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TG-MS analysis as tool for the evaluation of clay mixtures[1]

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Abstract

The evolved gases after thermal treatment of a series of clay samples are studied using on-line TG-MS and off-line TGA-GC-MS. © 1998 Published by Elsevier Science B.V. All rights reserved.

Keywords: Clay mixtures; Evolved gases; TG-MS

1. Introduction

During the heating cycle of clay mixtures, volatile compounds are released as a function of additives and the intrinsic properties of the clay, as well as organic and inorganic emission products have to be determined.

Four different clay types (M, K, I and B), containing several additives are evolved in this study; $CaCO_3$ is the most important additive present in different concentrations in each clay type.

In order to evaluate twenty clay mixtures with respect to their volatiles at high process temperatures, on-line TG-MS for a description of the thermal behaviour and the identification of their decomposition products is an important tool for an unambiguous characterization. Additional information on the nature of the organic emission products can be obtained, using the off-line coupling between TG and GC-MS.

2. Experimental

All TG experiments are performed with a TA Instruments 2000-951. The on-line coupled quadrupole mass spectrometer is a VG Fisons Thermolab. The off-line experiment is carried out on a Varian 3400 gas chromatograph, coupled to a Finnigan TSQ 70 quadrupole mass spectrometer.

The clay mixtures are homogenized before sampling. Four different clay types (coded K, B, M, I) with five different $CaCO_3$ concentrations are studied.

The TG experiments are carried out under an inert [1] helium atmosphere and under oxidative working conditions (air). The flow rate is 30 ml/min^{-1}. Samples are heated at a heating rate of 20°C min^{-1} from room temperature till 1050°C. The released volatiles are transferred on-line to a quadrupole mass spectrometer (mass range 10–150; SEM=950 V (air); SEM=1200 V (He).

For the off-line TG-GC-MS coupling, the evolved gases are collected in a cooled solution of dichloromethane. After the thermal treatment, the absorption solution is analyzed by GC-MS. Individual compo-

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[1] Dedicated to Prof. A. Kettrup on the occasion of his 60th birthday.

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nents are identified by their mass spectra through interactive library search.

3. Results

Typical TG and DTG curves for four different clay mixtures under helium and air are shown in Figs. 1–4. The ash residues of the different samples obtained in an air atmosphere are given in Table 1. As expected, an enhanced mass loss within the same clay type is function of the $CaCO_3$ content.

For each sample a series of mass-ions are selected for which the evolution as a function of time (temperature) is evaluated. These so-called ion-chromatograms enable to reveal the nature of the emission products during the thermal treatment. A list of selected ions is found in Table 2.

Table 1
Ash residues under oxidative conditions at 1000°C

Sample	Ash residue in w/w%	Sample	Ash residue in w/w%
K_1	95.3	B_1	90.3
K_2	94.1	B_2	88.4
K_3	92.8	B_3	86.8
K_4	91.7	B_4	85.7
K_5	89.7	B_5	84.5
M_1	95.5	I_1	94.5
M_2	94.3	I_2	93.3
M_3	95.65	I_3	91.8
M_4	90.9	I_4	90.4
M_5	89.55	I_5	88.7

3.1. M Samples

3.1.1. He atmosphere

The release of water over a broad temperature range (40–700°C) can be correlated with the different forms of

