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Kinetic study of the thermal degradation of lake aquatic humic matter by thermogravimetric analysis

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Abstract

Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) of different lake aquatic humic-solute fractions were investigated under atmospheric temperature and pressure. The samples were subjected for the destruction of organic matter within the 105–600°C range at a rate of 5°C/min. For each different humic-solute fraction, four-to-five partially overlapping thermal degradation stages were obtained from the shapes of the TG curves. A first-order approximation was applied to estimate the energy of activation for different multi-step degradation stages. A powerful reaction took place at 370–500°C for every acidic humic-solute fraction which indicated the decomposition of a very stable structural 'nucleus' with relatively strong bond energies. The results of TG-DTA demonstrate that the combination of the four diverse humic-solute pieces, isolated/fractionated by the XAD-technique in strongly acidic conditions, consisted of structural subunits the behaviour of which resembled that of the bulk of humic solutes isolated by the DEAE procedure. Apart from this, the diverse humic-solute fractions do not occur wholly independently in the bulk but are, to some extent, aggregated via different bondings. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermal analysis; Simultaneous TG-DTA; Aquatic humic substances; Biopolymers; Compositional elucidation

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1. Introduction

Thermal degradation techniques, such as thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA), have been applied for many years to elucidate structural features of decayed natural heterogeneous organic matter [1–6]. In view of the relatively low concentration of natural dissolved organic carbon (DOC), the aquatic humic matter must first be concentrated and isolated from other organic non-humic solutes for further studies. At present, the most frequently applied procedures for concentrating and fractionating aquatic humic matter (humic substances) at pre-adjusted acidity based on artificial 'hydrophobic' and 'hydrophilic' properties of organic solutes are the column chromatographic methods by non-ionic solids [7,8] (such as XAD resins or analogues). The fact that aquatic humic solutes possess an acidic character has been utilized for isolation of the bulk of humic solutes in one step from a freshwater sample without any pH adjustment. The most popular medium for this purpose [9–13] has been the DEAE cellulose, which is a weak anion exchanger with tertiary amine functional groups ($-OC_2H_4N(C_2H_5)_2$) bound to a hydrophilic matrix.

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Analytical pyrolysis has been proved to be a powerful tool in studying complex organic biomaterials. The structures of humic substances have been effectively studied by trying to identify the pyrolytically formed molecular fragments, most often by means of special mass spectrometric methods (e.g. [14–21]) either connecting the pyroprobe directly to the ion source of a mass spectrometer, or in combination with a gas chromatograph. The outcome of flash pyrolysis in a vacuum [21] pointed out clearly that various lake aquatic humic solutes isolated with different methods qualitatively contain the same structural subunits.

Until recently, few fundamental comparative thermogravimetric studies have been performed on biomaterials, such as humic substances or fossilized plants, recent or mature sediments, etc. It has been reported [22,23] that the onset of thermal evolution and the mass losses of soil organic matter by pyrolysis-field ionization mass spectrometry based on the resulting degradation fragments were in good agreement with the final outcome of TG and DTA data. Although the data obtained by the simultaneous TG-DTA are somewhat limited, the technique leads, without any complicated mathematical manipulations, to transition temperatures and mass changes in the materials.

The objective of the present study was to specify by simultaneous TG-DTA in atmospheric temperature and pressure the compositional similarity of different aquatic humic-solute fractions. The XAD technique at pre-adjusted acidity, extended with a given anion exchanger, and the DEAE procedure at original acidity of the water sample were applied parallel to the same lake-water sample for isolating different kinds of humic-solute fractions. Thermal analysis curves (TG, DTG, and DTA) and heat fluxes furnished important information for the patchwork in setting up the structural composition for an average heterogeneous humic-solute molecule.

