

# NIST Mass Spectral Libraries in the Context of the Circular Economy of Plastics

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Cite This: <https://doi.org/10.1021/jasms.4c00349>



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**ABSTRACT:** The Mass Spectrometry Data Center (MSDC) has recently started improving existing libraries and creating new ones for identifying and analyzing plastics-related compounds (PRC) and materials (PRM) as part of the NIST circular economy program. PRC are small molecules of dissimilar chemical nature; hence, to increase coverage, we have used three types of ionizations: EI, ESI, and APCI. PRM are solids that include polymers, polymer mixtures, and commercial plastics, so we have used pyrolysis-gas chromatography (py-GC-MS) to create a new searchable library. First, we have increased the coverage of the existing libraries by including as many as possible commercially available PRC. Then, for testing the libraries and to deconvolute complex PRM mixtures, we have analyzed extractable and leachable (E&L) samples and pyrolysis products from one hundred standards of the most common polymers and some of their mixtures using LC-MS/MS, GC-MS, and py-GC-MS. In collaboration with the FDA, the EPA, and other non-government institutions, we are applying techniques, libraries, and tools to areas of interest to the circular economy of plastics, health risk assessments, and environmental challenges.

## INTRODUCTION

Recently, NIST has launched a circular economy program to help stakeholders and innovators find solutions to minimize or eliminate economic waste (<https://www.nist.gov/circular-economy>). Plastics play a crucial role in this project. The circular process involves resource extraction, manufacturing, sales, use, collection, sorting, purification, and reprocessing, and poses many analytical challenges. The use of spectral libraries is generally still scarce in this area. Regarding solid plastics-related materials (PRM), Raman and pyrolysis GC-MS libraries have been proposed as reliable techniques.<sup>1,2</sup> However, libraries are relatively popular for identifying contaminants of plastics-related compounds (PRC) in foods and drugs, packaging, containers, etc.<sup>3,4</sup> Most efforts have been oriented to homemade nontargeted screening strategies based on high-resolution accurate mass spectrometry. Because of the large number of peaks in untargeted experiments and many low-abundance components, some arbitrary data reduction and software-based cleaning strategies are necessary, making it difficult to set standard criteria for false rate determination. Our objective with this commentary is to highlight recent additions of standard reference spectra to the NIST mass spectral libraries that may be very useful to support these strategies. Standard reference spectra are generated from pure samples and many spectra with no arbitrary cleaning procedures or software manipulations other than clustering.

The NIST Mass Spectrometry Data Center (MSDC) has been developing a comprehensive approach to PRC and PRM chemical analysis using mass spectrometry. This is oriented toward developing standards to support the research work in the circular economy of plastics. We have divided the work

into five stages: (i) build libraries that have complete coverage of PRC, (ii) test the libraries through the chemical analysis of extractable and leachable compounds (E&L) from standard polymers using liquid and gas chromatography coupled to mass spectrometry (LC-MS/MS and GC-MS), (iii) chemical analysis of standard polymers and polymer mixtures using pyrolysis gas chromatography–mass spectrometry (py-GC-MS) and chemical ionization (CI-GC-MS), (iv) multiple applications to commercial plastics that include, but are not limited to, identification of polymers in complex processes such as polymer sorting, catalytic depolymerization, pyrolysis, etc., (v) build a public repository for data and tools.

