Smoothing and derivative calculation of FT-IR spectra of coal by a modified least squares procedure

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Abstract

Fourier-Transform infrared spectroscopy (FT-IR) is an important method for the study of the structure of carbonaceous materials, such as coal, coke, carbon black, active carbon, and pitch. Smoothing and derivative calculation are routinely used for the interpretation of spectra.

Here we show the results of applying a least-squares procedure with osculating polynomials to obtain a mathematical model of the infrared spectra of coals, useful for smoothing, band resolution, peak finding, and data compression.

Key words: FT-IR, signal processing, coal.

Suavizado y obtención de derivadas de espectros de FT-IR de carbones minerales por un procedimiento modificado de mínimos cuadrados

Resumen

La espectroscopia de infrarrojo de transformada de Fourier (FT-IR) es un método importante para el estudio de la estructura de materiales carbonáceos, tales como carbón mineral, coque, negro de humo, carbón activado, y brea. El suavizado y cálculo de derivadas son usados rutinariamente para la interpretación de espectros.

En este trabajo nosotros mostramos los resultados de aplicar un procedimiento de mínimos cuadrados con polinomios osculantes a la obtención de un modelo matemático del espectro infrarrojo de carbones minerales, útil para suavizar, resolver bandas, localizar picos, y comprimir datos.

Palabras claves: Espectroscopía, infrarrojo, procesamiento de datos, carbón.

Introduction

Fourier Transform Infrared Spectroscopy (FT-IR) is an important tool for structural studies and quality control of many materials, including coal and others (e. g. coke, coal- tar pitch, petroleum pitch, minerals, plastics, and pharmaceuticals). The advantages of FT-IR over conventional infrared spectroscopy as an analytical tool have been resumed in the literature [1, 2].

We are interested in the applications of FT-IR to the analysis of coal, to complement or substitute other methods of analysis. However, the infrared spectra of carbonaceous materials present special characteristics: wide overlapping bands, low signal-to-noise ratio, and difficult to reproduce baselines [3,4]. Thus, special procedures need to be applied for data treatment and sample preparation [5-14].

Data treatment is necessary for band resolution and quantitative analysis. Fortunately, Fourier-Transform infrared spectrometers, that now are generally connected to a personal computer, permit to increase the signal-to-noise ratio by calculating an average of many scans. Smoothing, calculation of derivatives and other functions are routinely utilized for the analysis of infrared spectra of coal and other materials [4-14] and are available in commercial programs. For example, second- and fourth- derivative spectroscopy give the possibility of resolving overlapping bands, allowing for localization of "hidden" peaks and identification of components. Smoothing reduces noise, although severe smoothing may also cause loss of information. These points have been discussed by Maddams in his review [15].

Thus, difference spectroscopy [4, 10], smoothing and derivative calculation [4, 11], modeling with Lorentzian, Gaussian, and other functions [15], Fourier self-deconvolution [7, 16], and factor analysis [5, 6] have been applied to extract information from the infrared spectra of coal and other carbonaceous materials.

The method we propose is related to the algorithm most frequently used by chemists for smoothing and derivative estimation, published by Savitzky and Golay in 1964 [17]. They described simplified least-squares procedures (applicable to equally-spaced data, to a maximum width of 25 points) using integer convolution arrays derived from polynomials up to the sixth degree. Thus, smoothed values and derivatives could be estimated for the central point of symmetrical windows by a weighted moving-average, a highly efficient and fast procedure in digital computers. Equations to calculate arrays wider than 25 points [18], and procedures for calculating values for points other than the central one [19-21], have been recently published.

Here we present the results of using a program to calculate least-squares approximations with "osculating" polynomials (these are polynomials whose values *for given arguments* agree up to a certain order with those of a function and its derivatives [22]), variable window sizes, and points others than the window center.

Derivatives and integrals may be readily calculated from the polynomials. In addition, this approximation "compresses" the data, giving a reduced representation of the spectra.

