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Differential thermal analysis, thermogravimetry and pyrolysis–field ionisation mass spectrometry of soil organic matter in particle-size fractions and bulk soil samples

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Abstract

Differential thermal analysis (DTA), thermogravimetry (TG) and pyrolysis–field ionisation mass spectrometry (Py–FIMS) were compared in investigations of soil organic matter in particle-size fractions and bulk soil samples of two treatments (untreated and farmyard manure) of a 108 year old long-term agricultural experiment. The shapes of the DTA curves and Py–FIMS thermograms showed differences insofar as the latter were less resolved into distinct peaks and reached their maximum values at higher temperatures. The losses of weight obtained by the two methods were found to be strongly correlated. An adaption of the heating rates improved the conformity of the DTA, TG and Py–FIMS results. It is demonstrated that Py–FIMS yields additional information on the molecular chemical composition of soil organic matter by calculating the proportions of different compound classes based on relative abundances of characteristic FI signals. These results are essentially unaffected by different heating rates. Py–FIMS spectra were integrated for temperature ranges where DTA curves show marked reactions. Their evaluation improves the basis for the interpretation of the more common DTA and TG analyses of soil organic matter.

INTRODUCTION

Differential thermal analysis (DTA) and thermogravimetry (TG) provide information on the thermal behaviour of organic matter in soils and do not require expensive equipment. Therefore, these methods have long been used in studies of soil organic matter (SOM) in humic and organo-mineral fractions [1,2], as well as in bulk soil samples [3]. However, the interpretation of the detected thermal reactions with respect to the original substances is limited. Coupling TG with mass spectrometry (MS) may yield some additional information on the products of thermal breakdown, but for

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soil samples, only the detection of molecules of low mass, H_2O, CO_2, have been reported so far [4].

Recently, it has been shown that in-source pyrolysis in combination with field ionisation mass spectrometry (Py–FIMS) is a very promising technique for the characterisation of the molecular building blocks of soil organic matter [5,6], enabling the detection of molecular ions up to $m/z >$ 1400 [7]. In routine Py–FIMS analyses, a heating rate of 1.2 $K\ s^{-1}$ is used, which is approximately seven times higher than the heating rate usually employed for DTA and TG of soil materials (0.17 $K\ s^{-1}$). This may limit the comparability of DTA and TG data with those obtained by Py–FIMS. Different results have been reported on the influence of heating rates on the pyrolysis products registered by mass spectrometry. For amphiphilic acrylic copolymers it has been shown that the heating rate influences the degradation pathway and thus the pyrolysis products liberated [8]. In another study with low rank coals, it was found that the heating rate influenced to some extent the relative abundances of the FI signals [9]. On the other hand, a comparison of three different vacuum pyrolysis mass spectrometry techniques (pyrolysis–field ionisation mass spectrometry, thermogravimetry–low-voltage electron ionisation mass spectrometry and curie-point pyrolysis–low-voltage electron ionisation mass spectrometry) of a standard coal sample revealed that the distribution and type of primary pyrolysis products were largely independent of different heating rates over a wide range from 10^{-2} to 10^4 $K\ s^{-1}$ [10].

Therefore it seems appropriate to compare DTA, TG and Py–FIMS in soil organic matter studies in order to evaluate the possible influences of experimental conditions, e.g. heating rate, pressure and amount of sample, on the comparability of the data obtained, and to expand the molecular chemical basis for the interpretation of DTA and TG results.

Points of particular interest in this study are listed here.

(i) To determine similarities and dissimilarities in the DTA curves and the Py–FIMS thermograms obtained by plotting the total ion intensity versus the pyrolysis temperature, and in the weight losses measured directly by TG and calculated from Py–FIMS data, respectively.

(ii) To investigate the influence of different heating rates on the Py–FIMS thermograms and on the organic soil constituents detected.

(iii) To evaluate compound classes that produce characteristic thermal reactions which cause the main differences between different organo-mineral particle-size fractions and contrasting management practices.