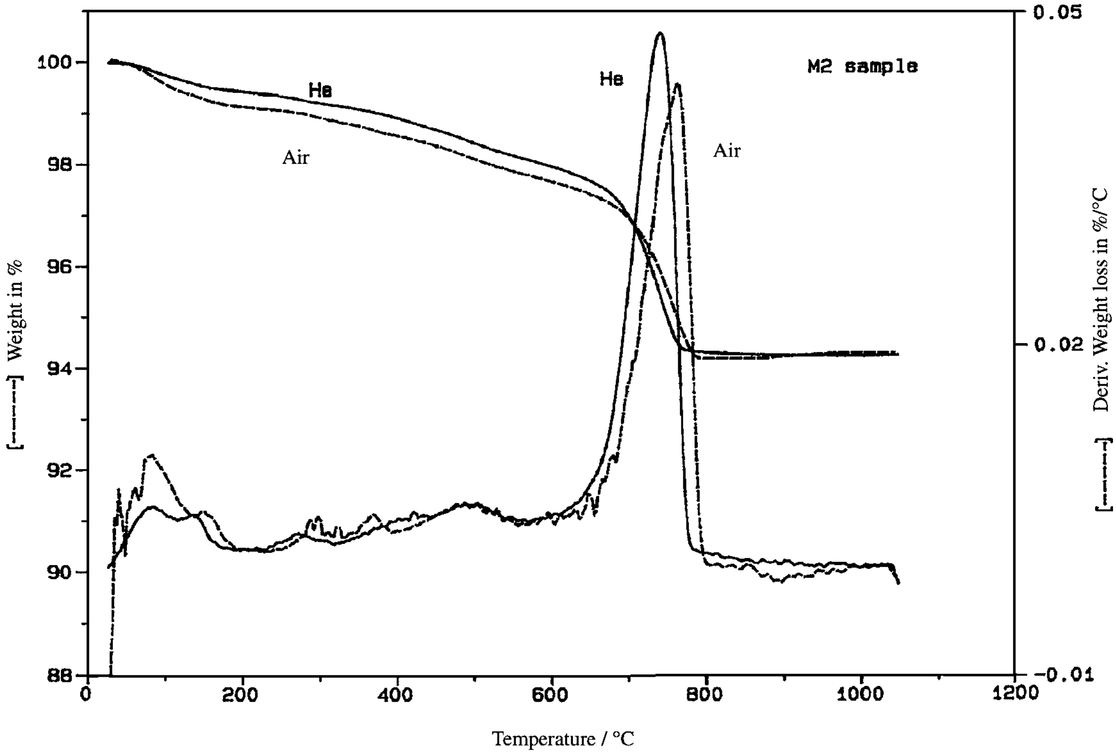

Fig. 1. TG-DTG plot of sample M_2 in He and air at a heating rate of 20°C min^{-1}.

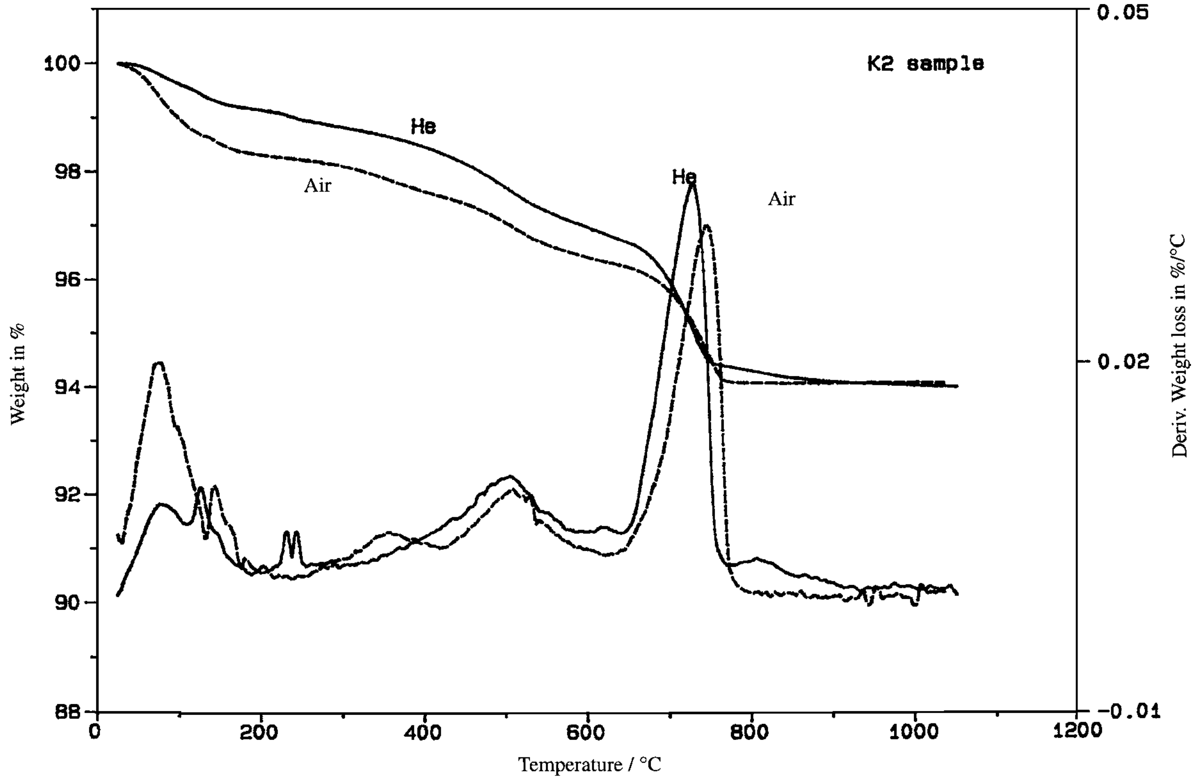

Fig. 2. TG-DTG plot of sample K_2 in He and air at a heating rate of 20°C min^{-1}.

