MICHAEL R. SCHILLING*
The Getty Conservation Institute
Los Angeles, CA, USA
mschilling@getty.edu
TOM LEARNER
The Getty Conservation Institute
Los Angeles, CA, USA
tlearner@getty.edu
*Author for correspondence

EVOLVED GAS ANALYSIS AS A TOOL FOR CHARACTERIZING PLASTICS

ABSTRACT

Evolved gas analysis (EGA) using a microfurnace pyrolyzer was shown to be an excellent tool for characterizing polymers and their additives in plastics. In tests of the SamCo, a reference set of plastics produced within the framework of the POPART project, the polymer type was correctly identified in three-quarters of the samples. Moreover, nitrocellulose could be identified with EGA from the presence of nitrogen oxide pyrolysis products, whereas these products are often not detected by pyrolysis-gas chromatography/mass spectrometry. Heart-cut gas chromatography/mass spectrometry, which uses the same microfurnace as EGA, was capable of isolating and analyzing plasticizers separately from the polymer, and detecting oxidized products from the thermal decomposition of unstabilized polypropylene.

RÉSUMÉ

L'analyse des gaz émis à l'aide d'un microfour à pyrolyse s'est révélée un excellent outil pour caractériser les polymères et leurs additifs dans les plastiques. En testant le SamCo, un ensemble de plastiques de référence défini dans le cadre du projet POPART, le type de polymère a été correctement identifié dans les trois quarts des échantillons. Par ailleurs, la nitrocellulose a pu être identifiée par analyse des gaz émis grâce à la présence des produits de pyrolyse de l'oxyde d'azote, alors que ces produits sont rarement détectés par chromatographie en phase gazeuse à pyrolyse-spectrométrie de masse. La chromatographie gazeuse de la fraction de cœur-spectrométrie de masse, qui utilise le même microfour que l'analyse des gaz émis, a permis d'isoler et d'analyser des plastifiants séparément du

INTRODUCTION

As plastic objects become more prevalent in museum collections, the need for comprehensive characterization of plastic composition and the assessment of degradation state grows (Blank 1990, Williams 2002, Shashoua 2008, Tsang 2009). Indeed, these are some of the priorities of POPART, an international collaborative research project about the preservation of plastic artefacts in museums.[1]

Given the vast number of synthetic polymers and the complexity of plastic formulations, versatile and sensitive analytical instrumentation is required for their complete characterization. Although Fourier-transform infrared spectrometry is often used for this purpose, the relatively high instrumental detection limit makes it difficult to identify additives present at low concentration, especially when multiple additives are present. Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is one of the few analytical techniques capable of both identifying the polymers and detecting trace levels of additives (Learner 2004, Rial-Otero 2009). Nonetheless, Py-GC/MS is not without its limitations. Py-GC/MS chromatograms of plastics often contain peaks from hundreds of compounds, and it can be a daunting task, indeed, to ascertain which compounds are uniquely characteristic of the polymer. Likewise, because many additives are present at low concentration, their peaks are consequently small and hard to detect, and the same may also be true of plastic decomposition products.

Evolved gas analysis (EGA) is a technique whereby temperature-resolved, volatile species generated from a sample placed within a microfurnace are analyzed using mass spectrometry. EGA curves, which appear in the form of total ion current versus temperature profiles, resemble the results from direct temperature-resolved mass spectrometry (DTMS). In DTMS, however, sample vapor is generated directly within the source of the mass spectrometer by the use of a heated filament, which permits the detection of larger mass fragments and improves the detection of labile compounds. Nonetheless, as will be shown later, microfurnace EGA offers several key advantages over DTMS, such as lower equipment costs, accommodation of larger and more heterogeneous samples, use of robust instrumentation that requires less maintenance and customized mass spectral libraries for compound identification.

SCIENTIFIC RESEARCH

EVOLVED
GAS ANALYSIS
AS A TOOL FOR
CHARACTERIZING
PLASTICS

LISBON 2011

polymère, et de détecter les produits oxydés provenant de la décomposition thermique du polypropylène non stabilisé.

RESUMEN

Se comprobó que la técnica conocida como *evolved gas analysis* (EGA) con un pirolizador de micro-horno era una excelente herramienta para la caracterización de polímeros y sus aditivos en plásticos. En pruebas de SamCo, un conjunto de plásticos de referencia producidos dentro del marco del proyecto POPART, el tipo de polímero fue identificado correctamente en las tres cuartas partes de las muestras. Además, la nitrocelulosa se podía identificar por EGA a partir de la presencia de productos de la pirólisis del óxido de nitrógeno, mientras que estos productos no se suelen detectar por espectrometría de masas o pirólisis en cromatografía de gases acoplada a espectrometría de masas. La cromatografía de gases acoplada a la espectrometría de masas del corte principal, que utiliza el mismo micro-horno que EGA, fue capaz de aislar y analizar plastificantes separados del polímero, y detectar productos oxidados de la descomposición térmica del polipropileno no estabilizado.

