



# An Ion Correlation Program for Deconvoluting Composite Mass Spectra Acquired Using a Direct Surface Ionization Source Interfaced to a Time-of-Flight Mass Spectrometer

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## Analytical Problem

Delineation of the dispersal area of chemicals after a flood, tidal surge, severe wind, leakage during transport, or explosion could require 100 or more wipe samples from surfaces or other types of samples. Rapid analyses, including identification of chemicals, are necessary to quickly allay public fear, characterize contaminated sites, and plan remediation after such natural or man-made disasters. Absent mass spectral library matches, elemental compositions of ions in mass spectra determined from exact masses, and relative isotopic abundances of the ions in isotopic clusters can lead to tentative identifications based on rapid searches of data bases. Semi-quantitation could better map the dispersal area into regions of low, moderate, and high levels of chemicals and provide data important for site remediation.

## Sampling Strategy

Figure 1 illustrates a hypothetical compass-based grid pattern for sampling that might be used to quickly map a dispersal area after an explosion. Wipe samples might provide non-detect and three levels of semi-quantitation. This example illustrates a northerly post-event distribution of a chemical. A second more detailed 10 x 10 grid over the area where moderate and high levels of the chemical were found could provide finer delineation of the contamination. A final set of wipe samples could document successful remediation.

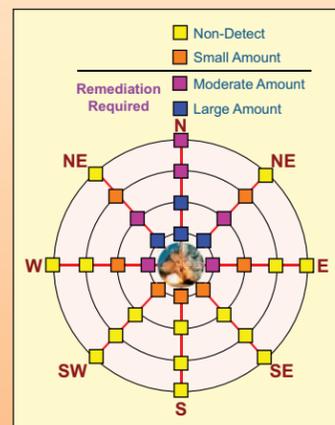


Figure 1. Compass-based grid for wipe sampling about an explosion site.

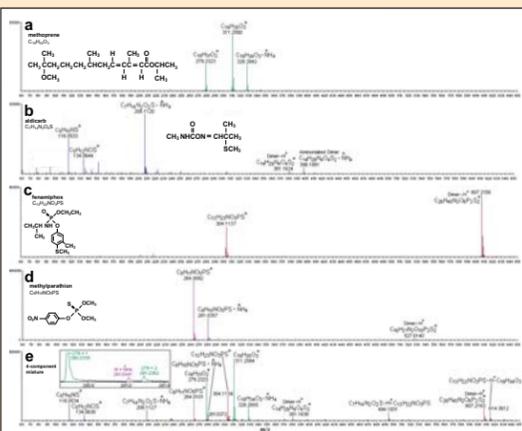
## Speed is Paramount

Extraction, cleanup, and chromatographic separation of components on 100 wipe samples could require much time and labor. But only 3-5 sec are necessary to acquire mass spectra for a cotton swab wipe sample in ambient air passing slowly through the metastable He beam of a Direct Analyses in Real Time (DART) ion source. Hence, from receipt of 100 wipe samples, the time required to acquire their mass spectra could be reduced at least 10-fold.

## The Tradeoff

Because multiple analytes will be present on surfaces, composite mass spectra will often be obtained. In Figure 2 are displayed averaged, centroided, mass spectra obtained by a DART/oa-TOFMS: mass spectra for four individual pesticides and a mass spectrum obtained for a mixture of the four compounds.

Figure 2. Averaged, centroided, DART/oa-TOF mass spectra for four individual pesticides and a mixture of all four.



Inset: averaged, profile-mode mass spectrum near m/z 281 showing baseline resolution between the monoisotopic profile of ammoniated methylparathion and the +2 profile from a methoprene product ion. The +1 profile of the methoprene product ion is also shown.

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## Correlating Ions

Table 1 lists the user inputs into an in-house Ion Correlation Program (ICP) and its outputs of possible ion and neutral loss compositions. For the m/z 328 and 208 ions, ion correlation of multiple fragment ions in the mass spectra in Figures 2a,b provided unique compositions for the precursor ion, product ions, and corresponding neutral losses. To determine unique compositions for the m/z 304 and 264 ions, the protonated dimer ions were considered. These ions must contain an even number of atoms of all elements except for H, for which an odd number of atoms is required. These restrictions provided a single composition for the protonated monomer ions. The analyst knew only that the analytes were pesticides. The unique compositions determined for all four pesticides using the ICP were found in the index of *The Pesticide Manual* (12th ed., British Crop Protection Council), which provided their identifications as methoprene, aldicarb, fenamiphos, and methylparathion.

Possible compositions for the protonated monomer ions 304.1137 and 264.0092 were used to provide upper and lower elemental limits for the dimer ions, 607.2159 and 527.0140, respectively. The ICP found two possible compositions for the m/z 264 monomer ion in the top part of Table 1d. These compositions provided the narrow elemental limit ranges in the bottom part of Table 1d. No compositions were found for the dimer ion for error limits of 2 and 3 mmu. The mass error was 3.3 mmu.

Table 1. User inputs into the ICP (elemental limits, ion type, exact mass error, and RIA error) and outputs (possible precursor ion, possible product ion, and possible neutral loss compositions) for the four analytes from Figure 2.

