

## Detailed GC/MS characterization of hot pressurized water (HPW) fractions and comparison to organic solvent fractionation

GC/MS qualitative characterization was performed on all acquired non-derivatized and derivatized fractions (chromatograms of derivatized diesel exhaust and urban PM extracts and non-derivatized wood smoke PM HPW extracts are enclosed as supporting information). Since this study focused mainly on unaccounted polar species, a quantitative analysis was performed on representative extracts specifically for carboxylic acids (Table S1) and carbohydrates. Several trends observed in the distribution of various analytes in different fractions are described in detail below.

### *Diesel Exhaust PM (SRM 2975)*

Diesel exhaust PM is generally considered to be a non-polar matrix; however, it is important to recognize that this is mostly due to its high content of EC. Thus, the non-polar character of EC should not be confused with the composition of OC. This was confirmed by finding a significant portion of OC in the polar fractions (Fig. 4), which was also consistent with the GC/MS responses (Fig. 1S). Diesel exhaust PM fractions obtained with a polar solvent (methanol) and polar HPW (50–150 °C) showed similar species extracted. In both extracts, derivatives of phthalic and naphthalic anhydrides, and nitro- and dinitrophenols were tentatively identified. Higher molecular weight species (MW 400–700), which we did not succeed to identify, were found in derivatized extracts of water-soluble and polar fractions obtained using both extraction systems.

In contrast to polar species, there was a difference in the extraction of less polar species. Oxy-PAHs were extracted by methylene chloride, whereas in HPW they were distributed over

the polar and mildly polar fractions. Furthermore, a significant portion of OC was extracted by *n*-hexane but not by steam or HPW at 250 °C (Fig. 4). Notably, the high GC/MS response of the *n*-hexane extract was mainly attributed to PAHs, but also to more polar ethyl hexyl phthalate, and dioctyl substituted phenylbenzylamine. On the basis of the response compared to the internal standard, it appeared that organic solvents were more efficient than HPW for the extraction of mildly polar and non-polar species such as oxy-PAHs, and PAHs.

#### *Urban PM (SRM 1648b)*

As for diesel exhaust PM, the distribution of OC among the fractions extracted (Fig. 4) corresponded to the overall GC/MS response of those extracts (Fig. 2S). In contrast to diesel exhaust PM, for which HPW was not an efficient extraction solvent for non-polar compounds, a higher occurrence of PAHs was found in the mildly polar fraction (extracted with 200–250 °C HPW). The following fraction (obtained with steam) consisted of alkanes and terpanes. Regarding the organic solvent extraction, PAHs, terpanes, and alkanes were found mainly in the *n*-hexane fraction.

As expected, more polar species were extracted with solvents of higher polarity. Mildly polar HPW (200–250 °C) extracted longer-chain organics such as monostearin, monopalmitin and monomyristin as well as myristic, palmitic and stearic acids. The same species were also observed in the *n*-hexane and methylene chloride fractions. Mildly polar compounds typical for wood smoke combustion, dehydroabietic and oxodehydroabietic acids, were found in the polar fraction of HPW (50–150 °C) and in mildly polar methylene chloride. The species identified above were relatively easy to find (due to a clean chromatographic pattern) in the HPW extracts. By contrast, due to interferences (solvent extracts consisted of many overlapping peaks) they

were confirmed in solvent extracts only based on the known retention times and characteristic ions in the mass spectra.

The polar and water-soluble fractions contained a significant portion of dicarboxylic acids and levoglucosan (*vide infra*). Among the other species identified in polar fractions obtained by both solvents were also pesticides (dichlorophenone and triazine). Moreover, we have observed a large number (~10) of unknown chlorinated species of a MW ranging from 412–626 (possibly originating from pesticides) in the derivatized polar HPW fraction. The occurrence of those species was also confirmed in organic solvent extracts.

