Compositional characterization of carbon electrode material: A study using simultaneous TG–DTA–FTIR

Naina Raje, Darshana A. Aacherekar, A.V.R. Reddy*

Analytical Chemistry Division, BARC, Mumbai 400085, India

ARTICLE INFO

ABSTRACT

Present work describes the application of thermal methods, especially the evolved gas analysis (EGA) for the compositional characterization of carbon electrode material with respect to its organic, amorphous and graphitic carbon content. Trace levels of organic carbon present in the amorphous carbon samples were determined qualitatively by using FTIR absorption spectroscopy. Amorphous and graphitic carbon content in synthetic mixture samples were determined quantitatively using simultaneous TG–DTA–FTIR measurements. FTIR system was calibrated using the measured absorption signal of the evolved carbon dioxide due to the decomposition of cadmium carbonate. Inter-comparison studies using TG–FTIR measurements show that simultaneous FTIR spectroscopy is an effective complementary quantitative measurement technique for thermogravimetric analysis involving the complex decomposition reaction processes.

1. Introduction

Since the historical application by Sir Humphrey Davy of graphite electrodes for electrochemical production of alkali metals, carbon materials have been widely used in both analytical and industrial electrochemistry. The advantages of carbon electrodes include low cost, wide potential window, relatively inert electrochemistry and electro catalytic activity for a variety of redox reactions. The diversity of carbon as an electrode material stems largely from its structural polymorphism, chemical stability, rich surface chemistry and strong carbon–carbon bonds present both internally and often between the carbon and a surface modifier [1]. Physical and analytical electrochemistry using carbon materials, depend on the electronic and chemical properties of carbon, which in turn, determine performance of the electrode. Thus, it becomes necessary, to consider those aspects of the material chemistry of carbon that dictate its electrochemical utility [2].

Most of the materials change their physical properties and chemical characteristics under the influence of temperature. The temperature specific information on material properties determined by thermal analysis is extremely useful for the identification of materials as well as evaluation of their purity and composition, polymorphism and structural changes, thermal stability and temperature limits of application, aging behavior, thermo-mechanical behavior, viscoelastic properties and processing conditions for shaping and casting. Material of organic, inorganic and biological origin could be characterized by thermal analysis [3].

Thermoanalytical methods are useful to systematically analyze the physico-chemical changes by application of programmed temperature variation for heating and cooling, and by application of specified sample atmosphere and pressure. The properties most often studied are specific heat and enthalpy changes, weight loss or weight gain, thermal expansion and gas evolution [4]. Evolved gas analysis (EGA) provides information on the nature and amount of volatile products as a function of temperature during the thermal decomposition of materials and these volatiles are analyzed using thermoanalytical methods and/or multiple techniques [5]. The simultaneous analysis approach is to monitor the evolved gaseous products in accordance with the decomposition reaction progress, such as in TG–FTIR and TG–MS on-line measurement techniques. Continuous mode involves in situ introduction of the gaseous products into the detector system using an interface coupling, such as TG–FTIR, and TG–MS. Main advantage of the continuous mode is its ability to perform simultaneous and continuous real time analysis [6,7].

Several methods are available for the determination of carbon in different matrices. Essentially in all these methods, total carbon present in the sample is oxidized to give carbon dioxide and the librated carbon dioxide is detected by using various detectors [8,9]. Thermogravimetric analysis (TG) has been used to

---

study both sewage sludge and coal burning providing a preliminary assessment of its fuel value and, the initial and final combustion temperatures as well as other relevant data such as maximum reactivity temperature or total combustion time [10–12]. Marta Otero et al. studied the combustion of sewage sludge and coal and compared the results with those obtained by TG. Non-isothermal thermogravimetric data were used to calculate the kinetic parameters [13]. TG–FTIR and TG–MS techniques have the ability to measure the simultaneous and continuous mass loss of materials as a function of temperature and monitor the gaseous products evolved as a function of temperature that account for the mass loss. Therefore these techniques are widely employed in the material science studies, e.g., in the study of coal pyrolysis and combustion, polymer degradation, evaluation of hazardous materials and thermal stability of materials [14]. Considerable work on characterizing materials, determining kinetic parameters and quantitative analysis of degradation products has been performed by TG–FTIR analysis [15,16].

Literature survey suggests that systematic studies on the characterization of carbon with respect to its various forms in the sample matrix are scarce. On-line detection of the nature of released gases or vapors is prime requirement to prove a supposed reaction, under either isothermal or heating conditions [17]. In view of this, present studies for the characterization of carbon electrode materials with respect to its organic, amorphous and graphitic carbon content have been carried out using the inherent ability of TG–FTIR technique. The results obtained are discussed in this paper.

2. Experimental

Experiments have been carried out using Netzsch Thermobalance (Model No.: STA 409 PC Luxx) coupled to Bruker FTIR system (Model No.: Tensor 27) via a heated Teflon capillary (1 m long, 2 mm i.d.). Pt vs. Pt 10% Rh thermocouple was used as the temperature sensor. TG–DTA data analysis was done using Proteus software from Netzsch.