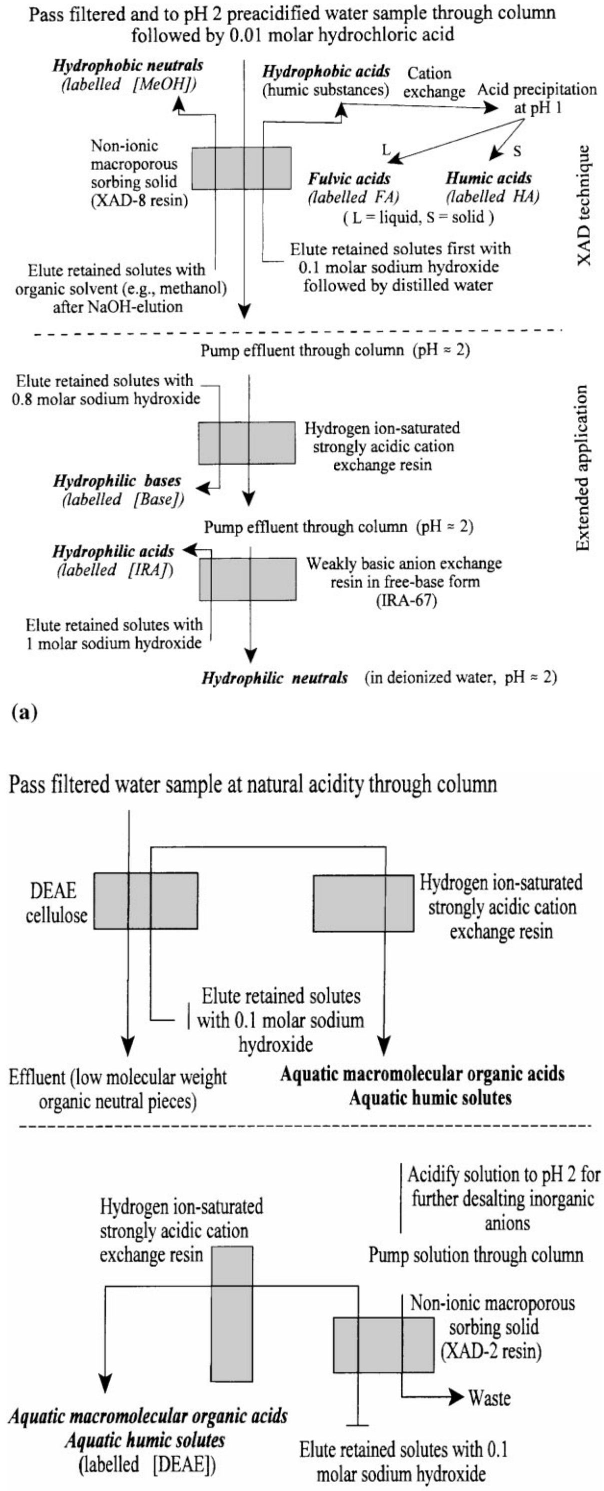
2. Experimental

2.1. Materials

Natural humic freshwater samples were collected from two lakes: Lake Savojärvi (S, SS), situated in a marshy region in southwestern Finland; and Lake Mekkojärvi (M1-M4), a small, forest-lake situated in the Evo district of Lammi in southern Finland. The aquatic Nordic humic and fulvic acids (No.HA and No.FA), used as commercial standards, were isolated with the XAD technique from the runoff water of a Norwegian mire. The basic characteristic properties determined and the pre-treatments carried out for the samples of a highly brown water were reported previously [12]. Different kinds of humic-solute fractions were isolated from the filtered freshwater samples (S, SS, M1, M2, M3 and M4) by two different chromatographic methods. The analytical flow chart of the XAD technique, including its multi-stage application (XAD resin→cation exchanger→anion exchanger; connected in sequence) and the DEAE procedure have been described in detail [12,13,24]. It is notable that the aquatic humic solutes (aquatic macromolecular acids) isolated by the DEAE procedure were not divided at pH 1 into distinct HA- and FA-type acids. The analytical procedures applied for isolation and fractionation of the DOC are shown in Scheme 1(a and b).

2.2. Thermal analysis

For the TG and DTA analyses, about 4 mg of sample were heated continuously from 20° to 600°C in an atmosphere of air (gas flow 100 $cm^3 min^{-1}$). Thermal analysis curves of the TG, DTG and DTA were recorded simultaneously using *SDT 2960 Simultaneous TG-DTA analyzer* (TA Instruments). The furnace was calibrated by using transition temperatures of indium and aluminium (156.6° and 660.4°C, respectively). The samples were dried in a desiccator before the measurements. The heating rate was 2°C min^{-1} from room temperature to 105°C for eliminating the residual moisture and the major part of the bound water, and then 5°C min^{-1} up to 600°C for destroying the organic matter and, finally, determining the ash content. The heating rate of 5°C min^{-1} was chosen for optimum conditions on the basis of experiments carried out on soil humic matter [25], since at slower rates the sensitivity is greatly reduced and at higher rates the reactions overlap to some extent and heat transfer (DTA effect) is reduced. Platinum crucibles were used and pure, dry pre-heated Al_2O_3 was used as an inert reference material in the reference crucible. To make the thermal



Scheme 1. (a) An analytical procedure for classification of the DOC at preadjusted acidity into ‘hydrophobic’ and ‘hydrophilic’ fractions. (b) Isolation procedure for aquatic organic macromolecular acids (aquatic humic solutes) by the DEAE cellulose.

properties of sample and reference more comparable, the sample was slightly diluted with the reference. The heat of combustion of different humic-solute fractions was measured by means of a adiabatic bomb calorimeter, *Gallenkamp CB-110*, using benzoic acid as reference.

3. Results and discussion

3.1. Quantities of different humic fractions

Retention [13] of organic solutes of the water sample SS at pH 2 from the DOC, according to Scheme 1(a), was as follows: SS.FA (49%), SS.HA (9%), SS.[MeOH] (4%), SS.[Base] (6%) and SS.[IRA] (20%). The DEAE procedure (Scheme 1(b)) retained 80% from the DOC as acidic humic solutes. Thus, the bulk of acidic organic solutes retained onto the DEAE cellulose at the natural acidity consisted of practically the same quantity of organic acids (82%) as given by the XAD technique at pH 2 for the diverse acidic humic-solute fractions of SS.FA, SS.HA, SS.[MeOH] and SS.[IRA].