Typical EGA results for plastics exhibit broad peak(s) originating from desorption and evaporation of low-molecular weight species, followed by a peak(s) due to pyrolysis and decomposition of high-molecular weight substances. In the present study, EGA was used to study a large collection of plastic reference specimens, where it was shown to be a rapid and accurate means of characterizing plasticizers and additives, and high-molecular weight polymeric species. Additional compositional information on selected plastic samples was obtained by using heart-cut gas chromatography/mass spectrometry (heart-cut GC/MS), a technique in which temperature-resolved EGA sample fractions are analyzed by GC/MS. A valve is used to direct the sample vapor that is evolved during a specified EGA fraction to a cryo-trap. Once the vapor from the fraction is fully collected, it is desorbed into the capillary GC column for GC/MS separation and analysis. In this way, multiple EGA temperature fractions of a plastic sample can be analyzed sequentially, making it possible to more fully understand the composition of each.

EXPERIMENTAL

Evolved gas analysis

The instrument used in this study was a Frontier Laboratories Ltd. PY-2020D microfurnace pyrolyzer. The microfurnace was mounted onto the split inlet of an Agilent Technologies 5975C inert MSD/7890A gas chromatograph/mass spectrometer via a heated syringe needle interface. A deactivated transfer line (Frontier Ultra ALLOY DTM EGA tube, 2.5 M × 0.15 mm) connected the GC inlet to the MS detector via a Frontier Vent-Free adaptor. The pyrolysis interface and GC oven were maintained at 320°C, and helium carrier gas was set to 1 ml/minute. The split injector was set to 320°C with a split ratio of 50:1 and no solvent delay.

A 50 µl stainless steel Eco-cup loaded with a sample that contained <100 µg of organic material) was placed into the cool upper zone of the microfurnace where it was purged with helium for three minutes prior to heating. Sample vapor was generated by ramping the temperature of the microfurnace from 100°C to 700°C at 20°C/minute, followed by a five minute isothermal period. The mass spectrometer was scanned from 10-600 amu. Polymers and volatile components were identified on the basis of their total mass spectra using the Frontier F-Search 2.0 program with libraries for polymers and their additives.

Pyrolysis-gas chromatography/mass spectrometry

GC conditions: Ultra ALLOY-5 column (30 M × 0.25 mm × 0.25 µm), helium at 1 ml/minute, split injector at 320°C with 50:1 split ratio, no solvent delay. GC oven program: two minutes at 40°C, 20°C /minute to 320°C, nine minutes isothermal. MS conditions: 10-600 amu, transfer line 320°C, source 230°C, quad 150°C. Samples were placed into 50 µl stainless steel Eco-cups, inserted into the pyrolyzer, purged with helium

SCIENTIFIC RESEARCH

EVOLVED
GAS ANALYSIS
AS A TOOL FOR
CHARACTERIZING
PLASTICS

LISBON 2011

for three minutes, then pyrolyzed for six seconds at 550°C. The pyrolysis interface was maintained at 320°C.

Heart-cut gas chromatography/mass spectrometry

Temperature-resolved sample vapor fractions were obtained by controlling the Frontier PY-2020D microfurnace pyrolyzer with a SS-1010E selective sampler and MJT-1030E microjet cryo-trap. The temperature ranges of the vapor fractions were obtained from separate EGA measurement results. A J&W DB-5MS-UI capillary column was used for separation (30 M × 0.25 mm × 0.25 μm). GC/MS measurement conditions were identical to those in the Py-GC/MS method.

Thermogravimetry

A Mettler Toledo TGA/SD TA851e with STARe software v. 8.10 was used. After three minutes at 30°C for purging the furnace, 2 mg powdered plastic samples were heated in open 70 μL alumina crucibles at 20°C/min to 1000°C. Nitrogen purge gas was set to 50 ml/min.
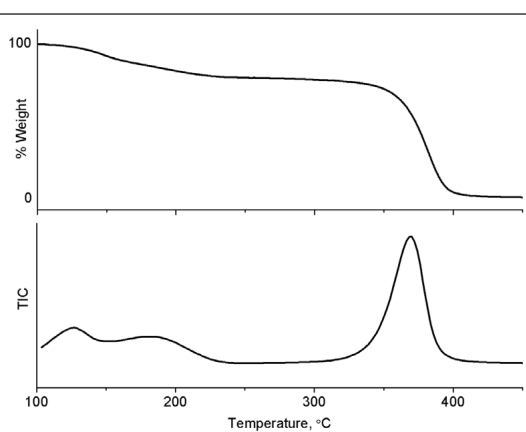
Samples

The SamCo reference collection was studied in its entirety using EGA. SamCo is a collection of 91 plastic reference samples, commercial items and artefacts developed in the POPART project.[1] A large portion of SamCo originated from *The ResinKit*, a set of 50 specimens of various plastics from a distributor in Woonsocket, RI, USA. A flexible sheet of cellulose diacetate was obtained from Goodfellow Cambridge Ltd., and a sheet of isotactic polypropylene, formulated without stabilizers for POPART, was provided by Jozef Rychly of the Polymer Institute of the Slovak Academy of Sciences, Bratislava.