Experimental

Infrared spectra of carbonaceous materials were obtained with a FT-IR spectrometer Model 1710 from Perkin-Elmer Corporation, using the diffuse reflectance method and taking the average of 100 scans. This number of scans was necessary to reduce the noise to an acceptable level. The detector was the triglycine sulphate (TGS) pyroelectric detector generally fitted to commercial FT-IR spectrometers. The samples were neat, pulverized (-200 mesh) coal. Spectra obtained were "exported" using the IRDM[TM] (Infrared Data Manager, Perkin-Elmer Corp.) program and processed with programs written by one of us (CEA) in the QuickBASIC[TM] (Microsoft Corp.) language. Standard least-squares procedures were followed [22]. "Synthetic" infrared absorption bands of Lorentzian [15] shape were generated using the formula $Y = A / \{1 + 4 * [(X - B) / C]^2\}$, where A represents maximum height, B the position of the maxima, and C the width at half height.

Results and Discussion

The procedure followed for smoothing and derivative calculation consisted in using ninth-degree polynomials ($Y = A0 + A1 * X + A2 * X^2 + A3 * X^3 + A4 * X^4 + A5 * X^5 + A6 * X^6 + A7 * X^7 + A8 * X^8 + A9 * X^9$) for approximating the data points inside "windows" of variable width. The result of such approximation is shown graphically in Fig. 1 for a section of a IR spectrum. It is clear that the calculated values do not "fit" at the ends of the windows. The fit is much worse when derivatives are calculated. Thus, values at the window extremes were calculated (using the central-point approximation) for the function and derivatives (1st., 2nd., 3rd., and 4th.) and the polynomials for each side were adjusted to give equal values for the function and derivatives (this is called "osculation" [22]) at those positions. This gave ten conditions for
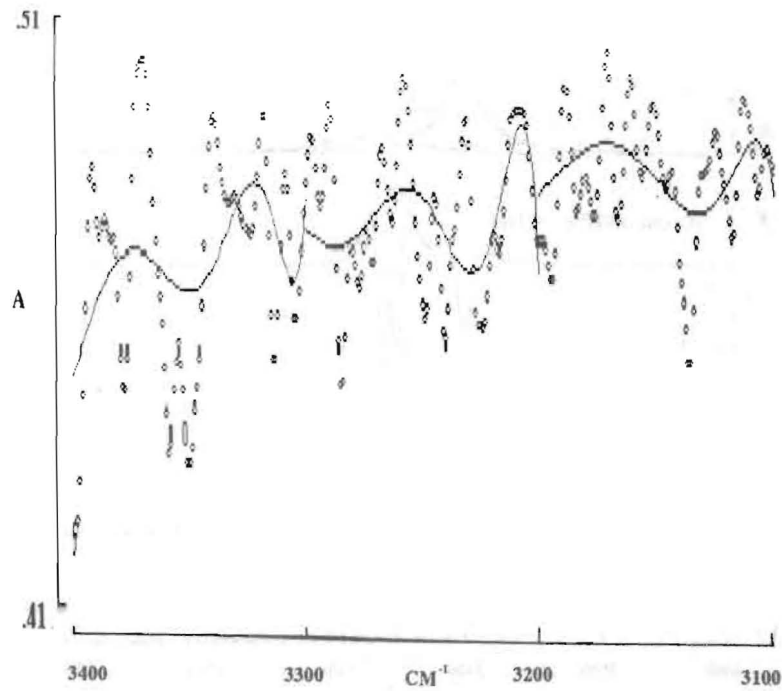
Figure 1. Part of an infrared spectrum. The continuous lines represent the polynomial approximation.
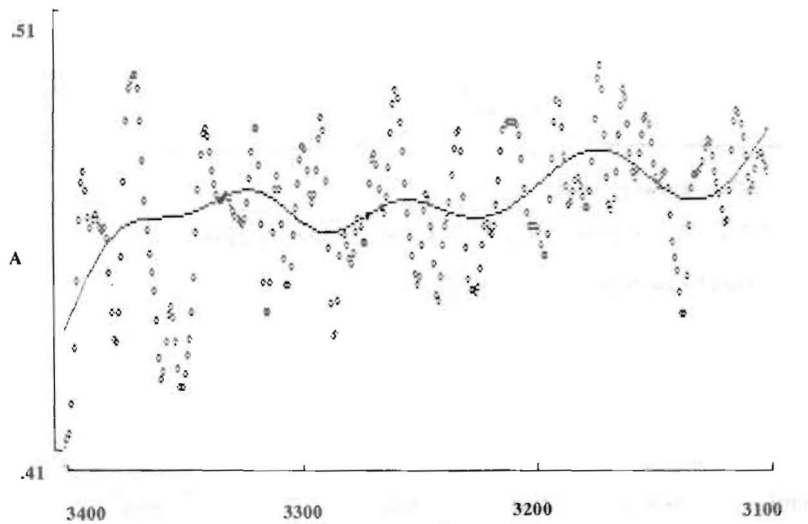

