Identification of Compounds in Water above a Pollutant Plume by High Resolution Mass Spectrometry

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Abstract

Identification of compounds in contaminated media is essential for determining sources of pollution and for assessing risks posed by the chemicals to ecosystems or human health. Eighty-five compounds were identified or tentatively identified in a 1-L extract of water sampled above a pollutant plume containing wastes from a chemical plant. Gas chromatography/high resolution mass spectrometry determined exact masses of apparent molecular ions and the exact masses and relative isotopic abundances of their +1 and +2 isotopic mass peaks, which provided their elemental compositions. Ion compositions, mass spectral libraries, the presence of related compounds, and knowledge of organic chemistry provided tentative identifications, half of which were confirmed by comparison of analyte retention times and mass spectra with those of standards.

Introduction

A chemical manufacturer for the rubber and plastics industries used over 100 chemicals for syntheses. For at least 30 years, some fractions of these chemicals, synthesis products, and their byproducts were transferred to a waste pond. After exposure to air, rain, solar radiation, and soil particles, fractions of these compounds, reaction byproducts, and transformation products had migrated into an underground plume 3/4 of a mile long and up to 1/3 of a mile wide. During droughts, water above the plume might be used as part of a nearby town's drinking water supply. It was therefore essential to identify as many of the compounds present in this water as possible in order to assess toxicological risk to humans and to provide a list of target compounds for evaluating the efficacy of drinking water treatments.

For the past decade, the Environmental Chemistry Branch (ECB) has characterized and identified compounds in complex environmental extracts using Ion Composition Elucidation (ICE) (Grange et al. 1998, 2001, 2003; Grange and Sovocool, 2003; Snyder et al., 2001), a high resolution mass spectrometric technique that measures both exact masses of ions and the relative abundances of the mass peaks heavier by 1 and 2 Da than the mass peak of the monoisotopic ion. The heavier mass peaks result from the presence of ions containing one or two atoms of heavier isotopes such as ^{13}C, ^{2}H, ^{15}N, ^{17}O, ^{18}O, ^{33}S, ^{34}S, ^{37}Cl, or ^{81}Br. A Profile Generation Model (PGM) calculates the possible compositions corresponding to the measured exact masses for the three mass peaks and the relative isotopic abundances of the +1 and +2 mass peaks based on the error limits of the measurements (Grange and Brumley 1997). This strategy fully exploits two independent physical properties of atoms, their masses and their isotopic abundances, to provide complementary discrimination among elemental compositions of ions.

While ICE was recently adapted for use with accurate mass triple quadrupole and orthogonal acceleration, time-of-flight mass spectrometers interfaced with HPLCs (Grange et al., 2005; Grange, Zumwalt, and Sovocool, 2006), this paper deals only with GC/HRMS application of ICE. Eighty-five compounds having a wide range of concentrations in the most complex extract of eighteen 1 L water samples were identified or tentatively identified.

Experimental

Field Samples. A total of 18 1-L water samples were collected from six locations at three

depths to survey the chemicals present. Six samples came from the water just above the plume. At each sampling site and depth, "ambient pH," "base extracted," and "acid extracted" samples were prepared by measuring the pH, adjusting the pH to 12-13 by addition of 6 N sodium hydroxide, or adjusting the pH to 2-3 by addition of 6 N sulfuric acid.

Extraction. Extraction of the analytes into methylene chloride and volume reduction to about 1 mL was performed as described in EPA Methods 625 (EPA Methods) and 1625 (EPA Methods). The extracts were then shipped on ice to the EPA's Environmental Sciences Division in Las Vegas.

Standards. Standards available from Aldrich (Milwaukee, WI) were purchased to confirm or refute tentative identifications of analytes based on comparisons of mass spectra and retention times.

Gas Chromatography/Mass Spectrometry (GC/MS). An HP 5890 GC (Wilmington, DE) containing a 30-m, 0.25-mm i.d., 0.25-μm film, Rtx-5 GC column (Restek, Bellfonte, PA), was interfaced to the mass spectrometer. The temperature program was 40 ^{o}C for 1 min, 7 C^{o}/min to 300 ^{o}C, and hold for 2 min.

A VG 70SE-250J double focusing mass spectrometer (VG, Danvers, MA, USA) acquired full scan data over a mass range of 50-600 Da at 1 s/scan using a resolving power of 1000 (10% valley definition). Selected Ion Recording (SIR) data were acquired with 25 ms dwell times for

each m/z ratio at resolving powers of 3,000 or 10,000. Ion source conditions were 70 eV electron ionization, a 500-μA filament current, an ion source temperature of 250 ^{o}C, a transfer line temperature of 280 ^{o}C, and a photomultiplier voltage of 350 V. The photomultiplier voltage was increased to 400 V and to 450 V to increase sensitivity when resolutions of 3,000 and 10,000 were used, respectively.

Mass spectral data acquired by a double focusing mass spectrometer at a resolving power of 10,000 provide exact masses accurate to within a few ppm. Unfortunately, at this resolving power full scans over wide mass ranges cannot be acquired rapidly enough to delineate GC peaks. However, SIR provides ion abundances for up to 25 pre-selected m/z ratios within 1 s when a VG 70SE mass spectrometer with B2.2 data system software is used. The m/z ratios usually chosen when using EPA analytical methods [*e.g.* Methods 8270 (EPA Methods), 8290 (EPA Methods), and 1613 (EPA Methods)] correspond to the maxima in mass peak profiles of ions arising from analytes and internal standards. Instead, to measure exact masses and relative isotopic abundances (RIAs), the SIR mode is used to monitor multiple m/z ratios across individual mass peak profiles. The areas under the chromatographic peaks for each m/z ratio are then plotted to provide the mass peak profiles in Figures 1b-d. The exact mass of each profile was obtained as the weighted average of several points across the top of the profile. Other groups have also employed the technique of monitoring multiple m/z ratios across individual mass peak profiles to obtain accurate exact masses (Vetter et al. 1999, Wu et al. 2002, Jörundsdóttir et al. 2006).

Relative to full scanning, SIR provides: (1) the speed necessary to make measurements of exact masses and relative isotopic abundances practical as chromatographic peaks elute; (2) about 100-fold greater sensitivity; (3) greater selectivity, since a higher resolving power can be used for low-level analytes; and (4) calibration stability, since a lock mass profile is scanned at the start of each SIR cycle for recalibration.

Ancillary Software. Disadvantages of using SIR to plot mass peak profiles are that only very narrow mass ranges can be monitored, which must be pre-selected based on an estimate of an analyte profile's exact mass, and that custom software on an ancillary computer is required. To compensate for narrow mass ranges, the multi-step approach illustrated in Figure 1 was employed.

First, a full scan was acquired using a resolving power of 1000 to provide the full mass spectrum of each analyte. The highest-mass monoisotopic ion (m/z 139 in Figure 1a) was selected for further study. Three SIR data acquisitions were made after using ASCII files of commands prepared by a Lotus 123 version 2.2 (Lotus Development Corp., Cambridge, MA) spreadsheet to automatically enter exact masses, resolving power, data file name, and other parameters into SIR menus.

The first SIR menu of m/z ratios covered the widest mass range using a 100-ppm mass increment, and data was acquired using a resolving power of 3000. The full mass peak profile

delineated by three points in Figure 1b provided an estimate of the exact mass of the m/z 139 ion and indicated only one m/z 139 ion was present. Other peaks in Figure 1b could result from calibrant or column bleed ions, but their ion chromatograms would reveal a constant or slowly increasing ion abundance, rather than a chromatographic peak (Grange et al. 2001).

The exact mass estimate from Figure 1b was used as the center mass to prepare the SIR menu to acquire the data displayed in Figure 1c, which were acquired using a 10-ppm mass increment and 10,000 resolving power. A full mass peak profile well delineated by about 10 points resulted, and the exact mass measured as the weighted average of the top several points was accurate to within 6 ppm. Using this mass error and assuming only atoms of C, H, N, O, and S were present in the ion, the measured exact mass of 139.02612 from Figure 1c yielded only one possible composition, $C_6H_5NO_3^+$. When P was also considered, two compositions were possible, and when P and F were considered, four possible compositions were found. When dealing with complex environmental extracts from a site for which a complete history is not available, numerous elements must be considered.

Because multiple compositions remained viable, the user picked a hypothetical composition from which center masses were calculated for the SIR menu that monitored the partial profiles displayed in Figure 1d for a monoisotopic ion and its associated +1 and +2 mass peaks. Because too few m/z ratios are available to delineate full profiles for these three ions and a calibration ion, only six m/z ratios each are used to delineate the top portions of the three analyte profiles and four m/z ratios capture the top portion of the calibrant ion. The relative

isotopic abundances of the +1 and +2 partial profiles were determined as the sum of the areas under the ion chromatograms for each m/z ratio used to plot the +1 or +2 partial profile divided by the sum of the areas used to plot the monoisotopic partial profile. Often, when ion abundances are low and the +2 profile relative abundance is less than 2%, the shape of the +2 profile is badly distorted due to insufficient ion abundance or the presence of mass interferences. In our experience, the possible composition with the fewest heteroatoms and lacking F atoms is usually correct. Hence, to acquire the data for Figure 1d, the last of the possible compositions for m/z 139.02916 ($CH_4N_4O_3F^+$, $C_2H_8N_2O_3P^+$, $C_4H_7NSF_2^+$, and $C_6H_5NO_3^+$) was chosen. The three exact masses and two RIAs provided by Figure 1d were entered into the PGM to determine which of the four possible compositions remained viable based on five comparisons between the measured values and values calculated for each composition.

Profile Generation Model. The PGM calculates the exact masses and RIAs for each composition that is possible based on the measured exact mass from the monoisotopic partial profile assuming an error limit of 6 ppm when the resolving power is 10,000. The error limit estimate was based on 15 data acquisitions for each of four standards using a resolving power of 20,000 (Grange et al. 1996; Grange and Brumley 1997). The largest observed mass error was 2.5 ppm. This value was rounded to 3 ppm and doubled when a resolving power of only 10,000 was used. This conservative estimate of the mass error ensured that compositions were not rejected that should be considered when low ion abundances or minor mass interferences were encountered. For the exact masses listed below, only three of 171 exact masses were measured with errors larger than 6 ppm.

For each composition, the five pairs of measured and calculated values are compared. An "X" is placed next to a calculated value when it is inconsistent with the measured value. Table 1 is the output from the PGM for the measured exact masses and RIAs obtained from Figure 1d. Only for the last composition, $C_6H_5NO_3^+$, were all five pairs of measured and calculated values in agreement.

The RIA error ranges result from several errors associated with partial profiles: consideration of (i) instrumental precision, (ii) isotopic abundance variation for each composition, (iii) offset error in monitoring the profiles if the wrong hypothetical composition is chosen to calculate the center masses of the profiles to be monitored, (iv) up to one mass increment of offset error by the data system, and (v) up to 10% error in the resolution. These errors are discussed in more detail elsewhere (Grange and Brumley 1997).

Results and Discussion

Total Ion Chromatograms. Figure 2 is the total ion chromatogram for the sample extract that provided the largest number of chromatographic peaks. The peaks are labeled with the apparent molecular ion compositions or largest fragment ion compositions determined from exact masses and RIAs using the PGM and with the names of identified or tentatively identified compounds. The wide linear dynamic range of the double focusing mass spectrometer allowed compositions to be determined for compounds that provided large, moderate, and small chromatographic peak areas. Aromatic and halogenated aromatic compounds commonly provide predominant molecular ions with distinctive isotopic patterns for compounds containing Cl or Br, which resulted in their compositions being determined for very small chromatographic peaks.