RESULTS

Comparison between EGA and TG

Thermogravimetry can be quite useful for determining whether or not a plastic contains plasticizers, because their volatility leads to weight loss upon heating (Price 2000, Schilling 2010). Figure 1 is an overlay of thermogravimetry (TG) and EGA data for a powdered sample of cellulose diacetate plasticized with diethyl phthalate (from Goodfellow). The three weight loss steps observed in the TG results give rise to an EGA curve with three peaks, although the first two are not well-resolved.

EGA is quite useful for identifying gases released during TG weight loss steps, and also for providing more precise definitions of the temperature limits of the steps. As in DTMS, mass spectra are obtained at each measuring point in the EGA curve, making it possible to calculate an average mass spectrum over the entire analysis, as shown at the bottom of Figure 2. Moreover, selected ion curves are useful for monitoring the evolution of individual volatile components. In Figure 2, the overlay of selected
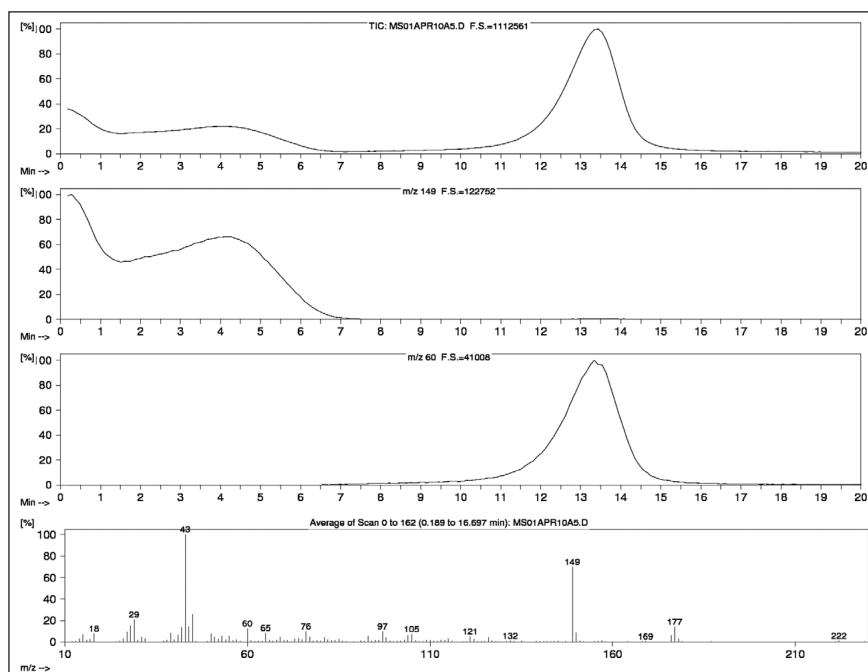
Figure 1

Results of thermogravimetry (top) and evolved gas analysis (bottom) for a sample of cellulose acetate from Goodfellow Cambridge Ltd

SCIENTIFIC RESEARCH

EVOLVED
GAS ANALYSIS
AS A TOOL FOR
CHARACTERIZING
PLASTICS

LISBON 2011

Figure 2
Evolved gas analysis results for Goodfellow cellulose acetate. Legend from top to bottom: total ion current; *m/z* 149; *m/z* 60; and average mass spectrum from 0.189 to 16.697 minutes

ion curves characteristic of diethyl phthalate (*m/z* 149) and pyrolytic cleavage of the acetate side-chains on the cellulose acetate polymer (*m/z* 60) indicates that the first two weight-loss steps are, in fact, due to plasticizer evaporation. Plasticizer evaporation is completed by 260°C, just after polymer decomposition begins. Plasticizer release from a polymer is a diffusion-controlled process, so the fact that the release appears in overlapping steps is consistent with the nature of the interaction of the plasticizer with the polymer, which is known to exhibit both molecular and structural behaviors (Skornyakov 1998).

Polymer identification using EGA with F-Search

Polymer identification by EGA is accomplished using the F-Search mass spectral library databases for polymers (Frontier 2010), as shown in Figure 3 for the Goodfellow cellulose acetate sample. The average mass spectrum was obtained over the portion of the EGA curve during which cellulose
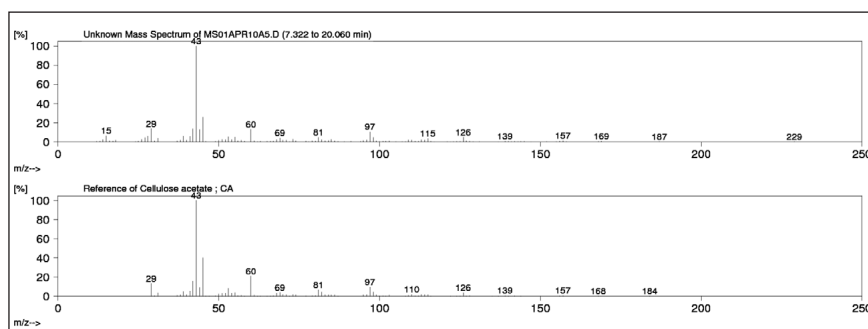

Figure 3
F-Search polymer identification results for Goodfellow cellulose acetate. Average mass spectrum (top) and cellulose acetate reference spectrum (bottom)

SCIENTIFIC RESEARCH

EVOLVED
GAS ANALYSIS
AS A TOOL FOR
CHARACTERIZING
PLASTICS

LISBON 2011

acetate pyrolyzed (from 7.3 to 20.06 minutes), thereby excluding the mass spectral contribution of the evaporation of plasticizer. The average mass spectrum gave a 96 percent match quality to cellulose acetate. Plasticizers can also be identified using the additive database; for the CA sample, the match to diethyl phthalate was 97 percent. In general, though, the match qualities tend to be lower because many plastics contain several additives, which can complicate the identification process.

