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Review

Applications of evolved gas analysis Part 1: EGA by infrared spectroscopy

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Abstract

The analytical applications of the evolved gas analysis (EGA) performed by infrared spectroscopy, for the period extending from 2001 to 2004, are collected in this review. By this technique, the nature of volatile products released by a substance subjected to a controlled temperature program are on-line determined, with the possibility to prove a supposed reaction, either under isothermal or under heating conditions.

Keywords: EGA; IR; Evolved gas analysis; Infrared spectroscopy

Contents

1. Introduction

The IUPAC Compendium of chemical terminology defines the evolved gas analysis (EGA) as "a technique in which the nature and/or amount of volatile product(s) released by a substance subjected to a controlled temperature program is (are) determined".

The possibility to on-line detect the nature of the released gases or vapors is fundamental to prove a supposed reaction, either under isothermal or under heating conditions.

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Among the different possibilities, thermo-analytical instruments, such as pyrolysers, thermobalances, differential thermal analyzers or calorimeters (but sometimes even simply temperature-controlled reactors), are the most commonly used tools to heat a sample under investigation. Thermogravimetry, in addition, is very useful for the quantification of each single gaseous evolution process as the result of an increasing thermal ramp or a defined isothermal temperature. These techniques have been successfully on-line coupled to perform evolved gas analysis. To obtain the IR spectra of the gases evolved during the programmed analysis, the thermo-analytical instrument is coupled with a FTIR spectrometer by means of a heated transfer line; the released vapors or gases are so transferred to the heated gas cell of the FTIR instrument, the temperatures of the cell and of the transfer line being independently selected.

The history of the EGA-FTIR and EGA-MS hyphenated techniques from the first attempts to 2000 has been previously reported [1–4].

In this paper, the applications of the evolved gas analysis performed by infrared spectroscopy for the period extending from 2001 to 2004 are proposed.

Many examples are reported from the literature, and often the references are generally obtained from the journals that specialize in thermal analysis. At least 50% of the applications of the evolved gas analysis are devoted to the polymers and to the inorganic compounds, and the review is consequently organized with two separate sections per year.

However, the number of publications on hyphenated techniques continues to grow in areas of specialized applications; as a consequence, it is not unusual for an article on the topic to appear in an unfamiliar journal or a trade-specific publication. The problem is that unless the terminology relating to the specifics of the hyphenated technique are present in the published keywords, the articles may be difficult to locate. As a result, certain important articles may have been overlooked, and the authors apologize for such inadvertent omissions.

2. 2001 applications

2.1. Polymers and inorganics

The real time evolution kinetics of formaldehyde, hydroxyacetaldehyde, CO and CO_2 during the pyrolysis of cellulose, Whatman 41, were studied in a fast evolved gas-FTIR apparatus (EGA) with a total of 10 compounds simultaneously detected in the gas phase by FTIR [5–7].

The thermal degradation of polyamide 6, polyacrylonitrile and of a polyurethane rigid foam was studied using two different thermal analyzers with coupled techniques for the evolved gas analysis (TA-MS and TA-FTIR) and two combustion devices by Herrera et al. [8].

FTIR evolved gas analysis was used to determine the thermal degradation behavior of epoxy resins blended with propyl ester phosphazene [9].

Mrozek et al. studied the thermal decomposition behavior of the manganese(II) complexes with glycine by FTIR evolved gas analysis [10].

FTIR-MS hyphenated EGA techniques were used to study the polymerization of monomeric reactants polyimides and to compare the results with other PMR-15 [11,12].

The thermal properties of the Europrene *cis* (*cis*-1,4-polybutadiene) were investigated taking into consideration both the method of the sample preparing and the atmosphere in the reaction zone [13].

Gases released during the conversion of $NH_4Zr_2(PO_4)_3$ to $HZr_2(PO_4)_3$ were identified by using TG-FTIR technique by Oi et al. [14], and the influence of electron beam irradiation on a polyurethane used in medical applications was evaluated by Guignot et al. [15].

The thermal degradation of poly(ε-caprolactam) and its copolymers was studied by Draye et al. by means of thermal analysis simultaneously on-line coupled both with Fourier transform infrared spectroscopy and mass spectrometry, in which the EGA gives credit to some blocky-like enchainment of the co-monomers [16].

By TGA-IR, *p*-hydroxymethylbenzyl chloride was proved to be an effective cross-linking agent in the reaction with polystyrene, and the potential applications in flame-retardancy were evaluated [17].

Uyar et al. studied the oxidative degradation of electrochemically synthesized *p*-toluene sulfonic acid doped polypyrrole by IR-EGA [18].

By on-line-coupled thermogravimetry-FTIR and thermal–desorption–pyrolysis–gaschromatography–mass spectrometry, four frothing agents used in the flotation of gold bearing sulfide minerals were characterized, and the possibility to identify any contamination present on unknown plants was shown [19].

Polymer/organically modified layered silicate nanocomposites, filled polymers with ultrafine phase dimensions, were studied by simultaneous TGA-FTIR-MS to obtain informations on the degradation products [20].