FTIR system used for the identification of IR absorbance in the mid IR region (400–4000 cm^{-1}) is equipped with liquid nitrogen cooled MCT detector and low-volume gas cell (8.7 mL) with a 123 mm path length and KBr windows. The adapter head of thermobalance, transferline and sample cell were heated to a constant temperature of 200 °C to avoid condensation of low volatile compounds. The FTIR compartment was continuously purged by high purity nitrogen and molecular sieves/silica gel were used to minimize the water and carbon dioxide background in the recorded spectra. The resolution of the collected spectra was set to 4 cm^{-1} and co-addition of 32 scans per spectrum with the scan speed of 20 kHz was applied. As a consequence, spectra were recorded with a temporal resolution of about 2.5 s, depending on the integration methods. FTIR data analysis was done using Opus (version 6.0) software from Bruker.

Simultaneous TG–DTA–EGA measurements were carried out individually on pure (5–200 mg) as well as on synthetic mixtures of amorphous/graphitic carbon electrode material/s (5–15 mg) in suitable air/inert atmosphere by heating from room temperature to 450–1200 °C at a heating rate of 5–10 K/min. The flow rate of high purity nitrogen was maintained at 100 mL/min. to transport the volatile products. Nitrogen was also used as protective gas to the thermobalance at a flow rate of 20 mL/min. FTIR system, connected to TG–DTA, was calibrated for quantitative analysis of carbon dioxide. Evolved carbon dioxide, due to the decomposition of analytical grade [Reanal, Budapest, Hungary] cadmium carbonate (5–150 mg) in air, was used as a calibration standard. Amorphous and graphitic carbon contents, present in the ratio of 2:1 respectively in the synthetic mixture samples (5–15 mg) have been determined quantitatively.
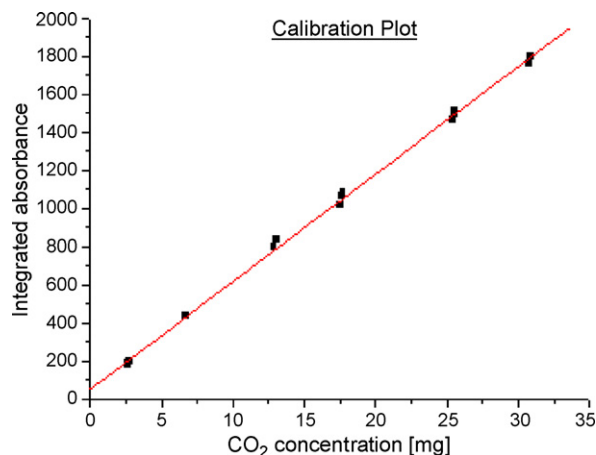

Fig. 1. Calibration plot used for quantitative determination of carbon dioxide.

3. Results and discussion

Calibration of TG–MS system using sodium bicarbonate for the quantitative determination of evolved carbon dioxide has been reported [18,19] but high temperature gas phasic interaction between simultaneously evolved H_2O and CO_2 is not clear. Decomposition of cadmium carbonate leads to the evolution of carbon dioxide only. Present studies involve the decomposition of cadmium carbonate (5–150 mg) in air at a constant heating rate and the evolved carbon dioxide during the decomposition process was used for calibration. The absorbance spectrum of carbon dioxide, extracted from the 3D FTIR spectrum matched well with the standard IR absorbance spectrum of CO_2 [20,21]. The absorbance signal corresponding to each temperature data block of the reaction region where the signal for carbon dioxide evolution is observed above baseline on absorption vs. temperature plot, has been integrated in the frequency region of 2215–2430 cm^{-1} and co-added to give the integrated absorbance of the reaction process. This integrated absorbance signal was plotted as a function of evolved carbon dioxide weight to obtain the calibration plot given in Fig. 1. A similar approach has been used for calibration of FTIR system using pulse calibration method by Marsanich et al. [22].

An excellent and reproducible linear relationship has been obtained between the integrated absorbance signal and the weight of evolved carbon dioxide in the decomposition of cadmium carbonate, in the mass range of 10–100 mg. Linearity range of the absorbance signal was observed to be within 2–30 mg of carbon dioxide weight. Correlation coefficient of 0.998 was obtained for CO_2 band at 2354 cm^{-1} which is in good agreement with the reported value of 0.995 obtained using pulse calibration method [23].

The present experimental investigations involve the measurement of evolved carbon dioxide due to the decomposition of sample matrix and therefore it is imperative to assess the possible contributions from inorganic carbon impurity present in the sample matrix. This was assessed as follows before proceeding for the analysis. Suitable amounts of the samples were taken and heated in thermobalance to 1200 °C at a heating rate of 10 K/min in inert atmosphere. The absorbance signal for carbon dioxide evolution was not seen, suggesting the absence of any inorganic carbon impurity in the sample matrix.