Compounds for which only a fragment ion composition was determined were characterized to the extent that the elemental composition of a large portion of the molecule was obtained. Compositional information was obtained for most of the discernable chromatographic peaks during this study.

Determining Ion Compositions. When fewer than three exact masses and two RIAs were measured reliably and multiple compositions remained viable, preference was given to compositions lacking F or P atoms, the composition with the fewest hetero atoms, compositions for which related compounds had been found, and to odd electron ions when four or more rings and double bonds were present, which suggested the presence of an aromatic ring and a stable molecular ion (except for phthalates). In addition, it was often assumed that at least 1/3 of each ion's mass was from C atoms. This eliminated carbonless compositions and those having very few carbon atoms relative to heteroatoms. Finally, if the +2 isotopic peak in the full scan mass spectrum was less than about 10%, Cl and Br atoms were not considered. In three instances, no compositions or no plausible compositions were found using the 6-ppm mass error limit; in these cases the error limit was increased to 12 ppm. In some cases, although a criterion was not met, the value measured still provided a basis for preferring a particular composition. For example, the %1 RIA was 7.02% for benzothiazole, which was outside of the acceptable range of 7.16-9.68% for $C_7H_5NS^+$. However, the maximum acceptable value for all other possible compositions was 5.51%. After a tentative identification has been confirmed, the assumptions made to choose that compound become irrelevant. The quality assurance is provided by the similar mass spectra and retention times for the analyte and standard.

Identified Compounds. The identifications of compounds in Table 2 were confirmed against standards based on similar mass spectra and retention times usually consistent within 2 s and always within 4 s. Numerous injections were made over several weeks and GC column degradation could shift retention times slightly. For a few aromatic compounds, two or more isomers remain possible due to a lack of available standards. In addition, a number of specific isomers were shown to be absent from the sample. Compounds not found in the sample were: 2,6-di-*tert*-butylphenol; 3,5-di-*tert*-butylphenol; 4-bromo-2-chlorophenol; 2-bromo-4-methylphenol; 3-bromotoluene; 3-bromo-o-xylene; 4-bromo-o-xylene; 2-chlorophenol; 3-methyl-2-nitrophenol; 3-methyl-4-nitrophenol; 5-methyl-2-nitrophenol; 2,3,4-trichlorophenol; 2,3-dichlorophenol; 6,7-dihydro-4(5H)-benzofuranone; and 4-bromo-3-methylpyrazole.

Tentatively Identified Compounds. The tentative identifications of compounds in Table 3 were not confirmed against standards. They were identified by considering the following factors: (1) the composition of the apparent molecular ions, (2) comparisons of the low resolution mass spectra to those in the NIST (NIST/EPA/NIH 2002) and Wiley (Wiley 2002) mass spectral libraries, (3) the presence of related compounds in the extract, (4) a list of chemicals of concern associated with the site provided by EPA Region 1, and (5) knowledge of organic chemistry.

Examples. *Halogenated Benzenes, Alkyl Benzenes , Phenols, and Cresols.* Chlorinated, brominated, and bromochlorinated compounds were found deriving from benzene, toluene, xylene, and other alkyl benzenes. Phenol and the cresols were found as were halogenated compounds deriving from them. Benzene, alkyl benzenes, phenol, and "alkylated phenol" were

used by the plant, but the halogenated derivatives were not and were apparently formed as transformation products. The halogenated phenols included singly or multiply chlorinated, brominated, chlorobrominated, iodinated, and bromoiodinated phenols. Multiple isomers differing in the position of attachment of the halogens to the benzene rings of many of the halogenated phenol compositions were found. The halogenated phenols were probably formed by electrophilic addition of Cl, Br, and/or I in water to the aromatic ring. Addition to the 2-, 4-, or 2- and 4- positions would be expected. Chlorination and oxidation by chlorine, chlorate, and hypochlorite likely also contributed.

Figure 3 provides nine background-subtracted mass spectra. Figures 3a-c are mass spectra for three halogenated phenols, 2-iodophenol, a bromoiodophenol, and a dibromoiodophenol. A standard was available only for the 2-iodophenol, but its confirmation provides support for the tentative identifications of the brominated iodophenols. Although iodine was not normally included as an element when using the PGM, the very small %1 RIA and %2 RIA indicated one or more elements lacking significant abundances of +1 and +2 isotopes was present. The dominant apparent molecular ion suggested aromaticity. Six C atoms would account for the observed %1 RIA, but only 72 of the 220 Da of the ion's mass. The presence of Cl and Br containing molecules in the extract made iodine a likely candidate. C_6I accounted for all but 21 Da of the molecular ion's mass.

For the bromoiodophenol isomer, a second composition also passed four of five criteria ($CHNO_{10}SBr^+$). Based on the presence of numerous other halogenated phenols, the composition $C_6H_4OIBr^+$ was chosen as far more likely. In addition,$C_6H_4OIBr^+$ is an odd electron ion and the

prominence of this probable molecular ion in the mass spectrum suggested the compound contained an aromatic ring, which would account for the 4.0 rings and double bonds (RDB) for this composition. Finally, 2-iodophenol was identified, and dibromoiodophenol was tentatively identified in the extract.

Hydrazine-carbonyl condensates. The mass spectra in figures 3d and 3e provide evidence for the presence of two hydrazine-carbonyl condensates. Two other compounds containing 2 N atoms with 3 rings and double bonds ($C_6H_{10}N_2O^+$ and $C_5H_7N_2OCl^+$) were also found. These compounds were not found in the NIST or Wiley libraries, but were suggested based on the use of hydrazine for chemical syntheses at the plant responsible for the pollutant plume.

Composite mass spectra. Mass spectra in Figures 3d and 3f were among those revealed to be composite mass spectra from coeluting analytes based on the ion compositions determined for apparent molecular ions and apparent fragment ions. In Figure 3d, the loss of 16 Da from the apparent molecular ion could correspond to a neutral loss of CH_4, O, or NH_2. However the ion compositions indicated that the m/z 240 and 224 ions were unrelated, even though the similar isotopic patterns suggested that both ions might contain the same set of halogen atoms. The possibility that the common loss of 43 Da accounted for the mass difference between the m/z 240 and 197 ions was also eliminated after the ion composition of the m/z 197 ion was determined. Clearly, determining ion compositions of multiple ions in a mass spectrum provided clarification of the origin of the ions. The isotopic patterns in Figure 3f for the m/z 250 and 186 ions indicated 2 and 1 Br atoms were present, respectively. The mass difference of 64 Da indicated these ions

arose from two different compounds, since the loss of a Br atom corresponds to 79 Da. In this example, one is well aware that two apparent molecular ions are present before determining their ion compositions.

Dichlorocarboxylic acid. Figure 3g provided a good NIST library match with a dichlorocarboxylic acid. This compound could be formed by hydrolysis of dichlobenil, which is a pesticide that might have been used for lawn care at the chemical plant. However, the purchased standard was not observed to elute when injected weeks after this mass spectrum was obtained. It is likely that as the column aged, the carboxylic acid retention time increased and its peak became extremely broad, or it did not elute at all.

Pseudo-isotopic pattern. The mass spectrum in Figure 3h appears to have an isotopic pattern for m/z 112, 114, and 116 characteristic of a compound containing 2 Cl atoms. However, determining the ion compositions of the m/z 112 and 114 ions refuted this supposition.

Mysteries remain. Figure 3i provides a simple mass spectrum for a prevalent compound not found in the NIST or Wiley libraries having five rings and double bonds. This compound has only been partially characterized. Some, but not all of its structural features have been deduced. A number of compositions for compounds and fragments of compounds were found that have not been assigned specific chemical structures. Numerous isomers are possible for most elemental compositions and if good library matches are not found, no tentative identification is possible. Similarly, the atoms in compound fragments can be assembled in multiple ways. In addition,

numerous background-subtracted mass spectra were essentially chemical noise. They arose from multiple compounds present at levels too low to investigate further. Finally, only a fraction of all compounds elute from a GC, and mass spectra from numerous other compounds might not have been obtained. It is unlikely that one could identify all of the compounds in such a complex mixture, but the ion composition elucidation strategy demonstrated herein greatly increased the number of compounds that were identified and tentatively identified relative to library matching of low resolution mass spectra alone.

Possible Sources of Other Compounds Found. Several additional phenolic compounds were also found: 2-hydroxyacetophenone, bromomethylisopropylphenol, tert-butylphenol, and 2-phenoxyphenol. In addition, benzoquinone, a known oxidation product of phenol, was found.

O-cresol was an often used reagent in the chemical plant and was found in the extract. Several oxidative coupling products of the cresols were found, which were consistent with the oxidative conditions at the plant. In Figure 4a are overlaid ion chromatograms for two m/z ratios used to plot points on the mass peak profiles for the m/z 214 ion seen in Figure 4b. The resolving power of 10,000 provided strong evidence that three isomers were present. The NIST library match for the most abundant isomer was for Pummerer's ketone [4a,9b-dihydro-8,9b-dimethyl-3(4H)-dibenzofuranone],

Alkanes, Alkenes, Alkyl Oxygenated Compounds and their Halogenated Analogs. Many hydrocarbon fragment ions and oxygenated hydrocarbon fragment ions were observed. Their elemental compositions indicated most were alkyl hydrocarbons or had one or two double bonds

and/or rings. Many of the fragments likely originated from branched-chain alkanes, alkenes, cycloalkanes and related alcohols, ethers, and carbonyl compounds that do not provide intact molecular ions in electron ionization mass spectrometry. This often prevented specific compound identification. Some may have originated from alkenes, alcohols, ethers, and "petroleum distillates" used at the nearby chemical manufacturing plant. Another likely origin would be from oils and other natural products, such as terpenes. Many of these compounds were likely oxidized and halogenated to produce many of the compounds listed in the tables. These compounds would be expected to be formed from disinfectant chlorination in the presence of endogenous bromide and iodide salts or from the use of bromide salts at the site. They would be expected to form in the presence of an oxidizing agent, like chlorine, used in water treatment. Historically, liquid chlorine was used at the site to produce hydrazine from excess urea for chemical production. An alternative possibility for the source might be from oxidation of bromide and iodide ions by chlorate or hypochlorite used at the site. Sodium bromide, chlorate and hypochlorite were also used.

Nitrophenol, Nitrocresol, and Bromonitrophenol. Nitration products of phenols were found, namely isomers of nitrophenol, nitrocresol, and bromonitrophenol. Nitrophenols were not used by the plant. Most likely, the different nitrophenols derived from the chemical reaction of phenol with the nitrates and nitrites present in the acidic waters. The plant used sodium nitrite and acid (nitrous acid) for chemical production. Nitrosophenols initially formed could have been oxidized to nitrophenols by oxygen or previously mentioned oxidizing agents.

Miscellaneous Compounds. Several cyclic silicone congeners probably consistent with an anti-foaming agent used at the site were observed. Bromoform, trimethylpentenes, bromodiphenyl ether and bis(2-ethylhexyl)phthalate, and diphenyl ether were also found.

