

Identification of Analytically Problematic Pollutants with a New Mass Spectrometric Technique

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Analytical chemistry plays a number of important roles for the EPA. Among them are characterization of contaminated sites and identification of pollutants in drinking water. For contaminated sites, discovering the source of pollution is often a major goal. For pollutants in drinking water, identification of the compounds is necessary before toxicity studies and risk assessment are possible.

Conventional Analysis

Capillary gas chromatography with low resolution mass spectrometric detection (GC/MS) is the most commonly used technique for analyzing samples. While the EPA has developed target lists of compounds, for which library mass spectra are available on most mass spectrometer data systems, only a small fraction of compounds generated in industrial processes is included in the libraries. Further, the low accuracy of the mass determined for ions can correspond to multiple elemental compositions. Finally, coelution of components from complex samples can yield poor, multiple matches with library mass spectra. Consequently, comparison of mass spectra with those in libraries often fails to identify components in these complex samples, and the compounds must be designated as "unknown".

An Impasse

When identification is essential, high resolution mass spectrometry (HRMS) is used to determine the "exact" (or "accurate") mass of the molecular ion formed from an unknown. If the ion's mass is less than 150 amu and it contains only C, H, N, O, P, or S atoms, its exact mass usually corresponds to a unique elemental composition (formula). From the unique composition and other information, the structure of the molecule can be deduced. However, most semi-volatile contaminants have molecular weights greater than 150 amu, and for a given exact mass, multiple compositions are possible.

A Solution

The Environmental Sciences Division (NERL, Las Vegas) has pioneered a new approach for determining unique compositions for larger-mass ions: Mass Peak Profiling from Selected Ion Recording Data (MPPSIRD)^{1,2} and a Profile Generation Model (PGM).³

Five Criteria Provide a Unique Composition

The number of molecular formulas possible for an exact mass increases rapidly with the mass of the ion. To determine unique compositions for ions with masses greater than 150 amu, four other measurements are made using MPPSIRD. In Figure 1 are shown mass peak profiles for two molecular ions and for the ions with masses 1 and 2 amu greater. The existence of higher isotopes for C, N, O, and S give rise to the M+1 and M+2 profiles. For the correct composition, the measured values of the exact masses of the three profiles and the abundances of the M+1 and M+2 profiles relative to the M profile must agree with the predicted values within the maximum error limits for each measurement. In this example, the exact mass of M for the two compositions is too similar to distinguish between them, but the exact mass of the M+2 profile and both relative abundances are sufficiently different to do so.

In Table 1, prepared automatically by the PGM, are listed compositions that are possible based on the exact mass of a molecular ion. For each composition, calculated values or ranges for each value considered are provided. The last line provides the experimental values. An "X" next to an entry indicates disagreement with the measured value, and the composition is rejected. Only one composition (#35) was consistent with the five measured values.

Comparisons of five measured values with the calculated values for each composition permits a unique composition to be determined for ions with masses up to 600 amu. Compositions can now be identified for a much larger fraction of the universe of environmentally significant compounds. Table 2 lists other advantages of MPPSIRD.

Table 2. Important Points about MPPSIRD

Advantages:

- More than 100 times greater sensitivity than full scans
- 6 times faster cycle time at 20,000 resolution, permitting delineation of chromatographic peaks
- Routine use of 20,000 resolution
 - provides lower error limits for exact masses, reducing number of possible compositions
 - improves selectivity through better discrimination against other ions with the same nominal mass

Disadvantages:

- Requires a double-focusing mass spectrometer (\$400-500K)
- Requires multiple data acquisitions

Other Demonstrated Applications:

- Rapid, sensitive, and selective screening for a target analyte
- Rapid identification and quantification of Aroclors based on congener distributions
- Confirmation for products of syntheses

Only MPPSIRD can provide elemental compositions and structural information for major and minor components in complex mixtures.

Potential Regulatory Tools

The ability to characterize the major components in complex samples could provide a scientific basis for assigning responsibility for clean-up costs when multiple sources of contamination are found. This approach could be especially useful when the responsible parties have kept inadequate records. Those involved in regulatory affairs should become aware of this capability and its potential to provide important evidence.