Figure 2. Same spectrum as in Fig. 1, approximated with osculating polymonials.

each polynomial; thus the need for ninth-degree polynomials. The result is shown in Fig. 2. Thus, the IR spectrum is approximated by a set of polynomials, from which derivatives, integrals or other parameters may be readily computed. For the initial point of each window (X = 0), values for the function and derivatives are easily calculated (Y = A0, Y'= A1, Y" = 2 * A2, etc.). These
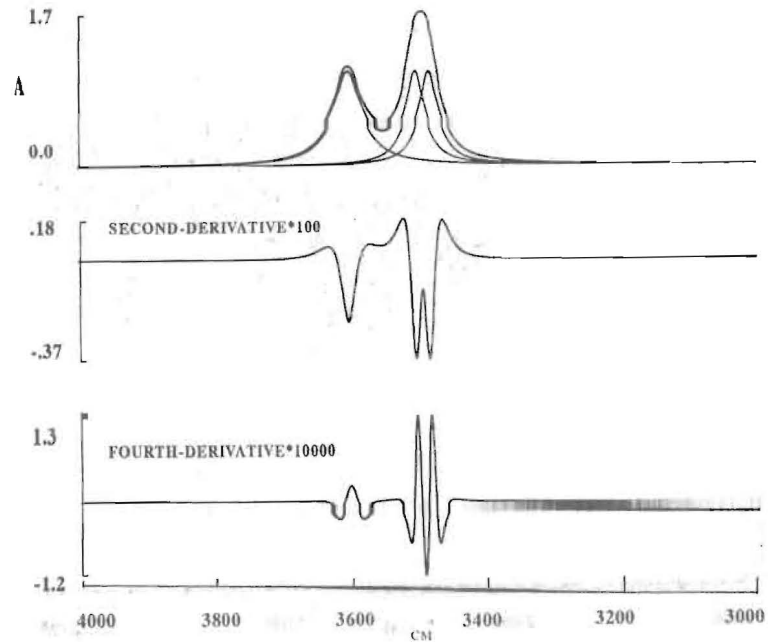
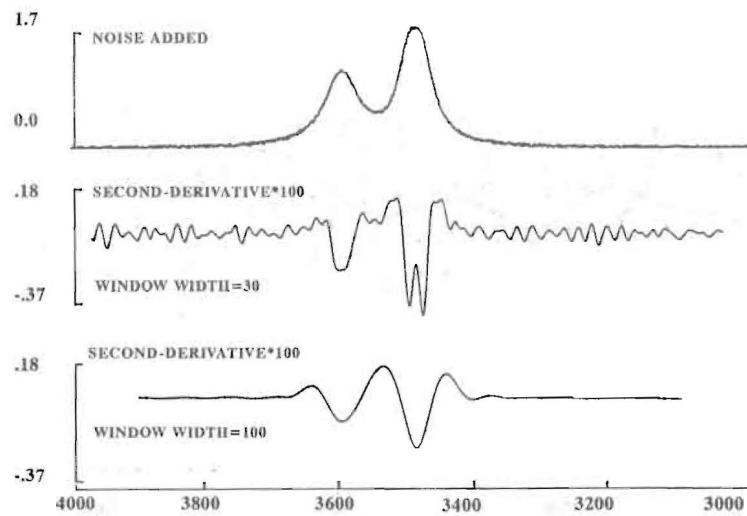Figure 3. Synthetic infrared bands and derivatives.