## NIST MASS SPECTRAL LIBRARIES FOR PLASTICS-RELATED COMPOUNDS

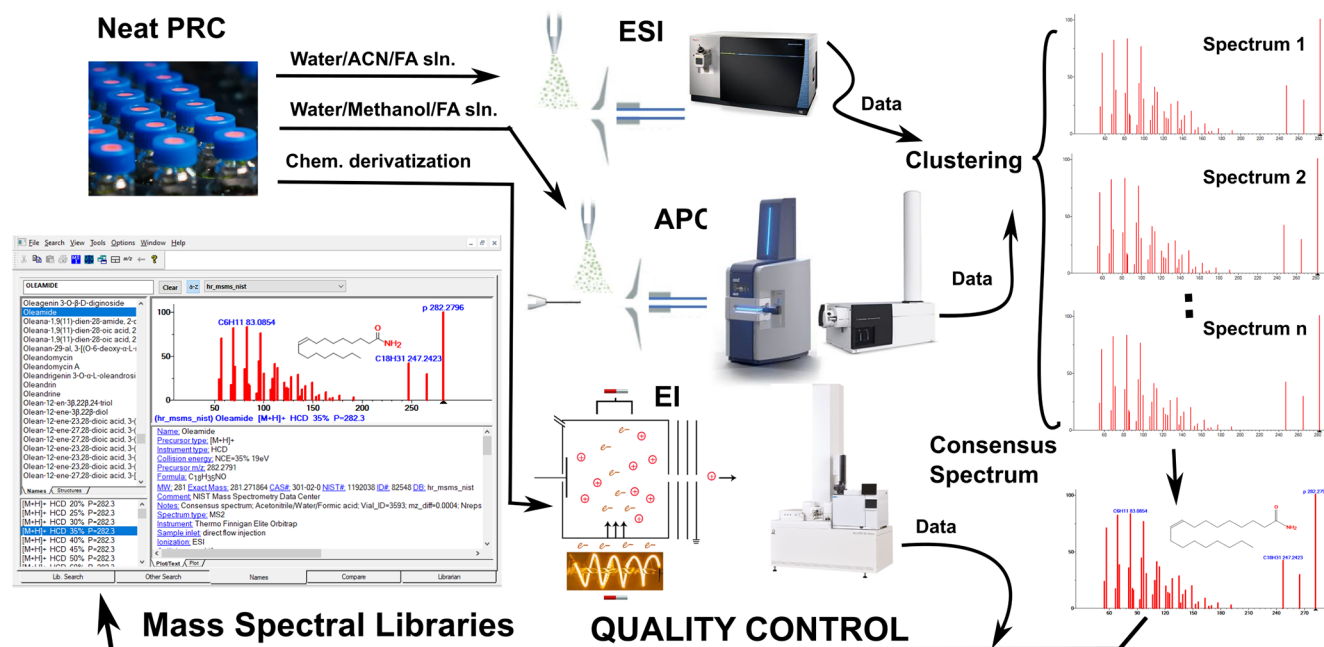
Expanding the scope of the NIST libraries has been a continuous effort, and new libraries are published every three years.<sup>5</sup> Figure 1a shows the significant steps in building libraries, sample procurement and preparation, ionization, acquisition of multiple spectra, spectral clustering, and quality control. In-house software was used for clustering, annotating, and building libraries.<sup>6–8</sup> It is worth adding that individual spectra are subjected to manual and software inspection to

