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Letter to the Editor

To the Editor-in-Chief
Sir,

EDit: a computer program to assist in the presentation of energy-dependent mass spectra

Energy-dependent mass spectrometry[1] (ED-MS) uses collision-induced dissociation[2] (CID) to fragment ions, generating a 2D projection (collision energy vs. *m*/*z*) of a 3D surface (the 3rd dimension, ion intensity, is on the axis perpendicular to the plane). The approach has most frequently been applied to electrospray ionization (EDESI),[3] but we have also shown that varying other parameters capable of fragmenting ions (temperature, laser power) can generate related maps.[4] Current mass spectrometry software does not allow facile production of ED spectra, as the 'Map' function produces an image that is difficult to manipulate and ill-suited for publication purposes. We present a program ('*EDit*') for conversion of MassLynx™ (Waters Corporation[5]) continuum spectra into a matrix format suitable for direct introduction into scientific graphing packages such as Origin®[6] or SigmaPlot®,[7] or even Excel®.[8]

To date, we have produced EDESI spectra using the Map function of the MassLynx software. This generates a plot with scan number (or time) on the *x* axis and *m*/*z* on the *y* axis in bitmap (.bmp) format. The appearance of the bitmap can be altered using various colour schemes, including one which may be user-defined by selection of appropriate colours (a greyscale being most suitable for publication purposes). Selecting a *Map Intensity Range* start value of >0 (e.g. 2%) minimizes the contribution of noise to the spectrum, and an end value of <100 similarly assists in the enhancement of minor peaks in the spectrum. Playing these two values off against one another makes for a clear, uncluttered map. Any graphics program, even one as simple as Microsoft® Paint,[8] allows transformation (rotation and reflection) of the data into a conventional format (*m*/*z* increasing left to right on the *x* axis). The spectrum summing all the data used to produce the map is added to the top of the spectrum, and the scale moved to the bottom of the map. The *y* axis is relabelled with cone (or collision) voltage replacing scan number. These procedures are time-consuming and the attainable resolution is limited by the bitmap format. A more convenient, flexible method is highly desirable.

The MassLynx™ proprietary file format (.raw) may be converted into ASCII format by use of the DataBridge program (part of the MassLynx™ suite). The resulting (.txt) file is not in a format suitable for scientific graphing programs, as it consists of sequential spectra listed as *m*/*z* vs. intensity (see Table 1).

The MassLynx software compresses the data by eliminating sequential zero intensity values, as is clear upon inspection of the list of data in Table 1. Each scan in the continuum spectrum is listed sequentially, and, even with the compression mentioned, the files are large (typically tens of MB). Graphing programs require data in a matrix format to plot 3D graphs, be this in the form of a color map, a contour map, or a 3D surface. We have written a program called '*EDit*', which converts the ASCII file into a matrix (in comma

Table 1. Part of the ASCII file produced from a .raw file using DataBridge

FUNCTION 1	
Scan	1
Retention time	0.052
49.7303	0
79.9002	0
79.9050	1
79.9098	0
90.1620	0
90.1671	1
90.1722	0
109.5832	0
109.5888	1
109.5944	0
153.5465	0
153.5531	1
153.5598	0
194.3987	0
194.4062	1
.....	.

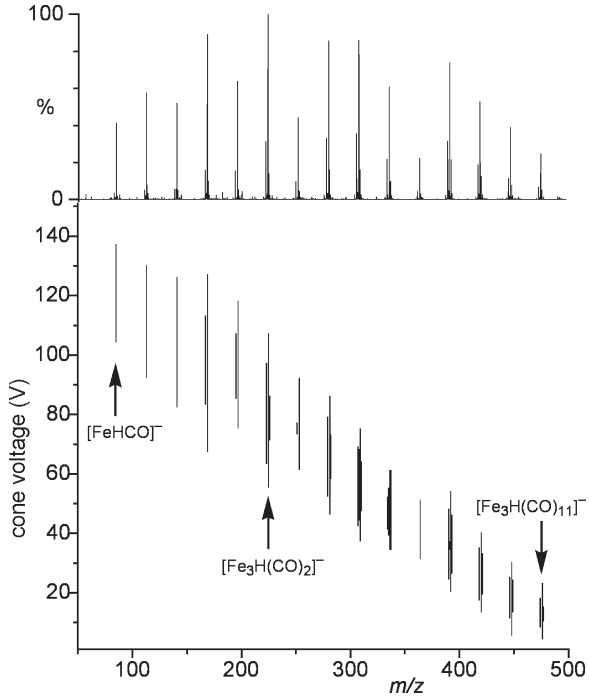

Figure 1. Image map EDESI-MS of $[Fe_3H(CO)_{11}]^-$, run in negative ion mode with methanol as the mobile phase, drawn using Origin®. The top spectrum is a summation of the 151 spectra used to generate the map.

separated value format, .csv, which is readable by all graphing programs) whose dimensions can be specified. Using typical parameters (e.g. a resolution of 1 $m/z \times 1$ scan), the reduction in file size is approximately a factor of 50 when taking raw data from a Micromass Q-Tof *micro* instrument.

Detailed instructions for the use of *EDit*, including screenshots, may be found in the supporting information ('*Step-by-step instructions for creating a 3D Origin plot from a MassLynx continuum file*'). The program itself may be freely downloaded,[9] along with source code, and is released as free software under the terms of the GNU General Public License (GNU GPL). *EDit* was developed for Microsoft® Windows[8] 2000 or XP operating systems using Microsoft® Visual Studio.NET C++;[8] however, the important sections of code (contained in the file 'MassSpecDataDlg.cpp') can be easily ported to any other operating system.

