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ADSORPTION OF HAZARDOUS ORGANIC POLLUTANTS BY CLAYS AND SOILS

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3. Executive Summary

The purpose of the present investigation is to study the adsorption of hazardous organic pollutants by clay minerals and by soils from Israel and the Czech Republic. The experimental work was carried out in Rez (Chech Republic) and Jerusalem (Israel). In Rez much effort was spent in order to develop techniques to study the microstructural changes occurring during the thermal treatments of the organo-clay complexed. The ETA heating and cooling curves were compared with DTA and TG heating curves of different organo-clay complexes data. There is a good correlation between the ETA curves and the DTA-TG curves of organo-clay complexes. ETA curves of different hazardous compounds were studied and the effect of the organic matter on the clay was interpreted.

Many experiments were carried out in Jerusalem to study the adsorption of hazardous materials by the different smectites. We studied the adsorption of phenol and dichlorophenols from organic solvents and by mechanochemical techniques. In this technique the clay is ground together with the phenol during 1, 3 , 5 and 10 minutes, which includes thermo-FTIR spectroscopy, thermo-X-ray diffraction, DTA and TG. For the thermo-FTIR study the samples were heated to evolve excess free. and the organo-clay complex is examined by thermal analysis.

We studied the adsorption of chlorophenols by simultaneous DTA-TG. From the area of a characteristic endothermic peak at 200-220°C, this technique may supply semi-quantitative information on the adsorption. In most cases the peak area show slight increments in the adsorption of complexed phenols due to grinding. The adsorption of common pesticides by clays and soils, the adsorption mechanism and the contribution of clays to this process were investigated.

4. Research Objectives

The principal work carried out in the present investigation was the study of the adsorption of hazardous materials by different expanding clay minerals such as smectites. The principal purpose of this study was: (1) to examine what might be the role of clay minerals in the migration of hazardous materials in soils and sediments and (2) to evaluate adsorbing agents for hazardous materials based on clay minerals for waste water purification.

There are several factors which play important roles in the adsorption process of organic matter by smectite minerals, and determine the stability of the organo-clay complexes. The most investigated factor is the exchangeable cation. In the interlayer space of the smectite mineral the cation may either be directly coordinated by the adsorbed organic compound or it may be bound to the organic species through a water molecule bridge. In the latter adsorption mechanism the polarizing power of the cation controls the acid strength of the bridging water molecules and this affects the type of bonding which is formed between the acidic water molecule and the organic adsorbed species. To conclude, the acidic behavior of the interlayer space, that is, the different acid adsorption sites and their contribution to the adsorption process have been widely investigated.

In the last twenty years it has been shown that, in addition to acid sites, the interlayer space has basic adsorption sites. Water molecules, via their oxygen atoms, may behave as proton acceptors and were shown to be adsorption sites of organic proton donors. Recently it has been shown that atoms of the oxygen plane of the silicate framework of the clay may react as electron pair donors. In other words, they may react as bases and adsorb Brønsted acids by accepting protons or Lewis acids by donating electron pairs. In the present investigation we examined the surface basicity properties of different smectites in order to find out the relationship between their basicity and the adsorption mechanism of the different hazardous materials.

We also studied by different methods of thermal analysis the thermal behavior of the hazardous material-clay complexes.

It was expected that this study will supply information about the stability of the complexes in general. Thermal analyses gives the evolution temperature of the organic compound. The higher this temperature is, the more stable is the organo-clay complex.

5. Methods and Results

Most of the different parts of this study were carried out equally in both laboratories, half was under the responsibility of Prof. Yariv from Jerusalem and half under the responsibility of Professor Belék from Rez. Some parts were done completely in Jerusalem and some completely in Rez. We shall therefore divide this section into work carried out in Jerusalem and that carried out in Rez.

Experimental Work carried out in Jerusalem

Methods: These are the principle methods used in Jerusalem for collecting data:

Adsorption of non-ionic hazardous compounds by smectite minerals was carried out from organic solvents. A clay film or powder was left in a solution of the organic compound for periods up to 6 months and the adsorption was investigated from time to time. Mechanochemical adsorption will be described later.

FTIR and XRD spectroscopy give information on the fine structure of the organo-clay complexes. For the FTIR study samples were prepared either as self- supporting films or as KBr disks. For the XRD oriented samples were prepared by slow sedimentation from suspension. FTIR and XRD spectra were recorded at room temperature before any thermal treatment and after heating the samples to different temperatures.

Thermal Analysis was carried out by DTA and TG.

Visible spectra of dye-clay complexes were recorded. For this purpose very dilute aqueous suspensions of dye-clay complexes were prepared.

Publications in peer-reviewed international journals

1. S. Yariv, "Thermo-IR-spectroscopy analyses of the interactions between organic pollutants and clay minerals," *Thermochimica Acta*: 234 (1996) 1-35.

This paper is a review article. It contains the characteristic IR spectra of the principal functional groups found in organic hazardous materials which originate from industrial and agricultural wastes, adsorbed on clay minerals. It also contains many spectra of hazardous agrochemicals adsorbed on clay minerals. The spectra are given as recorded at room temperature and after thermal treatments at various temperatures. To the best of our knowledge this was the first published collection of IR spectra of organo-clay complexes obtained with hazardous compounds. Infrared spectroscopy is one of the principal research tools in this research and this collection of spectra is essential for our study.

2. Z. Malek, V. Belék, D. Garfinkel-Shweky and S. Yariv, "The study of the dehydration and dehydroxylation of smectites by emanation thermal analysis," *Journal of Thermal Analysis*, 48 (1997) 8-92.

The study of thermal stability of the organo-clay complexes is carried out by emanation thermal analysis (ETA) in addition to DTA and TG. In this paper the ETA of smectites which were applied in our research is described and compared with DTA and TG. To the best of our knowledge this is the first paper to describe ETA of beidellite, saponite and laponite. The ETA thermograms were recorded in Rez and the DTA and TG thermograms in Jerusalem.

3. D. Garfinkel-Shweky and S. Yariv, "The determination of surface basicity of the oxygen planes of expanding clay minerals by acridine orange," *Journal of Colloid and Interface Science*, 188 (1997) 168-176.

Acridine orange is a cationic dye. It is adsorbed by smectites by the mechanism of cation exchange. After being adsorbed into the interlayer space it may accept a lone pair electrons of the clay oxygen-plane. In this reaction the lone pair electrons enter the antibonding π orbitals of the dye cation. This interaction is shown by a blue shift in the $\pi \longrightarrow \pi^*$ transition band in the electronic spectrum (visible spectrum).

The stronger the π bond, the longer the resulting blue shift. This study showed that the basicity of the O-plane decreases in the order: beidellite, montmorillonite, saponite, laponite. The basic strength of the O-plane has an effect on the adsorption mechanism of the hazardous compounds. This was shown in our study of the adsorption of phenol and phenol derivatives (see below).

4. E. Alayof, S. Yariv and Z. Gerstl, "Thermo-IR-spectroscopy study of the adsorption of tributhylazine by soil from the Jezreel Valley," *Journal of Thermal Analysis*, 50 (1997) 215-227.

Tributhylazine is an important herbicide. Its use has increased in recent years in Israel, replacing other s-triazines. We showed that the adsorption of this herbicide takes place mainly by the clay mineral montmorillonite. The adsorption takes place via the aniline group, the N being hydrogen bonded to the interlayer water molecules. After an aging period a new IR band appeared at 1745 cm^{-1}, attributed to CO-group. This band is intensified by heating the azine-clay complex. In previous studies on the adsorption of s-triazine herbicides, all investigators attributed a small band at 1730-1750 cm^{-1} in the spectrum of adsorbed triazines to protonated s-triazine.

In the present study we show that this band is intensified by heating and that the intensification of this band is accompanied by a drastic change in the spectrum and the disappearance of the s-triazine bands. This may indicate that, in addition to hydrolysis, the aging of s-triazine-montmorillonite complex is associated with a ring cleavage followed by polymerization of the decomposition product. These changes were not observed in the previous studies because the samples were not thermally treated.

5. A. Nasser, M. Gal, Z. Gerstl, U. Mingelgrin and S. Yariv, "Adsorption of alachlor by montmorillonites," *Journal of Thermal Analysis*, 50 (1997) 257-268.

Alachlor is a preemergence herbicide which has become popular for weed control in corn and soybeans. The adsorption of the herbicide by Na- and Al-polyhydroxy-montmorillonite was investigated by DTA, XRD, SEM and thermo-FTIR spectroscopy. The herbicide is adsorbed into the interlayer space of montmorillonite replacing part of the interlayer water. In this organo-clay complex, the interlayer water forms hydrogen bonds with N- or O-atoms of the tertiary amide group. Samples which were aged during six months degraded by hydrolysis to give mainly secondary amide. The reaction was catalyzed by Al-polyhydroxy-montmorillonite more than by Na-clay.

6. D. Ovadyahu, S. Shoval, I. Lapides and S. Yariv, "Thermo-IR-spectroscopy study of the mechanochemical adsorption of 3,5-dichorophenol by TOT swelling clay minerals." *Thermochica Acta*, 282/283 (1996) 369-383.
7. D. Ovadyahu, S. Yariv, and I. Lapides, "Mechanochemical adsorption of phenol by TOT swelling clay minerals. I, Thermo-IR-spectroscopy and X-ray study," *Journal of Thermal Analysis*, 51 (1998) 415-430.
8. D. Ovadyahu, S. Yariv, I. Lapides, and Y. Deutsch, "Mechanochemical adsorption of phenol by TOT swelling clay minerals." II, Simultaneous DTA and TG study," *Journal of Thermal Analysis*, 51 (1998) 431-447.

The last three publications deal with mechanochemical adsorption of hazardous materials by clay minerals. This technique was developed in the frame of the present research for the study of compounds which are hardly adsorbed from solvents. Adsorption of non-polar organic molecules by clay minerals for the study of organo-clay complexes and interactions is usually carried out from organic solvents. In many cases the amounts, which are adsorbed even after half a year by expanding clay minerals are very small and not sufficient for spectroscopic and thermal study of non-expanding clay minerals, which have a very low adsorption capacity. Combined mechanochemical adsorption/thermo-IR-spectroscopy and mechanochemical adsorption/DTA-TG techniques were developed in our laboratory for the study of chlorophenol-clay complexes of expanding clay minerals.

The mechanochemical adsorption of phenol and chlorophenols by laponite, saponite, montmorillonite, beidellite and vermiculite was investigated by thermo-IR-spectroscopy. In the mechanochemical adsorption study the clay is ground with excess phenol for 1, 3, 5 and 10 minutes. Spectra of the phenol-smectite ground mixtures are recorded in KBr disks, after leaving the disks for 3 days in a vacuum furnace at 115°C for the evolution of the excess phenol. In most cases, the first five minutes of grinding led to an increase in the intensity of the phenol bands relative to the characteristic bands of the clay. An additional five minutes of grinding resulted in a decrease of the phenol absorption bands. These observations indicate that the first five minutes lead to an increase in the adsorbed phenol, whereas longer grinding periods lead to desorption or decomposition of the adsorbed phenol. In the case of vermiculite, maximum adsorption is obtained after a grinding period of 3 minutes, whereas after 10 minutes no phenol bands are detected. In the case of laponite the intensities of the absorption bands after 10 minutes are similar to those after 5 minutes grinding. The absorbance of water bands was also affected by the time of grinding. They decreased in the first five minutes but increased with longer grinding periods. The fact that the water absorption bands decreased when the phenol absorption bands increased, indicates that the adsorbed phenol replaced interlayer water. Two configurations of phenol-water clay association were identified (types A and B). In configuration A, H-bond binds the phenol to the water molecule in which the former accepts a proton from the latter. In configuration B the phenol reveals acidic character. It forms hydrogen bonds with water molecules by proton donation. Due to the fact that phenol acidity is higher than that of water, configuration B is expected to be the principal adsorption product in all minerals. In beidellite and montmorillonite mainly configuration A is obtained after one minute grinding. Longer grinding periods are required to obtain configuration B. In saponite and laponite configuration B is obtained

immediately and longer grinding are required for configuration A to appear. In configuration A, protonation of the phenol renders the aromatic ring slightly positive and thus it may accept electrons into the π anti-bonding orbitals.

The mechanochemical adsorption of phenol by laponite, saponite, montmorillonite, beidellite and vermiculite was studied by simultaneous DTA and TG analysis. Fitting of the DTA curves showed four endothermic peaks in the r.t.—250°C temperature range. The first peak represents the melting of the excess crystalline phenol. The second peak represents the evolution of water. The third peak represents the boiling of water. The third peak represents the boiling of the free phenol. The fourth peak represents the evolution of adsorbed phenol. In the DTA curves of montmorillonite the fourth peak is not observed as a separate peak but as part of the third peak. Laponite, saponite and montmorillonite show a very small exothermic effect which follows the endothermic events. Laponite adsorbs the greatest amounts of phenol and shows a strong exothermic peak at 390°C. None of the other clays show this exothermic effect at this temperature.

Unpublished Results

The following investigations were carried out but the results have not yet been published.

1. Mechanochemical adsorption of 2,4 dichlorophenol by smectites. Grinding of the two solids together was carried out. For FTIR study KBr disks were used after the evolution of excess phenol by heating under vacuum at 115°C. The results are compatible with the fact that the acid strength of the phenol group in 2,4 dichlorophenol is higher than in the 3,5 dichlorophenol and consequently stronger hydrogen bonds are obtained. The mechanochemical adsorption was studied by thermal analysis.

2. DTA and TG of mechanochemical adsorbed 3,5 dichlorophenol. This is the continuation of the work published in the manuscript on the FTIR study of this compound adsorbed by clay minerals.

3. IR-spectroscopy and thermo-IR-spectroscopy in the study of the fine structure of organo-clay-complexes."

This is an enlargement of the review article on thermo-IR-spectroscopy of the adsorption of hazardous materials by clay minerals which was published in *Thermochimica Acta*. It contains information on clay complexes of hazardous and non-hazardous materials and other waste materials. It also covers the adsorption of neutral, cationic and anionic detergents such as long chain amines, ammonium, fatty acids and their anionic varieties. As well, it contains a summary of all the thermo-IR-spectroscopy studies which were carried out in our research project. It will be published in the book *Clay-organic complexes and interactions*.

US AID – Final Report

Research Project No. C-12-219

ADSORPTION OF HAZARDOUS ORGANIC POLLUTANTS BY CLAYS AND SOILS

Experimental work carried out at NRI Řež

1. Characterization of the dehydratation and dehydroxylation of reference smectite clays: Na-montmorillonite (Wyoming, U.S.A.), beidelite, saponite (both from Source Clay Minerals Repository, Columbia, Missouri, U.S.A.) and laponite (from Laporte Co. U.K.).
2. Characterization of sorption properties of the reference natural clays: montmorillonite, beidelite and laponite
3. Experimental determination of pH dependence of the sorption of the organic compounds 2,4 dichlorphenol (DCP) and Bengal Red dye (BR) by montmorillonite saturated with different inorganic cations, such as Li^+, Na^+, Cs^+, Mg^{2+}, NH_4^+, and the organic cations tetramethylammonium (TMA) and distearyldimethylammonium ($DSDMA^+$).
4. Comparison of sorption properties of montmorillonite clays saturated with different cations with regard to the two organic compounds DCP and BR. Thermogravimetry was used in the investigation of the stability of DCP bonding with various montmorillonite clays.
5. Characterization of structural parameters of montmorillonite due to its saturation with different exchangeable cations by means of X-ray diffraction.
6. Investigation of the effect of surfactant cation (distearyldimethylammonium, $DSDMA^+$) on sorption properties of bentonitic clays towards 2,4 dichlorphenol (DCP) and Bengal Red dye (BR). Sodium activated bentonite clay from Bavaria, Germany (denoted TIXOTON) and the organophilic clay products (denoted TIXOSORB and TIXOGEL), where Na cation was exchanged by $DSDMA^+$ to 50 % and 100 %, resp. were used in the investigation. Determination of pH dependence of the amount of adsorbed DCP and BR were determined for both organophilic modified bentonite products.
   Measurement of equilibrium isotherms for sorption of DCP and BR on organophilic modified bentonite products TIXOSORB and TIXOGEL.
7. Characterization of thermal stability of adsorbed DCP on montmorillonite organo-clays saturated with $DSDMA^+$ and the thermal stability of the substrate. Organo-clay complexes between DCP and organophilic bentonite product TIXOSORB (saturated with $DSDMA^+$ to 50 % extent) and TIXOGEL (saturated by $DSDMA^+$ to 100 %) were investigated. Thermal stability was characterized by thermogravimetry TG/DTG coupled by evolved gas analysis with mass spectrometric detection.
8. Characterization of thermal stability of adsorbed BR on montmorillonite organo-clays saturated with $DSDMA^+$, i.e. between BR and bentonite organophilic products TIXOSORB and TIXOGEL, respectively. Thermal stability was characterized by thermogravimetry TG/DTG coupled by evolved gas analysis with mass spectrometric detection.

9. Characterization of morphology changes taking place during heating montmorillonite saturated with $DSDMA^+$, non-contaminated and contaminated with DCP and BR, respectively X-ray diffraction patterns were used for the structure characterization, Emanation thermal analysis was used for the characterization of samples microstructure.
   Development of the mathematical model making possible to describe microstructure changes based on the changes of mobility of inert gas atoms serving as microstructural probe. Application of this model in the evaluation of the ETA results characterizing the behariour of non-contaminated and contaminated clay samples with organic compounds.

10. Investigation of the effect of various organic compounds on activated clay product TIXOTON, containing min. 65 % Ca-montmorillonite (activated by Na-carbonate), 6.5 % of calcite, 5.4 % of iron-oxide-hydroxide, quartz, mica and amorphous silica acid (not detectable by XRD). Following compounds representing different types of molecules were used in theinvestigation:
    5 % water solution of acetic acid (as organic acid)
    5 % water solution diethylamine (aliphatic amine- as organic base)
    5 % water solution of ethylenglycol (as neutral polar organic compound), and neat n--heptan (as aliphatic hydrocarbon- neutral non-polar organic compound).
    X-ray diffraction, IR spectroscopy, thermogravimetry TG/DTG coupled by evolved gas analysis with mass spectrometric detection and emanation thermal analysis were used for the characterization of the bentonite samples before and after interaction with respective organic compounds.

Results accomplished at NRI Řež

1. Dehydratation and dehydroxylation of smectites

The dehydratation and dehydroxylation of smectite clays, beidellite and montmorillonite (dioctahedral) and saponite and laponite (trioctahedral), were investigated by ETA, DTA, TG and X-ray diffraction. There are differences between the behaviors of di- and trioctahedral clays which are due to the differences in the ability of the exchangeable cations to migrate into hexagonal holes of the SiO_4^- network and due to the fact that the dehydroxylation and recrystallization of dehydroxylated trioctahedral smectites occur simultaneously, whereas a temperature gap of about 300 °C was observed between the dehydroxylation and the recrystallization of dioctahedral smectites. The results were published in [1]. Selected results of thermal behaviour of beidelite, montmorillonite and laponite are demonstrated as Figures 1, 2 and 3 in this report.

2. Results of 2,4 dichlorphenol sorption (DCP) test on natural smectite minerals

Samples of Na-montmorillonite beidelite and laponite were tested in order to check their sorption capacity for DCP. The sorption from aqueous solution containing 0.15 mg DCP/liter was compared at pH = 4. Following results were obtained (in % of the initially present DCP).

Na-montmorillonite	56 %
Beidelite	33.2 %
Laponite	13.6 %

As to the pH dependence of the sorption efficiency, we have found that it decreased with increasing pH in the range of pH 4–8. This behaviour is in agreement with the results obtained by Lee and other authors [2] for the sorption of pentachlorphenol on various clay minerals.

3. Sorption of 2,4 dichlorphenol (DCP) and Bengal Red (BR) dye on montmorillonites saturated with various cations

Sorption properties were measured by the batch equilibrium method. Preliminary experiments indicated that one hour shaking time on a rotating shaker was sufficient to obtain equilibrium. Nevertheless samples were shaken overnight (16–24 h). The sorption equilibrium isotherms for 2,4 dichlorphenol (DCP) and Rose Bengal dye (RB) on clays were performed in plastic vials. All vials were fitten with septa inserts in screw-top caps. Stock solutions of DCP (^{131}I and RB ^{131}I) were adjusted to various pH values with very small amounts of concentrated HCl or 1M NaOH solutions. The concentrations was 0.01–4.0 g/l. The DCP and BR compounds were labeled with ^{131}I radioisotope to make possible the radiometric detection of labeled DCP and BR. It was verified that the chemical properties of the labeled DCP and BR compounds did not differ from the properties of the original (non-labeled) samples.

Following equilibration, the solution and solid phase were separated by centrifugation. Aliquotes (3 ml) of the supernatant were taken from each sample. The concentration of DCP or BR was then determined by scintillation counter with gamma hole detector.

3.1. Results of DCP sorption tests

The DCP sorption by the samples of montmorillonite saturated with Na^+, Li^+, Cs^+, Mg^{2+}, Al^{3+}, NH_4^+ and tetramethylammonium (TMA^+) and distearyldimethylammonium ($DSDMA^+$) was compared at pH = 2.2. The experimental results are presented in Table 1 together with the values of basal spacings as structure characteristics of the monoionic montmorillonite samples.

Table 1

Sorption of DCP (in μg/g) by monoionic montmorillonites from an aqueous solution (0.15 mg/l), at pH = 2.2 and basal spacings d(001) (in nm) of air dried samples.

Clay Sample	DCP sorption %	Basal spacing d_{001} (nm)
Mont-Na-feed	61.6	1.24
Mont-Li	63.2	1.26
Mont-Cs	70.1	1.20
Mont-NH_4	65.8	1.20
Mont-Mg	65.4	1.50
Mont-Al	77.9	1.50
Mont-TMA	67.2	1.41
Mont-DSDMA	98.6	3.16

3.2. Characterisation of structure parameters and thermal behaviour

Structure parameters of montmorillonite clay with different cations were determined by X-ray diffraction patterns. The basal spacing d_{001} determined are listed in Table 1. Monovalent cations give rise to one water layer in the interlayer space. The di- and trivalent cations give rise to two water layers in the interlayer space whereas the large organic DSCMA cation gives an extremely high spacing.

Prior to sorption testing, the montmorillonite samples prepared were characterized by thermogravimetry coupled with evolved gas analysis from the viewpoint of their ability to dehydrate and dehydroxylate. The results were published in [3] and selected results are presented in this report in Figs. 4, a-d. The respective ETA curves are presented in Fig. 5.

Emanation thermal analysis used in this study made it possible to identify microstructure changes during heating homoionic montmorillonite samples saturated with different cations. Microstructure changes revealed by ETA, occur together with dehydration and dehydroxylation, which were confirmed by TG/DTG and EGA studies. They also occur with annealing of the amorphous particles of meta-montmorillonite and with its recrystallization to high temperature minerals, processes, which were previously confirmed by DTA, X-ray and expansion-contraction behaviour studies.

Information on the thermal stability of the amorphous meta-montmorillonite phase and its annealing temperature were obtained by ETA under „in situ" heating conditions. It appears that the fine-structure of the amorphous phase is determined by the acid strength of the exchangeable cation.

ETA, supplemented by TG/DTG abd EGA (MS) showed that the exchangeable cations (Na^+, Li^+, Mg^{2+}, Al^{3+}) have a great influence on the thermal behaviour of montmorillonite samples. The present study confirmed the hypothesis made earlier by Grim and Kulbicki [4] that exchangeable cations and admixtures have great influence on high temperature behaviour, and consequently on the formation of high temperature phases of montmorillonite. Different high temperature behaviour due to different cations may be due to differences in the fine structure of the meta-montmorillonite phase and also due to differences size and shape of initial tactoids and flocs.

3.3. pH dependence of DCP sorption

Results demonstrating the pH dependence of the DCP sorption efficiency for the montmorillonite samples saturated with various cations are depicted in Fig. 6. It was found that the DCP sorption efficiency decreased with increasing pH in all the range of pH = 1–10. However, the most intense decrease was observed the range of pH > 6 (for the feed Na-montmorillonite) and even at pH > 4 for montmorillonite samples saturated with various cations. We supposed that the treatment of the feed Na-montmorillonite mineral during the preparation of montmorillonite samples saturated with various cations affected not only interlayer distance but also surface properties of the samples. We supposed that in the DCP sorption in the range of pH = 4–10 dominate ionized species, such as dichlorphenolate anions, whereas in the range of pH < 4 the sorption of DCP molecules dominates. It was observed that there is a pH dependence of the relative sorption ability of montmorillonite for all studied cations with the exception of the long cation distearyldimethylammonium ($DSDMA^+$). These

results are in agreement with the hypothesis that pH > 7 the anionic species DCP are present. The decrease in adsorption of DCP at pH > 4 on the hydrophilic surface of the clay is probably caused by this fact.

For the hydrophobic surface of DSDM-modified montmorillonite the relative sorption of DCP is not influenced by pH, which reflects another mechanism of sorption, as the modification of montmorillonite by this large cation (DSDM) turns its surface properties into organophilic and its ion-exchange is hydrophobic.

The sorption behaviour we found for DCP agrees fairy well with the results of the literature data on the sorption of pentachlorphenol [2]. The results and methods used for the characterization of the DCP sorption on various montmorillonite samples are described in details in our paper [5].

3.4. DCP and water release from treated montmorillonite samples

We compared TG/DTG results of selected montmorillonite samples measured before and after their treatment with DCP containing aqueous solution. Thermogravimetry results of the non-contaminated montmorillonite samples with various cations are presented in this report as Figs 4, a-d, the TG/DTG curves of the respective montmorillonite samples treated with DCP are depicted as Figs. 7.a-d. From the comparison it followed that for the feed Na-montmorillonite as well as Li^{+}, Mg^{2+} and Al^{3+} monoionic montmorillonite samples, the increased mass loss in the temperature ranges 20-140 and 50-200, 50-205 and 50-250 °C resp. may correspond to the simultaneous release of DCP and water molecules. However it should be pointed out that the amount of DCP sorbed by the samples was so small that no DCP products were detected in the evolved gas analysis by MS, as it was under the limit of MS detection.

Immediately after the treatment the DCP sorbed samples contained up to 1.5 μg of DCP/100 mg of the sample. Considering that approx. 25 mg of the sample was used for the TG analysis, up to 0.4 μg of DCP could be involved in a sample. The DCP treated montmorillonite samples were stored 4 months before their characterization by means of TG/MS.

3.5. Results of BR sorption tests

The sorption of BR by the samples saturated with various cations was compared at pH = 2.3. The experimental values of the sorbed amount (in %) of the BR from water solution are given in Table 2.

Molecules of Bengal Red (chemical composition is disodium salt of 4,5,6,7-tetrachloro-2'4'5'7'-tetraiodo fluorescein) posses both phenolic and carboxylic functional group. It is to suppose that in the environmentally relevant pH's ranging from 4 to 8 both forms of water soluble organic molecule (DCP or BR) may be adsorbed.

Table 2

Differences in sorption properties of chemically modified montmorillonite characterised by basal spacings d_{001} of their structure*

Clay Sample	DCP sorption [%]
Mont-Na-feed	43.7
Mont-Li	53.4
Mont-Cs	67.7
Mont-Mg	44.7
Mont-Al	95.0
Mont-NH_4	96.0
Mont-TMA	59.2

The relatively highest BR sorption efficiency was observed with NH_4-montmorillonite. The relatively lowest one corresponds to the feed sample of Na-montmorillonite.

The pH dependencies of the BR sorption on montmorillonite saturated with various monoionic cations are presented in Fig. 8. The relatively highest sorption in the range of pH = 1.5–10 possessed NH_4^+ montmorillonite. Although the sorbed amount of BR on this sample at the low pH = 1.5 was 81 % it reached the maximum value at 96 % at pH = 2.3 and subsequently decreased to 5 % at pH = 7.

The pH dependencies of the BR sorption on montmorillonite samples saturated with other cations was found to be similar at least in the range of pH 1.5–4.5. For all samples the relatively highest sorption efficiency was observed at pH = 2.3. We have to keep in mind that molecules of BR dye contain both phenolic and carboxylic functional group. The BR ionized species deminate in the water. When comparing the sorption of various homionic montmorillontie samples, the effect of the hydration ability of various ions the acidity of the surface as well as other factors should be taken into account.

The increased sorption of Mg^{2+} montmorillonite towards BR dye in the range of pH 4.2 may be explained the charge of Mg^{2+} ions whereas all other clay minerals were saturated with monovalent ions.

3.6. Dehydration and dehydroxylation of BR treated Na-montmorillonite

From the comparison of TG/DTG – EGA results of the feed Na-Mont sample and BR sorbed Na-Mont (see Fig. 9.a,b) if followed that the presence of BR considerably affected water binding in the Na-Mont clay and its dehydration and dehydroxylation. The release of BR was detected in the temperature range 300–600 °C, i.e. the similar range as the release of water.

4. Sorption of 2.4 dichlorphenol (DCP) and Bengal Red (BR) dye on the bentonitic clay products TIXOTON, TIXOSORB and TIXOGEL

The effect of large distearyldimethylammonium ($DSDMA^+$ ion) on the sorption of DCP and BR on bentonitic clays was investigated on two types of organophilic modified bentonitic clay samples, where 100 % and 50 % of $DSDMA^+$ resp. of the cation exchange capacity CEC were occupied by DSDMA ions. The respective bentonite samples named TIXOGEL and TIXOTON were prepared industrially by SUDCHEMIE A.S. Munich, Germany using Ca-bentonite from German localities.

The pH dependencies of the sorption efficiency of the 100 % DSDMA montmorillonite (commercial product TIXOGEL) for both DCP and BR dye (see Fig. 10, curves 1 and 2) were observed. The DCP sorption capacity on 50 % DSDMA montmorillonite (TIXOSORB product) was independent (see Fig. 10, curve 3) as well.

