COMPUTER-ASSISTED INFRARED ANALYSIS OF HETEROGENEOUS WORKS OF ART

FULL PAPER

Paolo Calvini, Stefano Vassallo

Ministero Beni Culturali, S.B.A.P., Via Balbi 10, 16126 Genova, Italy

corresponding author:
paolo.calvini@tin.it

In this paper a simple elaboration of the infrared spectra of heterogeneous materials is outlined. The data processing method, based on the least-squares solution of overdetermined systems, allows the semiquantitative analysis of mixtures in terms of the spectra of their components. An application of the data processing logic to a two- and three-components mixture is shown, but the method can be applied to more components with no difficulty. The proposed algorithm requires few instructions in a spreadsheet macro and can be applied fruitfully to the Fourier transform infrared spectra of materials of historic and artistic value, which generally do not allow chemical manipulation for the analysis of the samples.

1   Introduction

It is well known that many chemical compounds often give rise to complex Fourier Transform Infrared (FTIR) spectra, characterised by the broad overlap of individual bands. Although the FTIR identification of chemical substances has been greatly simplified by the modern computer-searchable databases of spectra, the analysis of heterogeneous mixtures remains still difficult. Sometimes the presence of different individual components can be detected through the identification of some characteristics peaks and the mathematical elaboration of spectra (by absorbance ratio,[1,2] subtraction,[3] second derivative and deconvolution[4-7]) considerably helps the spectral interpretation. In other cases a chemical manipulation of heterogeneous mixtures is required in order to recognise the single components.[8]

The problem of FTIR analysis is greatly enhanced in the case of materials of historic and artistic value,[9, 10] where the limited amount of samples and the need for non-destructive analyses pose many constraints on the working procedure. To our knowledge another powerful algorithm, the least-squares curve-fitting of FTIR spectra,[11] has never been applied in the field of cultural heritage. The aim of this paper is to show how this simple numerical analysis might greatly

help in evaluating the different components of a mixture in a semi-quantitative way.

2   Materials and methods

Chemicals utilised as standard materials have been collected in the last years in our laboratory. Some of them are analytical grade, other have been accurately purified and analysed with the FTIR technique until their spectra corresponded to the literature data.

A Perkin-Elmer Spectrum One FTIR, equipped with the Universal ATR Sampling Accessory (ZnSe cell) and diamond window (~1.5 mm of diameter), was used to obtain 4 cm^{-1} resolution spectra in the 4000 - 550 cm^{-1} region, scanned 10 times. The ATR device allowed us to analyse the samples at room temperature and humidity, without any treatment of heating and KBr grinding.

3   Principle of the method

In order to better explain the proposed methodology let us suppose that we already know both the chemical composition of the mixture and the FTIR spectra of the individual components. If we neglect the physical-chemical interactions between the components (as implicitly assumed in all curve-fitting procedures), the overall absorbance A of the mixture at a given wavenumber (cm^{-1}) is given by

$$A = c_1 a_1 + c_2 a_2 + ... + c_n a_n \qquad (1)$$

where a_1, a_2 ... a_n are the absorbances of the n components at that wavenumber, and c_1, c_2 ...... c_n the unknown coefficients, proportional to the concentration of each component. It is well known that the n coefficients can be evaluated by means of a system of n equations like equation (1), taken at different n values of FTIR wavenumbers.

In an FTIR spectrum there are several hundreds data, while the mixture is composed of relatively few components and it may be difficult to select the few wavenumbers that allow the best solution of the system of n equations. In general, several equations like equation (1) can be written, and the presence of more equations than unknowns makes the system overdetermined. These systems will not give exact equality for each equation, but it is possible to calculate the unknown coefficients c_n so that the equations are as close to being satisfied as possible[12].

In short, the overdetermined system of equations can be written in a matrix form:
$$[a_{m,n}] |c_n| = |A_m| - |r_m| \qquad (2)$$

where $[a_{m,n}]$ is the matrix of the individual absorbance of the n-th component at m wavenumbers, while the vectors represent, respectively, $|c_n|$ the n unknown coefficients, $|A_m|$ the overall absorbance of the mixture at m wavenumbers and $|r_m|$ the residual vector, whose size should be minimised in order to satisfy the overdetermined system as closely as possible. A least-squares analysis of the size of the vector $|r_m|$ gives an algorithm for obtaining the solution to equation (2), i.e.:

$$[a_{m,n}]^T [a_{m,n}] |c_n| = [a_{m,n}]^T |A_m| \qquad (3)$$

where $[a_{m,n}]^T$ is the transpose of $[a_{m,n}]$.

