SELECTED POSSIBILITIES OF USING INFRARED SPECTROSCOPY IN CRIMINALISTICS

Abstract:
Infrared spectroscopy is one of the most commonly used spectroscopic methods in criminalistics, through which various kinds of criminalistic traces can be explored. It finds wide application in academic research, but also in research of forensic laboratories in order to obtain results applicable in criminalistic practice. The paper provides information about selected possibilities of using Fourier transform infrared spectroscopy and its modifications in investigation of specific criminalistic traces such as documents, banknotes, cosmetics, blood traces and adhesive materials.

Keywords:
infrared spectroscopy, chemometrics, paper, banknotes, hair cosmetics, lipstick, blood traces, adhesive tape
1. A BRIEF INTRODUCTION TO THE BASIC THEORETICAL BASIS OF INFRARED SPECTROSCOPY

Infrared spectroscopy (IR spectroscopy) is a physico-chemical method that deals with the measurement and evaluation of absorption spectra of substances in the wavelength range 800 nm to 1000 μm (wavelength range from 12500 to 10 cm\(^{-1}\)). The advantage of infrared spectroscopy is the possibility to study substances in all dimensions and states, such as liquid substances, solutions, pastes, powder samples, paints, gases, different surfaces, polymers, organic and inorganic compounds, biological samples, oils, catalysts, minerals, organometallic compounds. IR has its irreplaceable role in the identification of molecules, the detection of new compounds, the study of chemical equilibria and the kinetics of chemical reactions. This fact is also proved by the fact that IR spectroscopy is currently one of the most widely used analytical techniques. In the past, IR prism spectrometers used optical prisms as dispersion devices (1940s) and optical grids (1950s). The introduction of the Fourier transform and the use of interferometers in spectrometers have made significant progress in the field of chemical research (Milata et al., 2008).

During the clarifying of the basic principles of how infrared spectroscopy works and to understand its principles, we may ask at the outset why some compounds absorb infrared radiation only at certain wavelengths and some do not? In answering this question, we need to look at the molecular level of the substances studied. Each molecule has its own energy, which corresponds to the movements inside the molecule, which is manifested by protracting and shortening bonds, increasing and decreasing valence angles; these phenomena are called vibrations (Figure 1) (Milata et al., 2008).

![Figure 1: Some allowed vibrational movements in molecules (McMurry, 2007).](image)

The energy of a molecule does not change continuously, but is quantized, and therefore the molecule can be lengthened and shortened with certain frequencies that correspond to certain energy levels. McMurry, in his publication (2007), gives an example that focuses on the length of bonding between atoms and points out that the perception of chemical bond lengths cannot be understood as a fixed
value, but an average value, since the bonds constantly change their length in the context mentioned above. The 110 µm length oscillates at a certain frequency, alternately extending and shortening as a spring between two atoms. It further states that after radiation of a molecule by electromagnetic radiation, energy is absorbed when the frequency of electromagnetic radiation coincides with the frequency of vibration, resulting in (absorption of energy) an increase in the vibration amplitude (the „spring“ between two atoms lengthens and shortens a little bit more.) The principle of the method is that a certain frequency of radiation absorbed by a molecule corresponds to a certain molecular motion, allowing chemists to study different types of molecular vibrations by compounds by measuring their infrared spectrum. Chemical bonds are present in the molecule of the substance to be measured, which is of practical importance in the subsequent determination of the functional groups present in the molecule.

Infrared radiation is generally divided into near-infrared, NIR, 800-2500 nm, followed by middle-infrared, MIR, 2.5 - 25 µm, ie 4000-400 cm\(^{-1}\)) and in a far-infrared, FIR, 25-1000 µm, ie 400-10 cm\(^{-1}\)). Low-energy radiation in the far infrared region causes only a change in the rotational states of the molecules, and the effects of radiation in the middle and near infrared regions change the rotational and vibrant states of the molecule. From the point of view of structural measurements, the middle and far infrared region is the most interesting for chemists (Milata et al., 2008).

Interpretation of infrared spectra is difficult because the molecules of interest are often large, allowing for a considerable amount of valence and deformation vibrations. The resulting the infrared spectrum therefore contains many absorption bands, which in practice can be considered as a specific „fingerprint“ of a given compound. The „fingerprint“ area is usually in the range from 1500 cm\(^{-1}\) to about 400 cm\(^{-1}\), as the infrared spectra are the most complex. The principle is that if two compounds have an almost identical infrared spectrum, we can say that it is one and the same substance (McMurry, 2007).