**Received:** August 20, 2024

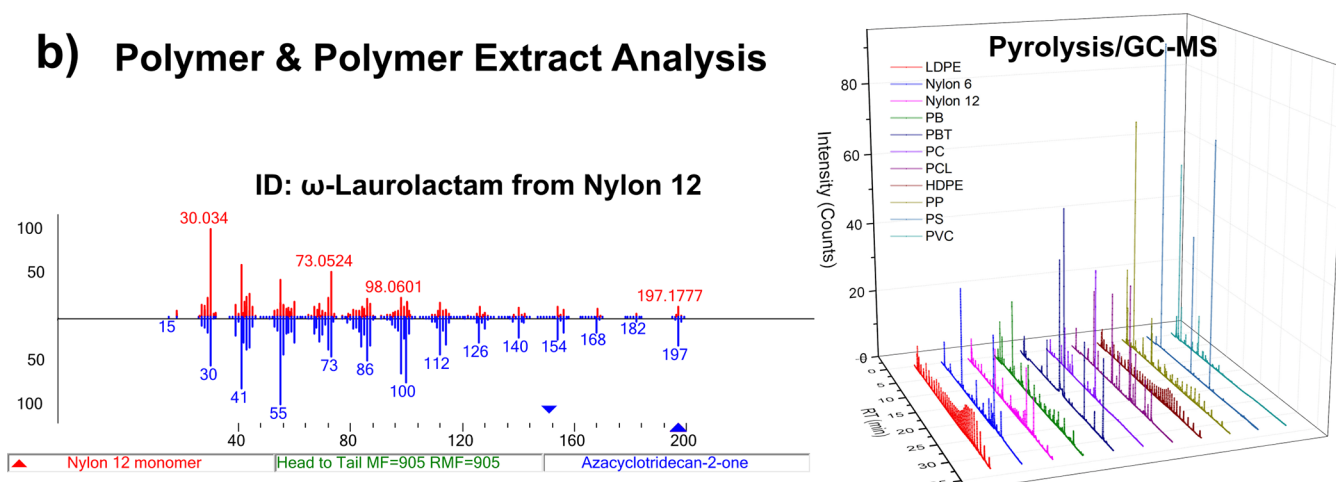
**Revised:** December 12, 2024

**Accepted:** December 16, 2024

## a) Data Acquisition & Mass Spectral Library Building



## b) Polymer & Polymer Extract Analysis



**Figure 1.** (a) Library building workflow includes pure compound procurement, sample preparation, infusion, ionization (ESI, APCI, EI), spectral acquisition, spectral clustering, consensus spectrum creation, and quality control (informatics and manual). (b) On the left side, a library match example is performed with the EI library,  $\omega$ -laurolactam, identified in a nylon-12 extract. On the right side are pyrolysis chromatograms for a set of the most used polymers.

validate fragmentation patterns and are revised by multiple researchers.

We started by increasing the number of PRCs in our libraries using three types of ionization: Electrospray Ionization (ESI), Electron Ionization (EI), and Atmospheric Pressure Chemical Ionization (APCI). Compounds have been selected and ordered based on a publication that collected more than 10,000 compounds, which include monomers, additives such as plasticizers, dyes, fire retardants, and processing aids of the plastics industry.<sup>9</sup> Most of these compounds are small molecules amenable to analysis by mass spectrometry. Each ionization type has a dedicated library. In previous work, we have shown that EI, ESI, and APCI ionizations provide full coverage for the chemical analysis of PRC.<sup>10</sup> In the following,

we discuss the essential elements of library building and significant updates regarding plastics and related materials.

### ■ NIST/EPA/NIH EI-GC-MS LIBRARY

As mentioned, the library spectra are obtained from pure compounds using appropriate chemical derivatization procedures.<sup>11</sup> Usually, Agilent 5977 Series MSD Systems and DB-5 ms GC Columns are used to obtain the spectra. The initial oven temperature is 50 °C, the ramp rate is 15 °C/min, the final temperature is 300 °C, and the hold time is 30 min.

In addition to the increased number of compounds, the 2023 version of the EI library enables the application of retention index and compound ubiquity to scoring and hit list formation for its over 347 K compounds. Each library compound is represented by either one or more experimental

Table 1. APCI Mass Spectral Library Identifications for the Polyethylene Extract Using 2-Propanol as the Extraction Solvent<sup>a</sup>

Name	Exp <i>m/z</i>	RT <sup>b</sup> (min)	1/K0 <sup>c</sup> (V s/cm <sup>2</sup> )	Lib <i>m/z</i>	DTXSID <sup>d</sup>	DP <sup>e</sup>	MP <sup>f</sup>	Use <sup>g</sup>
Tetradecamethylcycloheptasiloxane	519.1361	11.54	0.9938	519.1388	DTXSID8059348	869	10	? Organosilicon polymer production
Diphenylamine	170.096	0.44	0.62	170.0964	DTXSID4021975	900	6	Antioxidant
Oleamide	282.2785	11.12	0.8988	282.2791	DTXSID6027137	861	24	Processing aid
1,3:2,4-Bis(3,4-dimethylbenzylidene) sorbitol	387.1797	7.54	0.9129	387.1802	DTXSID4051297	937	5	Nucleating agent
Benzaldehyde	107.0493	0.32	0.4958	107.0491	DTXSID8039241	989	3	?
N,N-Dibutylformamide	158.1532	7.29	0.6331	158.1539	DTXSID3022114	845	3	Processing aid
Bis(3,4-dimethyldibenzylidenesorbitol)	415.2108	8.05	0.9702	415.2115	-	961	3	Nucleating agent
Tris(2,4-di- <i>tert</i> -butylphenyl) phosphate	663.4526	14.11	1.3289	663.4537	DTXSID20893779	856	5	Antioxidant
1-Methyl-2-pyrrolidinone	100.0758	1.12	0.4975	100.0757	DTXSID6020856	923	3	Solvent
1,6-Dioxacyclododecane-7,12-dione	201.1125	0.42	0.642	201.1121	DTXSID70228330	937	9	Cross-linking agent
Bis(2-ethylhexyl) phthalate	391.284	13.02	1.0082	391.2843	DTXSID5020607	954	6	Plasticizer
4-Vinylpyridine	106.0653	1.03	0.496	106.0651	DTXSID0051499	868	3	Anticorrosive coatings
3,5-Di- <i>tert</i> -butyl-4-hydroxybenzaldehyde	235.1687	9.07	0.7517	235.1693	DTXSID7057658	928	4	Antioxidant
Diisobutyl phthalate	279.1585	9.41	0.7891	279.1591	DTXSID9022522	967	5	Plasticizer

