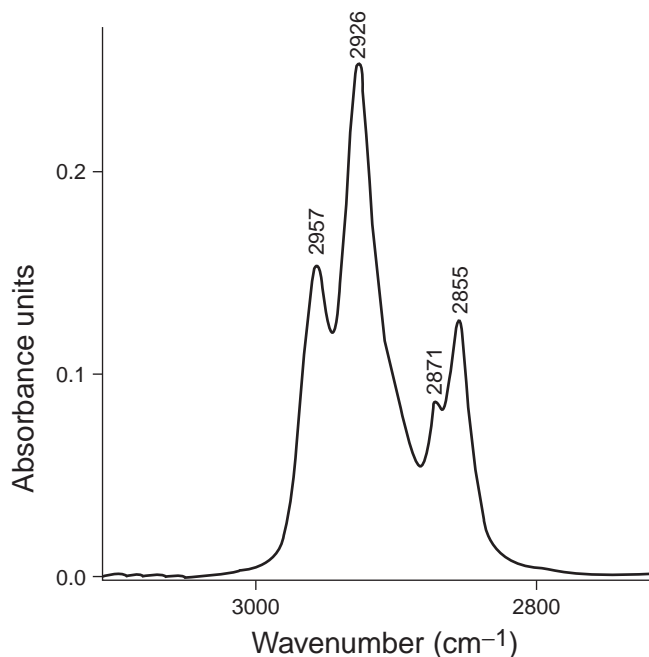

Figure 11 Characteristic absorption pattern of mineral oil extracted from a soil sample.

stretching bands in the extract. The limit of detection is in the order of 0.05 to 1 mg L^{-1}, depending on the extraction solvent and the pathlength of the liquid cell (1–5 cm typical). An example of the usual absorption pattern of a mineral oil is shown in Figure 11.

Up till now the extraction, prescribed in the protocols, has been carried out with halogenated hydrocarbons such as carbon tetrachloride and freon-113 as these solvents are IR transparent in the relevant wavenumber region 3200–2700 cm^{-1}. However, as result of the ozone-depleting effects of chlorinated fluorocarbons (CFCs), research is going on to alternative extraction methods without the use of these solvents. Several excellent alternatives for extraction and preconcentration have been proposed, such as adsorption filtration,[62] SPE, SFE, microwave-assisted extraction (MAE) and LLE in strongly reduced liquid volumes or in nonhalogenated solvents.[63] In parallel, ATR and DRIFT have been tested as alternative methods for the extinction measurement of the alkyl bands after evaporation of the solvent. The performances of several of the new methods are comparable or even better than the conventional ones with detection limits in the order of 0.005 ppb and a recovery of 90%.

Another alternative for the relatively elaborate extraction methods is direct screening by optical-fiber sensing. This in situ method is very fast but can only be applied for highly contaminated wet soils.[64]

4.14 Soil Characterization

IR spectrometry is commonly applied for the characterization of soil humic acid (HA) and fulvic acid (FA) fractions. HA and FA substances are complex organic macromolecules formed by degradation of biotic material such as cellulose, lignins, peptides, saccharides, etc. The large variety in the precursor structure combined with the many different parameters affecting the degradation process, results in an enormous diversity of the chemical and physical properties of humic substances. These properties play an important role in environmental analysis of xenobiotic compounds and for that reason the characterization is an important task. IR spectroscopy is a useful method for this purpose, particularly in the determination of the oxygen contents of humic and FAs. Information on the oxygen contents of both untreated as well as fractionized HAs and FAs can be derived from the position and the band pattern of the OH stretching bands around $3300\,cm^{-1}$, the strong absorbing symmetric and asymmetric $C(=O)-O-$ stretching vibrations at 1600 and $1400\,cm^{-1}$ and the $-C-O-C$ bands in the region $1200-1000\,cm^{-1}$, which are correlated to the presence of hydroxylic, carboxylic and ether groups, respectively.[65,66] Examples of the IR spectra of peat HA fractions are given in Figure 12.

An IR method, closely related to characterization of HA fractions, is the analysis of residual fractions that remain after microbiological degradation of contaminated soil.[67] In this application, IR spectrometry is used to determine oxidation products of the original contaminants.

Another way to classify humic substances is by pyrolysis GC/IR.[68] With this technique, HA and FA fractions are characterized by the identity of the different pyrolysis products such as acids, lactones, alcohols and phenols, and their relative abundance.

4.15 Inorganics and Asbestos

Occasionally, IR is used to determine the quantity of specific inorganics such as minerals and nitrates by means of conventional KBr measurements, DRIFT or photoacoustic IR.