When interpreting infrared spectra, we observe most often the position and shape of the absorption bands, their number and intensity (Milata et al., 2008). Most of the functional groups that the molecule contains characteristic absorption bands in the infrared spectrum, and their position does not change too much for each type of compound (McMurry, 2007). If we can identify individual absorption bands of functional groups, we gain valuable information about the structure of molecules, which is an important element in the complex identification of chemical substances. By way of illustration, we present the infrared spectrum of the organic compound hex-1-ene (Figure 2) and a table with characteristic absorption bands of selected functional groups (Table 1).
Since dispersive infrared spectrometers have their experimental limitations, the following section will focus on Fourier transform infrared spectroscopy, which uses an interferometer instead of a grid monochromator.

The basic type of interferometer is the Michelson interferometer (Figure 3), which has two perpendicularly oriented mirrors (A, B), of which mirror B is fixed and mirror A moves at a constant speed. Between the mirrors is located a beam splitter (C), which divides the unmodulated beam from the source on both

Table 1: Fields of occurrence of bands assigned to valence vibrations of X-H groups (Milata & Segľa, 2007).

| Wavenumber (cm⁻¹) | 
|------------------|---|
| 3600-3400        | 
| 3200             | s |
| 3000             | w |
| 2800             | w |
| 2600             | w |
| 2400-3600        | 
|                  | m |
|                  | m |
|                  | m |
|                  | m |
|                  | m |
|                  | m |

Figure 2: Example of hex-1-ene infrared spectrum (McMurry, 2007).
mirrors, recombines after the beam is reflected and outputs the interferometer as a modulated beam. If the incoming beam is monochromatic with a wave (cm⁻¹), the signal that comes from the interferometer passes through a series of max and min and produces an interferogram that contains all the spectral information that can be obtained from it by Fourier transform. In order to achieve optimal parameters of the infrared spectrum, it is necessary to realize a precisely defined movement of the mirror and an on-line connection to a computer that transforms the digitized value of the detected signal. The acquired values are stored in the computer memory (Miertuš et al., 1991; Milata et al., 2008).

Fourier transform infrared spectrometers (FT-IR spectrometers) are analytical instruments consisting of a source of infrared radiation, a laser-controlled interferometer, a sample optical part and a radiation detector. As mentioned above, the signal from the detector is digitized and processed by a computer. Silicon carbide (SiC, Globar) is the most common source for radiation from 5000-250 cm⁻¹ and the wolfram filament bulb is used for the near region (up to 10000 cm⁻¹) and for the far region (up to 20 cm⁻¹) mercury lamp interferometers are most commonly controlled by a helium-neon laser, with some manufacturers using Michelson interferometers (for example Bruker) and others using Fabry-Perrot interferometers (for example Nicolet). It is important to note that the spectral range of the interferometers depends on the beam splitter material (see Figure 3), which may be of germanium, resp. iron oxide. Polyethylene terephthalate (mylar) films, which are intended for the far infrared region and the spectral region are determined by the film thickness, can also be used (Milata et al., 2008; Tusami & Sakamoto, 2015).

In the next part of our paper we would like to point out selected possibilities of the use of infrared spectroscopy in the forensic research of forensic laboratories and academic workplaces, which try to apply the obtained results of research into routine forensic practice. This method has an irreplaceable role in the system of criminalistic practice activities. It is not possible to cover all areas in which infrared spectroscopy plays a major role in both research and forensic practice, so we decided to choose the following: examination of documents, notes and
banknotes, examination of cosmetics for hair and lips, designation of age of blood spots, examination of adhesive tapes and other adhesive materials.

2. INFRARED SPECTROSCOPY - EXAMINATION OF DOCUMENTS, NOTES AND BANKNOTES

In the area of investigation documents and notes, during the verifying their authenticity, ascertaining the origin, respectively, has big importance the investigation and characterization of paper, especially in connection with the falsification of documents and documents. It is important for law enforcement authorities and courts to establish whether the disputed document or document in dispute (for example a contract) has been handled, for example by exchanging sheets of paper.