Divalent transition metal ions coordination compounds with adrenaline [21] and imidazole-4-acetic acid [22] were studied by coupled TG-FTIR to prove the supposed decomposition mechanism.

2.2. Other applications

Investigations in pharmaceuticals were reported by Giron [23] and the characterization of the retinoic acid at the solid state by TG-FTIR evolved gas analysis and other spectroscopic techniques like X-ray diffraction, UV–vis, infrared diffuse reflectance, was reported by Berbenni et al. [24].

Bassilakis et al. applied the TG-FTIR analysis to predict yields and evolution patterns of selected volatile products as a function of feedstock characteristics and process conditions, in the attempt to get comprehensive biomass-pyrolysis models [25].

The thermal change of anodic alumina at high temperatures (around 950 °C) in a membrane was studied in detail by a simultaneous TG-DTA-FTIR apparatus [26].

To solve the problems related to the thermal changes in mixtures of minerals, the calcinations up to 800–950 °C of Israeli phosphorites were investigated by TG-IR and TG-MS-EGA [27].

The applications of thermal analysis coupled to FTIR, MS and GC–MS in the study of several materials, including organically modified clays, polymers and coal blends, were described by Xie and Pan [28].

The thermal oxidation of covellite was characterized by FTIR evolved gas analysis to determine the mechanisms induced by the temperature and the compounds that copper and sulfur form during the covellite transformations [29].

A study of alkaline earth metal titanates, in particular barium titanate $BaTiO_3$, was reported by Berbenni and coauthors since these compounds are widely used in the ceramics and electronic industries because of their high dielectric constant, ferroelectric properties and electrical resistivity [30].

The use of reduced pressure to expand the capabilities of TGA-FTIR coupled technique was reported by Jackson and Rager [31].

3. 2002 applications

3.1. Polymers and inorganics

Turel, in his 2002 review, cited several papers showing the usefulness of FTIR evolved gas analysis for the studies of the interactions of metal ions with quinolone antibacterial agents [32].

The processing (curing) chemistry involved in the polyamide formation was studied by simultaneous TGA-FTIR-MS techniques [33].

Py-FTIR and py-MS techniques were proposed to perform the evolved gas analysis to determine the decarbonylation of the equatorial amide ligand in cobalt(III) thiocyanate complexes by Amirnasr et al. [34]. Zinc(II) aliphatic carboxylate complex compounds were characterized by IR and MS evolved gas analysis by Andogova et al. [35].

Environmentally compatible polymers, such as poly(ε-caprolactone) and polyurethane were synthesized and characterized by FTIR evolved gas analysis [36,37].

TG-FTIR and TG-MS were applied for an unambiguous thermal characterization of intumescent coating material and were proposed as suitable methods in respect to quality assurance of such material [38]. The flame retardant effect of zinc sulphide in PVC materials was also investigated by both IR and MS evolved gas analysis [39].

The thermal decomposition processes of a model compound containing Mannich bridge and a series of polybenzoxazine model dimmers were investigated by Hemvichian et al. [40].

FTIR evolved gas analysis played an important role in explaining the phenomena of degradation related to the charge of polymer chain structures of F- and non-F-containing ladder polyepoxysilsesquioxanes in a study proposed by Wang et al. [41].

The synthesis and the thermoanalytical characterization (including FTIR-EGA) of uranyl complexes with oxalate by Curini et al. [42] and of unusual adrenaline complexes by Materazzi et al. [43] were reported.

Barontini et al. reported a FTIR-EGA methodology for the identification of azeotropic binary mixtures [44]. The gaseous products from the thermal decomposition of borazane BH_3NH_3 were determined by TG-IR and TG-MS [45].

Imidization of the precursor of a liquid crystalline polyimide was investigated using a thermogravimetric analyzer (TGA) coupled to FTIR (TG-IR), and the experimental evidences revealed that the rate and degree of imidization are functions of curing temperature and time [46].

3.2. Other applications

Giron reviewed the applications of coupled techniques (included EGA-FTIR) in pharmaceutical industry [47].

Hwu et al. described the applications of simultaneous TGA-FTIR-MS in the study of organically modified clays and clay-filled PMMA nanocomposites [48].

Kok proposed an interesting review on the applications of thermal analysis and evolved gas analysis in fossil fuel science [49].

Betaine compounds, complex lipids and transmethylating agents in biological systems, were studied by TG-FTIR to determine the thermochemical behavior under two different degradation conditions [50].

Cyanate ester resins were characterized by TG-FTIR and py-GC–MS techniques by Ramirez et al. [51].

T-jump/FTIR coupled technique allowed to determine the gaseous phase metal isocyanates during the flash pyrolysis of the energetic Group 1 element salts of mono-anionic and di-anionic 5-nitraminotetrazole [52]. Aminotetrazole were also studied by Lesnikovich et al. both by TG-FTIR and TG-GC–MS [53].

Two different pulse calibration techniques were compared and assessed to estimate the total quantities of evolved gaseous substances formed in FTIR-EGA runs [54].