Table 2
Selected mass-ions

m/e	Assignment
18	H_2O
44	CO_2
48 and 64	SO_2
55	aliphatic hydrocarbons
91	aromatic hydrocarbons

water (e.g. free water, hydrates, bound water, water evolved as a result of cure during the baking process) (Fig. 5). CO_2 is evolved at lower temperature which can be the result of in-situ reactions between organic acids and carbonates. The organic acids (humic and fulvic) can also undergo a decarboxylation reaction with a release of CO_2 at lower temperatures. At higher temperatures (600–700°C), the decomposition of carbonates results in an enhanced signal of *m/e* 44 (CO_2). SO_2 evolution starts at 400°C. Organic pyrolysis products are present in low concentrations in the 300–500°C range.

3.1.2. Air atmosphere

Changing the atmosphere results in nearly the same pattern for water evolution. The CO_2 emission is limited to the 250–800°C range. The dissociation of carbonates shifts to a higher temperature with respect to the experiment under inert working conditions (Fig. 6).

Organic compounds are not detected, probably because of complete oxidation reactions.

3.2. K samples

3.2.1. He atmosphere

The higher intensity of the mass ion 44 profile reflects the higher $CaCO_3$ content in comparison with the M sample (Fig. 7).

The profile of the water release shows less sequential transitions in comparison with the samples M.

SO_2 is released in three well-defined temperature ranges: 250–400°C, 400–650°C and 750–900°C.

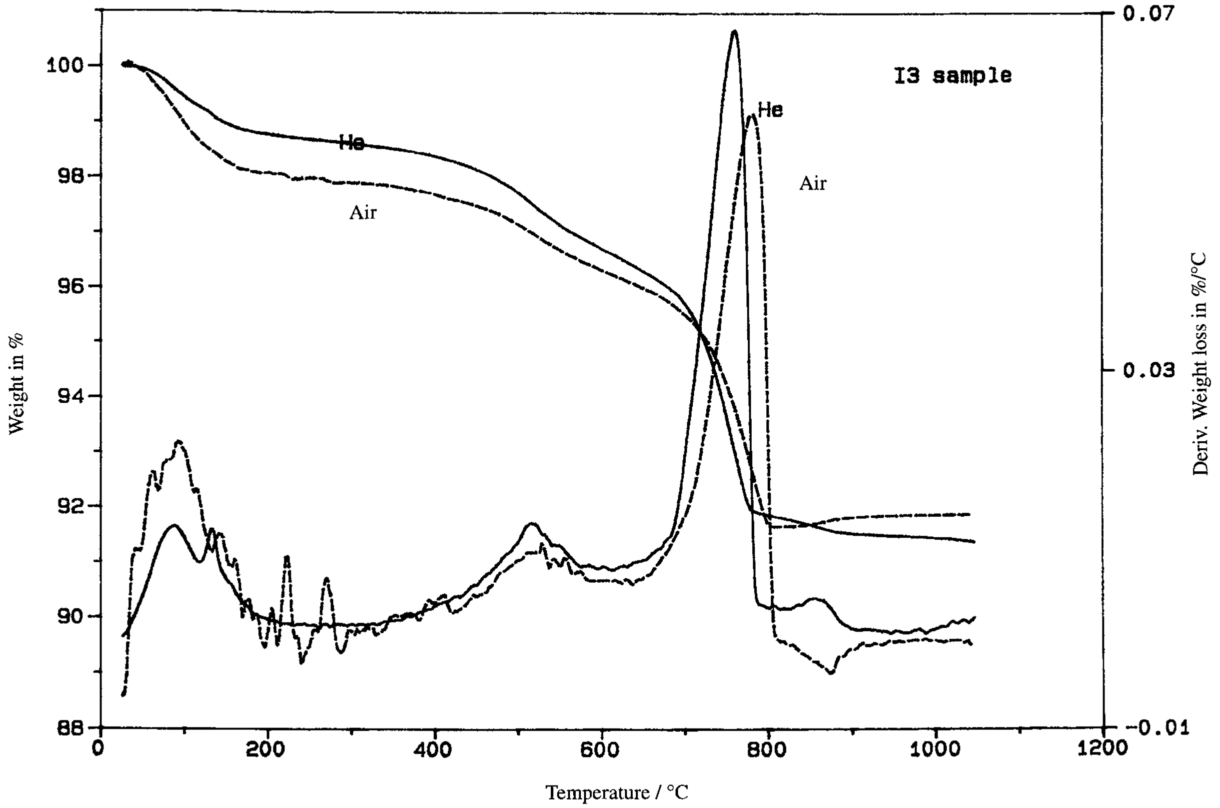

Fig. 3. TG-DTG plot of sample I_3 in He and air at a heating rate of 20°C min^{-1}.