The polymer types in the SamCo reference set were conclusively identified with at least 80 percent certainty for more than three-quarters of the SamCo reference set by searching the average mass spectrum against the standard F-Search polymer database, as shown in Table 1. The average mass spectra occasionally matched more than one polymer type. Many of these polymers were heavily plasticized, as was the case for PVC and cellulose acetate butyrate. Novon, an eco-friendly plastic formulated with starch and polyethylene (Novon 2010) was a secondary match for linear polyene-type plastics. Additionally, plastics formulated with styrene tended to give secondary matches to polystyrene. In summary, the difficulty in eliminating the mass spectral contribution of the plasticizer is one of the biggest impediments in obtaining a high-probability match for the polymer.

Identification of nitrocellulose

Nitrocellulose is one polymer that, traditionally, has been difficult to identify using Py-GC/MS. Peaks for camphor or alkyd plasticizers are obvious in the chromatographic results, whereas it was thought that pyrolysis of the nitrate groups forms gases that cannot easily be detected using positive-ion GC/MS (Learner 2004). Figure 4 shows the EGA curve and
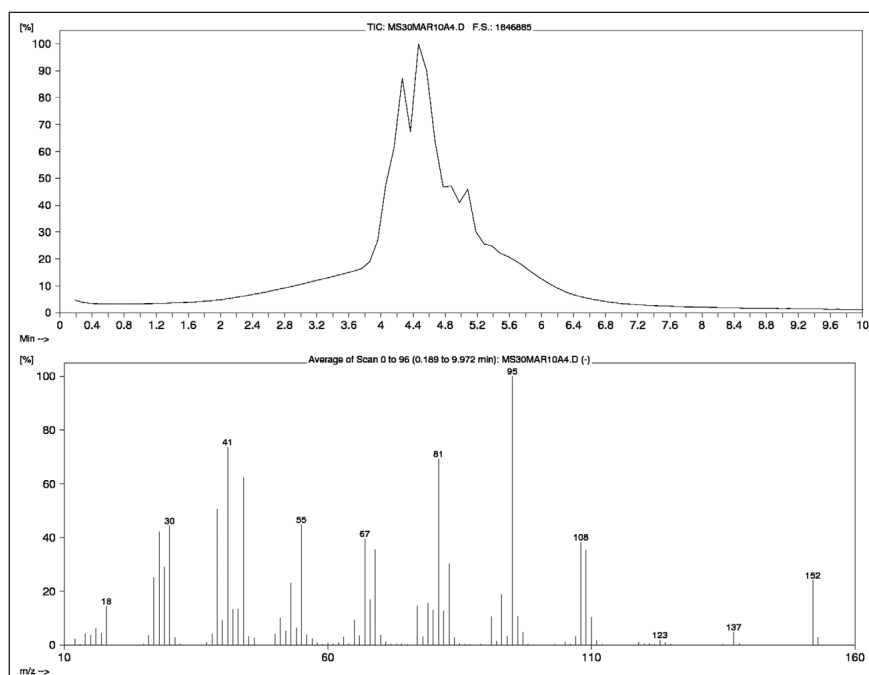

Figure 4
Evolved gas analysis results for cellulose nitrate (SamCo #9). Total ion current (top) and average mass spectrum from 0.189 to 9.972 minutes

5

SCIENTIFIC RESEARCH

EVOLVED
GAS ANALYSIS
AS A TOOL FOR
CHARACTERIZING
PLASTICS

LISBON 2011

average mass spectrum results for nitrocellulose (SamCo #9). Although the average mass spectrum is dominated by the spectrum of camphor, both *m/z* 30 and *m/z* 46 provide evidence for the presence of nitrogen monoxide and nitrogen dioxide, respectively. The selected ion curves in Figure 5

Table 1

F-Search library match results for polymers in SamCo reference set, from evolved gas analysis