As an example, a study published in 2010 in which the authors (Causin et al., 2010) examined 19 similar (visually indistinguishable) types of white office paper (80 g/m²) using X-ray diffraction analysis and infrared spectroscopy. They carried out this study in order to gain practical experience in the field of contract handling investigations, whereby offenders can exchange individual sheets of paper with a different text found in the contract of the original and the examination of anonymous letters. a disagreement on the structural and chemical composition of anonymous letter paper and papers detained by suspects may provide such information to investigators when guessing offenders sending anonymous letters repeatedly. In the case of contracts, the difference in the chemical composition and structure of the individual sheets of paper may indicate their handling. In this case, a comprehensive examination of the disputed document is required.

The use of X-ray diffraction analysis and infrared spectroscopy as non-destructive methods makes it possible to distinguish different types of white office paper from different commercial manufacturers based on differences in paper structure caused by paper processing, manufacturing conditions and chemical additives. To illustrate,
we show the infrared spectrum of Burgo Repro white office paper (80 g/m²) from Burgo (Figure 4).

Exciting and useful is the application of infrared spectroscopy in the examination and authentication of banknotes, printing techniques used and security features. In 2014, a study was published in which the authors (Sonnex et al., 2014) developed a methodology to identify fake English banknotes with a nominal value of £ 20 and £ 10 using infrared spectroscopy, an effective tool for their identification in the form of elaborated methodology for verification of banknotes authenticity using simple portable infrared spectrometers with Fourier transform. The principle of the method of investigation is based on detecting different chemical composition holographic bands and false holographic bands and different color contrasts of the printing inks used, respectively, inkjet cartridges in relation to the carrier substrate using an infrared microscope, especially in cases of more complex spectra that could not distinguish the original from the fake.

Figure 5: The example of infrared spectra (top - spectrum of original £ 20 banknote; bottom - three paper spectra of three £ 20 counterfeit papers) showing the characteristic peaks at 1400 cm⁻¹ that originate from the symmetrical valence vibrations of carbonate anionics of fake notes (Sonnex et al., 2014)
In similar way, Oliveira and his team (2018) used a portable infrared spectrometer operating in the near infrared range (950-1650 nm) and chemometric methods (SIMCA and SPA-LDA) for verifying the authenticity of Brazilian reals, respectively. Comparing their originals with seized counterfeits (the denomination was 20 BRL, 50 BRL and 100 BRL). Studies of a similar type arise, especially, in response to the continually improving digital technologies that make it possible to improve the print quality of computer printers and, at the same time, the commercial availability of fluorescent inks used in counterfeiting. The advantage of infrared spectroscopy when examining originals or counterfeits of seized banknotes is that it does not cause destruction of the carrier substrate, respectively. it does not damage the secured disputed material as a whole, providing valuable information on the chemical composition of the individual components of the banknotes. By comparing infrared spectra in combination with chemometric methods, it is possible to successfully distinguish the original banknote from the counterfeit.

3. INFRARED SPECTROSCOPY - EXAMINATION OF COSMETICS FOR HAIR AND LIPS

Trichological material (hair) is one of the most common and widespread forensic traces, which occurs at the scene of the crime in connection with a criminalistic relevant event. The basic technique used in the forensic investigation of trichological material is optical microscopy, which also has its limitations. However, there are currently studies using specifically modified Fourier transform infrared spectroscopy to determine whether or not the isolated trichological material (hair) has been colored with hair dye, which is ultimately important for closer identification, tipping or increasing the process of individualization, especially in cases where it is not possible to isolate a DNA molecule from trichological material.

Boll and his team (2017) published a study using ATR (Attenuated Total Reflectance) to analyze stained hair, distinguishing between the brands of dye products used and the dye used. The test samples used hair from men and women aged 16 to 34 years, different races and natural hair color, namely black, brown, blond, blond and red, which were afterward stained with the colors of „Revlon medium brown“, „Revlon black“, „Clairol Medium Brown“, „Clairol Black“, „Just for Men® Black“. The samples were stained in Petri bowles according to the instructions of the paint manufacturers, then rinsed with water and dried at room temperature for a week. Subsequently, they measured infrared spectra of colored hair and uncolored hair. By comparing the spectra, the authors were able to distinguish colored hair from uncoloured hair (Figure 6, A), to distinguish
individual colors from each other (Figure 6, B), as well as the color markers used (Figure 6, C). It should be pointed out that this is a method which is not commonly used in forensic practice but forms an important basis for its further elaboration, in particular in the field of time and sunlight, different shampoos and conditioners on colored trichological materials.

