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PYROLYSIS MASS SPECTROMETRIC MAPPING OF SELECTED PEATS AND PEATIFIED PLANT TISSUES

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Summary

Three peat types, a *Scheuchzeria* peat, a dark *Sphagnum* peat (Schwarztorf) and a light *Sphagnum* peat (Weisstorf), obtained from the peat deposit 'Meerstalblok' (The Netherlands), were chemically fractionated using dichloromethane, 70% ethanol and 0.1N potassium hydroxide as extractants. Extracts and residues were chemically characterised using in-source-pyrolysis-mass spectrometry. Mass spectrometric evidence for triterpenoids, tocopherols, sterols, steroids and wax esters was prominent in the dichloromethane extracts. Identical compounds were detected in thermally extracted fractions of the peats and peatified plants. The *Scheuchzeria* peat showed a spectrum characterised by a polysaccharide-lignin pattern, whereas both *Sphagnum* peat samples showed a spectrum characterised by polysaccharides.

A selective loss of polysaccharides and an alteration of the lignin macromolecule was observed in peatified *Calluna* wood, probably caused by the activity of brown rot fungi.

Introduction

Pyrolysis mass spectrometry (PyMS) is a very useful microanalytical technique for the characterisation of complex organic materials. Its rapidity and reproducibility, the minimal sample pretreatment, the low sample requirement (micrograms), and the universal applicability make this molecular characterisation technique ideally suited for the analysis of plant tissue on a microscale.

Curie-point pyrolysis quadrupole mass-spectrometry (Cu-Py-QMS), pyrolysis field ionisation mass spectrometry (Py-FIMS) and Curie-point pyrolysis gas chromatography-mass spectrometry (Cu-Py-GCMS) have been used for the characterisation of soils, peats and peatified plant remains. Analyses have been performed on soils (Haider & Schulten, 1985; Hempfling & Schulten, 1990), non-fractionated peat samples (Halma et al., 1984; Boon et al., 1986; Ryan et al., 1987; Durig et al., 1989), size fractionated peat samples (Bracewell et al., 1980; Ryan et al., 1987, Durig et al., 1989), handpicked plant remains (Boon et al., 1986; Smeerdijk & Boon, 1987; Boon et al., 1989; Stout et al., 1989), and wet chemical fractions, such as lipids (Ekman & Ketola, 1981) and humic acids (Meuzelaar et al., 1977). These studies reveal the complex chemical composition of peats, peatified plant remains and microscopically unrecognisable fractions. Polysaccharides, lignin and modified biodegraded lignins, polyphenols, suberins, cutins, various lipids and nitrogen and

sulfur containing compounds have been shown to be present in peat, but unfortunately many of these compounds were isolated from insufficiently characterised peat samples. Peat deposits are often built up of a complex mixture of tissue remnants from different plant species. This implies that each tissue contributes its own chemical fingerprint to the peat, a fact which is often overlooked. It has been shown that different plant parts selected from one peat deposit, contribute specific classes of compounds to the whole peat (Smeerdijk & Boon, 1987).

The complexity of peat becomes especially apparent when studied by microscopic techniques (Puffe & Grosse Brauckmann, 1963; Cohen & Spackman, 1977). Microscopy is an important tool in modern peat studies, especially when the anatomical aspects of the decomposition process in peat deposits are studied. Cohen & Spackman (1980), Stout (1988), and Stout & Spackman (1987, 1989) have demonstrated that tissue and cell wall architecture change significantly when plants are incorporated in the peat. The anatomical alterations during peatification reflect the chemical selectivity of the decomposition process. This chemical selectivity of the peatification has been demonstrated by pyrolysis mass spectrometry for woody tissues collected from a variety of sediments and peat deposits. Generally, a loss of polysaccharides and a preservation and structural modification of the lignin macromolecule, by demethylation and loss of oxygen functions, is observed in woody tissues (Hedges et al., 1985; Saiz Jimenez et al., 1987; Stout et al., 1988). Stout et al. (1989) have correlated these changes in chemistry with changes observed by fluorescence microscopy of the peatified cell walls.

Our study is part of an ongoing research program on the combined anatomical and mass spectrometric mapping of peatified plants, with the object of revealing the decomposition process on the tissue and cell wall level. This paper reports on the mass spectrometry of three peats and related handpicked peatified plant remnants. The potential of chemical extraction procedures and of online thermal extraction for the characterisation of these microsamples is explored.

Location, Materials and Methods

Location and samples

The peat samples under study were taken from the peat deposit 'Meerstalblok' (52° 41' N, 7° 02' E), an area located in the central part of the Bargerveen, which is a natural bog reserve southeast of Emmen in the eastern part of Drente Province (The Netherlands). The bog reserve is a remnant of the Bourtangerveen, a large peat area, which extended along the Dutch-German border. The peat was deposited during the Holocene in the Hunze valley, a northwest directed depression between the Drente plateau and the river dunes of the Ems (Ter Wee, 1962; Casparie, 1972; in Dupont, 1986).

The base of the peat section consists of sand overlain by a thin layer of Reed and Sedge peat. Afterwards, three layers, a *Scheuchzeria* peat, strongly decomposed old *Sphagnum* peat and *Eriophorum* peat respectively, were deposited. These thin layers are overlain by two thick layers consisting of strongly decomposed old *Sphagnum* peat (Schwarztorf) and well preserved young *Sphagnum* peat (Weisstorf) (Dupont 1986).

The top layer is disturbed by dead and living *Molinia* root material originating from a *Molinia* vegetation growing on the top soil. A stratigraphic map of the profile and a paleobotanical study of this section was presented by Dupont (1986).

For PyMS analysis, three different peat samples were collected from the section:
1. A *Scheuchzeria* peat, mainly composed of stem material of *Scheuchzeria palustris*. The peat was collected 30 cm above the base of the section.
2. A dark *Sphagnum* peat (Schwarztorf), mainly composed of Ericaceous (hair) root material, stems and leaves of *Sphagnum* section Acutifolia and some traces of *Calluna* twigs and *Eriophorum* stem remains. This type was collected 50 cm above the sandy base.
3. A light *Sphagnum* peat (Weisstorf), mainly composed of leaf and stem material of *Sphagnum papilosum* and some Ericaceous root material. Samples were taken 50 cm below the top of the peat profile.