Polymer (# of specimens)	Comments
> 90% Match Quality	
Polymer (# of specimens)	*Comments*
Acetal/Poly(oxymethylene) (2)	
Acrylic (2)	
Acrylonitrile-Butadiene-Styrene (2)	May also match acrylonitrile-styrene
Acrylonitrile-Styrene-Acrylate	May also match acrylonitrile-styrene
Polybutylene Terephthalate	
Polycarbonate (2)	
Cellulose Acetate (2)	
Polyethylene, various densities (5)	Also matches Novon
Silicone Rubber	
Polystyrene, various impact resistances (5)	
Styrene Acrylonitrile (2)	
Styrene Butadiene (3)	May also match polystyrene
Polytetrafluoroethylene	
> 80% Match Quality	
Polymer (# of specimens)	*Comments*
Cellulose Acetate Butyrate (2)	
Polyester, various types (3)	
Polyether-Ether Ketone	
Ethylene Vinyl Acetate	Also matches Novon
Melamine Formaldehyde (2)	Melamine also matches in additives library
Nylon 6	Also matches Nylon 6,6
Nylon 6,6 (3)	May also match Nylon 6
Polyphenylene Oxide	
Polypropylene (3)	
Shellac, various formulations (3)	
Silicone	Matches polydimethylsiloxane
Polyvinylidene chloride (Saran)	
Polyvinylidene fluoride	
Urethane Elastomer thermoplastic (4)	May also match polyethylene oxide, methylene diisocyanate-polylactone polyurethane
> 70% Match Quality	
Polymer (# of specimens)	*Comments*
Cellulose Acetate Propionate (3)	
Polyethylene Terephthalate	
Polyvinyl chloride, various types (4)	May also match acrylonitrile-vinyl chloride
Polyvinyl chloride/Polyvinyl acetate	May also match chlorinated polyethylene
< 70% Match Quality	
Polymer (# of specimens)	*Comments*
Epoxy	Also matches polycarbonate
Phenol-Formaldehyde (2)	Matches cresol-formaldehyde
Polyphenylene Sulfide	Cross-linker reduces match quality to 40
Polysulfone	
Urea-Formaldehyde	May also match Novon
Polyurethane (ester), flexible foam	Matches toluene diisocyanate-polyester polyurethane
Polyurethane (ether), flexible foam	29% match to toluene diisocyanate-polyether polyurethane
Natural Rubber (2)	Matches polybutadiene, may also match shellac

SCIENTIFIC RESEARCH

EVOLVED
GAS ANALYSIS
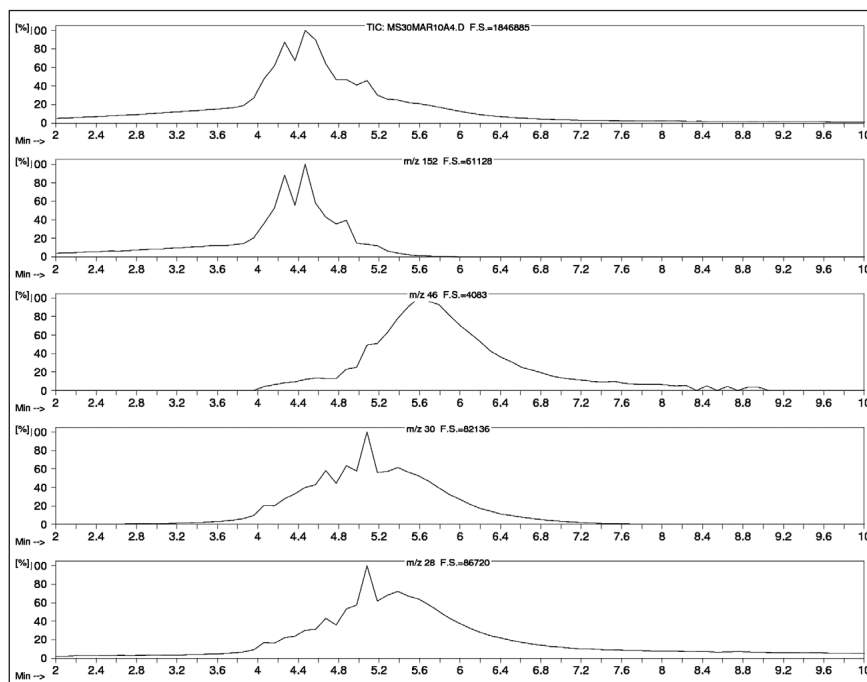AS A TOOL FOR
CHARACTERIZING
PLASTICS

LISBON 2011

Figure 5
Evolved gas analysis results for cellulose nitrate (SamCo #9). Legend from top to bottom: total ion current; *m/z* 152; *m/z* 46; *m/z* 30; and *m/z* 28

show evidence for the formation of nitrogen monoxide (*m/z* 30), nitrous oxide (*m/z* 28) and nitrogen dioxide (*m/z* 46) from the decomposition of nitrocellulose, which occurs soon after the bulk of the camphor (*m/z* 152) has evaporated. Ions from these permanent gases are often excluded in Py-GC/MS analyses because they are seen as contributing negatively to the background levels instead of adding confirmatory evidence for small gaseous compounds. The fact that they form during the middle of the EGA temperature ramp is consistent with their formation from pyrolysis instead of from air introduced during injection or other sources. Other studies that utilize a GC column capable of separating permanent gases have reported nitrogen oxides from pyrolysis of nitrocellulose (Moldoveanu 1998). Thus, this provides some justification for reducing the lower mass in a scan Py-GC/MS analysis protocol from 45 amu downwards to 10 amu. This adjustment would also aid in the Py-GC/MS identification of polyoxymethylene because formaldehyde, which as a molecular weight of 30, is formed almost quantitatively.

