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R. Hempfling<sup>a</sup>; H. -R. Schulten<sup>a</sup>

<sup>a</sup> Fachhochschule Fresenius, Department of Trace Analysis, Wiesbaden, F.R.G.

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# DIRECT CHEMICAL CHARACTERIZATION OF DISSOLVED ORGANIC MATTER IN WATER BY PYROLYSIS-FIELD IONIZATION MASS SPECTROMETRY

R. HEMPFLING and H.-R. SCHULTEN\*

*Fachhochschule Fresenius, Department of Trace Analysis, Dambachtal 20, D-6200 Wiesbaden, F.R.G.*

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The chemical composition of dissolved organic matter (DOM) in the leachates of moder profiles under mixed pine and oak forests was investigated by temperature-resolved pyrolysis-field ionization mass spectrometry (Py-FIMS). The FI-mass spectra of the freeze-dried samples from the 35- and 140-year-old forests show distinct differences. Temperature-resolved Py-FIMS indicates several steps of thermodesorption and thermal degradation of the organic materials due to free and chemically bound constituents. In the first step, these constituents are non-carbohydrate aliphatics volatilized between 100 and 200 °C. In the following steps of thermal evolution, carbohydrates, amino acids/peptides/proteins, and glycolipids are observed between 200 and 350 °C, followed by lignin subunits between 280 and 350 °C. Finally aromatic degradation products are recorded between 350 and 630 °C.

**KEY WORDS:** Dissolved organic matter, structural subunits, thermodesorption, thermal degradation, mass spectrometry.

## INTRODUCTION

Dissolved organic matter in water (DOM) percolating through soil horizons plays an essential role for plant nutrition, soil formation processes and water quality, as it affects the transport and availability of nutrients and inorganic/organic pollutants.<sup>1-4</sup> Recently the importance of DOM has also been discussed in the context of the impact of air pollutants on soil chemistry and subsequent humus disintegration.<sup>5,6</sup> As DOM from different environments varies strongly in chemical composition and physical properties,<sup>4,6,7</sup> the understanding of its biochemical and geochemical role in aquatic/terrestrial ecosystems requires elucidation of its molecular structures. However, due to the complexity of DOM, for this purpose time-consuming concentration, purification, fractionation, degradation, derivatization, and identification procedures have to be applied.<sup>8-11</sup>

A novel, rapid analytical technique for DOM that is based on thermal purification, fractionation, and degradation combined with mass spectrometric identification is temperature-resolved pyrolysis-field ionization mass spectrometry (Py-FIMS).<sup>12</sup> The only preparation step needed for this technique is concentration of the water sample by freeze-drying. The use of a soft ionization technique such

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\*Author to whom correspondence should be addressed.

as field ionization that preferably produces molecular ions, yields mass spectra that can be correlated with original structures of the sample. In a preliminary report,<sup>13</sup> it has been already shown that Py-FIMS can be used for the characterization of dissolved organic matter in ground water with  $4\text{ mg l}^{-1}$  of dissolved organic carbon (DOC).

The objective of this study is to evaluate the potential of the technique for the chemical characterization of DOM in soil leachates and, in general, organic matter in aqueous solutions on the basis of molecular substructures. In a first approach, for this purpose samples with a high content of dissolved organic carbon derived from forest humus were chosen.