Decomposition behavior of amorphous and graphitic carbon powder samples in air at the heating rate of 10 K/min is shown in Fig. 2. It can be seen from the extrapolated onset and offset temperatures on TG curves that oxidation of amorphous carbon in air takes place in the temperature region of 611–704 °C which is lower
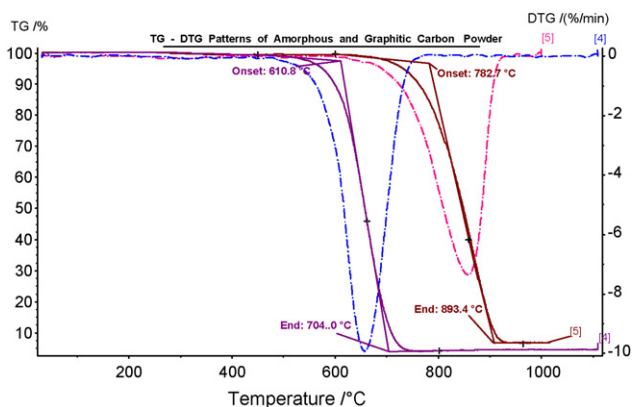
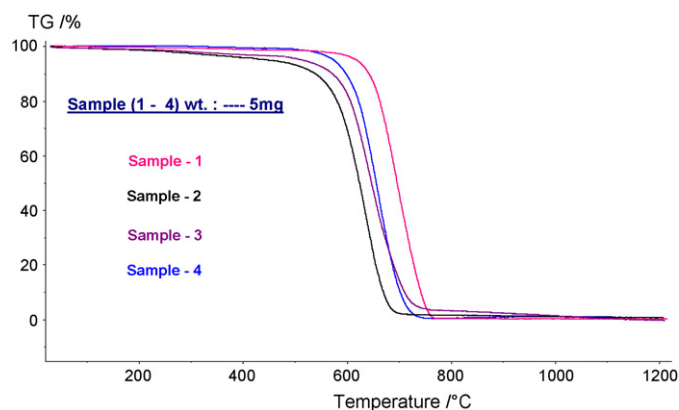**Fig. 2.** Decomposition pattern for amorphous and graphitic carbon.

Fig. 3. Recorded TG pattern for 5 mg sample weight.

by 150–200 °C than that of graphitic carbon [783–893 °C]. Thermo-analytical curves for the four amorphous samples obtained from different vendors, have been presented in Fig. 3. These TG curves have been corrected for the buoyancy effect [5,24] by applying suitable blank corrections. The corresponding total carbon content, the extrapolated TG onset temperature for the combustion process and the extrapolated offset temperature at which the reaction ceases have been listed in Table 1. TG_{onset} and TG_{offset} temperatures for, the samples 2, 3 and 4 are comparable except for sample 1 suggesting that these samples are of amorphous carbon. It can be seen from Fig. 3 and Table 1, that the thermoanalytical data based on 5 mg

Table 1
Simultaneous TG data observed for different carbon electrode samples.

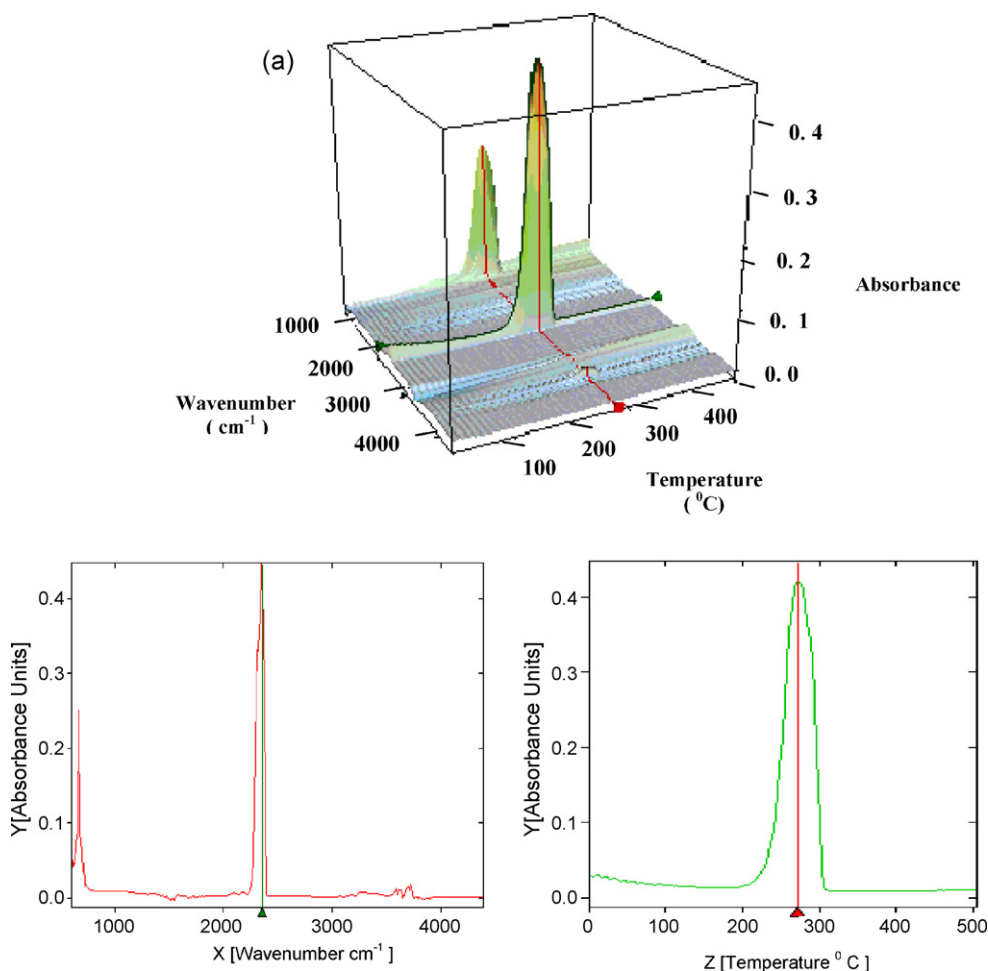| Sample No.	Sample wt. (mg)	Wt. loss (%)	TG_{onset} (°C)	TG_{offset} (°C)
1	4.92	98.0	652	747
2	5.01	96.8	587	707
3	5.43	97.2	593	686
4	5.33	98.6	613	705