Equation 3 is called the normal equation associated with the least-squares problem; it contains the same number of equations and unknowns and it can be easily solved (e.g., through the matrix inversion method) to obtain the values of the c_n coefficients of the individual components in the heterogeneous mixture (see Appendix for computational details).

With a careful selection of the allowable range of FTIR wavenumbers (which excludes, for instance, the absorbance region of water and carbon dioxide, as well as that of strongly interacting chemical groups), through the application of equation (3) to the n components of the mixture we should obtain a mathematically derived spectrum that closely matches the experimental FTIR spectrum of the mixture. If this is not the case, it may be argued that some further components contribute to the spectrum, or that most of the chemical groups strongly interact.

4   Some practical applications

In order to show the application of equation (3) a mixture of malachite with a proteinaceous binder (fish glue) was prepared, and the FTIR spectra of both the single components and the mixture were taken. This simple two-component mixture can be easily analysed with a trial-and-error procedure by means of the tuned difference already built up in the software of most FTIR spectrophotometers, but the algorithm of overdetermined systems gives the solution directly, as shown in Figure 1.

When more than two components are present, the trial-and-error difference cannot be performed easily, while the algorithm proposed in this paper still allows a simple solution.

Figure 2e, for instance, shows the FTIR spectrum of an ancient plaster. Looking only to the spectrum of Figure 2e we can hypothesise the presence of a sulphate group (figure 2a) from the two shoulders
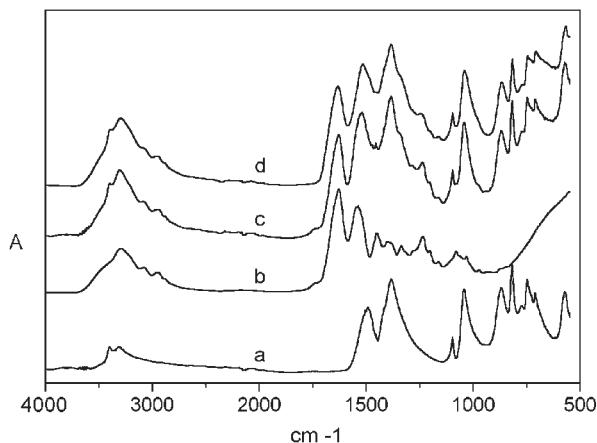
Figure 1. FTIR spectra of malachite (a), fish glue (b) and their weighted sum (c), compared with that of their mixture (d). The absorbance data (A) are proportional to the concentrations (as detected by the Infrared beam) and have been shifted onto the vertical axis to permit convenient comparisons.
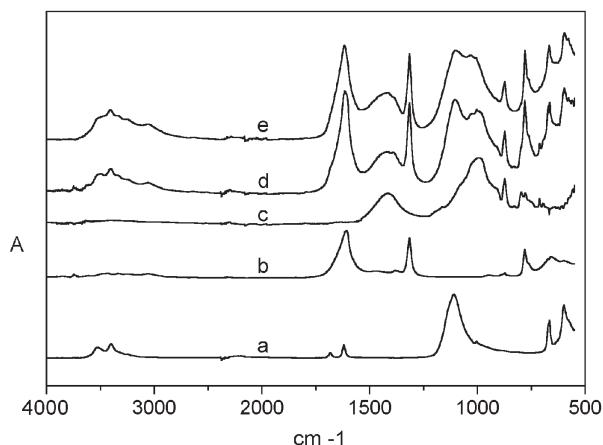

Figure 2. FTIR spectra of calcium sulphate dihydrate (a), calcium oxalate (b), calcarenite (c) and their weighted sum (d), as determined by overdetermined systems, compared with that of an ancient plaster (e). The absorbance data (A) are proportional to the concentrations and have been shifted onto the vertical axis to permit convenient comparisons.