EXPERIMENTAL

Materials

Soil samples from two treatments (U, unfertilised since 1878 and FYM, farmyard manure spread annually) of the Ewiger Roggenbau experiment

TABLE 1

Characteristics of the samples

	Treatment	Size fractions						
		fmc	cc	fs	ms	cs	sand	bss
% of soil (d.w.)	U	3.9	4.5	4.2	5.5	9.6	71.6	
	FYM	3.4	4.8	5.1	5.6	10.3	70.0	
C content (%)	U	4.78	5.24	5.82	3.36	0.54	0.34	1.24
	FYM	6.30	6.49	9.26	7.19	1.08	0.57	2.09
C/N ratios	U	9.4	7.9	14.9	20.7	15.4	21.2	15.13
	FYM	8.3	8.0	13.1	16.1	17.4	23.8	13.8
Dominant minerals [a]		I, ML, S	I, Q, F	Q, M, F	Q, F, M	Q	Q	

[a] I, illites; ML, mixed layers; S, smectites; Q, quartz; M, mica; F, feldspars; bss, bulk soil samples.

("Eternal rye cultivation") in Halle, Germany, were subdivided into organo-mineral particle-size fractions by ultrasonic disaggregation, wet sieving and sedimentation/decantation. The fractionation procedure is described in detail elsewhere [11]. The fractions obtained were fine-clay + medium-clay (< 0.63 μm, fmc), coarse-clay (0.63–2 μm, cc), fine-silt (2–6.3 μm, fs), medium-silt (6.3–20 μm, ms), coarse-silt (20–63 μm, cs) and sand (63–2000 μm). These represent a set of samples different in mineral composition, and in the amount and in quality (C/N ratios) of organic matter (see Table 1).

Pyrolysis–field ionisation mass spectrometry

For Py–FIMS, about 200 μg of the samples were thermally degraded in the ion source of a Finnigan MAT 731 mass spectrometer. All samples were heated in high vacuum from 50 to 750 ° C, routinely at a heating rate of 1.2 K s^{-1}. During the heating phase, about 50 magnetic scans per sample were recorded for the mass range 50–1000 dalton (single spectra). For two samples, the heating rate was reduced to 0.2 K s^{-1} in replicate measurements, whereby 185 and 200 scans, respectively, were registered. The Finnigan MAT data system allowed the integration of the single spectra resulting in summed spectra for selected temperature ranges as well as for the whole run. Thermograms of the total ion intensities were plotted against the pyrolysis temperature. Weight losses were computed from the Py–FIMS data by multiplying the intensities of the recorded ions with their molecular masses. From the obtained weight loss for each scan, weight losses in 100 K increments were calculated. A detailed description of the Py–FIMS methodology is given in ref. 12.

Differential thermal analysis and thermogravimetry

For DTA and TG analysis, about 300 mg of sample were heated continuously from ambient temperature to 1000 ° C at a heating rate of 0.17 K s^{-1} in an atmosphere of air. The DTA, TG and DTG curves were recorded simultaneously using a Q 1500-D derivatograph (MOM, Budapest, Hungary).

RESULTS AND DISCUSSION

Comparison of DTA curves and Py-FIMS thermograms, and weight losses

The DTA curves (Fig. 1) show endothermic (dehydration, dehydroxylation and quartz conversion) and exothermic reactions. The latter originate

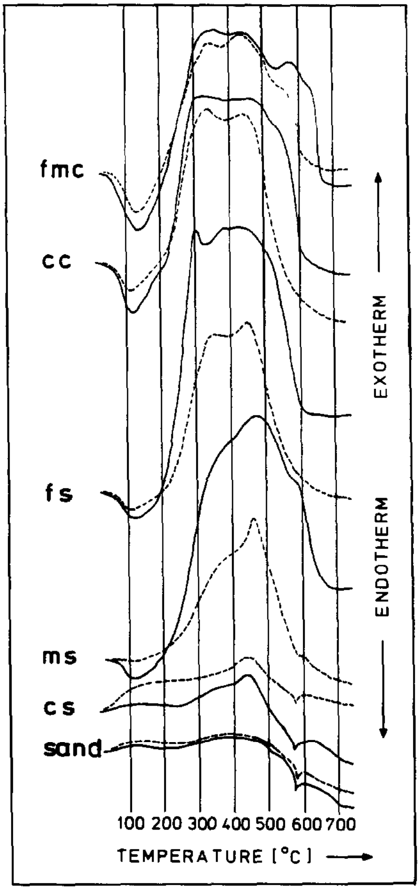

Fig. 1. DTA curves of organo-mineral particle-size fractions from two treatments of the "Ewiger Roggenbau" experiment: — — —, untreated; ———, farmyard manure; fmc = fine-clay + medium-clay, cc = coarse-clay, fs = fine-silt, ms = medium-silt; cs = coarse-silt.

