6.5 ORGANIC COMPOUNDS MEASURED IN $PM_{2.5}$ DURING NEOPS

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1. INTRODUCTION

Secondary formation of submicron ambient particulate matter occurs when organic and inorganic constituents having sufficiently low volatility condense onto preexisting particles in the atmosphere. The presence of the resulting submicron particles has led to three important environmental problems. First, visibility degradation leading to haze occurs due to light scattering imposed by these particles. This problem is especially pronounced in the Southeastern United States during the summertime because of high temperatures and high relative humidities (Sisler and Malm, 1994), which result in high levels of particle liquid water leading to increases in the particle diameter. Second, submicron particles are associated with changes in radiative forcing and may be expected to influence the factors leading to global climate changes (Charlson *et al.*, 1992). Finally, epidemiological studies (Schwartz *et al.*, 1996) have implicated fine particulate matter with increased mortality and morbidity in selected urban areas. Since the specific causal agents for observed adverse health effects are not presently known, it has become an important task to chemically characterize the specific organic components of ambient fine particulate matter as completely as possible.

The major components of fine particulate matter include hygroscopic salts (e.g., ammonium sulfate and ammonium nitrate), elemental carbon and organic carbon compounds (EC/OC), and liquid water incorporated in the particles. In the atmosphere, ammonium sulfate is generated through a secondary process involving sulfate acids and ammonia. Much of the organic carbon is formed also from secondary processes which can generate semivolatile and nonvolatile organic compounds which can partition to the particle phase. While ammonium sulfate and many other inorganic ions can be reliably measured using conventional filter techniques, the organic phase poses a more difficult problem because of the number of organic compounds produced through gas-phase reactions and gas-particle partitioning that occurs because of the semivolatile nature of organic compounds.

While measurements of the organic component of ambient aerosols have been made for numerous years, most studies have examined the production and partitioning of non-polar compounds from primary sources onto particulate matter (e.g., Rogge *et al.*, 1998). Only recently has an emphasis been placed on examining individual polar organic constituents formed as products from chemical reactions. These consideration have led to FTIR measurements of aerosol in environments that show a high fraction of polar and oxygenated compounds (Blando *et al.*, 1998). Hildeman and Saxena (1996) have also considered the importance of water soluble components in ambient $PM_{10.}$ In an attempt to gain further insight into the secondary organic components formed in ambient aerosol, smog chamber experiments have been conducted to generate secondary organic aerosol (SOA) in a controlled fashion.

Chamber studies which have examined the gas-aerosol partitioning of products from photochemical reactions have been conducted in numerous research studies (Odum *et al.*, 1996; Hoffman *et al.*, 1997; Kleindienst *et al.*, 1999; Edney *et al.*, 2000). These studies typically have examined aerosol formation from atmospherically-relevant reactions of C_7-C_{10} aromatic and biogenic compounds and determined the yield of condensible products. Recently, measured yields have been explained using theoretical considerations which treat secondary aerosol formation as a process involving equilibrium partitioning of components between the gas-phase and a mixed organic phase (Pankow, 1994). Thus, many constituents of secondary organic aerosol are found to be present in both the gas and particle phases with the distribution dependent on the vapor pressures of individual compounds and their activity coefficients in the condensed phase. Detailed product studies of the particle phase have also been conducted for the a-pinene-ozone system (Yu *et al.*, 1999; Jang and Kamens,

1999) and the toluene photooxidation system in the presence of oxides of nitrogen (Forstner *et al.*, 1997; Jang and Kamens; 2001; Edney *et al.*, 2001). The reaction of a-pinene with ozone has led to the formation of a series of diacids (e.g., pinic acid, nor-pinic acid), oxoacids (pinonic acid), and carbonyl compounds (e.g., pinonaldehyde, nor-pinonaldehyde). Most of these products are found in both in the gas and particle phases. For example, pinonaldehyde is found to exist predominately in the gas phase, while pinic acid is found mainly in the particle phase. SOA products from the toluene photooxidation was found to give rise to a series of unsaturated (Jang and Kamens, 2001) and saturated (Edney *et al.*, 2001) polyketones in addition to other products. These studies suggest that the identity of the particle-bound products could be dependent on the age of the collected particles.

We have conducted laboratory studies to examine the secondary organic aerosol production from highly oxidized mixtures of single aromatic hydrocarbons, biogenic hydrocarbon, and hydrocarbon mixtures representative of urban sources (Kleindienst *et al.*, 1999; Edney *et al.*, 2001; Kleindienst *et al.*, 2002). Secondary aerosol products from these experiments have been collected on filters and extracted to identify individual organic compounds associated with the aerosol. A series of polyketones results from the photooxidation of toluene in the presence of nitrogen oxides (Edney *et al.*, 2001). The compounds were identified by GC-MS following derivatization. The photooxidation of biogenic hydrocarbons in the presence of NO_x has produced numerous multifunctional organic compounds that are consistent with the product identifications given by Yu *et al.* (1999a) for the ozone/a-pinene system.

Only a limited number of studies have been conducted to determine the presence of chemical reaction products of biogenic or aromatic SOA products ambient atmospheres. Yu *et al.* (1999b) examined SOA products from two forested regions in North America. While some of the chamber identified biogenic reaction products were found in the both the gas and particle phases (e.g., pinic acid), hydroxypinonic acid was found only in the particle phase. Other studies (Kubatova *et al.*, 2000) have identified a series of substituted dicarbonylic acids from particulate matter collected at field sites in the Amazon, as well as, in Gent, Belgium. Edney *et al.* (2002) conducted measurements at a site in Research Triangle Park, North Carolina and have detected a number of the compound reported by Kubatova *et al.*, (2000).