The preparation and the characterization of promising multimetal oxide ceramic materials, such as super conducting cuprates and ferroelectric materials, were reported by Mullens et al. [55].

Since continuous monitoring of the evolution of moisture and carbon dioxide offers an interesting tool to determine reaction kinetics of non-enzymic browning and optimizing roasting processes, isothermal and dynamic heating of small specimens of hazelnuts in a differential scanning calorimeter (linked to a non-dispersive IR gas analyzer) was presented as a possibility to simulate roasting processes on a micro-scale [56].

4. 2003 applications

4.1. Polymers and inorganics

The thermal degradation of poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) was reported by Li et al. by IR-EGA and py-GC–MS-EGA [57].

A self-constructed fast infrared spectroscopic EGA equipment, based on a heatable optical cell adapted to a rapid scan FTIR spectrometer, which allows an on-line monitoring of the gas phase, was used to determine the decomposition pathways of nitrogen-rich substances as new components for energetic applications like gas generators [58].

The FTIR evolved gas analysis allowed to complete the characterization of the dimanganese complex with cyclobutanedicarboxylic acid [59].

Thermogravimetry coupled with IR evolved gas analysis was performed to characterize the thermal and the fire behavior of polypropylene flax compounds containing ammonium polyphosphate and expandable graphite as fire retardants [60].

Polyamide 6 (PA6) and PA6-clay nanocomposites prepared by melt compounding were the focus of a IR-EGA study proposed by Pramoda et al. [61], while a combined TG/IR and py-GC–MS study of poly(propylene carbonate) was reported by Li et al. [62].

1-Allylimidazole coordination compounds [63] and 4(5)-aminoimidazole-5(4)-carboxamide complexes [64] were synthesized and characterized by TG-FTIR evolved gas analysis by Materazzi et al. to prove the supposed decomposition mechanism. An aqueous metal-chelate gel precursor for $(Bi,La)_4Ti_3O_{12}$ was studied by Hardy et al. by means of several hyphenated techniques [65].

Rare earth elements carbonates were characterized by infrared evolved gas analysis in a study reported by Paama et al. [66].

Temperature-programmed desorption and decomposition with the on-line detection of the evolved gases by IR and MS techniques were applied to study the adsorbed pyridine on sulfated zirconium oxides, also promoted by platinum [67].

The formation of lithium ferrites ($LiFe_5O_8$ and $LiFeO_2$) from mechanically activated mixtures of Li_2CO_3–Fe_2O_3 has been studied using evolved gas analysis (TG/FT-IR) by Berbenni et al. [68].

A novel methodology for the screening of vapor–liquid enrichment in binary homogeneous systems is presented by Barontini et al. [69].

4.2. Other applications

The characterization of two biomass fuel (pelletised Miscanthus Giganteus and wood) was performed with measurement of gaseous products by IR-EGA, with a generally good fitting of model parameters to product-evolution data [70].

TG-FTIR was used to measure the organic content in a suite of coals of differing rank and compare these with the values determined by difference according to ASTM D3176-89 [71].

By using TG-FTIR analysis, the gas chemisorbed on graphite that has been milled for up to 1000 h was found to be a mixture of CO_2 and an unidentified gas, supposed oxygen [72].

The understanding of the evolution of volatile species during tobacco pyrolysis was the object of the work proposed by Wojtowicz et al. to improve product design and its evaluation [73].

Several techniques, among them a simultaneous TG-DTA-FTIR-MS, were applied to study the characteristics of the black powder [74].

The thermal treatment of torasemide form A, for pharmaceutical applications, resulted in several effects, all examined by FTIR and MS evolved gas analysis [75].

Chemometrics revealed a useful tool for the analysis of evolved gas during the thermal treatment of sewage sludge using coupled TG-FTIR [76].

The thermal decomposition gases of natural hydrotalcites carrboydite and hydrohonessite were determined by both IR and MS evolved gas analysis [77].

The thermal behavior in air of two Al nanopowders was determined using a simultaneous TG-DTA-FTIR-MS apparatus, to be compared to other Al nanopowders for which hazards results have been reported [78].

5. 2004 applications

5.1. Polymers and inorganics

In a study of different types of proton-conducting polymer blend membranes, when the principal membrane component is sulfonated polyaryletherketone, the TGA-FTIR coupled technique showed that the decomposition of the membranes splits off SO_2 at lower temperatures than in the pure substance [79].

The degradation of various poly(ε-caprolactone-block-1,4-dioxan-2-one) block polymers was investigated by TGA simultaneously coupled to a FTIR spectrometer and a mass spectrometer for evolved gas analysis [80].

The flame retardant mechanisms of red phosphorus, magnesium hydroxide and red phosphorus combined with magnesium hydroxide were studied in high impact polystyrene by means of Fourier transform infrared spectroscopy and mass spectroscopy evolved gas analysis [81].

The thermal degradation of various polymer nanocomposites was studied by TG-FTIR hyphenated technique and showed that evolved gases do not depend upon the type of nanocomposite and are qualitatively similar to those of the virgin polymer [82].