3.2. Thermoanalytical data measured for different humic-solute fractions

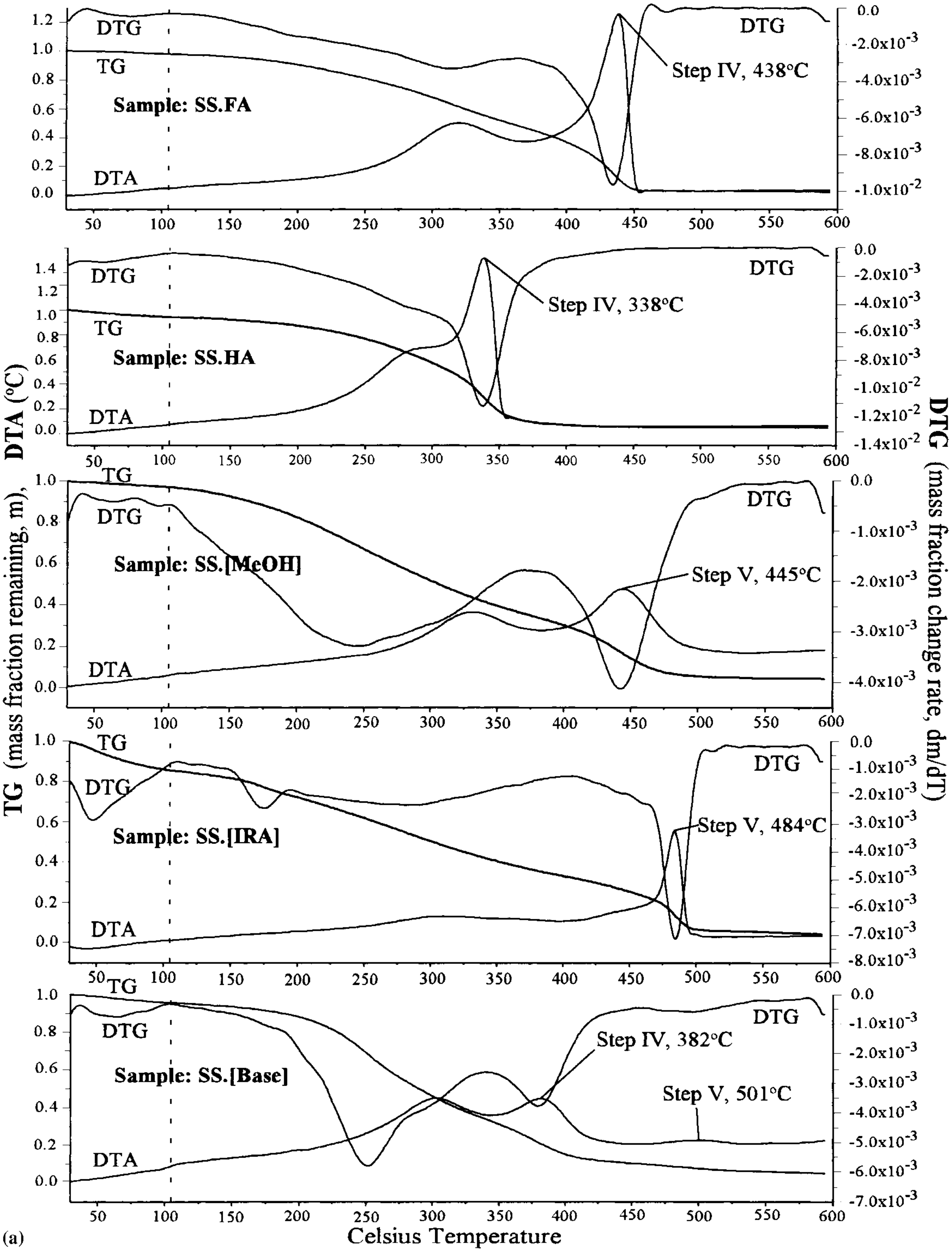
Fig. 1(a and b) illustrate thermal analysis curves (TG, DTG, and DTA; all normalized to the sample mass) recorded for different aquatic humic solutes. The TG curves of S.HA and SS.HA were practically similar (average correlation and variability 0.999 and 7%, respectively) within the 105–350°C range. Likewise, the thermal degradation of S.FA and SS.FA greatly resembled each other within the 105–450°C range (average correlation and variability 0.997 and 14%, respectively). Therefore, the thermal analysis curves were presented merely for the SS water sample. Correspondingly, the TG curves recorded for HA-fractions, isolated from the water samples M1-M4, conformed to each other (average correlation and variability 0.999 and 3%, respectively) within the 105–450°C range. The same tendency prevailed also with FA-fractions isolated from the M1-M4 samples (average correlation and variability 0.998 and 10%, respectively). For this reason, only mean shapes of TG curves for $M_{(1-4)}$.FA and $M_{(1-4)}$.HA are inspected. To sum up, the shapes of TG curves obtained for all FA-fractions isolated from the seven freshwater samples (S, SS, $M_{(1-4)}$ and No) closely resembled each other within the 105-450°C range (average correlation and variability 0.999 and 4%, respectively). A similar tendency of TG curves was also found for the HA-fractions isolated from the samples $M_{(1-4)}$ and No (average correlation and variability 0.999 and 3%, respectively) but not in the case of HA-fractions isolated from the samples S and SS (the end-point of pyrolysis was ca. 100°C lower from other HA-fractions and average variability 46%). The similarity stated above implies the remarkable finding that seasonal variation is presumably of minor importance on the primary structural composition of humic solutes even if the composition of certain characteristic humic-subfractions varies with different natural conditions [26].

The kinetic parameters from the mass loss vs. temperature data can be derived by one of several techniques or modifications thereof [27,28]. In this work, the calculation of kinetic quantities for the approximate thermal degradation reactions of solid humic-solute fractions ($A_{(s)}$) to gaseous components ($B_{(g)}$), $A_{(s)} \rightarrow B_{(g)}$, was based on the mathematical interpretations (1) and (2) derived by Horowitz and Metzger [29] and Broido [30], respectively. However, the actual situation is more complex because the substances under investigation are mixtures of several organic compounds (heterogeneous humic solutes) whose compositions or reactions are undefined. It has been stated [31] that heterogeneous reactions are not activated processes (with no activation energy) and that the only rate-controlling process is heat exchange between the reacting mass and its surroundings. The main aim of this study, however, was to study similarities/dissimilarities between different humic-solute fractions and estimate activation energies on the basis of first-order rate-controlling processes without mathematical descriptions [28,31,32] of different reaction mechanisms by multi-dimensional kinetic equations:

$$\ln\ln(y) = (E_a\Theta)/(RT_s^2) \tag{1}$$

$$\ln\ln(y) = -E_a/(RT) + \text{const} \tag{2}$$

where y is equal to $(W_0 - W_f)/(W - W_f)$, W being the weight remaining at a given temperature, W_0 and W_f



(a)

Fig. 1. (a) Thermal analysis curves for different humic-solute fractions in air. (b) Thermal analysis curves for different humic-solute fractions in air.