The periderm of Ericaceae side roots (ca.0.5-2mm in diameter), wood of *Calluna* twigs and *Sphagnum* stems were handpicked from the old *Sphagnum* peat and directly analysed by PyMS. Recent plant material was collected near the area of the peat deposit.

Extraction Procedure

Moist peat samples were freeze-dried and subsequently freezer milled at liquid nitrogen temperature for about 3 minutes in a Spex 6700 freezer mill. An amount of 200 mg of each peat sample was extracted sequentially with dichloromethane, 70% ethanol, and 0.1N potassium hydroxide. The peats were extracted in glass vials using a magnetic stirrer. During each extraction step, suspensions were flushed with nitrogen to prevent oxidation. After each step, the suspensions were centrifuged in order to separate extract and particulate residue. In this way, lipid fractions, ethanol extracts, humic acid fractions and the dilute alkali insoluble residues were obtained. Humic acid fractions were obtained by collecting the precipitate which was formed after acidifying the alkali extract. The alkali insoluble residue was desalted by repeated washing with Millipore-Q (CR) deionised water.

Pyrolysis Mass Spectrometry (PyMS)

Platinum filament pyrolysis was performed on a JEOL DX-303 double focussing mass-spectrometer connected to a JEOL DA-5000 data system. Solutions or suspensions of homogenised peat in water were applied to the inert metal (Pt, Rh) loop of the desorption probe and dried. After insertion of the probe in the mass spectrometer, the loop was resistively heated at a rate of 20 ^{o}C/s up to 800 ^{o}C. The pyrolysis products were ionised under 16 eV electron impact conditions in the ion source, which was kept at 180 ^{o}C. The accelerating voltage was 3kV. The scan cycle time over a mass range of 800 amu was one second.

Results

The chemical fractionation scheme described was designed as a gentle method for the solubilization of components with an increasing polarity, and was derived from a procedure for the purification of cell wall material (Fry, 1988). Soluble fractions and residues in each step were monitored by Py-EI-MS. We report here on the PyMS of

native peats, lipid extracts, and the alkali insoluble fractions, as well as on some selected plant remains isolated from the dark *Sphagnum* peat-layer.

Native peat and Calluna wood

The mass spectra of *Scheuchzeria* peat, light *Sphagnum* peat and dark *Sphagnum* peat, are shown in Fig.1. Markers of sugar and phenolic compounds were identified using PyMS data of Pouwels and Boon (1990). The mass spectrum of the *Scheuchzeria* peat is dominated by mass peaks from lignin, indicated by m/z 124, 137, 152, 164, 178, 180 (guaiacyl), m/z 154, 167, 180, 182, 194, 196, 208, 210 (syringyl), and in the higher mass regions, m/z 272, 302, 340, 358, 360, 370, 388, 400, 418 (dimeric lignin pyrolysis products). Mass peaks from polysaccharides (m/z 43, 57, 60, 73, 85, 112, 114, 126, 144) are relatively low in intensity, which points to a selective removal of polysaccharides during peatification. This decrease is demonstrated very well by comparison of fresh *Calluna* wood (Fig.2a) with peatified wood (Fig.2b). The fresh wood is characterised by mass peaks m/z 57, 60, 73, 112, 114, 126, 144, identified as polysaccharide-specific marker ions of hexose and pentose polymers, and by m/z 124, 137, 138, 150, 151, 152, 154, 180 and m/z 167, 180, 194, 196, 210 which are marker ions for guaiacyl and syringyl derivatives respectively. Furthermore, m/z 272, 302, 328, 340, 358, 370, 388, 418, assigned to dimeric lignin pyrolysis products, can be seen in the higher mass region. The mass spectrum of peatified wood (Fig.2b) is characterised by a significant reduction in intensity of polysaccharide marker ions and a retention of lignin derived peaks. However, the pattern of lignin marker ions is drastically altered towards a relative increase in guaiacyl mass peaks. This is evident in both the monomeric and dimeric lignin pyrolysis product ions. Moreover, ions of non-methoxylated compounds such as phenol (m/z 94) and dihydroxybenzene (m/z 110) are also more intense.

Mass peaks from complex polysaccharides i.e. m/z 43, 57, 60, 73, 85, 112, 114, 126, 144, are dominant in both *Sphagnum* peat samples (Fig.1 b,c), whereas lignin mass peaks (m/z 124, 138, 150, 164, 180, 194, 210) are rather low in intensity.

Dichloromethane soluble and thermally extractable lipids

The temperature resolved PyMS process allows separation between volatile fractions, thermally desorbed in an early stage of the temperature ramp (see insert in Fig. 4), and biopolymeric materials which are pyrolysed at a higher temperature. The temperature resolved PyMS appears to be especially useful for the analysis of lipids in extremely small plant tissue samples which are difficult to study by the usual solvent extraction method. Fig.3 and 4 show the partial mass spectra (m/z 200-800) of the dichloromethane extracts from the selected peat types and corresponding thermal extracts. The resemblance of these fingerprints is remarkable and reassuring, because it demonstrates that the thermal extraction process is relatively mild. Under both conditions, mass peaks (mainly molecular ions) are observed up to m/z 800. Compounds can be tentatively identified by comparison with PyGCMS data of Smeerdijk and Boon (1987) on peats and peatified tissues and with the mass spectral atlas of Mc Lafferty and Stauffer (1989).