The field study reported in this paper was conducted to determine the extent that photooxidation products identified in the laboratory experiments (Edney *et al.*, 2001) and in a prior field study (Edney *et al.*, 2002) are also found extensively in aerosol samples of the ambient atmosphere. Emissions of the precursor compounds, especially the biogenic hydrocarbons, are expected to be greatest in the summer; moreover, due to high solar intensity the extent of photochemical reaction is greatest during that season. In an effort to characterize the aerosol in a reasonably comprehensive manner, measurements were also made for the inorganic and organic constituents, and the total elemental and organic carbon associated with the aerosol.

The NARSTO Northeast Ozone/Particle Study (NEOPS) provided a venue for conducting sampling for organic compounds at a site in the eastern United States. A study in this location has the advantage that considerable additional measurements have been taken by other research groups that should aid in the interpretation of the organic particle data.

2. EXPERIMENTAL METHODS

2.1 Site Characteristics

The field study was carried at the NEOPS research site in Philadelphia, Pennsylvania, USA located at global coordinates N40E02.14'; W75E00.28'. The site was a grass-covered field approximately 0.01 km^2 in area, surrounded on three sides by a thin line of mixed deciduous and pine trees. The other side was bounded by the Delaware River. The immediate surrounding area consisted of corporate and industrial facilities and the NE suburban outskirts of Philadelphia. The research site was approximately 0.5 km SE of Interstate-95 and 2 km SW of the Bucks County, PA county line. Downtown Philadelphia and downtown Trenton, NJ were within a 30-km radius of the site. All sampler inlets were located on a wooden platform near the approximate center of the field, 2 m above the surface.

$PM_{2.5}$ samples were collected during three individual periods from 22-26 July 2001. Hot summertime conditions prevailed during the study period. Under these conditions, daytime high temperatures were above 35 C.

2.2. Sample Collection

Four collocated collectors were deployed to measure a comprehensive range of parameters associated with the particle phase. Filter-based measurements of the organic and inorganic constituents of fine particulate matter ($PM_{2,5}$ in this study) were made. These included a high volume organic sampler, a conventional quartz filter sampler for total organic analysis, a Teflon filter sampler for mass and inorganic constituents, and a multistage, low-pressure impactor for functional group analysis. All filter samplers were preceded by denuders to collect gas phase constituents that might present an interference for specified filter.

The high volume organic sampler consisted of a cyclone having a $PM_{2.5}$ cut point to reject coarse particles (i.e., aerodynamic particles in the range of 2.5 µm and higher). Following the cyclone, a glass denuder having an annular design with 8-channels was incorporated to collect volatile and semivolatile organic components in the gas phase. The denuder had a length of 60 cm and was coated with XAD-2 (Restek Corp., Bellefonte, PA) solid phase adsorbent. The XAD-2 was chemically bonded to the glass denuder surfaces using a proprietary technique (Gundel *et al.*, 1995). At the sampling flow rate of 150 L min^{-1}, the residence time of the airstream in the denuder was 200 ms a time sufficient for gas-phase components to be removed by the coated walls. Following the XAD-2 organic denuder, a 128-mm Teflon-impregnated glass fiber filter was used to collect the particulate matter in the air stream. These filters were pre-extracted with a 24-h Soxhlet extraction using high purity methanol followed by a second 24-h extraction with a 50:50 mixture of methylene chloride and acetonitrile. Following the glass fiber filter in the sampling configuration was a backup XAD-2 coated denuder for collecting semivolatile organic compounds from the filter. This second XAD denuder was 40-cm in length and had 5 annular channels. Under the sampling conditions, the residence time in the denuder was 24 ms.

The samples for total elemental carbon and organic carbon (EC/OC) were taken using a sampling train consisting of a carbon denuder followed by a filter holder containing three quartz filters. Samples were taken at a flow rate of 10 L min^{-1}. A parallel-plate, activated-carbon denuder was used to remove gas-phase constituents from the effluent prior to collection on quartz filters. The carbon denuder served to remove compounds contributing to the reported positive artifact (McDow and Huntzicker). The carbon denuder was housed in an aluminum enclosure and consisted of fifteen 3×15-cm carbon strips with a 2-mm separation. The residence time of the effluent within the denuder was 0.8 s. The initial quartz filter was used to collect the particulate matter. The use of the carbon denuder obviated the need for a backup filter to correct for a positive quartz filter artifact (Turpin *et al.*, 1994). However, backup quartz filters, while not quantitative were used to help evaluate the importance of a negative artifact from evaporation of semivolatile compounds from the first filter.

Teflon filters were employed for measurements of liquid water, total mass, and strong acid anions. A 24-cm carbonate denuder was placed ahead of the filter in the sampling train to collect strong acids and diacids (e.g., nitric and oxalic acids, respectively) that might be present in the gas phase. The denuder consisted of 4 annular glass channels with a 1.5-mm spacing (Part No., URG, Chapel Hill, NC) and coated with an aqueous 2% (w/w) sodium carbonate solution. Both before and after sample air collection, the Teflon filters were conditioned for 24 h at 19EC and at a relative humidity of 42%. Once the Teflon filters were weighed for the final time they were extracted with 10 mL of deionized water by sonication and analyzed for anions by ion chromatography (IC) using the analysis described below.

2.3 Mass, Liquid Water, Anion Analyses

The collection of $PM_{2.5}$ onto Teflon filters permitted an analysis for liquid water content of the aerosol using the procedure described by Speer *et al.* (1997). The technique involves measuring the aerosol-derived water uptake in an off-line in the chamber where the relative humidity (RH) is precisely adjusted over the range of 5 to 95%. At each RH reading, the absolute sample mass was measured to an accuracy of ±10 µg with a beta gauge. The mass of liquid water was found by subtracting the dry mass of the aerosol from the total aerosol mass at each RH value. The details of the measurements are described in a separate article (Speer *et al.*, 2002).