The effect of a curing agent on the thermal degradation of fire retardant brominated epoxy resins was reported by Balabanovich et al. [83].

Thermal degradation studies of alkyl-imidazolium salts and their application in nanocomposites were collected by Awad et al. [84].

Materazzi et al., by FTIR evolved gas analysis, proved the supposed decomposition mechanism of new solid-state 4(5)-aminoimidazole-5(4)-carboxamide complexes [85] and 4(5)-hydroxymethyl-5(4)-methylimidazole coordination compounds [86].

EGA by both FTIR and MS was the tool to study some flame-resistant modified segmented polyurethanes with 3-chloro-1,2-propanediol in the main chain [87].

Thermogravimetric analysis coupled to Fourier transform IR spectroscopy, TGA-FTIR, has been used real time to probe the degradation steps of polyamide 6 in highly pure N2 with constant rate-controlled heating [88].

A comparative study on thermal behavior of aminophylline and three theophylline compounds containing ethylenediamine analogs, has been carried out by using simultaneous TG-DTA and FTIR evolved gas analysis [89].

Identification and monitoring of gaseous species released during the thermal decomposition of Sn and Zn complexes with thiourea in flowing air atmosphere have been carried out up to 600 °C by both online coupled TG-EGA-FTIR and simultaneous TG-DTA-EGA-MS apparatuses [90–92].

Thermal studies of the interactions of solid Triprolidine hydrochloride, a well-known antihistamine drug which is reported as being photosensitive, with β-cyclodextrin indicated that interaction between the components occurs and it is possible that the TPH molecule may be least partially accommodated in the cavity of the BCD host molecule [93].

Tian et al. Demonstrated that the thermal decomposition atmosphere has evident effect on decomposition products of hydrated La(III), Pr(III) and Nd(III) methanesulfonates, and no effect on that of hydrated Ce(III), Yb(III) and Zn(II) methanesulfonates [94].

The combined TG-FTIR technique was employed to study the decomposition pathway of the cefadroxil complexes with transition divalent metals [95] and of manganese(II) complexes with α-amino acids [96].

In the EGA-FTIR spectrum of released gaseous species measured at the highest evolution rate by TG-FTIR, *trans*-1,4,5,8-tetraazodecalin, an aromatic 1,4-diazine and ethylenediamine can be identified as decomposition products of crystals of unknown origin, crystallizing spontaneously from ethylenediamine on standing [97].

A series of blends of polyoxymethylene (POM)/thermoplastic polyesterurethane (TPU) were investigated and it was found that incorporation of TPU into POM matrix resulted in increase of thermal stability of blends in comparison with pristine materials [98].

The surface composition of IrO_2 and SnO_2 thin films was monitored as a function of the firing temperature by a modified FTIR (emission cell) with a platinum sheet acting as a hot plate to heat up the sample on top [99].

5.2. Other applications

Giron and coworkers summarized in their review the different steps needed for a proper design and monitoring of the solid-state in pharmaceutical industry in order to fulfill the requirements of the guideline dealing with polymorphism of the International Conference of Harmonization [100].

The suitability of TGA-IR method for the analysis of the degree of substitution of acetylated starch was assessed in a paper by Elomaa et al. [101].

A computer program was developed to solve for the yield and rate of evolution of individual pyrolysis products which may be obtained from TG-FTIR or TG-MS analysis of the sample [102].

Due to the fact that coking can be adversely affected by weathering, MacPhee et al. reported a study regarding the detection of natural oxidation of coking coal by FTIR-EGA-mechanistic implications [103].

Computer-aided thermal analysis technique, incorporated with thermogravimetric and FTIR, was employed in studying the devolatilization of three thermal bituminous coals under packed bed pyrolysing conditions [104].

Evolved gas analysis by both FTIR and MS was applied for the characterization of model compounds and a synthetic coal to represent the pyrolysis behavior of coal by Arenillas et al. [105].

The degradation process of the chlorinated natural rubber from latex, used in the production of the raw materials for paints and adhesives because of its properties, was characterized by thermoanalytical techniques also coupled for the evolved gas analysis [106].

The pyrolysis of tobacco ingredients was performed to establish relationships between tobacco components and smoke products that are often difficult to unravel [107].

Besides that of the previously known H_2O and NH_3, evolution of two new gaseous products, N_2O and NO, which had not been reported earlier, has been detected and traced by both evolved gas analysis (EGA-FTIR and EGA-MS) methods in a study regarding ammonium paratungstate tetrahydrate, a starting material of WO_3 and tungsten production [108].

TG-FTIR of gaseous products from the decomposition of high energy materials suggested the evolution of NH_2CN/NH_3 and HCN as major decomposition products [109].

Three bio-fuels with or without additives and their fly ash samples were characterized using simultaneous TG-DTA-FTIR-MS; the results showed that the additives increase the reactivity of the bio-fuel during combustion [110].