Fig. 4. 3D FTIR spectrum of (a) organic carbon, (b) amorphous carbon, and (c) graphitic carbon.
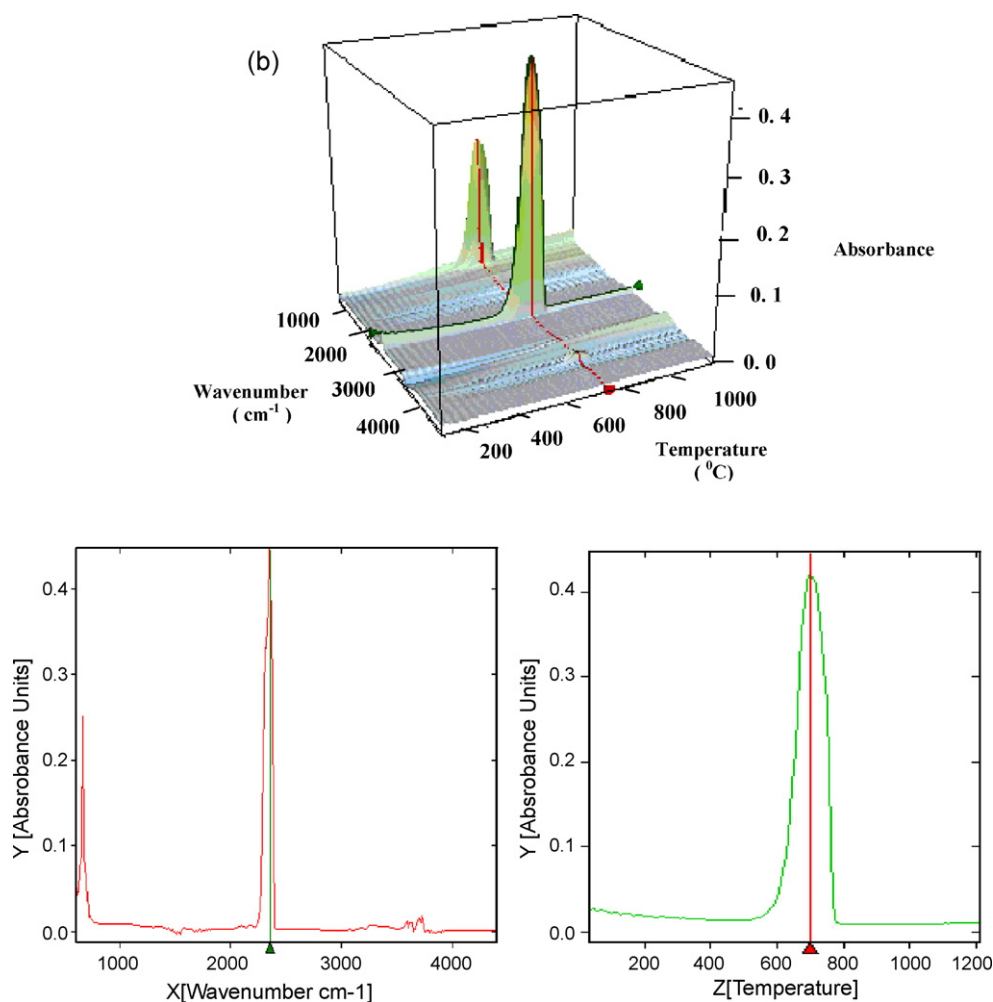
Fig. 4. (*Continued*).

sample are unable to provide any clue for the presence of organic carbon content in these samples though the observed weight loss on TG curve is in the range of 97–99%.

Carbon electrode materials are derived from bituminous coal having low volatile organic as impurity. Depending on the process from which the electrode material has been prepared, it may contain varying amounts of organic carbon [25]. 3D FTIR spectra for carbon dioxide evolution due to the oxidation of organic, amorphous and graphitic carbon powder samples in air have been shown in Fig. 4a, b and c respectively. On the basis of carbon dioxide signal above baseline on absorbance vs. temperature/wavenumber plots, it was found that the oxidation of organic carbon takes place in the temperature range of 195–330 °C while amorphous carbon gets oxidized between 535 and 803 °C and graphitic carbon at 650–930 °C. The influence of temperature (in TA chamber) on the shape and intensity of the MS/FTIR signals was studied and concluded as the integral intensity of the signal is independent of temperature [19,22]. Hence by observing the evolution of carbon dioxide at different temperatures, the organic, amorphous and graphitic carbon content in the sample could be identified, differentiated from each other and determined quantitatively.

Identification of organic carbon in amorphous samples was carried out by optimizing the experimental conditions in such a way that it results in suppression of the amorphous carbon oxidation. The determination procedure was adopted to increase the sample weight and stop the high temperature amorphous carbon oxi-