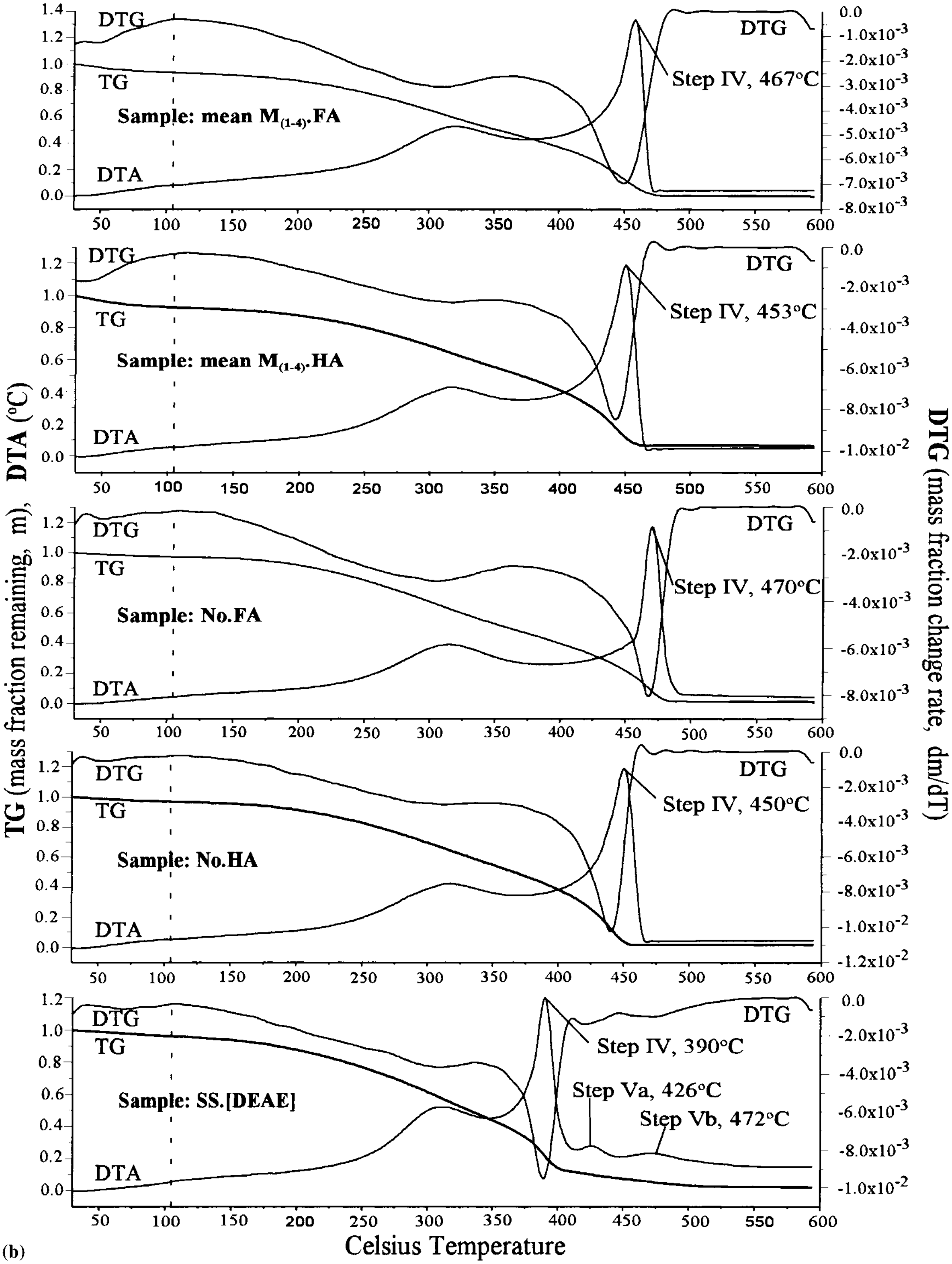


Fig. 1. (Continued)

the initial and final weights, respectively, E_a the activation energy, R the ideal gas constant (8.314 JK^{-1} mol^{-1}) and T_s (inflexion point) being defined as a reference temperature, where $1/y=1/e$ (e=2.718) and $T=T_s+\Theta$. A plot of the $\ln \ln(y)$ against Θ and $1/T$ should give straight lines whose slopes are related to the activation energies.

For every humic-solute fraction, reasonably good straight lines (the correlations of the graphical plots of Horowitz–Metzger and Broido were ca. 0.98) were obtained from which the activation energies for different temperature stages were computed (by the method of least squares). Thus, the first-order approximation for the thermal degradation of humic solutes studied is valid. It has been stated [27,33] that the Horowitz–Metzger approach will generate somewhat greater values for kinetic quantities as compared to other methods. Similarly, the activation energies obtained by the Horowitz–Metzger method were ca. 6% greater than those obtained by the method of Broido. For this reason, the mean values of these two methods were selected for the evaluation of the activation energies.