Before and after the measurement for liquid water, the Teflon filters were equilibrated at RH 42% for gravimetric analysis of the filters with an analytical balance (UMT-200, Mettler Corp., City, State) having a precision of 1 µg. Standard Class S weights were used before each weighing session for calibration and the estimated accuracy of these measurements was 5 µg. The Teflon filters were then extracted with 10 mL of deionized water and the extract was analyzed by IC. The constituents were separated with an AS-5 column (Dionex, Inc., Sunnyvale, CA) using a 2.2 *mM* sodium carbonate/2.8 *mM* sodium bicarbonate eluent operated isocratically with detection by electrical conductivity. Analyses were made for the anions: nitrate, sulfate, and oxalate. A similar analysis was made for the denuder tubes following extraction with deionized water.

2.4 Analysis of OC, EC, and Oxygenates

Ambient particulate matter was collected on quartz filters for analysis of the elemental and organic carbon content. Before sampling, the quartz filters were conditioned in a muffle furnace at 600EC for 4 h to vaporize residual background organic carbon. Following sample collection, the filters were analyzed by Sunset Laboratories, Inc. (Forest Grove, OR). The analysis for elemental and organic carbon was performed using a thermal-optical method (Birch and Cary, 1996).

Particulate matter was collected on 128-mm Teflon-impregnated glass fiber filters for measuring individual particle-bound organic compounds found in the ambient samples. The detailed organic analysis used a double derivatization technique with pentafluorobenzyl hydroxylamine (PFBHA) to derivatize carbonyl groups and bis(trimethylsilyl) trifluoroacetamide (BSTFA) to derivatize hydroxyl groups. Following collection, filter samples were Soxhlet extracted for 24 hours in a 50:50 (v/v) mixture of methylene chloride:acetonitrile (grade GC^2, Burdick and Jackson, Muskegon, MI) and spiked with 350 µL of a 160 µmol mL^{-1} solution of reagent grade PFBHA (Sigma-Aldrich, St. Louis, MO) in water. Gas-phase organic compounds collected on the 60-cm, 8-channel XAD denuder were extracted using 250 mL of a 50:30:20 (v/v) solvent mixture consisting of acetonitrile:methylene chloride:*n*-hexane, respectively. The analytes were extracted from the denuder through agitation using a repetitive end-over-end motion. Following this first extraction, an identical second extraction was performed. A third and final extraction was performed using 250 mL of DNPH-cleaned methanol in place of the three component mixture. In most cases, the analysis of the last two extractions indicated that the organic mass was almost entirely removed in the first extraction. 700 µL of the 160 µmol mL^{-1} PFBHA-water solution was added to each of the extraction liquids. Finally, to each of the filter and denuder extracts, 27 µg of D$_5$-benzaldehyde was added as an internal standard.

Following the derivatization with PFBHA, the samples were evaporated to dryness to remove all traces of solvent including water introduced as the PFBHA solvent. At dryness, the samples were dissolved into 850 µL of a 1:2 mixture of methylene chloride:*n*-hexane to which were added 50 µL of BSTFA and 100 µL of pyridine. The samples were allowed to react overnight at room temperature. Samples were then quantitatively transferred via filtration to injection vials and then heated at 70EC for a minimum of 2 hours to ensure complete reaction. 2 µL aliquots of the extracts were injected into a Thermoquest (Austin, TX) GCQ+ gas chromatograph-ion trap mass spectrometer (GC-ITMS) system having an injection temperature of 250EC. An RT$_X$-5 MS column (60-m × 0.25-mm × 0.250 µm film thickness; Restek, Inc., Bellefonte, PA) was used to separate the compounds. A set of blank Zefluor^{TM} filters were also analyzed using this procedure. The exposed filter and blank extract samples were analyzed by GC-ITMS in the positive chemical ionization (CI) mode over a *m/z* range of 50- 975 amu with methane as the CI reagent gas.

2.5 Analysis of GC/MS Chromatograms

Molecular weights of the pseudo-molecular ions of the PFBHA/BSTFA derivatives were used to determine the molecular weights of the photooxidation compounds. For compounds having carbonyl groups, characteristic ions include *m/z* 181 ($C_6F_5CH_2$-), as well as the pseudo-molecular ions M_d-197 and M_d+1 and M_d+29 from addition of H^+ and $C_2H_5^+$, respectively, where M_d is the molecular weight of the derivative. In principle, each of the non-acidic carbonyl groups should form a derivative, generating molecular weights for the derivatized compound of M_c+195, M_c+390, M_c+585 and M_c+780 for the mono-, di-, tri- and tetra-derivatives, respectively, where M_c is the molecular of the carbonyl oxidation product. Thus, for compounds derivatized with an odd number of oximes groups, the nitrogen rule holds and the molecular weight of the derivative will be odd. The available data (Edney *et al.*, 2001) suggest the some of the resulting oxime compounds may not be fully derivatized which is readily determined from the analysis.

The derivatization of OH groups by BSTFA results in the addition of a trimethylsilyl group, Si-$(CH_3)_3$, to the parent (or carbonyl-derivatized) molecule. Each derivatized OH group will add 72 amu to the molecule. Thus, two trimethylsilyl groups would be added to a diacid increasing its molecular weight by 144 amu. The major fragments from compounds derivatized with BSTFA include *m/z* 73 and 75 associated with the trimethylsilyl group, *m/z* 147 and 149 associated with the trimethylsilyl dimer, and similar pseudo molecular ions as above. For linear diacids the M-15 (loss of a methyl group) and M-89 (loss of O-Si-$(CH_3)_3$) fragments are generally the dominant peaks in the mass spectrum. If the OH group is associated with a carboxylic acid, an M-117 ion is frequently found in the spectrum. For linear dicarboxylic acids and tricarboxylic acids, the M+1 and M+29 adducts are generally very weak and in some cases below the noise level, even with chemical ionization. In some cases, M+73 and M+75 adducts are found in the mass spectrum. In most cases, the number of trimethylsilyl sites on the derivatized molecule must be deduced from knowledge of the chemical system and the range of reasonable molecular weights for parent molecule. This information taken together gives rise to information on the compound molecular weight and the number of carbonyl and OH groups associated with the parent molecule. However, the possibility of ambiguous molecular structures still exists.