Heart-cut analysis of plasticized cellulose acetate and polypropylene

The temperature ranges for plasticizer release and acetic acid formation, obtained from the EGA results, were used to establish the temperature parameters for subsequent heart-cut GC/MS analysis of the Goodfellow cellulose acetate. Figure 6 shows an overlay of heart-cut GC/MS chromatograms for two EGA temperature-resolved fractions: 100-320°C and 320-600°C. Release of diethyl phthalate (10.9 minutes) and triacetin (9.2 minutes) from the plastic was nearly quantitative in the first heart-cut fraction, with only a trace of acetic acid detected. During the second fraction, the polymer was completely thermally-degraded with release of the bulk of the acetic
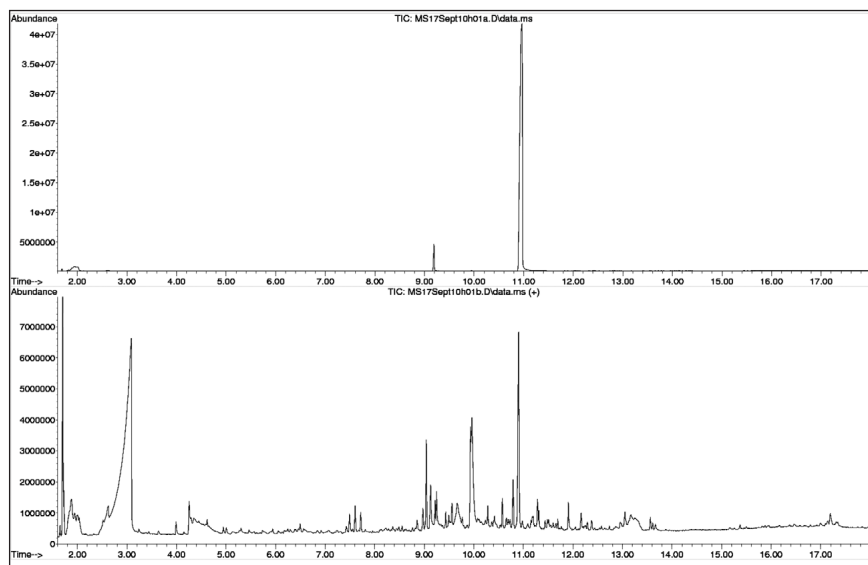
SCIENTIFIC RESEARCH

EVOLVED
GAS ANALYSIS
AS A TOOL FOR
CHARACTERIZING
PLASTICS

LISBON 2011

Figure 6

Heart-cut GC/MS chromatograms for two EGA temperature-resolved fractions from Goodfellow cellulose acetate: 100-320°C (top) and 320-600°C (bottom)
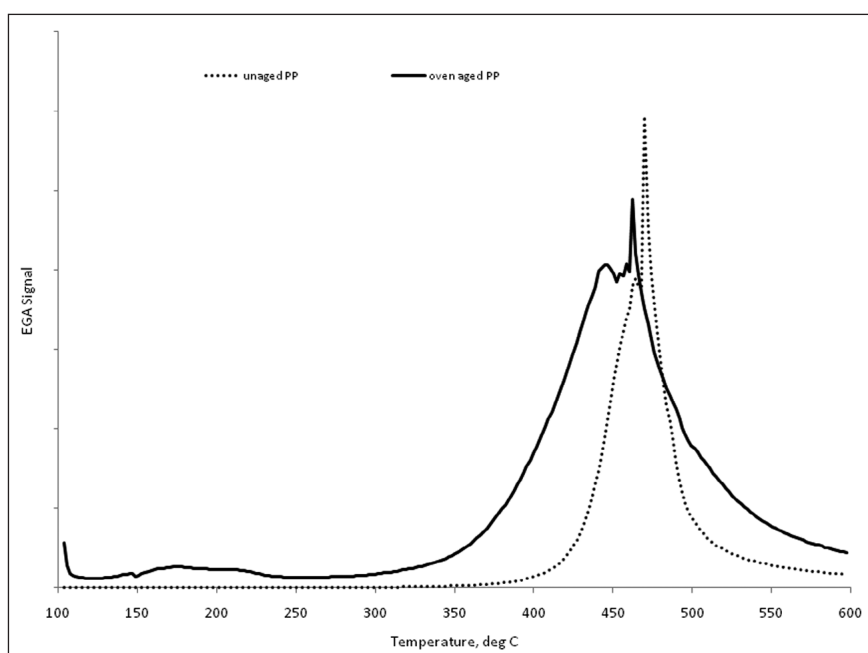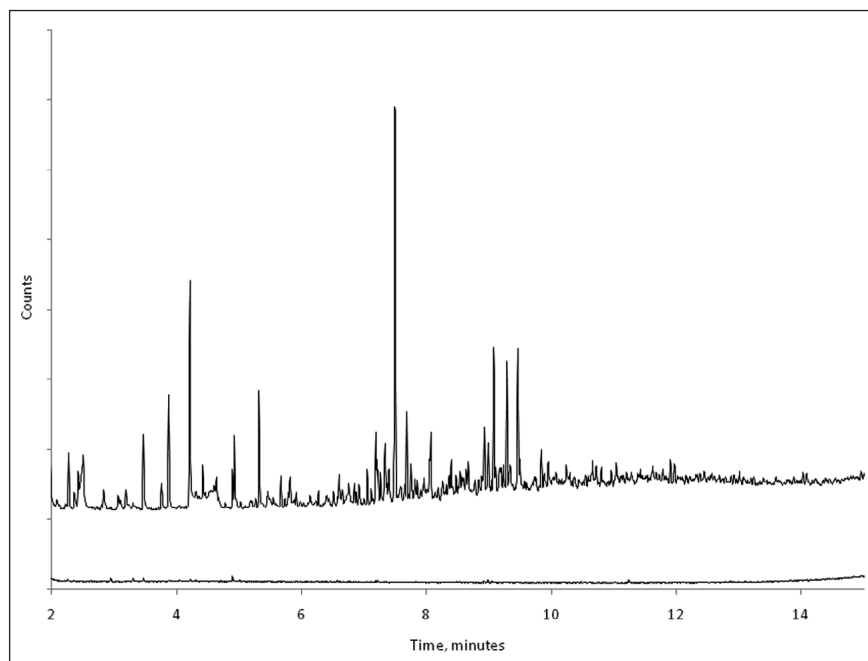