Pienpinijatham et al. (2018) were dealing with similar examination that analyzed the residues of cosmetic products applied to hair. The work was focused on spectral characterization of hair obtained from volunteer donors using ATR infrared spectrometer with Fourier transform and infrared microscope. They managed to spectrally distinguish hair from different persons of the same age on the basis of their different quality, characterize and spectrally identify the various
hair cosmetics for hair dyeing. By comparing the measured hair spectra of the victim who had been treated with cosmetic products, we can identify the used cosmetic hair product and if we have available trichological material secured from clothing, respectively of the perpetrator’s body, the analysis based on the characterization of hair and cosmetic hair products can contribute to increasing the individualization of forensic identification of persons. Again, however, it is a study that requires wider elaboration, the creation of a database of cosmetic hair products to be used by comparison experts in relation to the present disputed trichological material related to a criminalistic relevant event.

In the process of clarification criminalistic relevant events (for example life and health crimes), traces of lipstick on clothing, cups, paper or other surfaces may also appear as criminalistic traces, and their analysis is now logically justified. The development of non-destructive spectral methods makes it possible to investigate these traces as they can provide information from physical contact between people, places, and things. As an example, we present the latest study (Wong, Sauzier & Lewis, 2019) on differentiation, identification of lipsticks from different manufacturers, the aim of which was to develop a new methodology that will not destroy the criminalistic footprint, i.e. in situ approach. The authors analyzed a total of 40 lipsticks using molecular electromagnetic spectroscopy and ATR infrared spectroscopy in combination with chemometric methods to analyze and evaluate spectral data. To identify and determine differences between samples, the authors used the fact that each lipstick may have a different chemical composition and a different percentage of waxes, oils and specific additives (e.g. capsaicin, cinnamon, menthol). However, it should be noted that variations in the infrared spectra may be minimal (visually difficult to distinguish), therefore, it is necessary to use chemometric methods that allow subsequent differentiation. However, chemometric methods will not be discussed in more detail, as this is beyond the scope of the paper. The analysis itself has a great influence on the spectral characterization of the lip cosmetics drying process, so it is important that the secured traces and the comparative material are perfectly dried.

In the previous studies about the forensic examination of lip lipsticks were used chromatographic methods - high performance liquid chromatography (Reuland & Trinler, 1980; Sjöberg & Olkkonen, 1985), gas chromatography (Ehara & Marumo, 1998), thin layer chromatography (Misra et al., 1992), which show a significant discriminatory value, but the disadvantage of their use is that destruction of the sample is required. The use of Raman spectroscopy (Gardner et al., 2013) (non-destructive method) is also essential, but a limitation can be observed when fluorescence is formed, which in some cases makes it impossible to measure Raman spectra.
4. INFRARED SPECTROSCOPY - DESIGNATION OF AGE OF BLOOD SPOTS

Determining the age of blood spots found on different garment tops is particularly important when determining the timing of a criminal offense against life and health.

Bremmer and his team (2011a) examined the age of blood spots deposited on white cotton surfaces using visible spectroscopy. However, the use of this method appeared to be inadequate on various colored textile surfaces, so the logical result and solution to the problem was to use another spectral method.

Botonjic-Sehic and team (2009) published a study using near-infrared spectroscopy, which found that spectral changes in the spectral range from 1460 to 1860 nm allow estimating the age of blood spots on glass and gauze.

Edelman et al. (2012) published a study in which he also used infrared spectroscopy in the near infrared area to examine and determine the age of blood spots applied to differently colored cotton textile surfaces (white, black, red, green and blue). He took the benefit of the fact that infrared spectroscopy provides good results when examining blood spots on substrates other than white cotton. The principle of the method is based on the fact that blood released from the human body is subject to oxidation, i.e. hemoglobin is converted to oxyhemoglobin, then to methemoglobin, and this is subject to denaturation to hemichrome. This process is accompanied by color changes - the blood changes from red to brown (Bremmer et al., 2011b). Measurement of infrared spectra at certain times and their mutual comparison in the above-mentioned spectral range makes it possible to estimate the age of a blood spot based on the structural changes taking place in molecules containing the analyzed blood from the moment it left the human body changes during blood spot drying. More accurate results can be obtained in earlier periods of spectral analysis because chemical changes in blood are faster and more dynamic at the beginning of blood spot aging. High-performance liquid chromatography, electron paramagnetic resonance and atomic force microscopy have also been used to provide valuable information on the age of blood spots, but the methods are destructive, requiring special sample processing in the laboratory and specially trained personnel. Nowadays it is an effort to use infrared spectroscopy directly at the crime scene, for example in the form of portable infrared spectrometers or Raman spectrometers.
5. INFRARED SPECTROSCOPY - EXAMINATION OF ADHESIVE TAPES AND OTHER ADHESIVE MATERIALS