3. RESULTS AND DISCUSSION

Three sets of samples were collected for the analyses described above. The number for each sample was based on the filter type and the starting Julian date for the year, 2001. Collection times for each sample were 24 hours for Samples 203 and 204 and 48 hours for Sample 205. Mass flow readings for each sampler were taken and converted to total sample air volume for each sample type.

3.1 Inorganic Analysis

The results of the IC anion analysis for sulfate and nitrate is presented in Table 1. No other anions were present in measurable quantities. The predominant cation was undoubtedly ammonium. Since ammonium ion concentration was not measured its concentration was calculated under two assumptions regarding acidity. In the first case, it was assumed that the particle phase of the aerosol was completely neutralized with respect to sulfate and nitrate; in the second case, it was assumed that half of the sulfate was present in an acidic form, that is, as ammonium bisulfate. These assumption are reasonable given the fact that even if it is a assumed that the measured sulfate were present completely as ammonium bisulfate, an average reconstructed mass would decrease by only 5%. There is also the possibility for volatilization by ammonium nitrate but there was no basis to apply a correction due to possible volatization of ammonium nitrate. Values for the gravimetric masses are given in the Table 1.

3.2. Organic Analysis

Results for the measurement of elemental and organic carbon by thermal-optical analysis is presented in Table 1 and 2. Measurements were made for the front filter and two backup filters. The twenty four hour samples indicated an average organic carbon value of about 2.5 µg m^{-3}. The 48 hour sample showed an organic carbon value of 4.74 µg m^{-3}. For these samples, a parallel-plate carbon denuder was placed in line to remove gas-phase constituents (Eatough et al., 2001) from the sampling stream and thus we assume that the front filter collects particulate carbon only and the backup filters serve as an indication of the amount evaporated organic carbon from the front filter. In all three samples, the second filter together represented a small fraction of the front filter. The carbon fraction found on this backup filter varied widely from 8.0 to 11.9%.

Elemental carbon (EC) values were also made from particle collections on the front filter. In each case, the backup filters showed negligible EC concentrations and the values in Table 2 are solely from the first filter. Elemental carbon ranged between 0.39 and 0.64 µg m^{-3}. The fraction of EC to total carbon varied by a factor of two with a range between 9.0 and 18.1% and an average ratio of 13.7%.

While organic carbon is the quantity measured in this method, organic mass is usually the quantity of interest for interpretative purposes. Organic mass includes in addition to carbon, the other atomic constituents that make up organic molecules mainly hydrogen oxygen, and nitrogen. Until recently for ambient urban atmospheres, a value of 1.4 had frequently been used to convert organic carbon to organic mass (i.e., [OM]/[OC] ratio), where a high component of particulate carbon from primary emissions is present (Gray *et al.*, 1986). More recently, the works of Blando *et al.* (1998), Dick *et al.* (2001), and Turpin *et al.* (2001) have suggested that for rural or semirural areas where a primary emissions component to the particulate matter is considerably less emphasized and the sample appears to be highly oxidized, a value of 1.6 to 2.1 has been recommended. Analysis of chamber studies have been performed where a value of two for the [OM]/[OC] conversion factor was consistent with the carbon and mass data (Liang *et al.*, 1997; Kleindienst *et al.*, 1999).

For this study, the use of a value of 1.6 for the [OM]/[OC] conversion factor leads to organic mass values ranging between 3.8 and 7.6 µg m^{-3} for the three samples, as presented in Table 2. Following the assignment of the [OM]/[OC] ratio of 1.6, a comparison of the organic mass with the gravimetric mass shows that on average the organic mass component makes up 28.2% of the total mass during this study.

3.3 GC/MS Analysis of Derivatized Extracts

Derivatized extracts from the filter collections from FS01-203 to FS01-205 were analyzed by GC-ITMS using a double derivatization technique (Conver *et al.*, 2002). The total ion chromatogram for the three samples is shown in Figure 1. Previous FTIR spectra have shown that carbonyl compounds can be important constituents of the ambient aerosol. Therefore, an examination of the single-ion chromatogram of the *m/z* 181 fragment should give a measurement of all elutable carbonyl compounds. A selected ion chromatogram for *m/z* 181 is shown in Figure 2 for the three samples taken during the study. The mass spectrum for each carbonyl compound should include, in addition to the *m/z* 181 fragment, the M_d -197 fragment and the M_d +1 and M_d +29 adducts. If these mass are present, the molecular weight of the derivative is easily deduced. However, one or more of these masses being absent make the identification more ambiguous. As in the study of Edney *et al.* (2001), the polycarbonyl compounds that might be present in the sample were assumed to be singly derivatized if M_d was in the range *m/z* 195-390, doubly derivatized if M_d was in the range *m/z* 391-585, and triply derivatized if M_d was in the range *m/z* 586-780. Once the order of the derivative was determined, the molecular weight of the parent polycarbonyl compound, M_c, was determined by subtracting 195 from the single derivatives, 390 from the double derivatives, and 585 from triple derivatives.

The derivatization with BSTFA adds a trimethylsilyl group to each position containing an OH group either as an alcohol or carboxylic acid. This derivatization considerably improves the chromatography of compounds, for which the peak would otherwise tail considerably. Compounds derivatized with BSTFA are also found to produce characteristic peaks, including the fragments, *m/z* 73, 75 and M-15, M-89, M-117, and M-133, and adduct peaks M+1, M+29, M+73, and M+75. For a specific derivatized compound, not all peaks will be present and the relative intensity of the peaks are difficult to predict. For di- and tri-carboxylic acids as well as their substituted analogs, fragment peaks *m/z* 147 and 149 are almost always present. Finally, in some cases, the presence of an M-117 peak, indicates that at least one of the hydroxyl groups is associated with an organic acid.