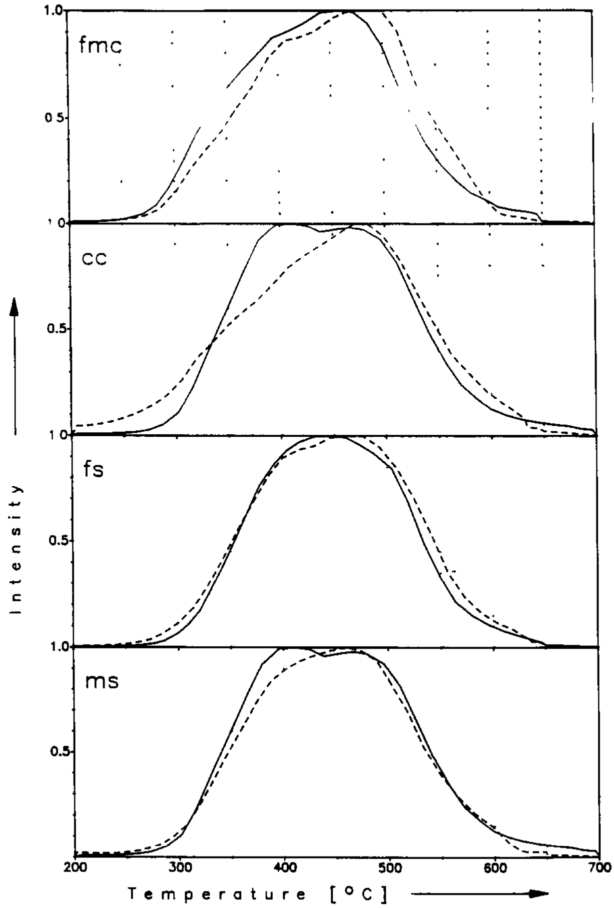

Fig. 2. Thermograms obtained by Py–FIMS of organo-mineral particle-size fractions from two treatments of the "Ewiger Roggenbau" experiment: — — —, untreated, ——— farmyard manure; heating rate 1.2 K s^{-1}.

mainly from the oxidation of organic matter and therefore exhibit remarkable differences between size-fractions and fertilisation treatments. These are (i) generally higher intensities of these reactions in fractions from the FYM treatment; (ii) a very intense reaction at around 580 °C in the fine-clay + medium-clay (FYM); (iii) a sharp exotherm effect at around 300 °C in the fine-silt (FYM); and (iv) in the medium-silt, the relative decrease of the exotherms between 200 and 400 °C compared to 400–500 °C.

The thermograms obtained by Py–FIMS are shown in Fig. 2. Compared with the DTA curves, they are less resolved into distinct reaction steps and reach their maximum values at higher temperatures, between 400 and 500 °C. The most similarities to the DTA curves are shown for fractions from the untreated variant where the two methods have similar distinct

TABLE 2

Thermogravimetry: weight losses of size fractions and bulk soil sample for 100 K increments. The two highest values for each sample are marked $^{+}$ (U) and * (FYM)

Temperature (°C)	Treatment	Size fractions						
		fmc	cc	fs	ms	cs	sand	bss [a]
20–100	U	1.92	2.05	1.60	0.75	0.14	0.06	0.42
	FYM	2.29	2.93	1.60	1.63	0.26	0.06	0.41
100–200	U	5.08^{+}	3.52	1.86	0.74	0.17	0.06	0.22
	FYM	5.48*	3.52	3.31	1.66	0.19	0	0.47
200–300	U	3.29	3.13	2.43	0.87	0.12	0.11	0.76^{+}
	FYM	4.13	4.78*	5.10*	2.47	0.26	0.07	0.67
300–400	U	3.35	3.78^{+}	3.84^{+}	1.84^{+}	0.27^{+}	0.17^{+}	0.75^{+}
	FYM	4.01	4.38	5.12*	3.90*	0.50*	0.25*	1.14*
400–500	U	3.90^{+}	4.24^{+}	3.45^{+}	2.07^{+}	0.41^{+}	0.24^{+}	0.70
	FYM	4.59*	4.52*	4.56	3.54*	0.56*	0.26*	0.91*
500–600	U	3.35	2.16	1.32	0.88	0.20	0.11	0.47
	FYM	3.94	2.77	2.14	2.23	0.28	0.17	0.50
600–700	U	0.57	0.70	0.48	0.34	0.12	0.06	0.14
	FYM	1.00	0.70	0.38	0.50	0.16	0.04	0.15

[a] Bulk soil sample.

reactions in the lower (300–400 °C) and higher (450–500 °C) temperature ranges.