## Mass Spectra Deconvolution

Using the ICP, composite mass spectra such as the one in Figure 2e can be deconvoluted based on exact masses and RIAs, rather than by chromatographic separation of analytes. Ions smaller than m/z 330 were assumed to be precursor ions, while the heavier ions were assumed to be protonated dimers, protonated combinations of two monomers, or their product ions. Table 2 lists the ions used for deconvolution. The measured exact masses and relative isotopic abundances (RIAs) of the ions in an ion's isotopic cluster in Table 2 were entered manually into the ICP to determine which ions could be correlated with each other.

m/z	%1 RIA	%2 RIA	Correlation	Composition
328.2855	22.64		[M+H] <sup>+</sup>	[C19 H34 O3 + NH4] <sup>+</sup>
311.2584	22.65	3.34	328	[C19 H34 O3 + H] <sup>+</sup>
304.1136	17.93		[M+H] <sup>+</sup>	[C13 H22 N O3 P S +H] <sup>+</sup>
279.2323	19.39		328	[C18 H31 O2] <sup>+</sup>
264.0101	11.54	5.84	[M+H] <sup>+</sup>	[C8 H10 N O5 P S +H] <sup>+</sup> + 3 others
208.1127	10.47	4.24	[M+H] <sup>+</sup>	[C7 H14 N2 O2 S + NH4] <sup>+</sup> + 1 other
134.0638			304, 208	[C5 H12 N O S] <sup>+</sup>
116.0534			304, 264, 208	[C5 H10 N S] <sup>+</sup>

Table 2. Exact masses and RIAs used to deconvolute the composite mass spectrum in Figure 2e.

## Ion Correlation Sequence

Table 3 illustrates the procedure used to determine which ions were related and which were not. Starting with the highest mass ion, each ion lower in mass was assumed to be a product ion. If this assumption was true, one or more possible compositions were found for both ions. If false, no compositions were found for either ion. Exact masses and the RIAs from Table 2 of correlated ions were re-entered for testing against the next lowest mass ion. This procedure was repeated until all ions had been tested for correlation. This process was then repeated for the m/z 304 ion, which was also a precursor ion. Likewise, each non-correlated, lower-mass ion (m/z 264 and 208) was treated similarly as a precursor ion.

328, 311	1:1
328, 311, 304	No compositions
328, 311, 279	1:1, 1:1, 1*
328, 311, 279, 264	No compositions
328, 311, 279, 208	No compositions
328, 311, 279, 434	No compositions
328, 311, 279, 416	No compositions

Table 3. Ion correlation procedure.

\*See Table 1a.

To restrict the upper elemental composition limit for the protonated monomer ion (m/z 304) for which a protonated dimer ion (m/z 607) was evident in Figure 2e, the procedure used above for the pure compound in Table 1c was first used to provide the correct composition for the m/z 304 ion. This composition then served as the upper elemental limit for attempted correlations with lower mass ions. This tactic avoided a false correlation with the m/z 208 ion based on an erroneous possible composition allowed when the protonated dimer ion was not considered.

In Figure 2e, the m/z 527 protonated dimer ion produced from the m/z 264 ion barely visible in Figure 2d was not seen. Hence, four compositions were possible for the m/z 264 ion. However, it was still found not to correlate with the other three analytes present.

The m/z 134 and 116 ions are compositional subunits of the m/z 208 from which they were formed, but also of other precursor ions. Hence, they cannot be used during deconvolution, since their origin is uncertain. This also occurs for common product ions such as m/z 91 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>) and 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>). An additional composition was possible for the m/z 208 ion, since it could no longer be exclusively correlated with the m/z 134 and 116 product ions.

All four analytes were found and unique compositions were determined for two of them.

## Future Work

Acquiring mass spectra under at least two conditions, one that discourages and one that encourages fragmentation, will provide important additional information. The relative abundance of precursor and protonated dimer ions will be greater when little fragmentation occurs and a larger number of product ions will be produced under the more energetic condition. Perhaps the product ions from the most easily fragmented precursor ion will be observed before other precursor ions fragment extensively. Perhaps the product ions last to appear will come from the last precursor ion to lose ion abundance. Such clues will further aid deconvolution of mass spectra. Ultimately, strategies that prove useful will be incorporated into an automated version of the ICP.

## Ion Correlation Program Details

- All possible compositions having at least -0.5 rings and double bonds (RDB), which are consistent with the elemental limits considered, exact masses and mass error limit, and RIA and RIA tolerance set by the user, are calculated for the precursor and product ions and stored for further processing. The precursor ion compositions are calculated first to establish upper elemental limits for the subsequent calculation of the possible product ion compositions.
- All possible neutral loss compositions are calculated based on the mass differences between the precursor ion and all product ions. The formulas characterized by an RDB value of no less than -2.0 are saved and stored for further processing.
- Those precursor ion compositions are rejected which cannot be derived by the summation of the number of atoms of each element in a product ion-neutral loss pair. This formula discrimination criterion is applied for each product ion exact mass.
- Product ion compositions that do not provide a remaining possible precursor ion when summed with a corresponding neutral loss composition are rejected, as are neutral loss compositions that do not provide a remaining possible precursor ion when summed with a corresponding product ion composition.

## Conclusion

The rapid sampling provided by the DART in ambient air will allow rapid delineation of areas of dispersed chemicals after natural or man-made disasters. Exact masses and RIAs of dimer, precursor, and product ions measured by the oa-TOFMS entered into the Ion Correlation Program to provide ion and neutral loss compositions will enable identification of one or more chemicals associated with such an event without recourse to time and labor intensive sample extraction, cleanup, and chromatographic separation. Deconvolution of mass spectra will also provide cleaner mass spectra for comparison with a mass spectral library after one is compiled.

The research described in the abstract for this poster has been published in the reference. The contents of this poster present our most current work.

More about using exact masses and RIAs for compound identification is available at: <http://www.epa.gov/nerlesd1/chemistry/ice/default.htm>

Reference: Grange, AH; Zurnwalt, MC; Sovocool, GW. Determination of Ion and Neutral Loss Compositions and Deconvolution of Product Ion Mass Spectra Using an Orthogonal Acceleration, Time-of-Flight Mass Spectrometer and an Ion Correlation Program. *Rapid Commun. Mass Spectrom.* 2006, 20, 89-102.