## MATERIALS AND METHODS

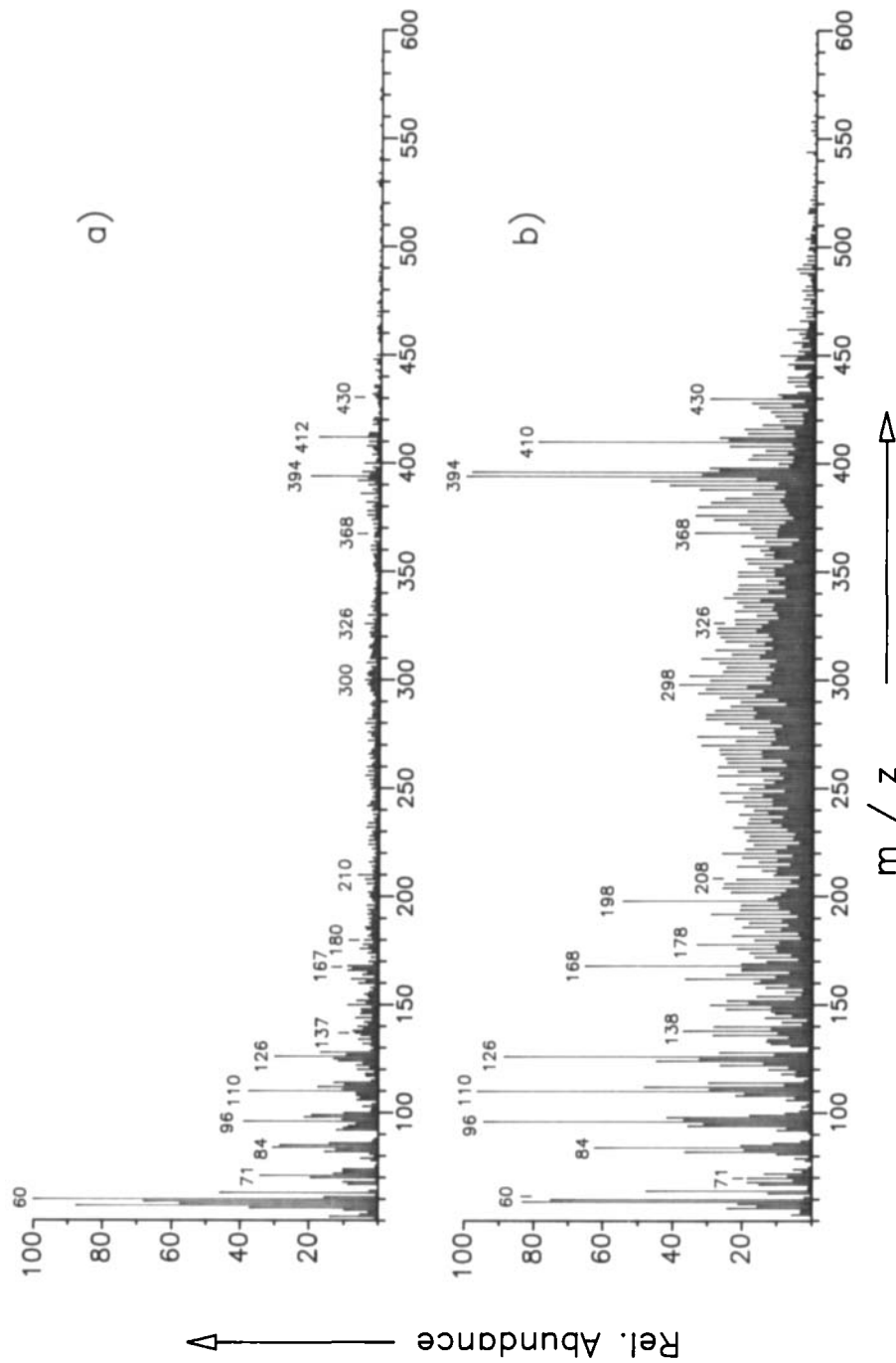
The samples analyzed were taken in two mixed *Pinus sylvestris/Quercus robur* forests in Berlin–Grunewald.<sup>14</sup> Soil leachates from the 35- and 140-year-old forests were collected in September 1989 by humus lysimeters that were positioned below the fermentation layers (Of horizons) in the two moder profiles over Dystric Cambisols. Samples were filtered through a membrane filter  $<0.45\ \mu\text{m}$  to separate DOM from particulate organic matter. The DOC content of the samples was determined by an oven DOC analyzer (Maihak, Tocar 2) resulting in  $60\text{ mg l}^{-1}$  for the sample from the 35-year-old forest and in  $168\text{ mg l}^{-1}$  for the sample from the 140-year-old forest. Prior to Py-FIMS analysis, the filtered water samples were freeze-dried.