The spectra of the peats are characterised by molecular ions and fragmentation products of monomeric compounds such as aliphatic hydrocarbons, ketones, alcohols, fatty acids, triterpenoids, tocopherols, steroids and long chain aliphatic esters. In the higher

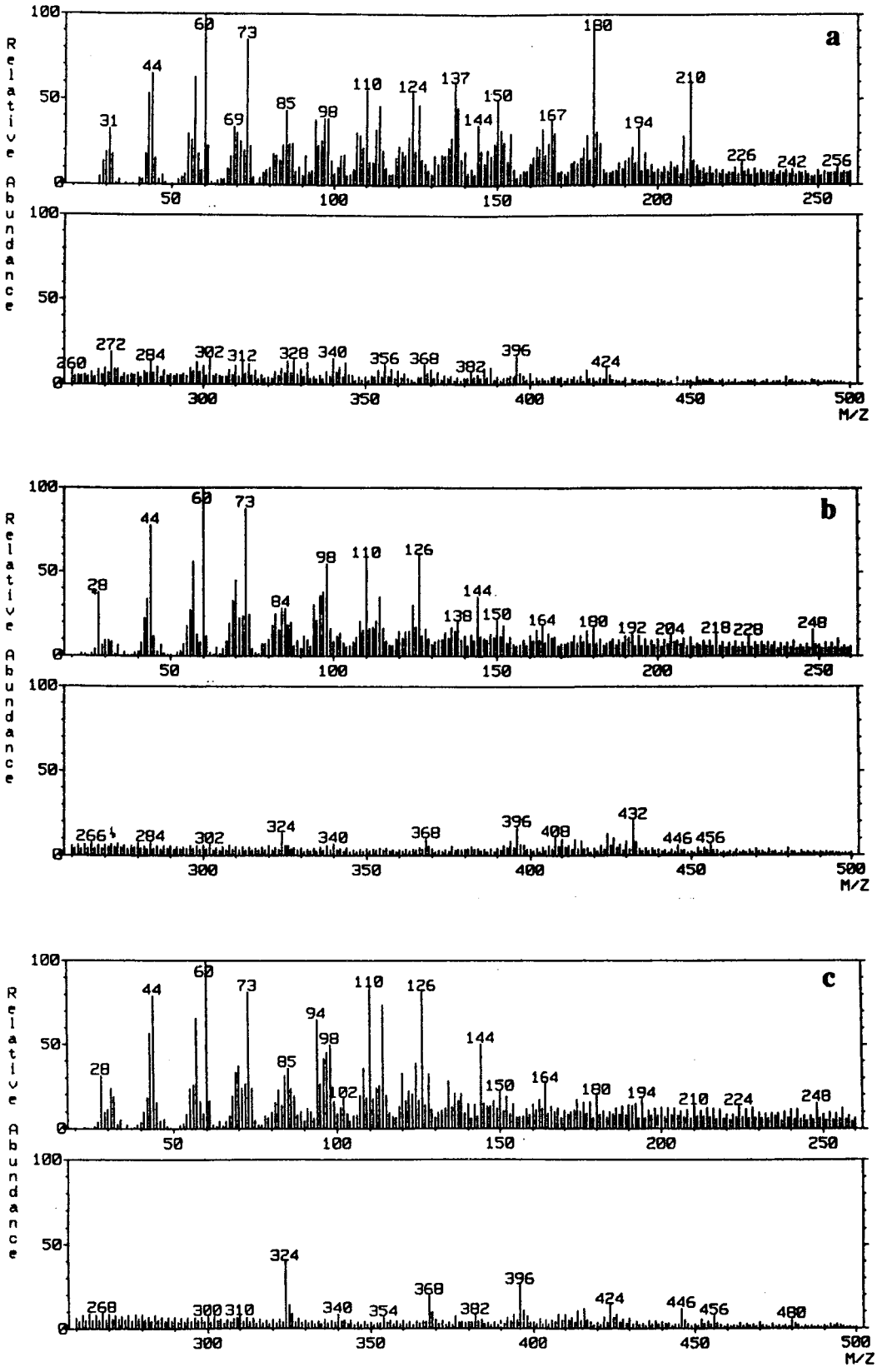

Fig.1. Time-integrated pyrolysis mass spectra of native peat types: *Scheuchzeria* peat (a), light *Sphagnum* peat (Weiss-Torf)(b), and dark *Sphagnum* peat (Schwarztorf) (c)