A similar trend was found for the weight losses (Tables 2 and 3). In the

TABLE 3

Pyrolysis–field ionisation mass spectrometry: weight losses of size fractions and bulk soil samples for 100 K increments. The two highest values for each sample are marked $^{+}$ (U) and * (FYM)

Temperature (°C)	Treatment	Size fractions						
		fmc	cc	fs	ms	cs	sand	bss [a]
50–100	U	0.017	0.038	0.002	0.002	0.007	0.003	0.100
	FYM	0.001	0.000	0.000	0	0.000	0	0.003
100–200	U	0.057	0.031	0.004	0.005	0.013	0.003	0.111
	FYM	0.002	0.003	0.000	0.001	0.006	0.000	0.002
200–300	U	0.054	0.091	0.052	0.027	0.087	0.096	0.053
	FYM	0.200	0.010	0.054	0.009	0.060	0.006	0.005
300–400	U	4.161	3.800	3.469	1.453	0.205	0.128	0.681^{+}
	FYM	6.009*	5.351*	4.568	5.376*	0.181	0.283*	0.824*
400–500	U	12.412^{+}	11.033^{+}	7.864^{+}	4.178^{+}	0.626^{+}	0.436^{+}	1.863^{+}
	FYM	15.025*	13.333*	12.349*	8.039*	1.119*	0.517*	2.654*
500–600	U	5.149^{+}	4.589^{+}	3.815^{+}	1.991^{+}	0.497^{+}	0.218^{+}	0
	FYM	4.398	5.096	5.493*	2.731	0.864*	0.064	0.813
600–700	U	0	0	0.148	0.057	0.038	0	0
	FYM	0.201	0.197	0.132	0.024	0.039	0.009	0

[a] Bulk soil sample.

TG analysis the highest losses per 100 K were measured between 300 and 500 ° C. Exceptions observed for the fine-clay + medium-clay fractions, and for the coarse-clay and fine-silt fractions (FYM treatment) can be explained by the contribution due to dehydration, in the case of the clay fractions, and of more thermolabile organic substances, in the case of the FYM treatment. The weight losses calculated from the Py–FIMS data reach their highest values between 300 and 600 ° C. It is remarkable, however, that despite different heating rates the two methods show similar relative enrichment of more thermolabile organic substances due to FYM application in some of the fractions. This is shown by the occurrence of the highest values of weight losses at lower temperatures in the FYM variant, marked (*) in Tables 2 and 3. From these data, in addition, significant correlations were derived between weight losses per 100 K obtained by the two methods, in particular in the range 300–700 ° C.

Influence of heating rate on Py–FIMS

For the fine-clay + medium-clay fractions from the two treatments, the heating rate of the Py–FIMS was reduced to 0.2 K s^{-1} and, thus, was similar to that of the DTA and TG analyses. At this heating rate the peaks in the Py–FIMS thermograms are shifted by approximately 20 K towards lower temperatures. The thermogram of the fine-clay + medium-clay of the untreated variant exhibits four distinct reaction ranges (around 340, 410, 460 and 530 ° C). It strongly resembles the corresponding DTA curve. In addition, the reaction between 400 and 500 ° C in the DTA appears to be subdivided into two distinct processes, as the Py–FIMS thermogram indicates (see Fig. 3 and compare with Figs. 1 and 2). This demonstrates that the heating rate has an influence on the shape of the thermograms obtained from Py–FIMS of soil organic matter. Consequently, the calculated weight losses were somewhat changed, so that a better agreement with the weight losses determined directly by TG is achieved. This is because the derived regression functions are more close to $y = x$ when the heating rates of the two analyses are similar. A visual comparison of the spectra of the fine-clay + medium-clay fractions recorded at different heating rates (not shown here) indicates a good agreement of the relative abundances of FI signals.

