Available on line www.jocpr.com

Journal of Chemical and Pharmaceutical Research

ISSN No: 0975-7384
CODEN(USA): JCPRC5

J. Chem. Pharm. Res., 2011, 3(1):590-596

Current analytical scope of Pyrolysis-Gas chromatography

Patel Vishal and Agrawal Y K*

Institute of Research & Development, Gujarat Forensic Sciences University, Gandhinagar, Gujarat, India

ABSTRACT

Pyrolysis is the technique for the breakdown of high mol wt substances into smaller components, so that they can be separated and analysed by chromatographic techniques like Gas chromatography. This technique offers various advantages like less sample requirement, easy preparation and moreover easier reproducibility. Though the initial cost is high, its use is not limited and follows varied applications which have been compiled in the paper.

Key words: Forensic, polymers, pyrolysis, PyGC, pyrolyzer.

INTRODUCTION

Pyrolysis a technique that is used in the analysis of biological and synthetic polymers.In pyrolysis, sample is heated up (mainly in vacuum or an inert atmosphere) to decompose into smaller units which are carried by a gas such as helium to the next instrument for characterization. Pyrolyzer is usually linked to a GC which can further be connected to detectors such as MS or FTIR [1]. Pyrolysis is ideally suited for one stage combination with gas chromatography. In pyrolysis-gas chromatography (PyGC) the fragments generated by pyrolysis are passed through the GC for separation and identification. Different pyrolysis devices can be directly connected to the gas chromatographic inlet system. Suitable gas chromatographic system can resolve a pyrolysate mixture into a highly specific pattern of peaks usually called a pyrogram. For identification purposes Davison, Slaney and Wragg applied gas chromatography to analyse pyrolysate. Their work had significant importance in the development of PyGC since it emphasized that the pattern of peaks in a pyrogram provided a characteristic fingerprint which could be used for identification of the original substance [2].

The applications basically focus on structure determination, qualitative and quantitative analysis of low level additives in polymers and kinetics of thermal degradation. PyGC is also useful in Forensic areas like document analysis, classification and differentiation of photocopy toners and the analysis of inks. Analysis of biological macromolecules like proteins, polysaccharides and lipids in Food, petrochemical source and environment is done through PyGC. Paint, adhesives, tapes, caulking, food packaging, rubber, plastic bottles, paper, ink, coatings and a full range of household and consumer products even are successfully analyzed using PyGC.

Application
2.1 Polymer analysis
2.1.1 Structure determination

Structure determination of the polymers by PyGC follows firstly structure determination for copolymers through trimmers with the next step being structure determination for homopolymers through tetramers or high oligomers. The copolymer structure or the monomer arrangement in the polymer chain can be determined by the triad intensities that have been studied previously, especially using a ^{13}C-nuclear magnetic resonance (NMR) technique. This concept has been adopted in PyGC study of the copolymer structures. The number average sequence length of a monomer 'A' in an A–B copolymer chain can be defined as n_A, where n_A equals the total number of 'A' monomers in the polymer chain divided by the total number of blocks of monomer 'A'. The formula can be expressed as:

$$n_A = \text{Total number of 'A'} \,/\, \text{Total blocks of 'A'} \qquad .....(1)$$

This definition and the formula associated with it have been used for polymer chain characterization for a long time [3]. The total number of 'A' monomers can be expressed with the triad terms as AAA+ (AAB+BAA) + BAB. The total number of blocks can be expressed with a triad term as (1 / 2) (AAB+BAA) +BAB. If the total number of monomers 'A' and the total number of blocks of 'A' can be expressed as these triad terms, the number-average sequence formula can be obtained based on the triad terms as follows

$$n_A = (n_{AAA} + n_{AAB+BAA} + n_{BAB}) / (1/2\, n_{AAB+BAA} + n_{BAB})$$

$$n_B = (n_{BBB} + n_{ABB+BBA} + n_{ABA}) / (1/2\, n_{ABB+BBA} + n_{ABA})$$

Based on the definition of the number average sequence length, it is easy to derive the next two formulas for the composition. The mole percentage can be calculated from the number average sequence length because, in a copolymer chain, the total number of block 'A' is either equal to total number of block of 'B' or different by one. Thus, the total number of blocks (either 'A' or 'B') will be cancelled in both numerator and denominator, the mole percent of 'A' will be equal to the total number of 'A' divided by the total number of monomers in the copolymer which is exactly the definition of mole percent. The composition formula in terms of the number-average sequence length can be expressed as follows:

$$\text{Mol \% of A} = n_A / (n_A + n_B)$$
$$\text{Mol \% of B} = n_B / (n_A + n_B)$$

The study of the styrene and butyl acrylate copolymer system has demonstrated that the statistical distribution of triad can be correlated to the trimers obtained from PyGC. If all eight trimers can be well resolved in the pyrogram along with their peak area, the number average sequence length as well as composition can be calculated from these trimer peak intensities [4]. The trimers produced from pyrolysis of polymers do not always exist as a component with three monomer units bonded together. Sometimes, the trimer may go through a decomposition to lose certain easy to lose fragments to form more stable compounds. An example is the vinyl chloride and vinylidene chloride copolymer system [5].