Aliphatic and aromatic compounds are evolved in the range 250–550°C (*m*/*e* 55 and 91 chromatograms).

3.2.2. Air atmosphere

Under oxidative conditions, the CO_2 profile is less complex. The SO_2 emission is shifted towards higher temperature. Moreover, the SO_2 emission decreases as a function of $CaCO_3$ content (Fig. 8).

3.3. I Samples

3.3.1. He atmosphere

The evolution of water is nearly identical to the K samples. SO_2 is liberated from 300°C in different stages. At higher temperature (750–850°C) SO_2 emission is still observed. Organic degradation products are formed in the 300–500°C range (Fig. 9) .

3.3.2. Air atmosphere

SO_2 emission is focussed at higher temperature (400–600°C). The CO_2 profile shows significant differences with the CO_2 profile found under inert conditions with a shift to higher temperatures (Fig. 10).

3.4. B samples

3.4.1. He atmosphere

SO_2 is evolved in two distinct steps in the temperature range 250–600°C. At high temperature SO_2 emission is still observed Fig. 11).

An increased concentration of organic degradation products is detected in comparison with the other samples (200–700°C). From the *m*/*e* 91 profile, it can be stated that the release of aromatic compounds occurs at a higher temperature with respect to the aliphatic products.

The profile of *m*/*e* 32 shows a signal at 550°C which can be assigned to the presence of H_2S.

In order to obtain more information on the nature of the evolved organic products, an off-line TG-GC-MS experiment is performed. From the list of identified

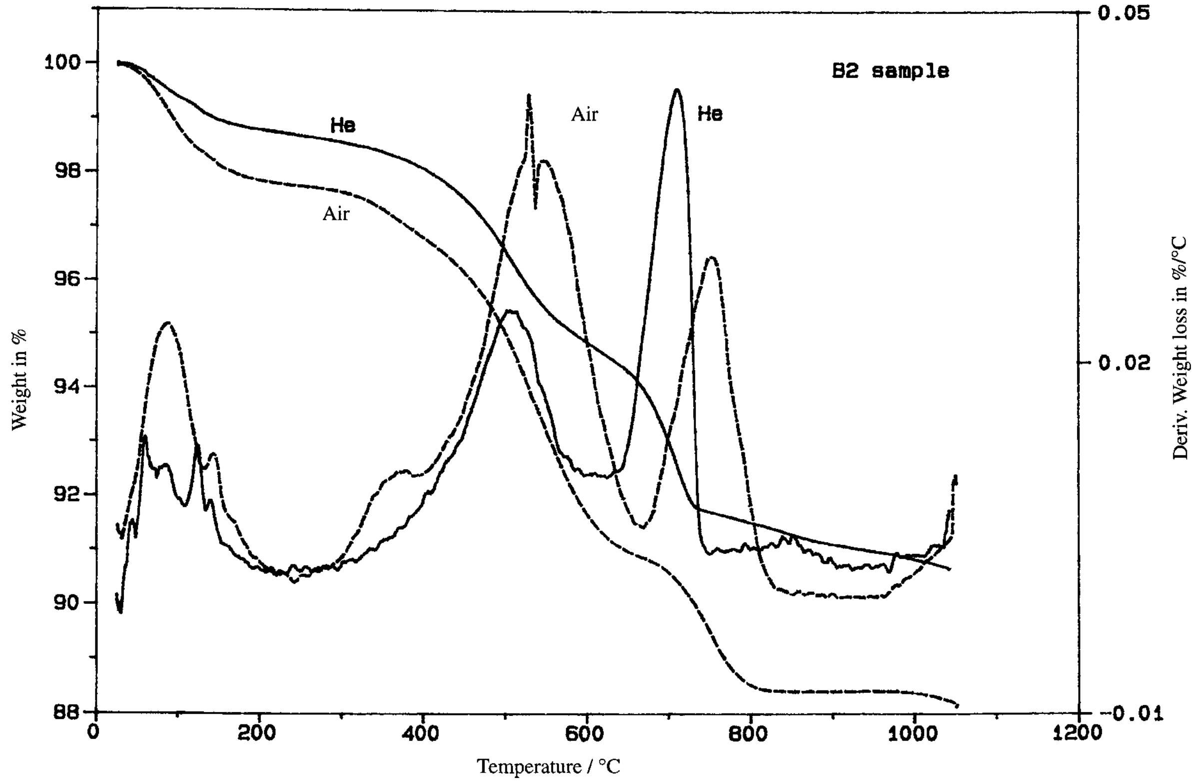

Fig. 4. TG-DTG plot of sample B_2 in He and air at a heating rate of 20°C min^{-1}.

