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**High molecular
weight compounds in
urban atmospheric
particles**

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Characterization of high molecular weight compounds in urban atmospheric particles

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Abstract

The chemical nature of a large fraction of ambient organic aerosol particles is not known. However, high molecular weight compounds (often named humic-like substances) have recently been detected by several authors and these compounds seem to account for a significant fraction of the total organic aerosol mass. Due to the unknown chemical structure of these compounds a quantification as well as a determination of their molecular weight is difficult. In this paper we investigate water soluble humic-like substances in ambient urban aerosol using size exclusion chromatography-UV spectroscopy and laser desorption/ionization mass spectrometry. A careful method evaluation shows that both methods complement each other and that both are needed to learn more about the molecular weight distribution and the concentration of humic-like substances. An upper molecular weight limit of humic-like substances of about 700 Da and a concentration of 0.2–1.8 $\mu\text{g}/\text{m}^3$ air can be estimated corresponding to 8–33% of the total organic carbon for an urban background site.

1. Introduction

Atmospheric aerosol particles play an important role in many atmospheric processes, such as scattering and absorbing solar radiation or cloud formation (Ramanathan et al., 2001; Breon et al., 2002). Aerosol particles smaller than 10 μm can penetrate deep into the human respiratory tract causing negative health effects (e.g., Dockery et al., 1993). Chemical components and physical properties of the aerosol particles critically influence these effects.

Atmospheric aerosols contain a significant fraction of organic components, up to 50% in mass (Seinfeld and Pandis, 1998). Although hundreds of compounds were identified, the chemical nature of the vast majority of the organic mass remains unknown. It was postulated that high molecular weight compounds contribute significantly to the organic aerosol mass (up to 40%) (Likens et al., 1983). Such substances have

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chemical characteristics that are similar to humic acids (HA) found in natural waters and soil, and the term “humic-like substances” (HULIS) was suggested (Havers et al., 1998). Several authors have analyzed this class of compounds, mainly using size exclusion chromatography methods (SEC) (Fuzzy and Zappoli, 1996; Zappoli et al., 1999; Krivácsy et al., 2000) or spectroscopic methods such as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), UV or fluorescence spectroscopy (Havers et al., 1998; Zappoli et al., 1999; Kiss et al., 2003). SEC is also a widely used and established technique in the field of humic acid analysis (Piccolo et al., 2001; Rausa et al., 1991).

Currently, only a few papers report an estimation of the molecular weight range and the concentration of high molecular weight compounds in atmospheric aerosols. Zappoli et al. (1999) estimated the concentration of HULIS by SEC with UV-VIS detection and found $0.6\text{--}2.5\ \mu\text{g}/\text{m}^3$ HULIS in aerosol with an upper limit for the molecular weight of 3000 Da using humic acid as standard. Krivácsy et al. (2000) also used SEC with UV and fluorescence detection to investigate atmospheric HULIS, confirming the previous results of Zappoli et al. (1999) concerning the chemical similarity of HULIS and HAs. The molecular weight distribution of HULIS was estimated by Kiss et al. (2003) with liquid chromatography – electrospray ionization mass spectrometry (HPLC-ESI-MS). These authors conclude that the molecular weight range of water-soluble high molecular weight compounds is not higher than 500 Da.

In this study we critically evaluate calibration procedures and present results of molecular weight range determinations of water soluble HULIS extracted from atmospheric particles by two different methods, SEC and laser desorption/ionization mass spectrometry (LDI-MS). Differences and limitations of the two methods are discussed and concentration estimates of HULIS are given using HA as a standard.

2. Experimental

Atmospheric aerosol particles were sampled in downtown Zurich, Switzerland, at an urban background site in August 2002. Particles smaller than 10 μm in diameter (PM10) were collected on pre-baked quartz fiber filters (140 mm diam.) with a high volume sampling system at a flow rate of 500 l/min (Model DA 80, Digitel, Hegnau-Volketswil, Switzerland). Three samples were collected continuously during 5 days, on 16–21 August, 21–26 August, and 28 August–2 September, respectively. Filters were then packaged into aluminum foils and stored in polyethylene bags at -28°C until analysis.