In the structure determination method, the first example is the stereo regularity study of polystyrenes (PSs). PyGC MS was able to detect and identify diastereoisomers such as tetramers and pentamers. The minimum requirement for a diastereoisomer is the inclusion of more than two asymmetric carbons in the molecule. This means that tetramers are the smallest possible candidates. In order to allow quantitative interpretation of data, the PyGC method was calibrated by a set of standards with known tacticity [6].The second example is the determination of the tacticity of various stereo regular poly(methyl methacrylate) (PMMA) which was done by separating the associated diastereometric tetramers. In this study, stereoisomer with slightly shorter retention times was also detected. Using the combination of two diastereoisomers, in addition to other stereo isomers, the ratio of different tacticity can be calculated. [7].

2.1.2 Qualitative and quantitative analysis

Recent development emphasises on the enhanced detection of chemical species in the polymers present in very low amount. The low amount of co monomer or other additives which were difficult to separate from the polymers may be identified by direct pyrolysis. In order to effectively detect those chemical species, other techniques along with pyrolysis can have added advantages. Pyrolysis with a trapping scheme has been developed in order to determine low level acrylic acid and methacrylic acid in emulsion polymer. The advantages of the trapping setup involve the flexibility of trapping solvent selection, sample accumulation and the option to choose the separation technique after the trapping. Low levels of acrylic acid and methacrylic acid were qualitatively detected in an emulsion polymer by this method [8].A similar technique has been applied to determine the acryl amide monomer in the emulsion polymer. The trapped pyrolysate mixture was separated and identified by GCMS. Because many other low level fragments elute at the same time, a single ion monitoring technique must be used to clearly catch the peak. It has been demonstrated in this study that the trapping technique is effective to detect low levels monomers of the acryl amide and methacrylamide in emulsion polymers [9].There is a study of composition analysis of multicomponent acrylic resins by PyGC. In this study, PyGC was used to analyze the composition of ethyl acrylate butyl methacrylate copolymers and ethyl acrylate styrene ethyl methacrylate terpolymers. The characteristic peaks of the pyrolysis products, up to the pentamers, were almost completely separated on the program [10].The quantification of end groups in anionically polymerized PMMA by PyGC has been studied and molecular mass distribution was determined. The characteristic fragments reflecting the end groups on the pyrogram of the PMMA were identified by comparison with those of a radically polymerized PMMA together with the mass spectra of the characteristic peaks on the resulting programs [11].

2.1.3 Kinetics of Thermal Degradation

Different types of polymers are continuously being pyrolyzed to investigate their thermal behaviour and degradation mechanism under different temperature conditions. In thermoplastic polymers, sulphur containing polymers such as poly(*p*-phenylene ether-sulfone) (PES) resin and a polysulfone resin (PSR) were studied by PyGC with Flame Ionisation Detector, Flame Photometric Detector and Mass Selective Detector. This study was done to evaluate the kinetics of Sulphur dioxide (SO_2) formation from PES and PSR by sequential pyrolysis [12].In thermo set polymers, PyGC was applied to study the thermal behaviour of some epoxy acrylic polymers based on phenol and para alkyl substituted phenols in the temperature range of 80–600^{0}C [13].A Curie-point PyGC has been applied to analyze the volume effects of stereo isomers of 2,4-diphenylpentane (a styrene dimer) and other styrene oligomers [14]. PyGC has been used in kinetic measurements of PSs and PMMA to deduce their thermal degradation mechanisms [15]. A thermocouple feedback-controlled resistive filament Pyrolyzer was used to study the kinetics and rates of degradation. PyGC MS analysis of glass fiber/vinyl ester has been reported [16].