A specific application is the analysis of asbestos (hydrated silica fibers) which is of concern owing to its assumed lung cancer causing properties. Although microscopy is usually the principal method for the determination of the type of asbestos, IR is often used for additional identification and confirmation. As demonstrated by Lang et al.,[69] IR can be used for the quantification as well. A method has been developed to quantify asbestos down to 0.01% by weight using an ashing technique to eliminate the cellulose matrix prior to absorption measurement.
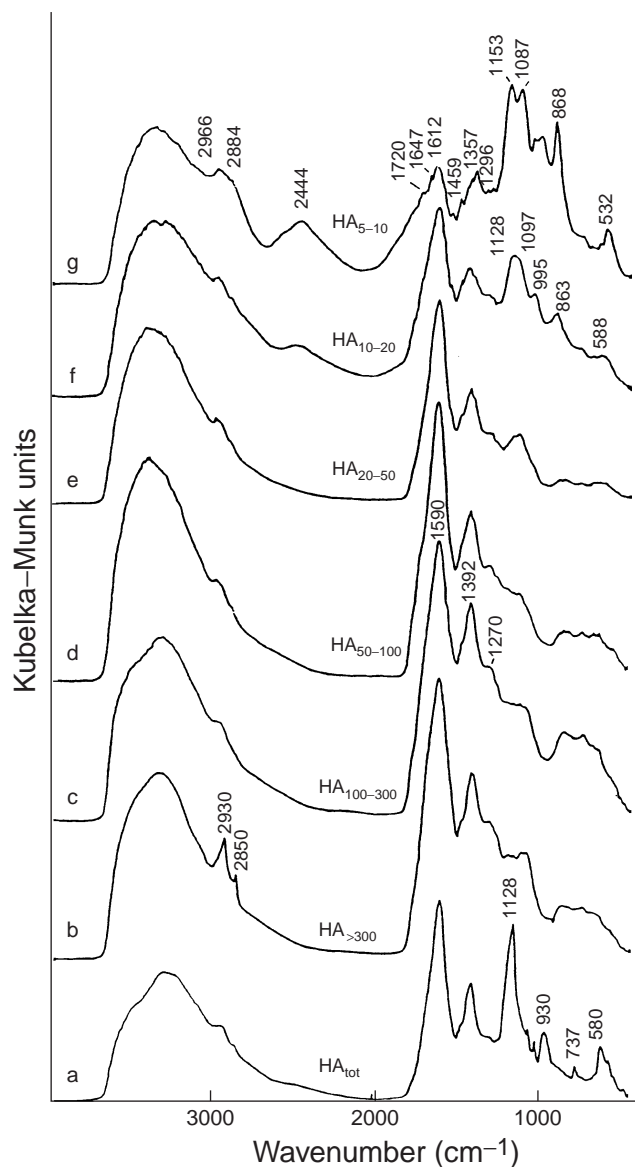

Figure 12 DRIFT spectra of peat HA. (Reproduced by permission of The Society for Applied Spectroscopy from O. Francioso, S. Sanchez-Cortes, V. Tugnoli, C. Ciavatta, L. Sitti, C. Gessa, 'IR, Raman and Nuclear Magnetic Resonance (^{1}H, ^{13}C and ^{31}P) Spectroscopy in the Study of Fractions of Peat HAs', *Appl. Spectrosc.*, **50**, 1165–1174 (1996).)

4.16 Polymer Characterization

For obvious reasons, the recycling of sorted plastics has a number of advantages over unsorted regeneration. IR is highly suited for the identification of polymers and for that reason the application of IR for polymer recognition in waste industry is logical. At present several methods for automated plastic-waste identification are being employed. All applications are based on a fast, remote recognition of polymers in a stream of waste.[70]

Examples of IR classification of (co)polymers for recycling purposes are found in the automobile industry, the regeneration of electronic equipment,[71] the identification of waste carpet materials and in sorting plastics from municipal solid waste.[72] The latter combines the spectral IR and NIR information with additional geometric information by means of a focal-plane IR imaging system.

4.17 Quality Assurance

As already noted, IR spectrometry is commonly used for confirmational purposes and identity control of analytical standards prior to performing qualitative and quantitative analysis. Confirmational analysis is important since unambiguous identification of substances with suspected toxic properties is subject to stringent forensic and regulatory requirements. Identity control is relevant as the growing importance of good laboratory practice (GLP) has increased the prescription of IR for the QC of analytical standards.

In general, the analytical procedure and the criterion for confirmation are described into detail in a Standard Operating Procedure (SOP) in accordance with requirements as proposed by the International Organization for Standardization (ISO). Several criteria and algorithms have been developed to express the similarity between two spectra in a reliable and useful number. Nowadays, the software of virtually all IR instruments offers this possibility while also less stringent peak-matching requirements[73] as well as criteria based on neural networks,[74] have been proposed as decisive criteria to confirm the identity of a standard or an analyte.