Figure 4. Second-derivative estimation with osculating polynomials.

values may be specially useful for comparison of spectra using those positions. Data compression is another benefit, for example, 100 data points may be represented by a ninth-degree polynomial (only 10 coefficients).

The mathematical functions utilized to generate synthetic IR spectra (Figs. 3-5) represent bands of the typical width found in infrared spectroscopy. As was indicated in the Introduction, second- and fourth- derivative spectroscopy
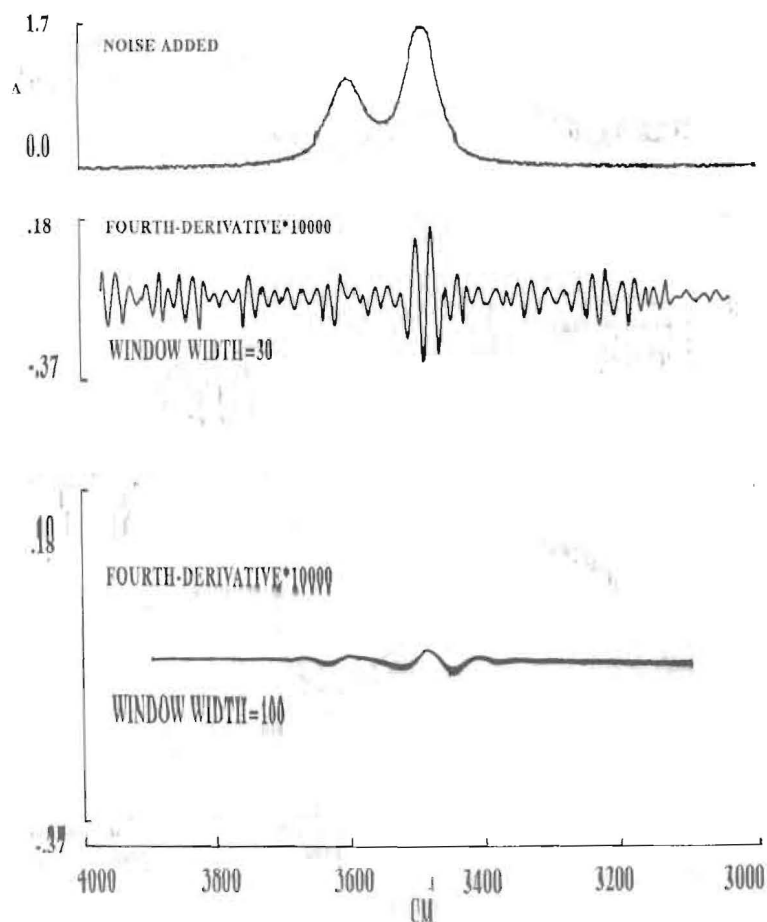
Figure 5. Fourth-derivative estimation with osculating polynomials.

give the possibility of resolving overlapping bands [15]. This is verified in Fig. 3, where a synthetic spectrum representing three over-lapping bands and its second- and fourth- derivatives are shown. Bands pointing upwards in the original spectra appear pointing downwards in the second derivative. This is only an ideal case, however, because "real" spectra always include noise. Figs. 4 - 5 represent the same spectrum with noise added, and its second and fourth-derivative *estimated* using our algorithm and different window widths. The wider window causes a loss in band resolution (compare the derivatives in Figs. 3-5). Resolution is improved as the window width is reduced; however, noise is amplified at the same time. Thus, the optimum window width will be the result of a compromise.