compounds (Table 3), it can be stated that the organic volatile fraction mainly consists of aromatic compounds, naphtalenes and some polycyclic aromatic hydrocarbons.

3.4.2. Air atmosphere

As observed for the M, K and I samples, the SO_2 emission is focussed at higher temperatures (600–900°C). This is also observed for the CO_2 emission where a more simple profile is found with a shift towards a higher temperature (Fig. 12).

Table 3
Compounds absorbed in a dichloromethane solution during the TG experiment on sample B_1 in He and identified by GC-MS

Acetic acid
Benzene, toluene, xylene, pyridine, styrene
Alkyl-substituted benzene compounds
Indene and methylindene
Methylbenzofurane
Dimethylbenzofurane
Naphtalene and alkylated naphtalene compounds
Biphenyl compounds
Flurorene

4. Conclusion

The use of on-line TG-MS experiments allows on unambiguous differentiation between different clay mixtures. There is a significant difference between the TG-MS results under He and those under air.

The SO_2 emission profile is dependent of the clay type. Experiments under helium and under air show significant features in the SO_2 emission profile within the same clay mixture. The organic fraction present in the clay mixtures are not only thermally decomposed (cracking pyrolysis conditions) but are also oxidized under air, resulting in a decrease of evolved organic gases.

The SO_2 and CO_2 emissions are more pronounced at higher temperatures under oxidative conditions. This can be explained in terms of interaction with

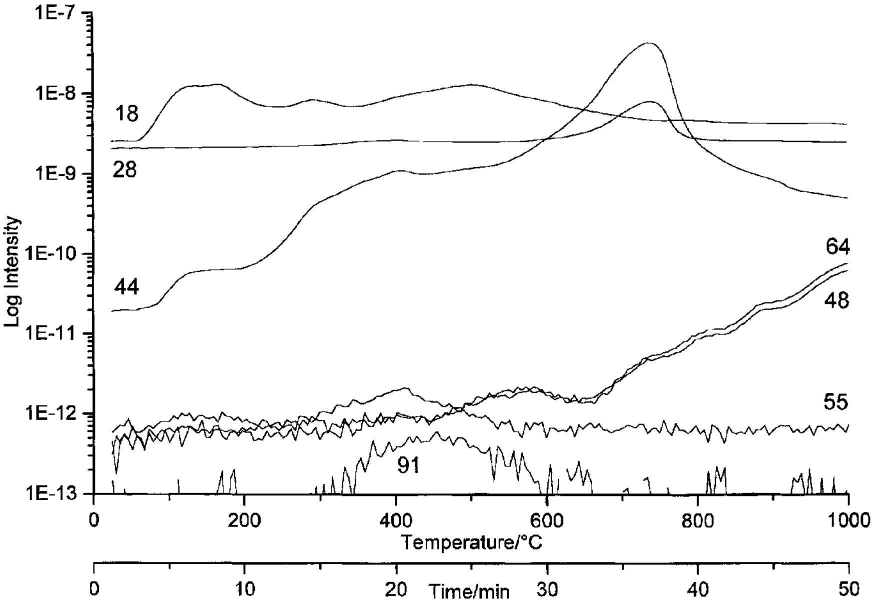

Fig. 5. Ion-chromatograms of gases released by heating sample M_2 in He as a function of time and temperature.