Once the water has been removed (105°C), the destruction of the organic material begins (Fig. 1(a and b)). The thermal degradation occurred in several partially overlapping temperature stages. For each humic-solute fraction, four-to-five separate thermal reaction steps were observed based on the DTG curves. The ignition temperatures of humic solutes were obtained from the DTA curves at onset temperatures. The mean information obtained from the TG, DTG and DTA curves for the different humic-solute fractions is presented in Table 1.

3.3. *TG curves related to bulk-compositional differences*

TG curves of 'hydrophobic' FA- and HA-samples in Fig. 1(a and b) point out that the primary structural composition of FAs is slightly more resistant against thermal degradation than that of the HAs. According to DTG peaks (Table 1), the sharpest changes of the mass losses take place at the end of thermal degradations for FAs at temperatures of 456±4°C and for HAs at 452±3°C and at 342°C. The increased stability obtained for FAs as compared to that of HAs agreed with the earlier results obtained by flash pyrolysis in a vacuum [21] and by CuO-oxidations [34,35]. On the contrary, it has been concluded [36,37] that the structure of the FAs is less stable against thermal stress under time-programmed heating in a vacuum than that of the HAs. Furthermore, it is generally believed [38–40] that light-induced structural degradation is more powerful for aquatic dissolved humic solutes of lower molecular weights, such as fictional FAs, than for fictional HAs with larger molecular sizes indicating more permanent structural composition of the latter. Actually, differences of thermal degradations obtained for different FAs and HAs studied were relatively minor and, therefore, it is difficult to draw solid conclusions about structural stability of FAs over HAs. The only drastic exception was met in the case of Lake Savojärvi (samples S and SS). The isolated HA-type fractions were now destroyed at much lower temperatures than their FA-homologues, indicating, at least in this case, an extremely unstable (e.g. loosely bound) structural combination of the fictional HA-solutes.

Table 1 indicates that the thermal degradation of the 'hydrophobic' FA- and HA-type solutes, isolated by the XAD resin at pH 2 from several lake water samples, took place, in any case, at four different reaction steps (I–IV) with different reactivities within temperature ranges of ca. (I) 105–223, (II) 223–378, (III) 378–439 and (IV) 439–465°C. The ignition of the FA-HA-type samples occurred at ca. 222. It is difficult to mark the limits for the end-point of the total water losses evaporated from bio-organic materials, but apparently a temperature stated close to 160°C agrees with the observations of this study [41,42]. The first reaction step (I) of thermal degradation, therefore, evidently consists of the evaporation of residual water in addition to small molecular organic pieces. Reactions, at lower temperatures (below ca. 370°C), of FA- and HA-type solutes in air have been often attributed to the elimination and decomposition of aliphatics (including cellulose) and functional groups (decarboxylation) [3,4], and those at higher temperatures (above ca. 400°C) to the thermal breakdown of aromatics ('nuclei'). It has been found [3] that phenolic groups of FA- and HA-type substances are more heat-resistant than carboxylic groups, but both are, at all events, eliminated below ca. 400°C. Furthermore, these two main functional groups in the FA-type soil humic substances have proved to be more heat-resistant than those in the HA. It has been also found [43] that

Table 1
Mean values of some kinetic quantities at different reaction steps obtained for different lake aquatic humic-solute fractions under atmospheric conditions

Fraction/Method	Ignition point in °C	DTG peaks in °C	DTA peaks/(°C)	Reaction step/(°C)	T_s/(°C)	E_a/(kJ mol^{-1})
S–SS–M$_{(1-4)}$–No.FA	220±1			I 105–(220±1)	197±1	72±2
S–SS–M$_{(1-4)}$–No.FA		313±1	318±1	II (220±1)–(364±2)	315±1	84±2
S–SS–M$_{(1-4)}$–No.FA		429±4	449±4	III (364±2)–(444±5)	422±4	197±13
S–SS–M$_{(1-4)}$–No.FA		456±4	462±5	IV (444±5)–(471±5)	459±4	620±42
M$_{(1-4)}$–No.HA	225±2			I 105–(226±2)	202±2	67±1
M$_{(1-4)}$–No.HA		316±2	316±2	II (226±2)–(392±4)	339±4	76±1
M$_{(1-4)}$–No.HA		429±4	429±4	III (392±4)–(433±4)	421±4	357±20
M$_{(1-4)}$–No.HA		452±3	452±3	IV (433±4)–(458±3)	448±3	623±25
S–SS.HA	211			I 105–211	189	68
S–SS.HA		288	291	II 211–305	281	121
S–SS.HA		312	318	III 305–335	326	302
S–SS.HA		342	345	IV 335–351	344	491
SS.[DEAE]	236			I 105–236	209	69
SS.[DEAE]		312	310	II 236–355	315	97
SS.[DEAE]		365	372	III 355–378	371	517
SS.[DEAE]		394	390	IV 378–400	392	630
SS.[DEAE]		420,474	426,472	Va,b 406–486	453	193
SS.[IRA]	220			I.a 105–157	141	100
SS.[IRA]		175		I.b 157–220	196	100
SS.[IRA]		288	305	II 220–340	294	84
SS.[IRA]		365	374	III 340–430	394	137
SS.[IRA]		443,461	438	IV 430–476	463	337
SS.[IRA]		480	484	V 476–494	487	906
SS.[MeOH]	206			I 105–206	182	77
SS.[MeOH]		246	332	II 206–342	286	71
SS.[MeOH]				III 342–394	374	216
SS.[MeOH]				IV 394–430	419	378
SS.[MeOH]		442	445	V 430–460	448	476
SS.[Base]	206			I 105–206	186	71
SS.[Base]		251,294	301	II 206–303	266	110
SS.[Base]				III 303–360	338	179
SS.[Base]		380	382	IV 360–395	382	367
SS.[Base]		495	501	V 430–537	493	167