The pH dependency for Ca-bentonite activated with Na-carbonate solutions (called TIXOTON products presented in Fig. 10, curve 4) for comparison. The sorption efficiency of TIXOSORB product towards DCP at pH 2.3 was lower by approx. 10 % as compared with TIXOGEL product of the hydrophilic bentonites product TIXOTON. The sorption efficience at pH = 2.3 was 62 % sorption decreased in the range of pH = 1.5–10. This behaviour is consistent with the assumption that dichlorphenolate ions were present in the solution.

5. Structure characterization of TIXOSORB and TIXOGEL bentonite products

Basal spacings d_{001} determined for bentonite clay products TIXOSORB and TIXOGEL (containing $DSDMA^+$ to 50 or 100 % CEC, resp.) were 35.09 Å and 31.55 Å, resp. Consequently, a larger interlayer distance corresponds to Ca-bentonite where 50 % of CEC was exchanged for $DSDMA^+$ than for the fully saturated bentonite with $DSDMA^-$. The respective XRD patterns are presented in this report as Fig. 11.a,b.

6. The equilibrium DCP and BR dye sorption isotherm for the organophilic found modified bentonite products TIXOSORB and TIXOGEL

The experimental techniques used for determination of the equilibrium sorption isotherms and the results obtained are described the experimental part of this report and in paper [6]. The curves are presented in this report as Figs. 12 .and 13.

6.1. DCP sorption equilibrium isotherms (Fig. 12)

The DCP sorption isotherms on TIXOGEL and TIXOSORB are presented in Fig. 12. The molecules of DCP (mol. mass 163.01) enter of the organophilic TIXOGEL clay in the amount 3.96 miliMole/g. From curves in Fig. 12 it follows that the sorption behaviour can be described by Langmuir sorption model. Considerably higher DCP sorption capacity was found on TIXOSORB as compared to TIXOGEL. We supposed that the larger C-spacing of TIXOSORB enhanced the sorption of DCP.

6.2. BR sorption equilibrium isotherms (Fig. 13)

The BR sorption isotherms on TIXOGEL and TIXOSORB are presented in Fig. 13. The large molecules of the BR dye (mol. mass 1018) enter organophilic TIXOGEL samples in the amount of 1.08 milimole/g. A higher sorption of BR TIXOGEL (organic carbon OC = 29 %) was observed than that on TIXOSORB (OC = 14.5 %). In both organoclays the long chained hydrocarbon groups, that are in direct contact with each other, are leading to the formation of a predominantly partitioning phase. We suppose, that the sorption mechanism for BR is simple partitioning into the organic carbon phase. Therefore, the BR sorption was found higher for 100 % $DSDMA^+$ saturated TIXOGEL that for the 50 % saturated TIXOSORB Langmuir type sorption isotherms were found.

7. Thermal stability of DCP organophilic bentonite complexes

Thermal behaviour of the organophilic bentonite products (TIXOTON and TIXOGEL) saturated by $DSDMA^+$ to 50 or 100 % extent resp. was characterized during heating in nitrogen at the rate of 5 K/min by means of thermogravimetry TG/DTG coupled with evolved gas analysis using mass spectrometric detection.

This method enabled as to determine temperature ranges of dehydration, dehydroxylation as well as temperature ranges where organic molecules sorbed on the clays were released.

Thermal behaviour of the TIXOSORB and TIXOGEL containing $DSDMA^+$ and DCP in various amount were compared with the thermal behaviour of the feed hydrophilic product TIXOTON, prepared by the treatment of Ca-bentonite with Na-carbonate solution. The results are published in [7] and are briefly described in this report.

7.1. TIXOTON bentonite product (Figs. 14)

The mass loss in the temperature range 40-100 °C (5.3 % of the sample mass) corresponds to the dehydration of the sample. The hydroxylation took place in the temperature range 280-700 °C. From the mass spectra of the evolved gases (m/z = 44 carbon dioxide) it followed that in the temperature above 300 °C the decomposition of calcite initially involved in the natural bentonitic clay sample took place.

7.2. TIXOSORB bentonitic product (Figs. 15)

On sample heating in nitrogen the dehydration was observed in the temperature range from 40 to 100 °C (mass decrease 1.46 % of the total sample mass). The dehydroxylation of the sample took place at temperatures above 300 °C. In this temperature range the release of CO_2 was also detected, corresponding to the decomposition of carbonate initially involved in the clay. The release of organic compounds resulting after thermal degradation of $DSDMA^+$ ions intercalated into montmorillonite was detected in the temperature range of 200-500 °C. (Corresponding DSMA fragments detected by MS were m/z = 57, 81, 83 and 85.)

7.3. DCP containing TIXOSORB (Figs. 16)

As it follows from the TG results, the sorption of DCP caused the decrease of water content in TIXOSORB bentonite, and the increase (by 5 % sample mass) of the amount of organic molecules. (The content of organic molecules in TIXOSORB before and after the DCP sorption were 28.2 and 33.2 % respectively.)

As it follows from the MS spectra of the released volatiles, the release of DCP (corresponding m/z = 162, 176 and 178) from the TIXOSORB sample was observed above 200 °C, reaching the maximum release rate at 300 °C.

Thermal degradation of TIXOSORB containing DSDMA was observed above 300 °C, as confirmed by the DTG maximum at 305 and 390 °C. The release of water originating from the dehydroxylation was observed by MS (m/z = 18) in the temperature range of 250-600 °C. The decomposition of carbonates was detected MS (m/z = 44 corresponding to CO_2 release) in the temperature range of 400 – 620 °C.

7.4. TIXOGEL bentonite products (Figs. 17)

As is follows from the TG results, the organophilic bentonite containing 100 % DSDMA involved no free water molecules. The amount of organic phase released on heating in the temperature range 200-400 °C (the maximum rate at the DTG maximum 376 °C) was determined as 38.6 % of the total sample mass.

The characteristic m/z of the degradation products of DSDMA released from TIXOGEL are m/z = 57, 85, 98, 112. These fragments corresponds to the aliphatic long chain amines.

7.5. DCP containing TIXOGEL (Figs. 18)

The total amount of organic phase in the DCP containing TIXOGEL was determined as 48.3 % of the total sample mass. Consequently 9.7 % of the total sample mass corresponded to DCP sorbed the sample. The characteristic temperature for the thermal decomposition of DCP-TIXOGEL determined by TG/DTG are 228, 316, 377 °C.

From the MS spectra it followed that the dehydroxylation of the clay mineral as well as the CO_2 release started at 300 °C. The release of DCP detected by MS (corresponding m/z = 162, 176 and 178) was observed already in the temperature range of 200-300 °C. No significant differences between the MS spectra corresponding to the DCP released from DCP containing TIXOGEL and TIXOSORB were observed.

8. Thermal stability of BR organophilic clay complexes

8.1. BR containing TIXOSORB (Fig. 19)

From TG results it followed that the dehydration of the sample (corresponding to the loss of 2.55 % or total sample mass) took place in the temperature range 40-100 °C. The mass loss observed in the temperature range 220-600 °C reflected the desorption of organic compounds from the sample, their degradation, dehydroxylation of the montmorillonite substrate

well as thermal decomposition of calcite initially present in the clay sample. From the difference of the mass observed on heating of BR – containing TIXOSORB and TIXOSORB before the BR-sorption, it followed that the amount of 11.8 % BR was sorbed by this clay product.

The MS spectra of the evolved gases during the heating revealed that the desorption of BR from TIXOSORB took place in the temperature range of 200-310 °C (corresponding m/z = 127, 142) whereas the release of DSDMA degradation products took place in the range of 300-500 °C (corresponding m/z = 55, 57, 58, 83, 85). Water release due to dehydroxylation of the sample (corresponding m/z = 18) was observed in the range 400-600 °C, the CO_2 release (corresponding m/z = 44) in the range 450-620 °C indicated thermal decomposition of calcite present in the initial clay.

8.2. BR containing TIXOGEL (Figs. 20)

From TG results it followed that the dehydration of the sample (corresponding to the loss of 0.8 % or total sample mass) took place in the temperature range 50-90 °C. The mass loss observed in the temperature range 220-600 °C reflected the desorption of organic compounds from the sample, their degradation, dehydroxylation of the montmorillonite substrate well as thermal decomposition of calcite initially present in the clay sample. From the difference of the mass observed on heating of BR – containing TIXOGEL and TIXOGEL before the sorption it followed that the amount of 11.6 % BR was sorbed by this clay product. Consequently, the BR amount sorbed on TIXOSORB and TIXOGEL was the same.

The MS spectra of the evolved gases during the heating revealed that the desorption of BR from TIXOGEL took place in the temperature range of 200-480 °C (corresponding m/z = 127, 142) whereas the release of DSDMA degradation products took place in the range of 300-500 °C (corresponding m/z = 55, 57, 58, 83, 85). Water release due to dehydroxylation of the sample (corresponding m/z 18) was observed in the range 250-300 °C was ascribed to the thermal decomposition of BR molecule, whereas in the range 450-620°C indicated thermal decomposition of calcite.

9. Morphology and microstructure changes

Results of Emanation Thermal Analysis of TIXOTON, TIXOSORB and TIXOGEL samples characterized differences in their morphology changes due to the degradation of DSDMA, dehydroxylation of the mineral substrate as well as annealing of highly diordered meta-phase structure. In the presence of DCP sorbed on TIXOSORB clay product the dehydroxylation and structure annealing took place in a more narrow temperature range. Moreover the formation of high temperature phases was enhanced. These results were presented in [7,8].

The developed mathematical model made it possible to evaluate the ETA curves characterizing morphology changes of the clay minerals treated with various cations and contaminated with different organic compounds.

The model and its application to the characterization of disordered materials by ETA is published in [21].

The decrease of interlayer distance due to of dehydration was characterized by the decrease of the radon release rate. Dehydroxylation and formation of meta-montmorillonite was reflected by an radon release rate increase, indicating the increased disorder of the clay mineral structure. Annealing of highly disordered meta-phase structure was characterized by the decrease of radon release rate, the intensity of the changes and temperature range ΔT in which the annealing take place were used as parameters for the description of the microstructure changes.

It was shown that the morphology changes observed in the series of the montmorillonite samples with various cations are closely related with sorption properties of the clays towards organic compounds.

10. Characterization of bentonite clays contaminated with various organic compounds

Bentonite clay product TIXOTON was used in the investigation of sorption behaviour towards DCP and BR. The clay contained min. 65 % Ca-montmorillonite which was activated by Na-carbonate, 6.5 % of calcite, 5.4 % of iron-oxide-hydroxide, quartz, mica and amorphous silica acid (not detectable by XRD).

As amount of sorbed organic compounds on the natural Ca-montmorillonite was negligible, the sodium activated product (TIXOTON) prepared from the Ca-bentonite product supplied by Sudchemie, Germany was used in this study.

The clay material was treated with four organic reagents, representing different types of environmentally relevant compounds encountered in municipal repositories. These are acetic acid, representing acids formed during the so called acid fermentation of organic substances; diethylamine, representing aliphatic amines and other bases formed at various decomposition processes; ethyleneglycol, representing alcohols and neutral polar substances encountered in leakage waters; and *n*-heptane, an important component of gasoline, a car fuel. The latter also represents other non-polar hydrocarbons, which are widely used as organic solvents. Aqueous solutions (5%) of the first three reagents were employed in the present study. This is the maximum concentration of these compounds, which may be encountered in leakage waters [9]. Heptane and water do not mix. Therefore, a neat liquid was used in this study.

10.1. Thermogravimetry characterization of contaminated clays

TG/DTG curves of TIXOTON treated with the various organic compounds were recorded in argon atmosphere, to avoid oxidation of the organic matter adsorbed by the clay. The TG data are summarised in Table 3. They all show two stages of mass- loss. According to the EGA (MS) curves, the first stage is attributed to the dehydration of interlayer and surface water and the second stage to dehydroxylation and evolution of organic matter. Mass-loss in the second stage of organo treated samples is always higher than in the untreated, indicating that all reagents were adsorbed by TIXOTON. However, they could be located either in the interlayer space of montmorillonite (diethylammonium cations and ethyleneglycol molecules), on its broken bonds (acetate anions) and on surfaces of other components of the TIXOTON (acetate and *n*-heptane).

Table 3

Basal spacings (d_{001}) of montmorillonite (nm) in TIXOTON before and after treatment with various organic compounds and after their regeneration by neutralisation

TIXOTON treatment	Basal spacings (nm) After freeze drying	Basal spacings (nm) after neutralisation
Untreated	1.49	-
Acetic acid	1.63	1.80
Diethylamine	1.34	1.35
Ethyleneglycol	1.58	-
Heptane	1.49	-

The basal spacings (d_{001}) of the montmorillonite fraction in the different TIXOTON samples are summarised in Table 4.

Table 4

Thermal mass-loss in the TG curves of TIXOTON untreated and treated with various organic compounds

TIXOTON Treatment	Temperature interval [°C] and Mass-loss [%]	
Untreated	20 – 120 6.51	200 – 750 2.69
Acetic acid	20 – 120 9.52	200 – 750 12.03
Diethylamine	20 – 280 1.0	280 – 750 7.96
Ethylenglycol	20 – 120 3.60	300 – 750 19.5
n-heptane	20 – 120 4.72	300 – 750 8.5

The strongest effect on the montmorillonite basal spacing was found after the treatment with the acetic acid solution. During this treatment interlayer Na^+ was exchanged by H^+. According to Barshad [10] a small fraction of the adsorbed protons enter the interior of the crystal to displace Al^{3+} which is now able to exchange residual adsorbed protons.

Clay minerals are sparingly soluble. Their aqueous dissolution is catalysed by protons [11]. Analysis of the supernatant revealed that the acid dissolves Al and Si from the octahedral and tetrahedral sheets of the clay, respectively [12,13]. With time, released Al is adsorbed by the clay, probably by the mechanism of cation exchange. The presence of Al^{3+} in the interlayer space of montmorillonite leads to a high water adsorption, as follows from the high thermal mass-loss in the dehydration stage below 200°C, shown by the TG results (Table 3) and the high basal spacing in the XRD pattern (Table 4). After titrating H-Al-TIXOTON suspension with a dilute solution of ammonium hydroxide (0.01 M) the basal spacing of mont-

morillonite increased to 1.8 nm. This is probably due to the fact that basic NH_3 molecules penetrated into the highly acidic interlayer space.

In aqueous solutions the basicity constants of aliphatic amines are somewhat stronger than that of ammonia. When montmorillonite is treated with aqueous solutions of aliphatic amines, ammonium cations are obtained in the cation exchange sites of the clay [14]. In an aqueous solution of diethylamine, part of the dissolved amine is protonated forming diethylammonium cations. During the treatment of TIXOTON with the aqueous solution of diethylamine, interlayer Na^+ is exchanged by diethylammonium cation. The XRD measurements show a lowering of d_{001} basal spacing from 1.49 nm to 1.34 nm (Table 4). The TG curve shows a very low mass-loss in the dehydration stage (Table 3). According to Yariv [15] hydrophobicity and large size of organic cations, lead to the disruption of the hydration structure inside the interlayer space of smectite minerals. Consequently, organic aliphatic ammonium cations restrict any swelling of the montmorillonite to 1.3-1.4 nm. In addition to electrostatic interactions, aliphatic diethylammonium cations are strongly bonded to the clay surface by van der Waals forces. These cations were not replaced by H^+ during titration of diethylammonium- TIXOTON suspensions with dilute acetic or hydrochloric acids. Montmorillonite in the acid treated diethylammonium-TIXOTON did not swell above 1.35 nm (Table 3).

The interaction of TIXOTON with ethyleneglycol solution caused a slight increase in the basal spacing of the montmorillonite to 1.58 nm (Table 4). This compound, although not cationic, has high dipole moment and dielectric constant (Table 5) and is adsorbed into the interlayer space.

Table 5

Organic reagents used in the present study, their properties and pH of their 5% aqueous solutions

Solution	Representing compound type	pH of 5% aqueous solution	Dielectric constant	Dipole moment	Solubility in water
Acetic acid 5 %	Organic acid	2.5	6.1	1.7	Unlimited
Diethylamine 5 %	Aliphatic amine organic base	12.1	3.6	1.5	Unlimited
Ethyleneglycol 5 %	Polyhydric alcohol Neutral-polar	4.2	38.7	2.3	Unlimited
n-heptane 100 %	Aliphatic hydrocarbon neutral non-polar	-	1.0	0	Water insoluble

Brindley [16] obtained with a neat ethyleneglycol and bentonite a basal spacing of 1.7 nm. According to MacEwan [17] the organic dipolar molecules are oriented between the surfaces of the clay in positions as flat as possible. A basal spacing of 1.7 nm is compatible with two layers of ethyleneglycol in the interlayer space. We observed a smaller swelling, probably because of using an aqueous solution. The boiling point of ethyleneglycol is 197°C. It is therefore obvious that the mass-loss in the first stage of the TG curve (below 120°C) is due to

evolved water. Table 2 shows that the amount of water after the treatment (3.6%) is less than before the treatment (6.5%), indicating that the adsorbed ethyleneglycol replaces water in the interlayer space. Only Si and no Al were observed by chemical analysis of the supernatant.

Dipole moment and dielectric constant of *n*-heptane are low (Table 5) and as expected, no chemical interactions of *n*-heptane with the montmorillonite component of the TIXOTON were detected by IR spectroscopy or XRD (Table 3). According to Clements [18] there are no interactions between non-polar organic molecules and interlayer cations of montmorillonite. The heptane molecules were adsorbed on the external oxygen planes of montmorillonite tactoids and on surfaces of other components of the TIXOTON. Janczak and Bialopiotrowicz reported [19] about small changes of the wetting power of the silicate surface caused by this type of organic solvents.

No effects on Si-O, Al-O and AlO-H bands in IR spectrum of montmorillonite in the feed TIXOTON were found after the treatment with the four organic compounds. This is an indication that the montmorillonite framework was almost not affected by the treatment with the organic compounds.

10.2. Characterization of microstructure using ETA data

The ETA curves of TIXOTON before and after treatment with the four organic compounds, recorded in argon atmosphere, are depicted in Fig. 21. In the ETA curve of the untreated TIXOTON the first maximum of radon emanation rate appears at a higher temperature compared with the curve of Na-montmorillonite (120 instead of 79 °C). This is due to the fact that TIXOTON contains iron hydrous-oxide and amorphous silica, which also lose at this stage physically adsorbed water but, unlike montmorillonite, do not collapse. In the range 250-600 °C TIXOTON shows three maxima (at 360, 550 and 600 °C) in the radon emanation rate, which do not appear in the curve of Na-montmorillonite. These breaks are attributed to the presence of iron hydrous-oxide and amorphous silica. The dehydroxylation of these compounds leads to an increase in the rate of radon emanation. With the rise in temperature the amorphous anhydrous oxides undergo crystallisation, followed by crystal growth [20], which decrease the rate of radon emanation. A break at 650 °C corresponds to the dehydroxylation of Na-montmorillonite followed by the annealing of the amorphous particles of the metaphase.

The ETA curves of the organo-TIXOTON complexes show that the aqueous solutions purified the samples to some extent from the non-montmorillonite components (Fig. 21, curves 2, 3 and 5). Acetic acid was the most efficient purifying agent (curve 3) and diethylamine was the least. It seems that the ETA curve of diethylammonium-TIXOTON (curve 2) results from the overlapping of radon emanation from all components of the clay material. The breaks at 330-600 °C are attributed to the dehydroxylation, crystallisation and crystal growth of the iron hydrous-oxide. The break at 800 °C is attributed to the amorphization and annealing of montmorillonite. Silica dissolves in alkaline solutions and it probably dissolved during the preparation of this sample. Aliphatic hydrocarbons do not dissolve the mineral components of TIXOTON. The ETA curve of *n*-heptane treated TIXOTON shows above 250 °C broad breaks (curve 4) probably due to the thermal charring of the residual heptane. The charcoal, which covers the particles, probably interferes to the different reactions.

In the first stage dehydration, the four organic treated samples show that the emanation rate decreases, indicating that the mass-loss is accompanied by collapse of the smectite. This is in contrast to the behaviour of samples saturated with inorganic cations, which first show an increase in the emanation rate and later show a decrease [22]. This supports the idea that the interlayer water structure is affected from the hydrophobic environment of the organic reagent [11]. At 120-250 °C there is a sharp rise in the emanation rate. This was not observed in the ETA curves of montmorillonite from Wyoming [23] and we attribute this rise to the evolution of water adsorbed on residual amorphous phases, which were not separated during the preparation of the organo complexes. In the temperature range of the second mass-loss stage (Table 3), the emanation rates continue to increase but to a smaller extent. At this stage organic matter and structural water are evolved. An amorphous meta-montmorillonite, which contains framework vacancies, is obtained during the dehydroxylation.

The decrease in the rate of emanation above 650 °C is diagnostic for the annealing of the amorphous meta-clay. In our previous study of the ETA of Wyoming montmorillonite saturated with different metallic cations we showed that the temperature at which the annealing begins, depends on the exchangeable cation. With mono-valent cations it begins at 650 °C but with di- or poly-valent cations it begins at about 800 °C. We attributed the different behaviour to differences in the fine structure of the amorphous phases and to differences in the size of the initial tactoids. Figure 21 shows that this temperature also depends on the treatment with the organic compound. Untreated TIXOTON shows the annealing from 650 °C. Annealing begins at a slightly higher temperature after the treatment with *n*-heptane, which is not adsorbed by montmorillonite. This reaction begins at 75 °C after the treatment with ethyleneglycol, which replaces water in the interlayer space. After treatments with diethylamine or acetic acid, which result in cation exchange reactions, the beginning of annealing is shifted to above 800 °C.

The reactions above 1000 °C are associated with the thermal recrystallization of the meta-clay phase and are affected by the composition of TIXOTON. Several breaks appear in the curve of untreated TIXOTON whereas only one break appears in the samples, which were purified. These results are published in [22].

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6. Description of project impact

Presentation in conferences and published articles arose a strong interest in the communities of clay scientists and environmentalists.

Professor Balék organized and chaired a workshop on *Thermal Analysis in Environmental Science* which took place during ESTAC 6, in Grado, Italy, on September 13, 1994. Professor Yariv was invited to present a lecture on the thermo-IR-spectroscopy for the study of the fine structures of complexes obtained from hazardous pollutants adsorbed by clay mineral. After the lecture, Professor Yariv was invited to prepare an advanced review on this subject. The review has been published in **Thermochimica Acta** (Vol. 274, pp. 1-35, 1996), and is now enlarged into a full chapter to be published in a special book on organo-clays.

Professor Yariv presented a lecture on this analytical method in the Workshop on Environmental Science in the biannual Conference of the "Israel Association for the Advancement of Mineral Engineering," Eilat, 9 November - 1 December 1994. A scientific paper was published in Hebrew in the Proceedings of the Conference and in the journal **Chimia**.

Professor Balék, Chairman of ICTAC Group for Environment studies by Thermal Analysis, was invited by the ICTAC 11 Organizing Committee to organize and chair a workshop on environmental problems. The workshop took place in August 1996, in Philadelphia, PA, USA, during the International Congress for Thermal Analysis, but Professor Balék, who arranged everything for this workshop, could not attend the conference for personal reasons. In this workshop Professor Yariv presented a lecture on the mechanochemical adsorption of hazardous materials by clay minerals. In December 1996 Professor Yariv presented a similar lecture on the mechanochemical adsorption of hazardous materials by clay minerals in Syncrude Oil Company Laboratories, Edmonton, Alberta, Canada. A lecture on the mechanochemical adsorption of hazardous materials by clay minerals was given by Mrs. Dalia Ovadyahu in February 1996, in the Meeting of the Israel Mechanochemical Group in Jerusalem. Mrs. Ovadyahu was a Ph.D. student of Professor Yariv. Professor Yariv is invited by the Organizing Committee of Solid State Chemistry-2000, Prague to present a key lecture on the mechanochemistry adsorption of hazardous materials by clay minerals.

7. Project Activities/Outputs

In the ESTAC 6 Meeting in Grado, Italy, a poster on the IR study of the adsorption of 2,4 dichlorophenol from organic solvent was presented by Mrs. Dalia Ovadyahu, from Jerusalem (a Ph.D. student of Prof. Yariv).

In the Meeting of the Israel Group of Mechanochemistry, Jerusalem, February 1995, Mrs. Dalia Ovadyahu (a Ph.D. student) presented a lecture on "The mechanochemistry adsorption of phenol by smectites."

In EUROCLAY ' 95 (Leuven, August 20-24, 1995) a poster "Electronic and IR-spectroscopy study of the basicity of the oxygen plane of Na-smectites treated with acridine organo was presented by Mrs. Diana Garfinkel-Shweky from Jerusalem, Jerusalem (a Ph.D. student).

In the Israel-Hungary binational conference on thermal analysis and calorimetry of materials, Ein-Boker, March 1996, Mr. Ahmed Nasser from Bet-Dagan (a Ph.D. student) presented a poster on "Differential thermal analysis of montmorillonites treated with alacholor."

In the Neubrandenburger (Germany) Industriemineral-Symposium, March 1997, Professor Yariv presented an invited lecture on "Surface acidity of clay minerals: Industrial examples." Some of the data in this presentation included information from the study of absorption of hazardous materials by clay minerals.

In the second Mediterranean Clay Meeting, Aveiro, Portugal, September 1998, Professor Yariv presented an invited lecture on "Adsorption of cationic dyes by smectite minerals." Some of the data in this presentation included information from the study of surface basicity of the O-planes, which is part of the present investigation on the adsorption of hazardous materials by clay minerals.

List of scientific publications and contributions to scientific meetings resulting from the US AID research Project No. C-12-219

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8. Project productivity

Most of the project was completed and experimental results covered adsorption of hazardous materials of different types by soil and clays.

Great effort has been made to develop techniques for the characterization of sorption properties of natural and modified clays by sophisticated thermal methods (ETA, DTA, TG). The surface basicity of the swelling clay minerals (smectites and to some extent also vermiculite), which were used in the present research, was studied. Also different methods of adsorption of organic hazardous pollutants and industrial wastes by clay minerals were examined by IR-spectroscopy and X-ray diffraction. For example, adsorption from solvents were compared with adsorption by mechanochemical techniques. We studied the complexes obtained in both techniques using the sophisticated thermal analysis (ETA) developed for organic clays. We studied (by thermo-IR and X-ray) the fine structures of the organo-clay complexes which were obtained in Rez from thermal analysis in order to obtain a better understanding of the mechanism of adsorption of hazardous materials by clays and soils.

The knowledge about the adsorption of surfactants by clay minerals was collected from the literature and is included in the review article "IR-spectroscopy and thermo-IR-spectroscopy in the study of organo-clay complexes."

9. Future work

In both laboratories we are planning to continue our collaboration. First, we have collected many results that we still have to discuss. For this purpose Professor Yariv will spend a few weeks in September in Rez. Secondly, we have in mind to continue with the same adsorption studies of hazardous compounds by clay minerals.

The mechanochemical adsorption which was developed has been shown to be an excellent method for the study of adsorption of any kind of organic material by different expanding and non-expanding clay minerals. In Jerusalem, we are now using this technique to study the adsorption of dyes by smectite minerals. We believe that this technique will become increasingly popular among clay scientists.

The Emanation Thermal Analysis proved to be a fundamental technique in the study of the thermal changes and stability of organo-clay complexes. We believe that in the future it will always accompany DTA and TG studies as a complementary technique. This is especially true for agrochemicals adsorbed on clay minerals.

Caption to Figures

Fig. 1. Thermal behaviour of beidelite during heating in dry air

Fig. 2. Thermal behaviour of montmorillonite during heating in dry air

Fig. 3. Thermal behaviour of laponite during heating in dry air

Fig. 4 Characterization of water release during nitrogen heating of samples

(a) feed Na-montmorillnite (Mont-Na), (b) Mont-Li, (c) Mont-Mg, d) Mont-Al

Fig. 5. Emanation Thermal Analysis of montmorillonite samples saturated with various cations

1 - feed Na-montmorillnite (Mont-Na), 2 - Mont-Li, 3 - Mont-Mg, 4 - Mont-Al

Fig. 6. pH dependencies of DCP sorption on homoionic montmorillonite samples saturated with various cations

Fig. 7. Thermogravimetry and evolved gas analysis results characterizing the release of DCP and water during heating in nitrogen of the DCP treated montmorillontie samples with cations

(a) feed Na-montmorillonite (DCP-Mont-Na), (b) DCP-Mont-Li, (c) DCP-Mont-Mg, (d) DCP-Mont-Al

Fig. 8 pH dependencies of BR sorption on montmorillonite samples saturated with various cations

Fig. 9. Characterization of thermal behaviour of Na-montmorillonite during heating in nitrogen of Na-montmorillonite non treated (a) and treated with BR containing aqueous solution (b)

Fig. 10. Comparison of pH dependencies for DCP and BR sorption on modified bentonite products:

Curves 1 and 2 correspond to the sorption of BR and DCP on TIXOGEL, resp. curves 3 and 4 to correspond the sorption of DCP on TIXOSORB and TIXOTON products, resp.