at about 3400 and 1090 cm^{-1}, while two bands at about 1600 and 1300 cm^{-1} suggest the presence of calcium oxalate (Figure 2b). By applying the proposed algorithm with these two standards alone, the misfit between the actual spectrum of Figure 2e and the mathematically derived one indicates that at least one third component contributes to the overall spectrum, and that this component should show a broad absorbance at about 1400, 1000 and 974 cm^{-1}, with some minor sharp spectral features in the 900-750 cm^{-1} region. These FTIR bands are typical of calcarenite (Figure 2c). After applying again the overdetermined systems procedure to the FTIR spectra of all the hypothesised components calcium oxalate + calcium sulphate + calcarenite = ancient plaster, the mathematically derived spectrum (Figure 2d) closely agrees with that of the unknown sample (Figure 2e). This agreement, which can be quantified by
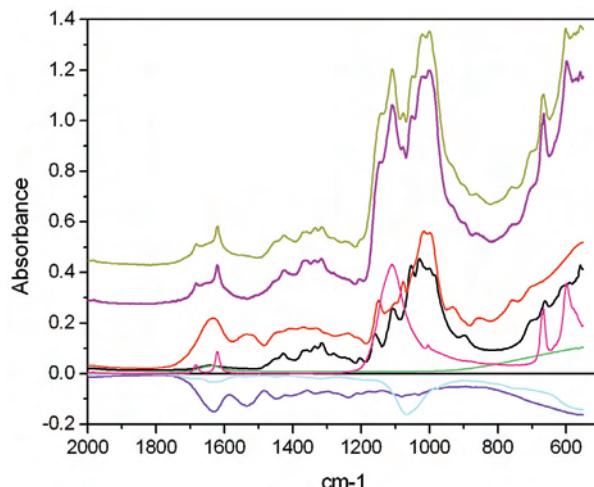

Figure 3 (bottom to top): FTIR spectra of hide glue (blue), ferrous sulphate (azure), water (green), calcium sulphate (magenta), cellulose (black), starch/hide glue (red) and their weighted sums (violet) compared with a XIX Century book leaf (dark green). The absorbance data (A) are proportional to the concentrations as detected by the Infrared beam. The absorbances of the weighted sums and of the book leaf have been shifted onto the vertical axis to permit convenient comparisons.

subtracting the FTIR data of Figure 2d from these of Figure 2e, indicates that no other components are present in a significant amount. Obviously, the whole procedure is a mixture of art and science[7] and can not be applied in a blind routine.

One of the main interesting features of the overdetermined systems algorithm is shown in the case study of Figure 3, where a brown book leaf of the XIX Century was examined. Figure 3 (top) shows its FTIR spectrum in the 2000-500 cm^{-1} region, where the spectrum of paper shows also the bands of sulphates (doublet at 1682 and 1619 cm^{-1}, strong absorbance at 1096 cm^{-1} and low-frequency doublet at 664 and 592 cm^{-1}) and starch (996 cm^{-1}, in the fingerprints region of cellulose). In order to verify the reliability of the curve fitting algorithm we compared this spectrum with a mixture of standards (bottom to top): hide glue, ferrous sulphate, water, calcium sulphate bihydrate, cellulose paper and (intentionally) a sample of starch/hide glue taken from a canopy of the same century. Figure 3 second-last shows the result of the algorithm, which closely matches the FTIR of the book leaf (top), but assigns a *negative* absorbance to ferrous sulphate and hide glue. This finding suggests that the glue of canopy contains more hide glue and iron sulphate than the coating of the book leaf.

5   Conclusions

The algorithm of overdetermined systems offers several advantages in analysing the FTIR spectra of heterogeneous mixtures. While both the tuned difference and the deconvolution of spectra rapid-

ly become impossible to treat against an increasing number of different components, the procedure shown in this paper does not change in a significant way and requires few rows of instructions in a spreadsheet macro. In fact, our spreadsheet allows detection up to 8 components. Generally, a mixture of more than 8 components yields an FTIR profile so rugged that no calculations can be performed on it.

Secondly, the normalisation of spectra is not required, since the solution of equation (3) directly gives the values of the concentration-related coefficients.

The drawback of the method is due to the necessity of a spectral database of standards built up with the same FTIR device utilised for the analysis of the unknown mixtures, owing to the problems of baseline correction and detector sensitivity in different modes of analysis (FTIR photoacoustic, ATR, KBr pellets, FTIR microscope).

However, if the reference spectra of the individual components have been stored once and for all in a spectral library, it should be easy to build a calibration curve at different ratios of concentration in order to perform a semiquantitative analysis of a mixture, at least in the simplest of cases.

6   References

1. J.L. Koenig, *The ratio method for analyzing infrared spectra of mixtures*, Appl. Spectr., 1977, **31**, 292-295.

2. J.L. Koenig, D. Kormos, *Quantitative infrared spectroscopic measurements of mixtures without external calibration*, Appl. Spectr., 1979, **33**, 349-350.

3. J. Grdadolnik, *Infrared difference spectroscopy. Part I. Interpretation of the difference spectrum.* Vibr. Spectr., 2003, **31**, 279-288.