Examples of experimental FT-IR spectra of coal are reproduced in Fig. 6. These spectra look similar, as is the case generally with coal [3,5]. We expected derivatives of the spectra to help us see graphically and evaluate numerically the differences between coals. However, it is necessary to keep noise low. Thus, a window width of 100 data points was used and found to give reproducible values of second- and fourth- deriv-

atives of spectra from different portions of the same macroscopic sample. It is important to compare these results with those obtained with the Savitzky- Golay method. Fig. 7 shows the second-derivatives obtained with both algorithms; the coincidence obtained is excellent. Our method, however, has the additional benefits of giving a mathematical model of spectra.

Fig. 8 shows one of the coal spectra together with its second- and fourth- derivatives calculted with our method. It is seen that the derivatives remove base line effects and narrow the bands, thus facilitating band location. The fourth derivatives may resolve additional bands, as is seen in this case with the shoulder located at 1660 cm^{-1}. The second derivatives of a section of the spectra of both coals are shown together in Fig. 9, displaying approximately the same number of bands at about the same positions. However, clear (and reproducible) differences in relative intensities of the bands are seen in this figure. Work to relate these intensities to physical and chemical properties of the coal samples is in progress.
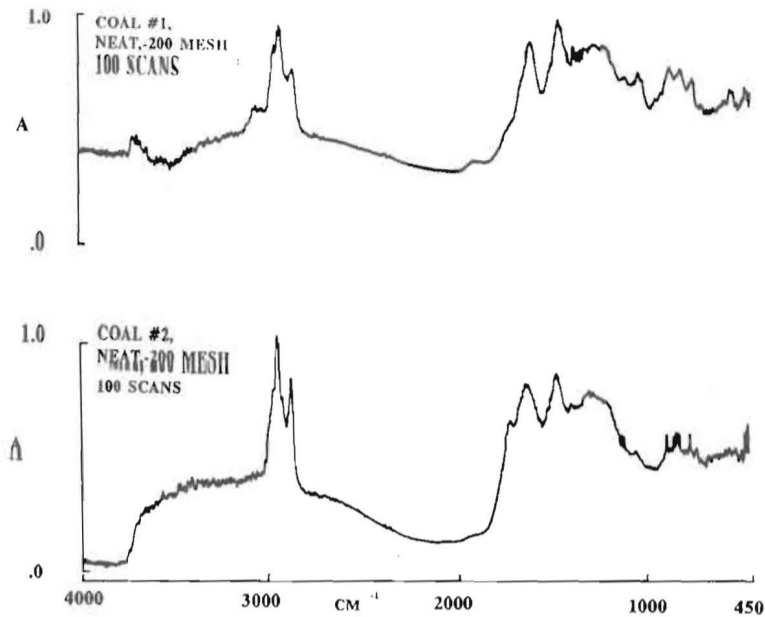
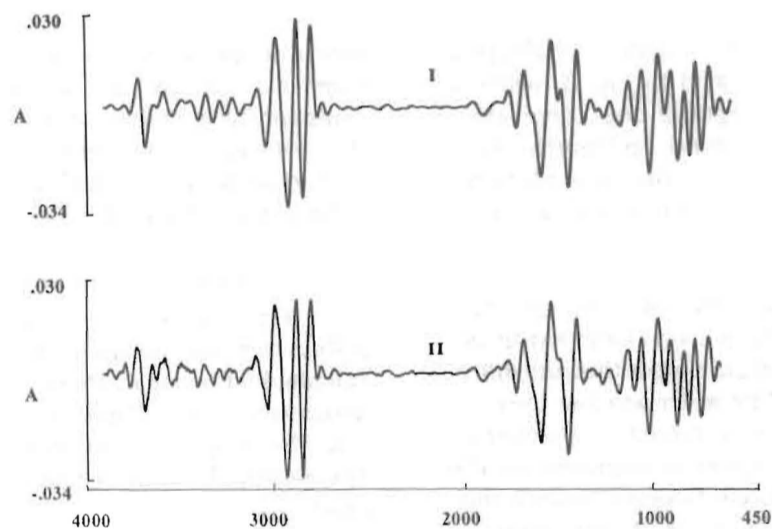Figure 6. Diffuse-reflectance spectra of two sub-bituminous coals.

Figure 7. Comparison of second-derivatives calculated using our algorithm (I) and
Savitzky-Golay's Method (II).