The combined thermogravimetric (TG) Fourier transform infrared (FTIR) techniques were used for studying the gaseous compounds evolved at thermooxidation of oil shale samples from different deposits (Estonia, Jordan, Israel) [111] and to investigate the thermal degradation behavior of materials containing brominated flame retardants under fire conditions [112].

Evolved gas analysis (IR- and MS-EGA) of volatiles was used to characterize the thermal behavior of commercial PVC cable insulation material during heating in the range 20–800 °C in air and nitrogen [113].

An infrared furnace and an arrangement of internals for heating of a packed bed of sample were the tools to realize an apparatus to determine the gases from a coal powder [114].

The burning rate data obtained by couplet TG-FTIR analysis indicated that triamino guanidinium azotetrazolate acts as an efficient energetic additive in composite modified double base (CMDB) propellant formulations in high-pressure region [115].

By FTIR evolved gas analysis, Jang and Wilkie showed that the main thermal degradation pathways of bisphenol A polycarbonate follow chain scission of the isopropylidene linkage, and hydrolysis/alcoholysis and rearrangement of carbonate linkages [116].

Evolution of gaseous products from ammonium paratungstate tetrahydrate, a starting material in powder metallurgy of tungsten, has been the subject of a complex thermoanalytical study reported by Szilágyi et al. [117].

The coupled TG-FTIR analysis of the evolved gases has revealed that in the lattice compound 1,4-diammoniumbutane bis(theophyllinate) the diamine is released as a whole molecule in the first decomposition step [118].

A combination of high resolution thermogravimetric analysis coupled to a gas evolution mass spectrometer combined with infrared emission spectroscopy has been used to study the thermal decomposition of synthetic hydrotalcites honessite ($Ni_6Fe_2(SO_4)(OH)_{16}{\cdot}4H_2O$) and mountkeithite ($Mg_6Fe_2(SO_4)(OH)_{16}{\cdot}4H_2O$) and the cationic mixtures of the two minerals [119].

In the review collecting the selected applications of thermal analysis, published on Analytical Chemistry, Vyazovkin reported several examples of evolved gas analysis performed by coupling thermoanalytical instruments and FTIR spectroscopy [120].

An interesting application of the FTIR evolved gas analysis was shown by Lunghi et al. [121]: a thermobalance or a flash pyrolyzer are employed to simulate accident conditions in process industries, with the analysis of more than 40 materials.