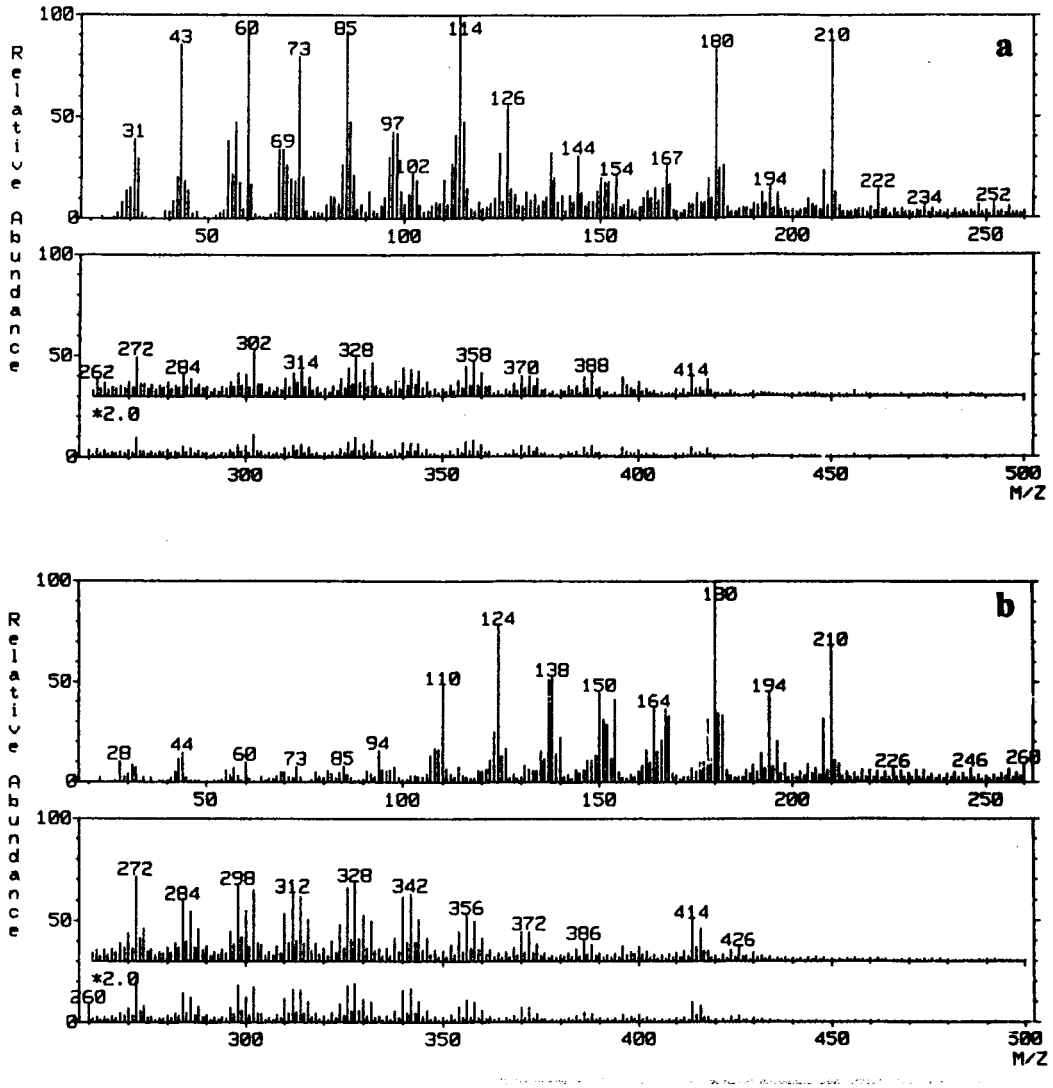

Fig.2. Time integrated pyrolysis mass spectra of fresh *Calluna* wood (a) and peatified *Calluna* wood (b)

mass range a series with masses m/z 592, 620, 648, 676, 704, 732, 760, 788 are assigned to long chain aliphatic wax esters with carbon chain length ranging from C_{40} to C_{54}, which are present in all peat types. Mass peak m/z 324, rather intense in the *Sphagnum* peat samples, is tentatively identified as 2-docosanone and n-tricosane. Mass peaks of sterols and their dehydrated isomers (steradienes) are observed at m/z 414 (C_{29}), 400 (C_{28}), 386 (C_{27}), and m/z 396, 382, 368. The steradienes have relatively high intensities in all peat types. Peaks with m/z 416 and 430, assigned as γ- and α-tocopherol, are detected in all peat types, although of low intensity. In the mass range from m/z 410 to 470, molecular ions of several types of triterpenoids can be observed (Smeerdijk and Boon, 1987). For example taraxerone (M^+ 424), taraxerol (M^+ 426), several compounds with a friedooleane skeleton (M^+ 426 and 428), and an unknown triterpenoid acetate (M^+ 470). A pentacyclic triterpenoid, showing a molecular ion with M^+456 and fragmentation ions at m/z 204, 205, 218 and 248, is tentatively identified as hydroxy-ursenoic acid. This compound appears to be relatively abundant in the *Sphagnum* peats. The mass peak m/z 432 from an unknown compound, is specific for the light *Sphagnum* peat. The identification of the various compounds is subject of further studies with chromatographic separation techniques and GCMS.

Microscopic investigation of the periderm of Ericaceae side roots (1-2 mm thick), showed distinct cell inclusions in these tissues. Periderm material of Ericaceous side roots was isolated from the dark *Sphagnum* peat by micromanipulation, homogenised and immediately analysed by PyMS. The time resolved pyrolysis profile, shown in Fig. 5, can be divided into a thermal extract (1) and a pyrolysate (2). The thermally extracted lipid fraction, obtained by integration between scan 20 and 35 , yields a mass spectrum with many molecular ion peaks which have been observed in Ericaceae roots (Smeerdijk and Boon, 1987). The mass peaks observed are also seen in the spectra of the peats, but in different relative amounts. No peaks for aliphatic wax esters in the mass range from m/z 500-800 could be detected. Therefore, only some of the lipids observed in the peats can be sourced to side root bark material. Results for other peatified plant tissues will be reported elsewhere.

Alkali insoluble fraction

The pyrolysis mass spectra of the peat samples obtained after alkali treatment are shown in Fig 6. The effect of mild alkali treatment is demonstrated by the mass spectra of the potassium-hydroxide extracted *Sphagnum* peats (Fig.6 b,c), showing a very significant decrease in the relative intensity of polysaccharide marker peaks (m/z 57, 60, 73, 112, 114, 126, 144). Solubilisation of polysaccharides is also observed in fresh *Sphagnum* tissues after similar treatment. The mass spectra of non-treated and alkali treated fresh *Sphagnum* tissues, as depicted in Fig. 7b and c, show a significant decrease in intensity of polysaccharide marker peaks in the alkali treated tissues. This points to the presence of loosely bound polysaccharides in the mosses. This polysaccharide fraction appears to be well preserved in the peatified *Sphagnum* tissue (Fig.7a), which may be an indication for the lack of suitable polysaccharidases in this peat forming environment.

In both alkali insoluble *Sphagnum* peat samples (Fig.6 b,c), a preservation of non-methoxylated phenolic compounds can be observed (m/z 94, 108, 110, 120). The