Additionally, Dibutyl phthalate, butylbenzylphthalate, di-2-ethylhexyladipate, and triphenyl phosphate were found. These compounds are plasticizers that were also found in the control water and are so ubiquitous as to be found almost everywhere.

Benzothiazole, a common rubber-related compound, was found and was probably consistent with industrial activities in the area. Several polycyclic aromatic hydrocarbons were found: biphenyl, naphthalene, anthracene/phenanthrene, and pyrene/fluoranthene. These may be components of oil or among combustion products, and are also practically ubiquitous.

Ongoing and Future work. Newer double focusing mass spectrometers no longer provide a macro language and a command line. Consequently, one cannot enter the name of an ASCII file containing macro language commands to prepare SIR menus and another ASCII file of instructions to display ion chromatograms over narrow windows, to integrate the areas under chromatographic peaks, and to save m/z ratios and areas in an ASCII output file. Hence, other types of mass spectrometers were investigated for determining ion compositions.

The mass error limits provided by both an accurate mass triple quadrupole mass spectrometer (AM3QMS) (Grange et al. 2005) and orthogonal acceleration, time-of-flight mass spectrometers (oa-TOFMSs) (Grange, Zumwalt, and Sovocool, 2006; Grange, et al., 2006) are greater than those for mass measurements made using the double focusing mass spectrometer. To

compensate, an Ion Correlation Program (ICP) was written to correlate precursor and product ions and thereby increase the mass of ions for which unique compositions could be determined based on larger mass errors.

A second advantage of using the ICP to correlate ions became apparent. Figure 3d illustrated that for composite mass spectra, determining the composition of the highest-mass, monoisotopic ion is often insufficient to reveal the source of the remaining ions through logical neutral losses from this ion. The ICP can help to characterize or tentatively identify multiple analytes providing a composite mass spectrum by determining the composition of all prominent ions in the mass spectrum and by correlating the related ions for each analyte (Grange, Zumwalt, and Sovocool, et al. 2006; Grange, et al., 2006).

The oa-TOFMS provided a major advantage by acquiring the necessary exact masses and RIAs for precursor and product ions from full scan data acquisitions. Hence, only two generic data acquisitions were required, one each at a low or high collisionally induced dissociation voltage, rather than the four data acquisitions including three that were analyte-specific depicted in Figure 1. Three data acquisitions, two of which were analyte-specific, were required when using the AM3QMS.

Both the AM3QMS and oa-TOFMS were interfaced to an HPLC. The double focusing MS will continue to be used for determining ion compositions for analytes introduced by GC. However, it may be possible to use the ICP to determine ion compositions from full scan data.

But acquiring full scan data at higher than 1000 resolving power will necessitate slower scan speeds that will not resolve chromatographic peaks, but rather yield composite mass spectra. In addition, the mass error will probably be larger. Correlating apparent molecular ions with fragment ions and deconvoluting mass spectra might provide numerous ion compositions and tentative identifications for analytes present at a high level and perhaps at moderate levels. ICE may still be necessary to determine compositions of ions present at low levels. If application of the ICP to full scan data is successful, the time to characterize or tentatively identify 100 analytes could be reduced substantially.

Conclusion

A methylene chloride extract of 1 L of water sampled above a pollutant plume contained hundreds of compounds. Many of the compounds yielded molecular ions for which the elemental compositions could be determined by measuring the exact masses of the monoisotopic ion and its +1 and +2 mass peaks and the relative isotopic abundances of the +1 and +2 mass peaks. Comparing the five pairs of measured and calculated values using a Profile Generation Model provided the correct composition. Often, for molecules not containing Cl or Br, the +2 isotopic peak abundance was very small or mass interferences were present, and only three comparisons could be made. This was also true for the +1 isotopic peak when Cl or Br atoms were present. Then multiple compositions were sometimes possible. In these cases, the composition with the fewest heteroatoms was usually correct. No apparent molecular ions or fragment ions were found to contain F atoms, and compositions containing F atoms were discarded. Compositions related to those of other compounds already found were also preferred. Knowledge of organic chemistry

was also considered when culling multiple possible ion compositions.

Forty-two identifications were confirmed based on comparisons of retention times and mass spectra with those of purchased standards. Forty-three tentative identifications remained. Many of these compounds were closely related to identifed compounds. Compounds that did not provide molecular ions could only be characterized by determining the composition of the largest observed fragment ion.

Longer lists of identified and tentatively identified compounds were compiled using ICE than could be compiled from data acquired with low resolving power. These lists could enable a more thorough assessment of the risk posed to humans by the water overlying the pollutant plume and would provide a more detailed inventory of compounds and transformation products for establishing one or more pollutant sources.

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References

Final drafts of Grange et al. articles through 2003 are available at http://www.epa.gov/nerlesd1/chemistry/ice/default.htm.

Grange, A. H., J. R. Donnelly, W. C. Brumley, and G. W. Sovocool. 1996. Determination of Elemental Compositions from Mass Peak Profiles of the Molecular (M), M+1, and M+2 Ions Anal. Chem. 68: 553-560.

Grange, A. H., and W. C. Brumley. 1997. A Mass Peak Profile Generation Model to Facilitate Determination of Elemental Compositions of Ions Based on Exact Masses and Isotopic Abundances. J. Amer. Soc. Mass Spectrom. 8: 170-182.

Grange, A. H., G. W. Sovocool, J. R. Donnelly, F. A. Genicola, and D. F. Gurka. 1998. Identification of Pollutants in a Municipal Well Using High Resolution Mass Spectrometry. Rapid Commun. Mass Spectrom. 12: 1161-1169.

Grange, A. H., L. Osemwengie, G Brilis, and G. W. Sovocool. 2001. Ion Composition Elucidation (ICE): An Investigative Tool for Characterization and Identification of Compounds of Regulatory Importance. International J. Environmental Forensics 2: 61-74.

Grange, A. H. and G. W. Sovocool, 2003. Identifying Compounds Despite Chromatographic Limitations: Organophosphates in Treated Sewage. LC-GC 21: 1072-1076.

Grange, A. H., P. M.Thomas, M. Solomon and G. W. Sovocool, 2003. Identification of Compounds in South African Stream Samples Using Ion Composition Elucidation (ICE). Poster: 51st ASMS Conf. on Mass Spectrom. & Allied Topics, Montreal, Ontario,

6/2-6/6. Available at: http://www.epa.gov/nerlesd1/chemistry/ice/sa.htm

Grange, A. H., W. Winnik, P. L. Ferguson, and G. W. Sovocool. 2005. Using a Triple Quadrupole Mass Spectrometer in Accurate Mass Mode and an Ion Correlation Program to Identify Compounds. Rapid Commun. Mass Spectrom. 19: 2699-2715.

Grange, A.H., M. C. Zumwalt, and G. W. Sovocool. 2006. 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. 20: 89-102.

Grange, A. H., R. B. Cody, Jr. and G. W. Sovocool, 2006. An Ion Correlation Program for Deconvoluting Composite Mass Spectra Acquired using a Direct Surface Ionization Source Interfaced to a Time-of Flight Mass Spectrometer. Poster: Pittsburgh Conference, Orlando, FL, 3/12-3/16. Available from author.

Jörundsdóttir, H., K. Norström, M. Olsson, H. Pham-Tuan, H. Hühnerfuss, A. Bignert, and C. Bergman. 2006. Temporal Trend of Bis(4-chlorophenyl) Sulfone, Methylsulfonyl-DDE and -PCBs in Baltic Guillemot (*Uria aalge*) Egg 1971–2001 – A Comparison to 4,4'-DDE and PCB Trends. Environ. Pollut. 141: 226-237.

NIST/EPA/NIH Mass Spectral Library, Version 2.0, Standard Reference Data Program, National Institute of Standards and Technology, U.S. Dept. of Commerce, NIST Mass Spectrometry Data

Center, Gaithersburg, MD 20899, 2002.

Snyder, S.A., K. L. Kelly, A. H. Grange, G. W. Sovocool, E. M. Snyder, and J. P. Giesy. 2001. Pharmaceuticals and Personal Care Products in the Waters of Lake Mead, Nevada, in Pharmaceuticals and Personal Care Products in the Environment: Scientific and Regulatory Issues; Daughton, C.G. & Jones-Lepp, T., Eds.; Symposium Series 791, Amer. Chem. Soc.: Washington, DC, 116-141.

Vetter, W., L. Alder, and R. Palavinskas, 1999. Mass Spectrometric Characterization of Q1, a C9H3Cl7N2 Contaminant in Environmental Samples. Rapid Commun. Mass Spectrom. 13: 2118-2124.

Wiley Registry of Mass Spectra, 6th ed. Palisade Corp., Newfield, NY.

Wu, J., W. Vetter, G. W. Gribble, J. S. Schneekloth Jr., D. H. Blank, and H. Görls. 2002. Structure and Synthesis of the Natural Heptachloro-1'-methyl-1,2'-bipyrrole (Q1) Angew. Chem. Int. Ed 41 10: 1740-1743.

EPA Methods

Appendix A to Part 136, Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Method 625 -- Base/Neutrals and Acids at http://www.epa.gov/waterscience/methods/guide/625.pdf

Appendix A to Part 136, Method 1625 Revision B -- Semivolatile Organic Compounds by Isotope Dilution GC/MS at http://www.epa.gov/waterscience/methods/guide/1625.pdf

Method 8270C, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) at http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8270c.pdf

Method 8290, Polychlorodibenzodioxins (PCDDs) and Polychlorodibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS) at http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8290.pdf

Method 1613, Revision B, Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS at http://www.epa.gov/waterscience/methods/1613.pdf

Tables

Table 1. Output from the Profile Generation Model based on the exact masses and relative isotopic abundances from the partial profiles in Figure 3d

Table 2. Compounds confirmed with standards by retention times and mass spectra

Table 3. Tentatively Identified Compounds

Figure Captions

Figure 1. (a) A low resolution mass spectrum and three outputs provided by a Lotus 123 spreadsheet using SIR data: (b) full profile, 100-ppm mass increment, and 3,000 resolving power; (c) full profile, 10-ppm increments, and 10,000 resolving power; and (d) partial profiles, 10-ppm increment, and 10,000 resolving power. The lock mass (m/z 142.99199) is a calibration ion from perfluorokerosene.

Figure 2. The total ion chromatogram for the extract containing the largest number of chromatographic peaks

Figure 3. Nine background-subtracted mass spectra for chromatographic peaks observed in the

total ion chromatogram in Figure 2.

Figure 4. (a) ion chromatograms for two m/z ratios of the mass peak profile, (b) a background subtracted mass spectrum for the most abundant isomer, and (c) the NIST library match for Pummerer's ketone.

