



# Putting Pollution on ICE

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## Introduction

When environmental pollution is detected, determining its source is critical to finding the best remedies, and to establishing responsible parties. The science of determining pollution sources is called environmental forensics. The identification of individual chemical contaminants provides a "fingerprint" of the pollution source, the keystone of environmental forensics. Contaminant identification is also essential for risk assessment.

Gas chromatography coupled to mass spectrometry, using a mass spectral library for comparison, is the EPA's workhorse for identifying compounds. Unfortunately, identification is much more difficult if a compound's mass spectrum is not present in a library, and this is often the case for pollutants that are most useful for identifying pollution sources.

## ICE - An Analytical Tool

The Environmental Chemistry Branch (ECB) in Las Vegas has developed a new mass spectrometric method, Ion Composition Elucidation (ICE), to determine unequivocally the elemental compositions, or chemical formulas, of a pollutant and its fragment ions in its mass spectrum. This information is a key to identifying a compound that does not have a library mass spectrum for comparison. Conventional high-resolution mass spectrometry determines elemental composition by measuring the exact mass of the molecular ion and comparing it to the exact masses of combinations of atoms of different elements. This method seldom provides a unique chemical formula if the mass of the ion exceeds about 150 atomic mass units (amu), due to the error limits of the measurement. ICE uses the relative abundances of the isotopes of elements, as well as their exact masses, to eliminate this drawback.

## ICE to Identify Municipal Well Water in NJ

Increased incidences of childhood cancer and leukemia were observed in Toms River, NJ. An extract of water from a municipal well that served 50,000 residents in the area was provided by EPA Region 2. The extract contained several closely related isomers (compounds with the same elemental composition). The mass spectrum of one of these compounds is shown in Figure 2. Conventional mass spectrometry performed in other labs did not identify these compounds. Using ICE, the compositions of the 11 ions that are labeled in Figure 1 were determined. The +1 and +2 isotopic peaks of the m/z 210 ion are not visible in the mass spectrum. Even so, the high sensitivity of ICE provided the exact masses and relative abundances of these two profiles.

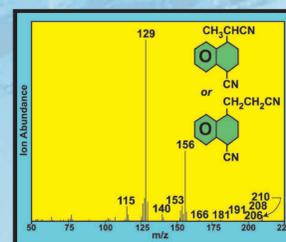


Figure 1. Mass spectrum and possible chemical structures of a compound found in municipal well water from Tom River, NJ.

As illustrated by Figure 2, these compositions narrowed the list of possible compounds to a number for which a search of the chemical and commercial literature was feasible. Such a search led to identification of the compound as one of the isomers shown in Figure 1 and convinced the party that produced these compounds to acknowledge their responsibility. To illustrate the scale of the reduction in possible compounds from the green ring to the blue ring, 342 NIST mass spectral library matches occurred when a mass of 210 Da was entered, while only 13 were found for the composition, C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>. Of course, none of the matches in the library were the correct isomer, or the compound would have been routinely identified.

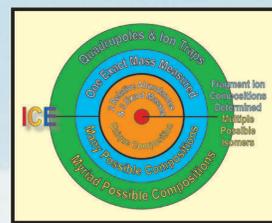


Figure 2. Target diagram illustrating the great reduction in possible compositions provided by ICE.

## Characterizing Superfund Sites

Superfund sites often contain a multitude of compounds. Each peak in the total-ion chromatograms in Figures 3a and 3b corresponds to at least one compound. For an extract of one Superfund site sample from a location in Region 3 (Figure 3a), using ICE to determine ion compositions for most of the predominant compounds revealed a family of benzothiazoles, which confirmed that a dye plant was primarily responsible for the site. For another Superfund site, ICE was applied to extracts supplied by Region 4 (Figure 3b). This revealed a family of compounds that contained multiple sulfur atoms, which were probably formed by bacteria, while other compounds containing chlorine atoms resulted from pesticide manufacturing. ICE provided the means to identify potentially responsible parties, whether they were industries or organisms!

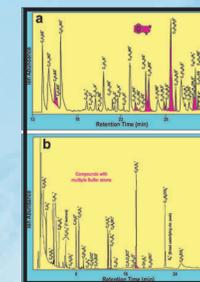


Figure 3. Total-ion chromatograms for extracts from Superfund sites. (a) A site where a dye manufacturer was primarily responsible; (b) a site where a pesticide manufacturer was primarily responsible for the man-made compounds.

## How ICE Works

To establish the elemental composition of an ion, ICE uses its exact mass, as measured by a high-resolution mass spectrometer, as well as the exact masses and relative abundances of two additional groups of ions. These additional groups arise from heavier isotopes of the ion's elements, such as <sup>13</sup>C, <sup>18</sup>O, and <sup>34</sup>S.

In Figure 4a, the calculated mass profile for an ion weighing 410 amu and the two profiles heavier in mass by 1 and 2 amu are shown, labeled with their calculated exact masses and relative abundances. The +1 and +2 profiles arise from groups of ions containing different combinations of atoms of heavier isotopes.

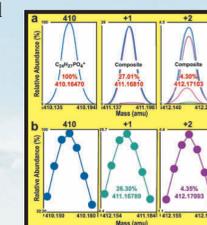


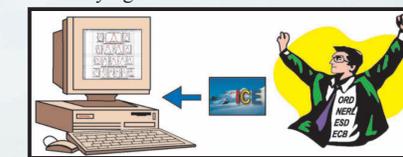
Figure 4. Calculated mass peak profiles for the C<sub>14</sub>H<sub>14</sub>N<sub>2</sub><sup>+</sup> ion (a) and partial profiles obtained experimentally (b).

Figure 4b depicts the experimental data that provide measurements of these values. Seven points along the top portion of each profile are monitored. Advantages in scan speed, sensitivity, selectivity, and mass calibration stability result from using this new type of data acquisition. Plugging this additional data into a Profile Generation Model written at the ECB provides the numbers of atoms of each element that comprise the ions observed in mass spectra. The fast scan speed allows the required data to be obtained as each compound enters the mass spectrometer for less than 10 seconds. This means compounds need not be isolated before study and that numerous compounds in a complex mixture can be studied conveniently.

ICE, which is simply a software package, requires a double-focusing, high-resolution mass spectrometer to provide its data. EPA Region 4 has recently procured such an instrument and ECB plans to transfer ICE to it. Two tutorial aids, "ICE is Nice" and "ICE is Easy," are animated PowerPoint presentations that provide the scientific basis of ICE and demonstrate step-by-step experiments using ICE to determine the compositions of ions. To learn more about ICE and its applications, see the web site:

<http://www.epa.gov/nerlesd1/chemistry/ice/default.htm>

This site contains a dozen ICE articles and a dozen ICE posters. In the next few years, ECB hopes to transfer this technology to several EPA regional labs as they acquire double focusing mass spectrometers, to many others who have such instruments, and possibly to an instrument manufacturer for inclusion within its data systems. Clearly, ICE expands the utility of these instruments for identifying environmental contaminants and their sources.



The joy of ICE!