High molecular weight compounds in the aerosol samples are compared with a humic acid standard (Aldrich).

2.1. Extraction

Six 15 mm diameter pieces of each filter were extracted with solvents of different polarity. In the literature extraction of HULIS from atmospheric particles is mostly described with basic solvent such as aqueous sodium hydroxide (Havers et al., 1998; Krivácsy et al., 2000). In this study, samples were extracted with milliQ water, aqueous 0.1M NaOH, tetrahydrofuran (THF) or toluene covering a range of polar and apolar extraction media.

Filters were first soaked in the solvent during 2 h and then sonicated for 15 min. The supernatant was then filtered (PVDF Filter, 0.45 μm pore size, Whatman) or centrifuged depending on the type of analysis performed. Humic acid standards were sonicated and filtered in the same way as the filter samples.

For both analysis methods performed, size exclusion chromatography and laser desorption/ionization mass spectrometry, the toluene and THF extracts showed no detectable signals indicating the very polar properties of atmospheric HULIS. Thus only water and NaOH extracts are considered in the following.

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2.2. Size exclusion chromatography (SEC)

Size exclusion chromatographic measurements were performed using a Waters Ultrahydrogel 120 column (300 mm×7.8 mm, hydroxylated polymetacrylate stationary phase), and a SHIMADZU System Controller (SCL-10Avp), a Solvent Delivery Module (LC-10Atpv) and a Diode Array Detector (SPD-M10Avp). UV spectra between 190–800 nm were recorded.

MilliQ water and NaOH extracts from the filter samples and from the humic acid standards were filtered with a PVDF filter (0.45 μm pore size, Whatman) prior to SEC analysis. An aqueous buffer solution (0.3M NaCl, 0.03M NH₄Cl, pH 10–11 adjusted with NH₄OH) at a flow rate of 1 ml/min was used as eluent (Krivácsy et al., 2000).

2.3. Laser Desorption/Ionization Mass Spectrometry (LDI-MS)

LDI-MS was performed to determine the molecular weight distribution of the compounds present in the ambient aerosol with an alternative method and to compare the results with the SEC measurements. The experiments were performed with a time-of-flight (TOF) mass spectrometer (Axima-CFR, KRATOS Analytical Shimadzu, Manchester, UK, laser wavelength 337 nm, pulse width 3 ns, repetition rate 10 Hz, linear mode, delayed extraction optimized for m/z=1000).

Filter samples were extracted as described above and centrifuged to separate the dissolved compounds from filter fibers and soot particles (the remaining solution was yellowish brown colored). For a direct comparison with SEC, the extracts were also filtered with the same filters as used for SEC analysis. After filtration, the LDI-MS spectra were essentially the same compared to the centrifuged samples however, with slightly lower signal intensities. Due to the high sodium content of the NaOH extracts, the LDI-MS were dominated by the Na⁺ adducts and a poor overall signal intensity was observed. Thus only milliQ water extracts were measured with LDI-MS and compared with SEC.

50 μl of the extract was directly added to the target stainless steel plate, the wa-

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ter was evaporated in a dessicator and the LDI-measurement was performed without further sample treatment. To assure a representative sampling, usually 1000 mass spectra were summed up, scanning over an area of about 0.25 mm². The laser power had to be kept in a narrow range in order to obtain sufficient signal but avoid fragmentation and plasma formation. In addition, small filter pieces were measured with LDI-MS without any further treatment in order to avoid artifacts due to extraction losses.

The addition of matrices, i.e., nicotinic acid, 2-(4-hydroxyphenolazo)benzoic acid (HABA), 6-aza-2-thiothymine (ATT), 3-aminoquinone (3 QA), 1,8,9-trihydroxyanthracene (Dithranol) was also studied, but did not improve the peak intensities significantly. Instead it increased the complexity of the spectra due to matrix peaks and matrix-sample molecule adducts. The presented LDI spectra were thus all recorded without any matrix addition.