#### *Wood Smoke PM*

Due to a high content of methoxyphenols, even a qualitative characterization of trimethylsilylated fractions was not feasible. The GC/MS characterization of underivatized wood smoke PM extracts (Fig. 3S) showed comparable results to those obtained in our prior research (Kubatova et al. 2006; Kubatova et al. 2004). Syringol and guaiacol derivatives were mainly extracted in the water-soluble (25 °C) and polar fractions (50–150 °C). Similarly as in our previous work, we have confirmed the occurrence of new syringylguaiacyl and disyringyl derivatives in the HPW mildly-polar fraction (50–150 °C) (Kubatova et al. 2006) as well as in the methylene chloride extract. Less polar species, such as oxy-PAHs and PAHs, were extracted at higher temperatures (> 150 °C). As for urban PM and in contrast to diesel exhaust PM, the majority of non-polar species (e.g., PAHs) were extracted with HPW at 200–250 °C rather than with steam. This suggests that matrix interactions affect which polarity solvent will extract particular species. In other words, polar solvents (methanol or 25–150 °C HPW) were more effective in disrupting the matrix-analyte interactions in polar matrices such as wood smoke and urban PM. However, these solvents were less effective for diesel exhaust PM, a non-polar matrix.

### *Extraction of Acids*

Highly polar species, such as dicarboxylic acids, are expected to be found mainly in the water-soluble fraction (Graham et al. 2002; Li and Yu 2005; Mader et al. 2004). However, our initial comparison of chromatograms suggested otherwise (Figs. 1S-3S). In order to look closer at the distribution of various acids among different polarity fractions, semi-quantification of 25 acids has been performed (Table 1S).

The total concentration of diacids showed that HPW was a more efficient extraction solvent than organic solvents. This would be typically attributed to the recoveries in the water-soluble fraction as observed for urban PM. However, except for urban PM, higher recoveries were obtained with HPW at higher temperatures (e.g., polar and mildly polar fractions). Thus, the extraction efficiency was not only strongly dependent on the analyte solubility in different solvents but also on the matrix composition and analyte-matrix interactions. We may speculate that this is due to interactions with matrix defined in terms of primary and secondary emissions. Wood smoke and diesel exhaust PM are representative of primary emissions. Therefore, PM constituents (diacids) were strongly embedded in the matrix requiring higher temperature HPW to achieve efficient extraction. By contrast, the formation of diacids in urban air is typically related to secondary atmospheric processes (Kawamura and Ikushima 1993; Kubatova et al. 2000), thus occurring on the surface of PM. The second explanation (which may still be consistent with the first explanation) is that matrices could break down at higher temperatures broke thus releasing lower molecular weight species.

In contrast to diacids, the extraction of monocarboxylic acids appeared to be favored by a sequential organic solvent extraction (Table 1S). It appeared that HPW was not efficient to

extract acids extracted with a non-polar solvent (i.e. *n*-hexane). A significant portion of these acids was recovered with steam from diesel exhaust PM (a non-polar matrix).