The examination of adhesive tapes, their fragments and other adhesive materials also has its justification in the framework of forensic investigation. This type of forensic track can be investigated in particular in cases of crimes against life and health, crimes against liberty and human dignity and crimes of general danger. In particular, adhesive tapes (e.g., electrical insulating tapes) may be used in the construction of improvised explosive devices, kidnapping, drug packaging, packaging of counterfeit medicines and nutritional supplements. The aim of the analysis of the above-mentioned type of criminalistic traces is a significant contribution to closer identification of offenders, respectively, their guessing (e.g. securing the aforementioned materials during a search by suspects). At the same time, it is important to note that these traces may also include textile fiber microstructures, biological material (DNA, hair), fingerprints, etc.

The examination and comparison of adhesive tapes and other adhesive materials secured from the crime scene in the context of a criminalistic relevant event and the obtained comparative materials is based mainly on the mensuration of physical characteristics and microscopic examination of the samples and transformation and pyrolysis gas chromatography with mass spectrometer. The techniques make it possible to identify the underlying material - polymer (polyvinyl chloride, polyethylene, butyl rubber) and other components (phthalates, adipic acid esters). The combination of these two methods makes it possible to significantly determine the proportion of organic substances in spore materials and subsequent comparison with the reference material. Inorganic substances (e.g. fillers, stabilizers, flame retardants), respectively. the elemental composition is detected and characterized by means of a scanning electron microscope with an energy-dispersive X-ray fluorescence spectrometry spectrometer (Martinez-Lopez, 2019). The chemical composition of adhesive tapes and other adhesive materials is specific to the manufacturers of such materials.

6. CONCLUSION

Application of Fourier transform infrared spectroscopy, resp. its technical modification (for example ATR infrared spectroscopy with Fourier transform) allows to investigate not only the forensic traces mentioned above, but also presents a vast range of possibilities in the investigation of other types of forensic traces, while beyond their contribution further analysis. These include, for example, investigating paints using chemometric methods (Muehlethaler, Massonnet & Esseiva, 2011; Falardeau, Moran & Muehlethaler, 2019), investigating the originality and geographical origin of tobacco products in connection with
tobacco counterfeiting (Omar, Slowikowski & Boix, 2019), investigating seized drugs and admixtures (the largest group of forensic traces investigated by IR spectroscopy) (Silva et al., 2018; Abiedalla et al., 2019; Liu et al. 2018, Ali, 2011), identifying new psychoactive substances (Pereira et al., 2018; Casale, Mallette & Guest, 2017), investigating and authenticating medicines, nutritional supplements and identifying fake pharmaceutical substances (Storme-Paris et al., 2010; Been et al. 2011; Dégardin et al., 2015; Dégardin et al., 2016).

In the end, it is not specified to provide a comprehensive overview and exhaustive calculation of possible applications of Fourier transform infrared spectroscopy into forensic practice. It focuses especially on the field of forensic research, in which infrared spectroscopy is not commonly used in our conditions. The paper is based mainly on foreign literature sources, where we can observe the increasing trend of using this method in academic research, research of forensic laboratories and application practice (e.g. crime scene - portable infrared spectrometers and portable Raman spectrometers). We can also notice the efforts of many authors of various studies to continually develop methodological procedures for investigating forensic traces, in which Fourier transform infrared spectroscopy provides valuable results not only in examining papers, banknotes, trichology, adhesive tapes, cosmetics, but also in printers pens, analysis of cross-strokes, paints, automotive paints, nail polishes, falsification of works of art, drugs, drug precursors, nutritional supplements, pharmaceutical substances. There are many analytical and spectral methods commonly used to investigate forensic traces in forensic laboratories. Nevertheless, the investigation is in some cases more time-consuming, requires special sample preparation, contains lot of specially trained personnel to operate the instrumentation (for example liquid chromatography, gas chromatography, mass spectrometry) and cannot be used directly at the crime scene. Infrared spectroscopy has its well-established place in the system of forensic examination methods, as it is a method that does not require special sample treatment, time consumption and sample handling is minimal, thus significantly reducing the risk of secondary contamination.

REFERENCES