References

[1] S. Materazzi, Appl. Spectrosc. Rev. 32 (4) (1997) 385–396.
[2] S. Materazzi, Appl. Spectrosc. Rev. 33 (3) (1998) 189–197.
[3] S. Materazzi, R. Curini, Appl. Spectrosc. Rev. 36 (1) (2001) 1–9.
[4] S. Materazzi, R. Curini, Appl. Spectrosc. Rev. 36 (2–3) (2001) 169–180.
[5] S. Li, J. Lyons-Hart, J.L. Banyasz, K.H. Shafer, Fuel 80 (2001) 1757–1763.
[6] J.L. Banyasz, S. Li, J. Lyons-Hart, K.H. Shafer, Fuel 80 (2001) 1809–1817.
[7] J.L. Banyasz, S. Li, J. Lyons-Hart, K.H. Shafer, J. Anal. Appl. Pyrol. 57 (2001) 223–248.
[8] M. Herrera, M. Wilhelm, G. Matuschek, A. Kettrup, J. Anal. Appl. Pyrol. 58–59 (2001) 173–188.
[9] B.L. Denq, W.Y. Chiu, K.F. Lin, M.R.S. Fuh, J. Appl. Polym. Sci. 81 (2001) 1161–1174.
[10] R. Mrozek, Z. Rzaczynska, M. Sikorska-Iwan, J. Therm. Anal. Calorim. 63 (2001) 839–846.
[11] W. Xie, W.P. Pan, K.C. Chuang, J. Therm. Anal. Calorim. 64 (2001) 477–485.
[12] W. Xie, W.P. Pan, K.C. Chuang, Thermochim. Acta 367–368 (2001) 143–153.
[13] G. Janowska, L. Slusarski, J. Therm. Anal. Calorim. 65 (2001) 205–212.
[14] T. Oi, K. Horio, R. Kikuchi, H. Takahashi, J. Therm. Anal. Calorim. 65 (2001) 305–308.
[15] C. Guignot, N. Betz, B. Legendre, A. Le Moel, N. Yagoubi, Nucl. Inst. Meth. Phys. Res. B 185 (2001) 100–107.
[16] A.C. Draye, O. Persenaire, J. Brozek, J. Roda, T. Kosek, Ph. Dubois, Polymer 42 (2001) 8325–8332.
[17] H. Yao, M.A. McKinney, C. Dick, J.J. Liggat, C.E. Snape, C.A. Wilkie, Polym. Degrad. Stab. 72 (2001) 399–405.
[18] T. Uyar, L. Toppare, J. Hacaloglu, Synth. Metals 123 (2001) 335–342.
[19] J.G. Dunn, N.G. Fisher, Thermochim. Acta 366 (2001) 157–166.
[20] W. Xie, Z. Gao, K. Liu, W.P. Pan, R. Vaia, D. Hunter, A. Singh, Thermochim. Acta 367–368 (2001) 339–350.
[21] S. Materazzi, C. Nugnes, A. Gentili, R. Curini, Thermochim. Acta 369 (2001) 167–173.
[22] S. Materazzi, E. Vasca, Thermochim. Acta 373 (2001) 7–11.
[23] D. Giron, J. Therm. Anal. Calorim. 64 (2001) 37–60.
[24] V. Berbenni, A. Marini, G. Bruni, A. Cardini, Int. J. Pharmac. 221 (2001) 123–141.
[25] R. Bassilakis, R.M. Carangelo, M.A. Wojtowicz, Fuel 80 (2001) 1765–1786.
[26] R. Ozao, H. Yoshida, Y. Ichimura, T. Inada, M. Ochiai, J. Therm. Anal. Calorim. 64 (2001) 915–922.
[27] K. Tonsuaadu, M. Koel, M. Veiderma, J. Therm. Anal. Calorim. 64 (2001) 1247–1255.
[28] W. Xie, W.P. Pan, J. Therm. Anal. Calorim. 65 (2001) 669–685.
[29] J.G. Dunn, C. Muzenda, Thermochim. Acta 369 (2001) 117–123.
[30] V. Berbenni, A. Marini, G. Bruni, Thermochim. Acta 374 (2001) 151–158.
[31] R.S. Jackson, A. Rager, Thermochim. Acta 367–368 (2001) 415–424.
[32] I. Turel, Coord. Chem. Rev. 232 (2002) 27–47.
[33] W. Xie, R. Heltsley, H.X. Li, C. Lee, W.P. Pan, J. Appl. Polym. Sci. 83 (2002) 2213–2224.
[34] M. Amirnasr, R. Houriet, S. Meghdadi, J. Therm. Anal. Calorim. 67 (2002) 523–533.
[35] E. Andogova, K. Gyoryova, F.A. Nour El-Dien, J. Therm. Anal. Calorim. 69 (2002) 245–253.
[36] H. Hatakeyama, J. Therm. Anal. Calorim. 70 (2002) 755–795.
[37] S. Hirose, T. Hatakeyama, Y. Izuta, H. Hatakeyama, J. Therm. Anal. Calorim. 70 (2002) 853–860.
[38] R. Kunze, B. Schartel, M. Bartholmai, D. Neubert, R. Schriever, J. Therm. Anal. Calorim. 70 (2002) 897–909.
[39] B. Schartel, R. Kunze, D. Neubert, A. Tidjani, Polym. Int. 51 (2002) 213–222.
[40] K. Hemvichian, A. Laobuthee, S. Chirachanchai, H. Ishida, Polym. Degrad. Stab. 76 (2002) 1–15.
[41] J. Wang, C. He, Y. Lin, T.S. Chung, Thermochim. Acta 381 (2002) 83–92.
[42] R. Curini, U. Tentolini, S. Materazzi, E. Vasca, T. Caruso, C. Fontanella, G. Palladino, Thermochim. Acta 387 (2002) 17–21.
[43] S. Materazzi, E. Vasca, U. Tentolini, S. Aquili, R. Curini, Thermochim. Acta 389 (2002) 179–184.
[44] F. Barontini, E. Brunazzi, V. Cozzani, Thermochim. Acta 389 (2002) 95–108.