Table 1. Output from the PGM based on the exact masses and RIAs from the partial profiles in Figure 1d*

m/z = 139.0269 ± 6 ppm Resolving Power: 10,000

#	RDB Range	Composition	Monoistopic Ion Exact Mass	(M+1) Profile Exact Mass	(M+2) Profile Exact Mass	%1 RIA Allowed Range (%)	%2 RIA Allowed Range (%)
1	1.5 2.5	$CH_4N_4O_3F$	139.02674	140.02645 **X**	141.03098 **X**	1.66 (1.17-2.29) **X**	0.61 (0.47-0.75)
2	0.5 1.5	$C_2H_8N_2O_3P$	139.02725	140.03003	141.03148 **X**	2.64 (2.18-3.18) **X**	0.63 (0.49-0.76)
3	1.0	$C_4H_7NF_2S$	139.02673	140.02952	141.02252 **X**	5.06 (4.14-5.05) **X**	0.38 (0.03-1.11)
4	5.0 6.0	$C_6H_5NO_3$	139.02694	140.03028	141.03168	6.89 (5.88-7.93)	0.78 (0.65-0.92)
Experimental Values:			139.02690	140.03027	141.03238	6.70	0.66

*The mass of the electron was not subtracted from ion masses. The calibrant ion closest in mass to each analyte ion was automatically chosen by the software and differed by no more than 7 Da from the analyte ion mass. Hence, this oversight had no significant effect on determining ion compositions. For example, 0.00055 Da, the mass of an electron, is 3.0 ppm of 180.98882 Da, the mass of a perfluorokerosene ion, and 2.9 ppm of 187.97772 Da, a mass about 7 Da greater. These two errors nearly cancel out.

Table 2. Compounds Confirmed with Standards by Retention Times and Mass Spectra

Note	Identified Compound	Apparent Molecular Ion or Fragment Ion (F)	Monoisotopic Ion Exact Mass (ppm Mass Error)	(M+1) Profile Exact Mass (ppm Mass Error)	(M+2) Profile Exact Mass (ppm Mass Error)	(M+1) Profile Relative Isotopic Abundance	(M+2) Profile Relative Isotopic Abundance
§	dibromochloromethane	$CHBr_2Cl^+$	205.81372 (+4.5)				
‡	Fragment	$CHBrCl^+$ (F)	126.89563 (+4.9)	127.89837 (– 0.2)	128.89341 (+5.1)	1.16	130.31
§‡	Bromoform	$CHBr_3^+$	249.76279 (–0.2)		251.76073 (–0.2)		264.91
§	p-benzoquinone	$C_6H_4O_2^+$	108.02103 (+4.2)				
§‡	Phenol	$C_6H_6O^+$	94.04147 (–4.1)	95.04491 (–3.6)	96.04691 (–4.5)	5.83	
§‡	Benzonitrile	$C_7H_5N^+$	103.04231 (+1.1)	104.04557 (+0.4)		7.26	
§‡	octamethylcyclotetrasiloxane	$C_7H_{21}O_4Si_4^+$ (F)	281.05181 (+2.3)			28.06	16.87
§‡	1,3-dichlorobenzene	$C_6H_4Cl_2^+$	145.96897 (–0.3)		147.96528 (–5.3)		57.87
§	1,4-dichlorobenzene	$C_6H_4Cl_2^+$	†		†		†
§	1,2-dichlorobenzene	$C_6H_4Cl_2^+$	†		†		†
§‡	2-bromotoluene	$C_7H_7Br^+$	169.97383 (+4.2)	170.97730 (+4.7)	171.97191 (+4.8)	7.80	90.89
§	4-bromotoluene	$C_7H_7Br^+$	†		†		†
§‡	2-bromophenol	$C_6H_5OBr^+$	171.95246 (+0.5)	172.95582 (+0.3)	173.95035 (0)	6.24	98.24
§	2-cresol	$C_7H_8O^+$	108.05750 (–0.1)	109.06053 (–3.5)			
§	4-cresol &/or 3-cresol	$C_7H_8O^+$	†	†			
§‡!	┌ 2-bromo-m-xylene | 2-bromo-p-xylene | 4-bromo-m-xylene └ 5-bromo-m-xylene	$C_8H_9Br^+$	183.98824 (–2.8)	184.99152 (–3.5)	185.98610 (–3.4)		
§‡	2,4-dichlorophenol	$C_6H_4OCl_2^+$	161.96397 (+0.3)	162.96732 (+0.1)	163.96168 (+4.1)		
§‡	2-iodophenol	$C_6H_5OI^+$	219.93957 (+4.8)	220.94311 (+5.5)		6.58	
§‡	4- &/or 3-iodophenol	$C_6H_5OI^+$	†	†		†	
§‡*	4- &/or 3-chlorophenol	$C_6H_5OCl^+$	128.00303 (+1.1)	129.00638 (+0.8)	130.00012 (+1.0)	6.21	28.96
§‡	Benzothiazole	$C_7H_5NS^+$	135.01366 (–4.5)	136.01735 (+0.1)	137.00957 (–4.3)		

§	4-methyl-2-nitrophenol	$C_7H_7NO_3^+$	153.04207 (–3.4)	154.04531 (–3.3)	155.04760 (+0.7)			
§	3-methyl-2-nitrophenol	$C_7H_7NO_3^+$	153.04188 (–4.6)			7.82		
§	2-bromo-4-chlorophenol	$C_6H_4OClBr^+$	205.91256 (–4.1)	206.91597 (–4.0)	207.91038 (–3.7)		133.42	
§	4-bromo-2-chlorophenol	$C_6H_4OClBr^+$	†	†	†		†	
§‡	2-bromomesitylene	$C_9H_{11}Br^+$	198.00450 (+0.5)		200.00221 (–0.9)			
§‡*	4- &/or 3-bromophenol	$C_6H_5OBr^+$	171.95246 (+0.5)	172.95582 (+0.3)	173.95035 (0)	6.25	98.24	
§‡	4-tert-butylphenol	$C_{10}H_{14}O^+$	150.10520 (+4.9)	151.10786 (-0.1)				
§‡	2,4-dibromophenol	$C_6H_4OBr_2^+$	249.86401 (+4.5)	250.86743 (+4.6)	251.86197 (+4.4)	6.84	191.94	
§‡	2,6-dibromophenol	$C_6H_4OBr_2^+$	†	†	†	†	†	
§	4-bromo-3-methylphenol	$C_7H_7OBr^+$	185.96720 (–4.4)		187.96518 (–4.5)	8.20	91.88	
§‡	Biphenyl	$C_{12}H_{10}^+$	154.07765 (–3.9)	155.08101 (–4.0)	156.08467 (–2.2)	11.92		
§‡	diphenyl ether	$C_{12}H_{10}O^+$	170.07320 (+0.2)	171.07666 (+0.6)	172.08038 (+5.3)	12.36		
§	dimethyl phthalate	$C_9H_7O_3^+$ (F)	163.03898 (–3.3)	164.04287 (–0.2)	165.04411 (–4.5)			
§#	2,4-di-*tert*-butylphenol	$C_{14}H_{22}O^+$	206.16627 (–3.9)	207.16999 (–2.4)		13.83		
§	DEET	$C_{12}H_{17}NO^+$	191.13046 (–2.7)	192.13354 (–3.5)				
§#	diethyl phthalate	$C_{10}H_9O_3^+$ (F)	177.05459 (–3.3)					
§	2,4,6-tribromophenol	$C_6H_3OBr_3^+$	327.77222 (–3.6)		329.77027 (–3.3)		287.72	
§‡	4-bromodiphenylether	$C_{12}H_9OBr^+$	247.98304 (–2.6)	248.9873 (+1.0)	249.9813 (–1.6)	12.40	94.90	
§‡#	anthracene/phenanthrene	$C_{14}H_{10}^+$	178.07764 (–3.4)	179.08240 (+4.3)		15.69		
§	Pyrene	$C_{16}H_{10}^+$	202.07741 (–4.2)	203.08099 (–3.2)	204.08511 (+0.5)		1.44	
§	Fluoranthene	$C_{16}H_{10}^+$	†	†	†		†	
§#	Triphenylphosphate	$C_{18}H_{15}O_4P^+$	326.07066 (–0.4)	327.07433 (+0.4)	328.07664 (–0.6)	20.37		

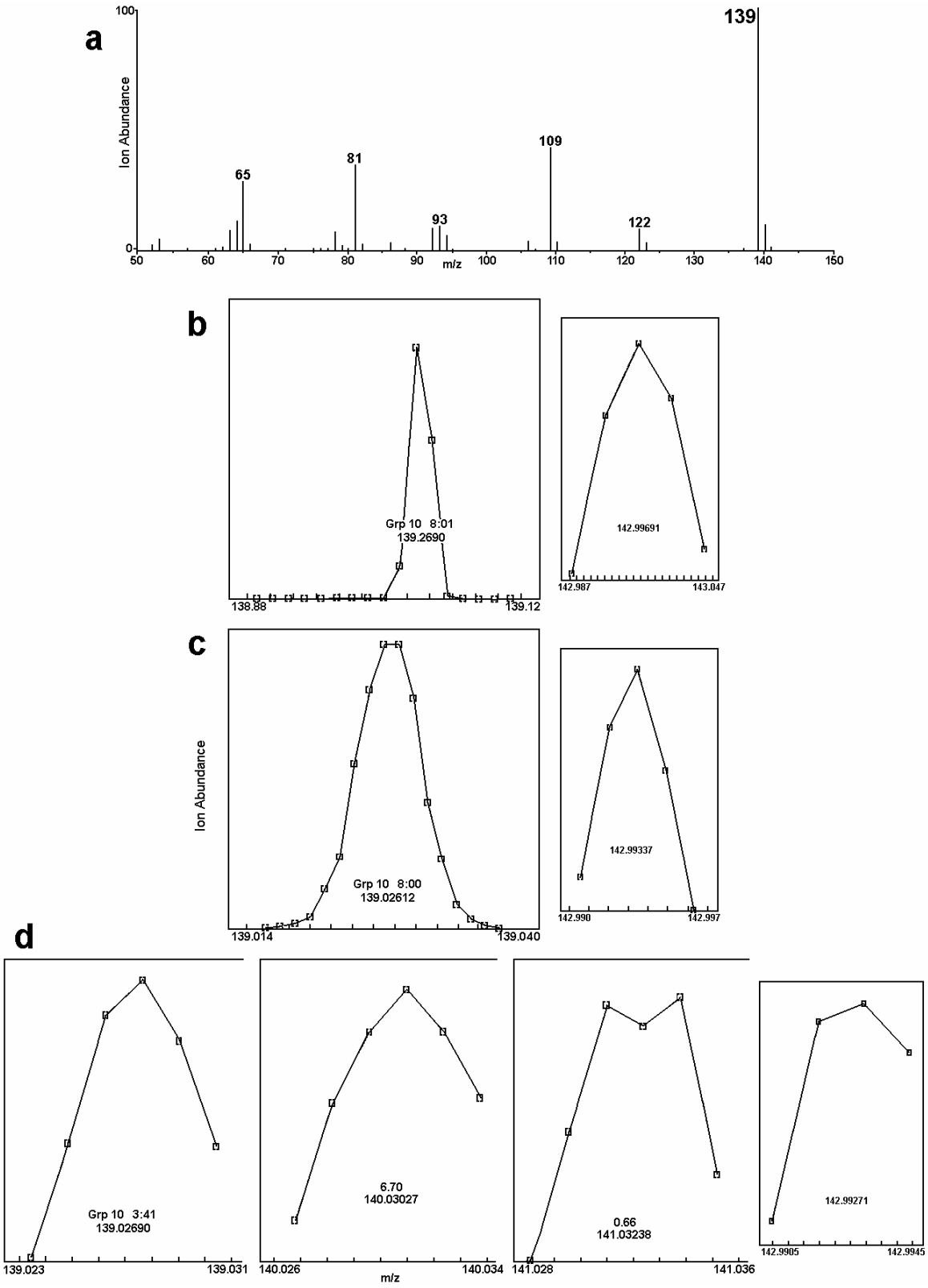
§ The tentative identification was confirmed using a purchased standard.
‡ Only one composition was possible. No assumptions regarding the presence of P or F atoms were necessary.
† The exact masses and RIAs were measured for a different isomer.
! These four isomers co-elute and cannot be distinguished from each other.
* The RTs for both standards were indistinguishable. The para isomer is more likely based on electrophilic reaction chemistry.
# Also found in the blank.