For temperature-resolved Py-FIMS, about  $100\ \mu\text{g}$  of the freeze-dried samples were filled into quartz crucibles and placed in the ion source of a Finnigan MAT 731 mass spectrometer.<sup>15</sup> The samples were heated by a heating coil in high vacuum ( $10^{-3}\ \text{Pa}$ ) from  $50$  to  $750\ ^\circ\text{C}$  at a heating rate of about  $1.2\ ^\circ\text{C s}^{-1}$ . The evolved thermodesorption/thermal degradation products were field-ionized and electrically registered on the mass spectrometer. During 10 min about 40 magnetic scans were recorded per sample in the mass range from  $m/z$  50 to 700 (single spectra). The Finnigan MAT SS 200 data system allows the integration of single spectra representative for an individual temperature range (section spectrum) or of all single spectra resulting in one summed spectrum. The plots of the ion intensities of the whole sum of FI mass signals recorded versus the heating temperature can be obtained as thermograms.

The sample preparation by freeze-drying and the introduction of the freeze-dried samples into the ion source at  $50\ ^\circ\text{C}$  and  $10^{-3}\ \text{Pa}$  implies the loss of low-boiling compounds. These compounds can be analyzed complementary by cryoadsorption methods using a stripping system with a cryotrap.<sup>16</sup>

## RESULTS AND DISCUSSION

The Py-FI mass spectra obtained from both samples (Figure 1) are characterized by distinct differences in signal patterns. These differences mainly refer to the



**Figure 1** Integrated Py-FI mass spectra of dissolved organic matter in humus leachates from (a) 35- and (b) 140-year-old forests. The registered integrated intensities of all FI signals are (a)  $2.8 \times 10^6$  counts and (b)  $6.2 \times 10^6$  counts. The calculated ratio of 1:2.2 for these integrated intensities corresponds to a certain extent with the DOC content of the original samples (ratio = 1:2.8).

**Table 1** Tentative assignments of chemical structures to mass signals obtained by Py-FIMS of DOM in forest soil leachates

<i>Mass signals</i>	<i>Compound classes</i>
m/z 58, 60, 68, 72, 74, 82, 84, 85, 86, 96, 98, 110, 112, 114, 126, 128, 132, 144, 162	carbohydrates
m/z 110, 124, 136, 138, 140, 148, 150, 152, 154, 156, 164, 166, 168, 178, 180, 182, 192, 196, 198, 208, 210, 212, 246, 260, 272, 284, 286, 298, 300, 302, 312, 314, 326, 328, 330, 332, 340, 342, 344, 356, 358, 360, 362, 372, 374, 376, 386, 388, 402, 416, 418	monomeric/dimeric lignin subunits
m/z 59, 67, 71, 79, 81, 83, 85, 93, 95, 97, 103, 107, 109, 117, 121, 125, 131, 137, 139, 147, 167, 185, 203	amino acids, peptides, proteins, N-acetyl amino sugars and other nitrogen-containing compounds
m/z 78, 92, 94, 104, 106, 108, 110, 116, 118, 120, 122, 130, 132, 134, 136, 148, 150, 162, 164, 176, 178, 186, 190, 192, 204, 206, 218, 220, 232, 234, 246, 248, 260, 262, 274, 276, 288, 290, 302, 304, 316, 318, 330, 332	benzene, phenol and their hydroxy, carboxy and alkyl derivatives
m/z 386, 388, 390, 392, 394, 396, 398, 410, 412, 414, 430	sterols, steranes, tocopherols
m/z 158, 172, 186, ..., 508	<i>n</i> -fatty acids
m/z 56, 58, 70, 72, 84, 86, ..., 532, 534	alkenes/alkanes

intensity of signals but not to their existence. The signal patterns can be interpreted using previous investigations on forest humus and aquatic humic substances by Py-FIMS (high resolution) and Py-GC/MS.<sup>17–20</sup> These studies allow the tentative assignment of chemical structures, produced out of organic constituents in the leachate to specific mass signals as summarized in Table 1. These structures and constituents are carbohydrates, monomeric/dimeric subunits of intact and biodegraded lignin, amino acids, peptides, proteins, N-acetyl amino sugars and other nitrogen-containing compounds, aromatic building blocks yielding benzenes, phenols and their hydroxy, carboxy and alkyl derivatives, and non-carbohydrate aliphatic building blocks yielding sterols, steranes and tocopherols, homologues series of *n*-fatty acids, and alkenes/alkanes.