dation reaction. Simultaneously measured DTG–EGA patterns for the decomposition of typical amorphous sample in air have been given in Fig. 5. The IR absorption spectrum was extracted from the Gram Schmidt curve and absorption band corresponding to H_2O or any other volatile product could not be seen in the absorption vs. wavenumber plot in temperature region of 31–450 °C. Absorption band could be seen only at 2354 cm^{-1} in the temperature region of 195–330 °C and this suggests the presence of CO_2 in this temperature region. Ensuring the presence of CO_2 only, as volatile, in the temperature region, the EGA pattern (Gram Schmidt) is being depicted in Fig. 5 for the direct correlation and interpretation between DTG and evolved gas signals. Effect of the optimized procedure can be seen from Fig. 5. When a larger sample weight [100 mg] was decomposed to 450 °C in air, the decomposition step between 195 and 330 °C temperature region could be seen on the DTG curve along with the corresponding gas evolution signal on EGA curve in the same temperature region. Also, these low temperature decomposition reaction signals were found to be missing on DTG–EGA curves when small sample weight [5 mg] was used and the reaction was observed above 500 °C. These observations shown in Fig. 5 suggest that the decomposition step corresponding to 195–330 °C temperature region is due to the oxidation of organic carbon present in the amorphous sample. As the concentration of organic carbon in the sample is low, it could not be seen with smaller sample weight. It is also possible that the small signal corresponding to organic carbon content would have been masked by the major matrix signal.
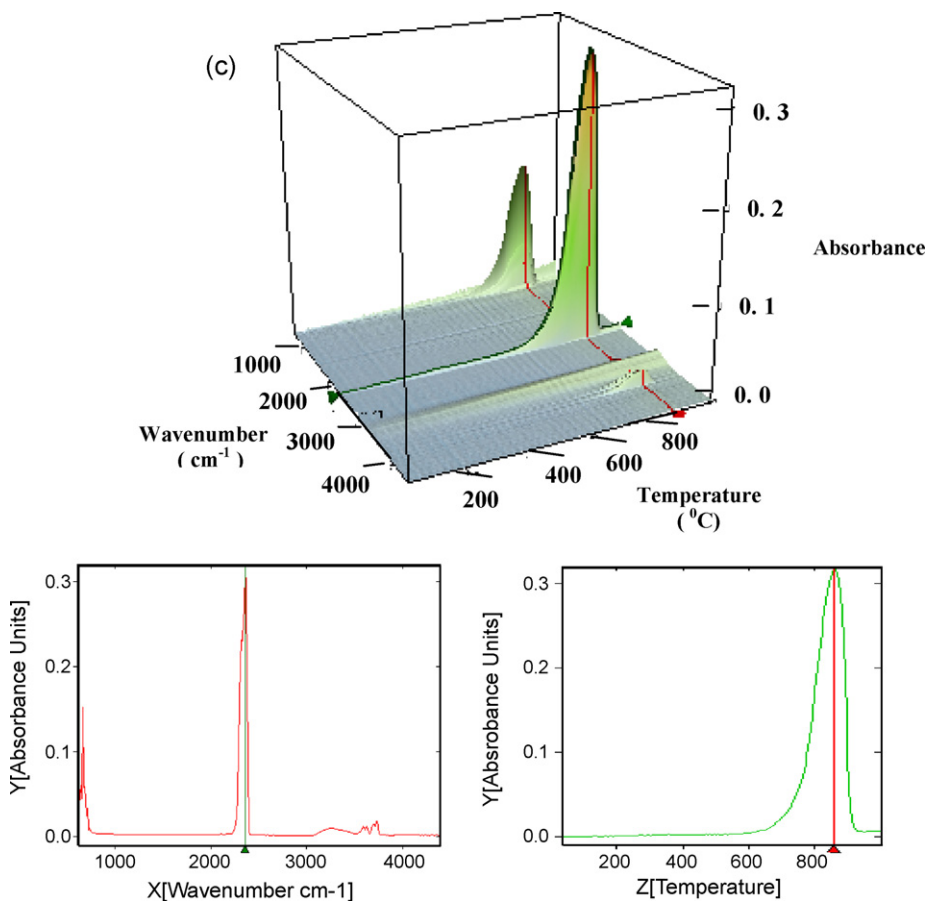
Fig. 4. (*Continued*).

Though the low temperature signals could be seen using larger sample weights, the signal intensity on TG/EGA curves was poor. To check for possible baseline shift or contamination, the sample was pretreated. Pretreatment was done by heating the sample to 500 °C in air and subsequently cooled to room temperature. Fig. 6 shows the effect of pretreatment on the amorphous carbon samples. When the decomposition pattern of pretreated sample was followed, the decomposition step in the temperature region of 195–330 °C was absent on DTG curve along with the corresponding gas evolution signal on EGA curve. These observations confirm that the low tem-

perature weight loss on DTG curve and simultaneous gas evolution on EGA curve are from the decomposition of sample at low temperature and it appears that the baseline drifts or any other possible contaminations are absent.

As discussed earlier, the combustion of organic carbon takes place at lower temperature. Hence amorphous carbon powder samples [200 mg] were heated in the thermobalance independently to 450 °C at a heating rate of 10 K/min in air atmosphere. Qualitative estimation of organic content in the amorphous carbon powder samples can be obtained by following the low temperature
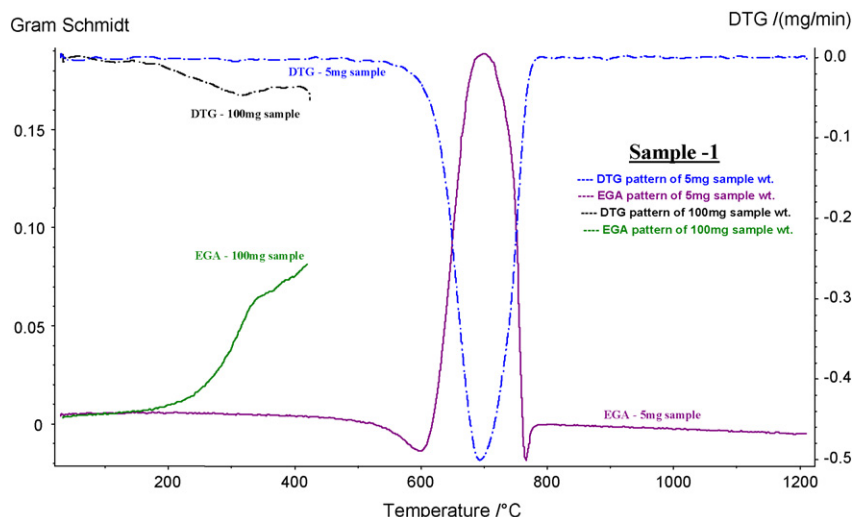