The composition of the organic matter of these and of the bulk soil samples was calculated on the basis of characteristic mass signals [5,13,14]. There are: for phenolics, m/z 94, 108, 110; for lignin monomers, m/z 124, 138, 150, 152, 164, 166, 178, 180, 182, 196, 208, 212; for lignin dimers, m/z 246, 260, 270, 272, 274, 284, 286, 296, 298, 300, 302, 310, 312, 314, 316, 326, 328, 330, 332, 358, 418; for mono- and polysaccharides, m/z 82, 84, 96, 98, 112, 114, 126, 128, 132, 144, 162; for fatty acids, m/z 340, 368, 396, 424, 452, 480, 508; and for alkanes/alkenes, m/z 154, 156, 184, 224, 226, 238,

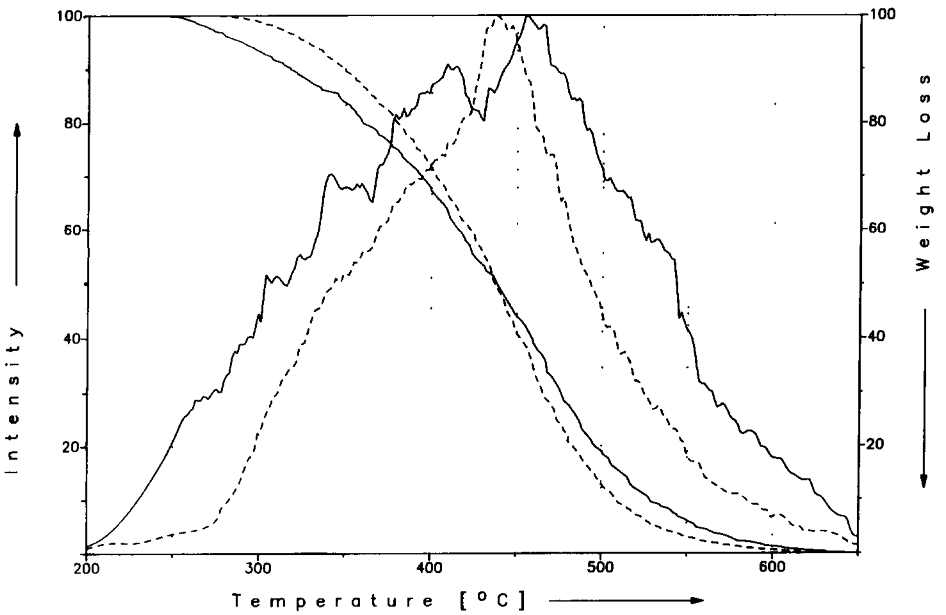

Fig. 3. Thermograms obtained by Py–FIMS of the fine-clay + medium-clay fractions from two treatments of the "Ewiger Roggenbau" experiment recorded at a lowered heating rate of 0.2 K s^{-1}: — — —, untreated; ———, farmyard manure.

240. Among the nitrogenous compounds present, nitriles, *m/z* 69, 71, 91, 103, 119, 147, amino-N/amides, *m/z* 59, 87, 93, 97, 113, 121, 135, 167, 185, and heterocycles, *m/z* 67, 79, 81, 95, 107, 109, 111, 123, 129, 131, 145, 153, 157, 159, 161, 171, 173, 175, 189, 203, were distinguished. A satisfying agreement between the relative amounts of the compound classes is obtained for the fine-clay + medium-clay sample of the untreated variant. Larger differences were found for lignin dimers, mono- and polysaccharides and heterocyclic nitrogen compounds in the FYM fine-clay + medium-clay (see Table 4). In addition to the influence of the different heating rates, an incomplete signal assignment cannot be excluded for this very complex organic material. In general, despite the discussed discrepancies, the spectra recorded at the different heating rates give the same indication of the composition of the samples and of the principal changes due to soil management. In summarising these facts and the above-mentioned correlations between weight losses obtained by TG and Py–FIMS, it is established that the pyrolysis products registered do indeed reflect the organic matter status of the samples, which is an essential prerequisite for the following interpretations.

