Waters™

응용 자료

Direct Real-Time Analysis of Volatile Organic Compounds From Biobased Plastics Using Soft Ionization ACQUITY QDa Mass Detection

Rachel Sanig, Jan-Christoph Wolf, Cristian Cojocariu

Waters Corporation, Plasmion GmbH

This is an Application Brief and does not contain a detailed Experimental section.

Abstract

This application brief highlights the use of a Plasmion SICRIT cold plasma ionization source coupled to a Waters ACQUITY QDa Detector to directly assess the volatile organic profiles in real-time of biobased plastic bags. This instrument system set-up demonstrated a cost-effective orthogonal technique that requires minimal sample preparation and allows for improved productivity of plastic products testing where speed, reliability, and flexibility of analysis is key. In addition, the small footprint of the analytical configuration would benefit at site analysis.

Benefits

Real-time, direct analysis of volatile organic compounds in recycled or biobased plastics materials for quality control of potentially harmful substances and unpleasant odorants in the raw material and final products

Introduction

In a world where 99% of plastic is made from chemicals sourced from fossil fuels; environmentally friendly materials are becoming more popular, with an increased number of manufacturers of consumer products adopting sustainable solutions for their plastic packaging. One such promising solution is biobased plastics that are synthesized from renewable materials from organic or plant-based sources. The main advantages of such materials are that most are recyclable, compostable, or biodegradable with relatively short degradation times. Consequently, biobased plastics can potentially be used for the same applications as oil-based plastics and have the potential to replace non-biodegradable film and single-use plastics. However, despite these advantages, further research is required to identify the best combination of raw materials, selectively and collectively, and to optimize the appropriate physicochemical properties of the resultant biobased plastics.

One important method for understanding the chemical processes involved in biobased plastic manufacturing is the analysis of volatile organic compounds (VOCs) in such materials. Often this type of analysis can elucidate the chemical processes responsible for thermal degradation during processing or during unwanted conditions. Biobased plastics, just as conventional plastics, need additives (such as plasticizers) or the addition of more chemicals since they are usually less stable and have a lower diffusion barrier than conventional plastics.[1] These chemicals may migrate from the packaging into the consumer product posing health risks or altering the product quality through emission of volatile odorant substances.[2] Quick, real-time profiling of the VOCs present in the final products can indicate compounds which can cause unpleasant odor or even potentially harmful volatile chemicals. Traditionally, VOC profiling is performed using static headspace or dynamic gas chromatography-mass spectrometry (GC-MS) or reaction-mass spectrometry. However, such techniques can require sample preparation, be costly, or have a large laboratory footprint.

In this application brief a novel analytical approach was employed to directly assess the volatile organic profiles in real-time of several biobased plastic bags using a Waters ACQUITY QDa Detector equipped with a cold plasma ionization source from Plasmion GmbH.

Experimental

Sample Preparation

Three different commercially available biobased plastic bags (BIOTEC GmbH & Co. KG) were analyzed in triplicate directly without any preparation except for cutting small pieces of similar weights of each plastic bag and placing into separate sample vials (Table 1).

Sample name	Description	Weight (mg)
C1 500	Bioplast 500	11.58
C2 400	Bioplast 400	11.61
C3 GF 106/02	Bioplast G2 106/02	11.66

Table 1. Biobased plastic bag cuttings.

Analytical Set-up

The analytical instrumentation used was a Waters ACQUITY QDa Detector coupled to a Soft Ionization by Chemical Reaction In Transfer (SICRIT) Ionization source (Plasmion GmbH, Germany) (Figure 1). This configuration allows for an easy to handle, small footprint analytical tool that can directly detect chemical components of a sample simply by holding the sample in front of the ionization source. In this process, the chemical components are driven into the ionization source directly via the negative pressure prevailing in the mass detector and are ionized during transfer. The ionization takes place in the inlet capillary by generating a cold, ring-shaped plasma. This means that the analytes pass through the plasma ring on their way into the mass detector, whereby the ionization or charge transfer takes place by reactive species and ultraviolet radiation. Since the analytes have no direct contact to the plasma, SICRIT is a "soft" ionization method, which means that the analytes are not fragmented, but remain intact. Moreover, the ionization mainly produces protonated $[M+H]^+$ species facilitating the identification of chemical molecular ions.[3]

In this set-up, samples were analyzed by holding the vial containing the cutting up to the SICRIT source for five seconds and the data was collected under the conditions outlined below. A small tube was attached to the SICRIT source to allow for easy direct sampling from the sample vials.