4.18 Chemometrics and Model Studies

Nowadays, chemometrics plays a very important role in IR spectroscopy. The fact that FT/IR instruments are inherently equipped with fast processors and large storage capacity for data acquisition, processing and manipulation has made it considerably easier to use chemometric techniques like discriminant analysis (DA), principal component analysis (PCA), partial least squares (PLS) regression and artificial neural networks (ANN). On the other hand, the need for application of these techniques has been urged by two developments. Firstly, the current instrumentation produces increasing amounts of spectral data in shorter time and spectra are currently obtained within a tenth of a second. Secondly, the development of two- and three-dimensional mapping facilities and the coupling to GC and LC, has manifolded the number of spectra to be handled. In order to facilitate or even admit the interpretation of this enormous amount of information, chemometrics are practically indispensable and have, therefore, become common sense in modern IR spectroscopy. Data reduction and data storage methods are applied to reduce the large amount of data to feasible proportions in terms of desk and memory space while multivariate calibration techniques have been incorporated into the standard instrument software for data manipulation and simplification of the interpretation. Besides, expert systems have been developed to enable unskilled spectroscopists to take advantage of unknown possibilities of IR spectrometry. Examples are the chemometrical systems that are used to assist in the structure elucidation of unknowns.[75,76]

Model studies are a valuable method to predict the course of processes when only a limited number of data is available or in case extended studies cannot be performed for practical reasons. Particularly, in large-scale processes such as environmental exposure and risk assessment, computerized models are indispensable. Several models, partly or fully based on IR spectroscopic data, are currently used for this purpose. An important additional advantage of IR spectrometry is the possibility to perform real-time and in situ measurements which enables the development and the validation of a model not only in the laboratory but also in real-life situations.

A good example are the computerized models that are used in studies of the greenhouse effect. These models take into account a variety of parameters such as the atmospheric and earth temperature, cloud cover, geographic coordinates, weather conditions and the composition of the atmosphere as a function of the altitude. Obviously, IR remote sensing is very well suited to provide the required qualitative and quantitative data of greenhouse and other gases. Moreover, the same technique can be used for the validation by monitoring the actual atmospheric composition and (photo)chemical processes.

Specific examples of model studies based on IR data are of those of Collete[77] and Nelson et al.[78] The first one applied PLS modeling of IR spectral data, to predict chemical and physical constants and distribution coefficients of a number of pollutants in order to estimate their environmental fate. The second one carried out a model study to determine the parameters that affect the formation of toxic constituents during incineration of wastes.

5 CURRENT POSITION AND FUTURE DEVELOPMENTS

At present, IR spectroscopy is a viable method for many applications in environmental analysis. The merits of the technique lie in its versatility and in the unique fingerprinting properties of the spectra. The first makes

IR the principal method for remote sensing and in situ measurements as illustrated by the applications in atmospheric studies and the classification of polymers. The second makes it, in principle, the method of choice for unambiguous identification. In trace analysis, however, mass spectrometry is superior in sensitivity and ease of operation and for that reason the role of IR is mainly restricted to QC and confirmational purposes.

Future applications should be seen in relation to developments in hard and software. The recent introduction of diode array detection in IR spectrometry is a good example of the ongoing attempts at innovation. Further development of this type of detection can be expected. Research will also focus on improvement of the sensitivity by means of dedicated detectors and tunable IR laser technology. At short notice, the ongoing demand for fast and robust methods will lead to the further development and optimization of dedicated, low-cost sensor type of instruments, particularly suited for routine and field measurements. As such, the growing interest in NIR spectrometry for routine tasks, currently performed with mid-IR techniques, will most likely continue.

Finally, it should be noted that the improvement of IR technology will be attended by similar developments of other analytical techniques. For that reason, the choice for application of an IR spectroscopic method has always to be judged in relation to the potential of alternatives which includes economical and practical considerations such as the availability of instrumentation and expertise.

ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectrometry
ANN	Artificial Neural Networks
ATMOS	Atmospheric Trace Molecule Spectroscopy
ATR	Attenuated Total Reflection
BTEX	Benzene, Toluene, Ethylbenzenes, and Xylenes
CFC	Chlorinated Fluorocarbon
CFC	Chlorofluorocarbon
DA	Discriminant Analysis
DRIFT	Diffuse Reflectance Infrared
FA	Fulvic Acid
FT	Fourier Transform
FT/IR	Fourier Transform/Infrared
GC	Gas Chromatography
GC/IR	Gas Chromatography/Infrared
GC/IR/MS	Gas Chromatography/Infrared/Mass Spectrometry
GC/MS	Gas Chromatography/Mass Spectrometry
GLP	Good Laboratory Practice
HA	Humic Acid
HPLC/UV	High-pressure Liquid Chromatography/Ultraviolet
IGC	Infrared Gas Cloud
IR	Infrared
ISO	International Organization for Standardization
LC	Liquid Chromatography
LC/IR	Liquid Chromatography/Infrared
LLE	Liquid–Liquid Extraction
MAE	Microwave-assisted Extraction
mid-IR	Mid-infrared
NIR	Near-infrared
PAH	Polyaromatic Hydrocarbon
PAS	Photo-acoustic Spectrometry
PCA	Principal Component Analysis
PCB	Polychlorinated Benzene
PCDD	Dibenzo-p-dioxin
PCDF	Dibenzofuran
PLS	Partial Least Squares
QA	Quality Assurance
QC	Quality Control
SFC	Supercritical Fluid Chromatography
SFE	Supercritical Fluid Extraction
SOP	Standard Operating Procedure
SPE	Solid Phase Extraction
SPME	Solid Phase Micro Extraction
UV	Ultraviolet
VOC	Volatile Organic Compound

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