2.2 Forensic Analysis

In forensic analysis, PyGC is often used by forensic chemists for document analysis, classification and differentiation of photocopy toners and inks analysis. Zimmerman and co workers analysed 35 different photocopy toners and respective machine copied documents in an attempt to establish a library of spectra from which an unknown toner extracted from a questioned document may be matched [17]. More recently multivariate statistics is used for the forensic discrimination of photocopy and printer toners [18]. Study of various proportions of solvents in different inks used in inkjet printings was also done by this technique [19]. Besides ink and photocopy toners, PyGC was employed for the forensic analysis of packaging tapes and the adhesives which was described by Li and co workers. They incorporated simultaneous methylation to measure the polar compounds [20]. Sakayanagi and co workers used PyGC/MS to identify 20 different products of colourless, transparent, pressure sensitive adhesive polypropylene tapes make this technique highly suitable for real forensic sample analysis [21]. Drugs like methamphetamine and its analogues were also investigated by Takayasu and Ohshima using PyGC/MS method for rapid analysis [22]. Forensic detection and analysis of condom and personal lubricants in sexual assault cases were also been proposed. Additional applications of PyGC in the field of forensic medicine and toxicology include the post-mortem alcohol analysis of the synovial fluid and its availability as a biological specimen for the prediction of blood and urine alcohol concentration in medico legal cases [23], and the rapid analysis of pesticide components in blood and urine [24].

2.3 Identification and differentiation of biological materials

Analysts have continued efforts to differentiate and identify biological materials like microorganisms. Goodacre and co workers detected a simple biomarker for the rapid detection of Bacillus spores using Curie point PyGC/MS technique [25]. A miniaturized PyGC system has also been proposed for the rapid detection and identification of bacteria and other pathogens. An interesting application described by Buckley and co workers involves use of PyGC/MS to analyse the complex organic balms on tissues and wrappings from paranoiac animal mummies in a view to understand the mechanism of preservation [26]. The compositional analysis of Copoly (dl-lactic/glycolic acid) generally applied to the devices for wound closure, orthopaedics and controlled drug release is also done by PyGC [27].

2.4 Analysis of biological macromolecules in food

Because of the ability to analyse complex molecules such as lipids, proteins and polysaccharides, foodstuffs have often been analyzed by PyGC. Halket and Schulten studied several whole foodstuffs like ground roast wheat meal biscuit, coffee, rosehip tea, chocolate drink powder, milk chocolate etc. and were able to differentiate them all by examining the molecular weight distributions of released volatiles and pyrolysis products in their spectra [28]. The identification and quantification of soy protein in ground beef has been reported [29]. Rapid PyGC/MS derivatization method for profiling of fatty acids in animal fats and vegetable oils is reported in many papers [30].

2.5 Agricultural Applications

Soil chemistry, more specifically soil structure and soil organic matter (SOM) dynamics and composition is investigated through PyGC. Nierop and co workers found out the differences in the chemical composition of SOM within one soil series from three differently managed fields in

Netherland [31]. Marinari and co-workers used carbon fraction pools and pyrolytic indices as an indication of SOM quality under organic and conventional management in central Italy [32]. Rodriguez and co workers evaluated chemical and structural properties of SOM under different agronomical practices of the Venezuelan central plains by measuring the relative abundance of volatile organic products produced through pyrolysis [33]. A comparison between organic and mineral fertilization in the investigation of chemical and biochemical changes in SOM had been reported, in which the detection of high levels of water soluble organic carbon and aliphatic pyrolytic products confirmed that mineral fertilization caused greater alteration of native SOM than the organic amendments [34].

2.6 Petrochemical Source Analysis

Pyrolysis techniques can also be applied for molecular characterisation of environmental kerogen and humic substances [35]. Petsch and co workers analysed the weathering profiles of organic carbon rich black shales in order to determine degradation and loss of organic matter during weathering and its role in the geochemical carbon cycle by PyGC [36]. Gonz´alez-Vila and co-workers analysed a set of kerogen concentrates using PyGC/MS both in the presence and absence of tetra methyl ammonium hydroxide (TMAH) to study their structural characteristics. Results show binding of considerable amounts of functionalized compounds to the macromolecular structure via ester and ether linkages [37]. Another area of geochemical research which has been greatly explored includes the compositional analysis of coal materials. The release behaviour of hydrocarbon components of pulverized coal has been investigated using PyGC [38]. The co pyrolysis of coal and petroleum residues had been studied by Suelves and co workers in an attempt to examine the synergetic effects on the yield of the main petrochemical pyrolysis products [39]. Additional research using PyGC includes the study of both volatile and non volatile organic compounds in extraterrestrial environments during planetary missions [40].