Compounds found in the filter extract of laboratory samples have been summarized by Edney *et al.* (2001). For all of the compounds, except glyoxal and methyl glyoxal, identifications must be considered tentative because standards are not available for these compounds. In some cases, however, even without chemical standards the identifications are unambiguous. For example, the triple derivative of 3-oxo-1,3-propanedial represents an unambiguous identification, since no other compound having a molecular weight of 86 can form three PFBHA derivatives. Most of the other identifications are fairly unambiguous given the precursors and conventional photooxidation mechanisms.

Compound identities have been found for biogenic and aromatic product species in the extracts of the denuder and filter samples. Biogenic oxidation products have been recently reported by Jang and Kamens (1999) and Yu *et al.* (1999) and are identical to those found during this study. Many of the biogenic products previously reported were found in the denuder samples, that is, in the gas phase. Several of the products (notably, pinonic and norpinonic acids), while detected in the gas phase were not found in the filter.

For the aromatic hydrocarbons, several oxidation products were also detected as seen given by Edney *et al.* (2001). In most cases, the mass spectra and identification of the compounds from irradiations of toluene/NO_X mixtures were the same as those found by Edney *et al*. (2001) using the PFBHA derivatization and Conver *et al.* (2002) using the PFBHA/BSTFA derivatization. Identified compounds ranged from dicarbonyl to tetracarbonyl compounds with the compound volatility decreasing as the number of oxygens bonded to the carbon skeleton increases. The peak areas of the aromatic oxidation products were found to be small in comparison to the total ion chromatographic peak areas.

As mentioned above, the selected ion(s) chromatogram from the mass spectrum can be used to generate ions indicative of specific species (e.g., *m/z* 181 for carbonyls). The selected ion chromatogram for *m/z* 147+149 fragments gives a chromatographic depiction of the diacids present in the sample which is shown in given in Figure 3. The chromatogram shows a number of large peaks which is far greater than the number of linear diacids typically found in an ambient sample. Linear diacids are typically found early in the chromatogram, since the BSTFA derivatization adds only 72 mass units per OH group to the parent compound; thus, for the diacids, 144 mass units are added to the parent compound. The derivatized oxalic acid compound is the earliest identified compound to elute although the spectrum is fairly nondescript, given a very weak M+1 peak and strong masses for *m/z* 73 and 149 only. The other diacids found from the analysis (malonic acid and higher diacids) show many more identifying ion peaks, particularly the M-15 and M-89 fragments.

The most notable aspect of the mass spectrum for the BSTFA derivative for the linear C_2-C_{11} diacids is the weak or even absent M+1 peak in the mass spectrum. By contrast, the M-15 and M-89 peaks are the strongest fragments that have molecular weight information. (While characteristic fragments, such as *m/z* 73, 149, or 181 serve to identify for specific compound classes, these masses alone provide no structural information on the molecular weight of the derivative.) This difficulty does not prevent identification of the linear diacids since retention times for the standards have been determined. For compounds for which there are no standards, the M-15 and M-89 peaks are essential for determining the molecular weight, when an M+1 peak is not substantially greater than the instrumental noise.

Substituted diacid have been previously reported in ambient samples (Kawamura and Gagosian, 1990; Kubatova *et al.*, 2000). While these previous studies used ester and trisilyl derivatization of the acid group to aid in the identification, no attempt was undertaken to derivatize the carbonyl group which tends to confirm the identification. In these samples, the initial derivatization of the keto (or acetyl) group results in compounds less volatile thus minimizing sample losses once the sample is taken to dryness. In Figure 4, mass spectra have been shown for (a) 3-acetylhexanedioic acid, (b) 3 acetylpentanedioic acid, and (c) 3-carboxylheptanedioic acid. 3-Acetylhexanedioic acid forms two BSTFA derivatives and one PFBHA derivative and has a derivative molecular weight (M_d) of 527 amu. Because of the nitrogen associated with the oxime group, the molecular weight of the derivative has odd parity (nitrogen rule), thus major fragments and adducts in the mass spectrum are of even parity. For this compound, the M-89 fragment at *m/z* 438 is found to be the base peak. Unlike linear diacids, this derivative has a relatively strong M+1 peak and a weaker M-15 fragment. The presence of *m/z* 181 and the M-197 fragment is used to predict the presence of a carbonyl group. Finally the presence *m/z* 149 peak (albeit weak) and M-117 fragment suggest the compound has acidic groups. With two trimethylsilyl groups and a single PFBHA group, 339 mass units are subtracted from the derivatized mass giving a compound mass of 188. The presence of acyl diacids have already been reported by Kubatova *et al.* (2000) to be present in ambient samples. This information taken together gives rise to the tentative assignment of the peak as 3-acetylhexanedioic acid.

Mass spectral assignments for the mass spectrum in panel (b) of Figure 4 follow in an analogous fashion as that for 3-acetylhexanedioic acid. Again the M-89 peak serves as the base peak; the intensity of the M-15 peak is considerably stronger than the spectrum in panel (a). The mass fragment for M-117 is relatively weak although clearly detected at *m/z* 396. Again the peaks, *m/z* 73, 149, and 181 are all relatively weak in this spectrum. The molecular weight of the derivative is found to be 513 amu and, again assuming one oxime and two trimethylsilyl derivatives are present, the molecular weight of the compound is found to be 174 amu. Using the same rationale as above, the mass spectrum is tentatively assigned to the compound, 3-acetylpentanedioic acid. In fact, the GC-MS spectrum shows three other compound differing by 14 mass units are also present in relatively high abundance among the elutable compounds.