Table 3. Tentatively Identified Compounds

Note	Tentatively Identified Compound	Apparent Molecular Ion or Fragment Ion (F)	Monoisotopic Ion Exact Mass (ppm Mass Error)	(M+1) Profile Exact Mass (ppm Mass Error)	(M+2) Profile Exact Mass (ppm Mass Error)	(M+1) Profile Relative Isotopic Abundance	(M+2) Profile Relative Isotopic Abundance
‡	Dichloroethylene	$C_2H_2Cl_2^+$	95.95331 (–0.5)	96.95627 (–4.8)	97.95046 (+0.5)		
‡	Dibromomethane	$CH_2Br_2^+$	171.85159 (–4.1)		173.84953 (–4.3)	1.08	203.37
‡!	Toluene	$C_7H_8^+$	92.06199 (–6.6)	93.06551 (–5.3)	94.06928 (–1.3)	7.11	
‡	2-methyl-1-butanal	$C_5H_{10}O^+$	86.07284 (–3.7)	87.07625 (–3.8)			
‡	Xylene	$C_8H_{10}^+$	106.07780 (– 4.2)	107.08132 (– 3.0)	108.08472 (–3.1)	8.13	
‡	Xylene	$C_8H_{10}^+$	106.07842 (+1.6)	107.08192 (+2.6)		8.25	
	Xylene	$C_8H_{10}^+$	†	†	†	†	
‡	3-decanol	$C_8H_{17}O^+$ (F)	129.12769 (–1.9)			9.92	
‡	Chlorotoluene	$C_7H_7Cl^+$	126.02363 (0)	127.02759 (+4.5)	128.02068 (–0.2)		
	Chlorotoluene	$C_7H_7Cl^+$	†	†	†		
	1,3-dibromo-3-methylbutane	$C_5H_{10}Br^+$ (F)	148.99652 (–0.5)		150.99438 (–1.1)		
‡	3,6-dimethyl-3-heptanol	$C_8H_{17}O^+$ (F)	129.12769 (–1.9)				
‡	alpha-methylbenzyl alcohol	$C_8H_{10}O^+$	122.07286 (–2.5)	123.07641 (–1.2)		9.50	
‡	acetyl hydroxy methylcyclohexane	$C_7H_{13}O^+$ (F)	113.09662 (–0.2)	114.09973 (–2.9)		8.12	
‡	Nitrophenol	$C_6H_5NO_3^+$	139.02690 (–0.3)	140.03027 (–0.1)	141.03238 (+5.0)		0.66
‡	Nitrophenol	$C_6H_5NO_3^+$	139.02641 (–3.8)	140.02965 (–4.5)	141.03102 (–4.7)	6.40	0.65
◊	decamethylcyclopentasiloxane	$C_9H_{27}O_5Si_5^+$ (F)	355.06904 (–4.1)	356.06952 (–4.7)	357.06716 (–4.3)	11.69	99.00
	2-hydroxy acetophenone	$C_8H_8O_2^+$	136.05256 (+1.0)	137.05638 (+4.1)	138.05737 (–3.6)		
‡	1-bromo-2-butanone	$C_4H_7OBr^+$	149.96873 (+4.7)		151.96672 (+4.8)		97.78
‡!	dibromochlorobenzene	$C_6H_3Br_2Cl^+$	267.82676 (–8.4)	268.82974 (–9.8)	269.82563 (–4.4)		224.16
‡	2,4,6-trichlorophenol	$C_6H_3OCl_3^+$	195.92505 (+0.5)	196.92833 (0)	197.92219 (+0.9)		
‡	bromomethylphenol	$C_7H_7OBr^+$	185.96720 (–4.5)		187.96518 (–4.4)	8.20	91.88
	5-bromo-4-hydroxy-m-cymene	$C_{10}H_{13}OBr^+$	228.01517 (+0.8)	229.01827 (–0.5)	230.01301 (+0.2)		104.43
‡#	surfynol 104	$C_{10}H_{15}O^+$ (F)	151.11218 (–0.7)	152.11571 (+0.1)	153.11858 (+0.7)	11.08	
‡	bromonitrophenol	$C_6H_4NO_3Br^+$	216.93831 (+3.9)		218.93542 (–0.2)		103.02

‡	bromonitrophenol	$C_6H_4NO_3Br^+$	216.93806 (+2.8)		218.93480 (–3.1)		99.00
‡	bromodichlorophenol	$C_6H_3OCl_2Br^+$	239.87462 (+0.8)		241.87240 (+1.5)		149.78
‡	dibromomethylphenol	$C_7H_6OBr_2^+$	263.87734 (–4.5)		265.86197 (–4.8)		
	dibromomethylphenol	$C_7H_6OBr_2^+$	†		†		
	bromoiodophenol	$C_6H_4OBrI^+$	297.84953 (+1.7)	298.85234 (–0.2)	299.84837 (+4.6)		99.58
	bromoiodophenol	$C_6H_4OBrI^+$	†	†	†		†
	bromoiodophenol	$C_6H_4OBrI^+$	†	†	†		†
	chlorodibromophenol	$C_6H_3OClBr_2^+$	283.82286 (–3.7)		285.82089 (–3.0)		240.09
	chlorodibromophenol	$C_6H_3OClBr_2^+$	†		†		†
	2-phenoxyphenol	$C_{12}H_{10}O_2^+$	186.06715 (–5.0)			12.77	
‡	4-methoxy-nitrobenzene	$C_7H_7NO_3^+$	153.04207 (–3.4)	154.04531 (–3.3)	155.04760 (+0.7)		
‡	Benzophenone	$C_{13}H_{10}O^+$	182.07322 (+0.3)	183.07661 (+0.3)	184.07867 (–4.6)	12.85	
	2-acetyl-6-methoxynaphthalene	$C_{13}H_{12}O_2^+$	200.08288 (–4.2)	201.08640 (–3.6)	202.08886 (–4.7)		
‡#!	2,2'-diethylbiphenyl	$C_{16}H_{18}^+$	210.13884 (–9.6)	211.14315 (–5.2)		17.90	
	dibromoiodophenol	$C_6H_3OBr_2I^+$	375.76124 (+4.6)		377.75767 (+0.5)		211.54
*#	butylbenzylphthalate	$C_{12}H_{14}O_3^+$ (F)	206.09385 (–2.1)		208.10120 (+5.6)	17.78	
‡*#	di-2-ethylhexyl adipate	$C_{14}H_{27}O_4^+$ (F)	259.18978 (–4.4)	260.19459 (+0.8)	261.19765 (+3.4)	17.68	
*#	bis(2-ethylhexyl)phthalate	$C_{16}H_{23}O_4^+$ (F)	279.15863 (–3.6)	280.16325 (+0.7)			

‡ Only one composition was possible. No assumptions regarding the presence of P or F atoms were necessary.
! 12-ppm mass error limits used.
† The exact masses and RIAs were measured for a different isomer.
# Also found in the blank.
* Fragment ion