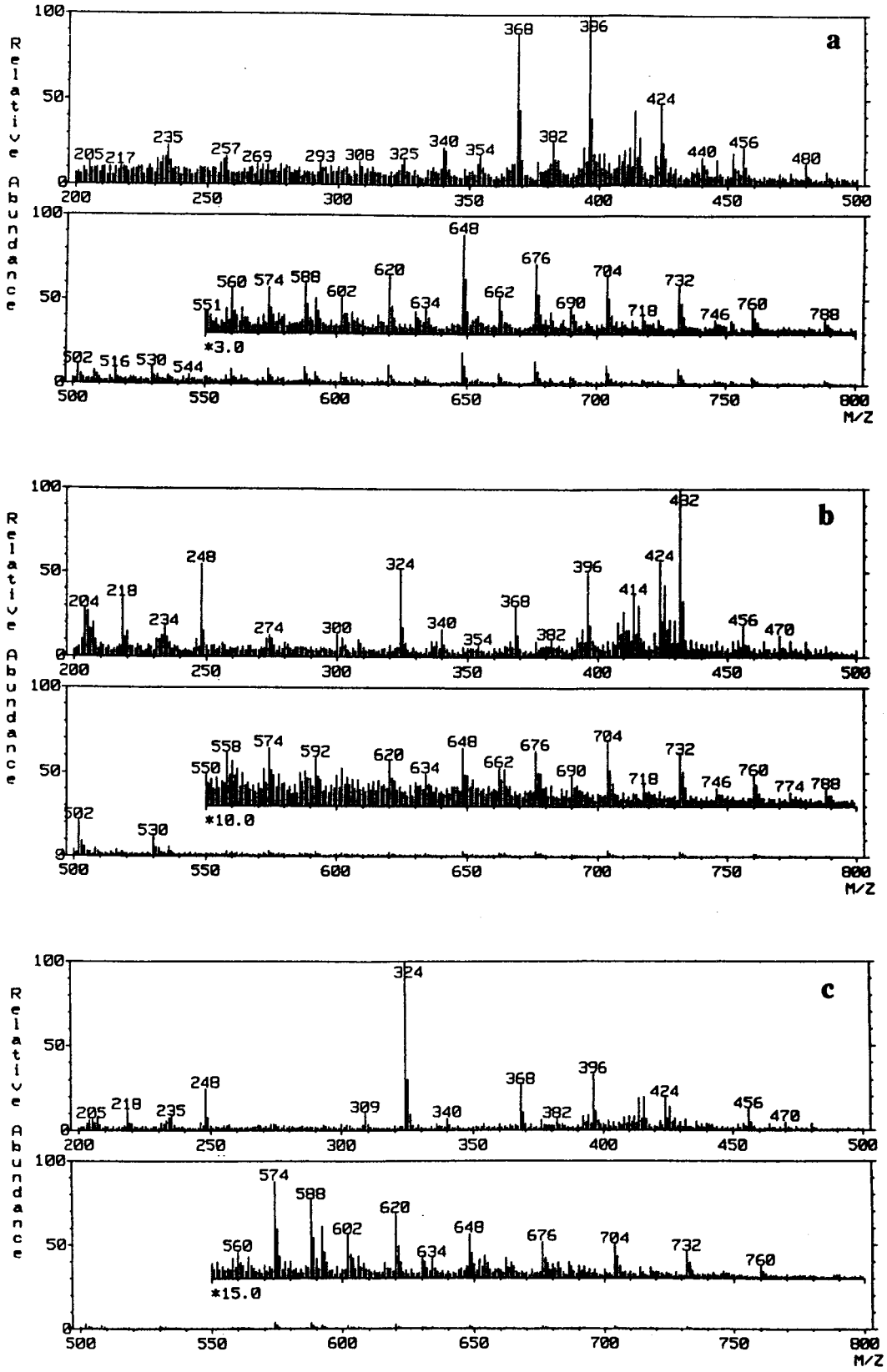

Fig.3. Time-integrated mass spectra of the dichloromethane-soluble lipids: *Scheuchzeria* peat (a), light *Sphagnum* peat (b) and dark *Sphagnum* peat (c).