4. P. Calvini, G. Martinelli, *Numerical processing of Fourier transform infrared spectra: a powerful tool in paper analysis*, in: K. Grimstead, Ed., *Preprints of the ICOM Committee for Conservation 9th Triennial Meeting, Dresden, 26-31 August 1990*, ICOM CC, Los Angeles, 1990, **Vol. II**, pp. 453-455.

5. P. Calvini, A. Gorassini, *FTIR-deconvolution spectra of paper documents,* Restaurator, 2002, **23**, 48-66.

6. A. Lórenz-Fonfría, E. Padrós, *Curve-fitting of Fourier manipulated spectra comprising apodization, smoothing, derivation and deconvolution*, Spectrochim. Acta A, 2004, **60**, 2703-2710.

7. R.J. Meier, *On art and science in curve-fitting vibrational spectra*, Vibr. Spectr., 2005, **39**, 266-269.

8. T. Hirschfeld, *Computer resolution of infrared spectra of unknown mixtures*, Anal. Chem., 1976, **48**, 721-723.

9. F. Casadio, L. Toniolo, *The analysis of polychrome works of art: 40 years of infrared spectroscopic investigations*, J. Cult. Her., 2001, **2,** 71-78.

10. J. Van der Weerd, A. Van Loon, J. Boon, *FTIR studies of the effect of pigments on the aging of oil,* Stud. Conserv., 2005, **50**, 3-22.

11. M.K. Antoon, J.H. Koenig, J.L. Koenig, *Least-squares curve-fitting of Fourier transform infrared spectra with applications to polymer systems*, Appl. Spectr., 1977, **31**, 518-524.

12. F. Scheid, *Numerical Analysis*, McGraw-Hill, New York, 1968.

7   Appendix

Table 1 shows an example of calculations, based on 9 FTIR wavenumbers and 4 standards (i.e., $[a_{m,n}] = [a_{9,4}]$), the sum of which should yield the FTIR absorbance of the mixture (i.e., $|A_m| = |A_9|$). The fourth standard (null column) allows a further FTIR standard, if necessary. Notice that not all the values of the null column can be set to 0, in order to avoid error messages during the matrix inversion step.

cm^{-1}	[$a_{m,n}$]				$|A_m|$
	standard 1	standard 2	standard 3	null	MIXTURE
1600	0.3055	0.0072	0.0150	0.0001	0.5380
1596	0.3064	0.0075	0.0160	0.0000	0.5570
1592	0.3084	0.0077	0.0180	0.0000	0.5780
1588	0.3101	0.0078	0.0200	0.0000	0.5940
1584	0.3121	0.0078	0.0220	0.0000	0.6080
1580	0.3162	0.0080	0.0250	0.0000	0.6240
1576	0.3221	0.0083	0.0280	0.0000	0.6450
1572	0.3269	0.0085	0.0300	0.0000	0.6660

Table 1. The [am,n] matrix and the |Am| vector of FTIR absorbances of a simulated mixture.

The transpose of $[a_{m,n}]$ (i.e., $[a_{m,n}]^T$) is

$[a_{m,n}]^T$								
0.3055	0.3064	0.3084	0.3101	0.3121	0.3162	0.3221	0.3269	0.3296
0.0072	0.0075	0.0077	0.0078	0.0078	0.0080	0.0083	0.0085	0.0085
0.0150	0.0160	0.0180	0.0200	0.0220	0.0250	0.0280	0.0300	0.0330
0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

and the left side of equation 3 (i.e., $[a_{m,n}]^T [a_{m,n}] |c_n|$) yields

0.8951	0.0225	0.0659	0.0000		c_1
0.0225	0.0006	0.0017	0.0000	**x**	c_2
0.0659	0.0017	0.0051	0.0000		c_3
0.0000	0.0000	0.0000	0.0000		c_4

where c_1, c_2, c_3 and c_4 are the unknown coefficients to be determined.

The right side of equation 3 (i.e., $[a_{m,n}]^T |A_m|$) yields

1.7364
0.0437
0.1293
0.0001

so that the matrix equation 3 with the same number of equations and unknowns is

0.8951	0.0225	0.0659	0.0000		c1		1.7364
0.0225	0.0006	0.0017	0.0000	x	c2	=	0.0437
0.0659	0.0017	0.0051	0.0000		c3		0.1293
0.0000	0.0000	0.0000	0.0000		c4		0.0001

and the unknown coefficients $|c_n|$ can be determined through the standard methods of matrix equations.

In the above example

c1	=	1.01113
c2	=	24.297
c3	=	4.37405
null	=	-120.867

where the actual value of the null standard does not matter, as it multiplies null absorbances.