a
Ion Abundance
100
0
139
109
81
65
93
122
50
60
70
80
90
m/z
100
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120
130
140
150
b
Grp 10 8:01
139.2690
138.88
139.12
142.99691
142.987
143.047
c
Ion Abundance
Grp 10 8:00
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139.040
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142.997
d
Grp 10 3:41
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139.031
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140.03027
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m/z
0.66
141.03238
141.028
141.036
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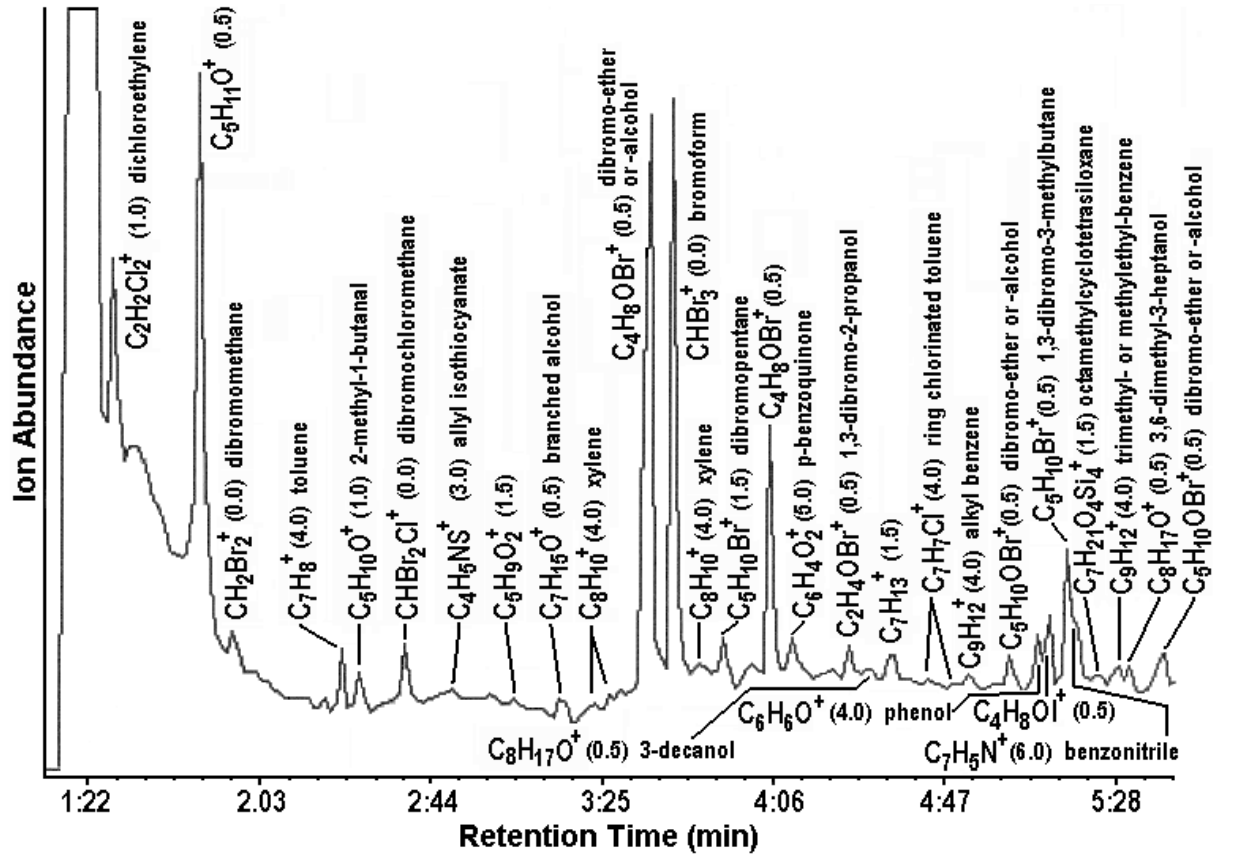
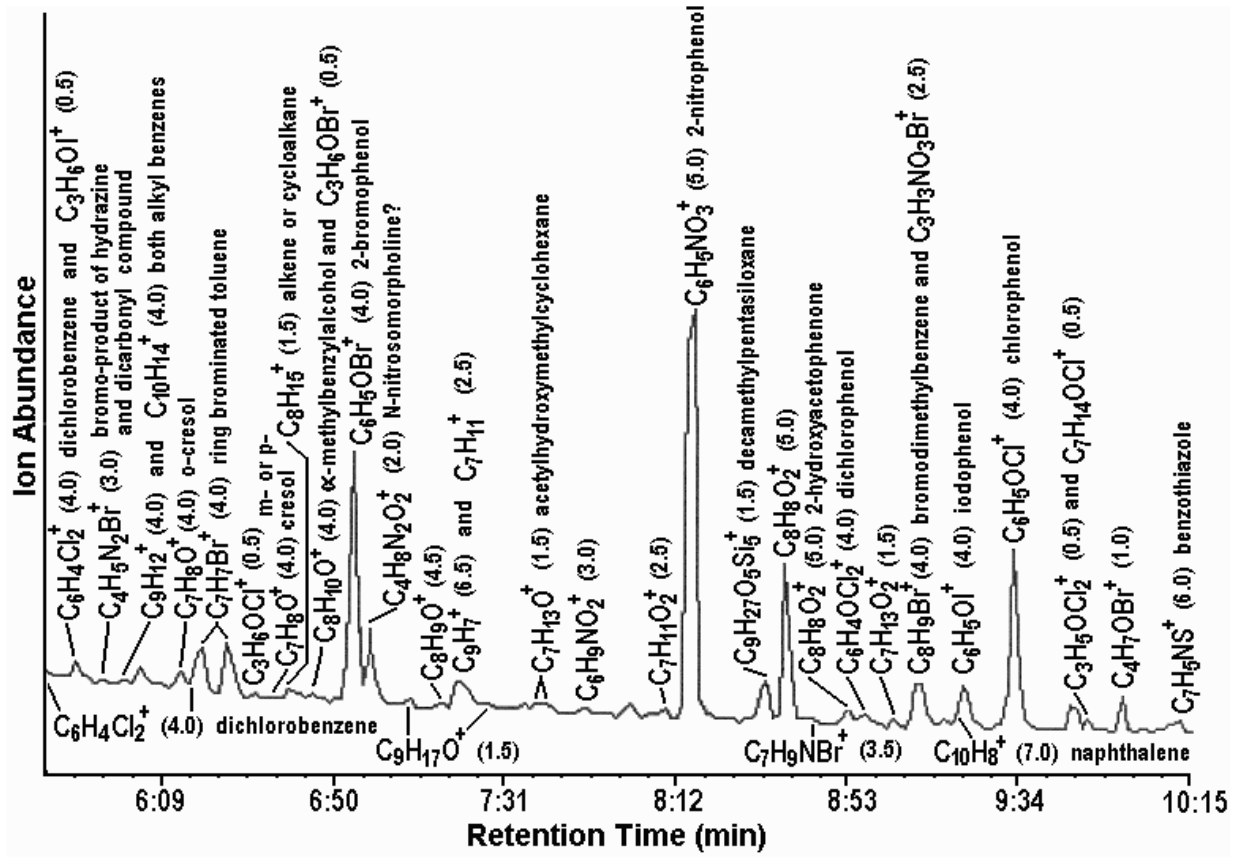
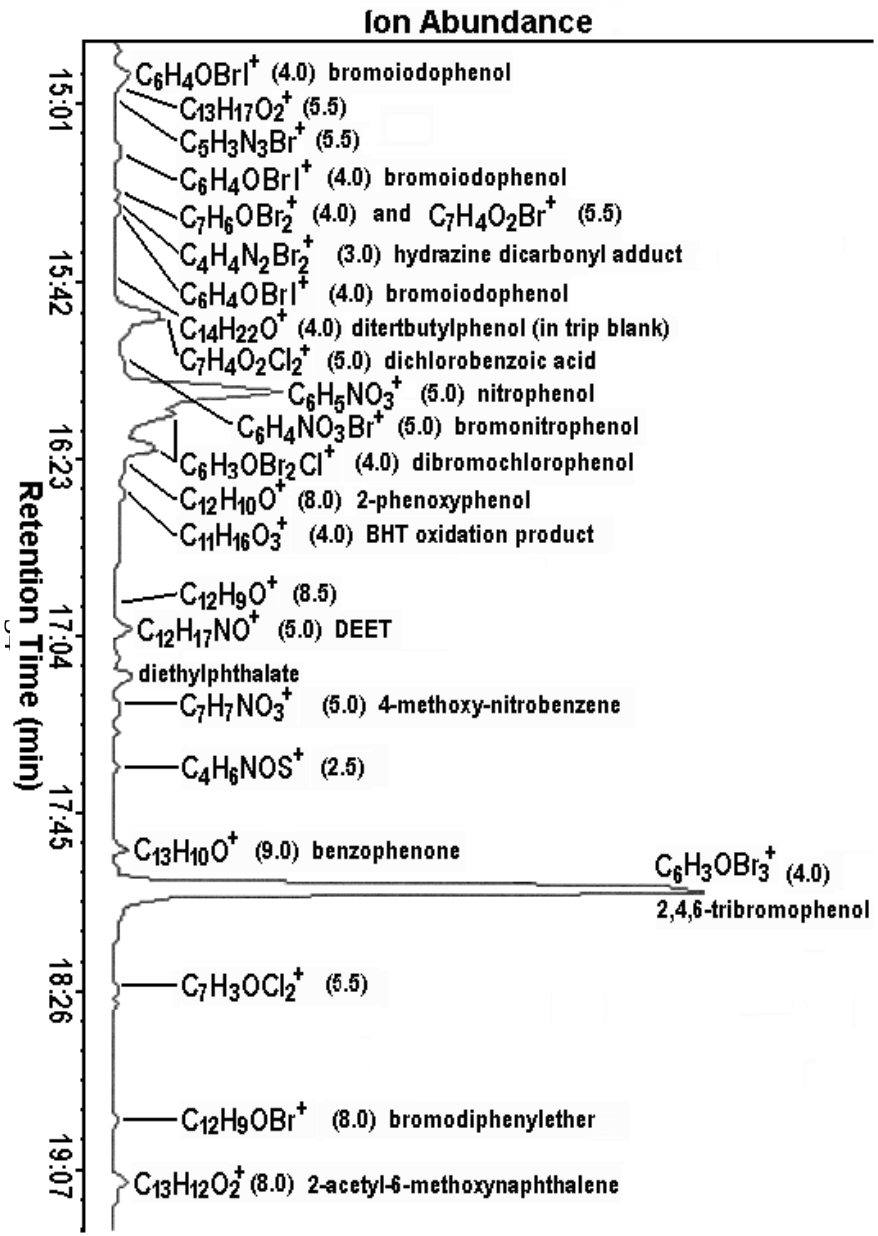
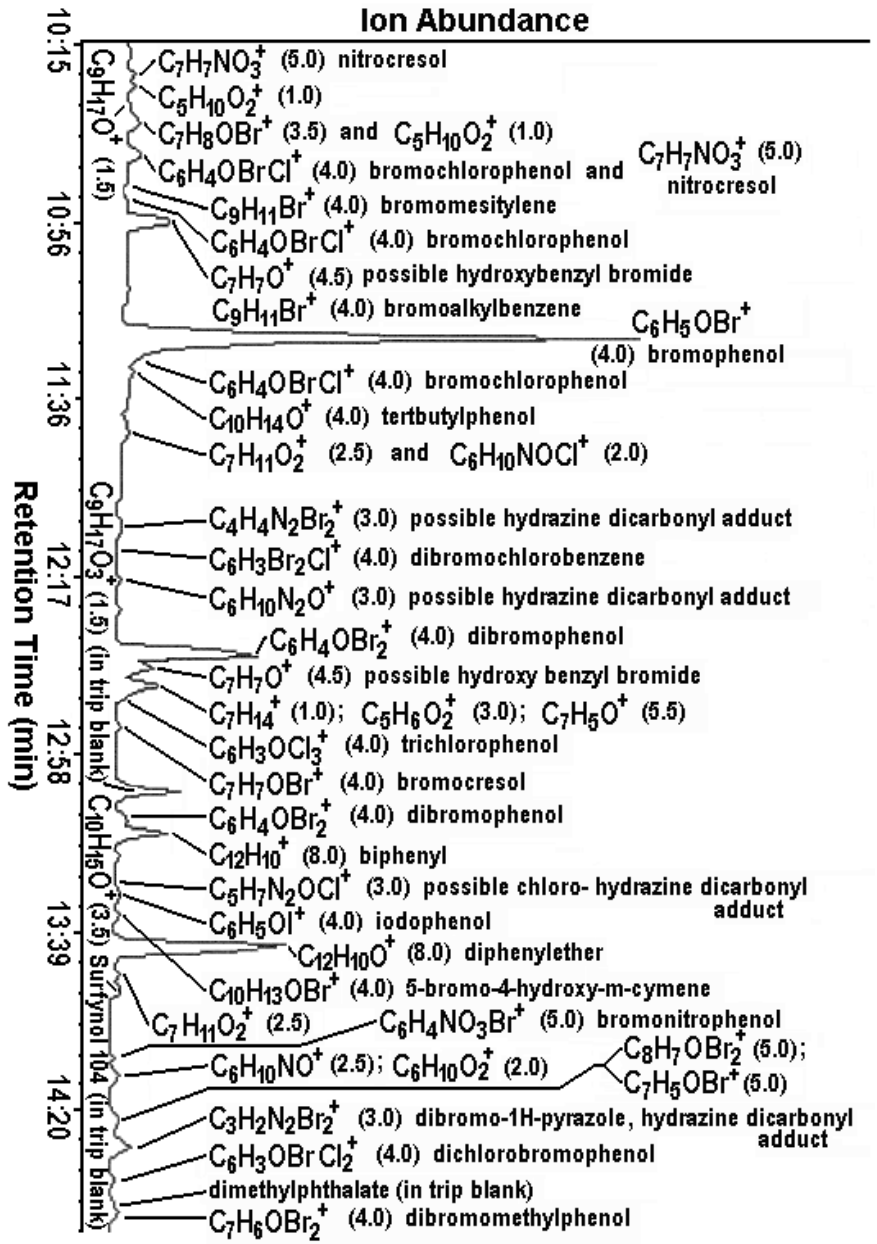
142.9905
142.9945

Figure 1.