Note: S and SS, water samples from Lake Savojärvi (1988 and 1994, respectively); M$_{(1-4)}$, water samples from Lake Mekkojärvi (1988, 1988, 1989 and 1990, respectively); No, water sample from a Norwegian mire. For abbreviations of different humic-solute fractions see Scheme 1(a and b).

ionization of carboxylic and, especially, phenolic groups leads to increased thermal stability of humic solutes. It has been recently demonstrated [22] that aliphatics, especially such as long-chain hydrocarbons and nitrogen compounds, also contribute to some of the thermal reactions above ca. 400°C.

It is clear from the foregoing that thermal reactions of humic-solute fractions can be expected to be extremely complicated. The kinetic quantities of reaction steps I and II for FA- and HA-type isolates were quite comparable with each other, thereby indicating structural similarity for the mass loss taking place at lower temperatures. However, the E_a of the reaction step III (intermediate stage between lower and higher degradation temperatures and appearing as shoulders in the DTG and DTA curves) was almost twofold for HA- in comparison to that of the FA-fraction, indicating a less stable structural composition for these particular parts of carbon skeletons of FAs. This supports the finding [21] that the carbon skeleton of the FAs breaks down slightly more strongly immediately at the beginning of flash pyrolysis in a vacuum under thermal impulse, than that of the HAs. The higher content [13,44] (ca. 1.3-fold) of phenolic groups in HA- compared to that in FA-fractions studied may, in some degree, contribute to the above property, and explain the finding that the bulk of FAs contain somewhat lesser stable separate structural subunits than the HAs even if the overall stability of FAs is somewhat greater. The rate of the degradation was definitely faster at the final temperature stage IV (ca. 440–550°C) for both FA- and HA-fractions than at the lower temperatures. In the same way, the activation energies of reaction steps IV were ca. two-to-ninefold compared to those at lower temperature stages (I–III), indicating that much more energy was required to exceed the bond dissociation energies for the transformation of the solid FA- and HA-reactants to gaseous products. Only in the case of Lake Savojärvi (S-SS), the E_a obtained for IV.FAs was noticeably greater than that for IV.HAs, establishing that, at least in this distinct case, the overall structural stability of FAs is much stronger than its HA-homologues. The aromaticity [12,24] in all FA-fractions studied was definitely smaller than in HA-fractions. Therefore, the higher content of aromaticity alone is not the only implication about the greater activation energy and stronger stability. After all, a common property for both, FAs and HAs, is that plenty of energy is required to break the structure of their organic subunits at the high-temperature stages (IV, above ca. 400°C), and when this high amount of energy is reached a very rapid degradation follows, indicating the existence of a highly stable structural 'nucleus' with strong bond energies.

Table 1 shows the kinetic quantities for different humic solutes isolated from the SS water sample at natural acidity in one step by anion exchanger, [DEAE], and from the effluent (pH 2) of the XAD-resin, firstly by the cation exchanger ('hydrophilic' bases, [Base]) and secondly by the anion exchanger ('hydrophilic' acids, [IRA]); moreover, the residuals extracted by methanol from the XAD-resin ('hydrophobic' neutrals, [MeOH]) are also given. According to Scheme 1(b), the SS.[DEAE]-fraction is essential for representing the combined bulk of different acidic humic solutes. The TG curves imply that the character of the thermal degradation of SS.[DEAE] is placed roughly between that of SS.FA and SS.HA. A more detailed critical examination points out that the intermediate reaction step III for SS.[DEAE] was more powerful (e.g. the E_a was ca. twofold) than that obtained for SS.FA or SS.HA. On the other hand, the E_a of the reaction step IV computed for SS.[DEAE] was fairly analogous with those of SS.FA and SS.HA. It is notable that the thermal degradation of SS.[DEAE], in addition to reaction step IV, opposite to SS.FA and SS.HA, produced two more decomposition steps within the temperature stage 406–486°C (reaction steps Va and Vb, DTG peaks at 420° and 474°C).

It has been stated previously [13,24], based on non-degradation studies, that the structural composition of acidic humic solutes obtained by the DEAE isolation procedure appears to be a given combination of the various 'hydrophobic' and 'hydrophilic' acidic solutes obtained at pH 2 by the multi-stage XAD technique (i.e. SS.[DEAE]≈SS.FA+SS.HA+SS.[MeOH]+SS.[IRA]). Also, the results obtained from CuO-oxidation studies [35] support this statement. Fig. 1(a and b) indicate that the thermal analysis curves of SS.[DEAE] indeed contain some signs of the above special 'hydrophobic' and 'hydrophilic' separate humic solutes (i.e. DTA peaks of SS.[DEAE] at 426° and 472°C compared with those of SS.[MeOH] and SS.[IRA] at 445° and 484°C, respectively) indicating their potential occurrence, as contributory factors, in the isolated humic-solute mixture of SS.[DEAE]. The TG curve estimated for the combined SS.FA–SS.HA–SS.[IRA]–SS.[MeOH] mixture, weighted by their proportions [13], was almost symmetrical at lower temperatures (<370°C) with the authentic TG curve measured for SS.[DEAE] (correlation 0.99, average variability ca. 3%). However, at higher temperatures (>370°C), the similarities between the calculated and authentic TG curves were considerably weaker (correlation 0.87, average variability ca. 41% for the combined TG). Evidently, the contributions of these individual humic-solute pieces at higher temperature ranges is overestimated by calculating the combined TG curve for the hypothetical mixture. A reasonable explanation is that the four acidic humic-solute pieces fractionated by the multi-stage XAD technique do not behave wholly independently in their isolated bulk mixture (i.e. in the SS.[DEAE]-fraction), but are more or less aggregated (cross-linked) via chemical bondings which lower the thermal barrier of decomposition. This aggregated nature does not come definitely into view by comparison tests based solely on non-degradational methods [13,24].

