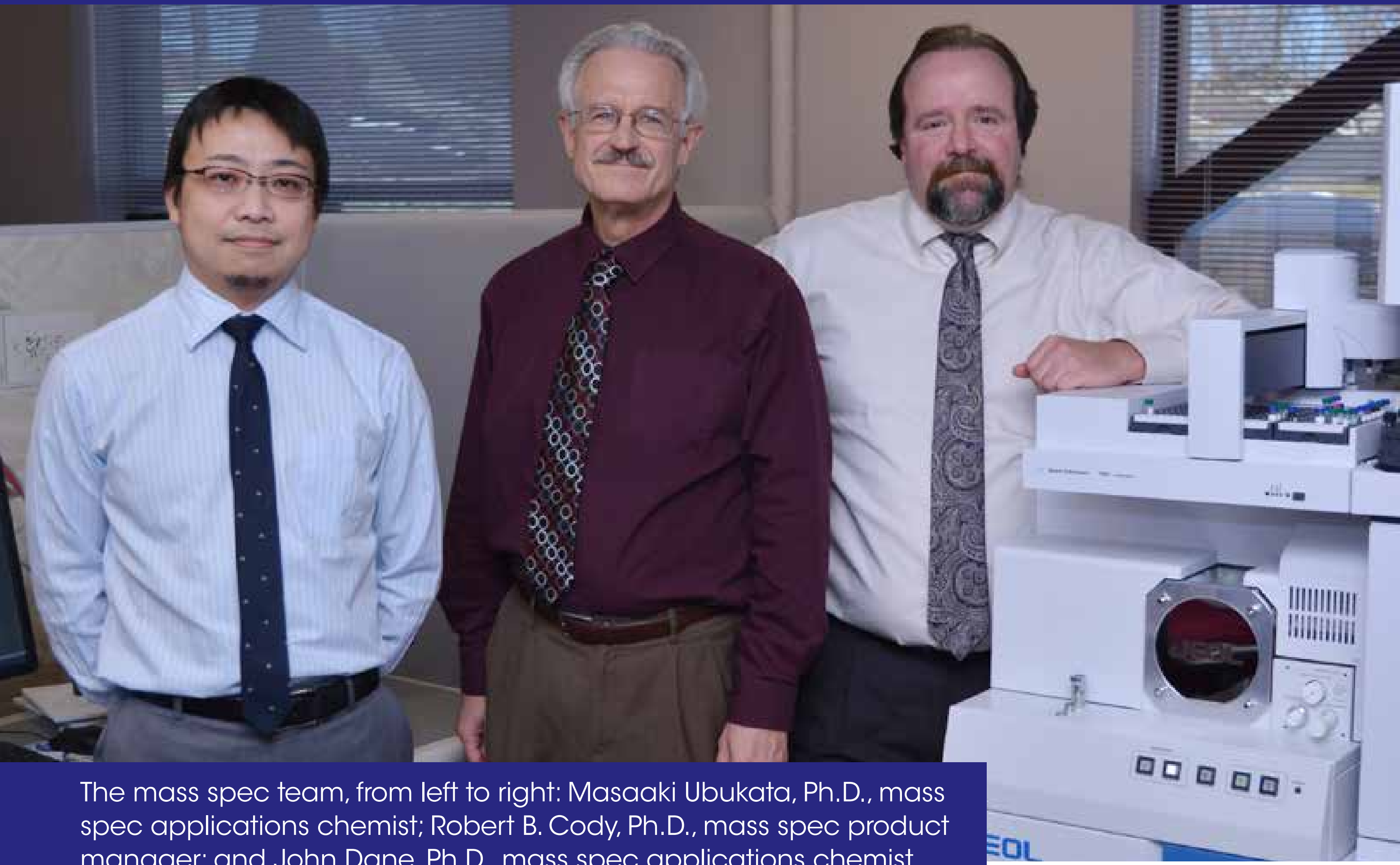

The mass spec team, from left to right: Masaaki Ubukata, Ph.D., mass spec applications chemist; Robert B. Cody, Ph.D., mass spec product manager; and John Dane, Ph.D., mass spec applications chemist.

From DUST to DATA

In a recent collaboration, Ontario's Ministry of the Environment and Climate Change recently collaborated with JEOL USA to identify pollutants found in electronics waste recycling using new analytical methods.

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Dust created by recycling electronics waste is known to emit pollutants that can find their way into the environment and contaminate air, land, and water. These pollutants are composed of complex compounds, many of which contain chlorine and bromine, elements found in the most persistent organic pollutants (POPs). Among these are socalled legacy contaminants such as polychlorinated biphenyls (PCBs), and polychlorinated terphenyls (PCTs), as well as brominated flame retardants such as polybrominated diphenyl ethers (PBDEs) and other emerging environmental contaminants.