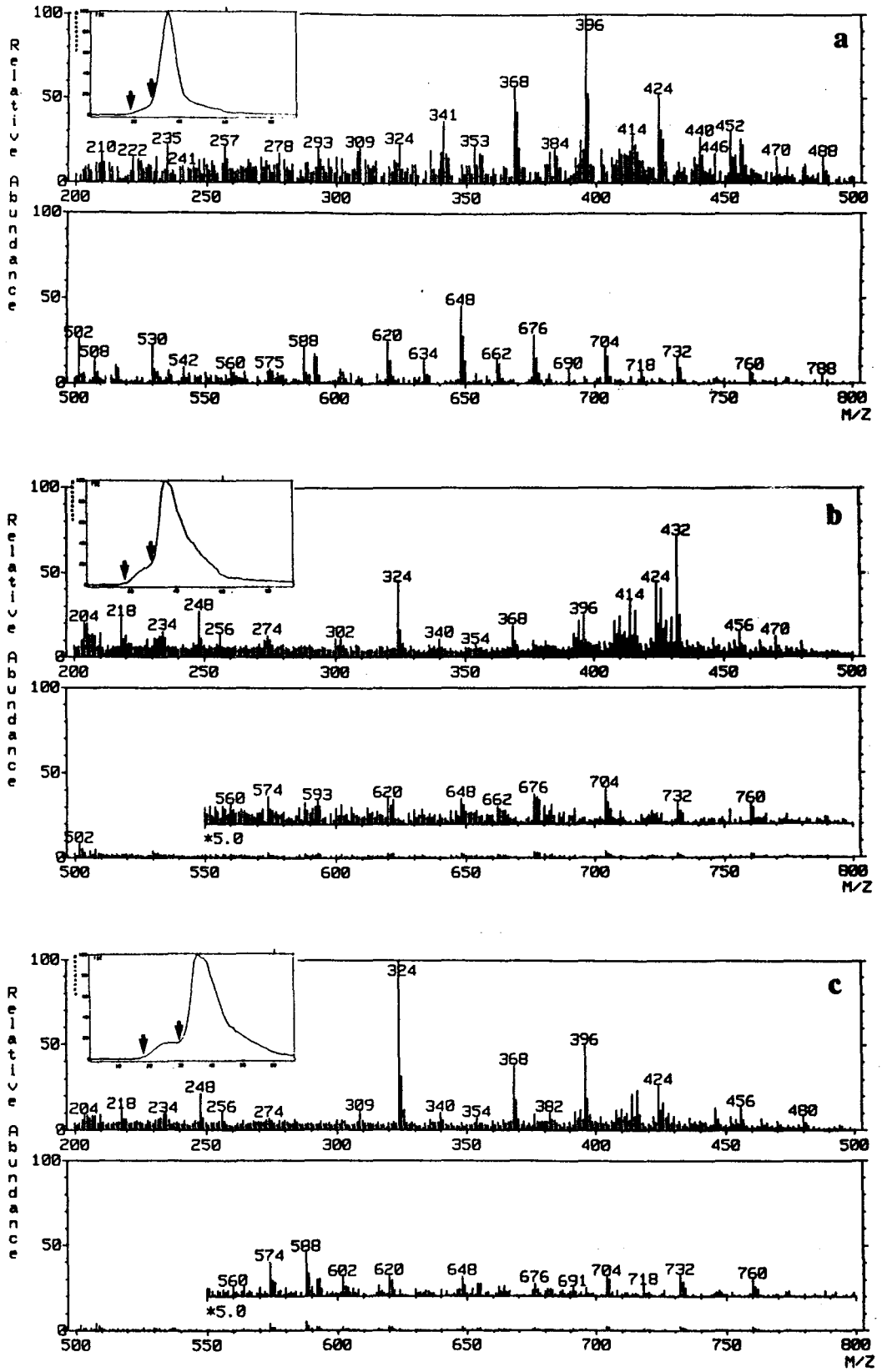

Fig.4. Mass spectra of the thermally extracted lipid fractions, obtained by summing spectra over the range indicated on the inset temperature profile:*Scheuchzeria* peat (a), light *Sphagnum* peat (b), dark *Sphagnum* peat (c) .

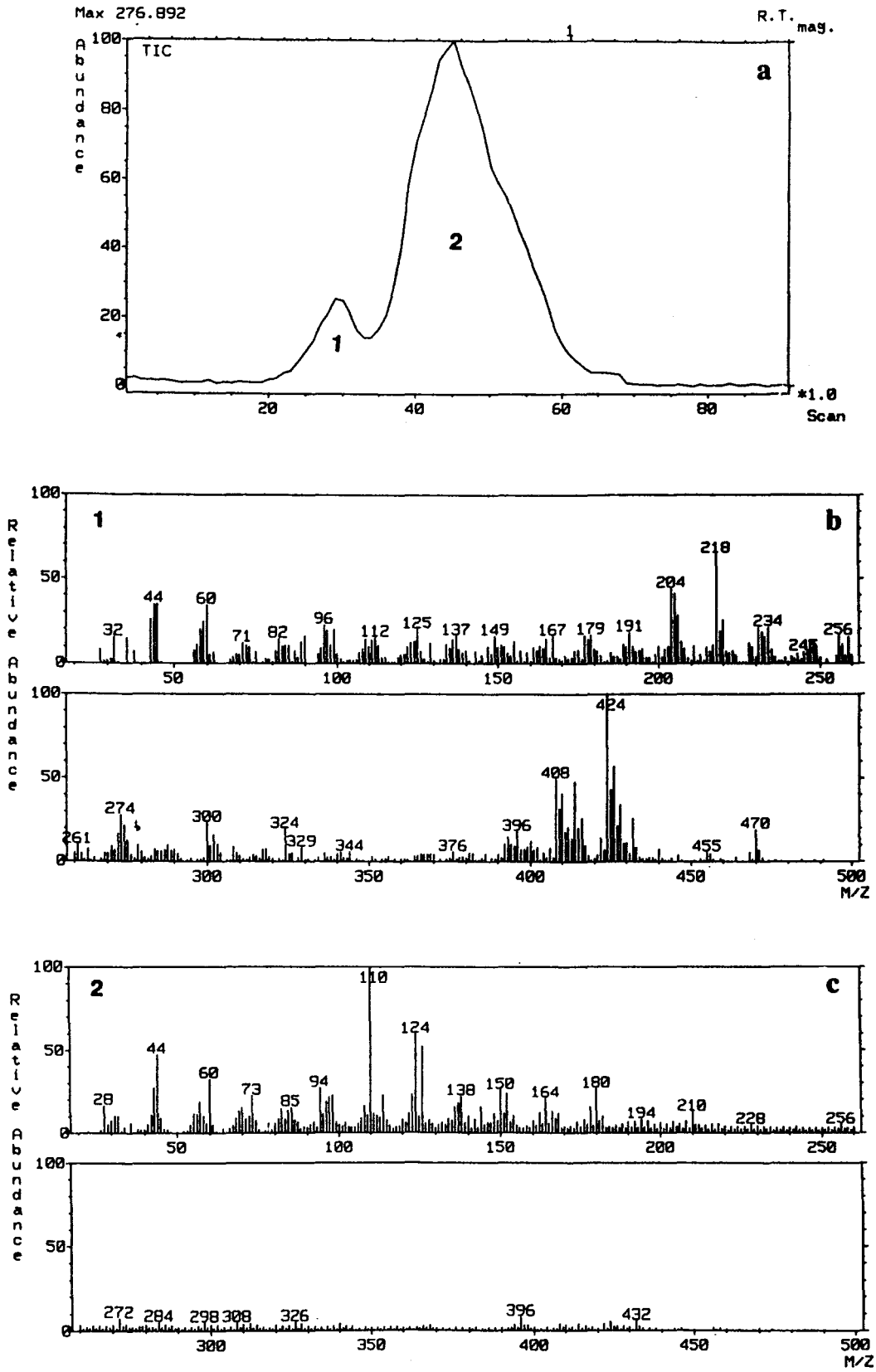

Fig.5.Temperature profile of the periderm of peatified Ericaceae root (a), the thermally extracted lipid fraction (mass spectral data integrated between scan 20 and 35) (b), the peatified polymer fraction (mass spectral data integrated between scan 35 and 70) (c).

predominance and preservation of these compounds can also be seen in the mass spectra of handpicked biodegraded *Sphagnum* stems (Fig.7a) and the alkali treated *Sphagnum* stems (Fig.7c). The nonmethoxylated compounds are probably pyrolytically derived from a resistant polyphenolic molecule grafted on the cell wall polysaccharides. Monomeric lignin marker peaks (m/z 124, 137, 138, 150, 152, 164, 180, 194, 210), are still observed in the *Sphagnum* peats (Fig.6 b,c) although less intense in the dark *Sphagnum* peat.