3. Results

3.1. SEC analysis

Size exclusion chromatograms of two extracts of the filter samples, in milliQ water and aqueous 0.1M NaOH, were compared. For both cases the size distribution of the extracted compounds is the same, but the peak intensity is about 30% higher for the 0.1M NaOH extract, most likely due to the polar and acidic character of HULIS making them more soluble in a basic extract than in water. The SEC analysis of all three filter samples show the same peaks with retention times between 5.5 min and 10.5 min. The relative peak intensities are also the same for all filters with the exception of the peak at 10.6 min (see Fig. 1a), which in sample number 2 (21–26 August) was three times larger than for the two other samples. However, at these low retention times only small compounds are expected, which are not the focus of this paper. The main peaks in the high molecular weight range are observed at 6.58, 6.93, and 7.64 min, respectively. Humic acid standards showed similar results with the main peak at 6.38 min (Fig. 1b).

The peak at 5.38 min includes compounds with a molecular weight higher than the exclusion limit of the column.

Several standards of different polarities were used for a molecular weight calibration, i.e., polyethylene glycols (PEG), polymethacrylic acids (PMA) and dicarboxylic acids.

For PEG and PMA standards with the same nominal mass retention time differences up to two minutes are measured as shown by the linear regression lines in Fig. 2. For an unknown compound this translates into large uncertainties for its molecular weight. For example, at a retention time of 6.5 min this difference corresponds to 500 Da and 3500 Da for the PMA and PEG calibrations, respectively. The carboxylic acids fit well into the calibration curve of PMA due to their very similar chemical structure. This size calibration comparison shows drastically that determining the molecular weight of high molecular weight compounds with unknown chemical structure has to be performed with great care and that either theoretical considerations or results from other experimental techniques are necessary to provide additional information on the true molecular size distribution of HULIS.

The described discrepancies of the size calibration are due to the chemical properties of the standards and their interaction with the stationary phase, resulting in a significantly lower retention time of PMA compared to PEG with the same nominal mass, a phenomenon that has been described in the literature (e.g., Perminova et al., 1998). The high pH (pH=11) of the eluent might explain this observation: it leads to a deprotonation of PMA, but also of the stationary phase of the SEC column (hydroxylated polymethacrylic acid). Electrostatic repulsion might cause PMA to interact less with the stationary phase than PEG, which is neutral and is not affected by the surface charges of the stationary phase, resulting in the faster elution of PMA.

The retention times of the main peaks of the chromatograms shown in Fig. 1 are indicated as cycles on the x-axis in Fig. 2. Using these two calibration curves the retention times of 6.6, 6.95 and 7.6 min correspond to 3300, 2400 and 1300 Da, respectively for a PEG-equivalent weight and to 400, 170 and 40 Da, respectively, for a PMA-equivalent weight. HULIS are rather polar compounds, as indicated by the extraction results with

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apolar solvents and consistent with literature data (Zappoli et al., 1999). Thus, it is expected that they are separated on the column similar to PMA. However, as can be seen in Figs. 1a and 2 some smaller peaks are present in the chromatogram of the aerosol sample that elute at retention time of 7.5 min (i.e., theoretical PMA-equivalent mass of 50 Da) and later, which cannot be explained by the PMA calibration. Thus, the compounds eluting late in the chromatogram seem to have polarity characteristics closer to the neutral less polar PEG. To get further insight into the most likely size distribution for these compounds other techniques, such as LDI-MS, have to be compared with SEC.

3.2. LDI-MS analysis

LDI mass spectra were recorded for water extracts of airborne particulate matter. No significant differences between the LDI spectra of all three filters were found. A mass spectrum of one of the three samples is shown in Fig. 3a. A broad range of peaks between m/z 100–600 is detected. Signals with lower intensities are present up to m/z 700 but no peaks were observed at higher mass. These findings are in good agreement with HPLC-ESI-MS analyses of HULIS by Kiss et al. (2003).