<sup>a</sup>The LC-MS/MS runs were carried out on a Thermo Vanquish LC coupled to a Bruker timsTOF PRO 2. Identifications are given as is. However, compounds found in blanks, suspected carryovers, matches to neutral losses, or in-source fragments were removed (only matches to  $[M + H]^+$  ions are included). <sup>b</sup>Retention time. <sup>c</sup>Inverse reduced ion mobility. <sup>d</sup>CompTox Chemicals Dashboard identifier. <sup>e</sup>Dot Product. <sup>f</sup>Matching Peaks. <sup>g</sup>Question marks in the column "Use" mean that the compound is not expected in this material.

retention index values or a reliable AI estimated value.<sup>12</sup> Compound ubiquity (or rare compound) corrections contain the number of citations for each compound among dozens of listings of chemicals of practical interest.

Regarding the coverage of the library for PRC, the EI-GC-MS library now comprises 394,054 spectra for 347,100 compounds, 3,285 of which are PRC.

### TANDEM MASS SPECTRAL LIBRARY

Although this library contains spectra from different instruments and experimental conditions, in recent times, the spectra are usually obtained by the infusion of a solution of the pure compound using a Thermo Ultimate 3000 nanoLC coupled to a Thermo Orbitrap Elite instrument. For these experiments, each compound is dissolved in a 50:50 water: acetonitrile solution containing 0.1% formic acid and injected for 1 h at a flow rate of ~300 nL/min). The MS settings are optimized to obtain a significant number of spectra, usually thousands, by using different MS/MS dissociation modes. The spectra are clustered and subjected to quality control to produce a consensus spectrum for the library.<sup>6-8</sup>

The NIST23 Tandem Mass Spectral Library<sup>13</sup> features an extensive collection of 2.4 million mass spectra for 51,000 compounds, a 60% increase from the previous release, with thousands of new compounds added annually. The library's central feature is the availability of high- and low-resolution mass spectra from collision cells and ion traps, in both positive and negative modes, using ESI and APCI ionization sources and MS<sup>n</sup> and various precursor types, including in-source ions. The library contains spectra of human and plant metabolites, pesticides, contaminants, drugs, sugars, bioactive peptides, lipids, and extractable and leachable compounds analyzed with ESI sources. This high-quality, comprehensive reference library is a crucial data source for compound identification and has been widely used in metabolomics, human health, environmental science, and other fields. The library includes more than 1300 PRC and contaminants.

### APCI MASS SPECTRAL LIBRARY

ESI and EI are well established in their field of applications. However, the use of APCI has been restricted to specific chemical classes. The experiments are similar to the ESI experiments, but the compounds are dissolved in a 2:98 water: methanol solution containing 0.1% formic acid, and conventional chromatography is used instead of nanoLC. The APCI library comprises 561 compounds (5,714 spectra), all PRC. It includes most compounds from the E&L Safety Information Exchange Consortium database (ELSIE; <https://www.elsiedata.org/elsie-database>). Surprisingly, many aromatic and branched hydrocarbons and compounds hardly ionizable in an ESI source, such as esters and ethers, show significant APCI ionization. Many APCI MS/MS spectra in the library have not been previously reported.

Overall, the number of PRC in the NIST mass spectral libraries is over 6,000 pure compounds and probably higher, depending on the criteria for determining which compounds are related to plastics. Table S1 of the Supporting Information lists the PRC and chemical structures available in the EI-GC/MS and ESI-LC-MS/MS libraries and reported in the ES&T article's list mentioned above. Table S2 lists the compounds and structures in the APCI-LC-MS/MS library.

It is worth noting that the chemical identification process using the tandem mass spectral libraries goes beyond library matching and develops into a multidimensional process.<sup>14-21</sup> For example, as shown in Table 1, mass accuracy, retention times, inverse reduced ion mobility, and/or collision cross-section values, and the expectation of finding a compound in a material based on its use are consistently used to increase reliability.