The output produced by the *EDit* program can be manipulated using graphing software to generate image maps, contour maps, or 3D surfaces. An image map is shown in Fig. 1. To aid in the assessment of the relative peak intensities, we generally include a conventional mass spectrum at the top of the map in which all the spectra used in the map are summed together (using the 'Combine' function in MassLynx).

The relative heights of crosspeaks in the EDESI spectrum may be depicted in the form of a 3D surface (Fig. 2), emphasizing that the EDESI map contains breakdown information[10] on all the ions in the spectrum. Rotation of the surface appropriately allows simultaneous viewing of all ion profiles.

A contour map can also be generated (Fig. 3), and this has the advantage of simplicity by eliminating distracting noise and very low intensity peaks by employing the simple precaution of setting the lowest contour value slightly higher than the noise. Alternatively, the z axis itself may be adjusted to eliminate noise, as it is not necessary to start the intensity axis from 0. The contour map presentation style is familiar to most chemists from 2D NMR spectra.

In summary, *EDit* enables the manipulation of multiple mass spectra (collected with MassLynx) using standard scientific graphing packages. The program should prove to be a useful tool in any application in which a variable is altered while multiple mass spectra are collected, such as reaction time (reaction monitoring), elution time (liquid chromatography), cone voltage (EDESI-MS), collision voltage (EDESI-MS/MS), etc.

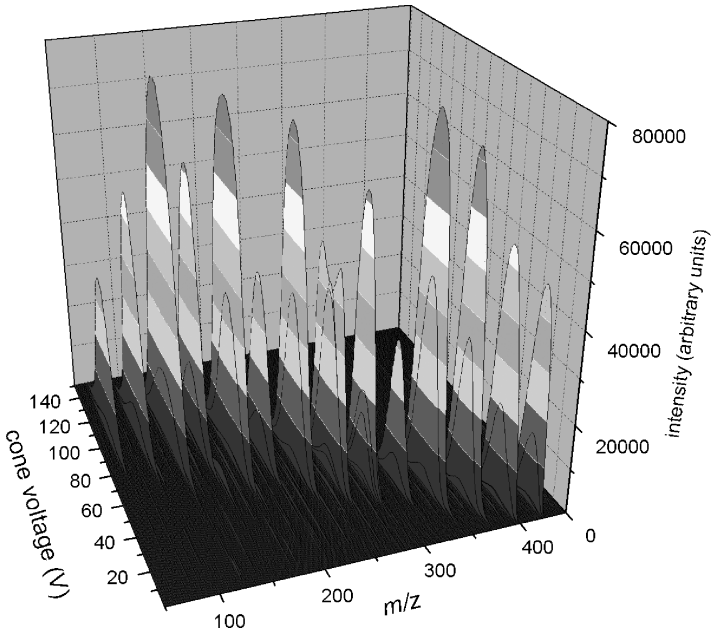

Figure 2. A 3D surface representation of the EDESI-MS data shown in Fig. 1, again drawn using Origin®.

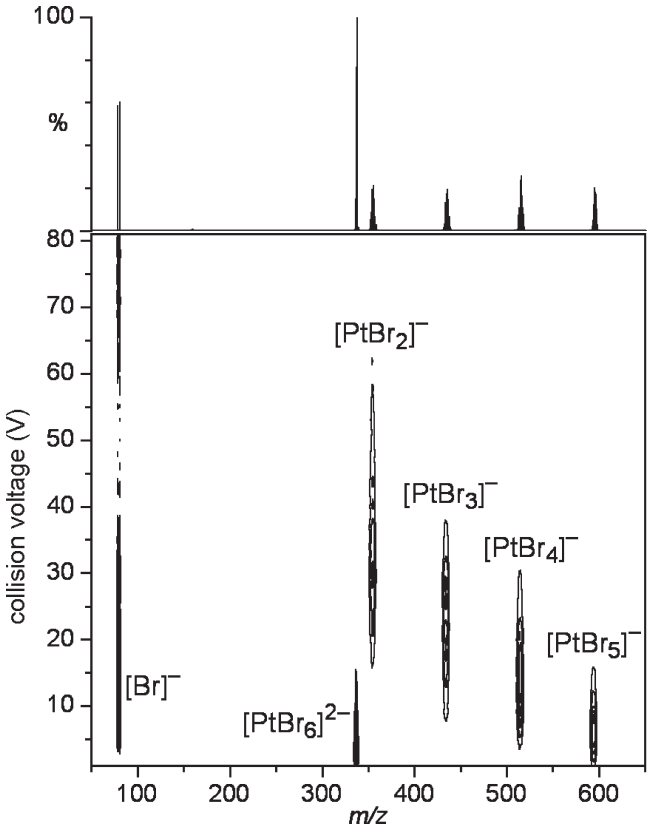

Figure 3. Contour map EDESI-MS/MS of $[PtBr_6]^{2-}$, run in negative ion mode with acetonitrile as the mobile phase, drawn using Origin®. The top spectrum is a summation of the 81 MS/MS spectra used to generate the map.

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Shamus L. G. Husheer[1], *Orissa Forest*[2], *Matthew Henderson*[2] *and J. Scott McIndoe*[2]*

[11]Department of Chemistry, The University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

[2]Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, BC V8W 3V6, Canada

**Correspondence to*: *J. Scott McIndoe, Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, BC V8W 3V6, Canada.*

E-mail: mcindoe@uvic.ca

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