Even after extraction with dilute alkali, solubilisation of polysaccharides is not evident in the *Scheuchzeria* peat spectrum (Fig.6a), in which a lignin-polysaccharide marker peak pattern is observed similar to the native peat. This points to the presence of a highly protected cell wall skeleton in the original *Scheuchzeria* plants, which is not modified during peatification.

Discussion

The preservation of polysaccharides in organic deposits has been observed by many authors (e.g. Halma et al., 1984; Boon et al., 1986; Smeerdijk & Boon, 1987; Moers, 1989) and has often been ascribed to a number of environmental factors, such as primary production, deposition rate and degree of anoxicity (Moers, 1989). Chemical environmental factors such as high acidity (pH 3) (Given & Dickinson, 1975), minimizing the activity of microorganisms, have been said to be the most important factors in explaining the preservation of compounds in ombrogenous bog deposits.

The selective removal of polysaccharides, as observed in the biodegraded *Calluna* wood, is probably caused by bio-degradative activities of brown rot fungi in the early stages of peat formation. These fungi are able to depolymerize polysaccharides non-enzymatically, leaving a residue of modified lignin (Crawford, 1981; Mulder et al., (in press)). According to Crawford(1981), alterations in the lignin polymeric macromolecule include demethylation of both the guaiacyl and syringyl moiety, as well as an increase in phenolic hydroxyl content and a loss of oxygen functions. Both loss of polysaccharides as well as a shift towards less oxygen containing phenolics in the lignin macromolecule have been observed in peatified wood samples by Hedges et al. (1985), Boon et al.(1986), Saiz Jimenez et al.(1987) and Stout et al.(1988).

The removal of polysaccharides in the *Sphagnum* peats by a mild alkali solution is probably not due to a weakening of the polymeric sugar system on peatification, because identical results are obtained when fresh *Sphagnum* tissues are treated in a similar way. Whether these polysaccharides are preserved in peatified *Sphagnum* tissues remains to be demonstrated. The isolated peatified *Sphagnum* stem shows a polysaccharide rich mass spectrum suggesting that no solubilisation occurs under peatification conditions, even though the alkali soluble polysaccharides are highly sensitive to biodegradation. This is not observed in the peatified plant tissues, which may point to some unknown protection mechanism. Anatomically these tissues also appear rather well preserved. The difference in polysaccharide solubility in mild alkali solutions between *Sphagnum* and *Scheuchzeria* peat might be due to the packaging of the polysaccharides inside lignified cell walls, which prevents enzymatic attack. This protection mechanism does not appear to be active in the *Sphagnum* samples.

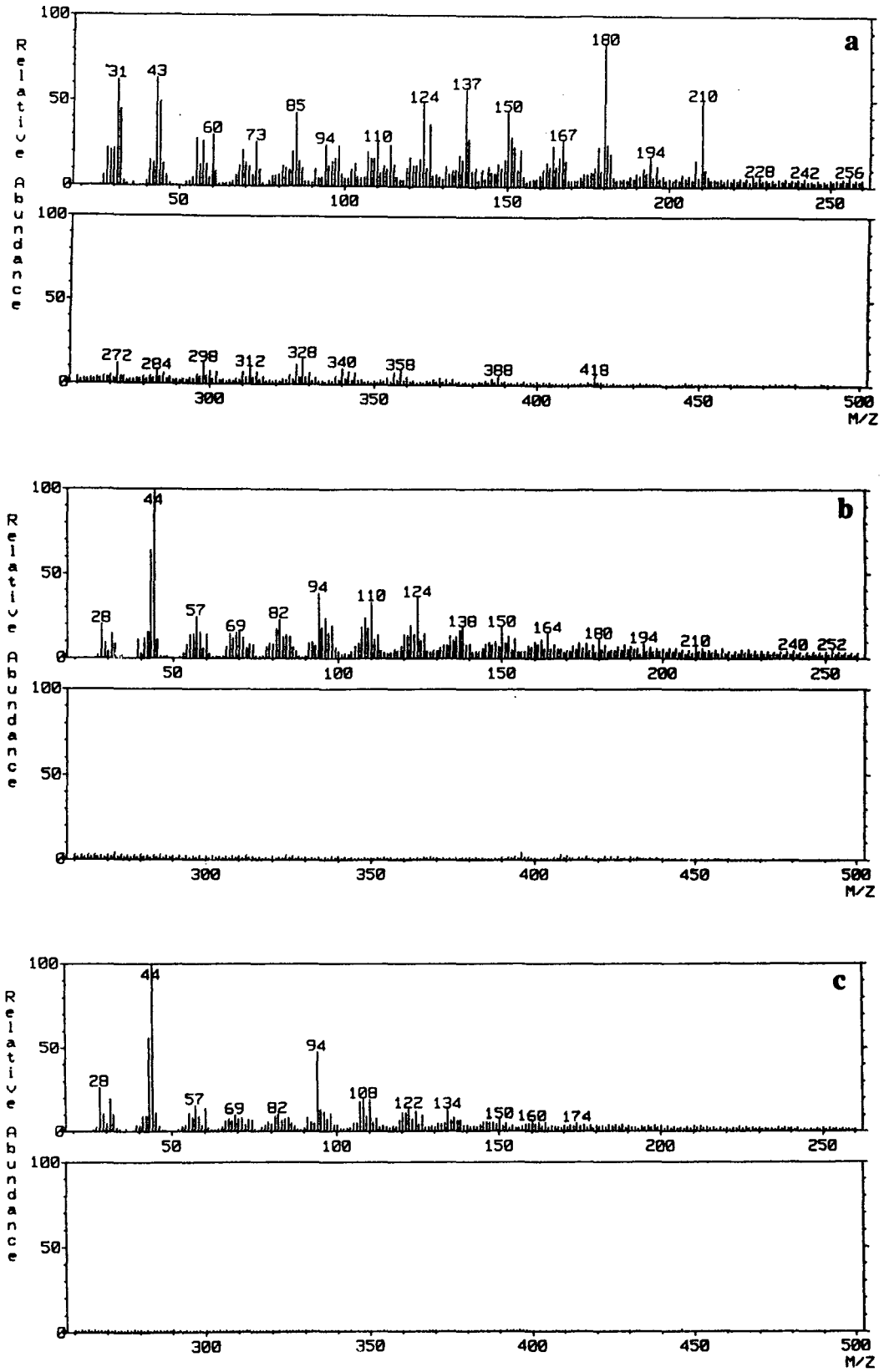

Fig.6. Time integrated pyrolysis mass spectra of alkali insoluble fractions: *Scheuchzeria* peat (a), light *Sphagnum* peat (b), dark *Sphagnum* peat (c).