In the LDI spectrum shown in Fig. 3a (insert) a sequence of peaks with a mass difference of m/z 14 and m/z 16 is observed in the mass range m/z 350–600. Recent studies found similar mass patterns in aerosols formed in smog chamber experiments and explained them mainly with oligomers formed from small carbonyls or dicarbonyls forming acetals (Tolocka et al., 2004; Kalberer et al., 2004). The similar pattern of these laboratory experiments and the spectrum shown here from field samples suggests that this kind of oligomers are also present in ambient aerosols.

Comparing the molecular weight determination from the LDI-MS measurements with the results of the two SEC calibrations and also considering the theoretical arguments discussed above, one can conclude that for the high end of the mass distribution the PMA calibration fits reasonably well to the LDI-MS results. This indicates an upper mass limit of organic compounds in urban aerosols of about 700 Da (equal to a re-

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tention time of 6.25 min for the PMA calibration). However, at this stage one cannot exclude that compounds with $m/z > 700$ are present in the ambient particles. They may have a very low ionization efficiency or fragment significantly in the LDI process, so that they may not be detected with the current method.

5 3.3. UV measurements

UV spectra between 190–370 nm of the aqueous aerosol extract are shown in Fig. 4. Traces a, b and c show spectra for retention times of 6.58, 6.93 and 7.64 min, respectively. Spectra at all three retention times are very similar, i.e., light absorbing properties do not seem to vary greatly for the different size fractions of the aerosol components. The humic acid standard (Fig. 4d) also shows a similar absorption spectrum. The absorption maximum is at 207 nm for both the aerosol components and the humic acid, and a shoulder at 260–290 nm is visible in both, which might be due to carbonyl functionalities absorbing at these wavelengths. However, between 210 and 240 the HULIS spectra show a more pronounced decrease than the humic acid standard.

15 These findings support results reported in the literature (Zappoli et al., 1999) where in addition also fluorescence and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra of humic acid and HULIS were compared. All these measurements indicate that humic acid is a suitable surrogate to obtain quantitative estimates by UV spectroscopy of HULIS in ambient aerosols.

20 3.4. Concentration determination

Based on the above described comparison a calibration curve with humic acid standards between 0.1–2.5 $\mu\text{g/ml}$ was used to estimate the HULIS concentration in atmospheric aerosols. Despite the considerations above, several assumptions are necessary to use humic acids as surrogate standards to quantify HULIS.

25 (i) Aerosol components identified so far on a molecular level (Seinfeld and Pandis, 1998; Rogge et al., 1993) have molecular weights mostly smaller than about 300 Da

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(e.g., alkanes up to C₂₁ or 6-ring PAHs). Therefore we define all compounds with a molecular weight >300 Da as HULIS. Accordingly, only the respective retention time windows of 5.8–6.61 min and 5.8–8.93 min (corresponding to molecular sizes >300 Da for the PMA and PEG calibration), respectively, were used in the quantitative analysis.

(ii) Consequently also the respective mass fractions of humic acid within these two retention time windows were used for the calibration. This, however, requires that throughout the chromatogram the extinction coefficient of humic acid components stays relatively constant.

(iii) In addition, a poor extraction efficiency of the HULIS from the filter material could lead to an underestimation of the HULIS concentration. Therefore extracted samples were compared with filter samples, which were measured directly with LDI-MS without extraction into a liquid. Figure 3b shows that the molecular weight distribution of such a direct LDI experiment is very similar to the extracted sample (Fig. 3a). Thus, it can be concluded that the extraction process is not affecting substantially the molecular weight distribution. However, spectra with poor mass resolution were obtained from these non-extracted samples, possibly due to electrical field distortion in the ion source caused by the rough filter surface.