Figure 7

Evolved gas analysis results for unstabilized, isotactic polypropylene: unaged (dotted line) and oven-aged for four hours at 120°C (solid line)

acid and the formation of typical pyrolysis products for cellulose acetate (Moldoveanu 1998). This example shows one of the main benefits of heart-cut GC/MS, which is easy detection of low-molecular weight additives.

Compared to polyethylene, polypropylene is extremely sensitive to thermal degradation and photo-oxidation because the secondary hydrogen on the polymer backbone is quite reactive in comparison to the primary hydrogen of polyethylene, which is why large amounts of stabilizers and anti-oxidants are incorporated into polypropylene formulations (Matisova-Rychla 1995). Unstabilized, isotactic polypropylene was analyzed with EGA before and after oven aging for four hours at 120°C (Figure 7). It is clear that a substantial

SCIENTIFIC RESEARCH

EVOLVED
GAS ANALYSIS
AS A TOOL FOR
CHARACTERIZING
PLASTICS

LISBON 2011

Figure 8

Heart-cut GC/MS chromatograms of low-temperature fractions for unstabilized, isotactic polypropylene: unaged (bottom) and oven-aged for four hours at 120°C (top)

quantity of low-molecular weight species is present in the thermally-aged sample. Heart-cut GC/MS analysis of the low-temperature fraction from 100-260°C (Figure 8) showed numerous oxidation products such as alcohols, aldehydes, ketones and carboxylic acids in the aged sample, whereas the result for the unaged sample was nearly blank.

DISCUSSION

A microfurnace-type pyrolyzer offers the user much more flexibility than does a Curie-point pyrolyzer or a probe-type pyrolyzer. By using the Frontier Vent-Free adaptor, the change from pyrolysis GC/MS to EGA can be accomplished in just a few minutes without requiring the vacuum system to be vented. A microfurnace pyrolyzer is much less expensive than a DTMS instrument because it is simply an accessory to an existing GC/MS. The deactivated EGA transfer line is far less sensitive than a capillary GC column to the corrosive effects of acids that form from the pyrolysis of PVC plastics and cellulose esters, thereby making it possible to test many samples on a single transfer line. EGA permits much larger samples to be tested by the use of small stainless steel cups, which is an important feature for materials that contain low concentrations of organic materials, whereas with Curie-point pyrolyzers tiny samples must be applied directly to the Curie-point wire from a suspension in solvent. The steel cups also make it easy to add derivation reagents to samples to improve their chromatography. Finally, the design of the microfurnace interface makes it possible to insert the sample into the cool section of the furnace and completely purge any air out of the system prior to pyrolysis without losing any volatiles, thereby eliminating the need for a multi-port switching valve like those used with probe-type pyrolyzers.

9

SCIENTIFIC RESEARCH

EVOLVED
GAS ANALYSIS
AS A TOOL FOR
CHARACTERIZING
PLASTICS

LISBON 2011

When identifying polymers, it is far easier to interpret EGA results using the F-Search library than it is to sift through numerous peaks in a Py-GC/MS curve. It can be quite a difficult task, indeed, to ascertain which of the many peaks in a GC pyrogram are characteristic of a given type of polymer. F-Search does have a Py-GC/MS feature that relies on summation mass spectra, but it is a bit more difficult to use than the EGA library.

Even with the relatively small F-Search database, it was possible to identify 75 percent of the samples, and so a larger, user-developed database would certainly improve the number of positive results. Therefore, the F-Search library matching results of the SamCo would be further improved by developing a user's spectral database, which is certainly one of the benefits of testing the SamCo. Such a library could be beneficial to the conservation community if it were shared with public organizations such as MaSC, the Mass Spectrometry and Chromatography Users' Group.