Detection of molecular subunits by Py–FIMS

The mass spectra of the bulk soil samples are shown in Fig. 4. They demonstrate clearly that additional information is obtained by Py–FIMS,

TABLE 4

Composition of the organic matter in the bulk soil samples and in the fine-clay + medium-clay fractions (fmc) evaluated from Py–FIMS data (% of the total ion intensity calculated according to the ref. 15) and influence of different heating rates on the results obtained

Class of compound	Untreated (U)			Farmyard manure (FYM)		
	soil [a]	fmc [a]	fmc [b]	soil [a]	fmc [a]	fmc [b]
Aromatics						
Phenolics	12.8	8.4	7.3	4.8	4.3	6.9
Lignin momomers	7.8	4.2	2.0	1.6	3.8	4.1
Lignin dimers	4.6	1.0	0.1	10.1	6.7	1.6
Aliphatics						
Alkanes/alkenes	3.1	0.4	1.0	1.7	1.2	1.4
Fatty acids	0.1	0	0	1.0	0.3	0
Mono- and polysaccharides	17.1	18.1	18.4	9.1	14.0	19.2
Nitrogen compounds						
Nitriles	1.4	3.4	3.6	1.5	1.8	1.8
Amino-*N*/amides	4.1	5.0	5.7	3.3	6.8	9.9
Heterocycles	13.6	15.0	18.6	9.1	9.2	14.9

[a] Spectra recorded at a heating rate of 1.2 K s^{-1}.

[b] Spectra recorded at a heating rate of 0.2 K s^{-1}.

which points to considerable differences in the molecular composition of organic matter due to the contrasting soil management. The sample from the FYM treatment yields far more signals, in particular in the higher mass range. The spectra and the evaluation of the compound classes (see above for the characteristic mass signals) indicate that the sample from the FYM treatment is enriched in lignin dimers and bound lipids such as fatty acids. The sample from the untreated soil shows more intense signals characteristic of phenolics, lignin monomers, mono- and polysaccharides and heterocyclic nitrogen compounds (see Fig. 4 and Table 4). These trends were also found in a previous study [15] for the fine-clay + medium-clay, and for the remaining size-fractions.

The integrated spectra in temperature ranges with marked DTA effects and peaks in the Py–FIMS thermograms of the fine-clay + medium-clay fractions, are shown in Figs. 5a–5c and 6a–6c. Characteristic molecules detected in all spectra are the pyrolysis products of mono- and polysaccharides, nitrogen compounds, C_4–C_8 alkanes and alkenes, and lignin decomposition products. In the spectrum of the "untreated" sample in Fig. 5a, signals related to mono- and polysaccharides predominate. Nitrogen compounds and lignin-derived molecular ions are less abundant. In the temperature range 450–470 ° C, nitrogen-containing molecules predominate, assigned, in particular, to heterocyclic nitrogen compounds such as pyrrole (*m/z* 67), pyridine (*m/z* 79), methylpyrrole (*m/z* 81) and others. In addition, the greater number of pyrolysis products from lignin is observed

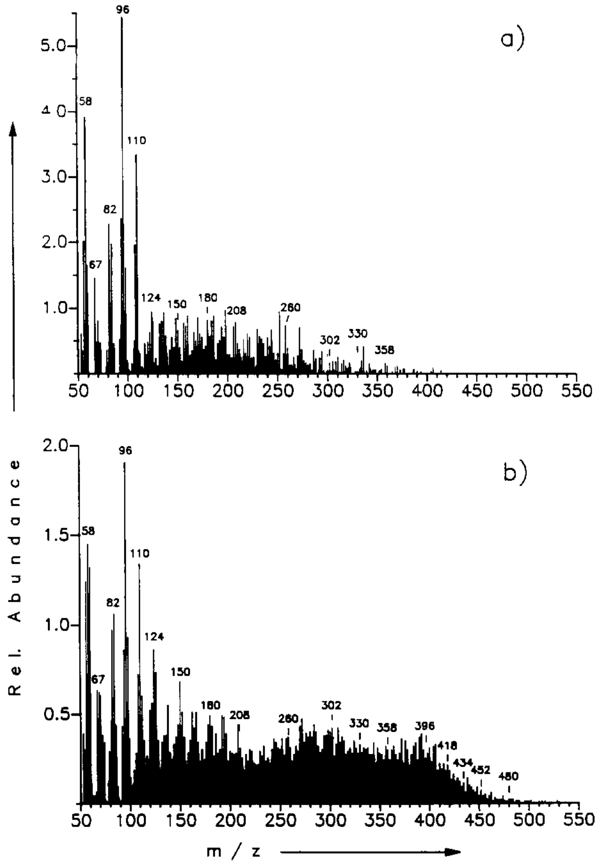

Fig. 4. Summed Py–FI mass spectra of the bulk soil samples from the untreated (a) and the farmyard manure plot (b) of the "Ewiger Roggenbau" experiment.