(iv) The extinction coefficient of the humic acid standard and HULIS (depending largely on the types and concentrations of chromophores) might be different for the same retention time window, which would introduce an error for the quantitative estimates. However, so far no better-defined alternatives to humic acid are available and the quantitative comparison with the total organic carbon (see below) indicates that the current estimates are reasonable. Thus, the quantitative results obtained here can be considered as “humic acid equivalent” concentrations.

Taking the above considerations into account the HULIS concentration (in humic acid equivalents) in the three urban aerosol samples was 0.23–0.52 $\mu\text{g}/\text{m}^3$ and 0.85–1.86 $\mu\text{g}/\text{m}^3$ for the PMA and PEG calibration, respectively (Table 1). This amounts to 8–10% and 30–33% of total OC (Szidat et al., 2004), respectively. As discussed above, it seems more likely that the PMA-calibration is more representative for the

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HULIS quantification, thus HULIS concentrations seem to account for roughly 10% of the water-soluble OC in these samples. Carbon-14 analyses of the same samples showed that 75–96% of total water-soluble OC is of biogenic origin (Szidat et al., 2004) suggesting that a large part of this aerosol fraction is possibly secondary aerosol mass.

5 Therefore it is not surprising that at this urban site significant amounts of HULIS are found, which are believed to be formed in secondary processes.

These HULIS concentrations are comparable to literature data, e.g. Zappoli et al. (1999) found HULIS concentrations of 0.6–2.5 $\mu\text{g}/\text{m}^3$ for samples collected in Italy.

4. Conclusions

10 We investigated humic-like substances (HULIS) in atmospheric aerosols by two different techniques, size exclusion chromatography and laser desorption/ionization mass spectrometry. LDI-MS was used for the first time to investigate HULIS from atmospheric aerosols. Different compounds, i.e., polyethylene glycol (PEG), poly-
15 methacrylic acid (PMA), and dicarboxylic acids, were used as standards for the molecular size calibration in the SEC experiments. Considering that HULIS are likely highly polar compounds (as extraction experiments with solvents of different polarity showed) the PMA and dicarboxylic acids are the better suited standards than PEG. Using the PMA calibration, an upper mass limit of about 700 Da for HULIS in urban aerosols can be estimated. These results are in good agreement with our LDI-MS measurements,
20 which showed a mass distribution in the same range. Direct LDI measurements of loaded filters, without extracting the aerosols showed a very similar molecular mass distribution, indicating that no substantial artifacts were introduced during the extraction work-up of the filter samples. Quantitative measurements, using humic acid as surrogate standard, showed that 0.2–1.9 $\mu\text{g}/\text{m}^3$ of HULIS are present in the urban particles collected in summer 2002 corresponding to 8–33% of the total organic mater in the aerosol.
25

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Table 1. HULIS concentrations in atmospheric urban aerosol. Quantified assuming different size calibration standards and % of HULIS of the total organic carbon.

Sampling time	HA-equivalent concentration of HULIS ($\mu\text{g}/\text{m}^3$) (PEG calibration) ^a	HA-equivalent concentration of HULIS ($\mu\text{g}/\text{m}^3$) (PMA calibration) ^b	% of OC (^b) using PEG calibration	% of OC (^b) using PMA calibration
16–21 August 2002	1.86	0.52	33	9
21–26 August 2002	0.85	0.23	30	8
28 August–2 September	1.58	0.48	32	10

^a see text and Fig. 2

^b OC data taken from Szidat et al. (2004)