Ion Abundance
$C_2H_2Cl_2^+$ (1.0) dichloroethylene
$C_5H_{11}O^+$ (0.5)
$CH_2Br_2^+$ (0.0) dibromomethane
$C_7H_8^+$ (4.0) toluene
$C_5H_{10}O^+$ (1.0) 2-methyl-1-butanal
$CHBr_2Cl^+$ (0.0) dibromochloromethane
$C_4H_5NS^+$ (3.0) allyl isothiocyanate
$C_5H_9O_2^+$ (1.5)
$C_7H_{15}O^+$ (0.5) branched alcohol
$C_8H_{10}^+$ (4.0) xylene
$C_4H_8OBr^+$ (0.5) dibromo-ether or -alcohol
$C_8H_{10}^+$ (4.0) xylene
$CHBr_3^+$ (0.0) bromoform
$C_5H_{10}Br^+$ (1.5) dibromopentane
$C_4H_8OBr^+$ (0.5)
$C_6H_4O_2^+$ (5.0) p-benzoquinone
$C_2H_4OBr^+$ (0.5) 1,3-dibromo-2-propanol
$C_7H_{13}^+$ (1.5)
$C_7H_7Cl^+$ (4.0) ring chlorinated toluene
$C_9H_{12}^+$ (4.0) alkyl benzene
$C_5H_{10}OBr^+$(0.5) dibromo-ether or -alcohol
$C_5H_{10}Br^+$(0.5) 1,3-dibromo-3-methylbutane
$C_7H_{21}O_4Si_4^+$ (1.5) octamethylcyclotetrasiloxane
$C_9H_{12}^+$ (4.0) trimethyl- or methylethyl-benzene
$C_8H_{17}O^+$ (0.5) 3,6-dimethyl-3-heptanol
$C_5H_{10}OBr^+$(0.5) dibromo-ether or -alcohol
$C_6H_6O^+$ (4.0) phenol
$C_4H_8OI^+$ (0.5)
$C_8H_{17}O^+$ (0.5) 3-decanol
$C_7H_5N^+$ (6.0) benzonitrile
1:22
2.03
2:44
3:25
4:06
4:47
5:28
Retention Time (min)


Ion Abundance
$C_6H_4Cl_2^+$ (4.0) dichlorobenzene and $C_3H_6OI^+$ (0.5)
$C_4H_5N_2Br^+$ (3.0) bromo-product of hydrazine and dicarbonyl compound
$C_9H_{12}^+$ (4.0) and $C_{10}H_{14}^+$ (4.0) both alkyl benzenes
$C_7H_8O^+$ (4.0) o-cresol
$C_7H_7Br^+$ (4.0) ring brominated toluene
$C_3H_6OCl^+$ (0.5) m- or p-
$C_7H_8O^+$ (4.0) cresol
$C_8H_{15}^+$ (1.5) alkene or cycloalkane
$C_8H_{10}O^+$ (4.0) α-methylbenzylalcohol and $C_3H_6OBr^+$ (0.5)
$C_6H_5OBr^+$ (4.0) 2-bromophenol
$C_4H_8N_2O_2^+$ (2.0) N-nitrosomorpholine?
$C_8H_9O^+$ (4.5)
$C_9H_7^+$ (6.5) and $C_7H_{11}^+$ (2.5)
$C_7H_{13}O^+$ (1.5) acetylhydroxymethylcyclohexane
$C_6H_9NO_2^+$ (3.0)
$C_7H_{11}O_2^+$ (2.5)
$C_6H_5NO_3^+$ (5.0) 2-nitrophenol
$C_9H_{27}O_5Si_5^+$ (1.5) decamethylpentasiloxane
$C_8H_8O_2^+$ (5.0)
$C_8H_8O_2^+$ (5.0) 2-hydroxyacetophenone
$C_6H_4OCl_2^+$ (4.0) dichlorophenol
$C_7H_{13}O_2^+$ (1.5)
$C_8H_9Br^+$(4.0) bromodimethylbenzene and $C_3H_3NO_3Br^+$ (2.5)
$C_6H_5OI^+$ (4.0) iodophenol
$C_6H_5OCl^+$ (4.0) chlorophenol
$C_3H_5OCl_2^+$ (0.5) and $C_7H_{14}OCl^+$ (0.5)
$C_4H_7OBr^+$ (1.0)
$C_7H_5NS^+$ (6.0) benzothiazole
$C_6H_4Cl_2^+$ (4.0) dichlorobenzene
$C_9H_{17}O^+$ (1.5)
$C_7H_9NBr^+$ (3.5)
$C_{10}H_8^+$ (7.0) naphthalene
6:09
6:50
7:31
8:12
8:53
9:34
10:15
Retention Time (min)


Ion Abundance
Retention Time (min)
15:01
15:42
16:23
17:04
17:45
18:26
19:07
$C_6H_4OBrI^+$ (4.0) bromoiodophenol
$C_{13}H_{17}O_2^+$ (5.5)
$C_5H_3N_3Br^+$ (5.5)
$C_6H_4OBrI^+$ (4.0) bromoiodophenol
$C_7H_6OBr_2^+$ (4.0) and $C_7H_4O_2Br^+$ (5.5)
$C_4H_4N_2Br_2^+$ (3.0) hydrazine dicarbonyl adduct
$C_6H_4OBrI^+$ (4.0) bromoiodophenol
$C_{14}H_{22}O^+$ (4.0) ditertbutylphenol (in trip blank)
$C_7H_4O_2Cl_2^+$ (5.0) dichlorobenzoic acid
$C_6H_5NO_3^+$ (5.0) nitrophenol
$C_6H_4NO_3Br^+$ (5.0) bromonitrophenol
$C_6H_3OBr_2Cl^+$ (4.0) dibromochlorophenol
$C_{12}H_{10}O^+$ (8.0) 2-phenoxyphenol
$C_{11}H_{16}O_3^+$ (4.0) BHT oxidation product
$C_{12}H_9O^+$ (8.5)
$C_{12}H_{17}NO^+$ (5.0) DEET
diethylphthalate
$C_7H_7NO_3^+$ (5.0) 4-methoxy-nitrobenzene
$C_4H_6NOS^+$ (2.5)
$C_{13}H_{10}O^+$ (9.0) benzophenone
$C_6H_3OBr_3^+$ (4.0)
2,4,6-tribromophenol
$C_7H_3OCl_2^+$ (5.5)
$C_{12}H_9OBr^+$ (8.0) bromodiphenylether
$C_{13}H_{12}O_2^+$ (8.0) 2-acetyl-6-methoxynaphthalene


Ion Abundance
Retention Time (min)
10:15
10:56
11:36
12:17
12:58
13:39
14:20
$C_9H_{17}O^+$ (1.5)
$C_9H_{17}O_3^+$ (1.5) (in trip blank)
$C_{10}H_{15}O^+$ (3.5) Surfynol 104 (in trip blank)
$C_7H_7NO_3^+$ (5.0) nitrocresol
$C_5H_{10}O_2^+$ (1.0)
$C_7H_8OBr^+$ (3.5) and $C_5H_{10}O_2^+$ (1.0)
$C_6H_4OBrCl^+$ (4.0) bromochlorophenol and $C_7H_7NO_3^+$ (5.0) nitrocresol
$C_9H_{11}Br^+$ (4.0) bromomesitylene
$C_6H_4OBrCl^+$ (4.0) bromochlorophenol
$C_7H_7O^+$ (4.5) possible hydroxybenzyl bromide
$C_9H_{11}Br^+$ (4.0) bromoalkylbenzene
$C_6H_5OBr^+$ (4.0) bromophenol
$C_6H_4OBrCl^+$ (4.0) bromochlorophenol
$C_{10}H_{14}O^+$ (4.0) tertbutylphenol
$C_7H_{11}O_2^+$ (2.5) and $C_6H_{10}NOCl^+$ (2.0)
$C_4H_4N_2Br_2^+$ (3.0) possible hydrazine dicarbonyl adduct
$C_6H_3Br_2Cl^+$ (4.0) dibromochlorobenzene
$C_6H_{10}N_2O^+$ (3.0) possible hydrazine dicarbonyl adduct
$C_6H_4OBr_2^+$ (4.0) dibromophenol
$C_7H_7O^+$ (4.5) possible hydroxy benzyl bromide
$C_7H_{14}^+$ (1.0); $C_5H_6O_2^+$ (3.0); $C_7H_5O^+$ (5.5)
$C_6H_3OCl_3^+$ (4.0) trichlorophenol
$C_7H_7OBr^+$ (4.0) bromocresol
$C_6H_4OBr_2^+$ (4.0) dibromophenol
$C_{12}H_{10}^+$ (8.0) biphenyl
$C_5H_7N_2OCl^+$ (3.0) possible chloro- hydrazine dicarbonyl adduct
$C_6H_5OI^+$ (4.0) iodophenol
$C_{12}H_{10}O^+$ (8.0) diphenylether
$C_{10}H_{13}OBr^+$ (4.0) 5-bromo-4-hydroxy-m-cymene
$C_7H_{11}O_2^+$ (2.5)
$C_6H_4NO_3Br^+$ (5.0) bromonitrophenol
$C_6H_{10}NO^+$ (2.5); $C_6H_{10}O_2^+$ (2.0)
$C_8H_7OBr_2^+$ (5.0); $C_7H_5OBr^+$ (5.0)
$C_3H_2N_2Br_2^+$ (3.0) dibromo-1H-pyrazole, hydrazine dicarbonyl adduct
$C_6H_3OBrCl_2^+$ (4.0) dichlorobromophenol
dimethylphthalate (in trip blank)
$C_7H_6OBr_2^+$ (4.0) dibromomethylphenol