[45] F. Baitalow, J. Baumann, G. Wolf, K. Jaenicke-RoBler, G. Leitner, Thermochim. Acta 391 (2002) 159–168.
[46] K.P. Pramoda, S. Liu, T.S. Chung, Macromol. Mater. Eng. 287 (2002) 931–937.
[47] D. Giron, J. Therm. Anal. Calorim. 68 (2002) 335–357.
[48] J.M. Hwu, G.J. Jiang, Z.M. Gao, W. Xie, W.P. Pan, J. Appl. Polym. Sci. 83 (2002) 1702–1710.
[49] M.V. Kok, J. Therm. Anal. Calorim. 68 (2002) 1061–1077.
[50] J. Suuronen, I. Pitkanen, H. Halttunen, R. Moilanen, J. Therm. Anal. Calorim. 69 (2002) 359–369.
[51] M.L. Ramirez, R. Walters, R.E. Lyon, E.P. Savitski, Polym. Degrad. Stab. 78 (2002) 73–82.
[52] B.C. Tappan, R.W. Beal, T.B. Brill, Thermochim. Acta 388 (2002) 227–232.
[53] A.I. Lesnikovich, O.A. Ivashkevich, S.V. Levchik, A.I. Balabanovich, P.N. Gaponik, A.A. Kulak, Thermochim. Acta 388 (2002) 233–251.
[54] K. Marsanich, F. Barontini, V. Cozzani, L. Petarca, Thermochim. Acta 390 (2002) 153–168.
[55] J. Mullens, K. Van Werde, G. Vanhoyland, R. Nouwen, M.K. Van Bael, L.C. Van Poucke, Thermochim. Acta 392–393 (2002) 29–35.
[56] R. Perren, R. Kunzli, F. Escher, Chimia 56 (2002) 265–269.
[57] S.D. Li, J.D. He, P.H. Yu, M.K. Cheung, J. Appl. Polym. Sci. 89 (2003) 1530–1536.
[58] S. Loebbecke, H. Schuppler, W. Schweikert, J. Therm. Anal. Calorim. 72 (2003) 453–463.
[59] Z. Rzaczynska, A. Bartyzel, T. Glowiak, Polyhedron 22 (2003) 2595–2599.
[60] B. Schartel, U. Braun, U. Schwarz, S. Reinemann, Polymer 44 (2003) 6241–6250.
[61] K.P. Pramoda, T. Liu, Z. Liu, C. He, H.J. Sue, Polym. Degrad. Stab. 81 (2003) 47–56.
[62] X.H. Li, Y.Z. Meng, Q. Zhu, S.C. Tjong, Polym. Degrad. Stab. 81 (2003) 157–165.
[63] S. Materazzi, K. Kurdziel, U. Tentolini, A. Bacaloni, S. Aquili, Thermochim. Acta 395 (2003) 133–137.
[64] S. Materazzi, G. D'Ascenzo, S. Aquili, K.M. Kadish, J.L. Bear, Thermochim. Acta 397 (2003) 129–134.
[65] A. Hardy, K. Van Werde, G. Vanhoyland, M.K. Vaan Bael, J. Mullens, L.C. Van Pouche, Thermochim. Acta 397 (2003) 143–153.
[66] L. Paama, I. Pitkanen, H. Halttunen, P. Peramaki, Thermochim. Acta 403 (2003) 197–206.
[67] R.W. Stevens, S.S.C. Chuang, B.H. Davis, Thermochim. Acta 407 (2003) 61–71.
[68] V. Berbenni, A. Marini, P. Matteazzi, R. Ricceri, N.J. Welham, J. Eur. Ceram. Soc. 23 (3) (2003) 527–536.
[69] F. Barontini, E. Brunazzi, V. Cozzani, Thermochim. Acta 408 (1–2) (2003) 17–29.
[70] W. de Jong, A. Pirone, M.A. Wojtowicz, Fuel 82 (2003) 1139–1147.
[71] J.P. Charland, J.A. MacPhee, L. Giroux, J.T. Price, M.A. Khan, Fuel Process. Technol. 81 (2003) 211–221.
[72] N.J. Welham, V. Berbenni, P.G. Chapman, J. Alloys Compd. 349 (2003) 255–263.
[73] M.A. Wojtowicz, R. Bassilakis, W.W. Smith, Y. Chen, R.M. Carangelo, J. Anal. Appl. Pyrol. 66 (2003) 235–261.
[74] R. Turcotte, R.C. Fouchard, A.M. Turcotte, D.E.G. Jones, J. Therm. Anal. Calorim. 73 (2003) 105–118.
[75] J.M. Rollinger, Cs. Novak, Zs. Ehen, K. Marthi, J. Therm. Anal. Calorim. 73 (2003) 519–526.
[76] J.H. Ferrasse, S. Chavez, P. Arlabosse, N. Dupuy, Thermochim. Acta 404 (2003) 97–108.
[77] R. Frost, M.L. Weier, M.E. Clissold, P.A. Williams, J.T. Kloprogge, Thermochim. Acta 407 (2003) 1–9.
[78] D.E.G. Jones, R. Turcotte, R.C. Fouchard, Q.S.M. Kwock, A. Turcotte, Z. Abdel-Qader, Propellants Explos. Pyrotech. 28 (2003) 120–131.
[79] J. Kerres, A. Ullrich, M. Hein, V. Gogel, K.A. Friedrich, L. Jorissen, Fuel Cells 4 (1–2) (2004) 105–112.
[80] J.M. Raquez, P. Degee, R. Narayan, P. Dubois, Macromol. Chem. Phys. 205 (2004) 1764–1773.
[81] U. Braun, B. Schartel, Macromol. Chem. Phys. 205 (2004) 2185–2196.
[82] S. Su, C.A. Wilkie, Polym. Degrad. Stab. 83 (2004) 347–362.
[83] A.I. Balabanovich, A. Hornung, D. Merz, H. Seifert, Polym. Degrad. Stab. 85 (2004) 713–723.
[84] W.H. Awad, J.W. Gilman, M. Nyden, R.H. Harris, T.E. Sutto, J. Callahan, P.C. Trulove, H.C. DeLong, D.M. Fox, Thermochim. Acta 409 (2004) 3–11.
[85] S. Materazzi, S. Aquili, C. Bianchetti, G. D'Ascenzo, K.M. Kadish, J.L. Bear, Thermochim. Acta 409 (2004) 145–150.
[86] S. Materazzi, S. Aquili, S. De Angelis Curtis, S. Vecchio, K. Kurdziel, F. Sagone, Thermochim. Acta 421 (2004) 19–24.
[87] K. Pielichowski, D. Slotwinska, Thermochim. Acta 410 (2004) 79–86.
[88] N. Huang, J. Wang, Beijing Ligong Daxue Xuebao 24 (2004) 182–188.
[89] M. Ban, J. Madarasz, G. Pokol, S. Gal, Solid State Ionics 172 (2004) 587–589.
[90] J. Madarász, P. Bombicz, M. Okuya, S. Kaneko, G. Pokol, J. Anal. Appl. Pyrol. 72 (2004) 209–214.
[91] J. Madarasz, M. Krunks, L. Niinisto, G. Pokol, J. Therm. Anal. Calorim. 78 (2004) 679–686.
[92] J. Madarász, P. Bombicz, M. Okuya, S. Kaneko, G. Pokol, Solid State Ionics 172 (2004) 577–581.
[93] V.J. Ndlebe, M.E. Brown, B.D. Glass, J. Therm. Anal. Calorim. 77 (2004) 445–457.
[94] J. Tian, H. Jiang, H. Gong, Z. Sun, J. Therm. Anal. Calorim. 77 (2004) 825–831.
[95] R. Mrozek-Łyszczek, J. Therm. Anal. Calorim. 78 (2004) 473–486.
[96] M. Sikorska-Iwan, R. Mrozek-Łyszczek, J. Therm. Anal. Calorim. 78 (2004) 487–500.
[97] M. Bán, J. Madarász, P. Bombicz, G. Pokol, S. Gál, J. Therm. Anal. Calorim. 78 (2004) 545–555.
[98] K. Pielikowski, A. Leszczynska, J. Therm. Anal. Calorim. 78 (2004) 631–637.
[99] E. Horvath, J. Kristof, R.L. Frost, N. Heider, V. Vagvolgyi, J. Therm. Anal. Calorim. 78 (2004) 687–695.
[100] D. Giron, M. Mutz, S. Garnier, J. Therm. Anal. Calorim. 77 (2004) 709–747.
[101] M. Elomaa, T. Asplund, P. Soininen, R. Laatikainen, S. Peltonen, S. Hyvarinen, A. Urtti, Carbohydr. Polym. 57 (2004) 261–267.
[102] A.A. Rostami, M.R. Hajaligol, S.E. Wrenn, Fuel 83 (2004) 1519–1525.
[103] J.A. MacPhee, L. Giroux, J.P. Charland, J.F. Grandsen, J.T. Price, Fuel 83 (2004) 1855–1860.
[104] V. Strezov, J.A. Lucas, L. Strezov, J. Anal. Appl. Pyrol. 71 (2004) 375–392.
[105] A. Arenillas, C. Pevida, F. Rubiera, R. Garcia, J.J. Pis, J. Anal. Appl. Pyrol. 71 (2004) 747–763.
[106] H. Yu, S. Li, J. Zhong, K. Xu, Thermochim. Acta 410 (2004) 119–124.
[107] R.R. Baker, L.J. Bishop, J. Anal. Appl. Pyrol. 71 (2004) 223–311.
[108] J. Madarász, I.M. Szilágyi, F. Hange, G. Pokol, J. Anal. Appl. Pyrol. 72 (2004) 197–201.
[109] M.B. Talawar, R. Sivabalan, N. Senthilkumar, G. Prabhu, S.N. Asthana, J. Hazard. Mater. 113 (2004) 11–25.
[110] Q.S.M. Kwok, D.E.G. Jones, G.F. Nunez, J.P. Charland, S. Dionne, J. Therm. Anal. Calorim. 78 (2004) 173–184.
[111] T. Kaljuvee, J. Pelt, M. Radin, J. Therm. Anal. Calorim. 78 (2004) 399–414.
[112] F. Barontini, K. Marsanich, V. Cozzani, J. Therm. Anal. Calorim. 78 (2004) 599–619.