The mass spectrum of the tricarboxylic acid is shown in panel (c) of Figure 4. For this spectrum, *m/z* 405 is the base peak and together with the *m/z* 331 peak suggest that they are identified as the M-15 and M-89 fragments in the molecule. Similar to what was found for dicarboxylic acid, the M+1 peak is extremely weak and generally at the level of the noise. However, the M+29 peak is reasonably strong and provides confidence in assigning the M+1 ion as *m/z* 421. Thus the molecular weight of the derivative, M_s, can be reasonably assigned as 420 amu. The absence of an M-197 peak suggests that a carbonyl group is not present. The presence of the *m/z* 149 peak suggest that the compound has at minimum two OH groups and the somewhat unusual M-147 peak at *m/z* 273 indicates loss of a trimethylsilyl dimer, a fragment not seen in the spectrum of diacids. The three trimethylsilyl groups associated with the derivative renders an M_C of 204 amu and the tentative identification of the compound is 3-carboxylheptanedioic acid. This compound has been previously detected in the work of Kubatova *et al.* (2000). The complete set of substituted dicarboxylic acids found on the filter samples awaits additional analysis of the total ion spectrum.

DISCLAIMER

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Table 1. Major components of the ambient aerosol during selected periods of NEOPS.
(All units are µg m^{-3}.)

Sample	Sulfate	Nitrate	OC	Mass
-0203	4.78	0.16	2.89	18.3
-0204	5.65	0.14	2.39	17.0
-0205	8.01	0.08	4.74	20.5

Table 2. Carbon components of the ambient aerosol during selected periods of NEOPS.
(All units are µg m^{-3}; fractions are in percent)

Sample	OM	EC	fraction EC	Organic fraction of mass
-0203	4.62	0.64	10.7	25.2
-0204	3.82	0.39	8.0	22.5
-0205	7.58	0.47	11.9	37.0

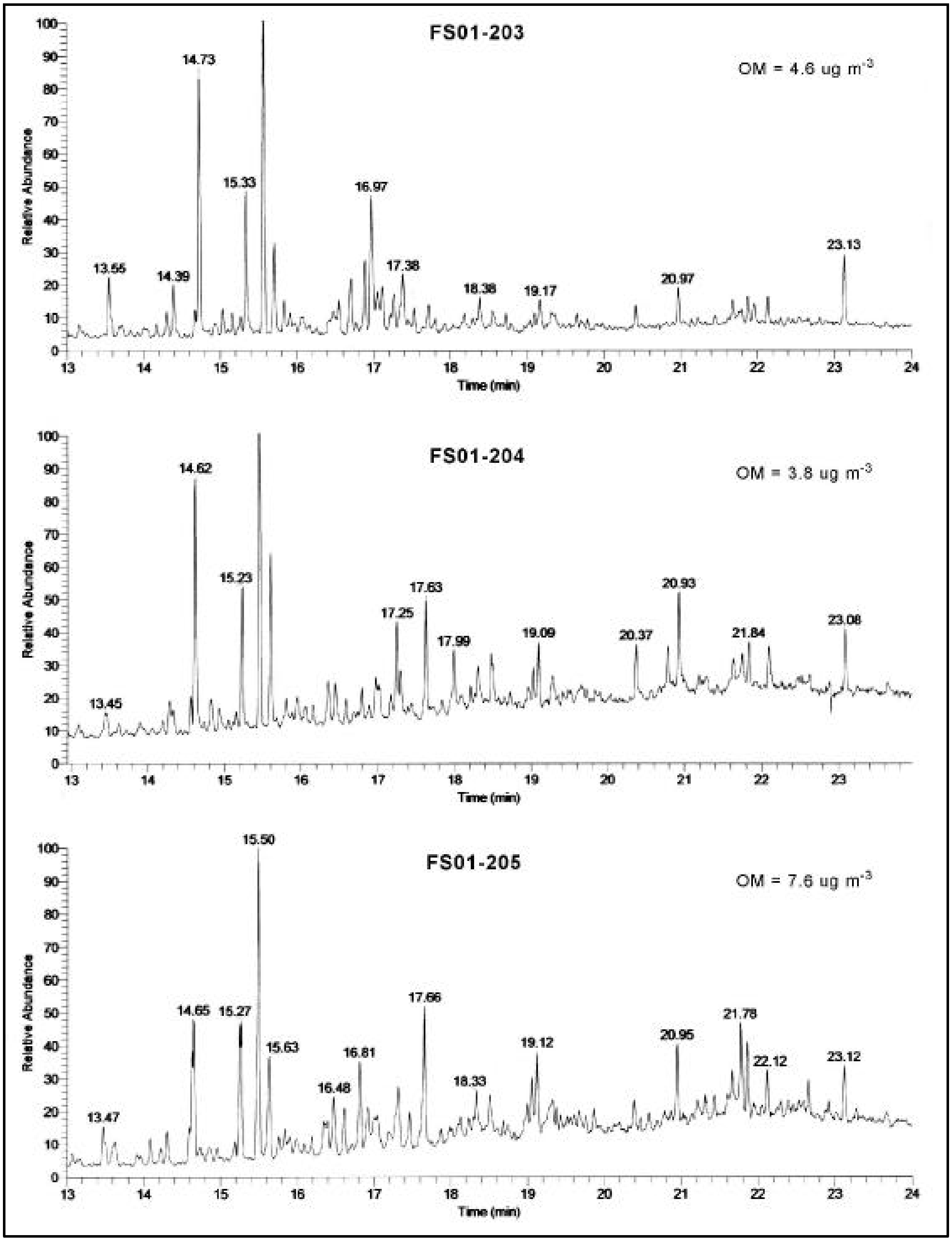

Figure 1. Total ion Chromatograms from derivatized filter extracts at NEOPS site from 22-25 July 2001.

