National Institute of Standards and Technology
U.S. Department of Commerce

The Role of Mass Spectrometry in the Circular Economy of Plastics. Deconvolution of Mass-Spectral-Data Derived from Extracts of Polymer Mixtures

Yamil Simón-Manso, Tytus Mak, Edward P. Erisman, Kelly H. Telu, Xiaoyu Yang, Yuxue Liang, William E. Wallace, and Stephen E. Stein
Mass Spectrometry Data Center, Biomolecular Measurement Division, National Institute of Standards and Technology (NIST), Gaithersburg, Maryland 20899, USA

Introduction

The circular economy aims to eliminate waste by designing durable, reusable, repairable, and refurbish-able products (https://www.nist.gov/circular-economy). For plastics, this circular process, i.e., resource-extraction, manufacturing, selling, using, collecting, sorting, purifying, and reprocessing presents many challenges at different levels. For example, plastics sorting is dominated by unreliable manual techniques and only recently spectral-methods in the form of Raman-spectroscopy libraries have been proposed.

The NIST Mass Spectrometry Data Center (MSDC) has been working on a comprehensive approach to the chemical analysis of plastics-related compounds (PRC) using mass-spectrometry. Three types of ionizations, ESI, APCI, and EI have been used for increasing the number of PRC in our libraries. In this work, chromatographic profiles of compounds in our libraries have been used for the deconvolution of data from degraded polymers and mixtures.

Methods

Several polymer mixtures, with a number of components ranging from two to five, were extracted using different solvents and temperatures. Multiple runs of each extract were recorded at 3 different collision energies by using gradient elution and two types of ionization, APCI and ESI on a QTOF-6530. LC runs were performed using reversed-phase (C18/2.1x100mm/MPA: water-FA, MPB: methanol-FA). EI spectra were recorded using Agilent 5977-GC/MSD and 8890-GC systems. In-house software was used for clustering, annotating, and building libraries. For the deconvolution of mixtures, a linear combination of the chromatographic profiles of individual polymer extracts acquired under the same conditions was used as a template, and the coefficients were optimized to minimize the variance between the model prediction and the mixture data.

Contact information : Yamil Simon (ysimon@nist.gov)
NIST Mass Spectrometry Data Center; Visit chemdata.nist.gov website

Results and Discussion

Preparatory work

Recently, we have shown that EI, ESI, and APCI ionizations provide full coverage for the analysis of PRC. Since then, the MSDC has been working towards the improvement of the NIST mass spectral libraries regarding these compounds. With the number of PRC in the upcoming 2023 release of the libraries approaching all known PRC, simple-and-robust applications for the detection and quantification of PRC in complex mixtures, which may be difficult to analyze using other measurements, are important. In the context of a circular economy, the deconvolution of polymer fingerprints derived from mixtures can be applied to sorting, recycling, degradation, pyrolysis, etc., although the implementation may involve some engineering beyond the scope of this work.

Polymer Mixture Extractions

We have extracted mixtures of polyethylene, polypropylene, polystyrene, polycaprolactone, and nylon-6 using isopropanol and hexane at 50 °C for 24 hours at a ratio of 5 mL/g as it was done in previous work for the individual polymers. All extracts have been analyzed using LC-MS/MS, while the GC-MS work is still in progress. The data was processed and the major peaks (above 5% of the base peak) were identified using the most recent versions of the NIST libraries. Retention times and maximum peak intensities have been collected and used for the model (individual-polymers), and mixture data.

Deconvolution

In most cases, the deconvolution models have confirmed the identities of the polymers and the proportions of the polymers in the mixtures with high precision. The monomers are always present in the extracts with small amounts of other compounds, e.g., nylon-6/isopropanol extract contains Caprolactam, cis-2-Penten-1-ol, Cyclohexanol, etc. However, more challenging tests, using commercial polymers, random samples, or degraded polymers are still in progress. Eventually, similar work will be performed using pyrolysis data from polymers and polymer mixtures instead of extracts.

Software and Web Resources

Software have been developed for data visualization, organization, validation of MS data. The chemical structures of PRC were subjected to careful curation and registered in the EPA CompTox Chemicals Dashboard.

Conclusion

The incoming NIST23 includes more than 8,000 PRC. A comprehensive approach for the deconvolution of polymer extracts from mixtures using mass spectrometry has been developed.