### PYROLYSIS GC-MS MASS SPECTRAL LIBRARY

The NIST mass spectral libraries include only pure small molecules. Therefore, polymer data and pyrolysis product



spectra were implemented in a separate database and searchable library.

We have performed py-GC-MS of polymers and their mixtures; for this purpose, using a filament-type pyrolyzer (Gerstel-Pyro) connected to a high resolution time-of-flight mass spectrometer (JEOL, GC-Alpha) equipped with electron ionization and multiple soft ionization techniques, i.e., field, photo, and chemical ionization. The method ramps pyrolysis up to 650 °C at 10 °C/s (note that higher temperatures pyrolyze a specific polymer to a greater extent, and individual polymers will start to pyrolyze at different temperatures) using the following chromatographic conditions: GC column: 15 m × 25 mm × 25 μm RXISHT (high temp); flow 1.2 mL/min; oven ramp 40 °C (3 min) 15 °C/min to 400 °C (2 min) for late eluting pyrolysates.

A demo library that includes polyethylene, isotactic polypropylene, isotactic poly(1-butene), polystyrene, polycaprolactone, Nylon-6, Nylon-12, polycarbonate, polyvinyl chloride, poly(butylene terephthalate), poly(acrylic acid), poly(vinyl alcohol), polysulfone, nylon-6/6, nylon-11, cellulose, methylcellulose, ethyl cellulose, phenoxy resin, polyacetal, polyacrylonitrile, and polyacrylamide is available with the [Supporting Information](#) and also included is an R shiny script to search the polymer library. It converts AMDIS \*.elu output to \*.mspec for batch searching the library using MSPepSearch with RI constraints and gives a final score for the polymer. Some challenges remain, e.g., poor chromatographic peak shapes for highly polar pyrolysates. Also, the automation and visualization of the process are still limited (preprocessing in AMDIS and lack of graphical representation of the chromatogram or spectra in the R Shiny script).

Although some useful commercial pyrolysis libraries exist—for example, Frontier Lab (<https://www.frontier-lab.com/products/multi-functional-pyrolysis-system/255177/>) and the product from CDS Analytical, Inc. MSChrom + Py-GC-MS Database (<https://www.cdsanalytical.com/py-gc-ms>)—they are mostly restricted to being used in a nonbatch processing mode and are not fully searchable. Also, these libraries usually generate a spectrum by averaging all of the spectra for a given sample. These average spectra are then used to identify samples or deconvolute data from mixtures (polymers). In our approach, we characterize each pyrolysis product individually and export all spectra that pass the quality control procedure to a library of individual pyrolysis products. This procedure does not produce reference data. However, py-GC is one of the few techniques for analyzing PRM (solids). We use this library to deconvolute complex polymer mixtures using the spectra of individual pyrolysates. The library is freely available.

## ■ EXTRACTABLE AND LEACHABLE TESTING

To test the libraries, LC-MS/MS, py-GC-MS, and CI GC-MS and the new version of the mass spectral libraries were employed to analyze E&Ls and pyrolysis product samples from one hundred standards of the most used polymers. The Polymer Sample Kit, Catalog #205 from Scientific Polymer Products Inc., has been utilized. This kit contains diverse polymers, including polyolefins, vinyl polymers, polyesters, polyamides, polycarbonates, and others. Polymers and polymer mixtures consisting of a few components (two to five) were extracted using different solvents, temperatures, and weight (surface area) to volume ratios.

The extractions were performed using three solvents, water, isopropanol, and hexane, at 50 °C for 24 h at a 10 mg/mL ratio

adapted from previous work,<sup>14</sup> adding extra precautions. Due to the volatility of most organic solvents, we have used closed pressure-resistant glass vessels with a headspace of two-thirds of the container volume and a shaker with shaking and temperature control.

Multiple extraction samples were analyzed at six different collision energies using gradient elution and two types of ionization (APCI and ESI) on an Agilent 6530 QTOF and a Bruker timsTOF Pro 2. The latter instrument allows for collecting collisional cross-sectional (CCS) data. LC-MS runs were performed using reversed-phase chromatography (C18/2.1 × 100 mm, mobile phase A: water-0.1% formic acid (FA), mobile phase B: acetonitrile-0.1%FA).