2.7 Environmental Analysis

Applications of PyGC in environmental science continue to grow, with the benefits in fingerprinting of environmental samples [41].Particulate organic matter (POM) suspended in water have been analysed by pyrolysis technique. Yildiz and co workers used PyGC/MS to investigate suspended POM in open and coastal waters of the southern Black Sea and found evidence in the pyrograms of 23 marker compounds characteristic of chlorophylls, lipids, carbohydrates and proteins formed during pyrolysis [42]. Characterisation of particulate organic matter in marine sediments was also done by PyGC. Fabbri and co workers had compared pyrolytic and lipid markers in the Adriatic Sea using semi quantitative PyGC/MS and classical GC/MS [43]. PyGC/MS method was also applied for the analysis of the UVb absorbing compounds in small numbers of pollen, spores and other microscopic entities [44].

2.8 Characterizations of Art Materials

PyGC technique is applied for the characterisation of proteinaceous binders such as animal skins or bones, egg and milk in artistic paintings [45]. Natural resins are used as a main ingredient in varnishes and binding media which have also been analysed [46]. Several studies are done for the analysis of different artist's paintings. Chiavari and co workers analysed lipid materials used in paint layers by an in situ pyrolysis and silylation method [47]. Natural dyes used in art work, namely madder, curcuma, saffron and indigo, have also been analysed by PyGC/MS [48]. Bonaduce and Colombini used PyGC/MS to characterize beeswax from a sculpture called "The Plague" [49].

2.9 Miscellaneous [50]

a) Analysis of hair samples.
b) Analysis of bathroom cleaners for surfactants.
c) Human hair composition.
d) Identification of cosmetic filler substances (such as PMMA or siloxane) used for augmentation purposes in human skin.
e) Identification of chitin in sensory hairs of silkmoth olfactory sensilla.
f) Determination of sulfur in sulphur containing amino acids: methionine, cystine, and cysteine.
g) Analysis of thermal decomposition by products of betaines.
h) Profiling of fatty acids in traces of lipids obtained from human skin, vegetable oil, and cosmetic lotions.
i) FBI analysis of paint traces in hit and run investigations.
j) Thermal degradation analysis of amino acids in fingerprint residues.

CONCLUSION

PyGC has evolved to become a routine analytical tool for the characterisation and differentiation of macromolecules both biological and synthetic. Analytical scope of PyGC is improved by using various thermal analysis equipments. Introduction of laser pyrolysis is a new phenomenon for PyGC where laser energy is used as fragmentation source and has facilitated controlled pyrolysis of specific regions on a sample, giving data on the molecular compositional units of the macromolecules. Also newer pyrolyzers have been developed to address the issues of sample losses and discrimination of high molecular weight compounds and further research promises to expand the horizons of the application of the technique.

REFERENCES

[1] TP Wampler. Applied Pyrolysis Handbook, 2nd Edition, M. Dekker, New York, **1995**; 2-12.
[2] WHT Davison; S Slaney; AL Wragg; Cham. Ind. (London), **1954**; 1356.
[3] JC Randall; Academic Press, New York, **1977**, 41.
[4] FCY Wang; BB Gerhart; PB Smith; *Anal. Chem*., 67, **1995**, 3536.
[5] FCY Wang; PB Smith; *Anal. Chem*., 68, **1996**, 425.
[6] T Nonobe; H Ohtani; T Usami; T Mori; H Fukumori; Y Hirata; S Tsuge; *J. Anal. Appl. Pyrolysis*, 33, **1995**, 121.
[7] T Nonobe; S Tsuge; H Ohtani; T Kitayama; K Hatada; *Macromolecules*, 30, **1997**, 4891.
[8] FCY Wang; BB Gerhart; CG Smith; *Anal. Chem.*, 67, **1995**, 3681.
[9] FCY Wang; BB Gerhart; *Anal. Chem*., 68, **1996**, 3917.
[10] S Mao; H Ohtani; S Tsuge; *J. Anal. Appl. Pyrolysis*, 33, **1995**, 181.
[11] H Ohtani; Y Takehana; S Tsuge; *Macromolecules*, 30, 1997, 2542.
[12] P Almen; I Ericsson; *Polym. Degrad. Stab*., 50, **1995**, 223.
[13] CN Cascaval; D Rosu; I Agherghinei; *Polym. Degrad.Stab*., 52, **1996**, 253.
[14] M Wada; S Fujishige; S Uchino; NJ Ohguri; *Anal. Appl.Pyrolysis*, 33, **1995**, 149.
[15] DM Bate; RS Lehrle; *Polym. Degrad. Stab*., 53, **1996**, 39.
[16] N Regnier; B Mortaigne; *Polym. Degrad. Stab.*, 49, **1995**, 419.
[17] J Zimmerman; D Mooney; MJ Kimmett; *J. Forensic Sci*., 31, **1986**, 489.
[18] WJ Egan; RC Galipo; BK Kochanowski; SL Morgan; EG Bartick; MLMiller; DC Ward; RF Mothershead II; *Anal. Bioanal. Chem*., 376, **2003**, 1286.
[19] F Partouche; B Espanet; C Villena; C Murie; International Conference on Digital Printing Technologies, **2005**, 216.
[20] N Tzamtzis; A Pappa; A Mourikis; *Polym. Degrad. Stabil*., 66, **1999**, 55.