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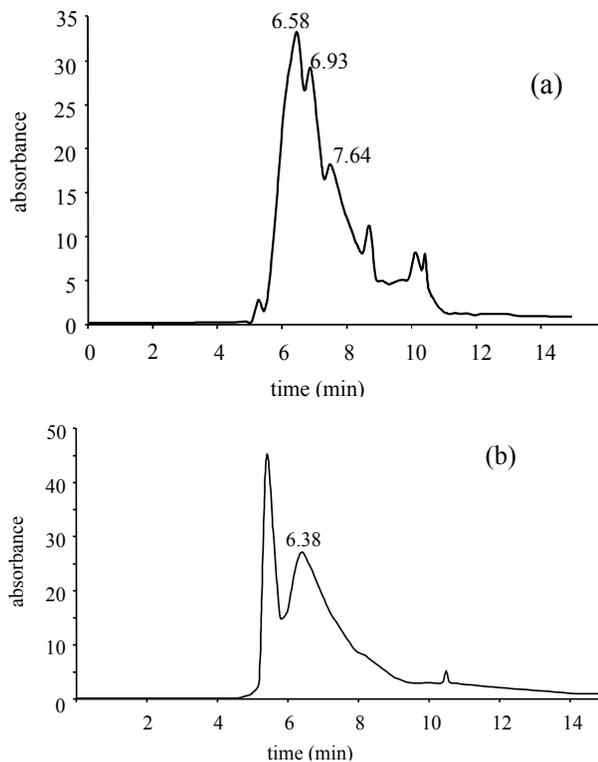


Fig. 1. Size-exclusion chromatogram of the 0.1 NaOH extract of atmospheric aerosols collected in downtown Zurich **(a)** and humic acid standards **(b)**.

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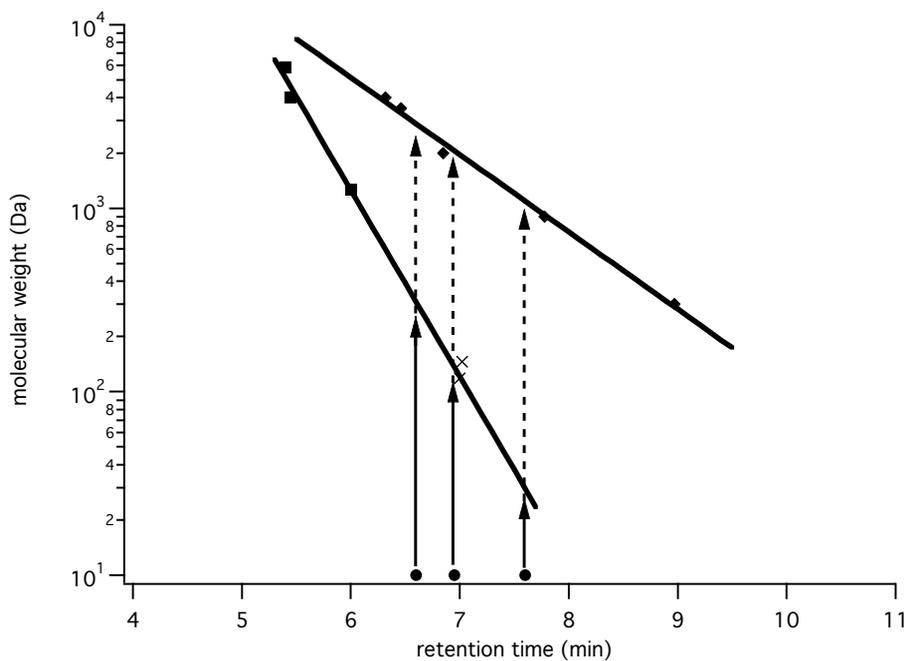


Fig. 2. Size calibration of SEC column with PEG (◆), polymethacrylic acid (■), dicarboxylic acids (×) and retention times of HULIS (●).