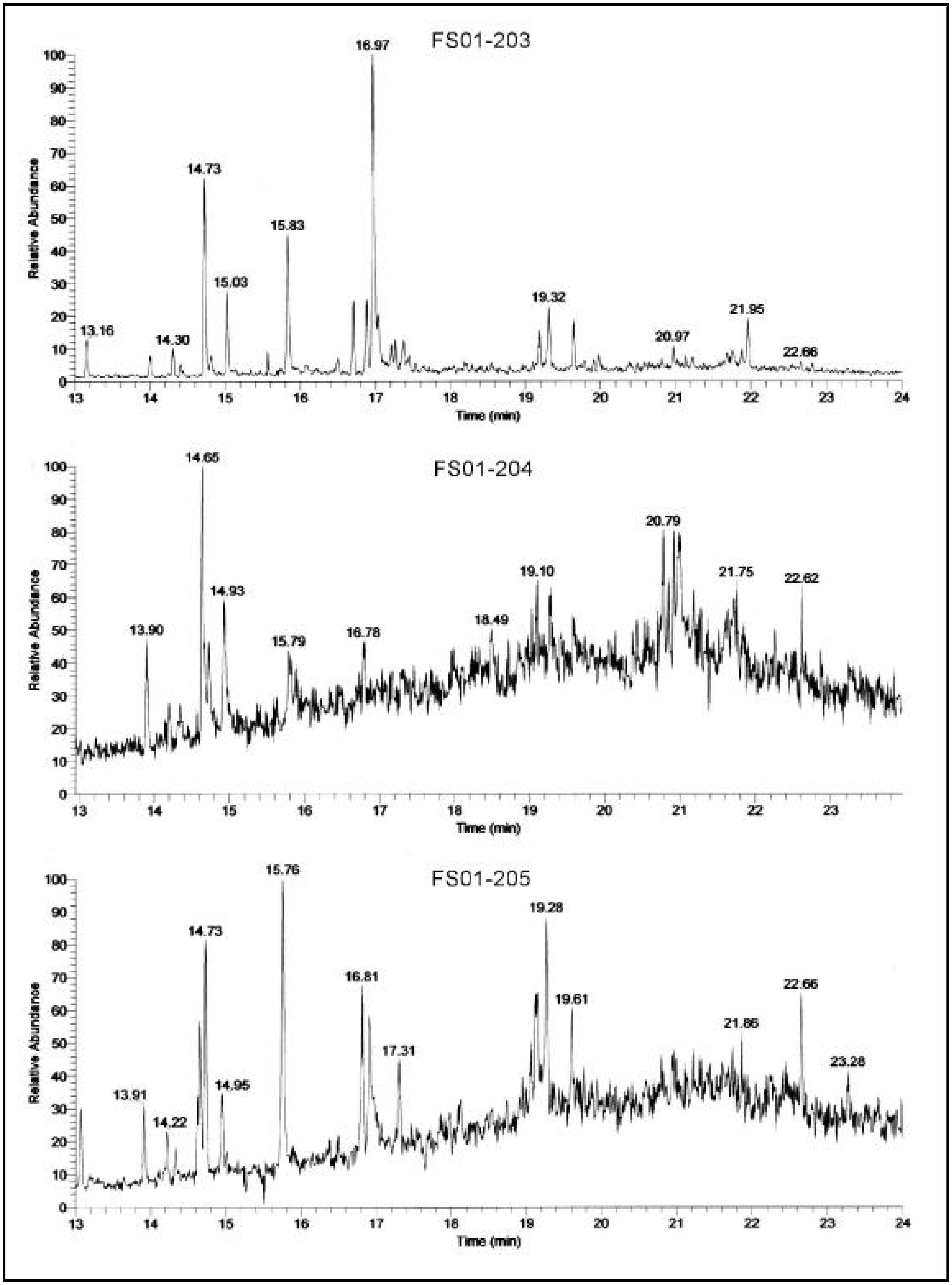

Figure 2. Selected ion chromatogram (m/z=181) of extract samples from NEOPS study. The m/z 181 ion is indicative of carbonyl compounds present in the sample.