In the sample from the 35-year-old forest (Figure 1a), signals related to N-acetyl amino sugars (e.g. m/z 137, 167), intact lignin subunits (e.g. m/z 180, 210), and products of thermal scission of functional groups (e.g. acetic acid at m/z 60) show relatively high abundances, while in the sample from the 140-year-old forest (Figure 1b) signals related to oxidatively biodegraded lignin subunits (e.g. m/z 168, 178, 198, 208), condensed lignin subunits (e.g. m/z 298, 326), *n*-fatty acids (e.g. m/z 368, 396, 410) and unsaturated ethylcholestanes (m/z 388, 390, 392, 394) are more abundant.

In the following the possibility of a more detailed discussion of the chemical composition of DOM by temperature-resolved Py-FIMS is demonstrated for the sample shown in Figure 1b. The thermogram obtained demonstrates that the thermal evolution of the DOM analyzed occurs between 100 and 630 °C (Figure

2). The shape of this curve allows to distinguish individual steps of thermodesorption and thermal degradation processes in the temperature ranges 100–200 °C, 200–300 °C, 300–350 °C, and 350–630 °C. The bulk of the material investigated is evolved between 300 and 475 °C.

For studying the fractionated thermal evolution of characteristic constituents and compound classes, single spectra of different temperature ranges were integrated to section spectra (Figure 3). These section spectra allow to discern which constituents exist in free or bound form in the sample.

In the temperature range of 100 to 200 °C (Figure 3), the mass signals in the registered mass range mainly refer to paraffinic compounds such as alkenes/alkanes ( $C_4$ – $C_{29}$ ) and fatty acids ( $C_{16}$ – $C_{25}$ ). These compounds are thermally desorbed from the bulk of dissolved organic matter.

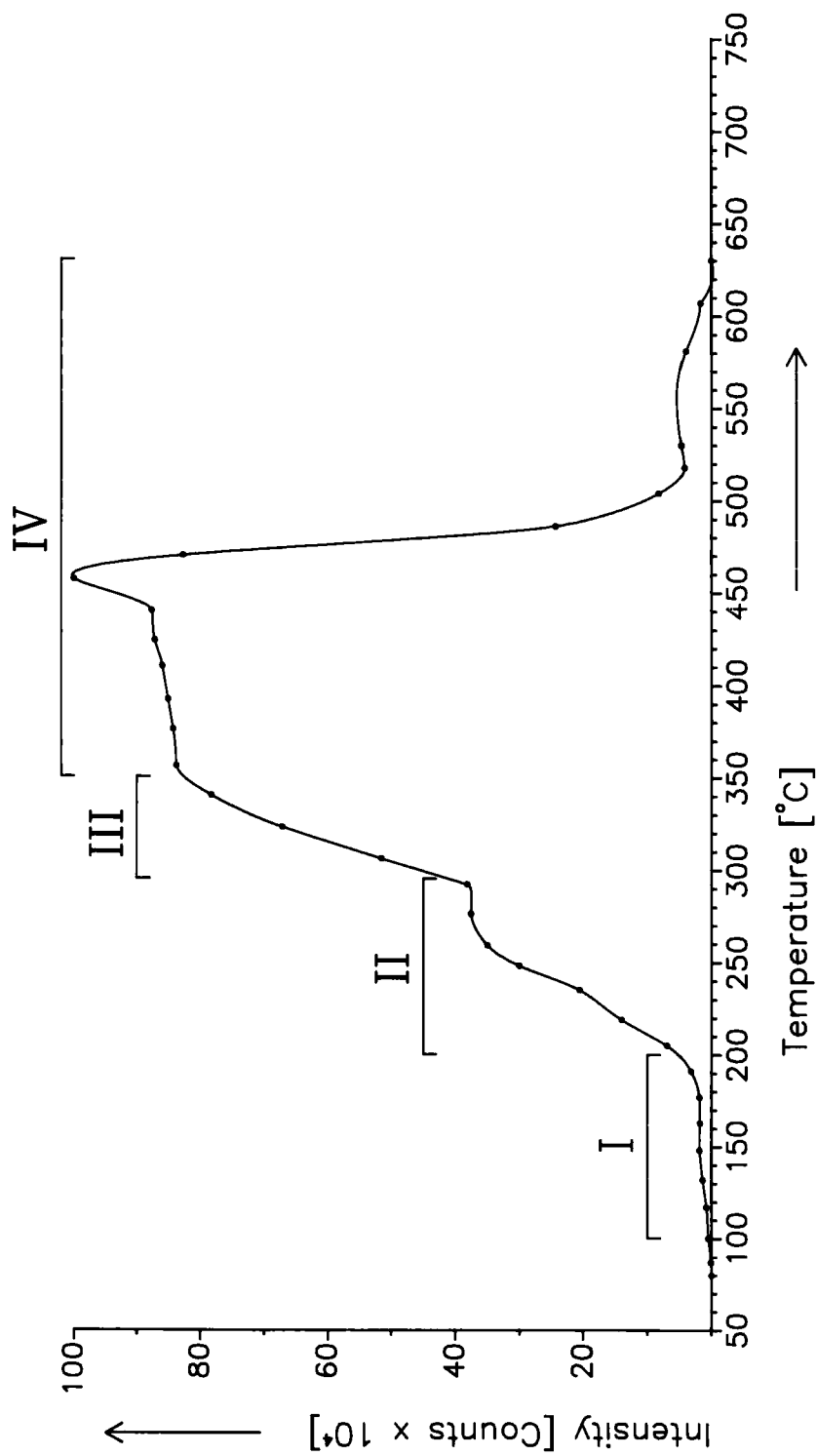
With increasing temperature, the pattern of signals changes significantly. Between 200 and 300 °C (Figure 3), the signals indicate the evolution of compounds related to carbohydrates, N-acetyl amino sugars, biodegraded lignin and non-carbohydrate aliphatics such as alkenes/alkanes, *n*-fatty acids, and unsaturated ethylcholestanes. The evolution of these compounds seems to be the result of thermodesorption *and* thermal degradation. The simultaneous evolution of non-polar and polar constituents in this temperature range offers an explanation for the high contribution of lipids to DOM<sup>10</sup>, suggesting that the spectra recorded represent to a large extent glycolipids that are thermally degraded.