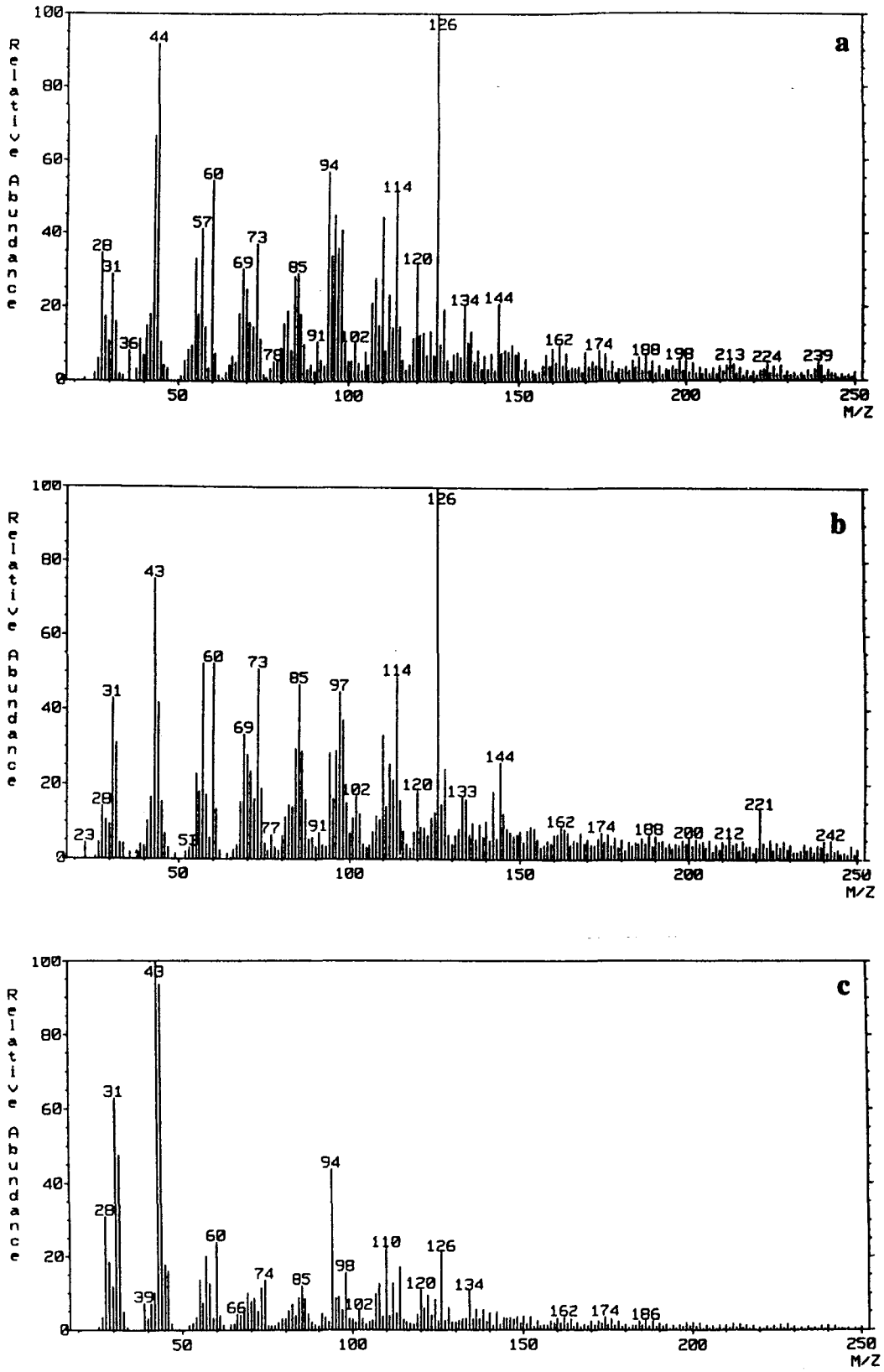

Fig.7. Time integrated pyrolysis mass spectra of handpicked peatified *Sphagnum* stem (a), fresh *Sphagnum* stem (b), alkali treated fresh *Sphagnum* stem (c).

Despite the fact that lignin is not present in the cell walls of *Sphagnum*, mass peaks of methoxylated phenolics are observed in the *Sphagnum* peats. These lignin compounds almost certainly originate from intermixed lignin rich material such as Ericaceous roots and *Eriophorum* stems.

Periderm material of Ericaceae roots, handpicked from the dark *Sphagnum* peat, showed a lipid fraction somewhat similar to the fraction isolated from the *Sphagnum* peat mixture. The fact that no lipid compounds were detected in selected *Sphagnum* tissues, indicates that some of the lipid compounds in the mixed peat originate from intermixed Ericaceous roots, but other sources are to be investigated such as *Eriophorum* and *Calluna* stems. The long chain wax esters, detected in the three peats, were not present in the selected plant parts investigated so far. The origin of these wax esters is still obscure, but one of the possible sources might be the cell walls of pollen, which can be found in rather high concentrations in peat deposits (Faegri and Iversen, 1989). The time course of pyrolysis of Ericaceous periderm demonstrates that on line thermal extraction of tissues obtained by microsurgery is a very useful method for the separation of volatile compounds from small samples. Using this method it is possible to characterise lipid fractions on a microscale, and simultaneously to get an insight into the modifications in the cell walls during peatification.

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