Tables of exact masses and elemental compositions of molecular ions, fragment ions, and neutral losses provide strong evidence for identifying pollutants. The elemental composition of a compound limits its identity to a number of structural isomers. Knowing the elemental compositions of fragment ions and of neutral losses from the molecular ion greatly reduces the number of possible isomers. A search can be made of chemical inventories and for industrial processes that might generate one or more of the isomers. Finally, mass spectra and chromatographic retention times of suspect compounds can be compared with those of environmental contaminants to confirm the identity of dumped chemicals.

MPPSIRD and the PGM are fully developed. The peer-reviewed references provide the theoretical basis and document the development of MPPSIRD and the PGM. Two examples of the utility of elemental compositions of ions for solving real-world problems will now be illustrated.

A Complex Sample from a Superfund Site

MPPSIRD and the PGM were used to characterize a tar-like sample from a Superfund site.⁴ From the total ion chromatogram (TIC), 47 chromatographic peaks were investigated. Elemental compositions were determined for the presumed molecular ion. A portion of the TIC labeled with the unique composition identified for each peak is shown in Figure 2. In addition, compositions were determined for presumed molecular ions from four compounds that did not provide chromatographic peaks by using a heated insertion probe to introduce the diluted sample into the ion source. At least 25 compounds provided the C₈H₇NS⁺ ion (m/z 149.0299) characteristic of benzothiazoles, which was tracked using 20,000 resolution to discriminate against potential interferences such as the C₈H₅O₃⁺ ion (m/z 149.0239), a common interference formed from phthalates. The finding that a majority of the compounds contained the benzothiazole moiety was consistent with the known source of this contamination, a nearby dye manufacturer. Single, good library matches for low resolution mass spectra were found for several low-mass compounds, most of which were not benzothiazoles. Characterization of the complex mixture with MPPSIRD and the PGM provided elemental compositions for large-mass ions from components that accounted for most of the mass of the sample and provided the chemical information needed to confirm the source of the waste.

Identification of Well Contaminants

MPPSIRD and the PGM were used to determine the elemental composition of several isomers contaminating a municipal well that serviced 50,000 people in an area where an increased incidence of childhood cancer was observed.⁵ The number of candidate isomers was greatly reduced by determining exact masses for 10 fragment ions, many of which were present in very low abundance. Unique compositions constrained by the number of atoms of each element in the molecular ion corresponded to the exact masses of the fragment ions and neutral loss fragments. With fewer isomers to consider, mass spectral interpretation was simplified, and searching of mass spectral data bases (for compounds with similar structural features) and the chemical literature was more rapid. These isomers were identified as products of styrene:acrylonitrile polymerization. Virtually identical mass spectra and retention times for a standard confirmed the identifications. The mass spectra for one isomer found in both the well water and the standard are shown in Figure 3.

Figure 1. Calculated mass peak profiles for the molecular ion and the ions with 1 amu and 2 amu greater masses for elemental compositions of C₂₄H₂₈N₂S₂ (top set) and C₁₉H₂₇O₃N₃P (bottom set).

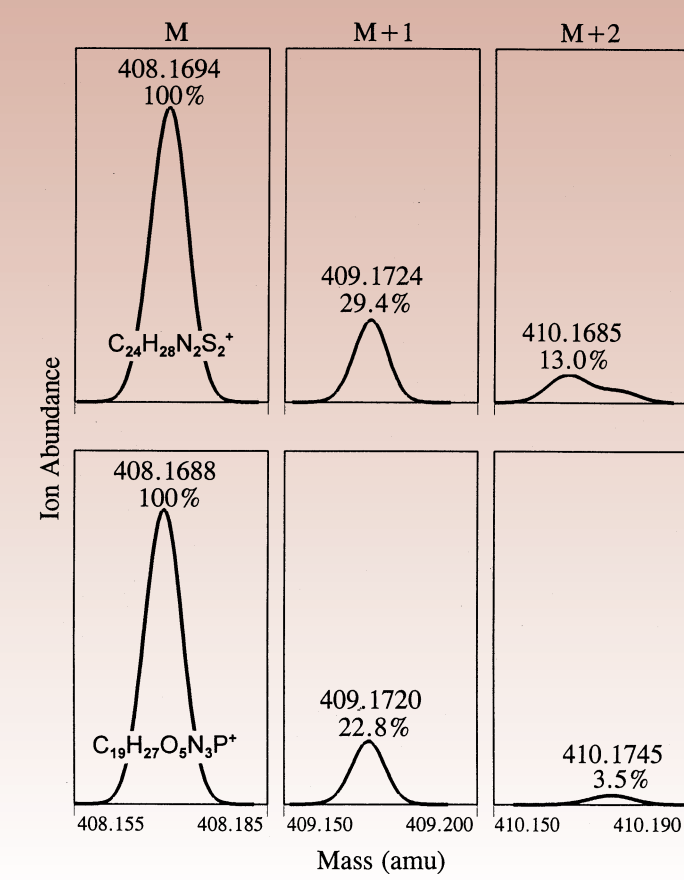


Table 1. PGM Output: Elemental compositions and quantities useful for distinguishing among them.