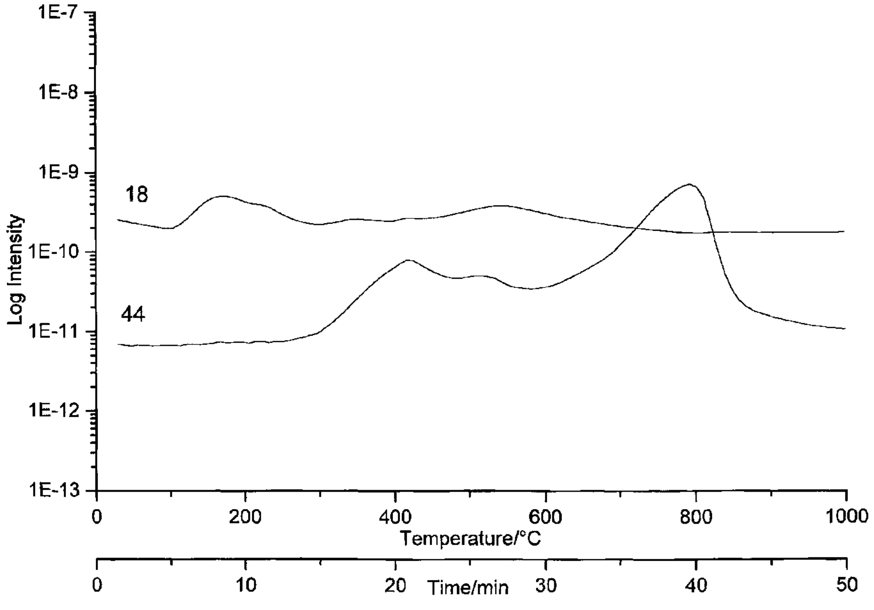

Fig. 6. Ionchromatograms of gases released by heating sample M_2 in air as a function of time and temperature.

the matrix which can induce a catalytic decomposition under inert conditions, resulting in a shift to lower temperatures. Working under oxidative conditions can result in an inhibition of this decomposition process with the formation of mainly oxidation products.

The GC-MS analyses of a B sample under inert conditions confirms the presence of aromatics as pyrolysis products of the organic fraction. The identification of fluorene and biphenyl compounds can be assigned to the formation of polycyclic aromatic

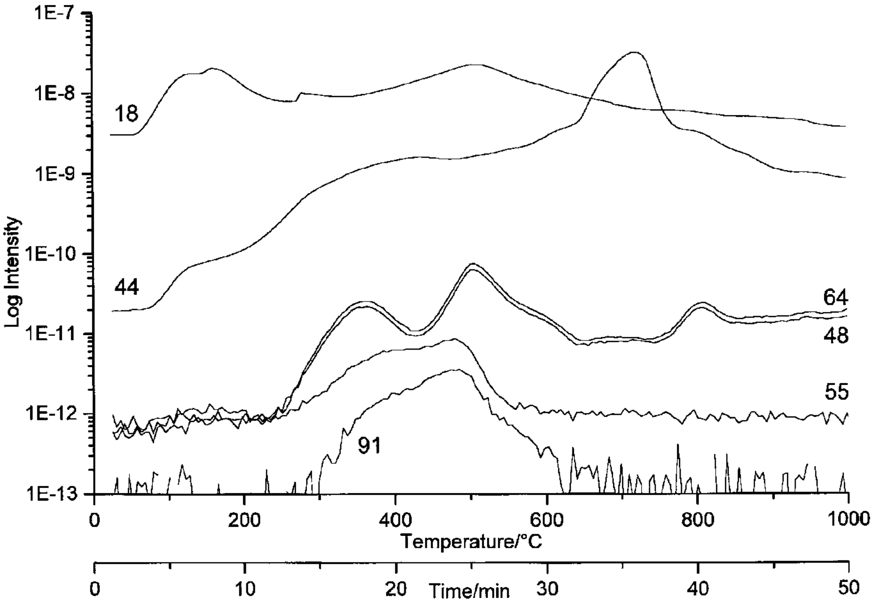

Fig. 7. Ion-chromatograms of gases released by heating sample K_2 in He as a function of time and temperature.