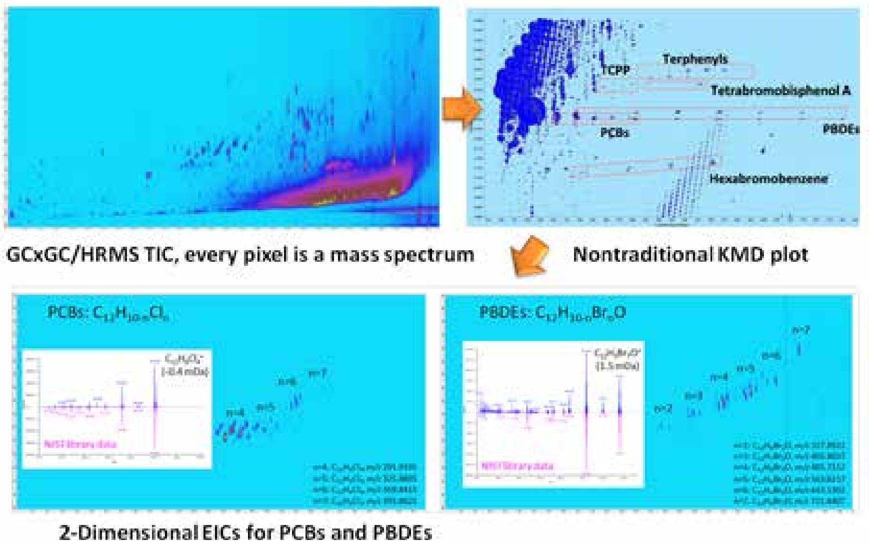
The Ontario Ministry of the Environment and Climate Change (Ontario MOE) recently collaborated with JEOL USA, a supplier of analytical instruments including mass spectrometers, electron microscopes, and NMR spectrometers, to analyze the complex composition of the dust swept from the floor of an electronics recycling facility in Canada. Such a collaboration falls within the Ontario MOE's mandate which includes using science and research to develop policies, legislation, regulations and standards, along with enforcing compliance with the province's environmental laws and tracking environmental progress over time.

The collaboration with JEOL grew out of informal discussions at the 5th Multidimensional Chromatography Workshop held at the Ontario MOE in January 2014. Researchers at the MOE had previously applied a data-processing method called a Kendrick Mass Defect (KMD) Plot to identify families of pollutants in high-resolution mass spectra. Because the JEOL AccuTOF-GCV combines comprehensive two-dimensional gas chromatography (GCxGC) with high-resolution mass spectrometry (HRMS), it seemed possible that the KMD approach could be extended to GCxGC/HRMS data.

KMD Plots were originally developed in the 1960s by Edward Kendrick at Esso Research and Engineering Company in New Jersey to apply a simple data transformation technique to interpret high-resolution mass spectra of complex petroleum samples. HRMS data can be represented graphically by constructing a KMD Plot, which can then be used to guide the interpretation of high-resolution mass spectra for highly complex mixtures. The traditional KMD Plot is used to find families of compounds that have the same core composition, but differ only by the degree of alkylation (that is, the number of CH_2 substitutions). 'Non-traditional' KMD Plots can also be applied to find other families of compounds, for example those that differ by the number of chlorines, bromines, or hydroxyl groups. To date, only a few publications (all from JEOL customers) have appeared in the literature combining GCxGC analysis with high-resolution mass spectra.

The Ontario MOE provided the dust sample for analysis, and JEOL analyzed the samples with the objective of finding polyhalogenated contaminants. A GC system combined with a ZX2 GCxGC thermal modulator from Zoex Corporation and the JEOL AccuTOF-GCv 4G high-resolution time-of-flight mass spectrometer were used for the analyses. The testing yielded enormous data sets detailing the many compounds present in these samples. The number of compounds revealed in just a single GCxGC/HRMS analysis made identification and interpretation a challenge for any lab. New software capabilities were needed to assist in the interpretation of the huge volume of data.

FIGURE 1. Non-targeted Analysis for Dust from Electronics Recycling Facility with GCxGC/EI and Nontraditional Dendrick Mass Defect Plot



Consequently, JEOL worked closely with GC Image and the University of Nebraska-Lincoln on a new software tool for the special KMD analysis. GC Image developed the new software tools, which were used to identify families of polyhalogenated contaminants in the mass spectra of the dust that were then mapped back onto the 2D chromatogram for further analysis and interpretation.

This approach allows researchers to find the proverbial "needle-in-the-haystack" contaminants in complex mixtures and paves the way for discovery of new or unexpected polyhalogenated compounds that may be widely distributed in the environment. As an example, a compound with the elemental composition $C_{11}H_7NO_2Cl_5^+$ was identified from its electron ionization (EI) mass spectrum. Its origin and purpose is not yet known, but its structure is similar to the Dechlorane family of flame retardants. Being a composite of dust from a consumer electronics recycling facility, it may be widely distributed in the environment.

The solution for making sense of all this data was found in this combination of new techniques and reported in a collaborative publication by JEOL USA, the Ontario MOE, GC Image, and the Zoex Corporation. The paper has been accepted for publication in the *Journal of Chromatography A.* The forthcoming article is entitled "Analysis of electronics waste by GCxGC combined with high-resolution mass spectrometry: using accurate mass information and mass defect analysis to explore the data", and is authored by Masaaki Ubukata, Karl J. Jobst, Eric J. Reiner, Stephen E. Reichenbach, Qingping Tao, Jiliang Hang, Zhanpin Wu, A. John Dane, and Robert B. Cody (doi:10.1016/j.chroma.2015.03.050).

Conclusion

New software tools were developed to interpret the large data sets obtained from comprehensive two-dimensional gas chromatography (GCxGC) combined with high-resolution mass spectrometry (HRMS). The software borrows and updates an old technique (Kendrick mass defects) from the petroleum industry and applies it to identifying environmental contaminants in GCxGC/HRMS data. Furthermore, this updated technique can be adapted for possible applications to many other problems. ***LPN***