at this temperature, e.g. syringylethane (*m/z* 182), syringylpropene (*m/z* 1984) and sinapylaldehyde (*m/z* 208) (Fig. 5b). This is also true for the range 530–540 °C. Some signals, e.g. *m/z* 142, 154, 168, 182, 184, 252, can be tentatively assigned to alkanes and alkenes (Fig. 5c). For the spectra of the FYM sample, in general, the same trends in the relative abundances of compounds at the various temperatures are observed. It is noticeable that among the nitrogen compounds, nitriles and amino-*N*/amides appear to be favoured. The strong signal at *m/z* 113 in Fig. 6b is assigned to aminomethylfuran, which has been found to contribute to a large extent to the differences between the size-fractions due to the farmyard manure application [15]. The pyrolysis products of lignin are detected over a wider mass range, in particular in the spectra at higher temperatures, where lignin dimers appear at $m/z > 246$. This indicates that the lignins are less decomposed microbially in the FYM treatment sample. Thus, the above-mentioned changes in the organic matter quality of this sample are con-

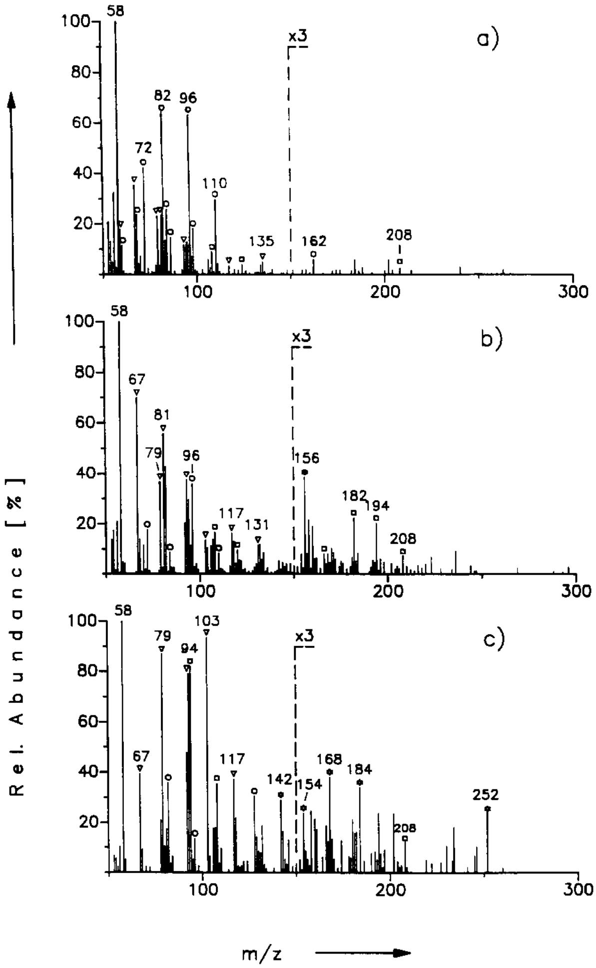

Fig. 5. Integrated Py–FI mass spectra of the fine-clay + medium-clay fraction from the untreated plot: a, 336–360 ° C; b, 452–467 ° C; c, 527–543 ° C; ○, mono and polysaccharides; ▽, N-compound; □, lignin fragments; ☆, alkanes, alkenes, fatty acids.

firmed. The signal patterns in Fig. 6b and c indicate the occurrence of homologous series of long chained alkanes/alkenes, partly up to C_{30}.