Analytical Conditions

Acquisition mode:	Full Scan
Mass range:	30–1250 Da
Ionization mode:	ESI+
Capillary voltage:	0.8 kV
Cone voltage:	30 V
Source temperature:	100 °C
Probe temperature:	40 °C

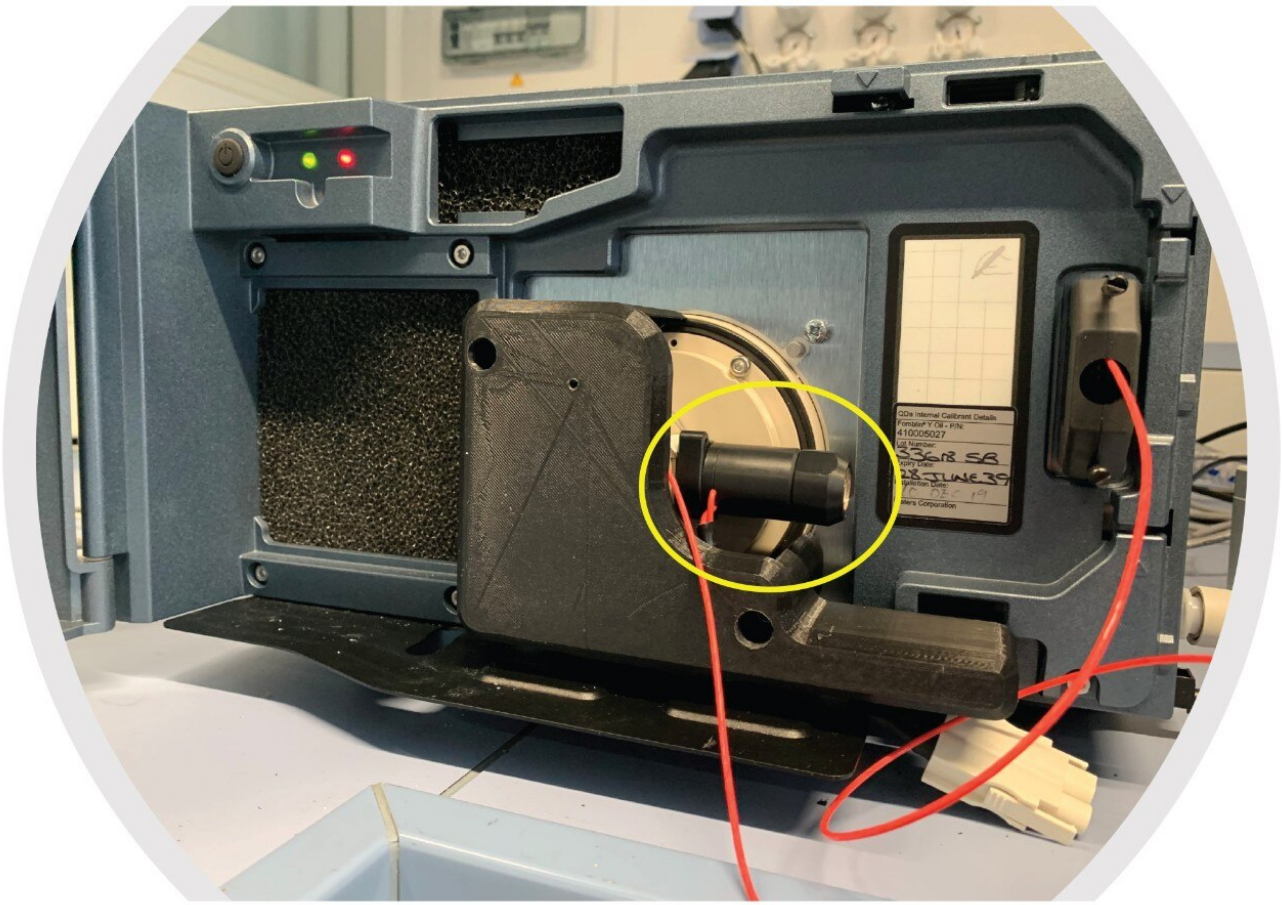

Figure 1. Plasmion SICRIT coupled to a Waters ACQUITY QDa Detector.

Results and Discussion

The experiment started by analyzing a procedural blank to assess the background level of the VOCs and benchmark the mass spectrometer baseline signal. This was followed by three technical replicate analyses of each biobased plastic bag. An example of the total ion current (TIC) chromatogram is shown in Figure 2[A].

Assessment of the mass spectra averaged over each acquisition revealed compounds present in all samples. This can be seen with the extracted ion chromatogram (XIC) of *m/z* 141 (Figure 2[C]), which is putatively assigned to 8-nonenal, a chemical odor often found in plastic containers and bags.[4] SICRIT-QDa analysis

indicated that traces of this chemical were present in all three samples, with sample C1 500 (>50% biobased) containing less of this compound perhaps due to a higher percentage of biobased polymers as compared to samples C2 400 (>40% biobased) and C3 GF 106/02 (>20% biobased).

Further investigation of the data revealed significant differences between the biobased plastic bag samples analyzed, for example, in the extracted ion chromatogram (XIC) of *m/z* 147 (Figure 2[B]).