Fig. 5. Effect of optimized conditions on DTG–EGA patterns of amorphous carbon sample.
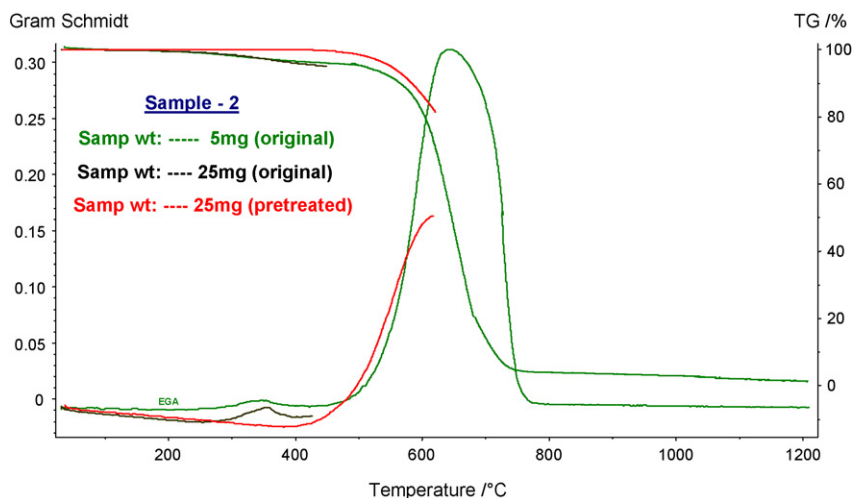
Fig. 6. Effect of pretreatment on TG–EGA patterns of powdered amorphous carbon sample.
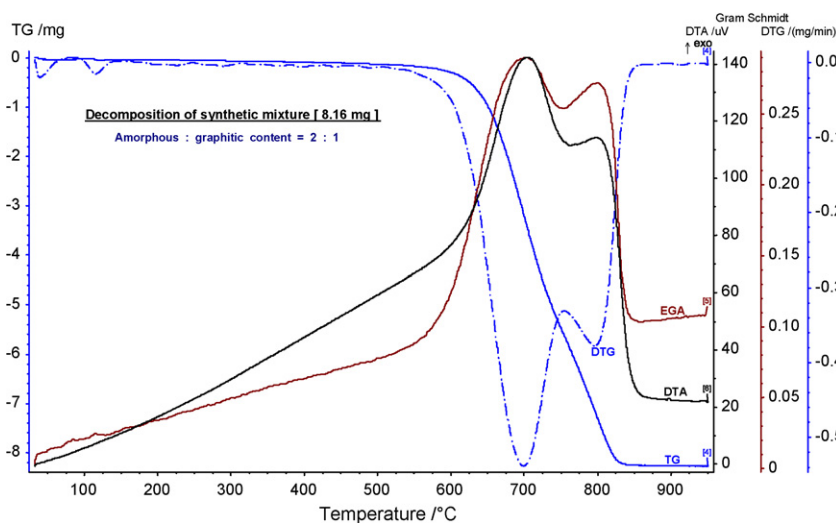

Fig. 7. Blank corrected TG–DTA–EGA curves of synthetic mixture decomposition [amorphous:graphitic carbon = 2:1].

[195–330 °C] carbon dioxide evolution and corresponding absorption signal on IR spectra. It was found that sample 4 has the least amount of organic carbon content present while samples 2 and 3 have comparable amounts of organic carbon content. The organic content in amorphous samples could not be determined quantitatively due to its low concentration in the samples. This is because the amount of the evolved carbon dioxide could be lower than the detection limit of the instrument [Fig. 1] used.

Simultaneous TG–DTA–EGA measurements were carried out in air for synthetic mixtures prepared by taking the amorphous and graphitic carbon contents in 2:1 ratio with sample weights in the range of 5–15 mg and heating in thermobalance at the rate of 10 K/min from room temperature to 1000 °C. The blank corrected TG–DTA and Gram Schmidt curves for the typical synthetic mixture [8.16 mg] have been shown in Fig. 7. The exothermic heat effects on DTA curve in the temperature region of 525–925 °C with
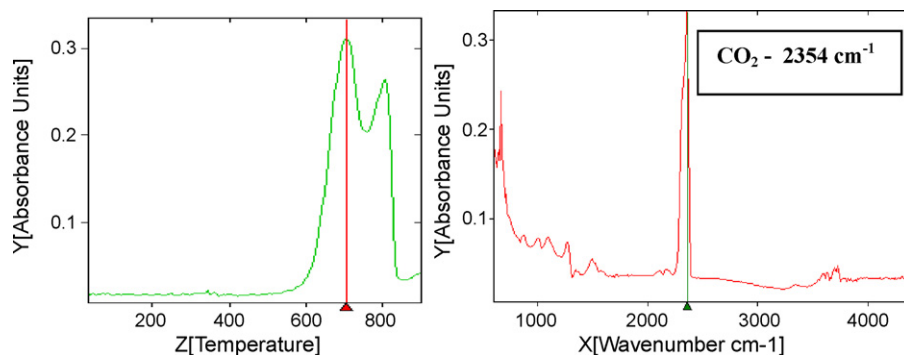