In the temperature range of 300 to 350 °C (Figure 3), glycolipids are still thermally degraded, but in addition signals relating to pyrolysis products of peptides/proteins and an increasing contribution of monomeric/dimeric pyrolysis products of biodegraded lignin appear. The temperature range for the thermal evolution of lignin subunits between 280 and 350 °C corresponds to temperatures where the thermal scission of  $\beta$ -arylether linkages occurs, confirming that the biodegraded lignin subunits still exist as polymers in DOM. The dominating signal at  $m/z$  168 indicates vanillic acid, a typical product of the oxidative biodegradation of lignin. The relative increase in intensity of the signal at  $m/z$  110 in relation to  $m/z$  96 and 126, if compared to the temperature range 200–300 °C, demonstrates an increasing contribution of catechol, a further typical product of oxidative lignin biodegradation.

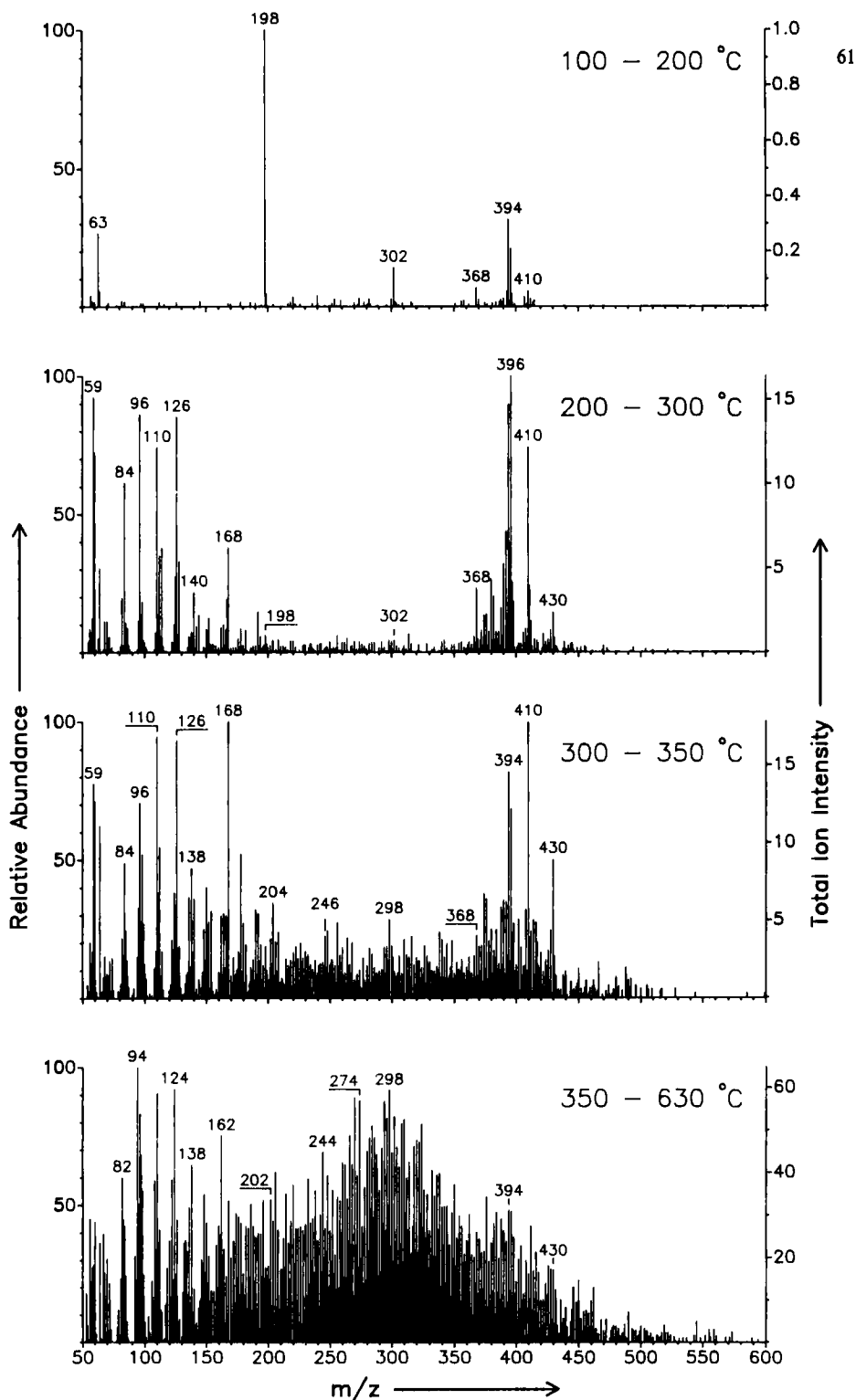
The temperature range of 350 to 630 °C (Figure 3) shows mainly aromatic subunits. These subunits are related to benzene and phenol and their hydroxy, methoxy and alkyl derivatives. Most likely these compounds result from thermal degradation of a macromolecular aromatic network and/or from aromatization of aliphatic subunits of this network.

## CONCLUSIONS

To the best of our knowledge, the described methodology represents the first approach of a rough chemical characterization of dissolved organic matter in soil leachates on the basis of molecular structures. As shown, this technique allows to



**Figure 2** Plot of the ion intensities versus the heating temperature (thermogram) of DOM in a forest humus leachate. Four distinct temperature ranges are indicated by I-IV; the corresponding section spectra are shown in Figure 3.



**Figure 3** Py-FI section spectra of dissolved organic matter in a forest humus leachate. The temperature ranges correspond to I-IV in Figure 2. The ordinates give the relative abundances (left) and the total ion intensities (right) in per cent.



differentiate between DOM from various forests possibly due to the age of the forests or to site conditions. The most suitable chemical information can be obtained with Py-FIMS from polar samples in the section spectra representing the temperature range 100 to 350 °C. In this range either thermodesorption or hydrogen transfer reactions and thermally induced solvolysis occur, leading to the volatilization of original compounds or of thermal decomposition products directly related to original subunits of DOM. Thus, Py-FIMS is shown to be a promising technique for a fast, sensitive, and rough chemical characterization of major constituents of DOM on a molecular basis.

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