The thermal degradation of the 'hydrophilic' SS.[IRA]-fraction was a case of its own. The degradation proceeded at first at a relatively slow, constant speed and with a low activation energy, until a very sharp and powerful decomposition with extremely high activation energy took place at ca. 470°C. This small molecular weight SS.[IRA]-fraction was the most acidic [13] (ca. 9 meq/g) of all, and the content of aliphatics [24] was exceptionally high (ca. 42%). Presumably, the fairly stretched 'core' of the SS.[IRA]-fraction consists of an uncomplicated integrated entity with very few cross-linkings to other 'cores'. In contrast, the thermal degradations of the 'hydrophilic neutral' SS.[MeOH]- and, especially, 'hydrophilic base' SS.[Base]-fractions proceeded from the beginning to the end with relatively slow, constant speed and with low activation energies without any drastic changes in mass losses, indicating loosely bound structural combinations and almost a total absence of stretched 'cores'. As a slight exception, SS.[MeOH]-fraction indicated a tendency towards high activation reactions at high temperatures (ca. 400–500°C). Nevertheless, the content [24] of aromatics (ca. 14%) of the slightly acidic, small-molecular weight SS.[MeOH]-fraction was the smallest and that of aliphatics (ca. 52%) the greatest of all, thus affording an opportunity for aliphatics to contribute to the thermal reactions above 400°C. The nitrogen content [13] of the SS.[Base]-fraction was the greatest (> or $\sim$4%) and, hence, some organic nitrogen compounds may contribute to the minor thermal reactions occurring at ca. 500°C.

3.4. Heat fluxes of degradation reactions evaluated from the DTA curves

It has been stated in the literature [28] that there is a relationship between the 'active area' of a DTA curve and the heat evolved. For evaluating the heat fluxes evolved at different temperature stages during thermal degradation of different humic-solute fractions, a relationship between the heat flux and the area of DTA was estimated. The heats of transitions of lead, indium, silver and aluminium at their transition temperatures (23.1/327.5, 28.6/156.6, 104.4/961.9 and 400.1/660.4 $\mathrm{J g^{-1}/^{\circ}C}$, respectively) were applied for this purpose. A linear relationship was obtained with a correlation of 0.999:

$$y = -0.00406 + 0.20609x \qquad (3)$$

where y is the heat flux (J/mg of sample) and x the integrated area of the DTA curve (area/mg of sample).

Fig. 2(a) shows the calorimetric heats evolved by the combustion of different humic-solute fractions at constant volume in an atmosphere of oxygen. A reasonable correlation (0.85, average variability ca. 13%) was obtained between the heat fluxes of different humic-solute fractions calculated from the integrated areas of DTA curves (thermal degradation range, 105–550°C) and measured by a bomb calorimeter. Fig. 2(b) shows the distribution of heat evolved at different temperature stages (based on DTA curves) during the progress of thermal degradation of different humic solutes.

The heat of combustion (Fig. 2(a)) of HAs was regularly somewhat greater (ca. 12%) than that obtained for FAs. According to Fig. 2(b), the heat liberated at high temperatures (ca. 370–550°C, decomposition of 'aromatic nuclei') in the case of HAs was significantly greater (ca. 1.2-fold) than that obtained for FAs. This was in good accordance with the fact that the content of aromatics was also greater (ca. 1.2-fold) in HAs than FAs [12,24]. The heat liberated at lower temperature stages was, by contrast, practically the same for both, HAs and FAs. According to the heat fluxes obtained from DTA curves at different temperature stages, the differences between the FA- and HA-type humic fractions were minor.

The profile of the heat fluxes obtained (Fig. 2(b)) for SS.[DEAE] at different temperature stages was, however, totally different from those of SS.FA and SS.HA. The most indicative difference was that the degradation of structural subfractions of SS.[DEAE] at high temperatures (>370°C) took place at three different temperature stages (Fig. 1(b)): the main decomposition at DTA (1) 390°C (reaction step IV)

