Available online at www.sciencedirect.com
SCIENCE DIRECT®
Talanta 68 (2006) 489–496
Talanta
www.elsevier.com/locate/talanta

Review

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

S. Materazzi*, A. Gentili, R. Curini

Department of Chemistry, University of Rome "La Sapienza", p.le A. Moro 5-00185, Rome, Italy

Received 17 January 2005; received in revised form 20 March 2005; accepted 27 April 2005
Available online 25 May 2005

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.

* Corresponding author. Tel.: +39 0649913616; fax: +39 06490631.
E-mail address: stefano.materazzi@uniroma1.it (S. Materazzi).

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.04.055

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].