Fig. 11. X-ray diffraction patterns of the modified organophilic bentonite products TIXOSORB (a) and TIXOGEL (b)

Fig. 12. Equilibrium sorption isotherms of DCP on TIXOSORB (curve 1) and TIXOGEL (curve 2)

Fig. 13. Equilibrium sorption isotherms of BR dye on TIXOSORB (curve 1) and TIXOGEL (curve 2)

Fig. 14. Thermal stability of TIXOTON bentonite products characterized during heating in nitrogen by thermogravimetry TG/DTG coupled with MS

Fig. 15. Thermal stability of TIXOSORB orgahophilic bentonite products characterized during heating in nitrogen by thermogravimetry TG/DTG coupled with MS

Fig. 16. Thermal stability of DCP treated TIXOSORB characterized during heating in nitrogen by thermogravimetry TG/DTG coupled with MS

Fig. 17. Thermal stability of TIXOGEL orgahophilic bentonite products characterized during heating in nitrogen by thermogravimetry TG/DTG coupled with MS

Fig. 18. Thermal stability of DCP treated TIXOGEL characterized during heating in nitrogen by thermogravimetry TG/DTG coupled with MS

Fig. 19. Thermal stability of BR treated TIXOSORB characterized during heating in nitrogen by thermogravimetry TG/DTG coupled with MS

Fig. 20. Thermal stability of BR treated orgahophilic bentonite products characterized during heating in nitrogen by thermogravimetry TG/DTG coupled with MS

Fig. 21. Results of emanation thermal analysis characterizing microstructure changes taking place during heating argon of TIXOTON product before and after treatment with different organic compounds

curve1: TIXOTON – non treated, curves 2–5: TIXOTON treated with diethylamine, acetic acid, n-heptan and ethylenglycol, respectively

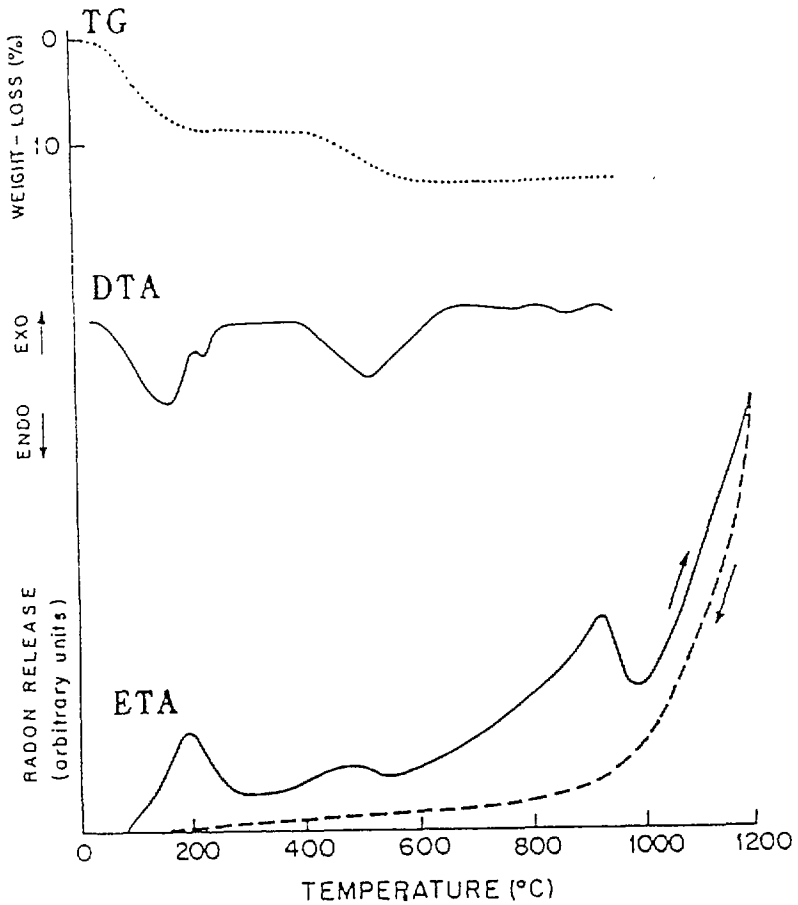


Fig. 1 Thermal behaviour of beidelite during heating in dry air

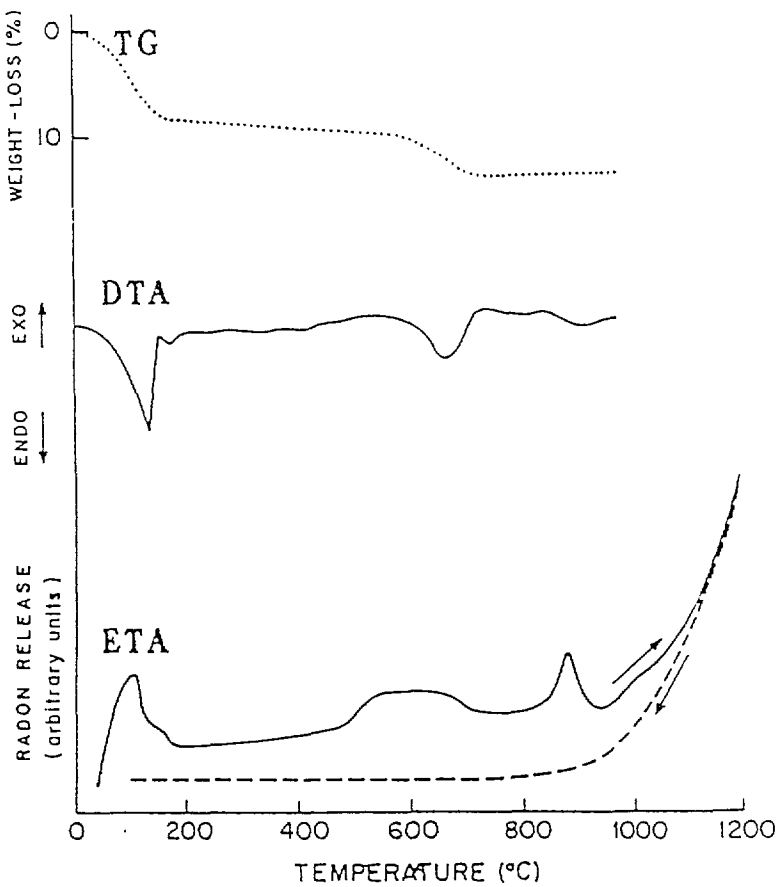


Fig. 2. Thermal behaviour of montmorillonite during heating in dry air

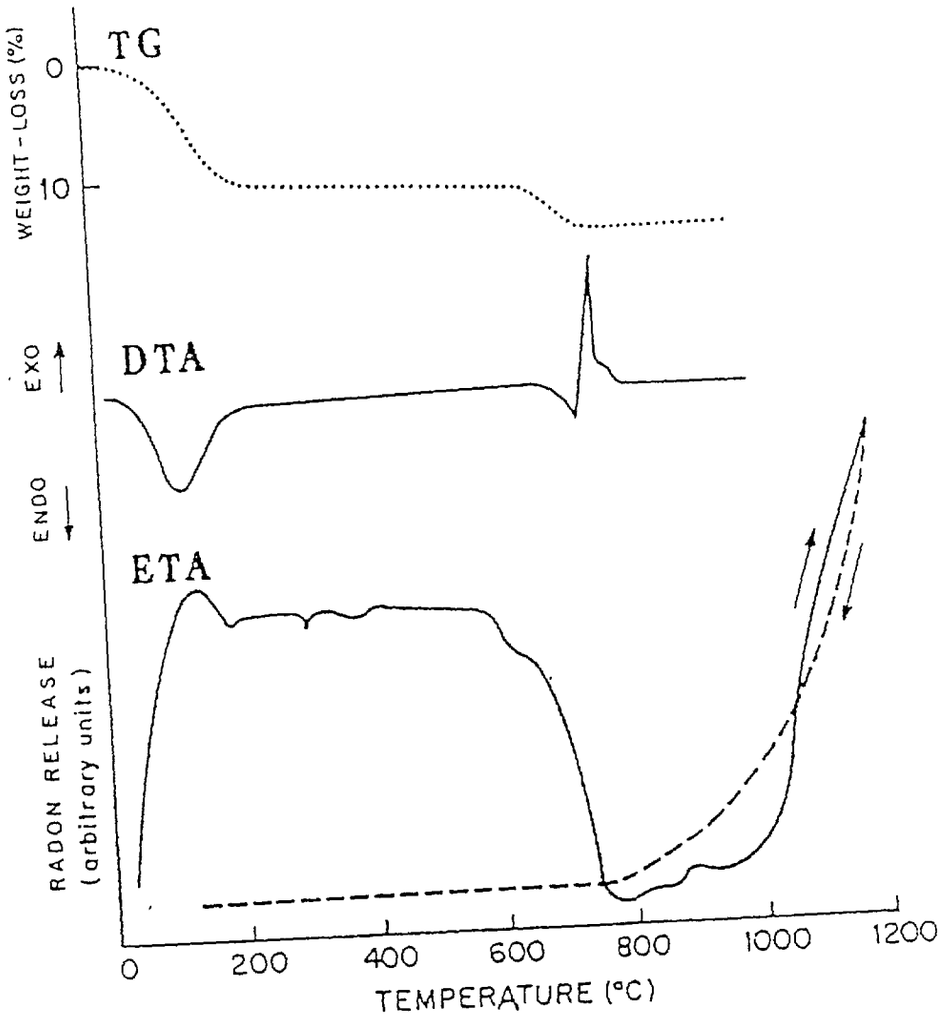
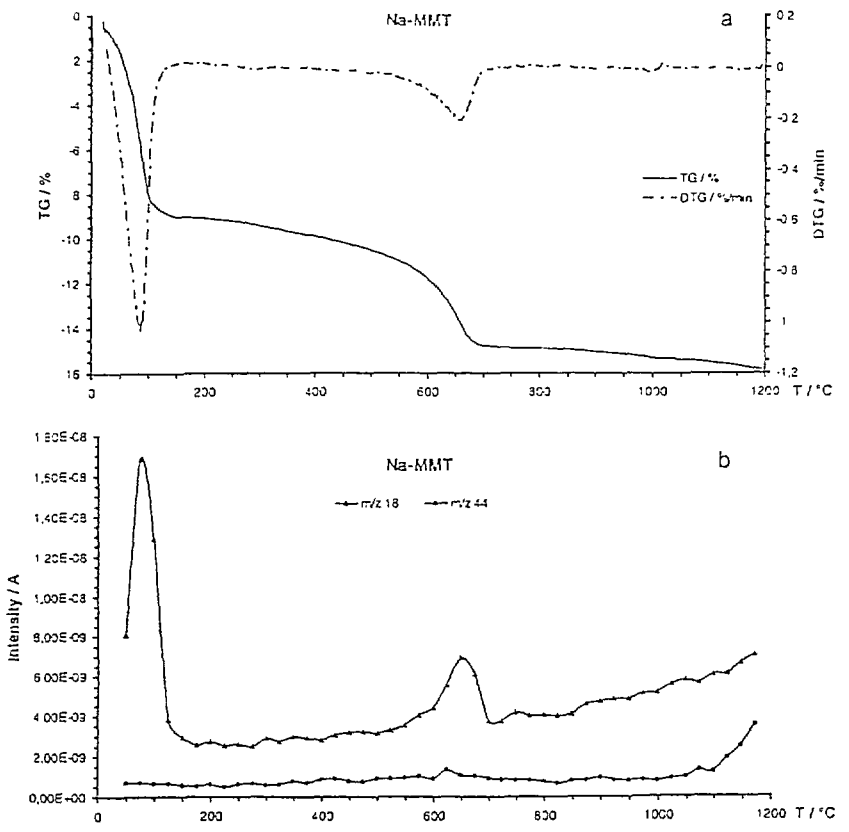


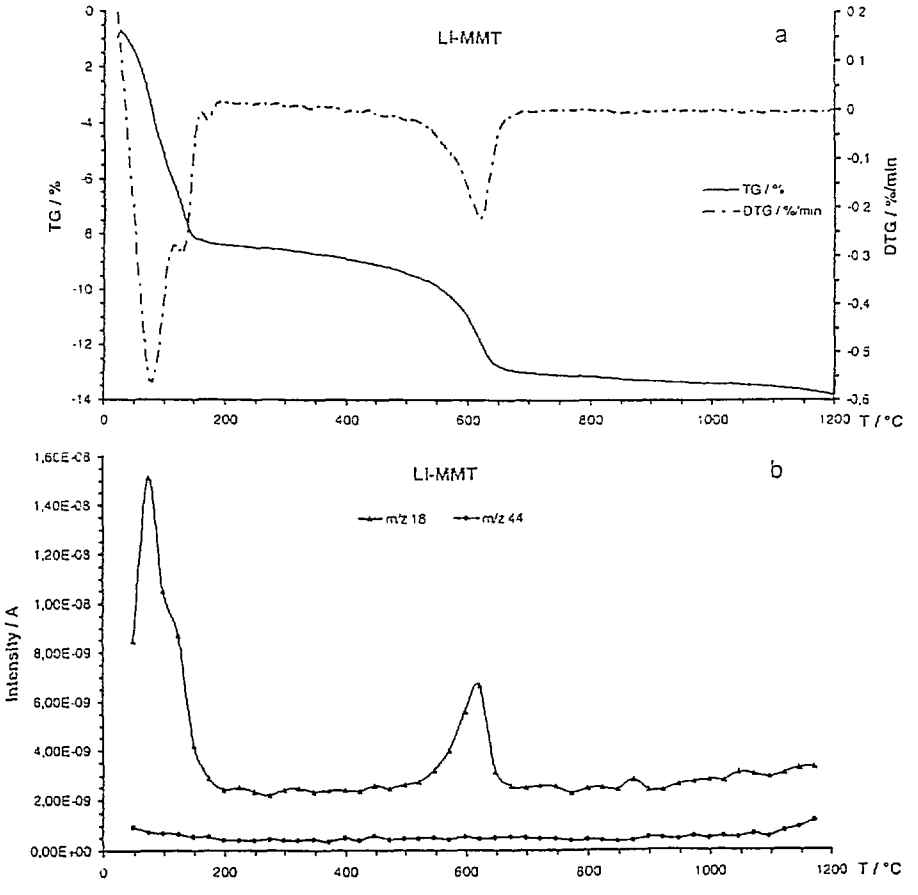
Fig. 3. Thermal behaviour of laponite during heating in dry air

Characterization of water release during nitrogen heating of samples

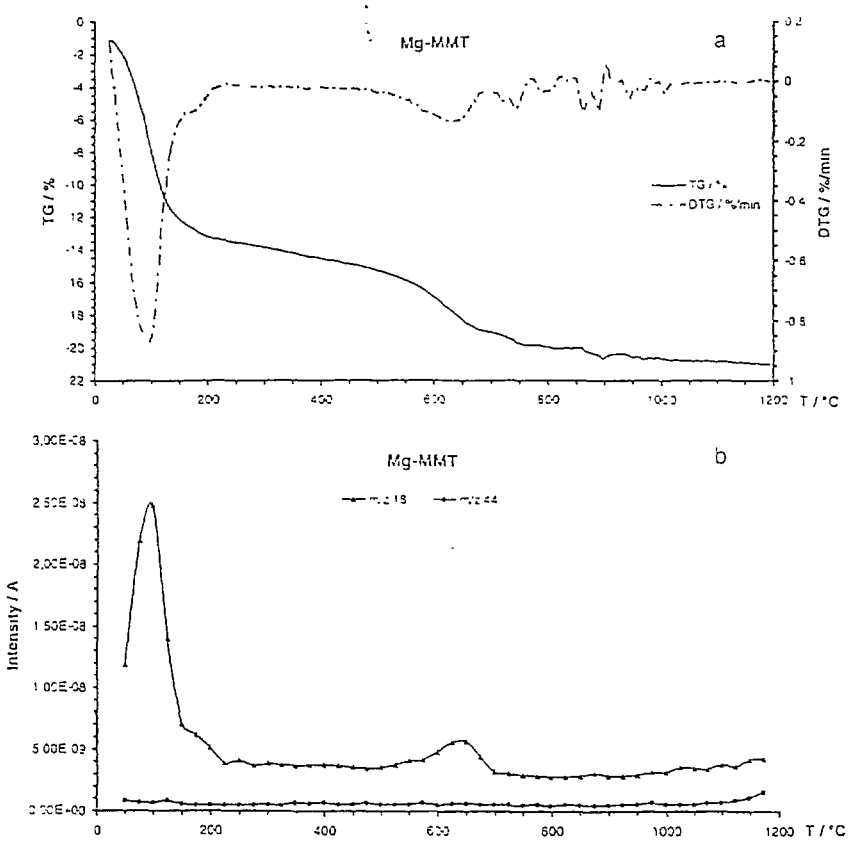
(a) feed Na-montmorillnite (Mont-Na), (b) Mont-Li, (c) Mont-Mg, d) Mont-Al



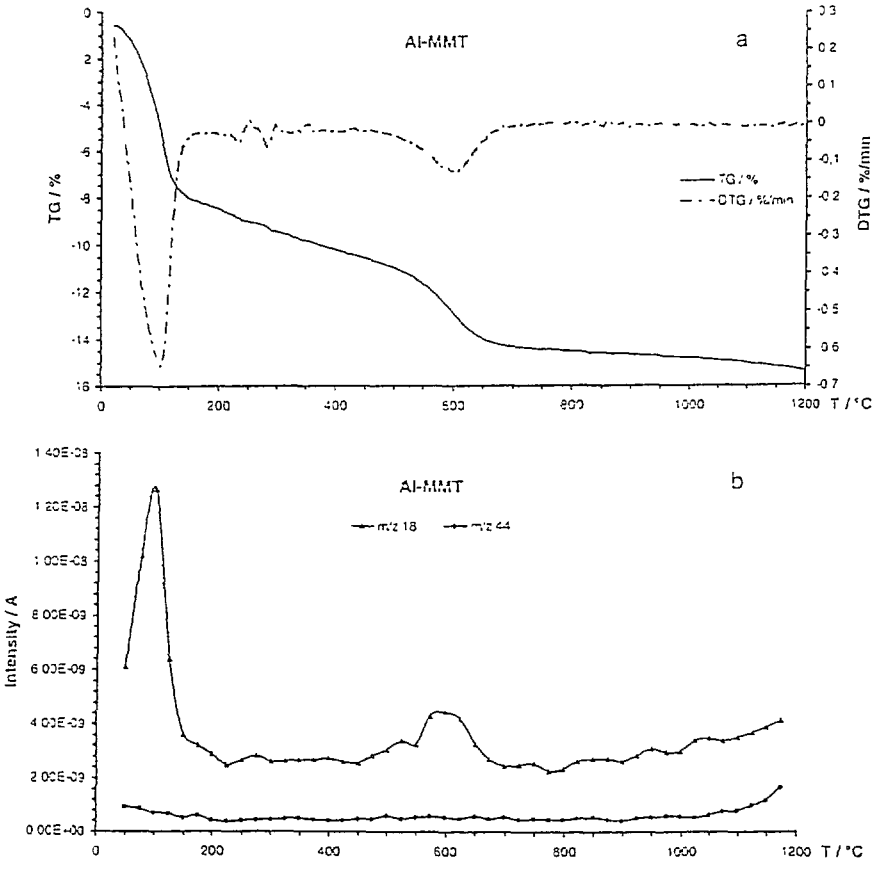
l Characterisation of water release taking place during heating in nitrogen of Na-montmorillonite (Upton, Wyoming, USA)
a) TG and DTG curve, b) EGA curve (mass spectrometric detection M 18 corresponding to water release, 44 to carbon dioxide)



Characterisation of water release taking place during heating in nitrogen of montmorillonite saturated with lithium ions; a – TG and DTG curve, b – EGA curve (mass spectrometric detection M 18 corresponding to water release, 44 to carbon dioxide)



Characterisation of water release taking place during heating in nitrogen of montmorillonite saturated with magnesium ions; a – TG and DTG curve, b – EGA curve (mass spectrometric detection M 18 corresponding to water release, 44 to carbon dioxide)



Characterisation of water release taking place during heating in nitrogen of montmorillonite saturated with aluminium ions; a – TG and DTG curve, b – EGA curve (mass spectrometric detection M 18 corresponding to water release, 44 to carbon dioxide)

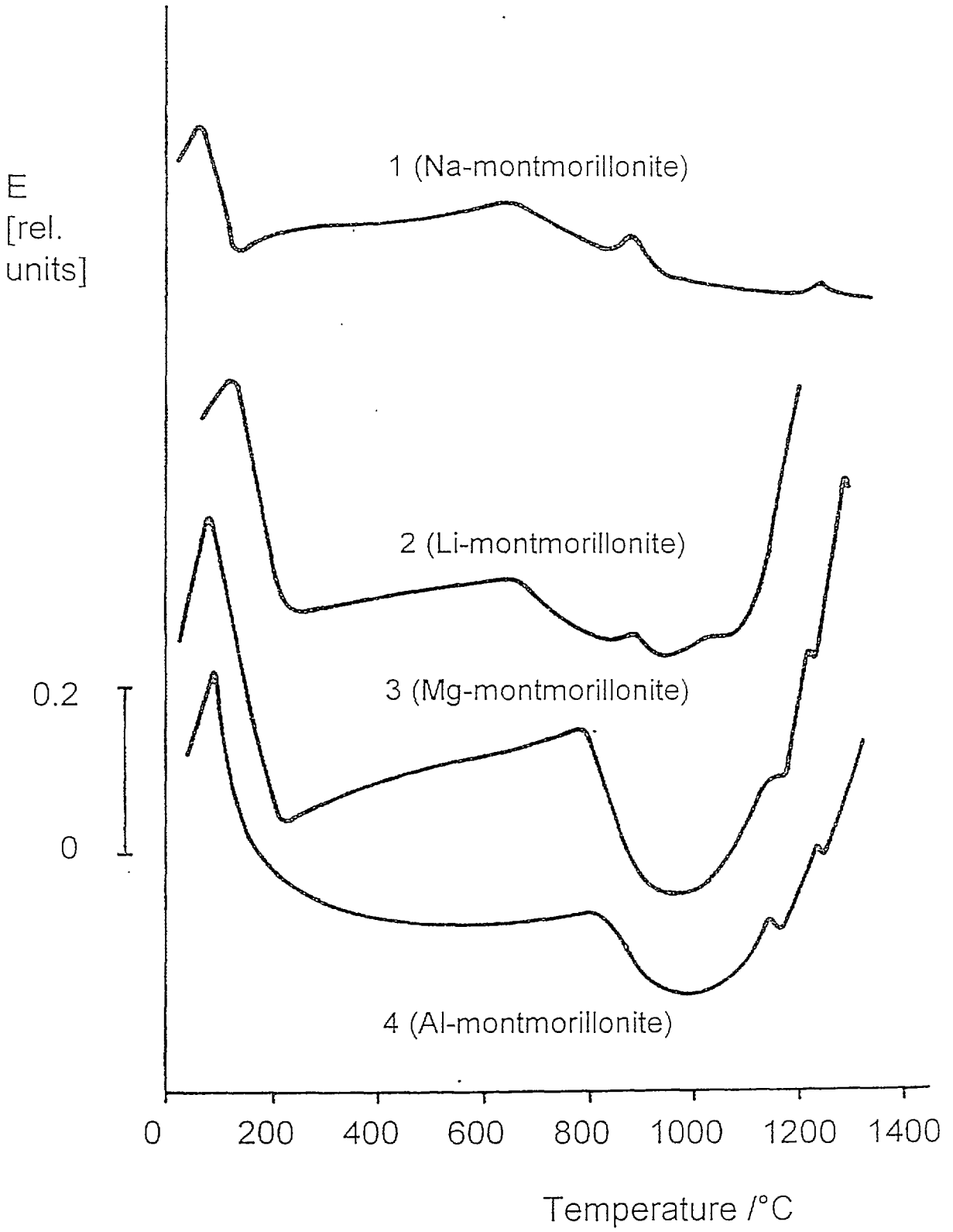


Fig. 5 Results of ETA of montmorillonite samples during heating in argon; 1 – Na-montmorillonite (Upton, Wyoming, USA), 2 – montmorillonite saturated with lithium, 3 – montmorillonite saturated with magnesium, 4 – montmorillonite saturated with aluminium

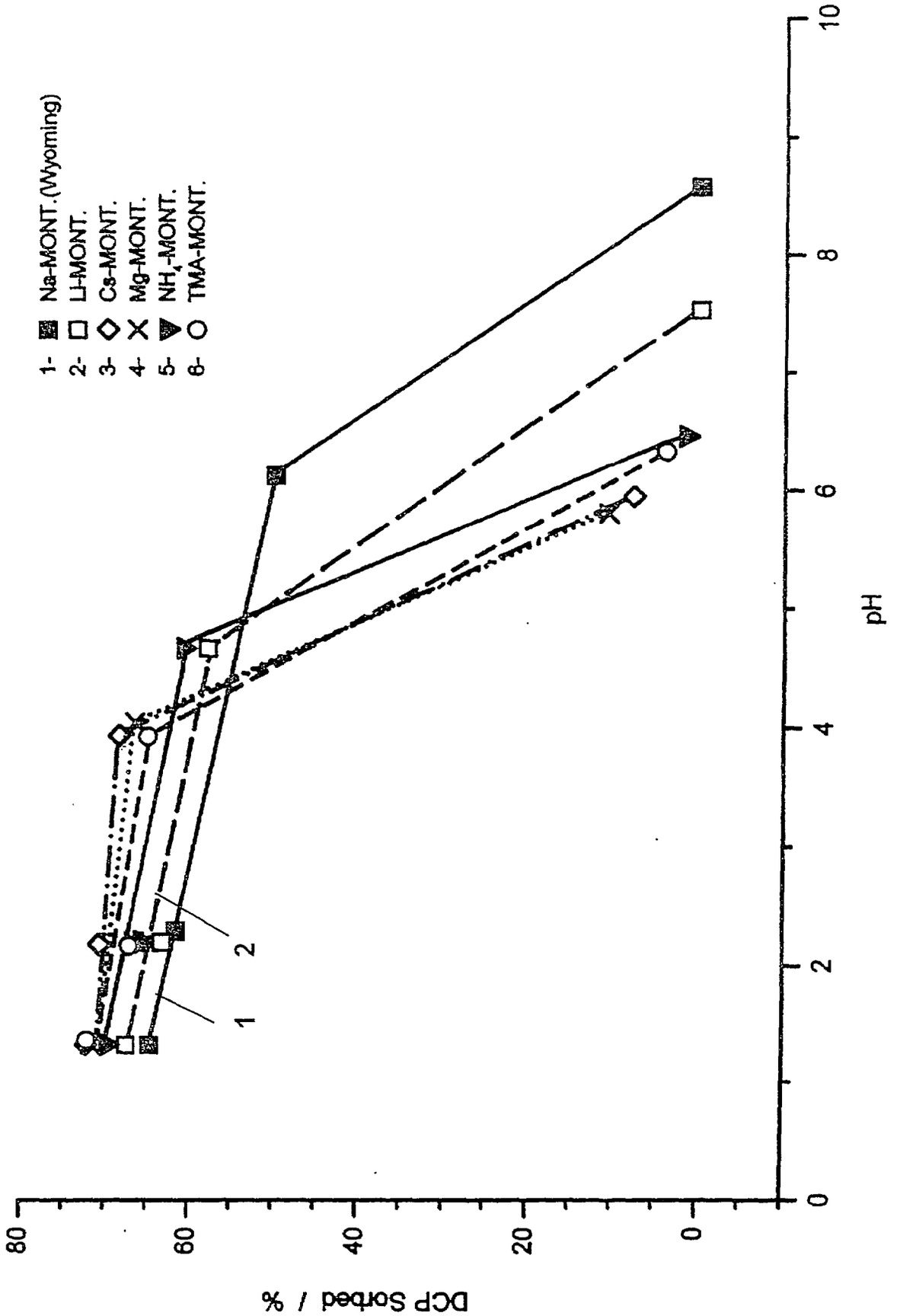
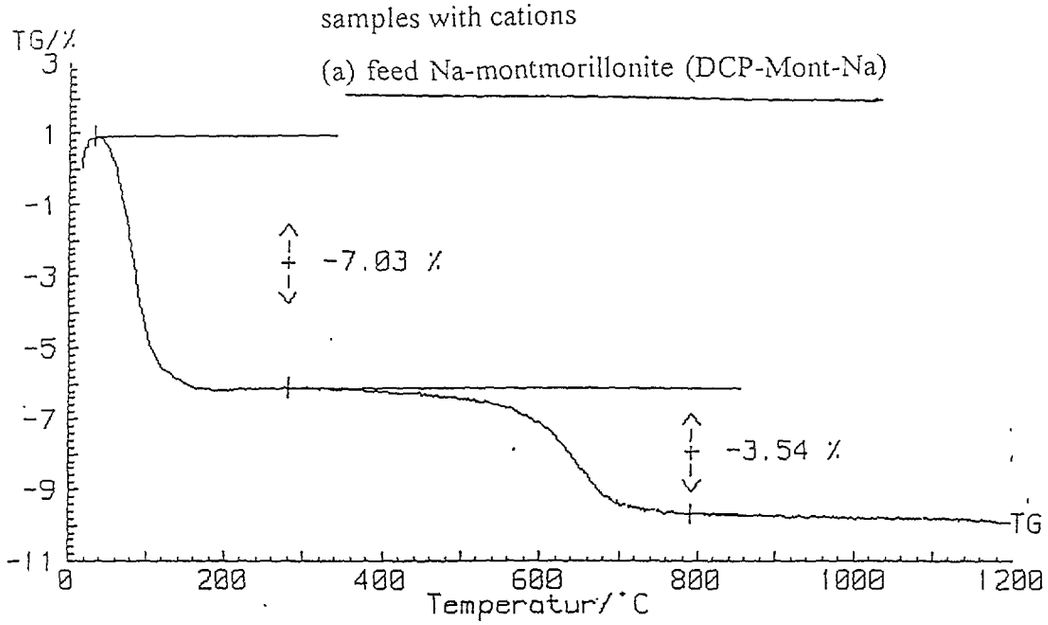