All extracts were analyzed by using LC-MS/MS. GC-MS experiments are in progress. For polar polymers, the corresponding monomers were usually found in the extracts with smaller amounts of other compounds; for example, the nylon-6/isopropanol extract contains caprolactam, cis-2-penten-1-ol, cyclohexanol, and other small molecules.

The data was processed, and the major peaks (above 1% of the base peak) were identified using the most recent versions of the NIST libraries. [Table 1](#) shows the hits list for the polyethylene IPA extract using timsTOF data and library matching the APCI library.

Library identification depends on the number of compounds in the library, the nature of the compounds, the quality of the spectra, and the library search algorithm, among other factors. The hit lists from LC-MS/MS experiments for different polymers fluctuate between 10 and about 100 compounds. [Table 1](#) is not very extensive compared to existing publications.<sup>3,4</sup> There are several reasons for that. We have used pelletized polymers, so they are less rich in additives than terminated materials used in consumables. However, they are commercially available as “standards,” so other researchers can reproduce our data. Also, we used milder experimental conditions to perform the extractions; the main reason is that plastics leach micro- and nanoparticles into the solution in a high proportion, contaminating columns and instruments and affecting reproducibility. Reports of particle leaching have been documented before.<sup>22,23</sup> This has also been demonstrated in our laboratory using Flow Imaging Microscopy experiments. For example, we observed that particle size distributions change dramatically and continuously during and after polymer extractions if the particles remain in contact with the solvent. See [Supporting Information](#) for the experiment using 50-μm polyethylene particles in IPA. This topic is beyond the subject and scope of this commentary and will be published elsewhere. It is worth mentioning that [Table 1](#) shows the hit list of the most challenging polymer and the smallest library (tandem APCI). The library contains only standard reference spectra, no in-silico or spectra derived from untargeted analysis. We have hundreds of these hit lists of E&L identifications corresponding to different polymers using the EI-GC/MS, ESI-LC-MS/MS, and the APCI libraries. We have shared six of them in the [Supporting Information](#) (see tables from [Table S3](#) to [Table S8](#)). All these data will be freely available in public repositories such as the EPA CompTox Chemicals Dashboard.<sup>24</sup> On the other hand, the GC-MS experiments for all polymers show more populated hit lists containing between 400 and 1200 identifications (see tables from [Table S10](#) to [Table S22](#) in the [Supporting Information](#)). The NIST EI-GC-MS contains spectra of almost half a million compounds, many of which are PRC. These lists are provided “as is,” only

subtracting hits found in the blanks. We must remark that these identifications are derived from matching standard reference spectra.<sup>25</sup>

Regarding identifying compounds not commercially available in their pure form, we use a different type of library called the Annotated Recurrent Unidentified Spectra (ARUS) library. These libraries are built from multiple recurrent spectra found in the untargeted analysis that do not match any spectra in the NIST mass spectral libraries in a direct search.<sup>14–21</sup> Then, they are annotated using a procedure called hybrid search.<sup>18</sup> Table S9 contains the hit list of a hybrid search that included more than 200 compounds. These spectra are added to an ARUS library with the suggested annotation. Other high-quality spectra that do not find a match in a hybrid search are added to the ARUS library as known unknowns.

## DECONVOLUTION OF POLYMER MIXTURES

For the analysis of the polymer mixtures, the polymers were first identified by spectral matching. Then, the deconvolution of mixtures was performed using a linear model based on the chromatographic profiles of individual polymers, using retention time (retention index for GC-MS) and peak area acquired under the same conditions as those for the mixture; the coefficients were optimized to minimize the variance between model prediction and mixture data. In most cases, the deconvolution models confirmed the identities of the polymers and the proportions in the mixtures. Although these mixtures are simple compared to commercial polymers, the aim is to provide a reliable and consistent reference for metrology when analyzing commercial plastics. More challenging tests are underway in our laboratory using commercial polymers, catalytic depolymerization products, and environmentally degraded polymers. Also, recently, we have incorporated techniques such as Multivariate Curve Resolution (MCR)<sup>26</sup> into the workflow of deconvoluting polymer mixtures.

Similar work was performed using py-GC-MS. Figure 1b shows an example of pyrolysis product identification and a set of polymer pyrograms.