[113] M. Beneš, N. Milanov, G. Matuschek, A. Kettrup, V. Plaček, V. Balek, J. Therm. Anal. Calorim. 78 (2004) 599–619.
[114] V. Strezov, J.A. Lucas, T.J. Evans, L. Strezov, J. Therm. Anal. Calorim. 78 (2004) 385–397.
[115] R. Sivabalan, M.B. Talawar, N. Senthilkumar, B. Kavitha, S.N. Asthana, J. Therm. Anal. Calorim. 78 (2004) 781–792.
[116] B.N. Jang, C.A. Wilkie, Polym. Degrad. Stab. 86 (2004) 419–430.
[117] I.M. Szilágyi, J. Madarász, F. Hange, G. Pokol, Solid State Ionics 172 (2004) 583–586.
[118] M. Bán, J. Madarász, P. Bombicz, G. Pokol, S. Gál, Thermochim. Acta 420 (2004) 105–109.
[119] R.L. Frost, K.L. Erickson, Thermochim. Acta 421 (2004) 51–58.
[120] S. Vyazovkin, Anal. Chem. 76 (2004) 3299–3312.
[121] A. Lunghi, L. Gigante, P. Cardillo, V. Stefanoni, G. Pulga, R. Rota, J. Hazard. Mater. A116 (2004) 11–21.