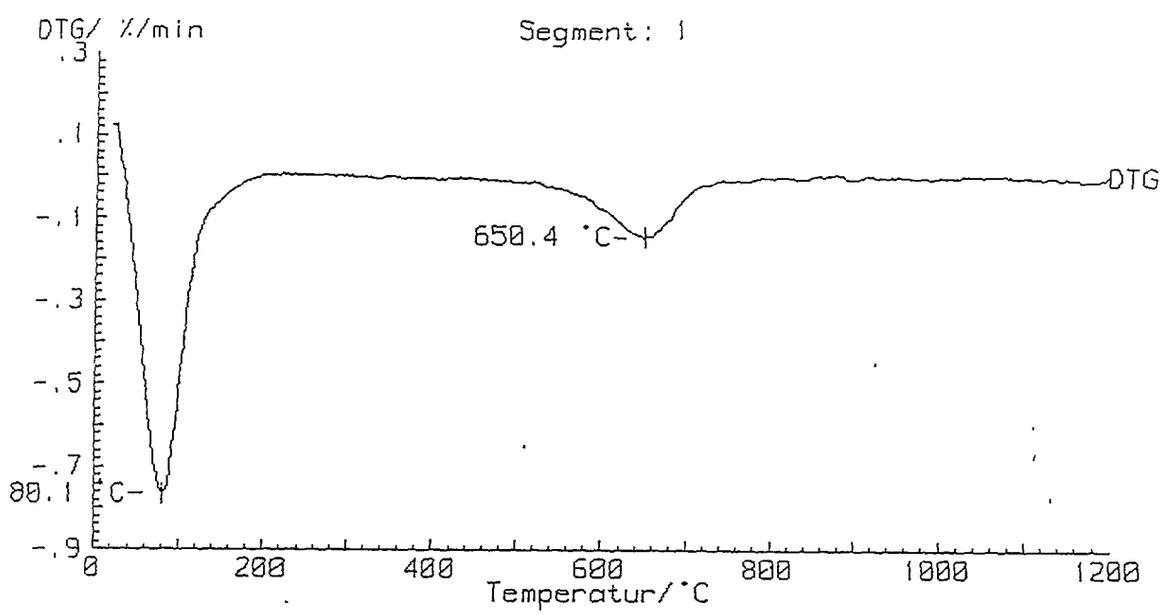
Fig. 6. pH dependencies of DCP sorption on homoionic montmorillonite samples saturated with various cations

Fig 7a Thermogravimetry and evolved gas analysis results characterizing the release of DCP and water during heating in nitrogen of the DCP treated montmorillontie samples with cations

(a) feed Na-montmorillonite (DCP-Mont-Na)



VERSUCHSNR.	M41-NaMMT-DCP	PROBE	Na-MMT-DCP	25.24
DATUM	13 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



VERSUCHSNR.	M41-NaMMT-DCP	PROBE	Na-MMT-DCP	25.24
DATUM	13 Aug 1996			
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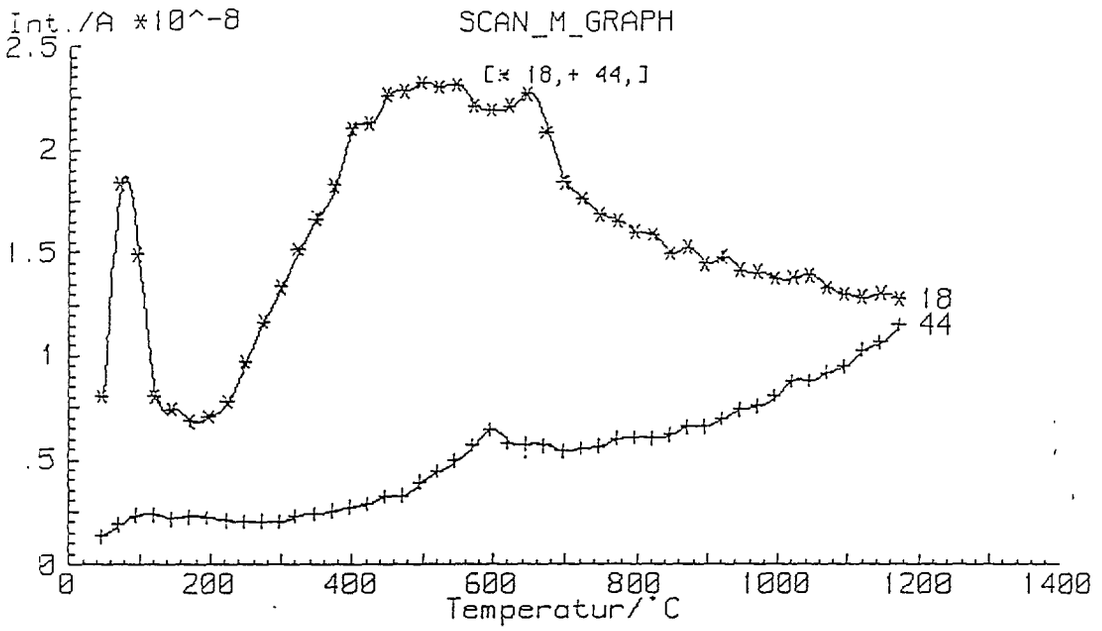
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



VERSUCHSNR.	M41-NaMMT-DCP	PROBE	Na-MMT-DCP	25.24
DATUM	13 Aug 1996			
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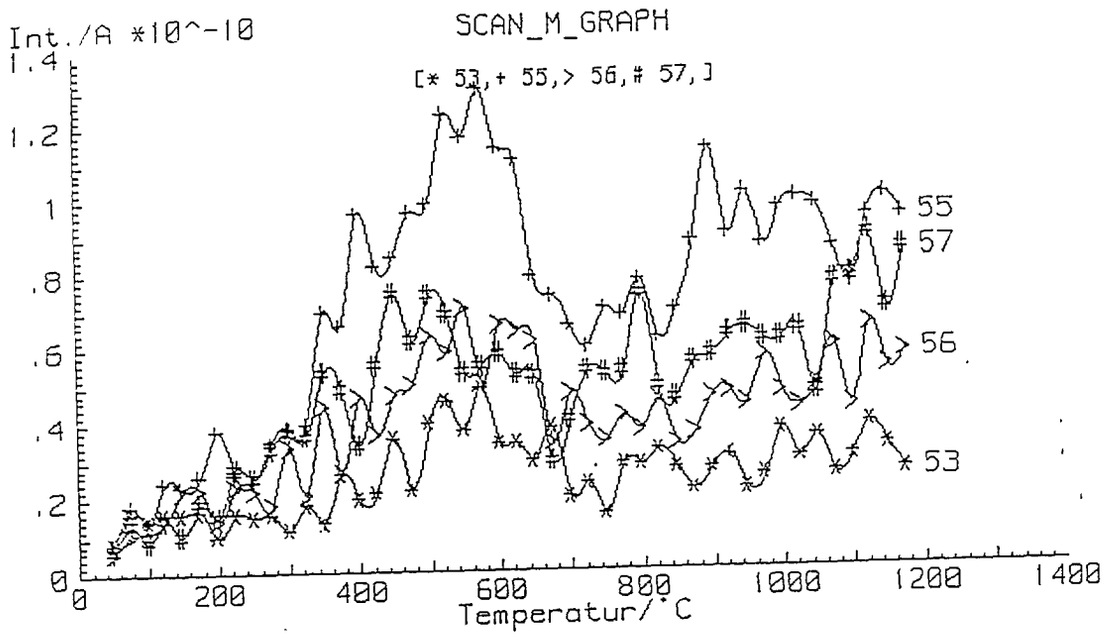
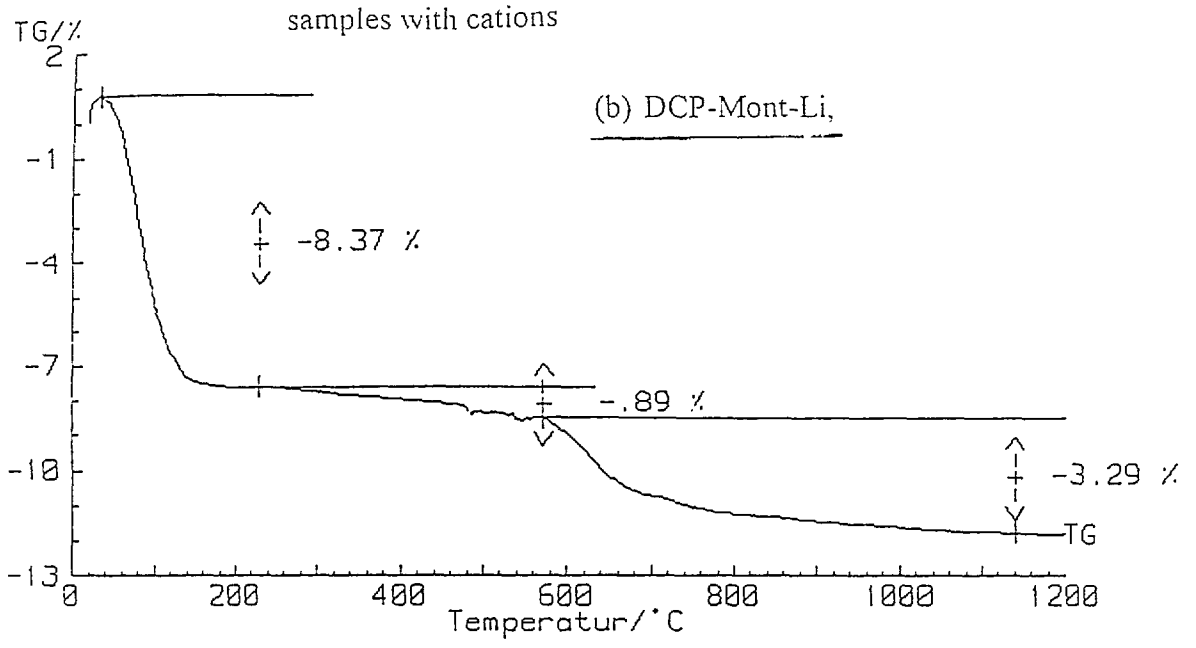
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



VERSUCHSNR.	M41-NaMMT-DCP	PROBE	Na-MMT-DCP	25.24
DATUM	13 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	

Fig. 7b Thermogravimetry and evolved gas analysis results characterizing the release of DCP and water during heating in nitrogen of the DCP treated montmorillontie samples with cations



VERSUCHSNR.	M49-Li-MMT-DCP	PROBE	Li-MMT-DCP	24.5
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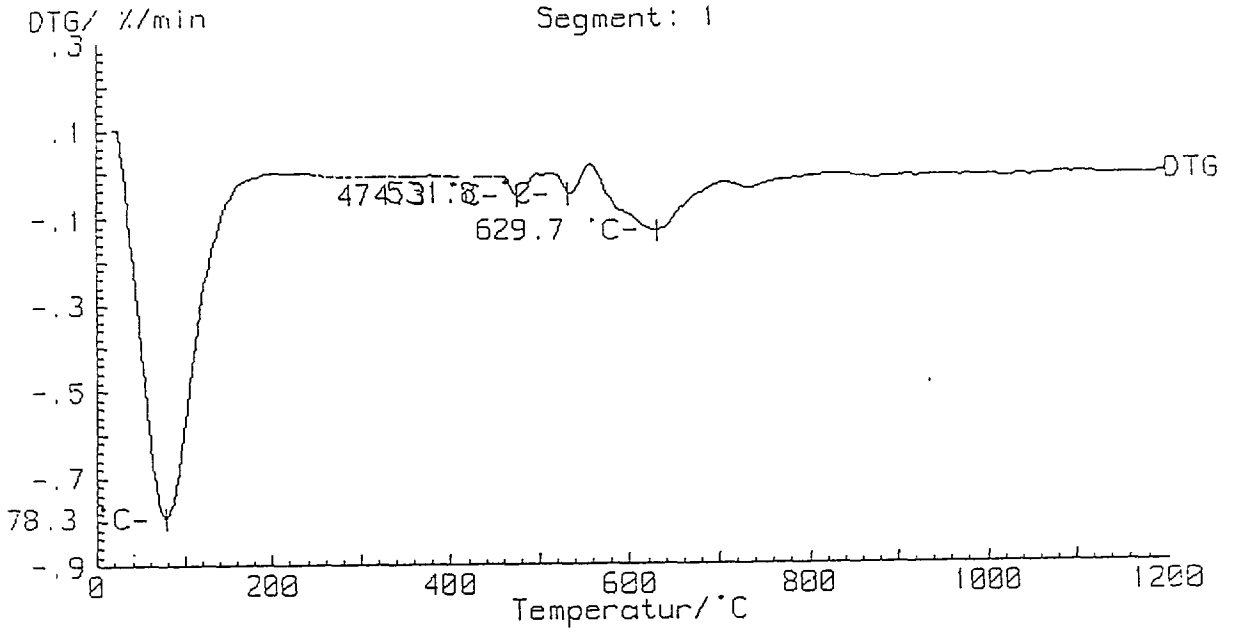
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



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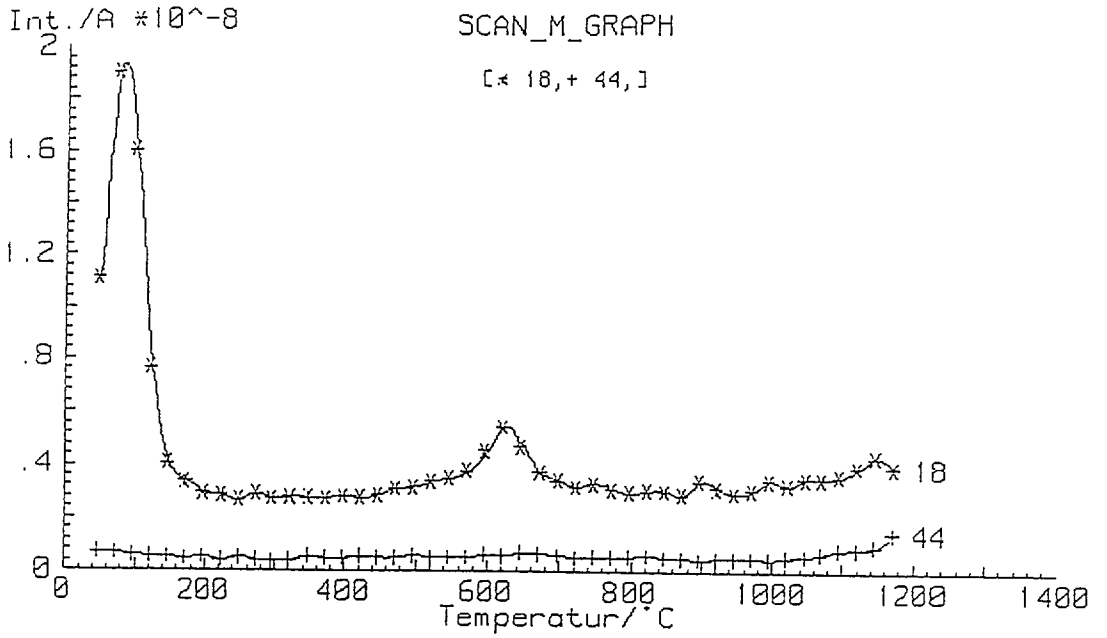
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



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OPERATEUR	CN			
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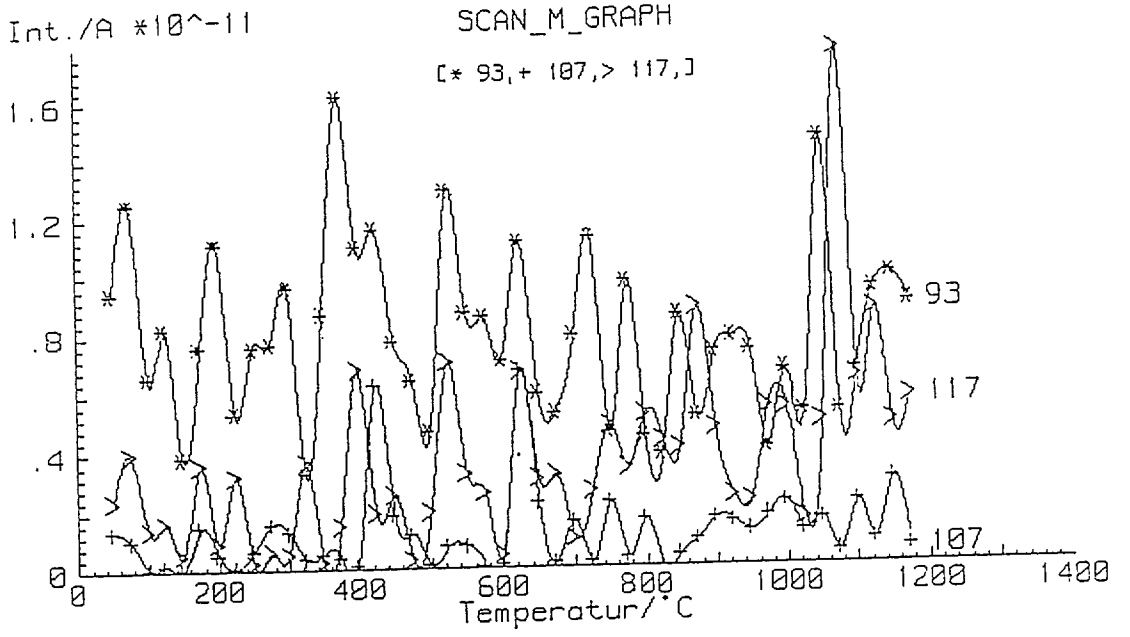

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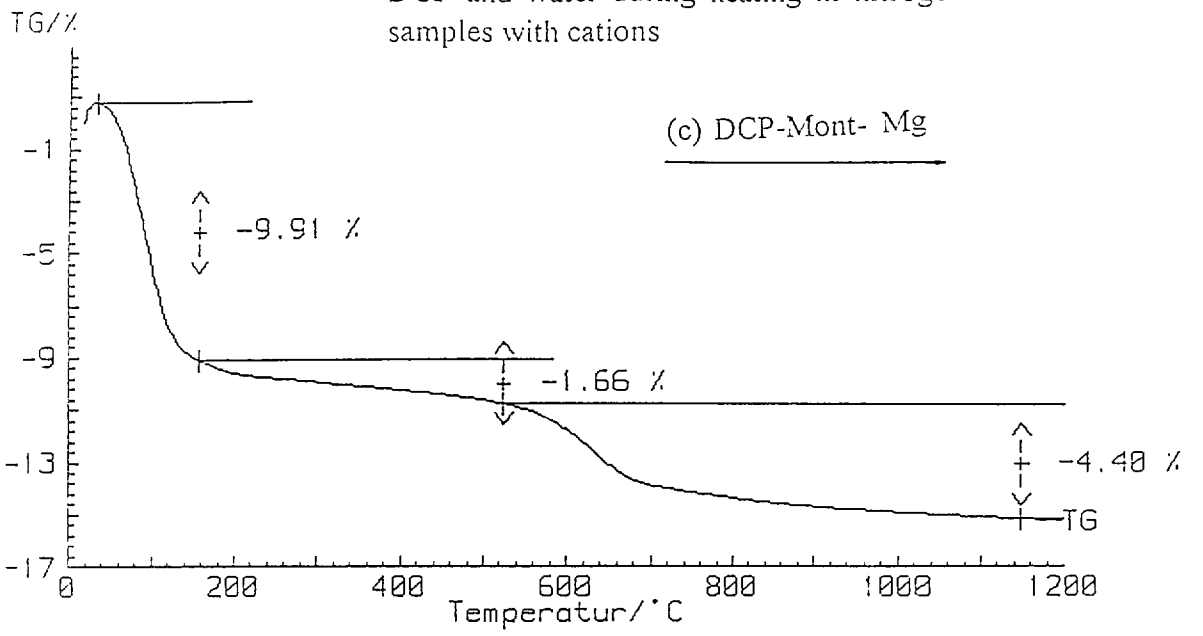
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	

Fig 7c Thermogravimetry and evolved gas analysis results characterizing the release c DCP and water during heating in nitrogen of the DCP treated montmorillont: samples with cations



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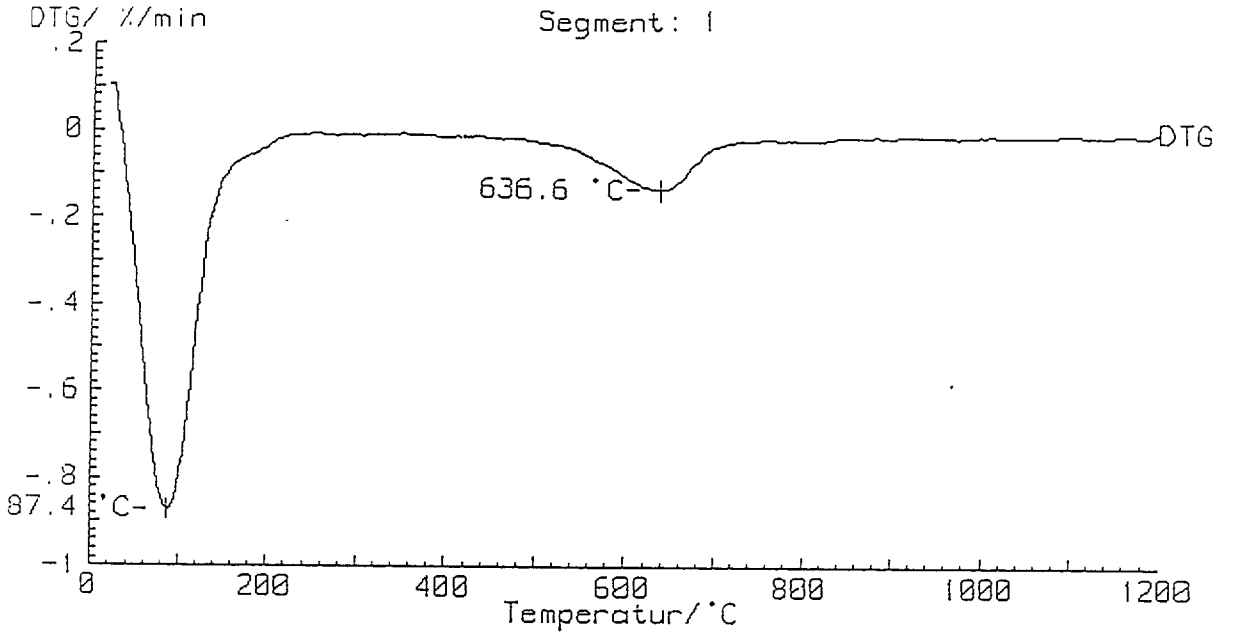
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



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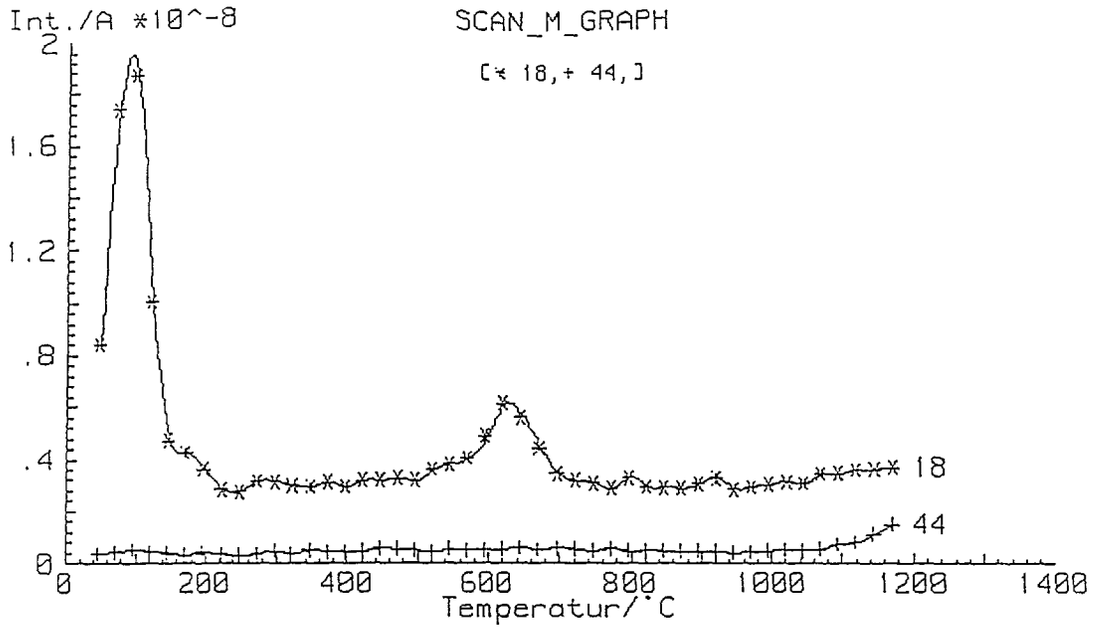

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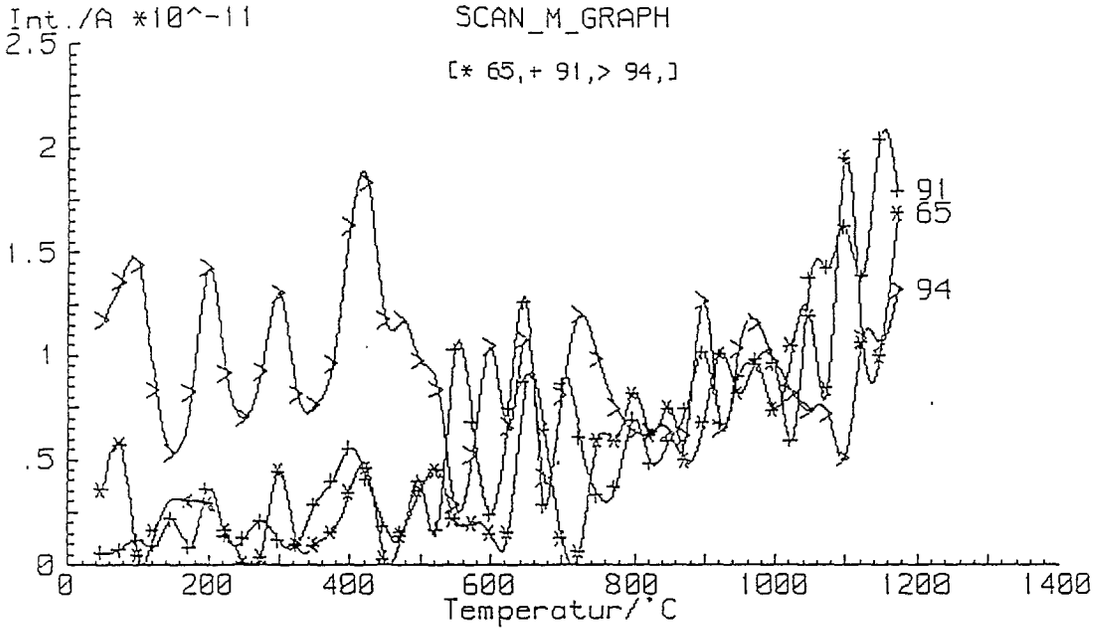

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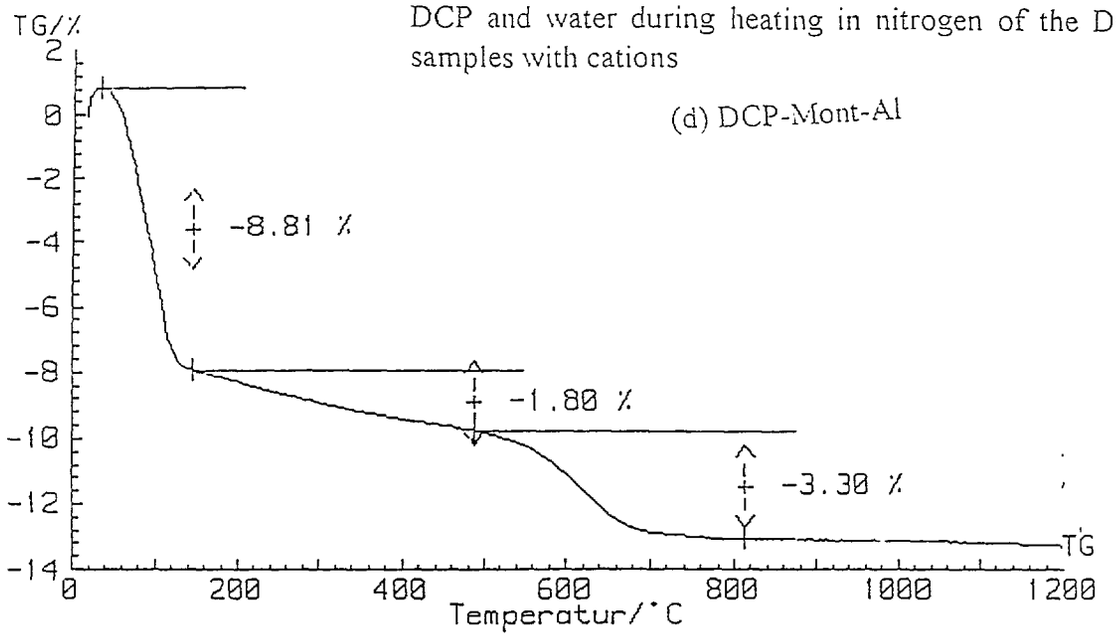
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	

Fig 7d Thermogravimetry and evolved gas analysis results characterizing the release of DCP and water during heating in nitrogen of the DCP treated montmorillontie samples with cations