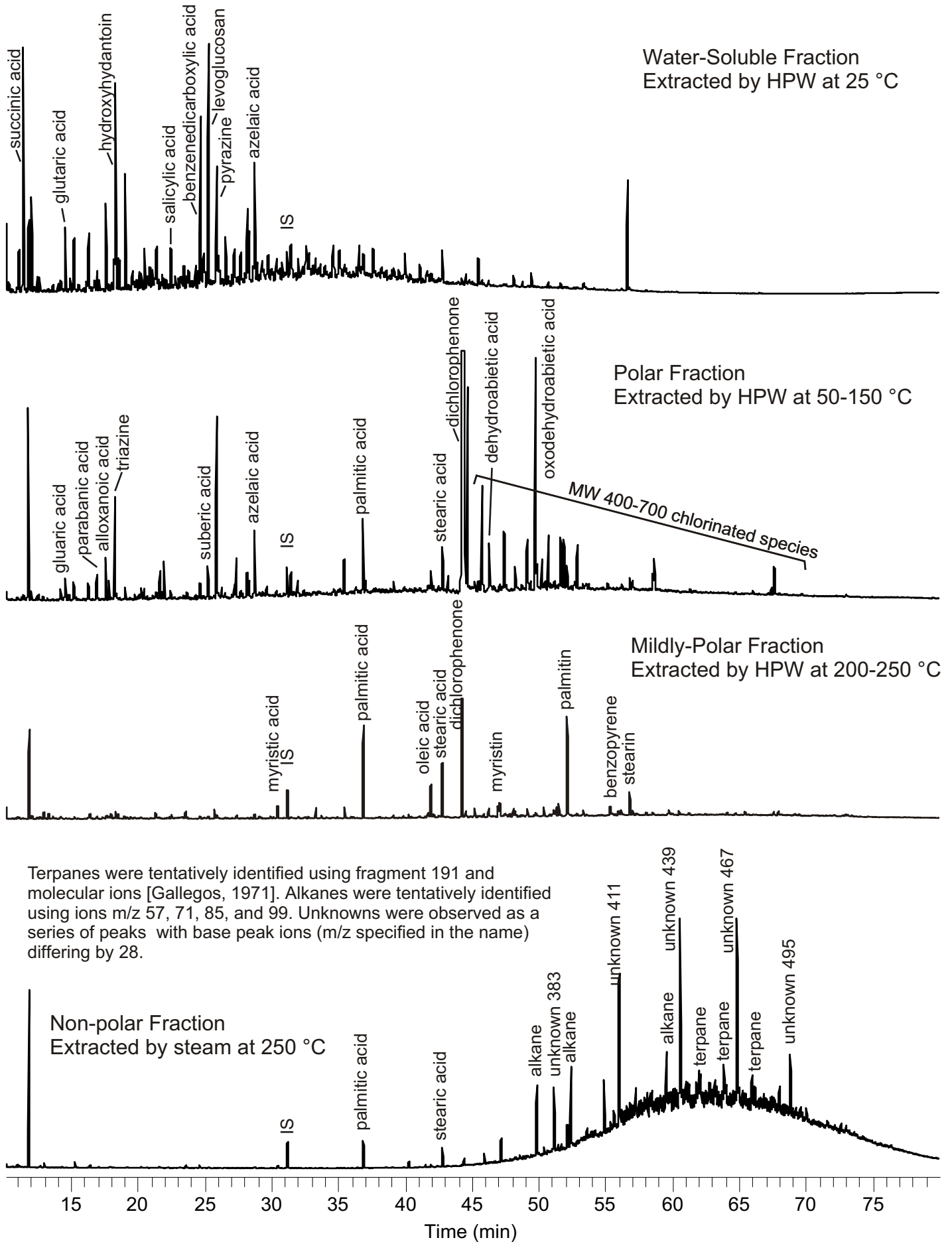
The differing total concentrations of diacids and some monocarboxylic acids may pose a question about the accuracy of these data. However, some of the recoveries of aromatic acids and also monocarboxylic acids (extracted from diesel exhaust PM) were similar (Table 1S). This observation suggests that differing recoveries observed for diacids and some monocarboxylic acids were due to matrix-analyte interactions.

#### *Extraction and Occurrence of Carbohydrates*

As expected, levoglucosan and several other anhydrosugars were observed mainly in the water-soluble fraction, and in lower amounts in polar and mild polarity HPW fractions of wood smoke and urban PM (totaling in 2600 and 185  $\mu\text{g/g}$  of original PM, respectively). The recoveries were comparable to those obtained by organic solvents in polar and mildly polar fractions (data not shown). With the exception of iso-erythritol (1650  $\mu\text{g/g}$ ) and D-ribose (270  $\mu\text{g/g}$ ) in wood smoke PM no other carbohydrates were detected. Both of these carbohydrates were distributed over water-soluble, polar and mildly polar fractions). Notably, iso-erythritol was not confirmed in organic solvent extracts.



Figure 1. GC/MS chromatograms of derivatized (trimethylsilylated) HPW extracts of diesel exhaust PM. The acids and compounds with hydroxylated groups were all identified as trimethylsilyl derivatives. All chromatograms are shown in the same proportion to the internal standard to allow for comparison of the signal abundance.



Terpanes were tentatively identified using fragment 191 and molecular ions [Gallegos, 1971]. Alkanes were tentatively identified using ions  $m/z$  57, 71, 85, and 99. Unknowns were observed as a series of peaks with base peak ions ( $m/z$  specified in the name) differing by 28.

Figure 2. GC/MS chromatograms of derivatized (trimethylsilylated) HPW extracts of urban PM. The acids and compounds with hydroxylated groups were all identified as trimethylsilyl derivatives. All chromatograms are shown in the same proportion to the internal standard to allow for comparison of the signal abundance.