Fig. 8. Amorphous carbon oxidation profile as a function of temperature/wavenumber in the synthetic mixture.
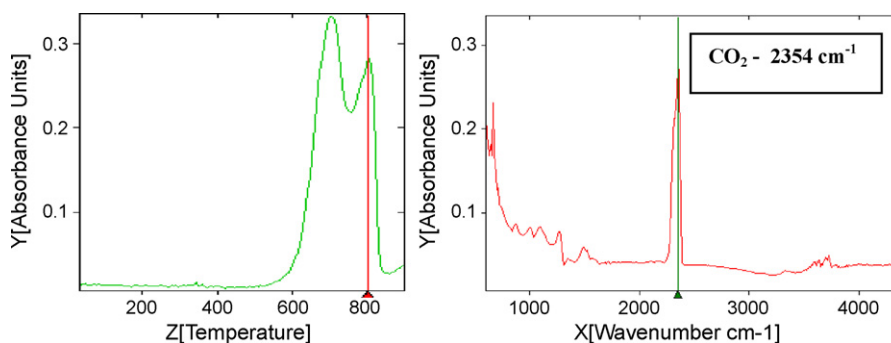
Fig. 9. Graphitic carbon oxidation profile as a function of temperature/wavenumber in the synthetic mixture.

Table 2
Inter-comparison of quantitative analysis using theoretical, FTIR and TG data.

	S.No.				
	1	2	3	4	5
Wt. of synthetic sample (mg)	6.42	8.01	8.16	10.06	12.58
Wt. of amorphous carbon content in synthetic sample (mg)	4.28	5.36	5.48	6.72	8.40
Wt. of graphitic carbon content in synthetic sample (mg)	2.14	2.65	2.68	3.34	4.18
Amount of CO_2 evolved due to amorphous carbon content in synthetic sample (mg)	16.59	20.01	20.22	25.28	31.10
Amount of CO_2 evolved due to graphitic carbon content in synthetic sample (mg)	8.16	10.15	9.58	12.35	15.17
Amount of carbon due to amorphous CO_2 content in synthetic sample (mg) ± error (%)	4.52 ± 5.61	5.46 ± 1.87	5.51 ± 0.55	6.89 ± 1.69	8.48 ± 0.95
Amount of carbon due to graphitic CO_2 content in synthetic sample (mg) ± error (%)	2.23 ± 4.20	2.77 ± 4.52	2.61 ± 2.61	3.37 ± 0.90	4.14 ± 0.96
Amount of total carbon due to total CO_2 content in synthetic sample (mg) ± error (%)	6.75 ± 5.14	8.23 ± 2.75	8.12 ± 0.49	10.26 ± 1.99	12.62 ± 0.32
TG wt. loss due to amorphous carbon content in synthetic sample (mg) ± error (%)	4.37 ± 2.10	5.37 ± 0.20	5.57 ± 1.64	6.75 ± 0.44	8.36 ± 0.48
TG wt. loss due to graphitic carbon content in synthetic sample (mg) ± error (%)	2.13 ± 0.47	2.62 ± 1.13	2.66 ± 0.74	3.38 ± 1.18	4.19 ± 0.24
TG wt. loss due to total carbon content in synthetic sample (mg) ± error (%)	6.50 ± 1.24	7.99 ± 0.25	8.23 ± 0.86	10.13 ± 0.70	12.55 ± 0.24
Ratio of amorphous:graphitic carbon content in the sample (theoretical)	2.00	2.02	2.04	2.01	2.01
Ratio of amorphous:graphitic carbon content in the sample ± error (%) (FTIR)	2.03 ± 1.50	1.97 ± 2.48	2.10 ± 2.94	2.04 ± 1.49	2.05 ± 1.99
Ratio of amorphous:graphitic carbon content in the sample ± error (%) (TG)	2.05 ± 2.50	2.04 ± 0.99	2.09 ± 2.45	1.99 ± 1.00	2.00 ± 0.50

simultaneous weight loss on TG/DTG curve and gas evolution on the EGA curve indicate the oxidation of carbon sample resulting in the evolution of carbon dioxide. The observed doublet in Fig. 7 on DTA and EGA curves correspond to independent oxidation of amorphous and graphitic carbon in the mixture. Although the two weight loss steps are not well resolved on TG curve, they can clearly be distinguished by following the DTG pattern. It can be seen from TG–DTG shown in Fig. 7 that weight loss of 5.57 mg, in the temperature region of 520–755 °C corresponds to the amorphous carbon content whereas 2.66 mg weight loss in the temperature region of 755–925 °C corresponds to the graphitic carbon content in the synthetic mixture sample. The total weight loss in the temperature range of 525–925 °C is 8.23 mg corresponding to the oxidation of total carbon. Figs. 8 and 9 represent the absorption profiles of evolved carbon dioxide as a function of temperature and wavenumber for amorphous and graphitic carbon content respectively in the synthetic mixture sample. It can be seen from Figs. 8 and 9 that CO_2 evolved in the temperature region of 520–755 °C and 755–925 °C correspond to the oxidation of amorphous and graphitic carbon respectively in the mixture. The integrated absorbance in the temperature region of 520–755 °C and 755–925 °C has been correlated to corresponding evolved carbon dioxide weight using the FTIR calibration plot [Fig. 1] for quantitative determination of amorphous and graphitic content respectively in the synthetic mixture sample/s. Five independent TG–FTIR measurements were carried out for synthetic mixture samples and the measured data have been compared with corresponding theoretical values. The results have been given in Table 2 along with the percentage relative error. It can be seen from Table 2 that overall accuracy of the analysis for TG measurements is within 1% and is within 3% for simultaneous FTIR measurements except for the sample with 6 mg weight. This may be due to the sample weighing error. Table 2 shows that the overall accuracy for FTIR analysis

could be improved by taking more amount of synthetic mixture sample.