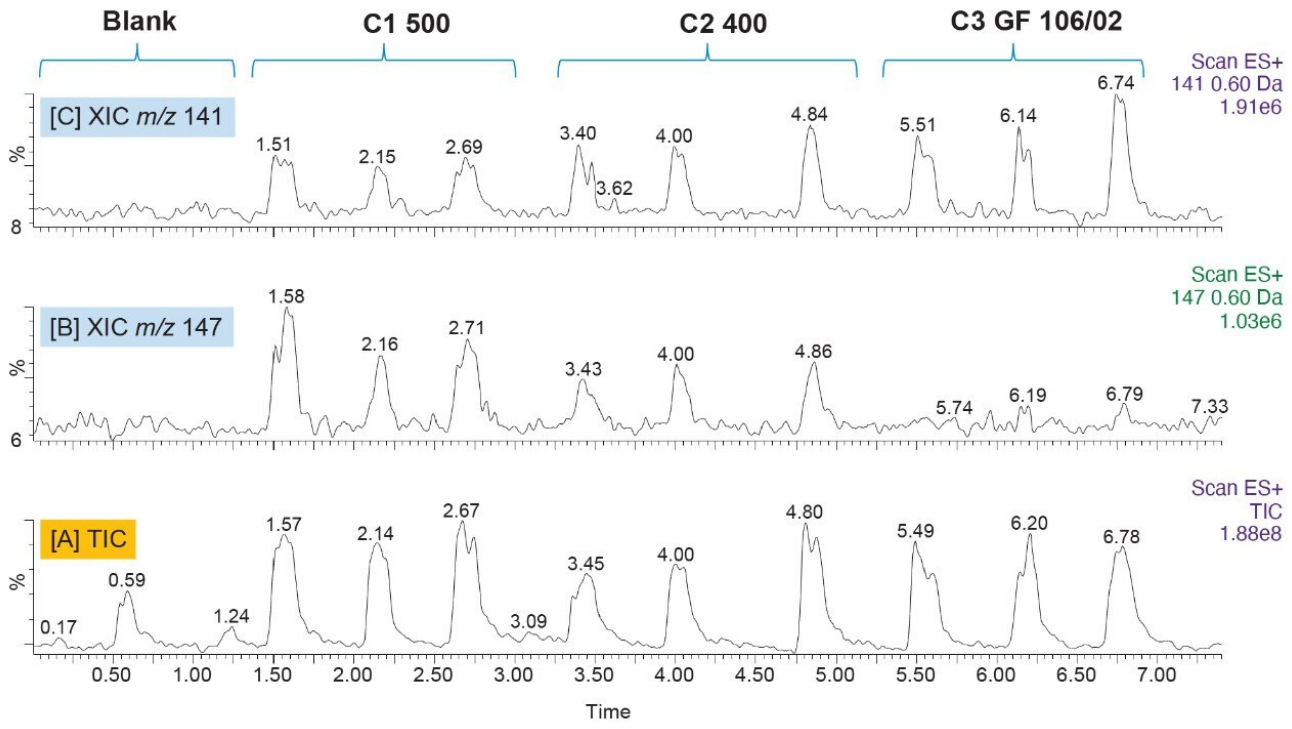

Figure 2. [A] Total ion chromatogram (TIC) of the blank and the three plastic bags acquired in triplicate. [C] Extracted ion chromatogram (XIC) of 8-nonenal (m/z 141, $[M+H]^+$) and [B] XIC of m/z 147, $[M+H]^+$, indicating differences between the biobased plastic bag samples analyzed.

Most likely a plasticizer compound, *m/z* 147, was most abundant in C1 500 and C2 400 samples, and absent in the C3 GF 106/02 sample which can be seen more clearly when the XICs are overlayed in Figure 3. Interestingly, the sample C3 GF 106/02 is described by the manufacturer as plasticizer-free which is in line with this finding.