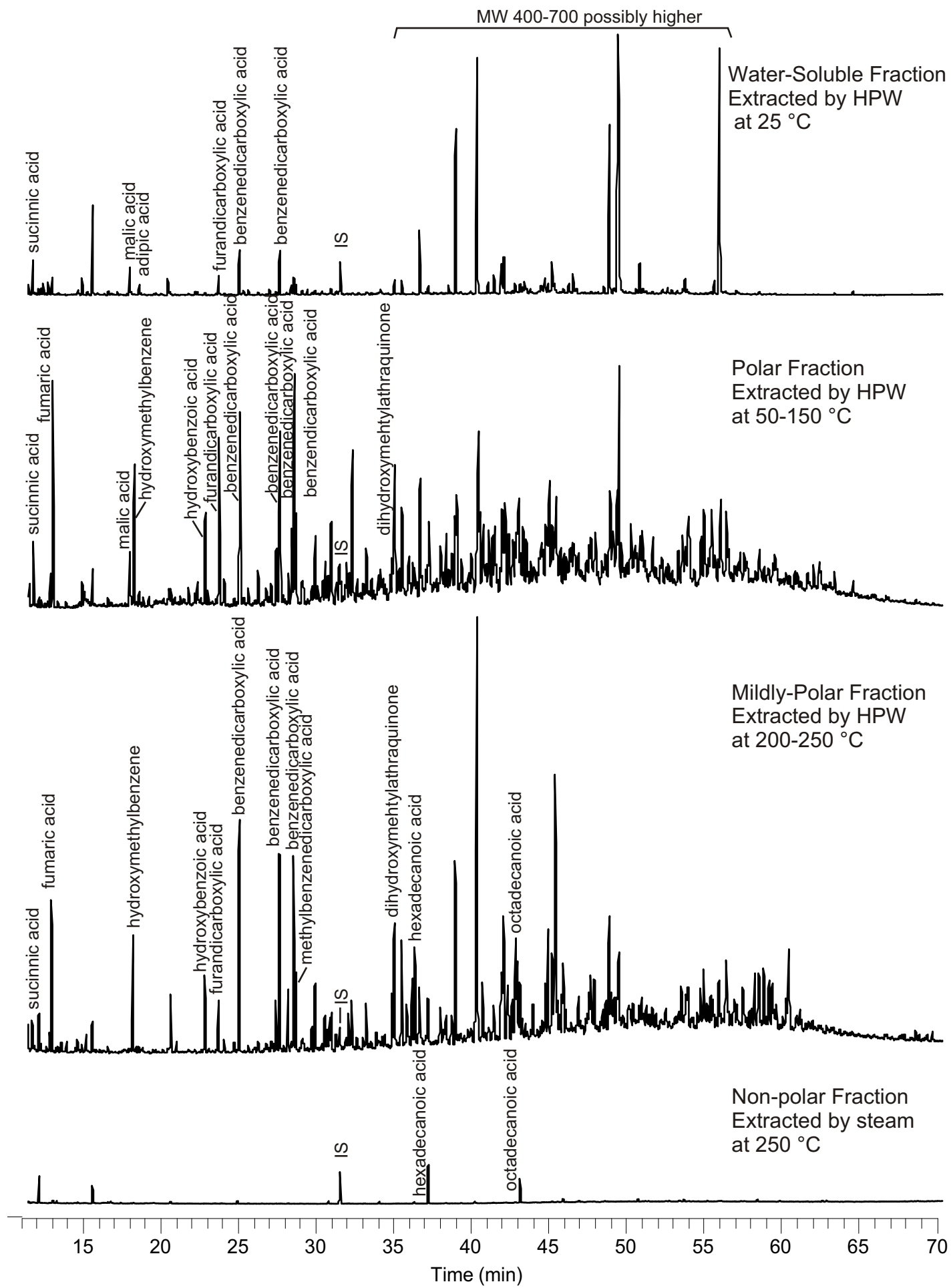


Figure 3. GC/MS chromatograms of underivatized (trimethylsilylated) HPW extracts of wood smoke PM. The acids and compounds with hydroxylated groups were all identified as trimethylsilyl derivatives. All chromatograms are shown in the same proportion to the internal standard to allow for comparison of the signal abundance.