#	RDB	Composition	M	M+1	M+2	%M+1	%M+2	Range
1	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1678	1662	8.9	3.6-10.1	4.3-5.9
2	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
3	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
4	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
5	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
6	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
7	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
8	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
9	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
10	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
11	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
12	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
13	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
14	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
15	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
16	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
17	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
18	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
19	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
20	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
21	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
22	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
23	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
24	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
25	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
26	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
27	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
28	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
29	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
30	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
31	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
32	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
33	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
34	2.0	CH ₂ O ₂ N ₂ S ₂	1697	1682	1688	10.4	3.6-11.7	4.3-5.9
35	12.0	C ₁₉ H ₂₇ O ₃ N ₃ P	1694	1725	1665	28.8	(26.1-31.5)	10.0 (8.7-11.7)
Experimental Values:			1694	1723	1657		30.3	10.9

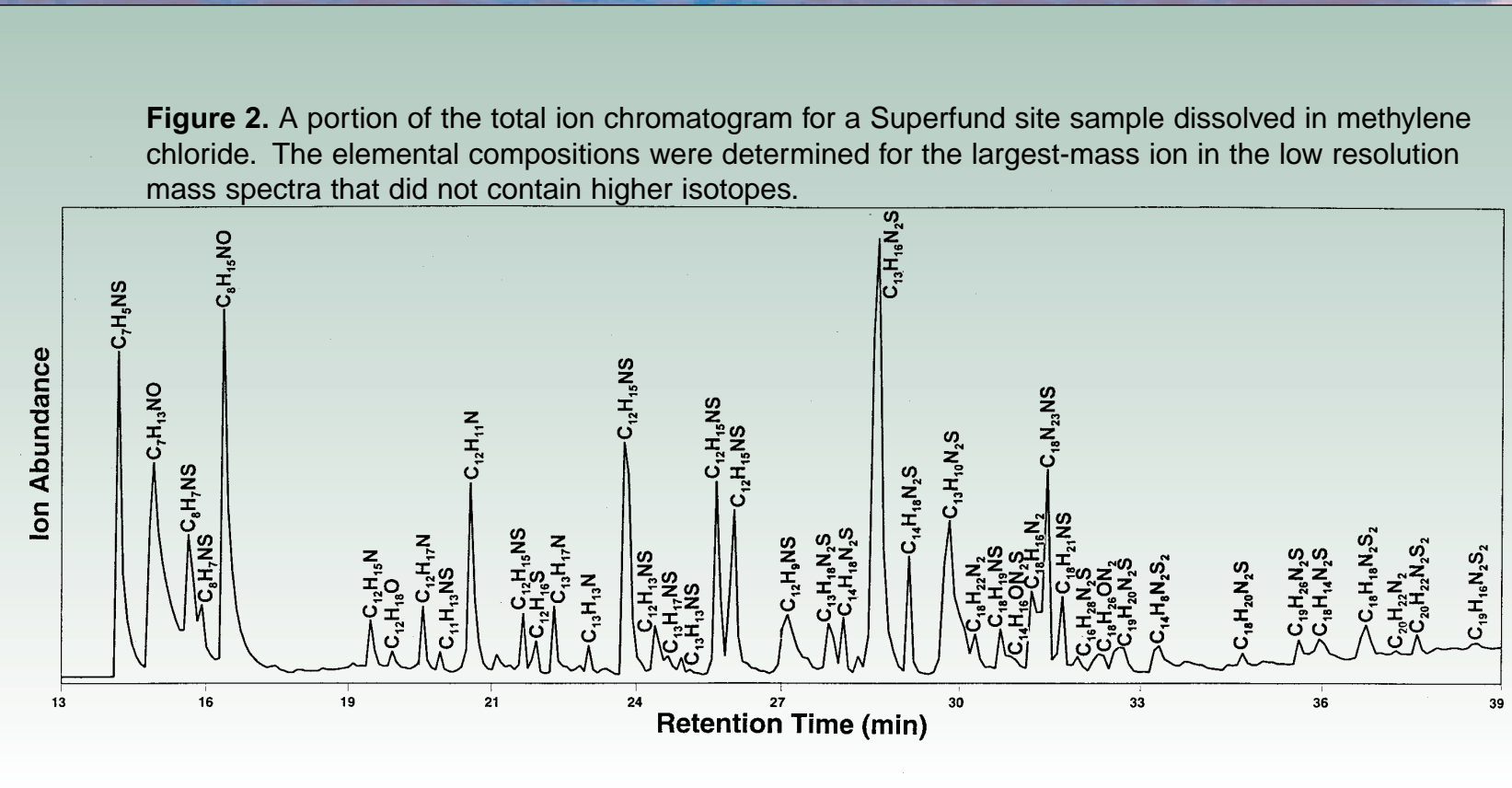
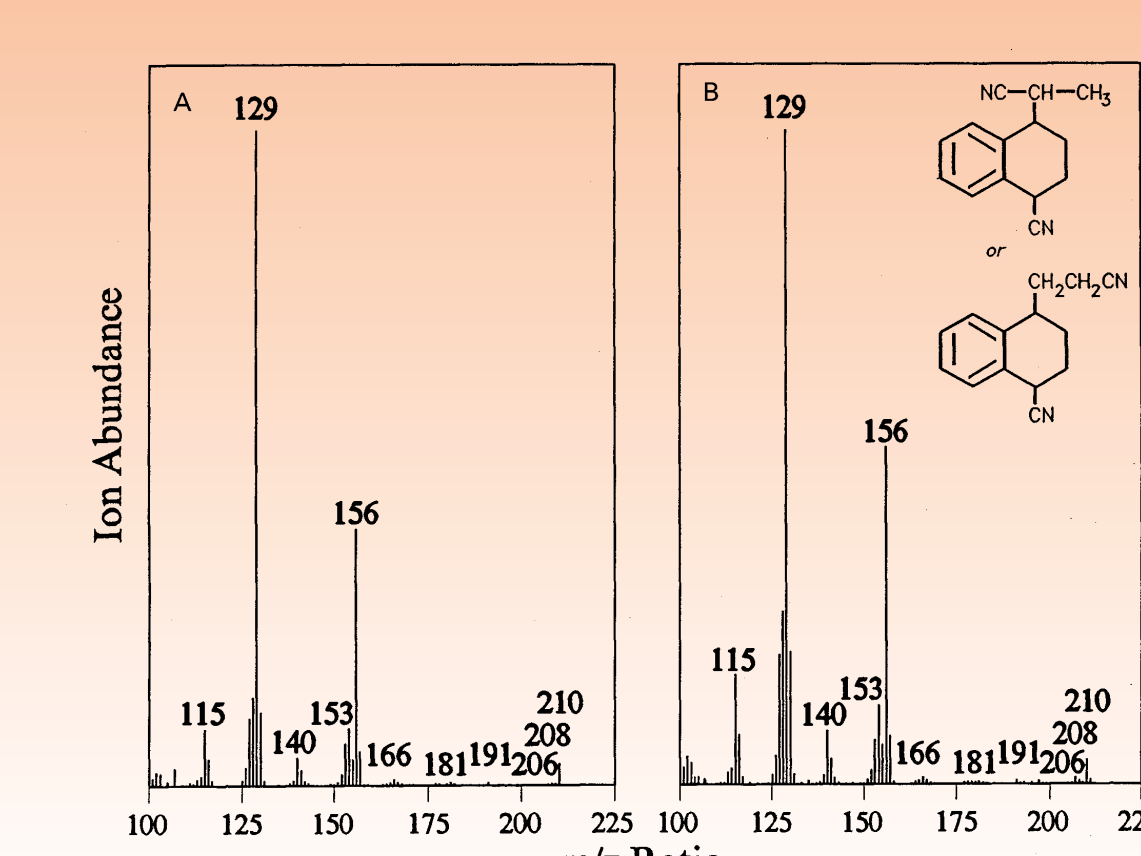


Figure 3. Low resolution mass spectrum for (A) an isomer in an extract of water from a municipal well and for (B) an isomer in a standard collected from a styrene:acrylonitrile polymerization process.



References

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