(d) DCP-Mont-Al



VERSUCHSNR.	M46-Al-MMT-DCP	PROBE	Al-MMT-DCP	25.6
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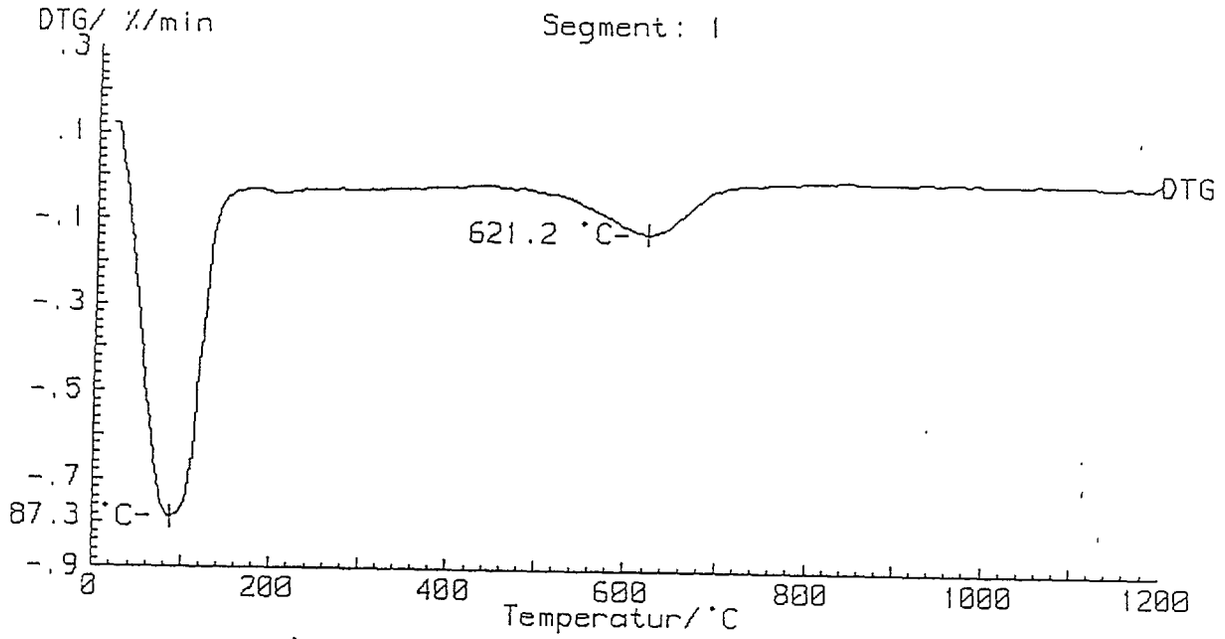

VERSUCHSNR.	M46-Al-MMT-DCP	PROBE	Al-MMT-DCP	25.6
DATUM	16 Aug 1996			
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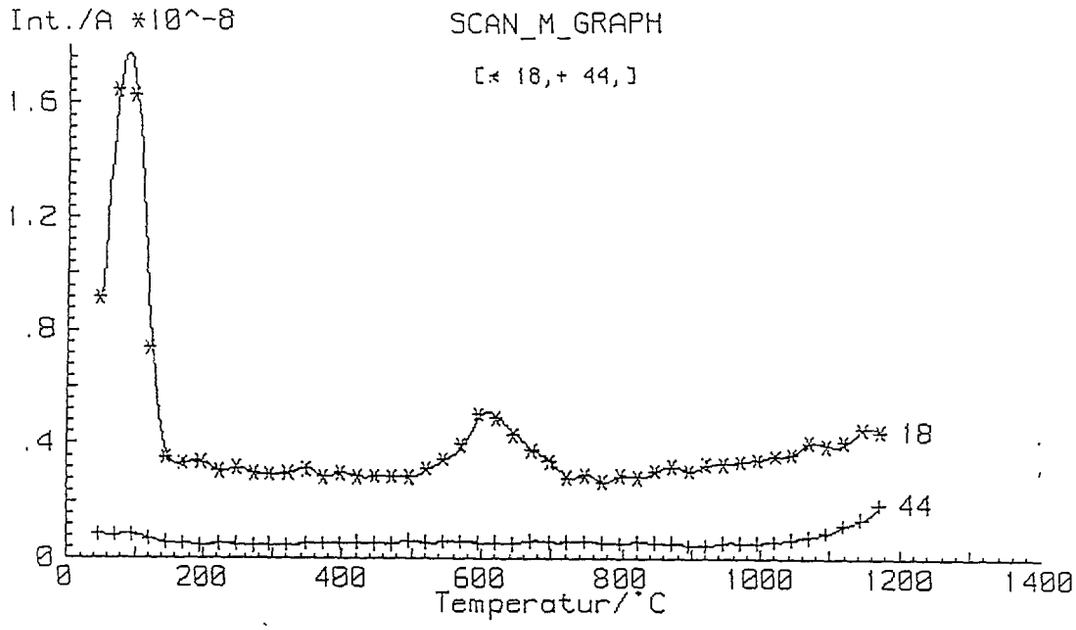
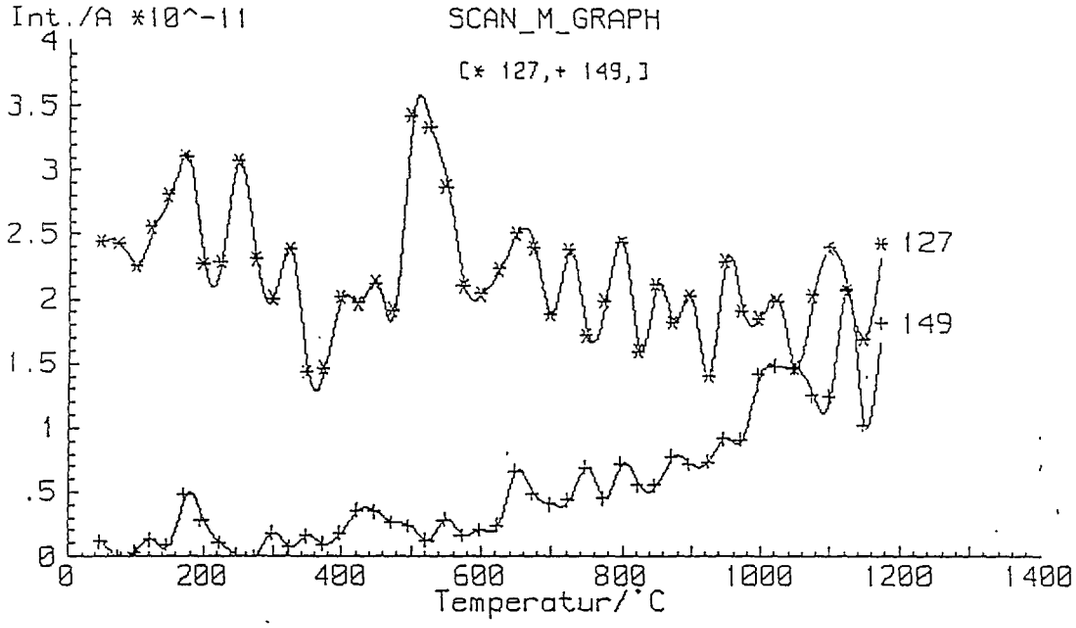
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



VERSUCHSNR.	M46-Al-MMT-DCP	PROBE	Al-MMT-DCP	25.6
DATUM	16 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



VERSUCHSNR.	M46-Al-MMT-DCP	PROBE	Al-MMT-DCP	25.6
DATUM	16 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	

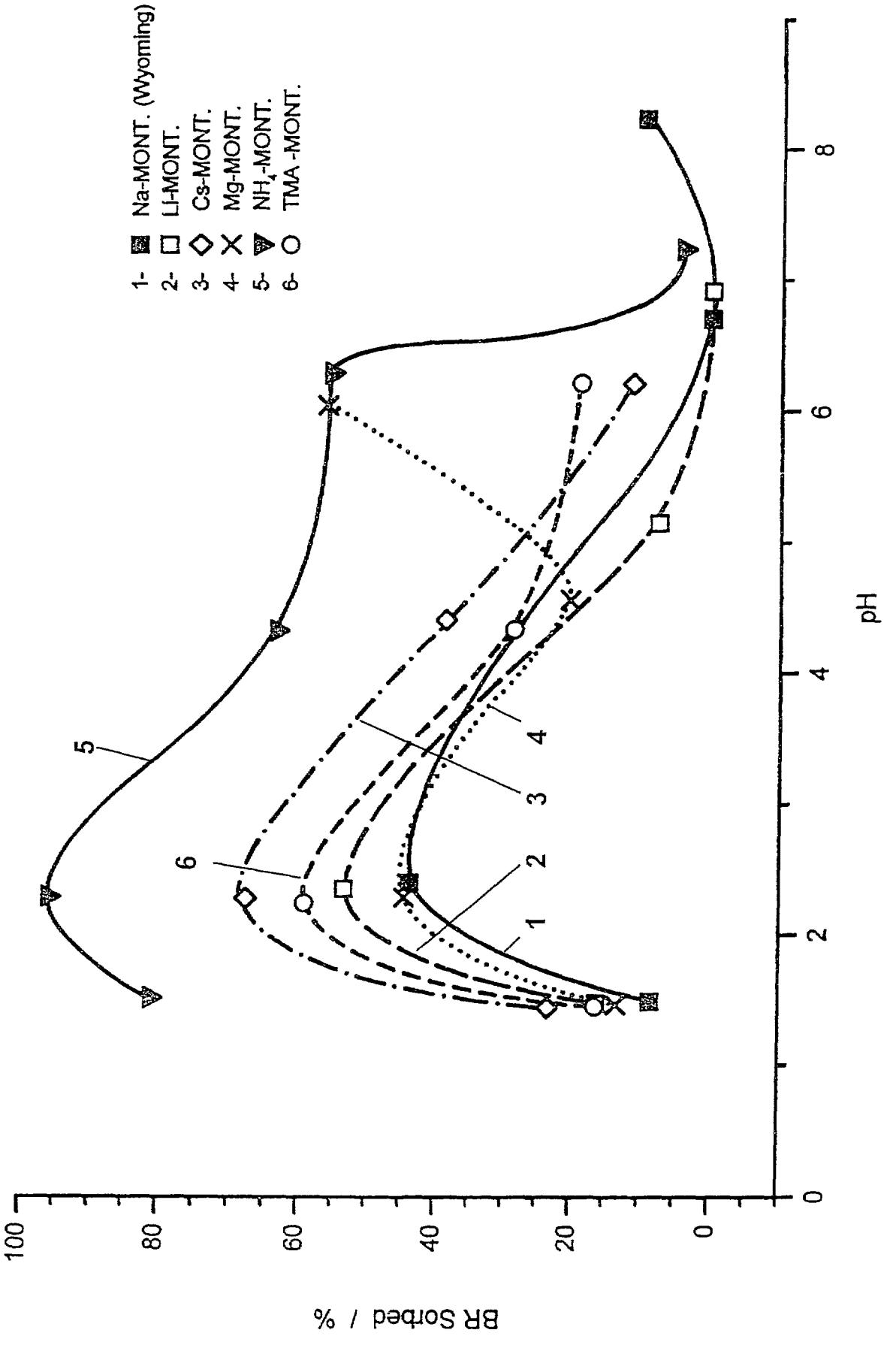
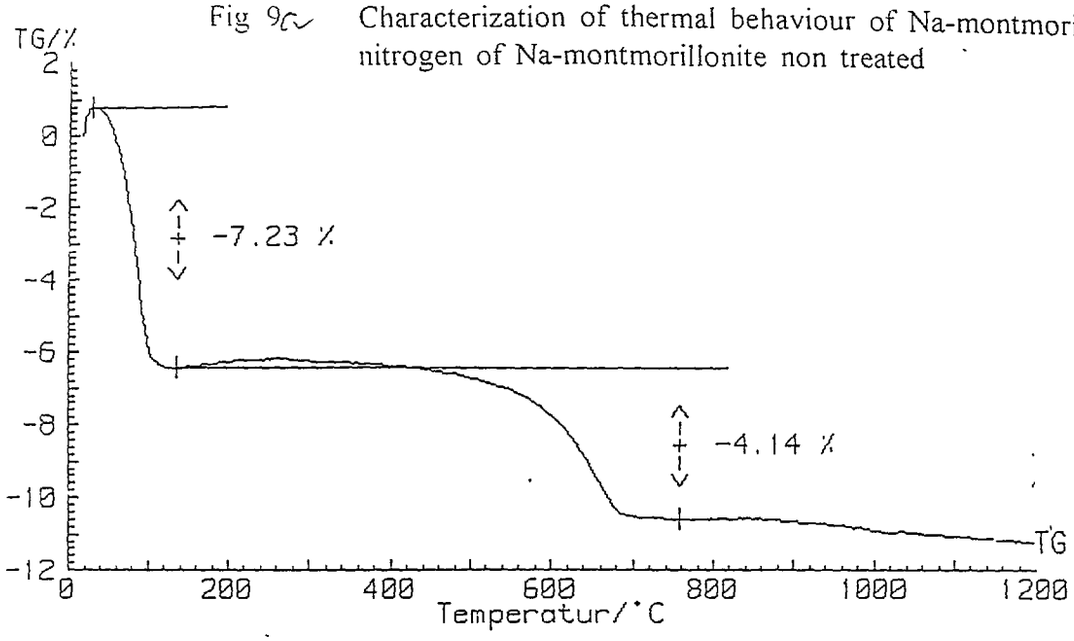
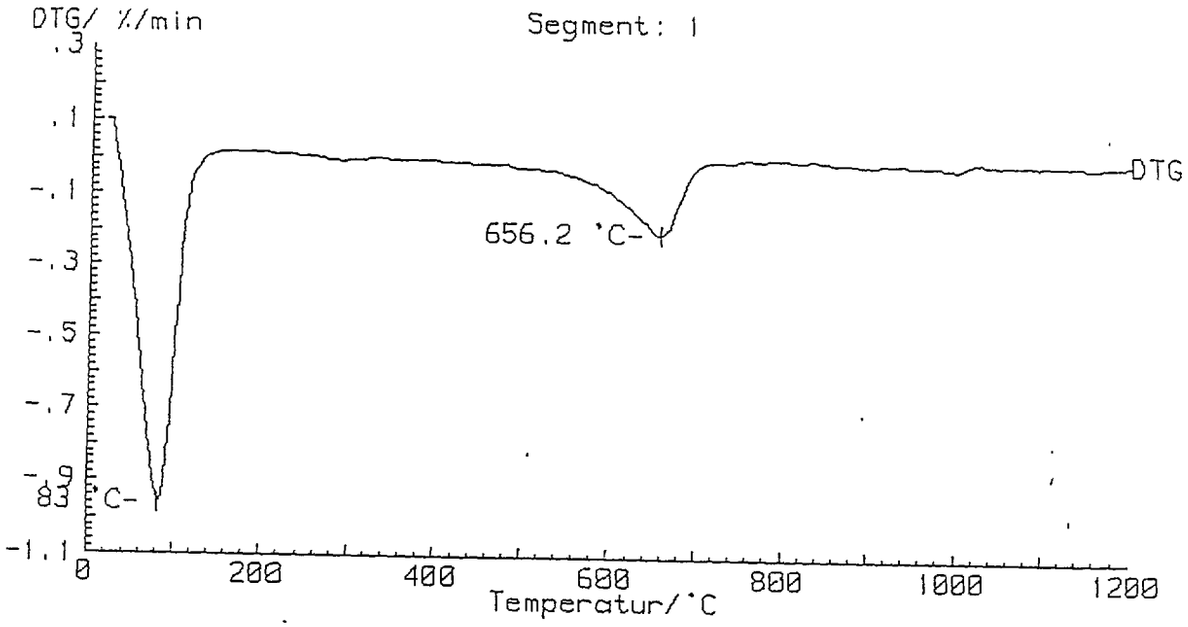


Fig. 8 pH dependencies of BR sorption on montmorillonite samples saturated with various cations

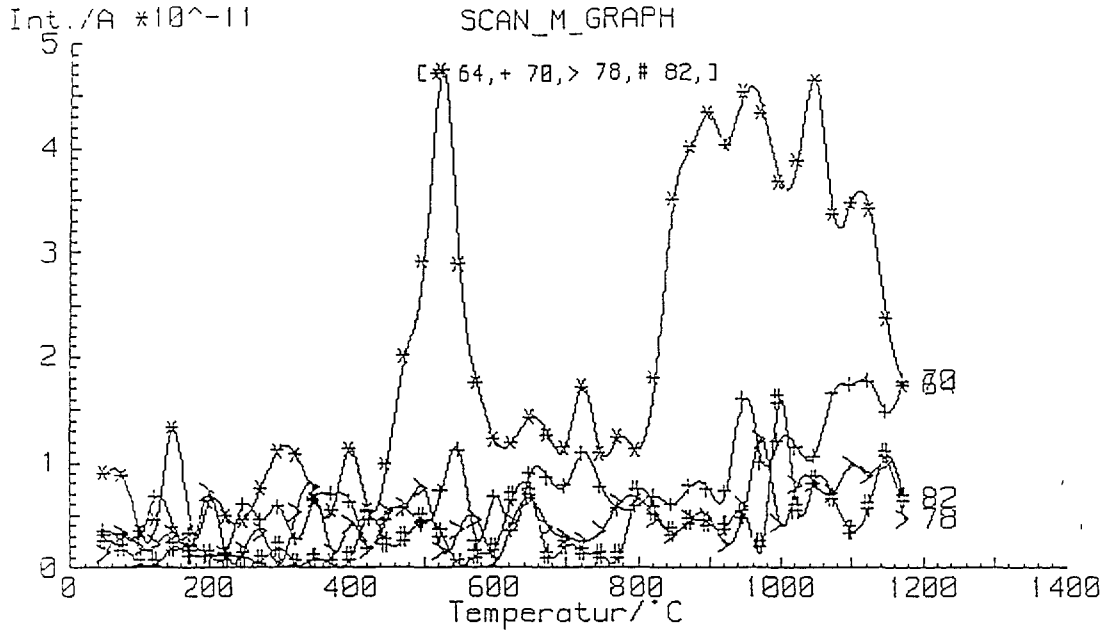
Fig 9c Characterization of thermal behaviour of Na-montmorillonite during heating in nitrogen of Na-montmorillonite non treated



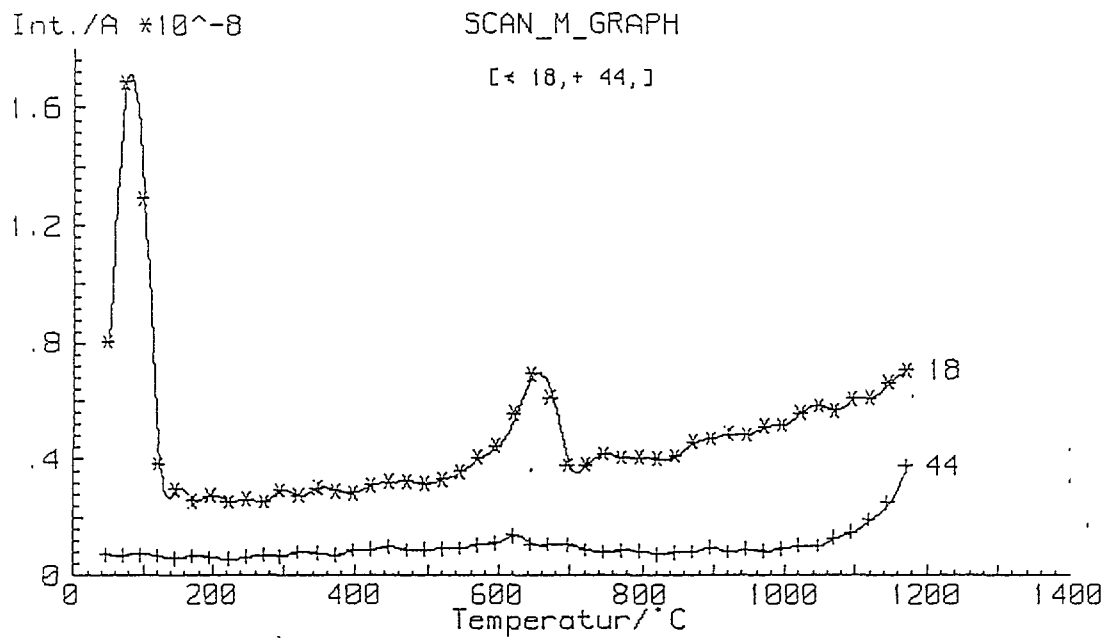
VERSUCHSNR.	M43-NaMMT	PROBE	Na-MMT(WYOMING) 25.32
DATUM	13 Aug 1996		
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/
OPERATEUR	CN		
NETZSCH	409/429-403	BEMERKUNG	S C A N



VERSUCHSNR.	M43-NaMMT	PROBE	Na-MMT(WYOMING) 25.32
DATUM	13 Aug 1996		
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/
OPERATEUR	CN		
NETZSCH	409/429-403	BEMERKUNG	S C A N

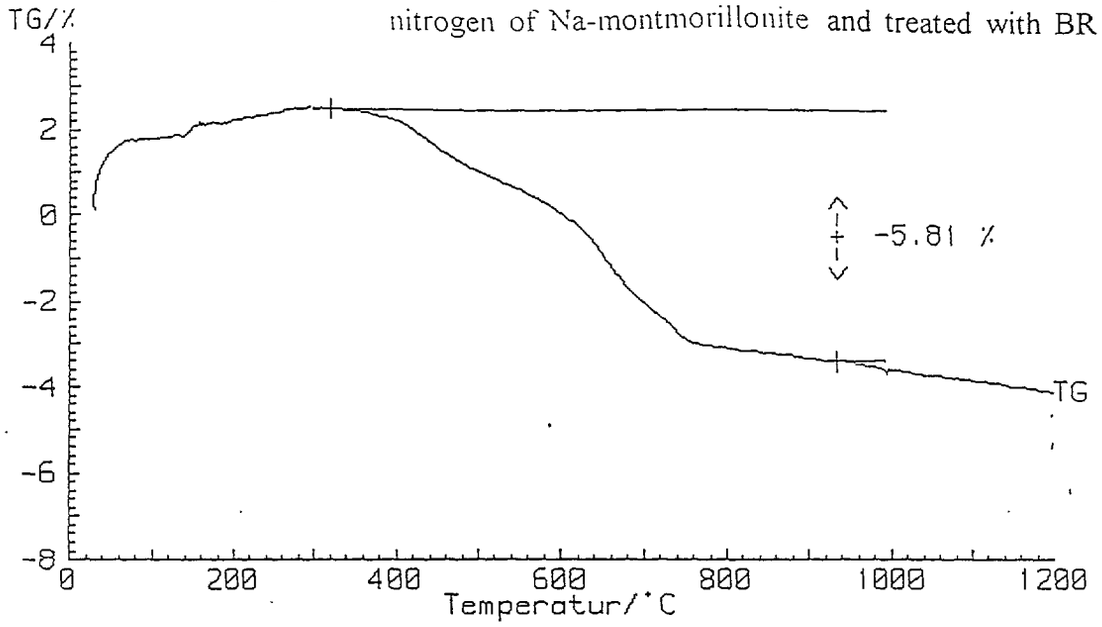


VERSUCHSNR.	M43-NaMMT	PROBE	Na-MMT(WYOMING) 25.32
DATUM	13 Aug 1996		
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/
OPERATEUR	CN		
NETZSCH	409/429-403	BEMERKUNG	S C A N

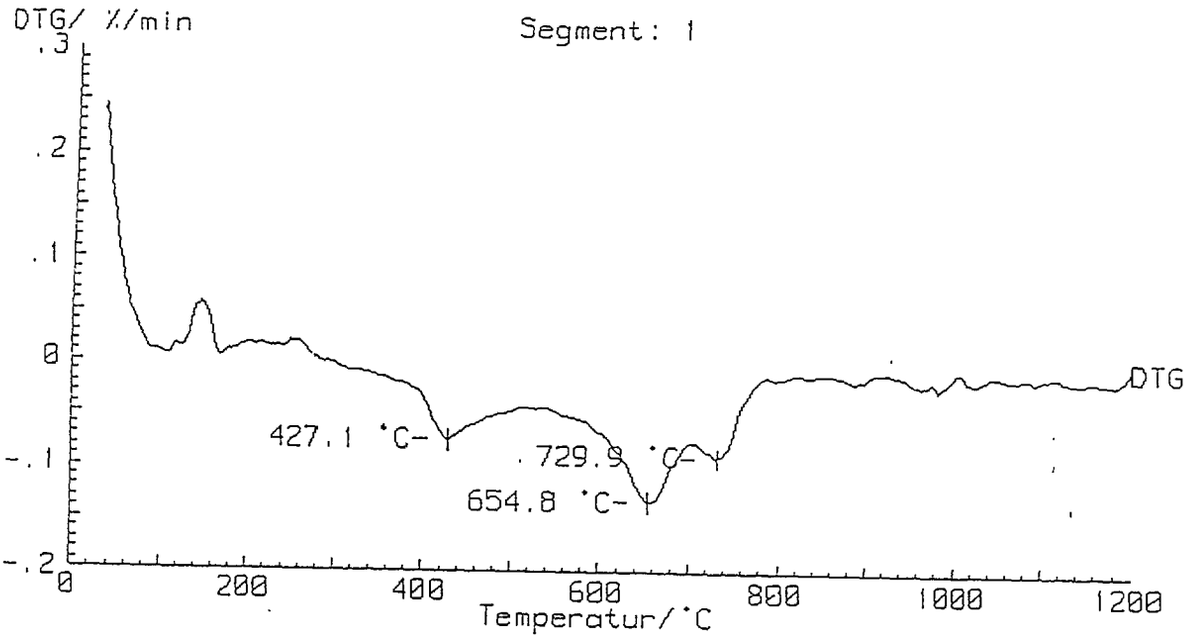


VERSUCHSNR.	M43-NaMMT	PROBE	Na-MMT(WYOMING) 25.32
DATUM	13 Aug 1996		
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/
OPERATEUR	CN		
NETZSCH	409/429-403	BEMERKUNG	S C A N

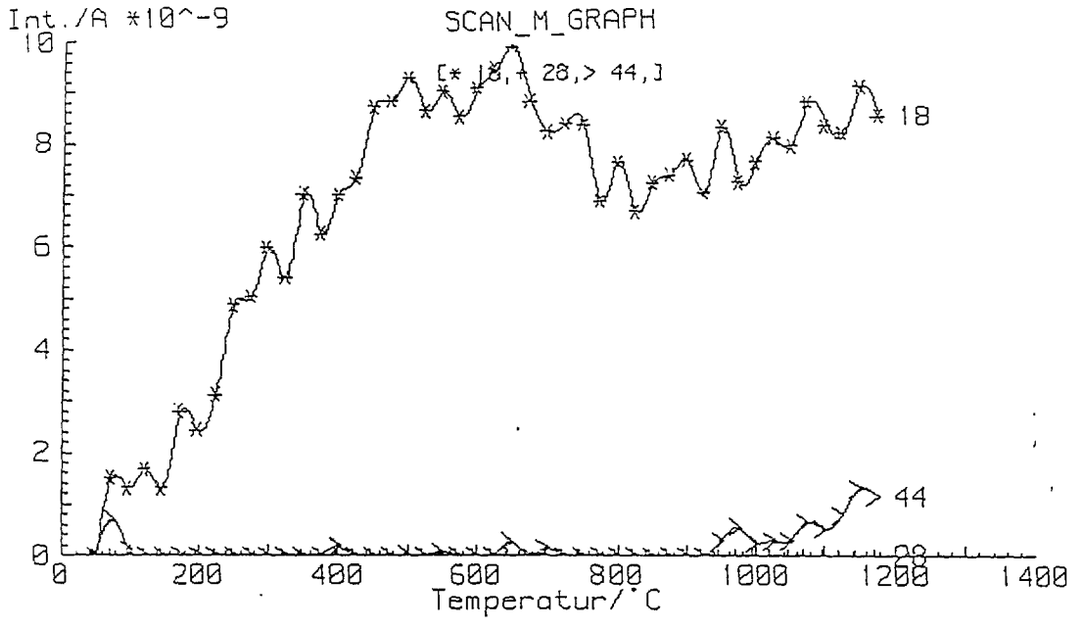
Fig 9b Characterization of thermal behaviour of Na-montmorillonite during heating in nitrogen of Na-montmorillonite and treated with BR containing aqueous solution



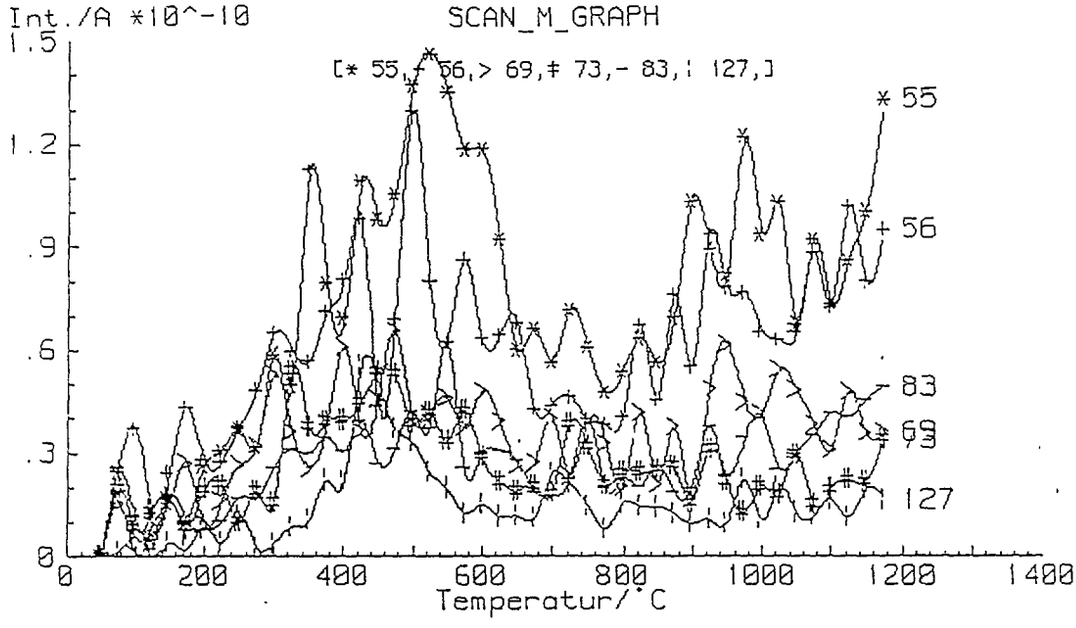
VERSUCHSNR.	M41-NaMMT+BR(2)	PROBE	NaMMT+BR (2)	25.3
DATUM	2 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



VERSUCHSNR.	M41-NaMMT+BR(2)	PROBE	NaMMT+BR (2)	25.3
DATUM	2 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