## OTHER APPLICATIONS AND DATA DISSEMINATION

A valuable byproduct of this work has been the identification of many E&L contaminants in NIST Standard Reference Materials of human blood urine and breast milk,<sup>15–20</sup> as well as in CHO cells and culture media.<sup>21</sup> We have identified many phthalates and phthalate metabolites, bisphenol A, and other pollutants in these samples. Usually, this type of analysis requires many analytical techniques, as outlined by ISO standards, USP-compliant testing, and governmental and international regulations.<sup>27</sup> Also, in collaboration with the FDA, we have begun analyzing many plastics used in biomedical applications such as infusion bags, drug containers, orthopedic casts, etc.

The plastics-related compounds mentioned in this work were curated, registered, and shared through the EPA CompTox Chemicals Dashboard.<sup>24</sup> Just as versions of the ELSIE list are available on the Dashboard (<https://comptox.epa.gov/dashboard/chemical-lists?filtered=&search=ELSIE>), new chemicals resulting from this work, and future iterations, will be added to the Dashboard for public dissemination.

## ASSOCIATED CONTENT

### Data Availability Statement

All data generated with this project is available upon request until a local repository is completed.

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jasms.4c00349>.

Title page and list of supporting tables (PDF)

PRC NISTMS library (XLSX)

Acrylonitrile butadiene copolymer, hexane, negative mode (XLSX)

Cellulose propionate, isopropanol, positive mode (XLSX)

Methylvinylether maleic acid copolymer, isopropanol, positive mode (XLSX)

Poly-1-butene isotactic, isopropanol, positive mode (XLSX)

Purified Zein, isopropanol, negative mode (XLSX)

Methylvinylether maleic acid copolymer, isopropanol, positive mode (XLSX)

Methylvinylether maleic acid copolymer, isopropanol, positive mode, hybrid search (XLSX)

Nylon 6 (XLSX)

Nylon 12 (XLSX)

Polybutylene terephthalate (XLSX)

Poly-1-butene, isotactic (XLSX)

Polycaprolactone (XLSX)

Polycarbonate MW36000 (XLSX)

Polycarbonate MW45000 (XLSX)

Polyethylene, low density (XLSX)

Polyethylene (XLSX)

Polypropylene isotactic (XLSX)

Polystyrene MW1200 (XLSX)

Polystyrene MW260000 (XLSX)

Polyvinyl chloride (XLSX)

Compounds and structures in the APCI-LC-MS/MS library (TXT)

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Y.S.-M., conceptualization with the support of S.E.S. and W.E.W.; E.P.E., GC-data acquisition, and interpretation of pyrolysis data; Y.L., X.Y., P.N., tandem mass library data acquisition, and interpretation; M.C.B., Y.S.-M., T.B., A.Z. APCI (and ion mobility data) acquisition, and interpretation; J.Y., S.W., A.Z., Y.S.-M. techniques for extractable and leachable analysis; T.M., X.Y., A.J.W. informatics and software; A.J.W., DSSTox database and CompTox Chemicals Dashboard; Y.S.-M., manuscript preparation, and figure; Y.S.-M., T.M., M.C.B., W.E.W., and S.E.S., reviewing and editing the manuscript.

### Notes

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The authors declare no competing financial interest.

PRC chemical structures: <https://www.epa.gov/comptox-tools/comptox-chemicals-dashboard>.

Software and Web Resources: Software was developed for processing, visualizing, organizing, and validating MS data. Most of the software is available at <http://chemdata.nist.gov>. The pyrolysis mass spectral library demo is freely available: [https://chemdata.nist.gov/download/other\\_libraries/PolymerPyrolysis.zip](https://chemdata.nist.gov/download/other_libraries/PolymerPyrolysis.zip). The full version will be freely available soon. To install the NIST library browser, go to <https://chemdata.nist.gov/dokuwiki/doku.php?id=chemdata:nistlibs>, download the installation program, and follow the instructions. Notice that identifications based on library matching are not authentic and always require additional validation. The polymers used in this work are not pure. They are just less complex than commercial materials.

### ACKNOWLEDGMENTS

The authors thank Dr. Kathryn Beers for her suggestions and insights on plastics and the financial support of the NIST Circular Economy Program. They also thank Dr. Nirina R. Andriamaharavo and Dr. Anzor Mikaia for their valuable comments about the GC-MS library work.

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