Journal of Molecular Structure 924–926 (2009) 504–513

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Computer analysis of ATR-FTIR spectra of paint samples for forensic purposes

Małgorzata Szafarska [a], Michał Woźniakiewicz [a], Mariusz Pilch [b], Janina Zięba-Palus [c], Paweł Kościelniak [a,c,*]

[a] Jagiellonian University, Faculty of Chemistry, Laboratory for Forensic Chemistry, Ingardena 3, 30-060 Kraków, Poland
[b] Higher Vocational School in Tarnow, Mickiewicza 8, 33-100 Tarnów, Poland
[c] Institute of Forensic Research, Westerplatte 9, 31-033 Kraków, Poland

ARTICLE INFO

Article history:
Received 3 September 2008
Received in revised form 25 November 2008
Accepted 27 November 2008
Available online 14 December 2008

Keywords:
ATR-FTIR
Paints
Forensic investigations

ABSTRACT

A method of subtraction and normalization of IR spectra (MSN-IR) was developed and successfully applied to extract mathematically the pure paint spectrum from the spectrum of paint coat on different bases, both acquired by the Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) technique. The method consists of several stages encompassing several normalization and subtraction processes. The similarity of the spectrum obtained with the reference spectrum was estimated by means of the normalized Manhattan distance. The utility and performance of the method proposed were tested by examination of five different paints sprayed on plastic (polyester) foil and on fabric materials (cotton). It was found that the numerical algorithm applied is able – in contrast to other mathematical approaches conventionally used for the same aim – to reconstruct a pure paint IR spectrum effectively without a loss of chemical information provided. The approach allows the physical separation of a paint from a base to be avoided, hence a time and work-load of analysis to be considerably reduced. The results obtained prove that the method can be considered as a useful tool which can be applied to forensic purposes.

1. Introduction

Paints and coatings are frequently encountered as types of materials that are submitted to forensic science laboratories in a wide variety of cases. These mainly include vehicular hit-and-runs, burglaries [1], devastations of building elevations (graffiti) [2], and painting robberies and fabrications [3]. The most common forensic samples are smears of automobile coatings transferred to another car or to a pedestrian's clothes during a traffic accident. The paint evidence can be also crushed paint transferred to the tools used for breaking-in or as a weapon, and finally paint flakes derived from a point of entry at a break-in [4].

Chemical investigations of paint samples are mainly focused on comparison of the evidence material with the reference one. Chemical composition of paint fragments are subjected to a variety of experiments, including microchemical tests for solubility and indicative reactions [5]. Then, the instrumental analysis follows, including the application of such instrumental analytical techniques as: the scanning electron microscopy with the energy dispersive X-ray spectrometry (SEM–EDX) [6], X-ray fluorescence (XRF) [7,8], the laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) [9], pyrolysis-gas chromatography with the mass spectrometry (Py-GC/MS) [5,10,11], as well as Raman and FTIR microspectrometry [12] in transmission and reflection modes, including attenuated total reflectance (ATR) technique [13].

ATR is widely used for rapid obtaining infrared spectra of complex materials which are too opaque or thick for standard transmission methods, e.g. linoleum, toothpaste, plastic [14], crystals, fibers, viscous liquids and surface coatings [15]. It combines the advantages of the non-destructive fast sampling system with the excellent sensitivity and low detection limits [16,17]. Another feature desirable in a forensic context is its ability to analyze the paint coat without its prior physical separation from a base. However, in such a case it often happens that the reflection spectrum obtained is the reflection of the paint and base spectra superimposed to each other and, consequently, the analytical identification of the paint is very difficult or even impossible in practice. This is the reason that this study is aimed to develop a mathematical method allowing the paint and base ATR spectra to be effectively separated from each other.

2. Background

2.1. Problem

An example of the problem mentioned above is shown in Fig. 1. It is seen that the spectrum of a paint can be significantly different from the spectrum of the same paint placed on the base. Strong absorption caused by the base is able to deform weaker paint

* Corresponding author. Address: Jagiellonian University, Faculty of Chemistry, Laboratory for Forensic Chemistry, Ingardena 3, 30-060 Kraków, Poland.
E-mail address: koscieln@chemia.uj.edu.pl (P. Kościelniak).