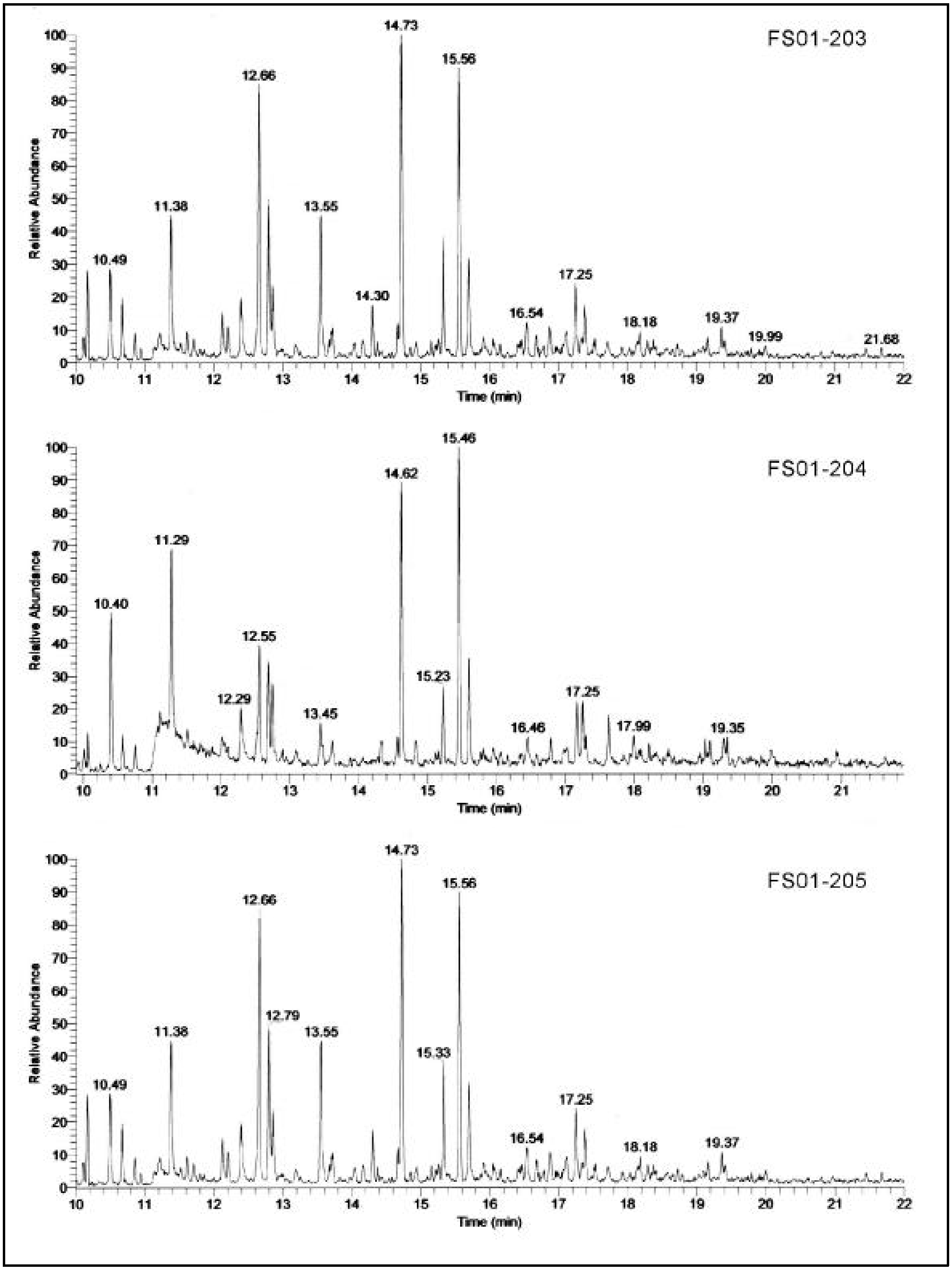

Figure3. Selected ion chromatogram (m/z=147+149) of extract samples from NEOPS study. The m/z 147+149 ions are indicative of dihydroxy compounds present in the sample.

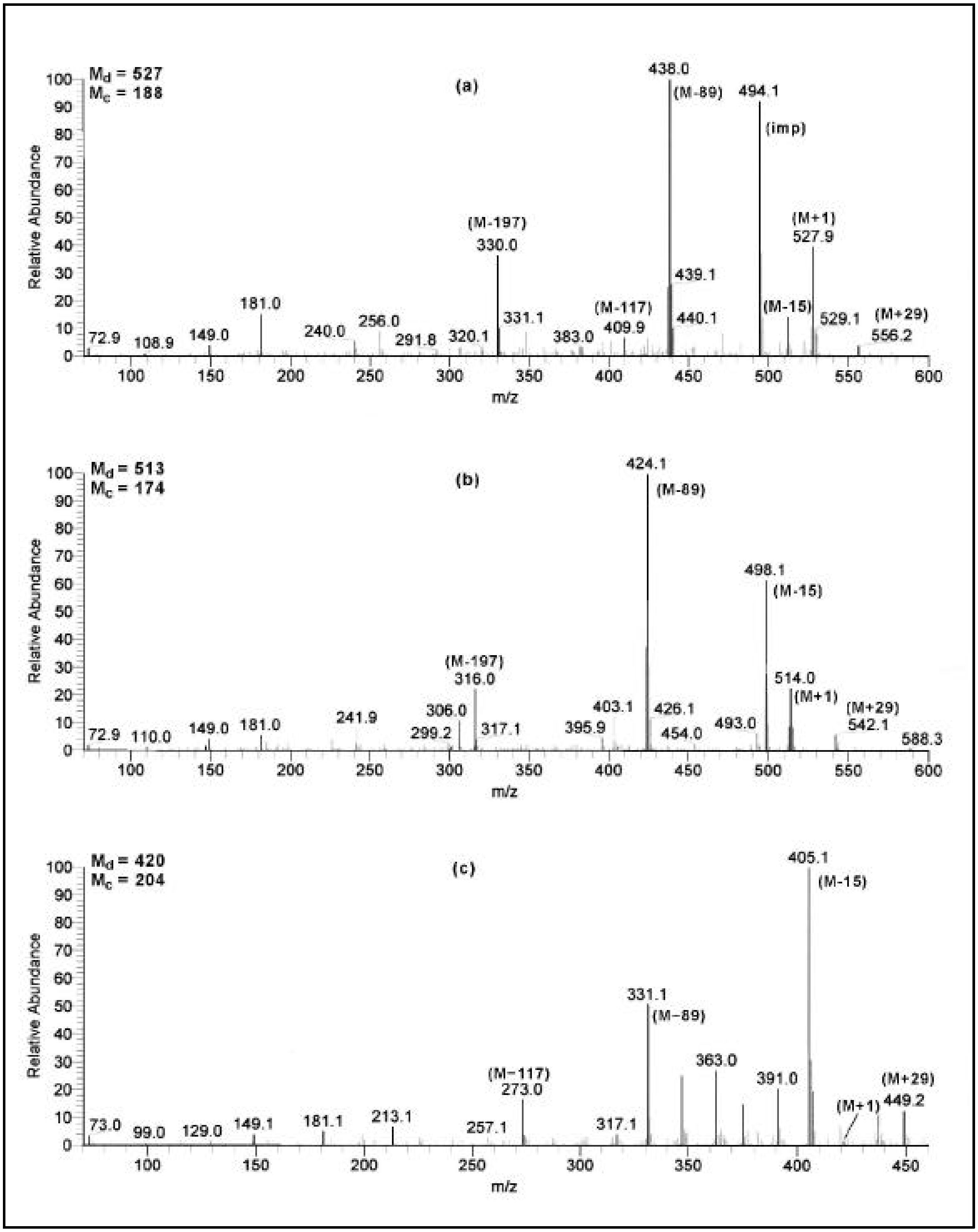

Figure 4. Mass spectra of substituted diacids. Spectra given for (a) 3-acetylhexanedioic acid, (b) 3-acetylpentanedioic acid and (c) 3-carboxylheptanedioic acid.