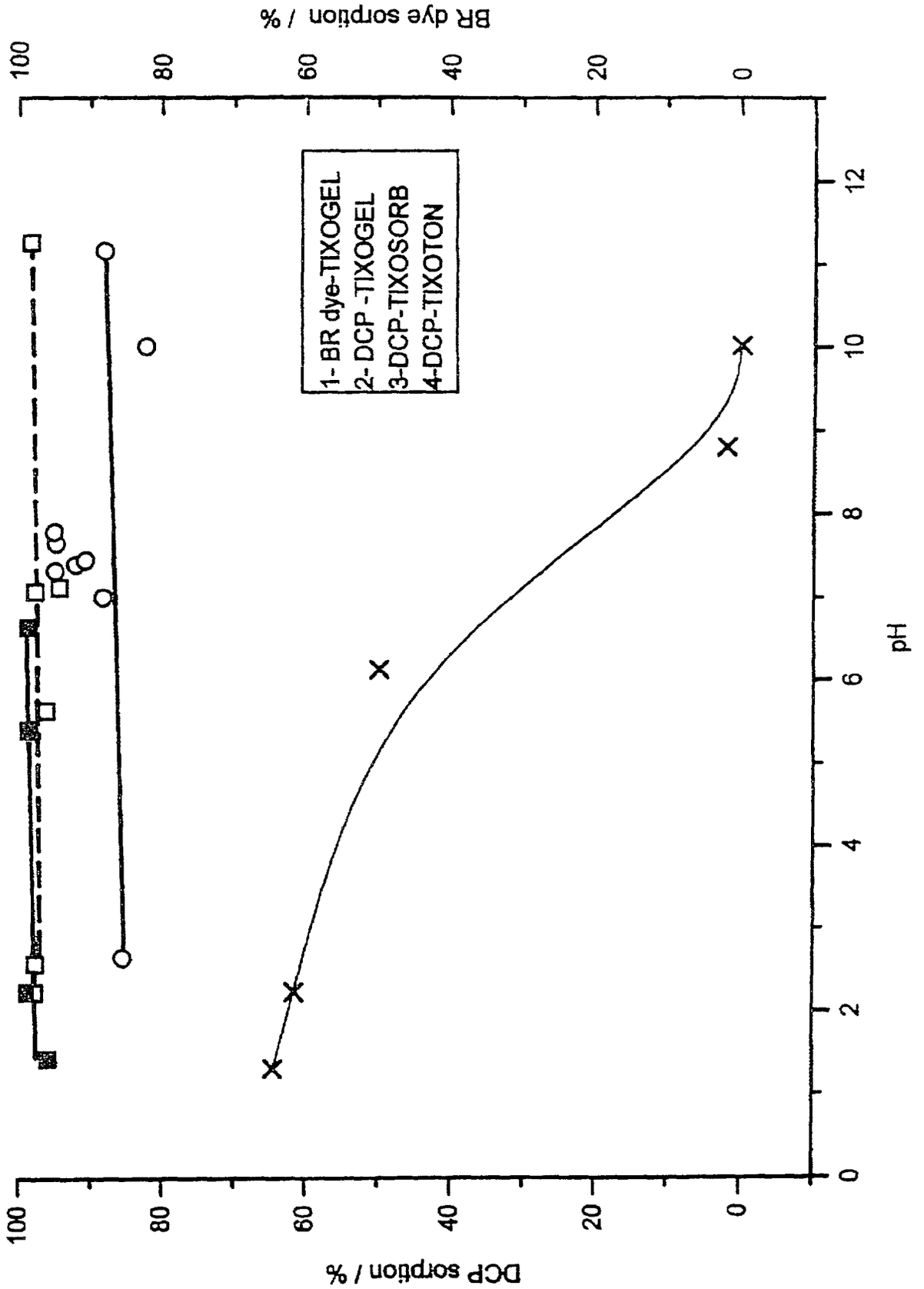
VERSUCHSNR.	M41-NaMMT+BR(2)	PROBE	NaMMT+BR (2) 25.3
DATUM	2 Aug 1996		
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/
OPERATEUR	CN		
NETZSCH	409/429-403	BEMERKUNG	S C A N

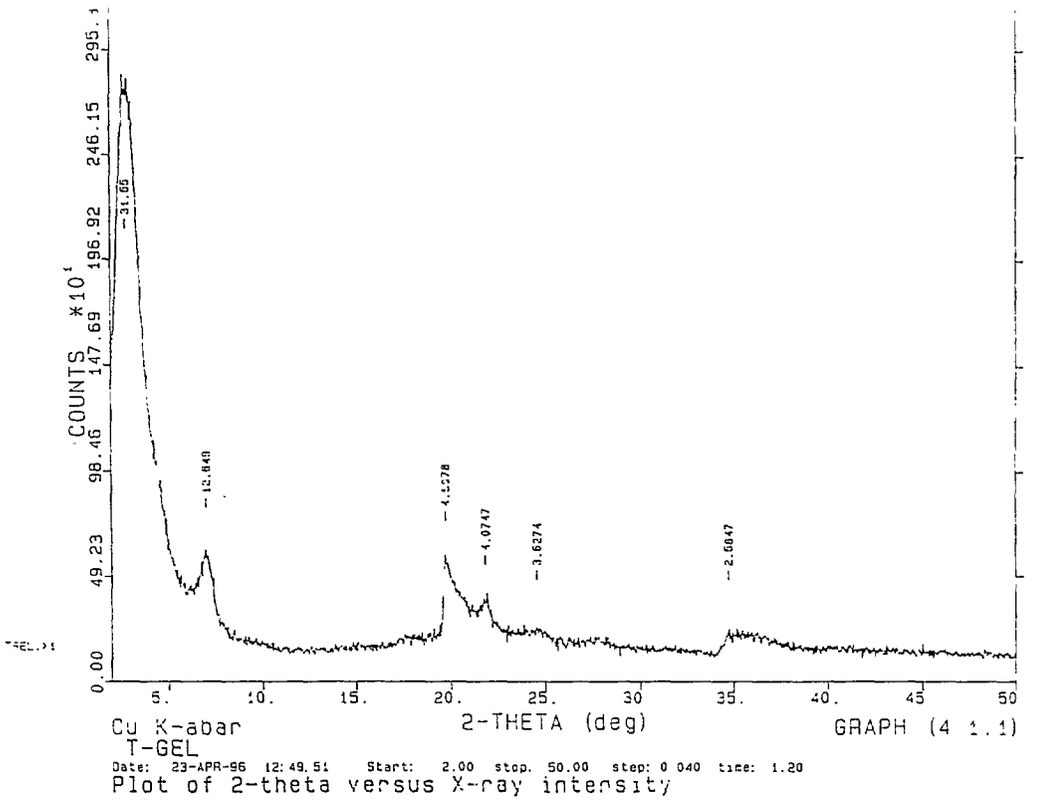


VERSUCHSNR.	M41-NaMMT+BR(2)	PROBE	NaMMT+BR (2) 25.3
DATUM	2 Aug 1996		
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/
OPERATEUR	CN		
NETZSCH	409/429-403	BEMERKUNG	S C A N

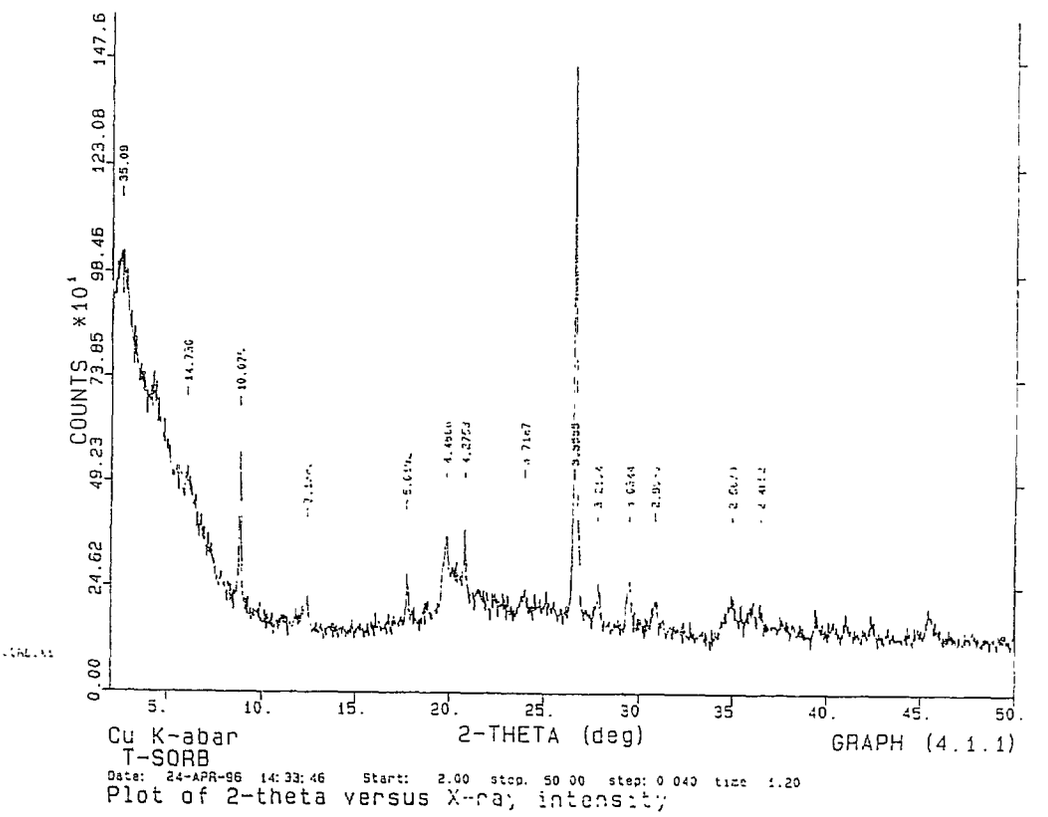
Fig 10 Comparison of pH dependencies for DCP and BR sorption on modified bentonite products:

Curves 1 and 2 correspond to the sorption of BR and DCP on TIXOGEL, resp. curves 3 and 4 to correspond the sorption of DCP on TIXOSORB and TIXOTON products, resp.





(a)



(b)

Fig. 11. X-ray diffraction patterns of the modified organophilic bentonite products TIXOSORB (a) and TIXOGEL (b)

Fig. 12 Equilibrium sorption isotherms of DCP on TIXOSORB (curve 1) and TIXOGEL (curve 2)

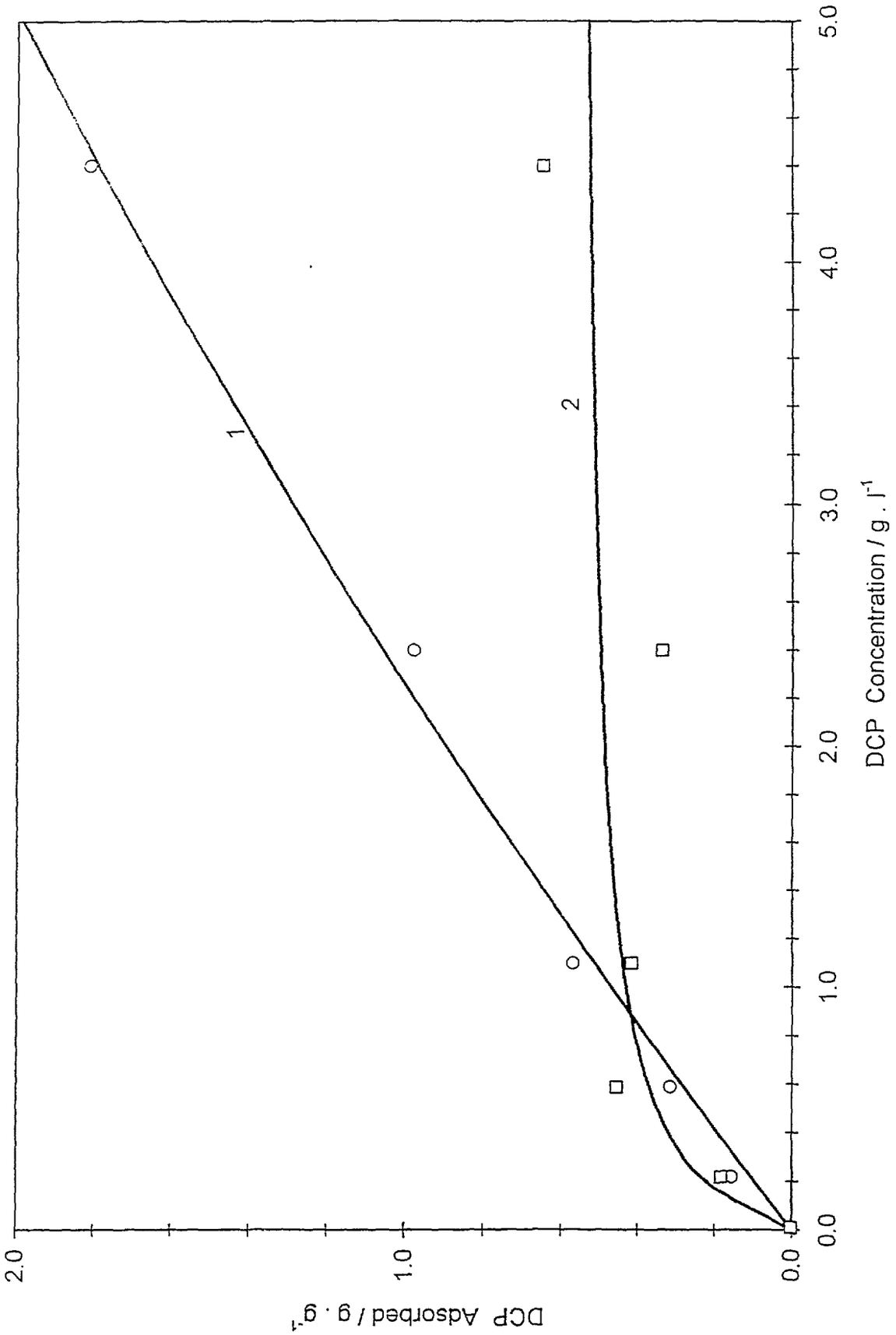


Fig 13. Equilibrium sorption isotherms of BR dye on TIXOSORB (curve 1) and TIXOGEL (curve 2)

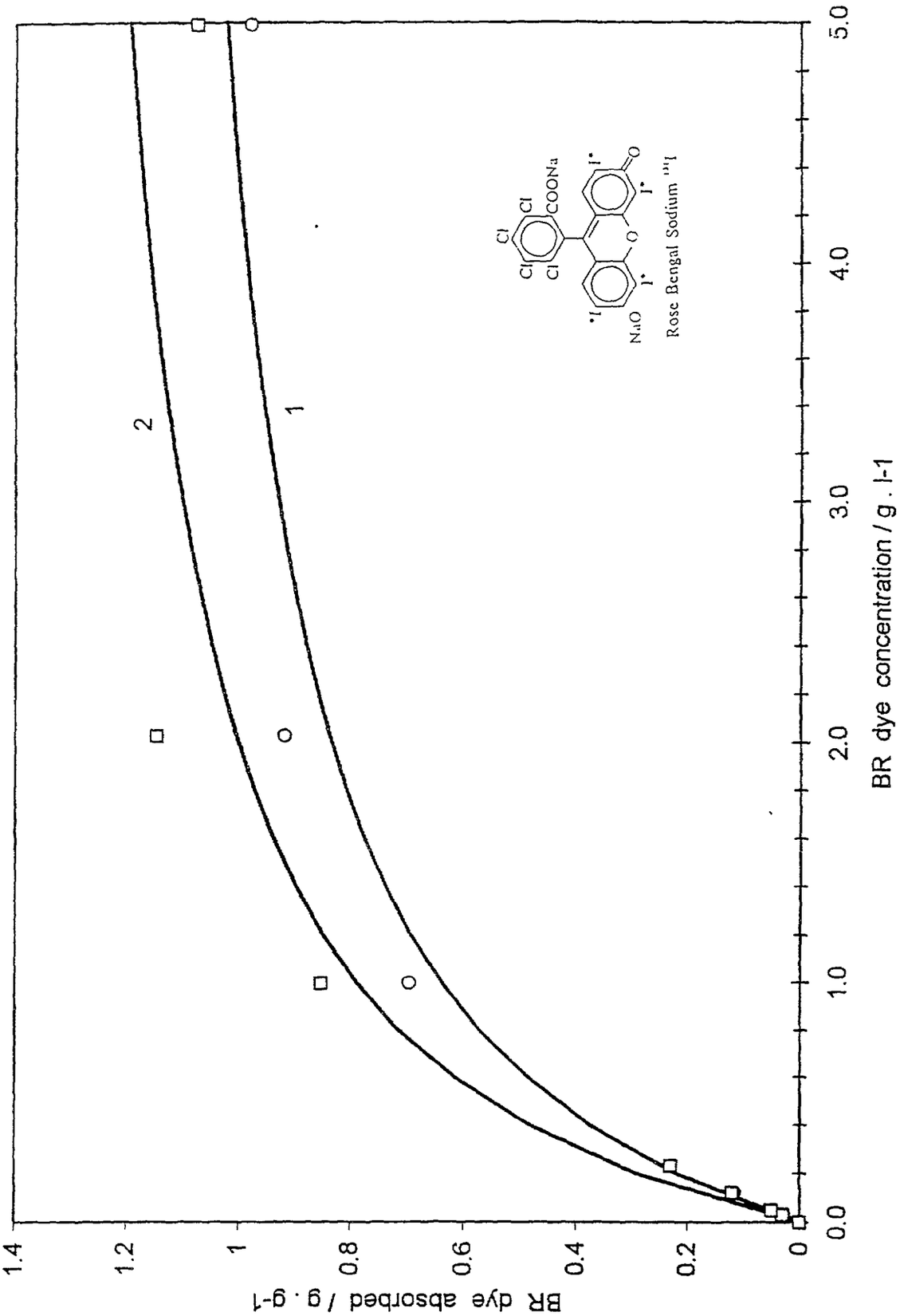
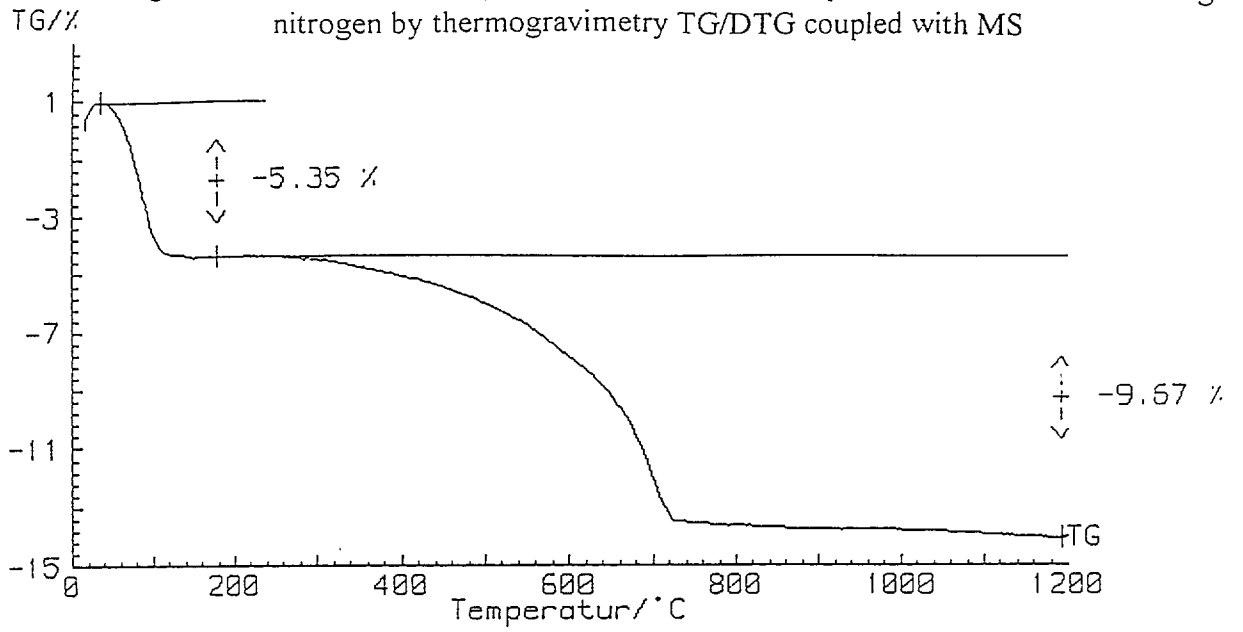
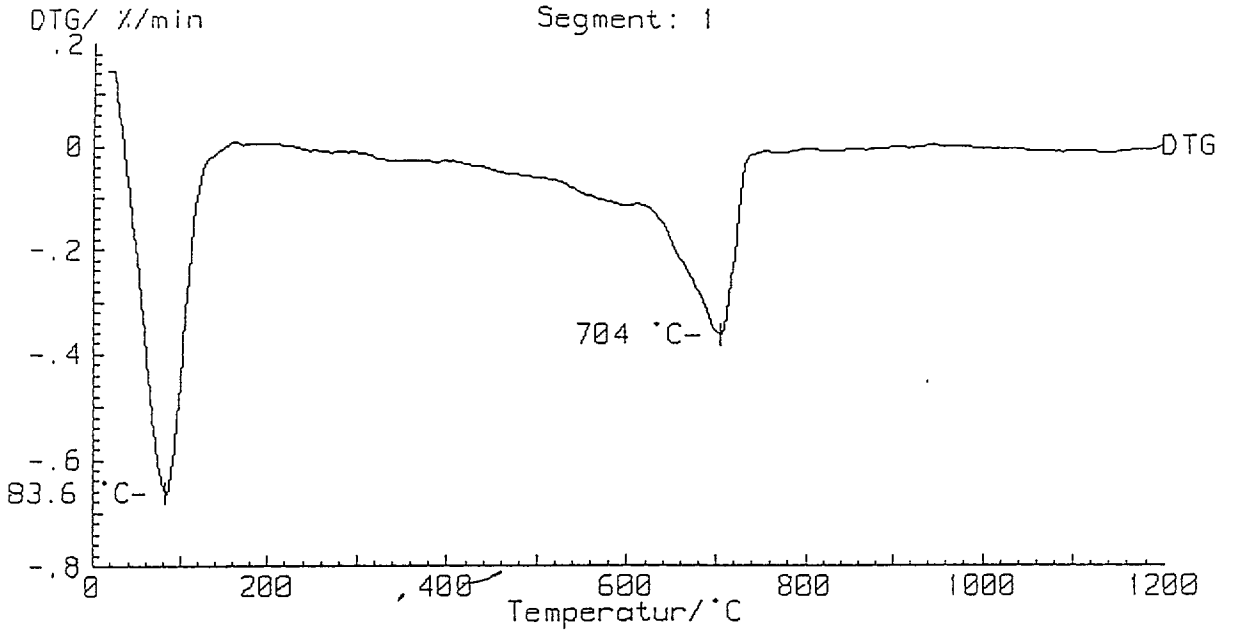


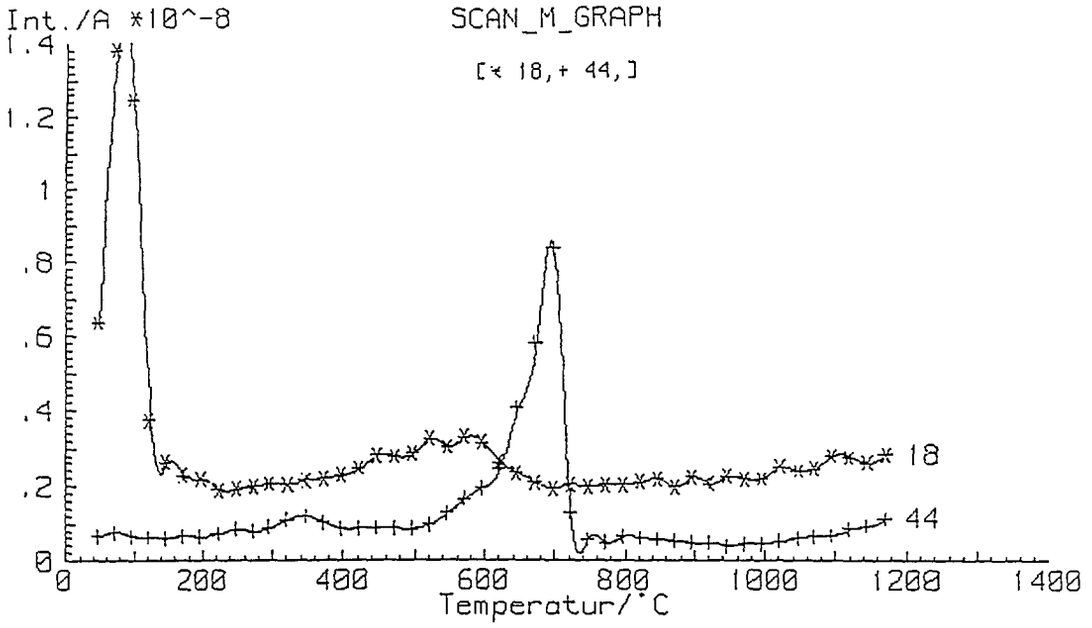
Fig 14 Thermal stability of TIXOTON bentonite products characterized during heating in nitrogen by thermogravimetry TG/DTG coupled with MS



VERSUCHSNR.	M54-Tixoton	PROBE	Tixoton	25.99
DATUM	28 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	

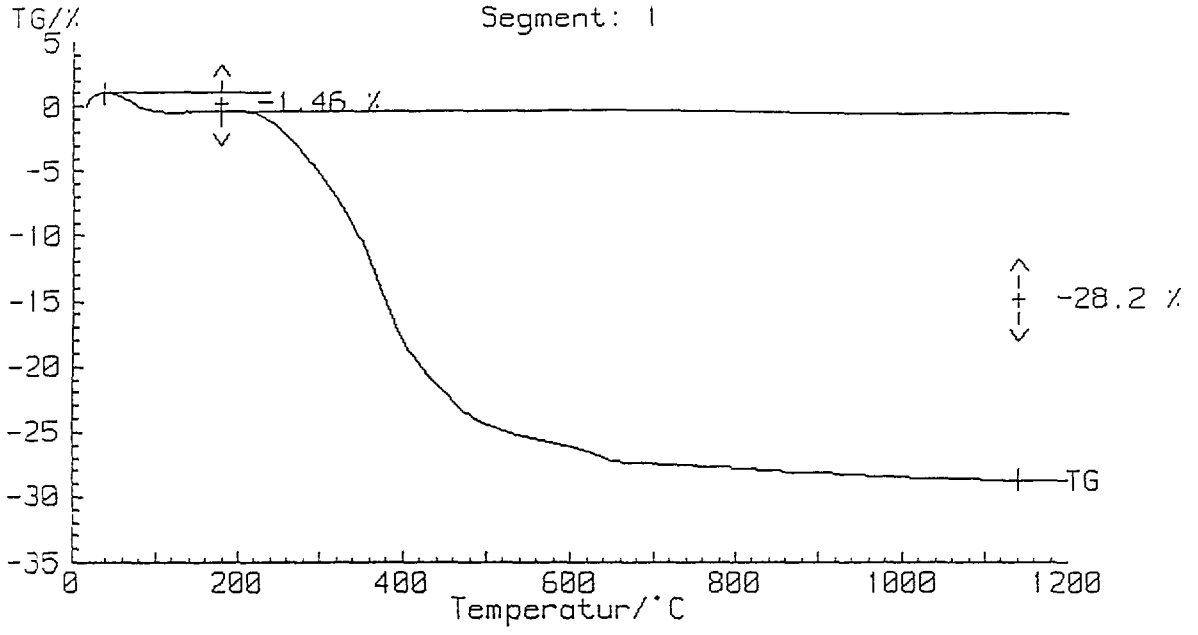


VERSUCHSNR.	M54-Tixoton	PROBE	Tixoton	25.99
DATUM	28 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	

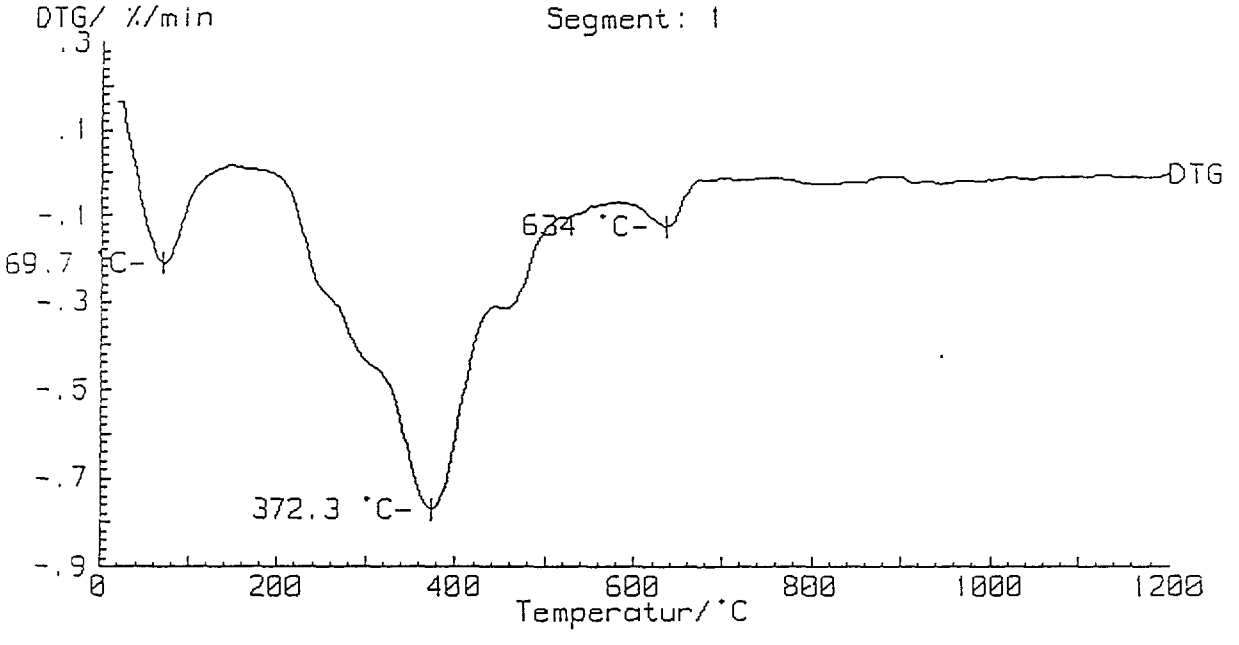


VERSUCHSNR.	M54-Tixoton	PROBE	Tixoton	25.99
DATUM	28 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	