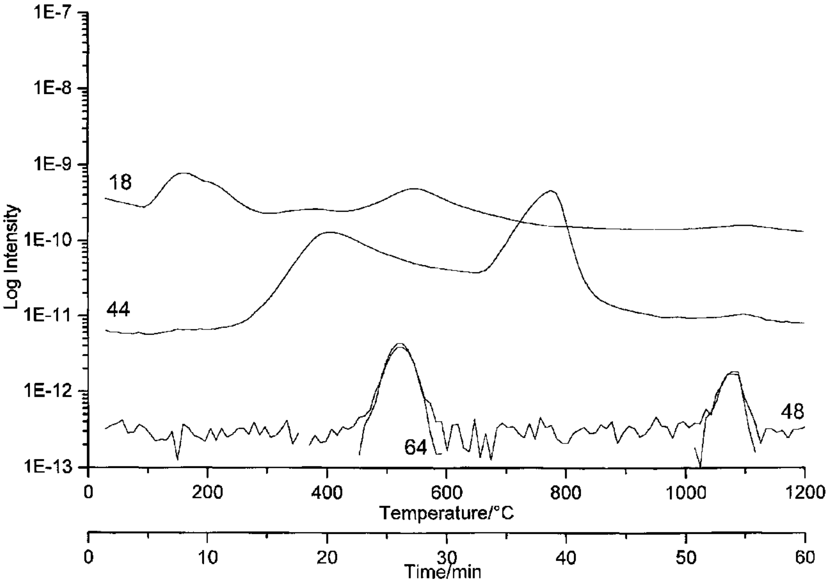

Fig. 8. Ion-chromatograms of gases released by heating sample K_2 in air as a function of time and temperature.

compounds (carbonization process) which is less probable under oxidative working conditions.

The obtained results are useful data for the evaluation of the composition of clay mixtures, additives, process parameters, emission products and clean-up techniques.

This experimental approach of evaluating different clay samples with respect to their thermal behaviour

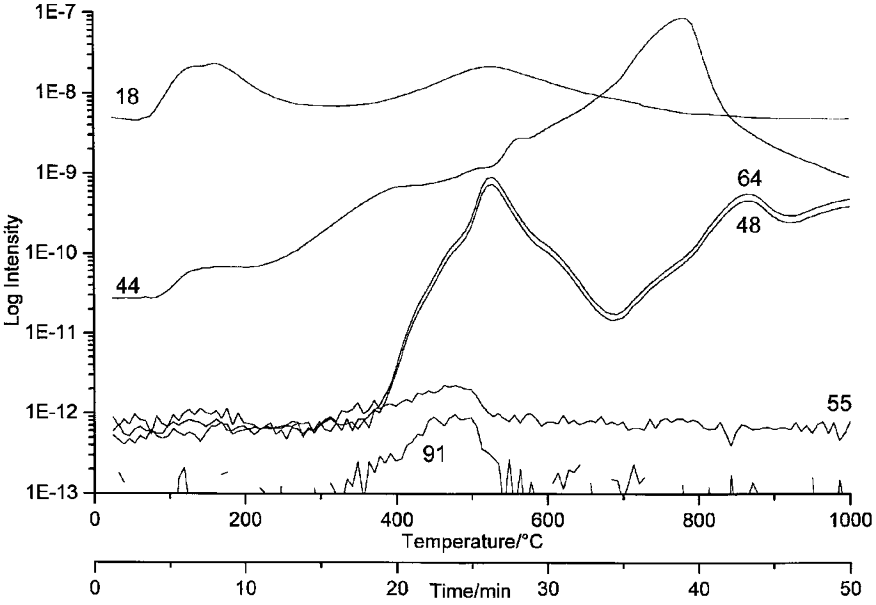

Fig. 9. Ion-chromatograms of gases released by heating sample I_5 in He as a function of time and temperature.

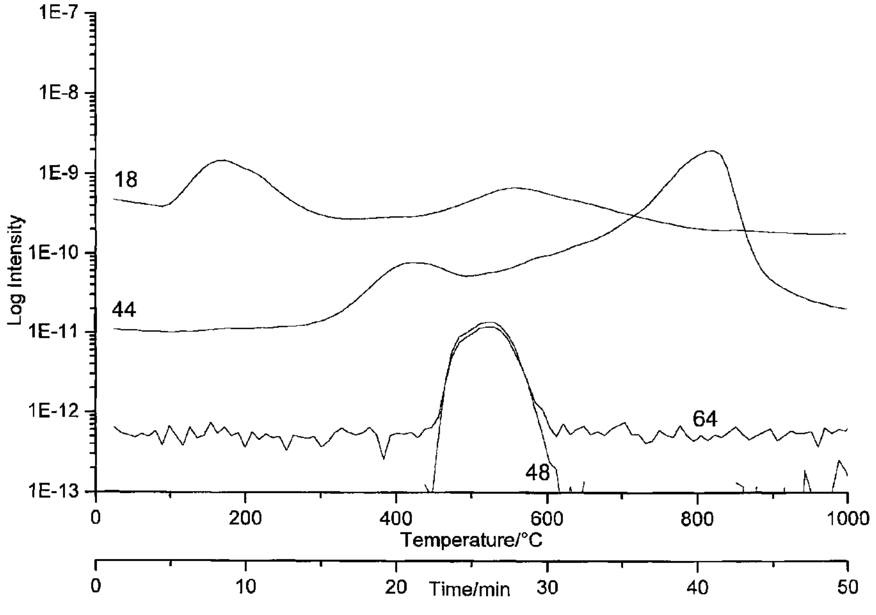

Fig. 10. Ion-chromatograms of gases released by heating sample I_5 in air as a function of time and temperature.

and emission products illustrates the performance and capabilities of coupled TG techniques.