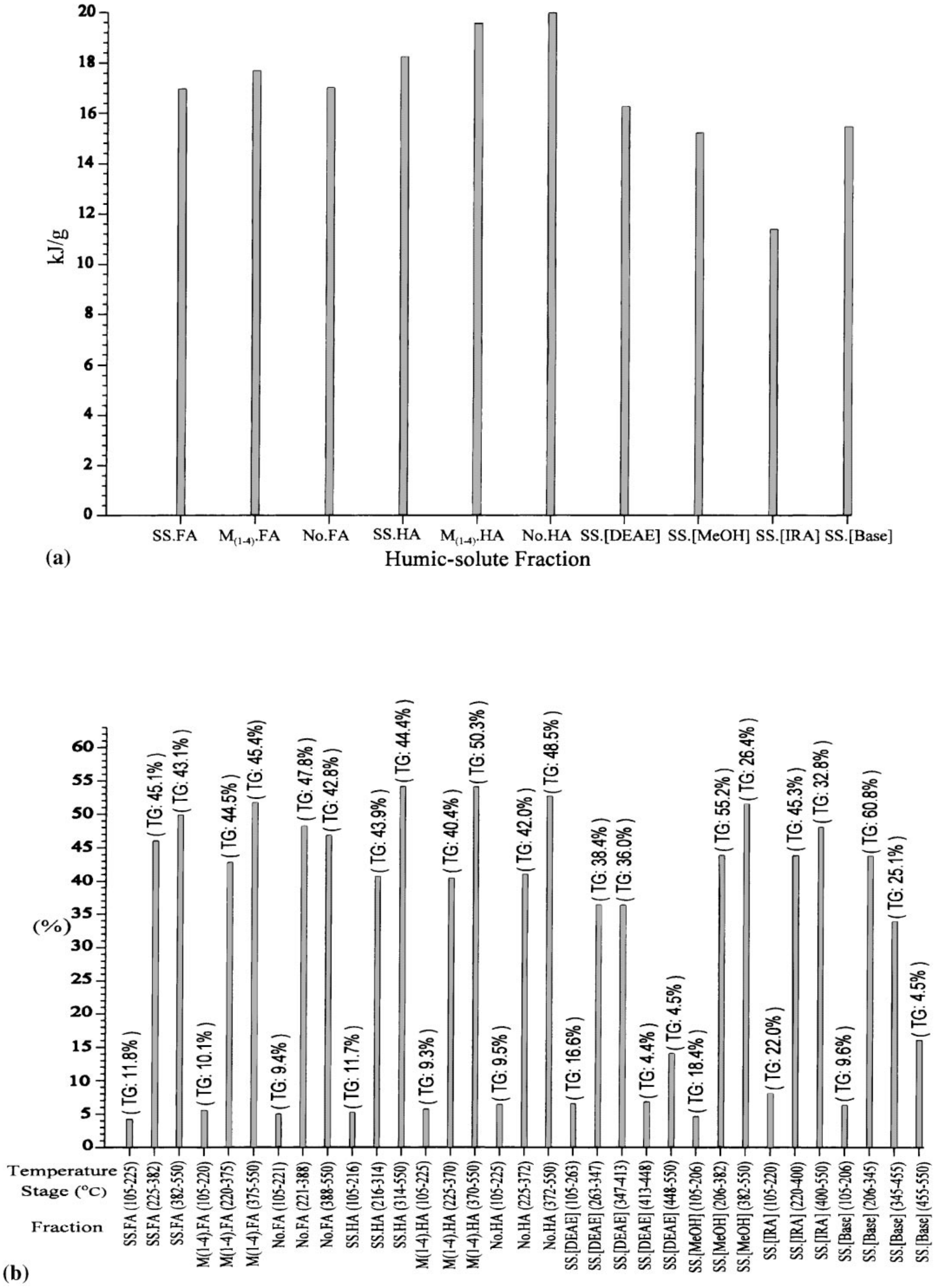


Fig. 2. (a) Calorimetric heats of combustion at constant volume of different humic-solute fractions. (b) Percent of heat fluxes obtained from DTA curves for different humic-solute fractions at different temperature stages (the corresponding percentages of fractions reacted, according to TG curves, in parenthesis).

and two minor ones at DTA (2) 426° and (3) 472°C (reaction steps Va and Vb), instead of a single main decomposition as was the case with SS.FA- and SS.HA-solutes (in Fig. 1(a): reaction steps IV at DTA 438° and 338°C, respectively). The total heat flux (J/g) estimated for the combined SS.FA–SS.HA–SS.[IRA]–SS.[MeOH] mixture weighted by their proportions [13] was only slightly smaller (ca. 8%) than that measured for the actual SS.[DEAE]-fraction verifying the concept about the structural composition of different acidic humic solutes (i.e. SS.[DEAE]$\approx$SS.-FA+SS.HA+SS.[MeOH]+SS.[IRA]).

The high-temperature degradation of the SS.[DEAE]-fraction at DTA 426° and 472°C (in Fig. 1(b): Va and Vb, respectively) was energetically relatively powerful even though their proportion of TG was rather small (in Fig. 2(b): 4.4 and 4.5%, respectively). The heat fluxes in kJ/g liberated at reaction steps Va and Vb were relatively ca. 1.5- and threefold to that obtained for the reaction step IV during degradation of SS.[DEAE]-solutes. Furthermore, the combined results of Fig. 2(a and b) indicate that the heat flux liberated at the reaction step Vb of SS.[DEAE]-fraction was relatively ca. threefold to that obtained for the reaction step V of the SS.[IRA]-fraction.

This crude evaluation, considering experimental errors, speaks for the very complex aggregated nature of humic solutes in their non-fractionated mixture. The ratios of heat fluxes liberated at reaction steps V of SS.[IRA]- and SS.[MeOH]-fractions (Fig. 1(a)) to the contents of aromatics were remarkably higher (ca. 1.5- and threefold, respectively) than those calculated for the reaction steps IV of different FAs and HAs (Fig. 1(a and b)). Therefore, it is not likely that only aromatics contribute to the heat liberated but certain aliphatics must also decompose at higher temperatures (>400°C). The same conclusion is, to some extent, valid in the case of FAs and HAs since the mass loss at higher temperaturs was ca. 1.6-fold to that of the aromatics.

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