EGA tends to work best for identifying the most abundant plasticizer in a plastic, whereas heart-cut Py-GC/MS provides a much better alternative for detecting additive mixtures and additives at low concentration because the peaks from polymer degradation are largely absent in low-temperature heart-cut fractions. It was also possible to expand the range of identifiable additives through the use of the NIST MS Search 2.0 program, which aided in the identification of melamine in a sample of melamine formaldehyde plastic. One final advantage of EGA is the capability to assess the relative evaporation rates of polymer additives, which would be useful when studying the aging behavior of plastics.

Results from EGA can be helpful for evaluating CHNS data for plastic objects, particularly the elemental ratios of C/N, C/O and C/H. Knowledge of the base polymer composition, primarily the monomer composition and the type of additives present in a plastic, could be factored into the elemental ratio calculations, which would result in more consistent results. This refinement would be advantageous for studying polymer oxidation or aging reactions.

CONCLUSION

Evolved gas analysis using a Frontier microfurnace pyrolyzer was shown to be a rapid, versatile and accurate technique for characterizing plastics that is capable of identifying a wide range of polymers and additives. Using F-Search to evaluate EGA measurement data was successful in identifying the polymers in three-fourths of the SamCo reference set of plastics from the POPART project. Nitrocellulose could also be identified by EGA on the basis of the detection of oxides of nitrogen that were generated after the camphor plasticizer had evaporated. Used in conjunction with EGA, heart-cut GC/MS can be a powerful tool for detecting additives in plastics, even when present at low concentration, and is helpful for assessing the effects of polymer aging.

SCIENTIFIC RESEARCH

EVOLVED
GAS ANALYSIS
AS A TOOL FOR
CHARACTERIZING
PLASTICS

LISBON 2011

ACKNOWLEDGEMENTS

NOTES

[1] A consortium of mostly European institutions and laboratories involved in the care or study of modern and synthetic materials obtained funding from the European Commission to initiate a three-year project entitled Preservation Of Plastic ARTefacts in museum collections (POPART). The objective of the project is to develop a strategy to improve preservation and maintenance of three-dimensional plastic objects in museum collections. Specific aims of the project include identifying risks associated with the exhibition, cleaning, protection and storage of plastic artefacts, plus the establishment of recommended practices (Lavedrine 2010). The GCI is participating in the project as an unfunded partner.

REFERENCES

FRONTIER LABORATORIES LTD. 12 Nov 2010. Brochure on F-Search program. http://www.frontier-lab.com/product/catalogue/F-Search.pdf.

LAVEDRINE, B., and A. FOURNIER. 2010. POPART: an international collaborative research project about the preservation of plastic artefacts in museums. http://popart.mnhn.fr/.

LEARNER, T.J.S. 2004. *Analysis of modern paints*. Los Angeles, CA: J. Paul Getty Trust.

MATISOVA-RYCHLA, L., J. RYCHLY, J. VERDU, L. AUDOUIN, and K. CSOMOROVA. 1995. Chemiluminescence and thermogravimetric study of thermal oxidation of polypropylene. *Polymer Degradation and Stability* 49(1): 51–55.

MOLDOVEANU, S. 1998. *Analytical pyrolysis of natural organic polymers*. Amsterdam: Elsevier Science B.V.

NOVON JAPAN INC. 6 Nov 2010. Development of ECO-3. http://www004.upp.so-net.ne.jp/novon/english1.html.

PRICE, D.M., D.J. HOURSTON, and F. DUMONT. 2000. Thermogravimetry of polymers. In *Encyclopedia of analytical chemistry*, ed. R.A. Meyers, 8094–8105. Chichester: John Wiley & Sons Ltd.

RIAL-OTERO, R., M. GALESIO, J. CAPELO, and J. SIMAL-GÁNDARA. 2009. A review of synthetic polymer characterization by pyrolysis–GC–MS. *Chromatographia* 70(3/4): 339–348.

SCHILLING, M., M. BOUCHARD, H. KHANJIAN, T. LEARNER, A. PHENIX, and R. RIVENC. 2010. Application of chemical and thermal analysis methods for studying cellulose ester plastics. *Accounts of Chemical Research* 43(6): 888–896.

SHASHOUA, Y. 2008. *Conservation of plastics: materials science, degradation and preservation*. Oxford: Butterworth-Heinemann.

SKORNYAKOV, I.V., and V.P. KOMAR. 1998. IR spectra and the structure of plasticized cellulose acetate films. *Journal of Applied Spectroscopy* 65(6): 911–918.

TSANG, J., O. MADDEN, M. COUGHLIN, A. MAIORANA, J. WATSON, N.C. LITTLE, and R.J. SPEAKMAN. 2009. Degradation of 'Lumarith' cellulose acetate: examination and chemical analysis of a salesman's sample kit. *Studies in Conservation* 54(2): 90–105.

WILLIAMS, R.S. 2002. Care of plastics: malignant plastics. *WAAC Newsletter* 24(1). http://cool.conservation-us.org/waac/wn/wn24/wn24-1/wn24-102.html.