Conclusions

A algorithm has been developed for representing the data points of infrared spectra with a set of osculating polynomials. This mathematical model lets us compress the data and estimate derivatives and integrals. The comparison of different samples of coal is demonstrated to be possible through the use of derivatives. Work is in progress to try to relate parameters calculated from this model to physical and chemical properties of the coal samples.
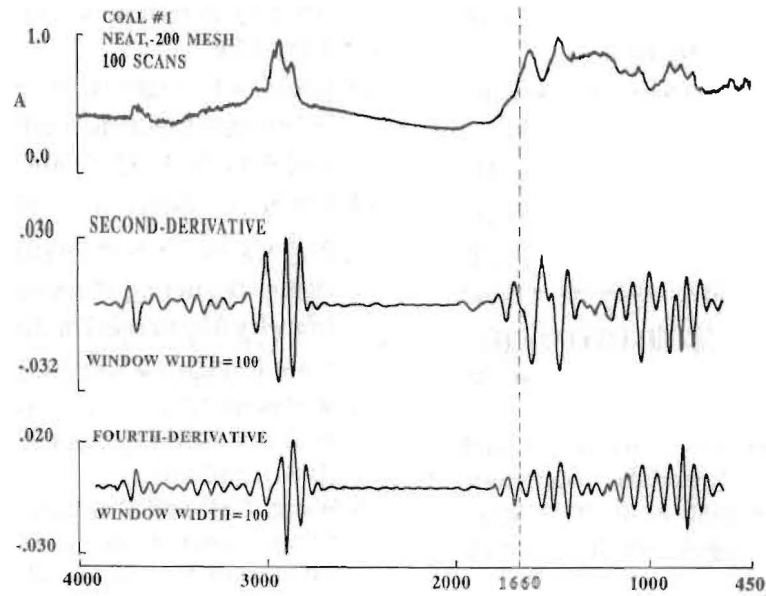
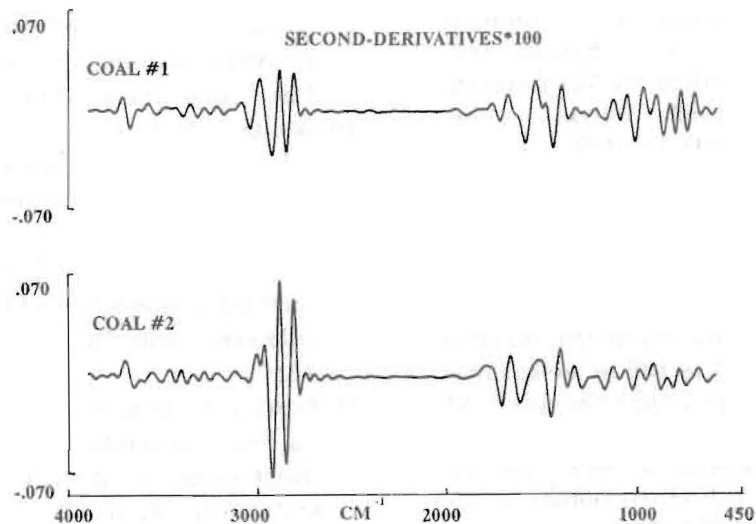Figure 8. Diffuse reflectance spectrum and derivatives.

Figure 9. Comparison of the second-derivative spectra of coal No. 1 and No. 2 (see Fig. 6).

Acknowledgement

References

1. Griffiths, P. R. and De Haseth, J. A.: "Fourier Transform Infrared Spectrometry", Wiley-Interscience 1986.

2. De La Cruz, C. I.: "Principios operacionales y ventajas de FT-IR en Química Analítica", Revista de la Sociedad Venezolana de Química, 13 (1) (1990), 16-19.

3. Elliot, M.A. (Ed.): "Chemistry of Coal Utilization", 2nd. Suppl. Volume, Wiley 1981.

4. Painter, P.C., Snyder, R.W., Starsinic, M., Coleman, M.C., Kuehn, D.W. and Davis, A.: "Concerning the Application of FT-IR to the Study of Coal: A Critical Assessment of Band Assignments and the Applications of Spectral Analysis Programs", Appl. Spectrosc. 35 (5) (1981), 475-485.