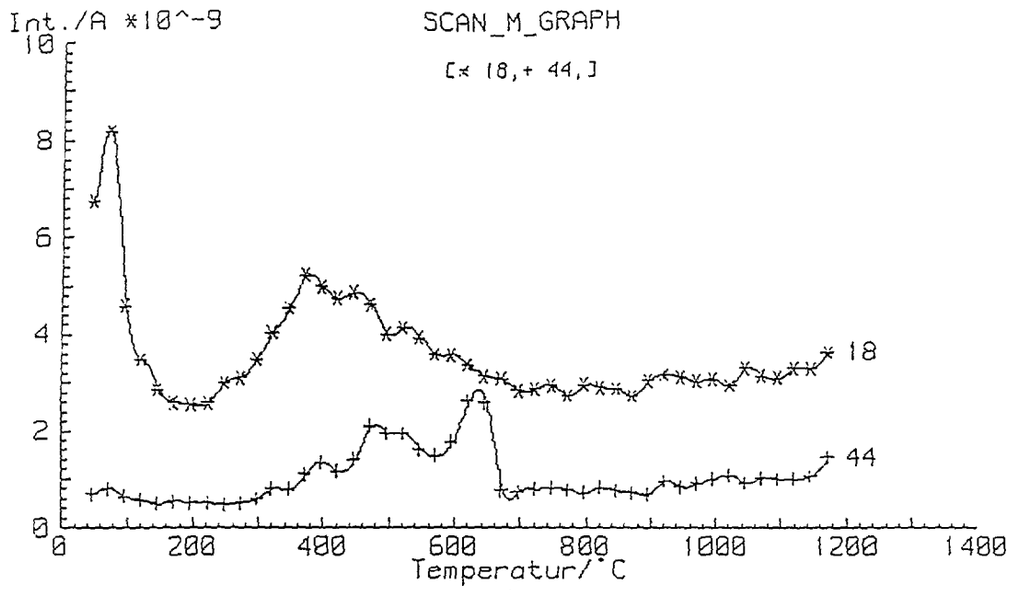
Fig 15. Thermal stability of TIXOSORB orgahophilic bentonite products characterized during heating in nitrogen by thermogravimetry TG/DTG coupled with MS



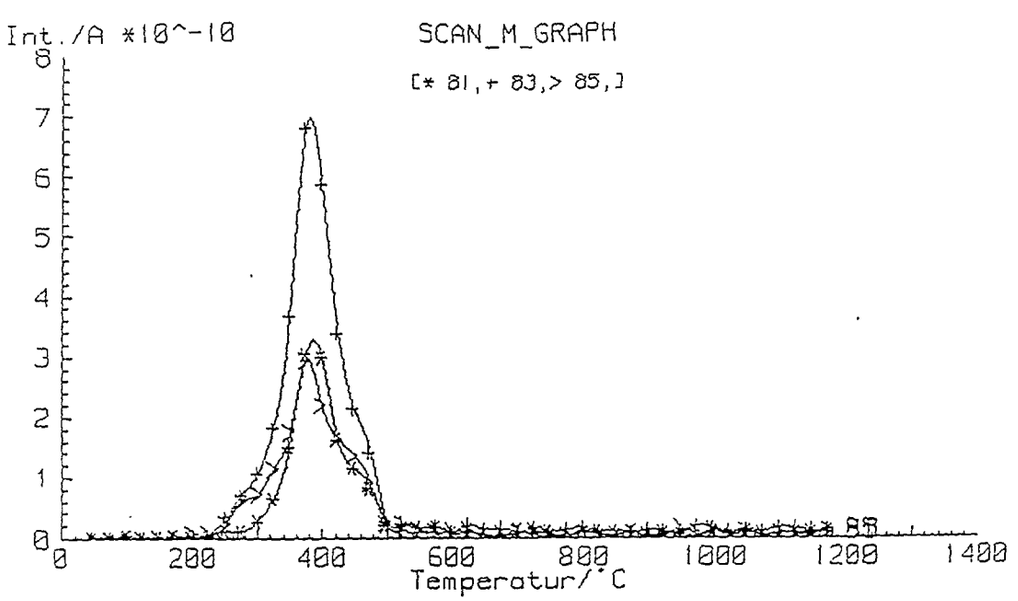
VERSUCHSNR.	M52-Tixosorb	PROBE	Tixosorb	26.12
DATUM	27 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



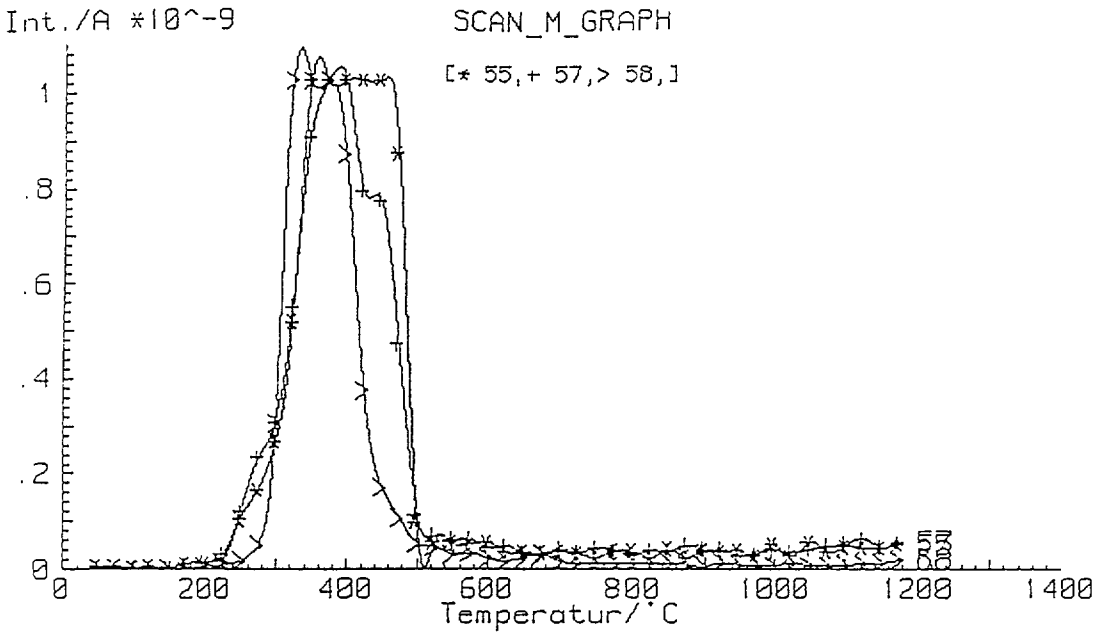
VERSUCHSNR.	M52-Tixosorb	PROBE	Tixosorb	26.12
DATUM	27 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



VERSUCHSNR.	M52-Tixosorb	PROBE	Tixosorb	26.12
DATUM	27 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	

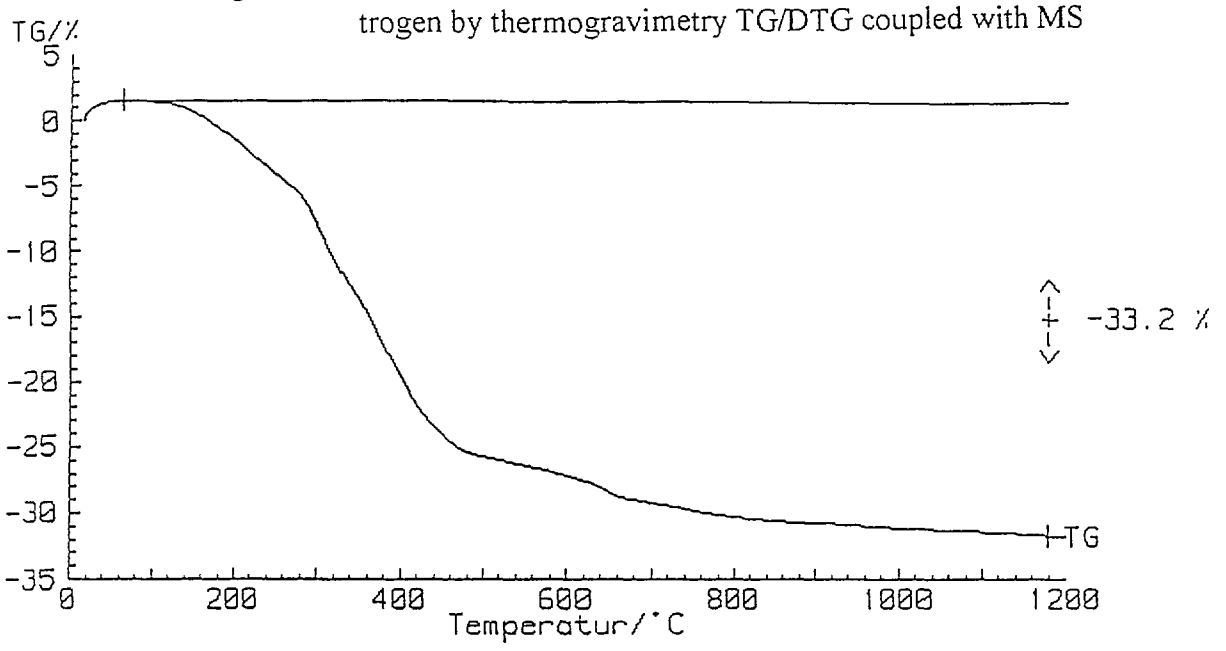


VERSUCHSNR.	M52-Tixosorb	PROBE	Tixosorb	26.12
DATUM	27 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	

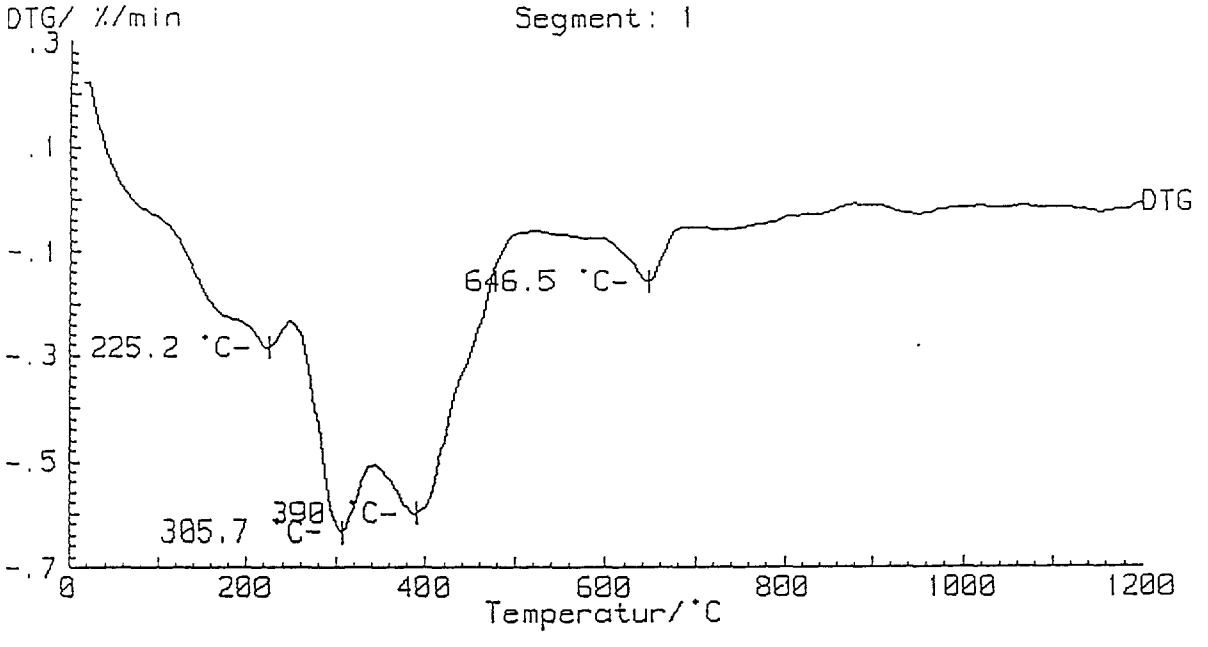


VERSUCHSNR.	M52-Tixosorb	PROBE	Tixosorb	26.12
DATUM	27 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	

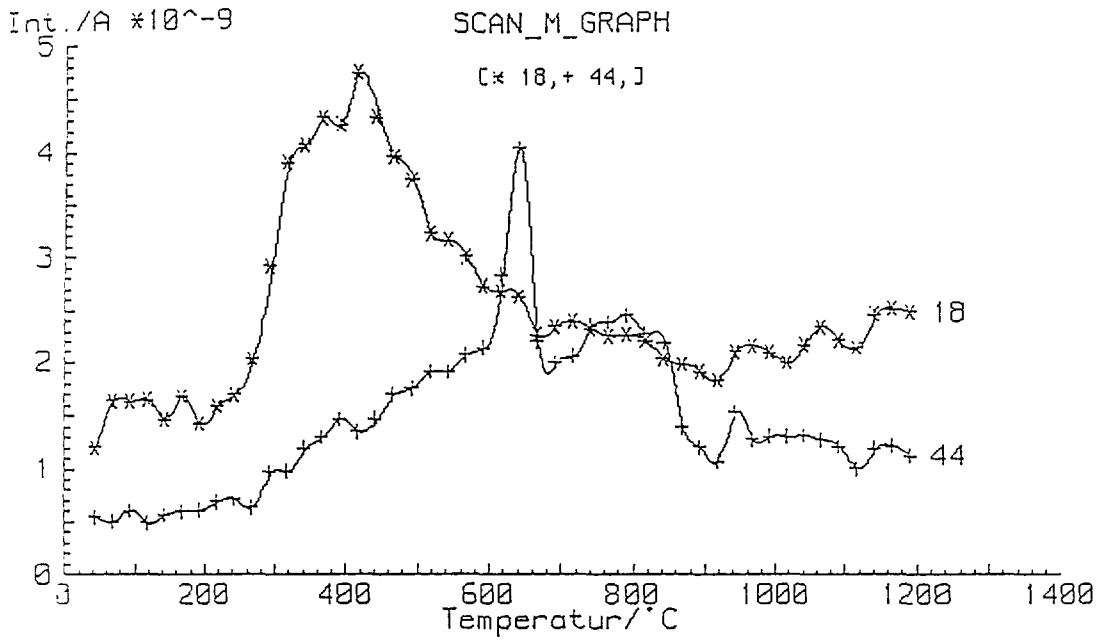
Fig. 16. Thermal stability of DCP treated TIXOSORB characterized during heating in nitrogen by thermogravimetry TG/DTG coupled with MS



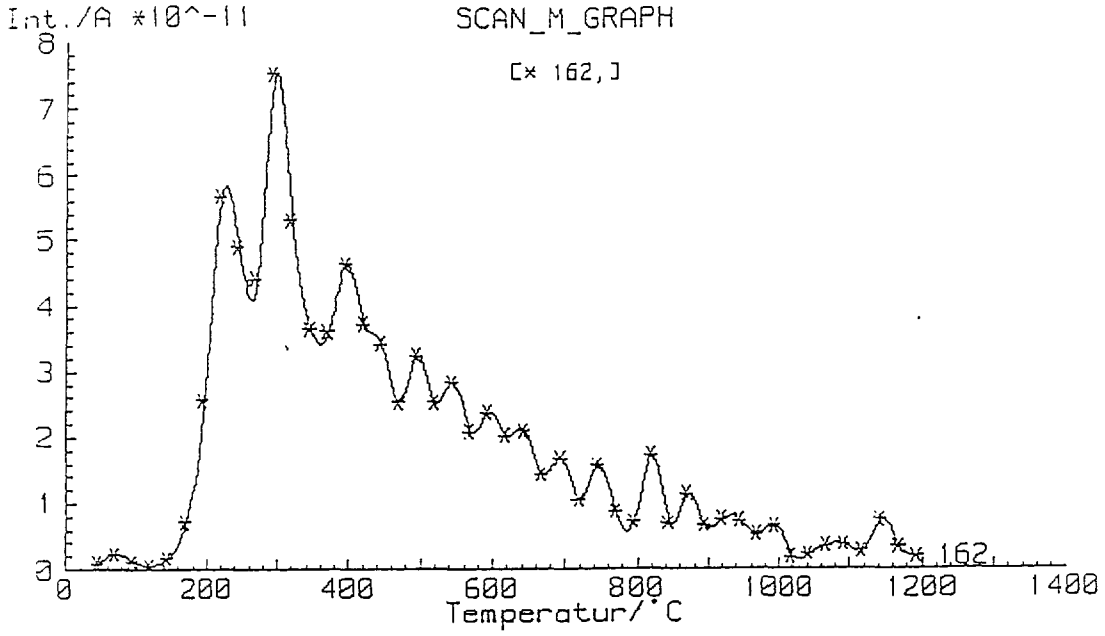
VERSUCHSNR.	M63-TixosorbDCP	PROBE	Tixosorb+DCP	25
DATUM	4 Oct 1996	REFERENZ	Al203	25
LABOR	IOeC TA-Labor	ATMOSPHÄRE	Stickstoff/ca.	100 mL
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N + DTA	



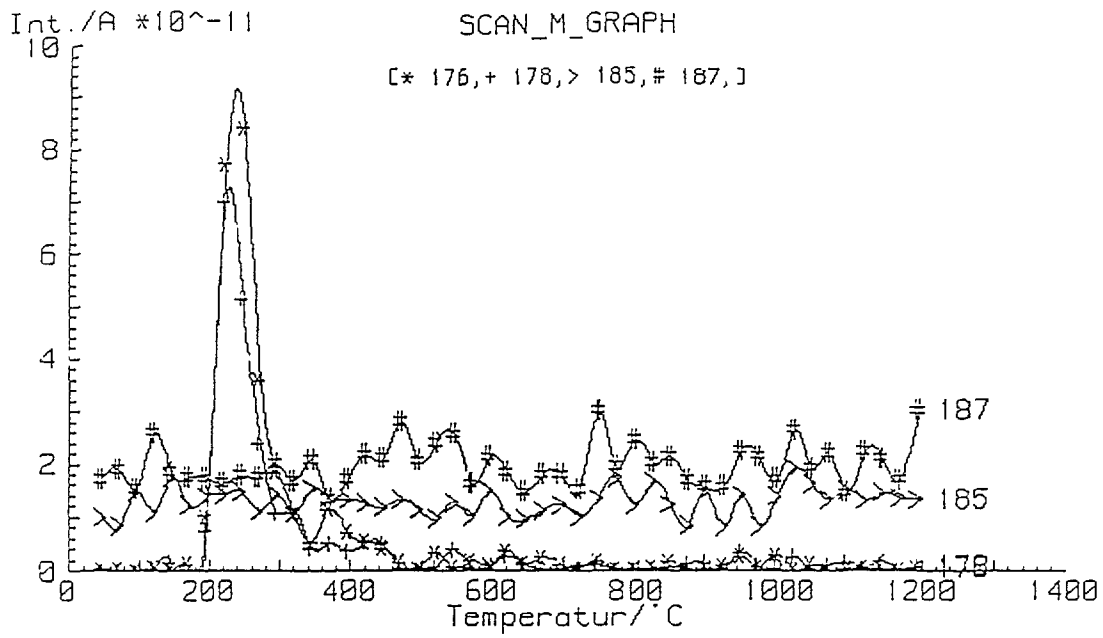
VERSUCHSNR.	M63-TixosorbDCP	PROBE	Tixosorb+DCP	25
DATUM	4 Oct 1996	REFERENZ	Al203	25
LABOR	IOeC TA-Labor	ATMOSPHÄRE	Stickstoff/ca.	100 mL
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N + DTA	



VERSUCHSNR.	M63-TixosorbDCP	PROBE	Tixosorb+DCP	25
DATUM	4 Oct 1996	REFERENZ	Al203	25
LABOR	IOeC TA-Labor	ATMOSPHÄRE	Stickstoff/ca.	100 mL
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N + DTA	

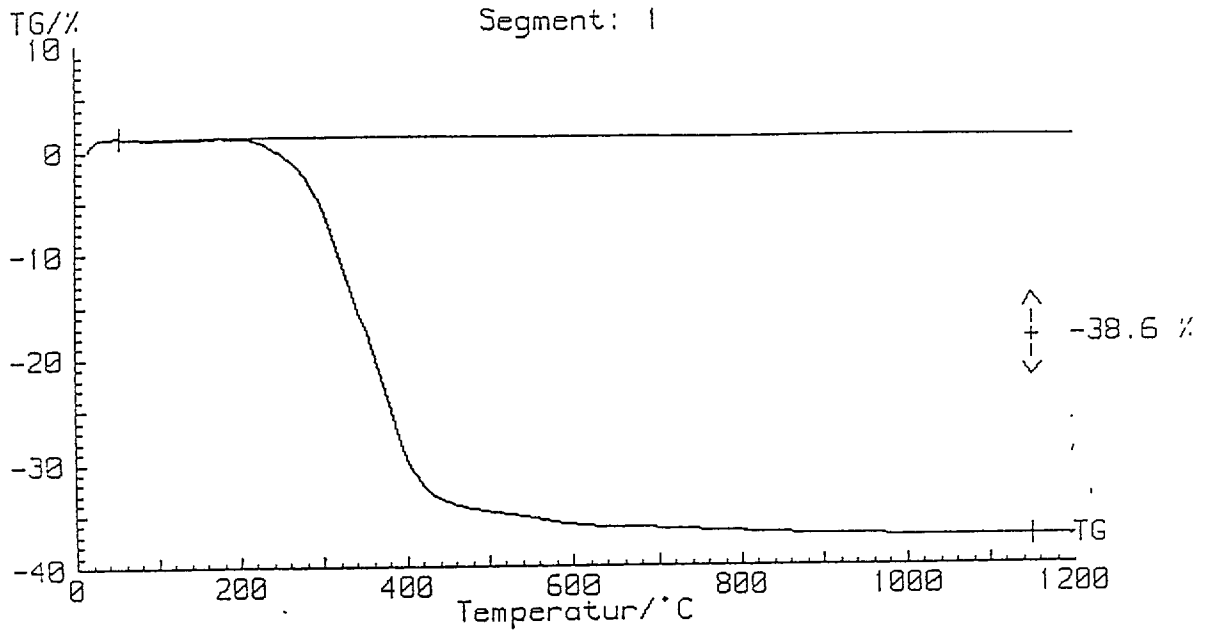


VERSUCHSNR.	M63-TixosorbDCP	PROBE	Tixosorb+DCP	25
DATUM	4 Oct 1996	REFERENZ	Al203	25
LABOR	IOeC TA-Labor	ATMOSPHÄRE	Stickstoff/ca.	100 mL
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N + DTA	

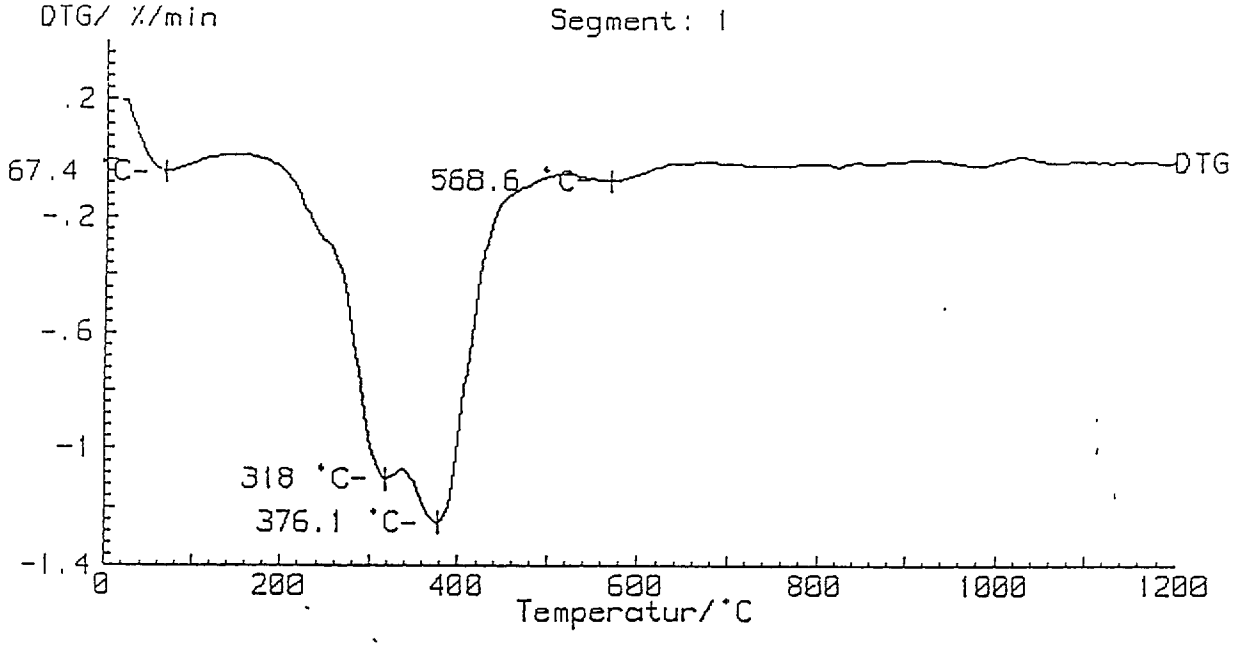


VERSUCHSNR.	M63-TixosorbDCP	PROBE	Tixosorb+DCP	25
DATUM	4 Oct 1996	REFERENZ	Al203	25
LABOR	IOeC TA-Labor	ATMOSPHÄRE	Stickstoff/ca.	100 mL
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N + DTA	

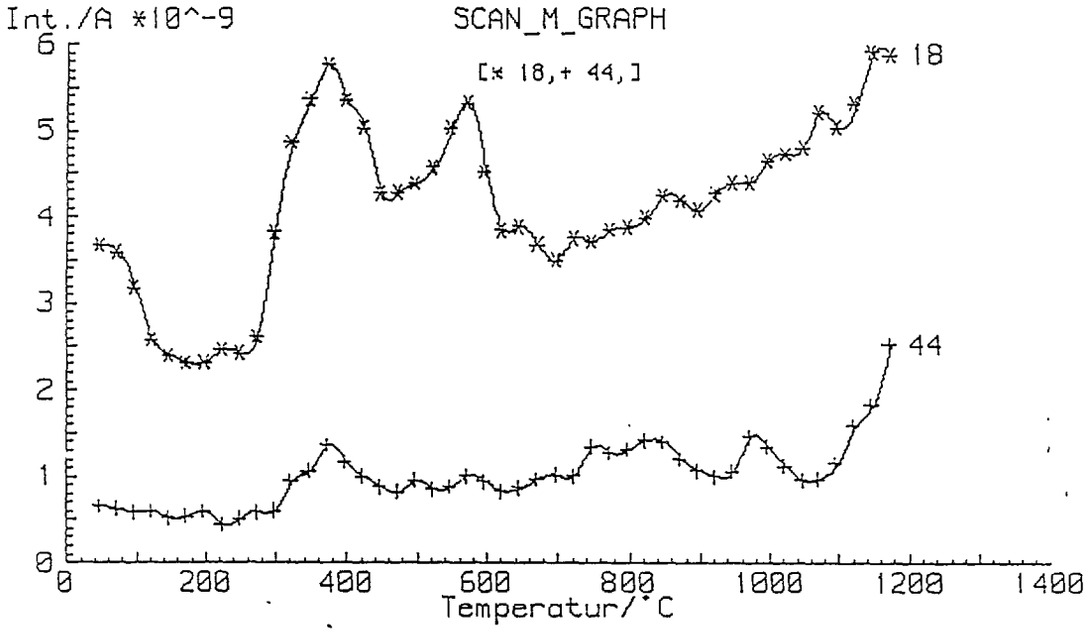
Fig. 17. Thermal stability of TIXOGEL orgahophilic bentonite products characterized during heating in nitrogen by thermogravimetry TG/DTG coupled with MS



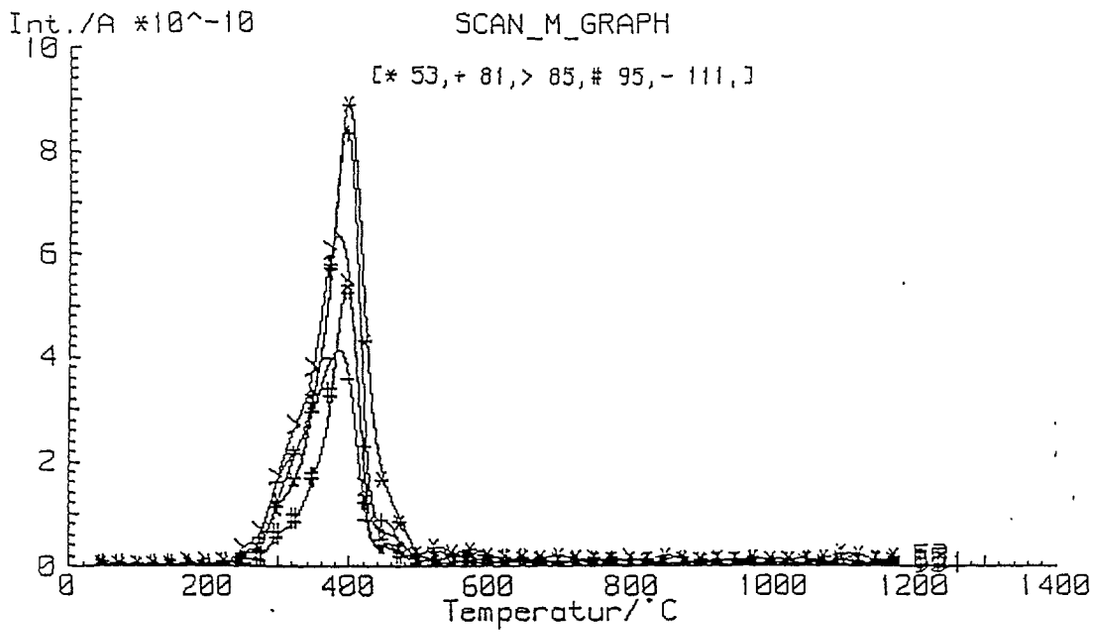
VERSUCHSNR.	M44-TIXOGEL	PROBE	TIXOGEL	25.19
DATUM	14 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