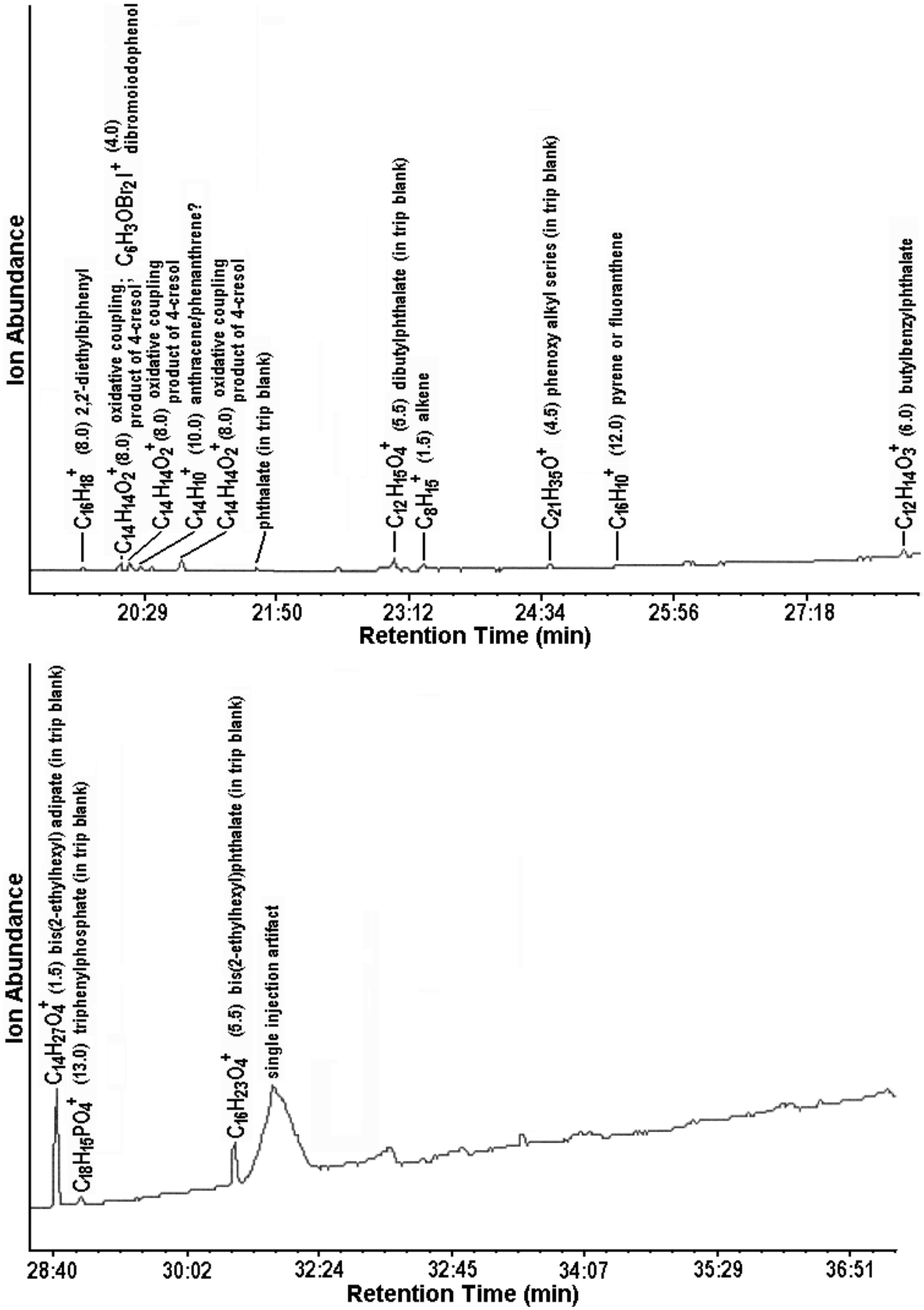

Ion Abundance
C16H18+ (8.0) 2,2'-diethylbiphenyl
C14H14O2+ (8.0) oxidative coupling product of 4-cresol
C6H3OBr2I+ (4.0) dibromoiodophenol
C14H14O2+ (8.0) oxidative coupling product of 4-cresol
C14H10+ (10.0) anthracene/phenanthrene?
C14H14O2+ (8.0) oxidative coupling product of 4-cresol
phthalate (in trip blank)
C12H15O4+ (5.5) dibutylphthalate (in trip blank)
C8H15+ (1.5) alkene
C21H35O+ (4.5) phenoxy alkyl series (in trip blank)
C16H10+ (12.0) pyrene or fluoranthene
C12H14O3+ (6.0) butylbenzylphthalate
20:29
21:50
23:12
24:34
25:56
27:18
Retention Time (min)
Ion Abundance
C14H27O4+ (1.5) bis(2-ethylhexyl) adipate (in trip blank)
C18H15PO4+ (13.0) triphenylphosphate (in trip blank)
C16H23O4+ (5.5) bis(2-ethylhexyl)phthalate (in trip blank)
single injection artifact
28:40
30:02
32:24
32:45
34:07
35:29
36:51
Retention Time (min)

Figure 2.

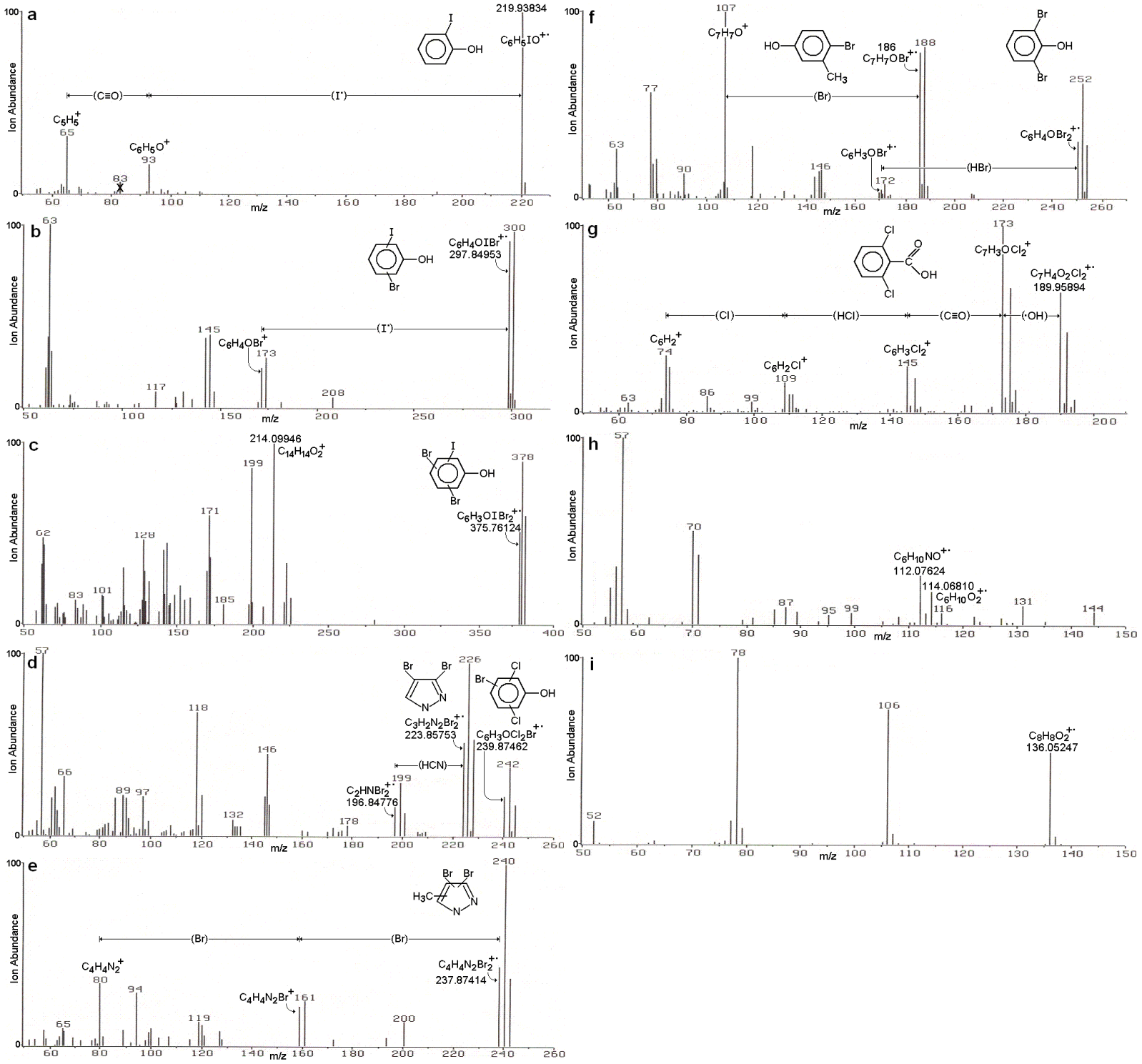

a
b
c
d
e
f
g
h
i
Ion Abundance
m/z
(C≡O)
(I•)
(Br)
(HBr)
(Cl)
(HCl)
(OH)
(HCN)
219.93834
C6H5IO+•
C6H5+
C6H5O+
C6H4OIBr+•
297.84953
C6H4OBr+
214.09946
C14H14O2+
C6H3OIBr2+•
375.76124
C3H2N2Br2+•
223.85753
C6H3OCl2Br+•
239.87462
C2HNBr2+•
196.84776
C4H4N2+
C4H4N2Br+
C4H4N2Br2+•
237.87414
C7H7O+
C7H7OBr+•
C6H4OBr2+•
C6H3OBr+•
C7H3OCl2+
C7H4O2Cl2+•
189.95894
C6H2+
C6H2Cl+
C6H3Cl2+
C6H10NO+•
112.07624
C6H10O2+•
114.06810
C8H8O2+•
136.05247

Figure 3

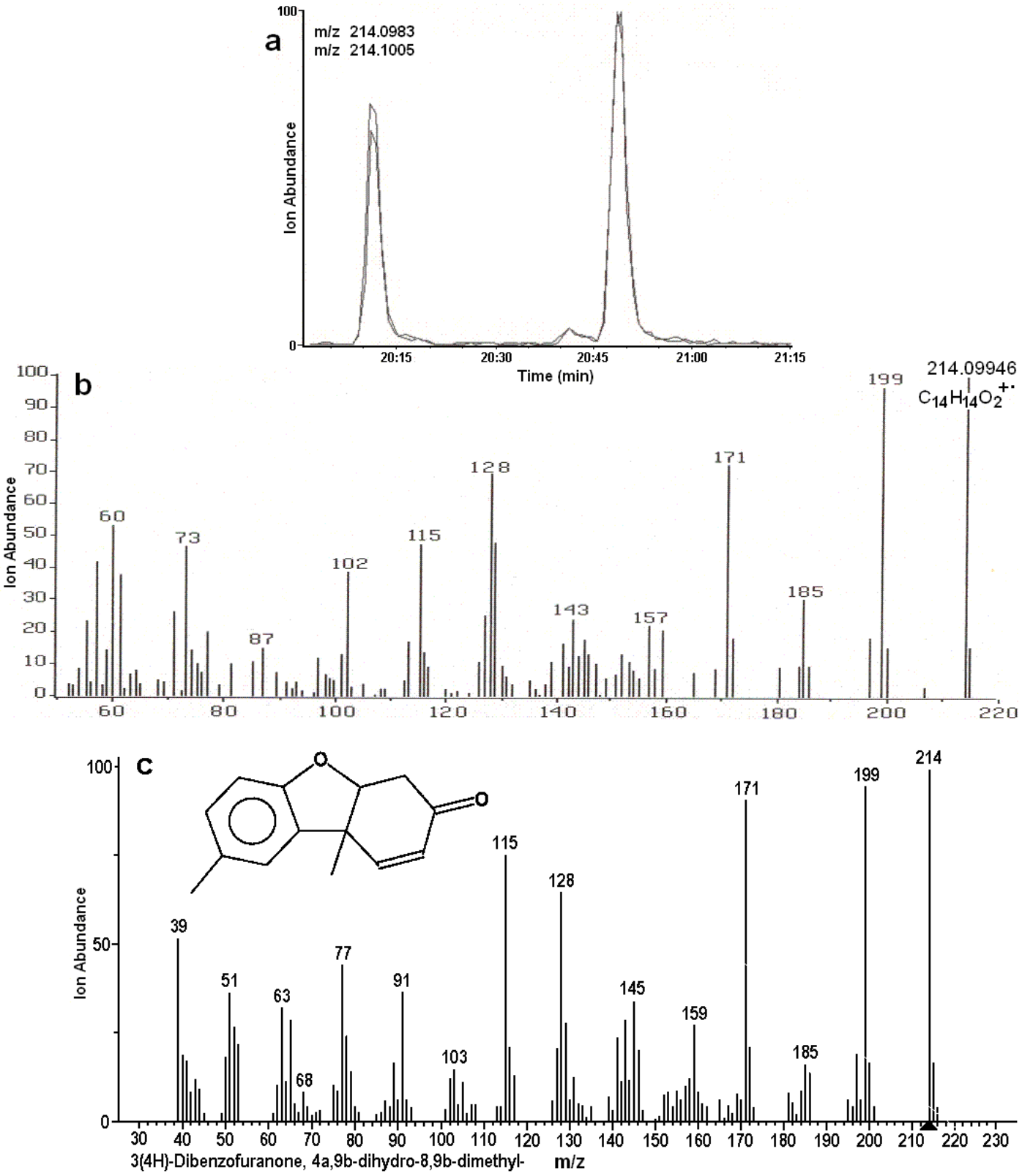

a
m/z 214.0983
m/z 214.1005
Ion Abundance
Time (min)
b
214.09946
C14H14O2+·
Ion Abundance
c
3(4H)-Dibenzofuranone, 4a,9b-dihydro-8,9b-dimethyl-
m/z

Figure 4.