5. Fredericks, P.M., Lee, J.B., Osborn, P.R. and Swinkels, D.A.J.: "Materials Characterization Using Factor Analysis of FT-IR Spectra. Part 1: Results", Appl. Spectrosc. 39 (2) (1985), 303-310.

6. Fredericks, P.M., Lee, J.B., Osborn, P.R. and Swinkels, D.A.J.: "Materials Characterization Using Factor Analysis of FT-IR Spectra. Part 2: Mathematical and Statistical Considerations", Appl. Spectrosc. 39 (2) (1985), 311-316.

7. Kauppinen, J.K., Moffatt, D.J., Mantsch, H.H. and Cameron, D.G.: "Fourier Self-Deconvolution: A Method for Resolving Intrinsically Overlapped Bands", Appl. Spectrosc. 35 (3) (1981), 271-276.

8. Fredericks, P.M., Kobayashi, R. and Osborn, P.R.: "Rapid analysis of coal blends by diffuse reflectance FT-IR spectrometry", FUEL 66 (11) (1987), 1603-1608.

9. Fuller, E.L., Jr. and Smyrl, N.R.: "Chemistry and Structure of Coals: Hydrogen Bonding Structures Evaluated by Diffuse Reflectance Infrared Spectroscopy", Appl. Spectrosc. 44 (3) (1990), 451-461.

10. Painter, P.C., Sobkowiak, M. and Youtcheff, J.: "FT-IR study of hydrogen bonding in coal", FUEL 66 (7) (1987), 973-978.

11. Supaluknari, S., Larkins, F.P., Redlich, P. and Jackson, W.R.: "An FTIR Study of Australian Coals: Characterization of Oxygen Functional Groups", Fuel Processing Technology 19 (1988) 123-140. PA

12. Fredericks, P.M. and Moxon, N.T.: "Differentiation of in situ oxidized and fresh coal using FT-IR techniques" FUEL 65 (11) (1986) 1531-1538.

13. Cooke, N.E., Fuller, O.M. and Gaikwad, R.P.: "FT-IR spectroscopic analysis of coals and coal extracts" FUEL 65 (9) (1986) 1254-1260.

14. Iwata, H., Gunji, N., Mametsuka, H. and Kaihara, M.: "New Measurement Methods for Highly Scattering Samples in FT-IR Spectrometry (Scattering Dilution Method)", NKK Technical Review 58 (1990) 78-83.

15. Maddams, W. F.: "The Scope and Limitations of Curve Fitting", Appl. Spectrosc. 34 (3) (1981), 245-267.

16. Wang, S.H. and Griffiths, P.R.: "Resolution enhancement of diffuse reflectance i.r. spectra of coals by Fourier self-deconvolution", FUEL 64 (1985), 229-236.

17. Savitzky, A. and Golay, M.J.E.: "Smoothing and Differentiation of Data by Simplified Least Squares Procedures", Anal. Chem. 36 (8) (1964) 1627-1639.

18. Madden, H.H.: "Comments on the Savitzky-Golay Convolution Method for Least-Squares Fit Smoothing and Differentiation of Digital Data", Anal. Chem. 50 (9) (1978), 1383-1386.

19. Wentzell, P.D., Doherty, T.P. and Crouch, S.R.: "Frequency response of Initial Point Least Squares Polynomial Filters", Anal. Chem. 59 (2) (1987), 367-371.

20. Bialkowski, S.E.: "Generalized Digital Smoothing Filters Made Easy by Matrix Calculations", Anal. Chem. 61 (11) (1989), 1308-1310.

21. Gorry, P.A.: "General Least-Squares Smoothing and Differentiation by the Convolution (Savitzky-Golay) Method", Anal. Chem. 62 (11) (1990), 570-573.

22. Scheid, F.: "Numerical Analysis", McGraw-Hill 1978.