[21] M Sakayanagi; Y Konda; K Watanabe; Y Harigaya; *J. Forensic Sci*., 48, 1, **2003**, 68-76.
[22] T Takayasu; T Ohshima; *Jpn. J. Forensic Tox*., 18, 2, **2000** ,146-147.
[23] T Oshima; T Konda; *Jr. Forensic science International*., 90, **1997**, 131-138.
[24] T Takayasu; T Ohshima; T Kondo; *Leg. Med*., 3, **2001**, 157.
[25] R Goodacre; B Shann; RJ Gilbert; EM Timmins; AC McGovern; BK Alsberg; DB Kell; NA Logan; *Anal. Chem*., 72, 2000, 119.
[26] SA Buckley; KA Clark; RP Evershed; *Nature*, 431, 2004, 294.
[27] K Urakami; A Higashi; K Umemoto; M Godo; C Watanabe; K Hashimoto; *Chem. Pharm. Bull*., 49, 2001, 203.
[28] JM Halket; HR Schulten; Z Lebensm; *Unters. Forsch*., 186, 1988, 201.
[29] SK Raghavan; CT Ho; H Daun*; J. Chromatogr*., 351, 1986, 195.
[30] JM Challinor; *J. Anal. Appl. Pyrol*., 37, **1996**, 185.
[31] KGJ Nierop; MM Pulleman; JCY Marinissen; *Soil Biol. Biochem*., 33, **2001**, 755.
[32] S Marinari; K Liburdi; G Masciandaro; B Ceccanti; S Grego; *Soil Till.Res*., 92, **2007**, 10.
[33] B Rodriguez; M Espana; E Cabrera De Bisbal; *Interciencia*, 29, **2004**, 461.
[34] S Marinari; G Masciandaro; B Ceccanti; S Grego*; Bioresour. Technol*., 98, **2007**, 2495.
[35] S Yamamoto; H Yoshioka; R Ishiwatari; *Bunseki Kagaku*, 56, **2007**, 71.
[36] ST Petsch; RA Berner; TI Eglinton; *Org. Geochem*., 31, **2000**, 475.
[37] FJ Gonzalezvila;A Ambles; JC delrio; L Grasset; *J. Anal.Appl. Pyrol*., 58/59, **2001**, 315.
[38] J Jin; Z Zhang; J Zhang; Huagong Xuebao/*J. Chem. Ind. Eng*., 58, **2007**, 217.
[39] I Suelves; R Moliner; MJ Lazaro*; J. Anal. Appl. Pyrol*., 55, **2000**, 29.
[40] F Raulin; R Sternberg; D Coscia; C Vidal-Madjar; MC Millot; B S´ebille; G Israel; *Adv. Space Res*., 23, **1999**, 361.
[41] DM White; DS Garland; L Beyer; K Yoshikawa; *J. Anal. Appl. Pyrol*., 71, **2004**, 107-118.
[42] YC ObanYildiz; G Chiavari; D Fabbri; AF Gaines; G Galletti; S Tu˘grul; *Marine Chem*., 69, **2000**, 55.
[43] D Fabbri; F Sangiorgi; I Vassura; *Anal. Chim. Acta*, 530, **2005**, 253.
[44] P Blokker;DYeloff; P Boelen; RA Broekman; J. Rozema; *Anal. Chem*., 77, **2005**, 6026.
[45] MP Colombini; F Modugno; *J. Sep. Sci*., 27, **2004**, 147.
[46] S Prati; S Smith; G Chiavari; *Chromatographia*,59, **2004**, 227.
[47] G Chiavari; D Fabbri; S Prati; *Chromatographia*, 53, **2001**, 311.
[48] MJ Casascatalan; MT Domenechcarbo; *Anal. Bioanal. Chem*., 382, **2005**, 259.
[49] I Bonaduce; MP Colombini; *J. Chromatogr*. A, 1028, **2004**, 297.
[50] EG Malawer; Cosmetiscope, New York Society of Cosmetic Chemists, 14, **2008**, 1 (http://www.nyscc.org)