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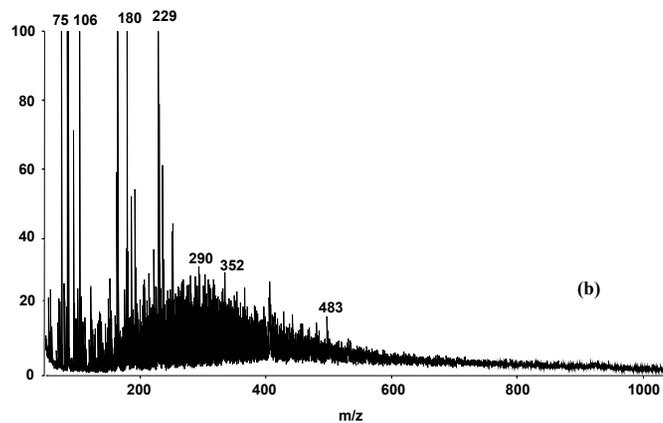
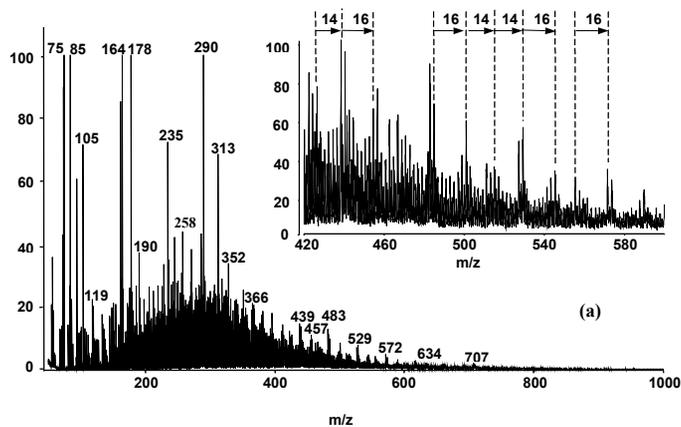


Fig. 3. LDI mass spectra of **(a)** HULIS from a water extracted filter and **(b)** a not extracted filter. The insert (a) shows an expanded view of the spectrum. Repetitive peaks of $\Delta m/z$ 14 and 16 are visible.

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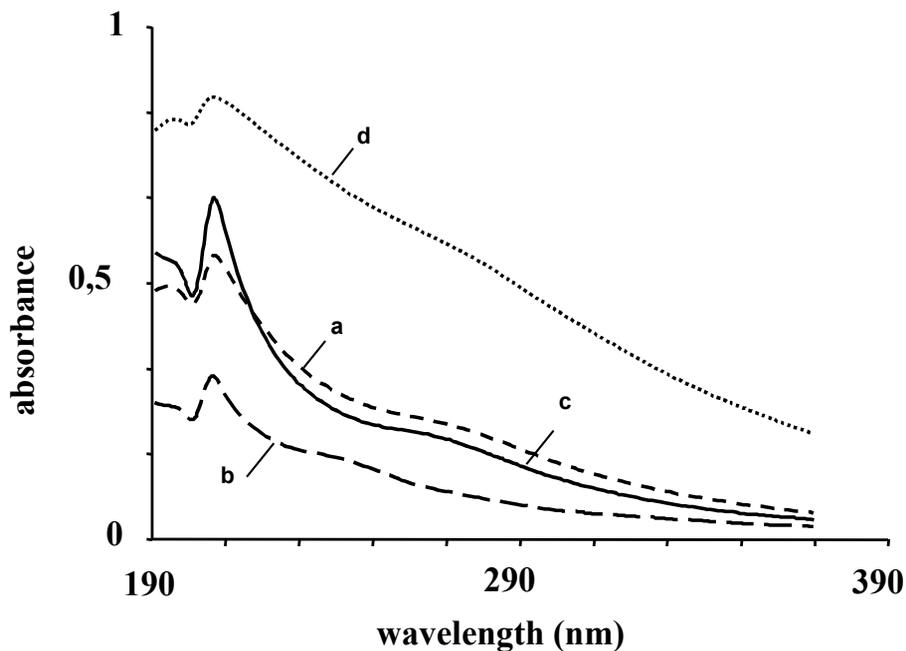


Fig. 4. UV spectra of (d) a HA standard at 6.36 min retention time (see Fig. 1b) and of HULIS at retention times of (a) 6.58 min, (b) 6.93 min and (c) 7.64 min of the water extracted filter (see Fig. 1a).

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