In previous DTA and TG studies of soil organic matter, lower temperature reactions have often been attributed to the decomposition of aliphatics, e.g. cellulose, and those at higher temperatures to the thermal breakdown of aromatics [2–4]. Our results, obtained by the direct detection of molecular ions of the pyrolysates, demonstrate that aliphatics such as long chained hydrocarbons and nitrogen compounds also contribute to the thermoreactions above 400 ° C (Figs. 5b and 5c, and 6b and 6c). It is suggested that the thermal stability of these compounds results from their incorporation into a stable "network" of differently linked organic

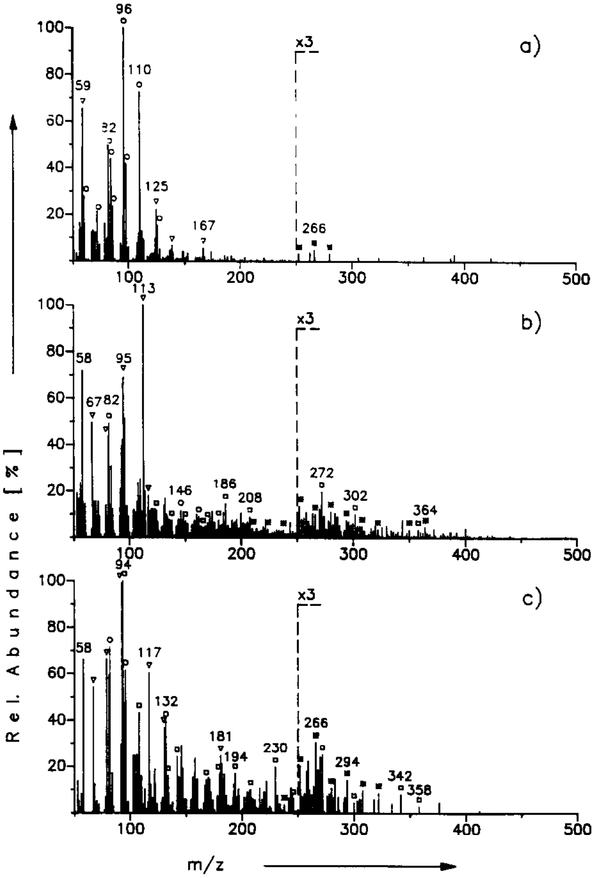

Fig. 6. Integrated Py–FI mass spectra of the fine-clay + medium-clay fraction from the farmyard manure plot: a, 338–347 ° C; b, 425–447 ° C; c, 526–543 ° C. For details see Fig. 5.

molecules and from strong associations with the minerals, probably partly in interlayer spaces.

CONCLUSIONS

The comparison of DTA, TG and Py–FIMS show that differences in the results obtained are caused by the different sample properties measured, namely heat flux (DTA) versus volatilisation and generation of molecules during heating (Py–FIMS), and weight loss of organic and mineral matter (TG) versus the summed weight of the detected molecular ions (Py–FIMS). Different experimental conditions, e.g. heating rates, pressure and amount of sample, may also contribute to disagreement between results. The adaption of the heating rates improves the comparability of the thermograms and weight losses obtained by the two methods. From the strong correlations between the weight losses measured directly by TG and those calculated from the FI signals, it is concluded that the volatiles and the pyrolysis products registered by Py–FIMS are representative of the organic matter originally present in the samples. The results obtained from the integrated spectra enable an improved interpretation of the DTA and TG investigations of sample sets of this and other field experiments. As an example, on the basis of spectra at 300 ° C (recorded at nearly the same heating rate as the DTA, not shown here) it is very probable that the strong DTA peak of the fine-silt sample in Fig. 1 is due to mono- and polysaccharides, which originate from less decomposed plant material.

Despite some differences in the shapes of the curves and in the weight losses, DTA, TG and Py–FIMS indicate the same changes in soil organic matter due to management, in particular, the enrichment of more thermolabile organic substances in the samples of the FYM plot, which appear to be largely attributed to mono- and polysaccharides as indicated by the integrated spectra in the lower temperature ranges. In addition, this variant contains more organic matter which is also liberated at higher temperatures. These are decomposition products of lignin, nitrogen compounds and probable long-chained alkanes/alkenes. It is concluded that these components, cross-linked with each other and strongly associated with the mineral matrix, represent a very stable part of the soil organic matter. Their appearence in the untreated soil, which has been cultivated intensively without any fertilisation for more than 100 years, implies a considerable resistance to biodegradation.

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