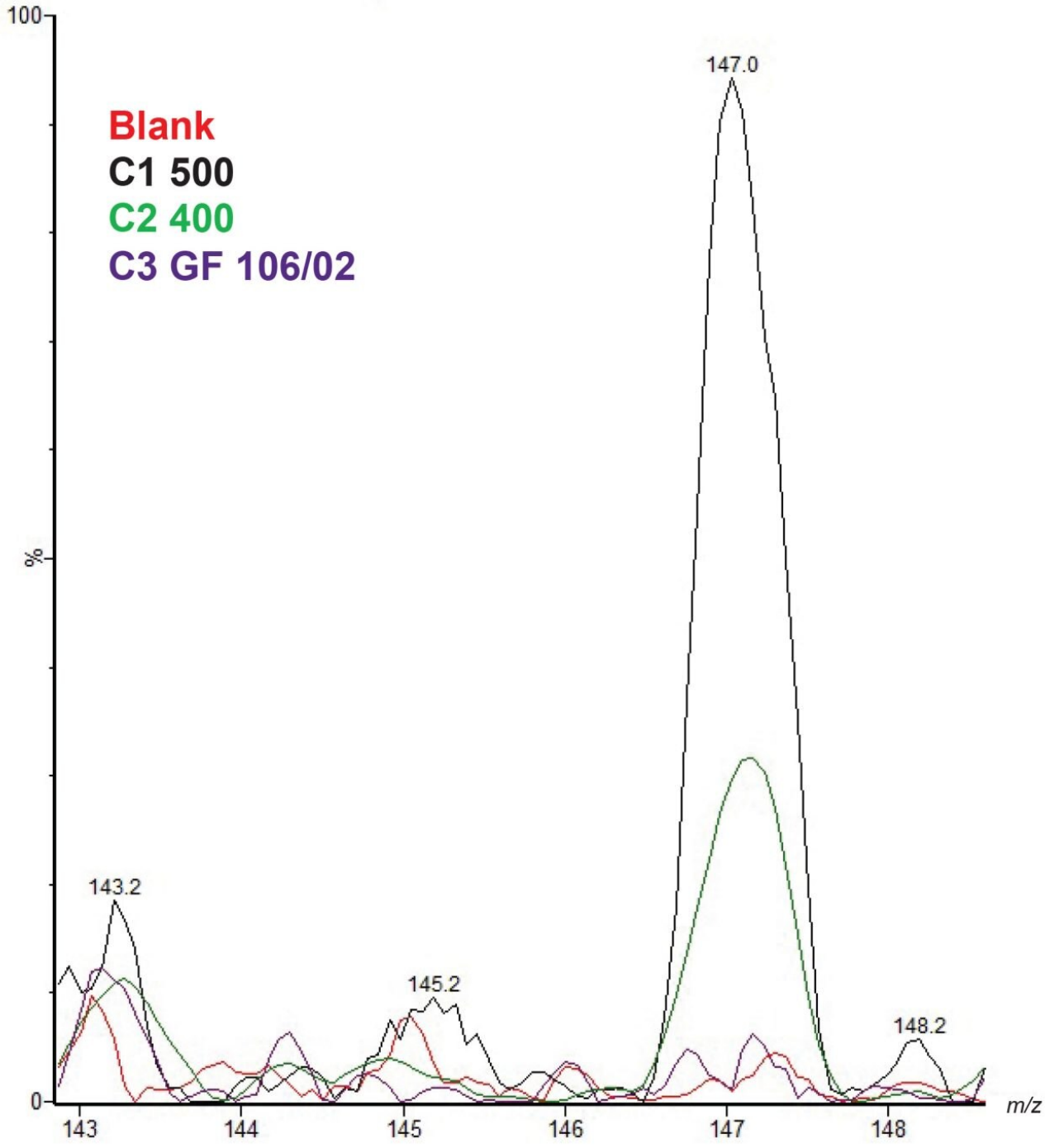

Figure 3. Overlayed XIC of m/z 147 showing higher abundance of this compound in sample C1 500 and C2 400 and absent in sample C3 GF 106/02.

Conclusion

These preliminary results demonstrate that the Waters ACQUITY QDa Detector coupled with SICRIT soft ionization represents a viable option for analytical laboratories aiming to profile the volatile organic compounds in biobased plastic products such as plastic bags. This analytical configuration is a cost-effective orthogonal technique that requires minimal sample preparation and allows for improved productivity of plastic products testing, aiming to quality control check the batch-to-batch quality of finished products where speed, reliability, and flexibility of analysis is key. In addition, the small footprint of the analytical configuration would benefit at site analysis with the Waters ACQUITY QDa detector containing an internal calibrant to assist simple instrument start up for fast and easy system operation.

References

1. Cecchi T., de Carolis C. "Assessment of the Safety of BioBased Products." Chapter in: Biobased Products From Food Sector Waste. *Springer, Cham*. 2021. DOI: 10.1007/978-3-030-63436-0_10.