0022-2860/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.molstruc.2008.11.048

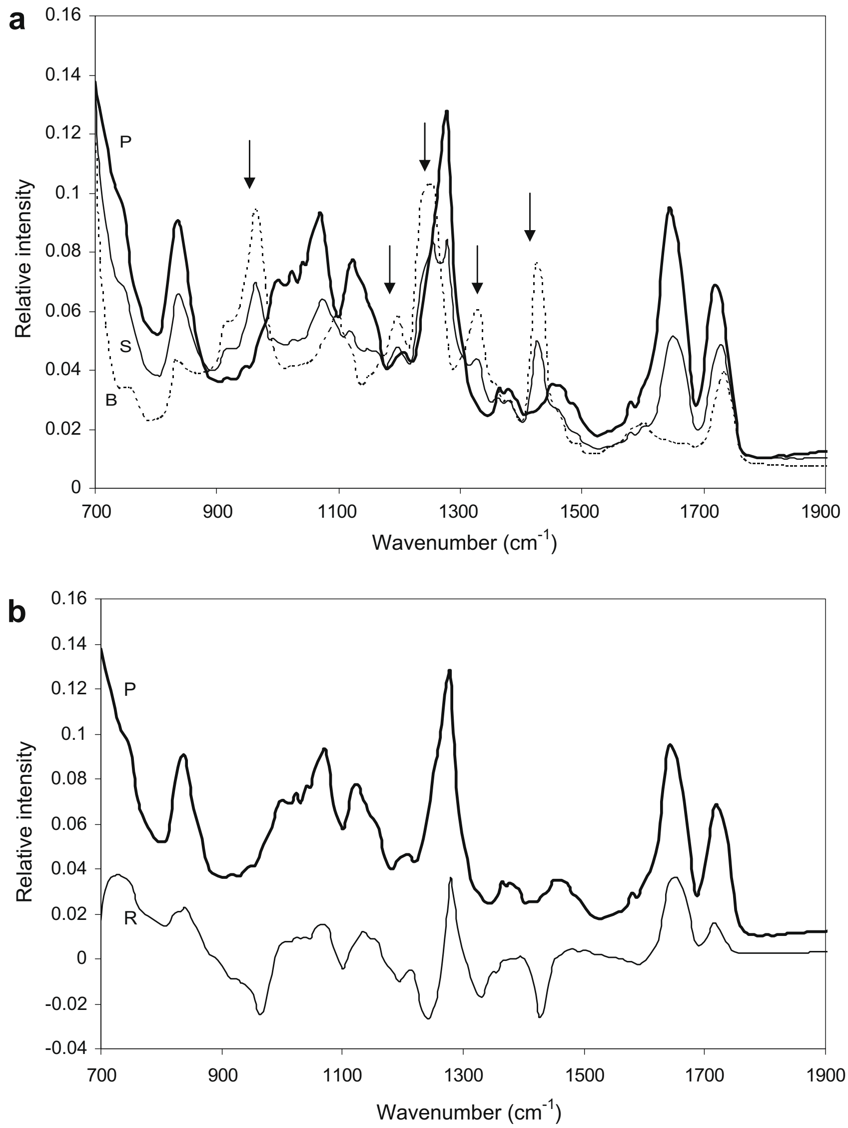

Fig. 1. ATR spectra: (a) of pure Montip paint (*P*), of the base (plastic foil) (*B*), of Montip paint on the plastic foil (*S*), and (b) obtained by direct subtraction of spectrum *B* from spectrum *S* (*R*) (the bands originating from the base are marked by arrows).

bands or even to overlay them (see Fig. 1a). Due to this fact, several additional base bands are exhibited.

If assumed that the spectrum of a paint placed on a base is a sum of the paint and base spectra, the base bands could be theoretically removed from the sample spectrum by the simple process of subtraction. Unfortunately, in such a case the risk is that the spectrum obtained after this treatment can lose some valuable information. In particular, as seen in Fig. 1b, the spectral region of 900–1200 cm^{-1} (useful to identify alkyd subclass of the resin) is considerably disturbed. The point is that any fluctuation of the band parameters in terms of shape, intensity, halfwidth and frequency can be expressed after subtraction as bands with disrupted shapes or even as new bands with either positive or negative intensities. Such effect is seen in Fig. 1 but general characterization of this problem was discussed by Grdadolnik [18].

Practically, there are several factors that affect the original sample spectra and indirectly the result of the subtraction. The first one is the inappropriate samples concentration which causes too large absorption of the base. Consequently, in the subtractive result serious oversubtractions appear. Another factor is connected with the measuring and collecting spectra: the sample spectrum should be acquired under the same condition as the base spectra, as any differences produce different background absorption which causes many problems in subtraction procedure [19].

The conclusion is that the mathematical approach separating the paint and base spectra effectively has to include some additional procedures over the simple subtraction process.

2.2. Methodology

The method proposed is based on the series of normalization and subtraction processes, hence it is named the method of subtraction and normalization of IR spectra (MSN-IR).

According to the MSN-IR approach the following three spectra are recorded within the same range of wavenumbers (i.e. they are consisted of the same number *n* of measurement points):

- the sample spectrum (*S*), i.e. the spectrum of unknown paint placed on a base,
- the base spectrum (*B*), i.e. the spectrum of the same base, on which the paint is placed,
- the paint spectrum (*P*), i.e. the spectrum of a paint being expected to have the same chemical composition as unknown paint (the reference spectrum).