It can be seen from Table 2 that when the two decomposition steps corresponding to the oxidation of amorphous and graphitic carbon are not well resolved on TG curve, the error associated with the measurement of amorphous and graphitic content, using TG and FTIR techniques becomes comparable. Measured data on the ratios of the two components clearly indicate that for such type of complex decomposition reaction processes, quantitative evolved gas analysis is indispensable and serves as a suitable inter-comparison technique for TG measurements.

4. Conclusion

Organic, amorphous and graphitic carbon contents present in the sample were identified by measuring the carbon dioxide evolution using simultaneous evolved gas analysis with FTIR as a detection technique. Qualitative determination of traces of organic carbon present in the amorphous/graphitic carbon matrix was done by modifying the experimental conditions. Enhancement of the signal due to the oxidation of organic carbon present in the matrix was achieved by taking a large amount of the sample and keeping the reaction temperature below 500 °C to suppress the matrix oxidation signal.

Linearity range, for carbon dioxide determination with FTIR detection, was obtained as 2–30 mg using decomposition of cadmium carbonate. Amorphous/graphitic contents present in the synthetic samples were determined quantitatively using TG/FTIR measurement techniques. Results show that simultaneous FTIR spectroscopy is an effective complementary quantitative measurement technique for thermogravimetric analysis involving the complex decomposition reaction processes.

Acknowledgements

References

[1] K. Kinoshita, Carbon Electrochemical and Physical Properties, John Wiley and Sons, New York, 1988.
[2] R.L. McCreery, Chem. Rev. 108 (2008) 2646–2687.
[3] J.W. Hellgeth, in: J.M. Chalmers, P.R. Griffiths (Eds.), Handbook of Vibrational Spectroscopy, vol. 2, John Wiley and Sons, New York, 2002, p. 1699.
[4] T. Daniels, Thermal Analysis, Kogan Page Ltd., London, 1973.
[5] W.W. Wendlandt, Thermal Analysis, IIIrd ed., John Wiley and Sons, New York, 1985.
[6] J. Chiu, Anal. Chem. 40 (1968) 1516.
[7] F. Zitomer, Anal. Chem. 40 (1968) 1091.
[8] V.K. Manchanda, M.S. Subramanian, Fresen. Z. Anal. Chem. 290 (1978) 302.
[9] M.K. Ahmed, R. Geetha, N.K. Pandey, S. Murugesan, S.B. Koganti, B. Saha, P. Sahoo, M.K. Sundararajan, Talanta 52 (2000) 885.
[10] L.F. Calvo, M. Otero, B.M. Jenkins, A.I. García, A. Morán, Thermochim. Acta 409 (2004) 127.
[11] M.B. Folgueras, R.M. Díaz, J. Xiberta, I. Prieto, Fuel 82 (2003) 2051.
[12] L.F. Calvo, M.E. Sanchez, A. Moran, A.I. Garcia, J. Therm. Anal. Calorim. 78 (2004) 587.
[13] Marta Otero, X. Gomez, A.I. Garcia, A. Moran, J. Therm. Anal. Calorim. 93 (2008) 619–662.
[14] W. Xie, W.P. Pan, J. Therm. Anal. Calorim. 65 (2001) 669–685.
[15] C.L. Putzing, M.A. Leugers, M.L. Mckelvy, G.E. Mitchell, R.A. Nyquist, R.R. Papenfuss, L. Yurga, Anal. Chem. 66 (12) (1994) 51R.
[16] W.M. Groenewoud, W. de Jong, Thermochim. Acta 286 (1996) 341–354.
[17] S. Materazzi, A. Gentili, R. Curini, Talanta 68 (2006) 489–496.
[18] M. Muller-Vonmoos, G. Kahr, A. Rub, Thermochim. Acta 20 (1977) 387.
[19] M. Maciejewski, A. Baiker, Thermochim. Acta 295 (1997) 95–105.
[20] D.A. Skoog, F.J. Holler, T.A. Nieman (Eds.), Principles of Instrumental Analysis, fifth edn., Harcourt College Publishing, USA, 1998, p. 388.
[21] NIST chemistry web book standard reference database No. 69, June 2005 release (http://webbook.nist.gov/chemistry).
[22] K. Marsanich, F. Barontini, V. Cozzani, L. Petarca, Thermochim. Acta 390 (2002) 153–168.
[23] F. Eigenmann, M. Maciejewski, A. Baiker, Thermochim. Acta 440 (2006) 81–92.
[24] M. Maciejewski, C.A. Muller, R. Tschan, W.D. Emmerich, A. Baiker, Thermochim. Acta 295 (1997) 167–182.
[25] Carbon electrodes having stabilized binders derived from the entire organic fraction of bituminous coal, document type: United States Patent and Patent Number: 4,072,599.