2. Osorio, J. "Comparison of LC-ESI, DART, and ASAP for the Analysis of Oligomers Migration From Biopolymer Food Packaging Materials in Food (Simulants)." *Analytical and Bioanalytical Chemistry*. 2021. DOI: 10.1007/s00216-021-03755-0.
3. M. Weber, J-C. Wolf, C. Haisch. Gas Chromatography–Atmospheric Pressure Inlet–Mass Spectrometer Utilizing Plasma-Based Soft Ionization for the Analysis of Saturated, Aliphatic Hydrocarbons, *Journal of the American Society for Mass Spectrometry.* 2021 32 (7), 1707–1715. DOI: 10.1021/jasms.0c00476.
4. Robert A. Sanders, David V. Zyzak, Thomas R. Morsch, Steven P. Zimmerman, Peter M. Searles, Melissa A. Strothers, B. Loye Eberhart, Amy K. Woo. Identification of 8-Nonenal as an Important Contributor to "Plastic" Off-Odor in Polyethylene Packaging, *Journal of Agricultural and Food Chemistry.* 2005 53 (5), 1713–1716. DOI: 10.1021/jf048395j.

Acknowledgements

Jan-Christoph Wolf - Plasmion GmbH

Rachel Sanig, Cristian Cojocariu - Waters Corporation

Featured Products

ACQUITY QDa Mass Detector <https://www.waters.com/134761404>

MassLynx MS Software <https://www.waters.com/513662>

720007504, January 2022