Other applications in material research and environmental applications have been described elsewhere, demonstrating the power of the combination of TG with relevant detection systems (FT IR, AAS, IC, ICP, MS potentiometry, XRF, ...) for qualitative and quantitative analyses of the gases evolved by materials such

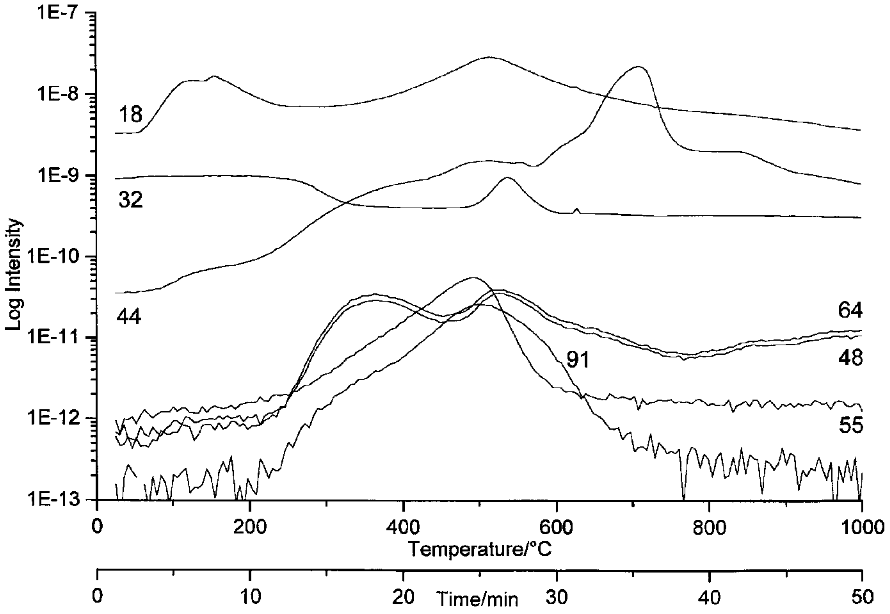

Fig. 11. Ion-chromatograms of gases released by heating sample B_2 in He as a function of time and temperature.

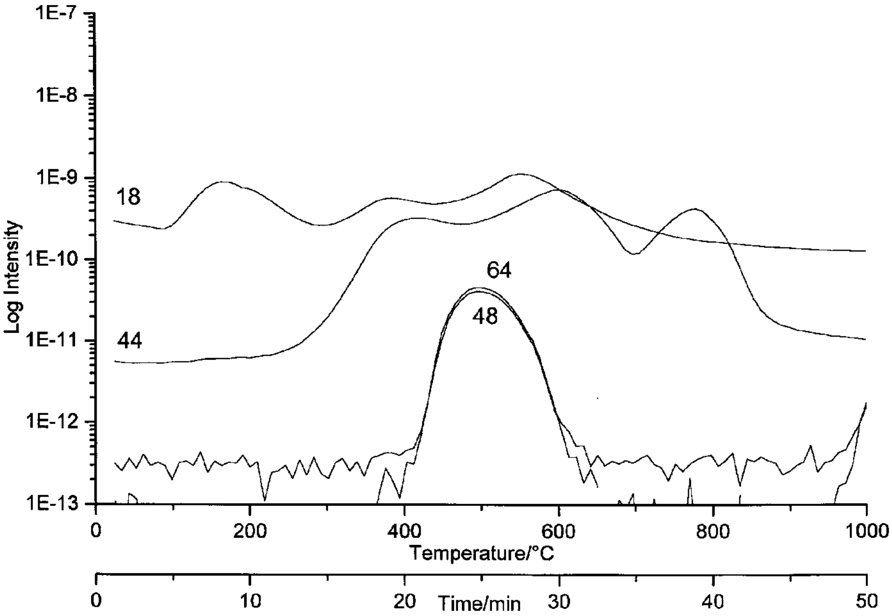

Fig. 12. Ion-chromatograms of gases released by heating sample B_2 in air as a function of time and temperature.

as high T_c superconductors [1], polystyrene [2], polyethylene [3], coal [4], Kortemark clay [5], ferroelectrical PZT [6] and a flame retardant for polymers [7].

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