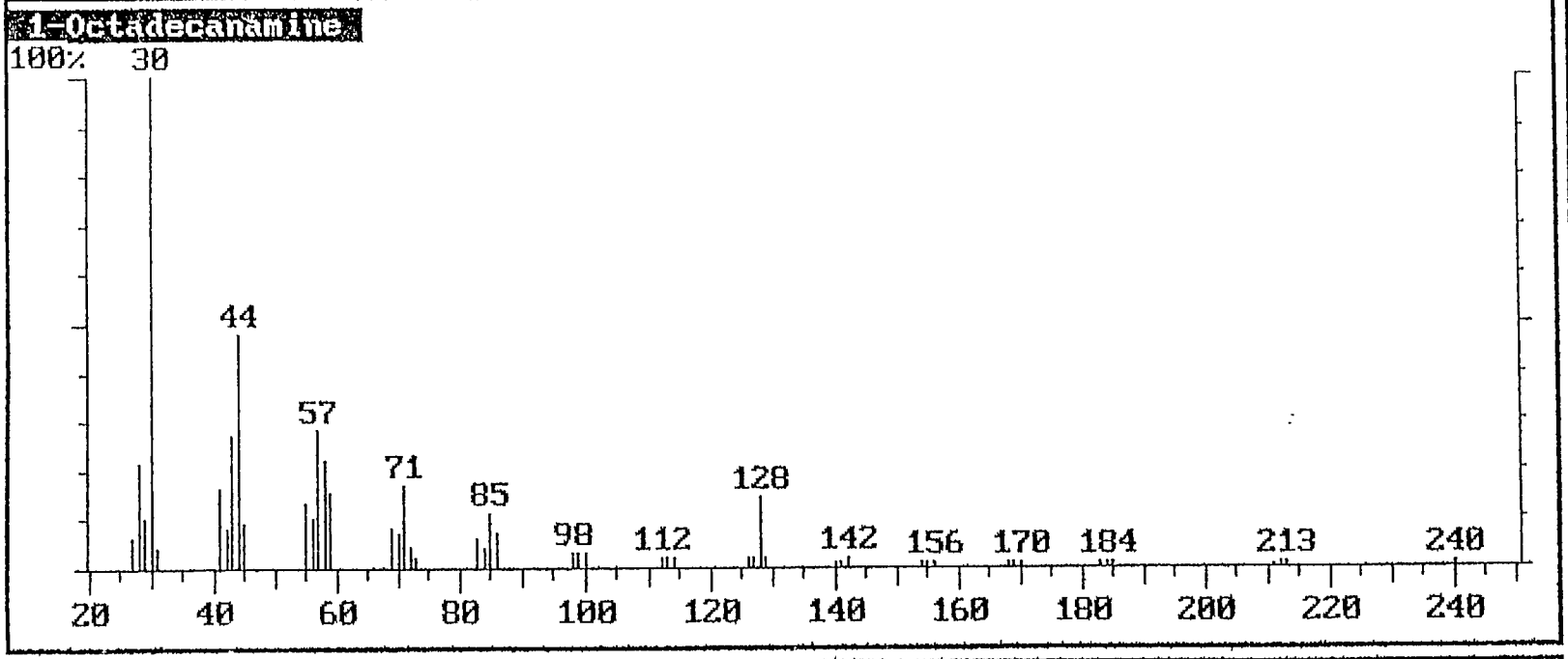
VERSUCHSNR.	M44-TIXOGEL	PROBE	TIXOGEL	25.19
DATUM	14 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



VERSUCHSNR.	M44-TIXOGEL	PROBE	TIXOGEL	25.19
DATUM	14 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



VERSUCHSNR.	M44-TIXOGEL	PROBE	TIXOGEL	25.19
DATUM	14 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



Entry Statistics
File: NIST
Entry: 37603
Peaks: 50
Mol Wt: 269
CAS#: 124-30-1
C18.H39.N

Mass	Int	Mass	Int	Mass	Int	Mass	Int	Mass	Int
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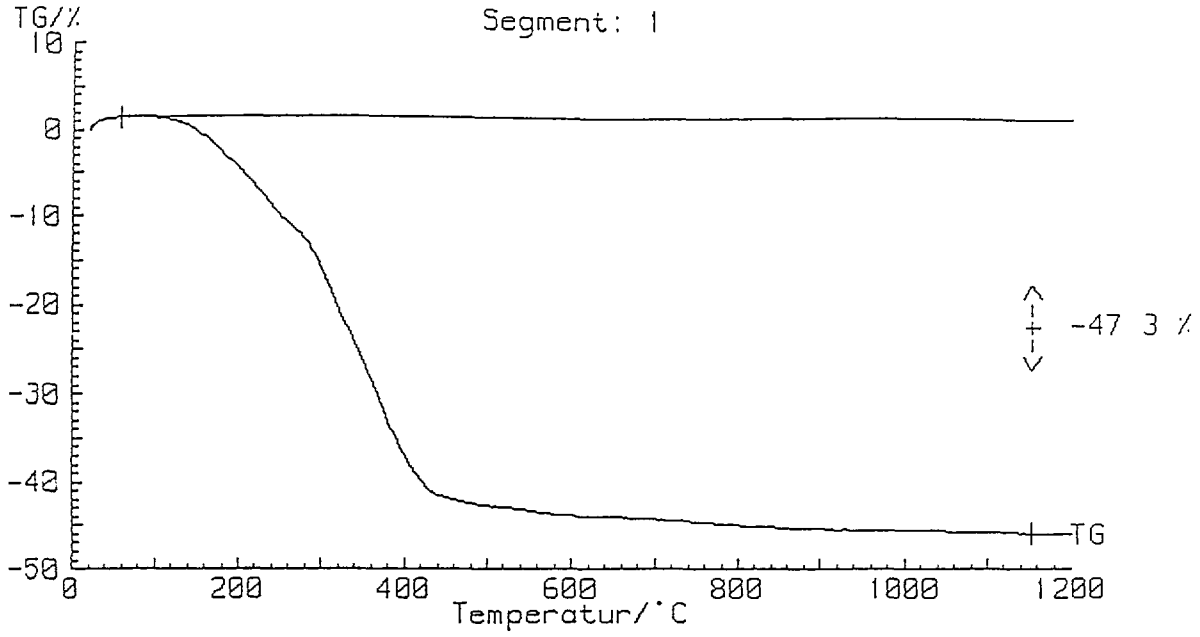
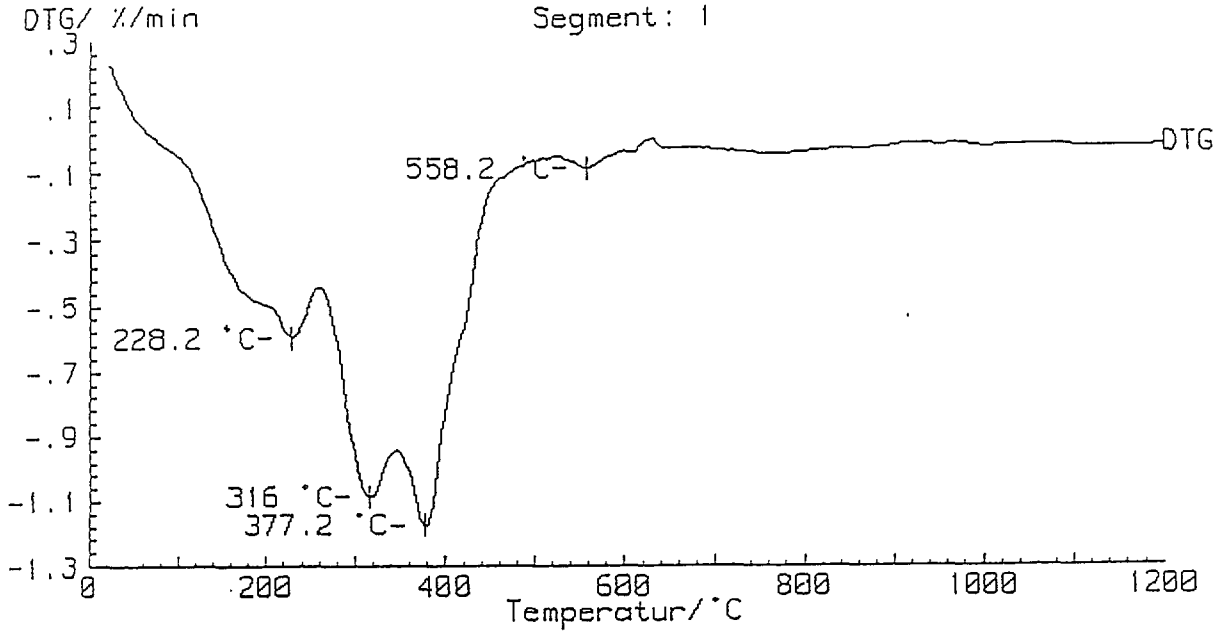
28	21139	56	10018	84	3998	127	2022	169	873
29	10018	57	28033	85	10983	128	14016	170	965
30	100000	58	21966	86	6985	129	2022	183	689
31	4090	59	14935	98	3033	140	1011	184	1011
41	15992	69	7996	99	2987	141	1011	185	827
42	7996	70	7031	100	3033	142	2022	211	505
43	27159	71	16865	112	2022	154	689	212	873
44	48023	72	3998	113	2022	155	919	213	1011
45	9099	73	1976	114	1976	156	1011	240	689

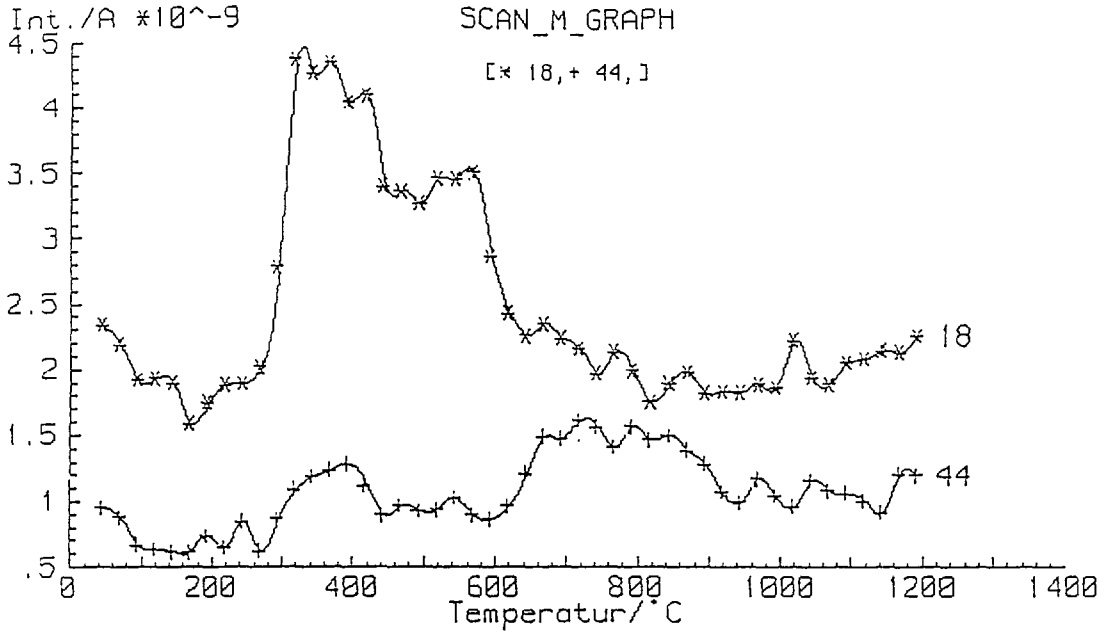
Fig. 18. Thermal stability of DCP treated TIXOGEL characterized during heating in nitrogen by thermogravimetry TG/DTG coupled with MS



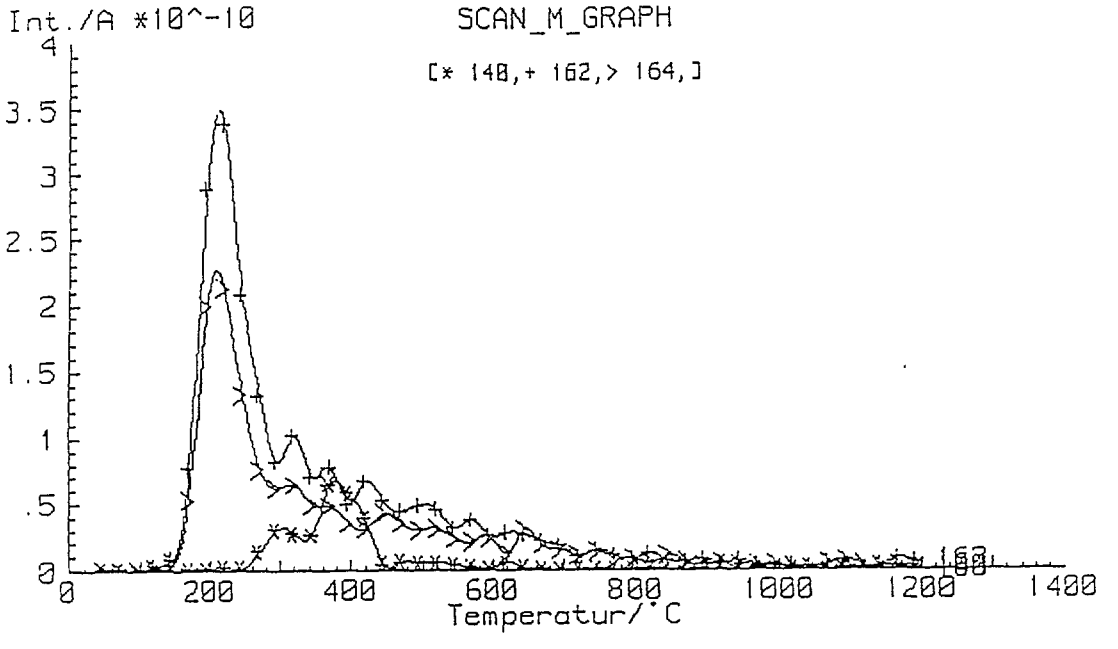
VERSUCHSNR.	M65-Tixogel+DCP	PROBE	Tixogel+DCP	25
DATUM	7 Oct 1996	REFERENZ	Al2O3	25
LABOR	IOeC TA-Labor	ATMOSPHÄRE	Stickstoff/ca.	100 mL
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N + DTA	



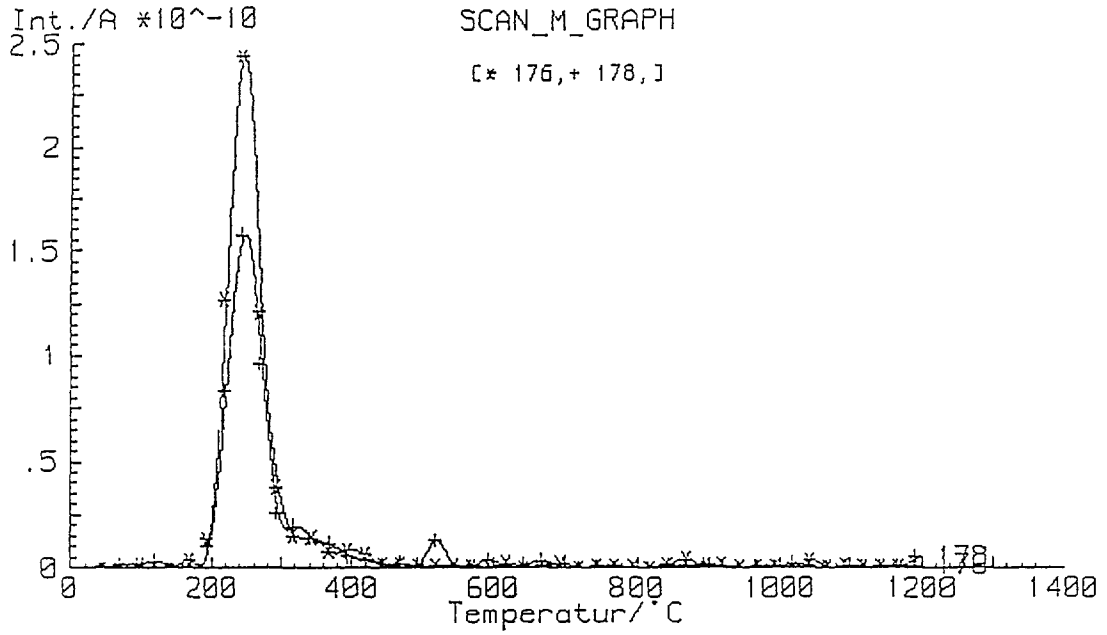
VERSUCHSNR.	M65-Tixogel+DCP	PROBE	Tixogel+DCP	25
DATUM	7 Oct 1996	REFERENZ	Al2O3	25
LABOR	IOeC TA-Labor	ATMOSPHÄRE	Stickstoff/ca.	100 mL
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N + DTA	



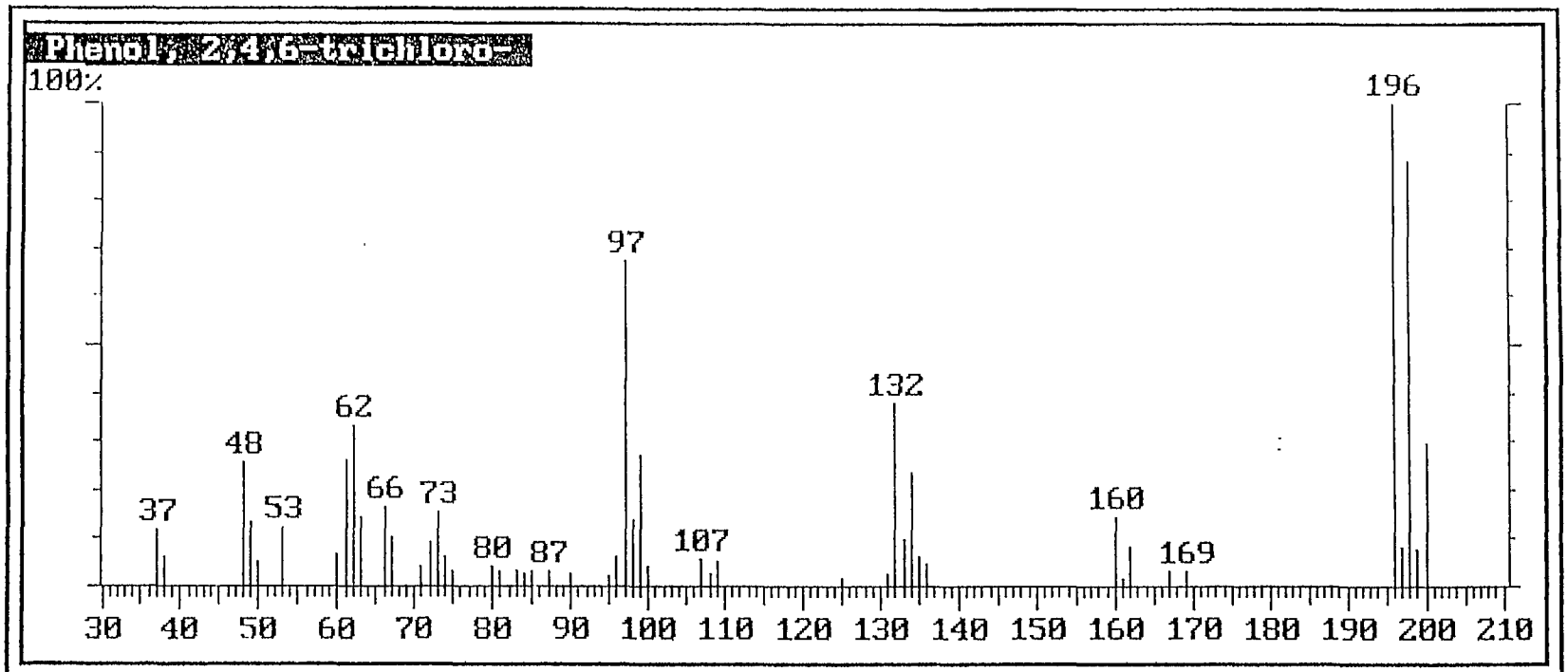
VERSUCHSNR.	M65-Tixogel+DCP	PROBE	Tixogel+DCP	25
DATUM	7 Oct 1996	REFERENZ	Al2O3	25
LABOR	IOeC TA-Labor	ATMOSPHÄRE	Stickstoff/ca.	100 mL
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N + DTA	



VERSUCHSNR.	M65-Tixogel+DCP	PROBE	Tixogel+DCP	25
DATUM	7 Oct 1996	REFERENZ	Al2O3	25
LABOR	IOeC TA-Labor	ATMOSPHÄRE	Stickstoff/ca.	100 mL
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N + DTA	

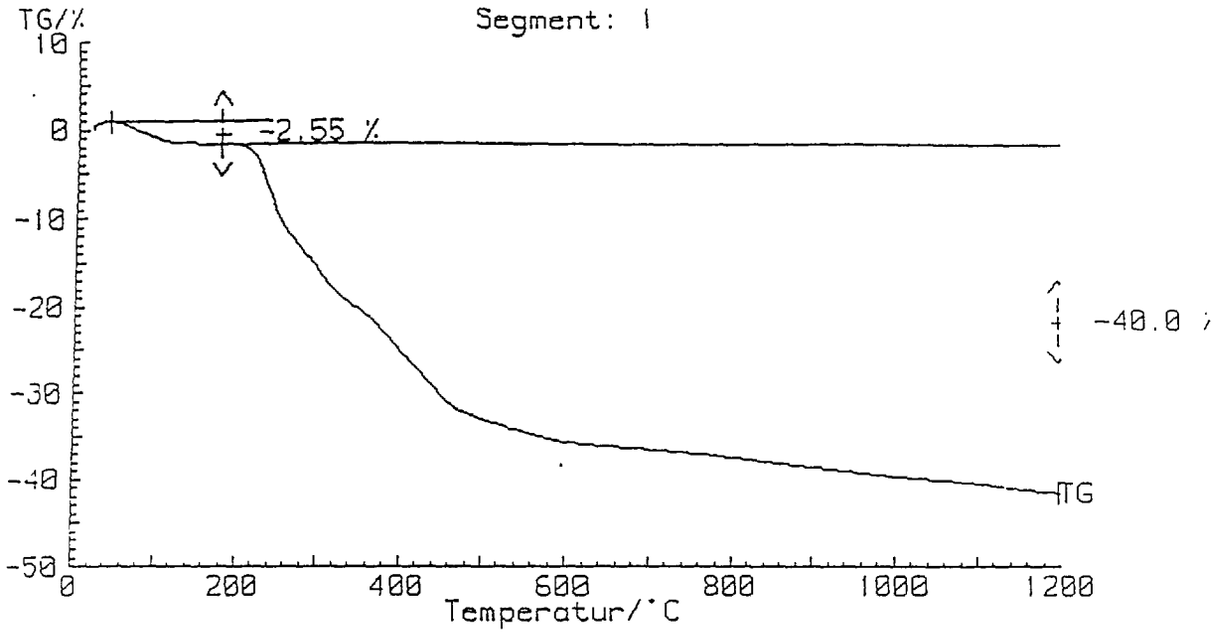


VERSUCHSNR.	M65-Tixogel+DCP	PROBE	Tixogel+DCP	25
DATUM	7 Oct 1996	REFERENZ	Al2O3	25
LABOR	IOeC TA-Labor	ATMOSPHÄRE	Stickstoff/ca.	100 mL
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N + DTA	

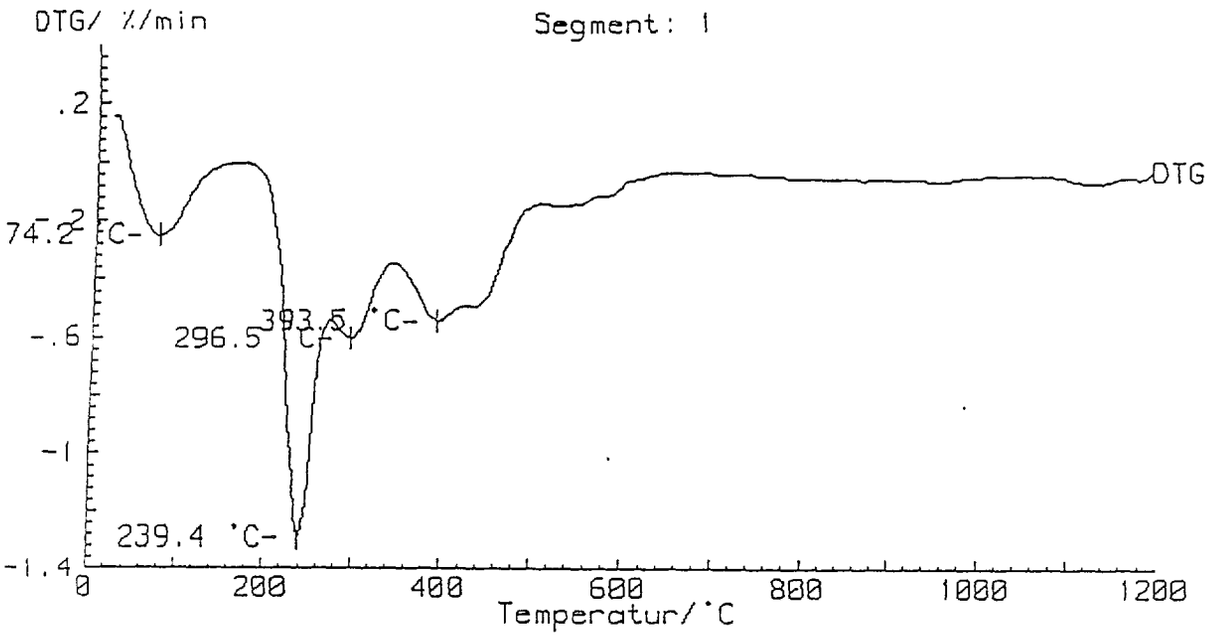


Entry Statistics	Mass/Int		Mass/Int		Mass/Int		Mass/Int		Mass/Int	
File: NIST	37	11411	66	15915	84	2402	107	5405	160	14114
Entry: 21646	38	6006	67	9909	85	2702	108	2102	161	1201
Peaks: 50	48	25225	71	3603	87	2702	109	4804	162	7807
Mol Wt: 196	49	13213	72	9009	90	2402	125	1501	167	2702
CAS#: 88-06-2	50	5105	73	15315	95	1801	131	2102	169	3003
----------	53	12012	74	6006	96	6006	132	37537	196	100000
C6.H3.Cl3.O	60	6306	75	2702	97	67267	133	9309	197	8108
	61	25825	80	3603	98	13513	134	23423	198	88288
	62	33033	81	2702	99	27027	135	5705	199	7207
	63	14114	83	3003	100	3903	136	4504	200	29729

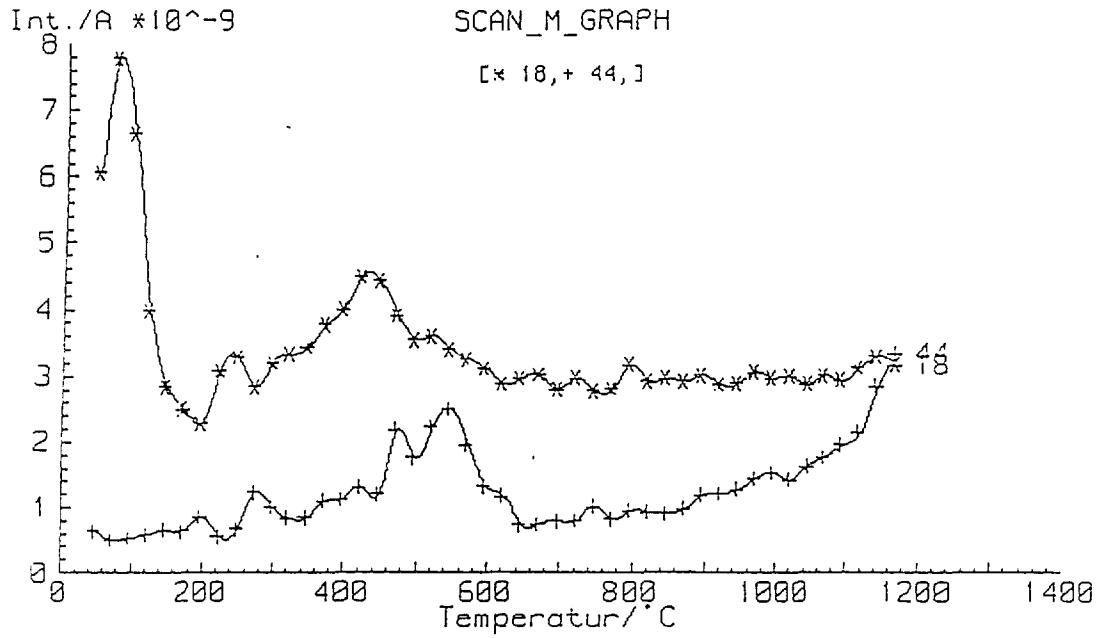
Fig. 19. Thermal stability of BR treated TIXOSORB characterized during heating in nitrogen by thermogravimetry TG/DTG coupled with MS



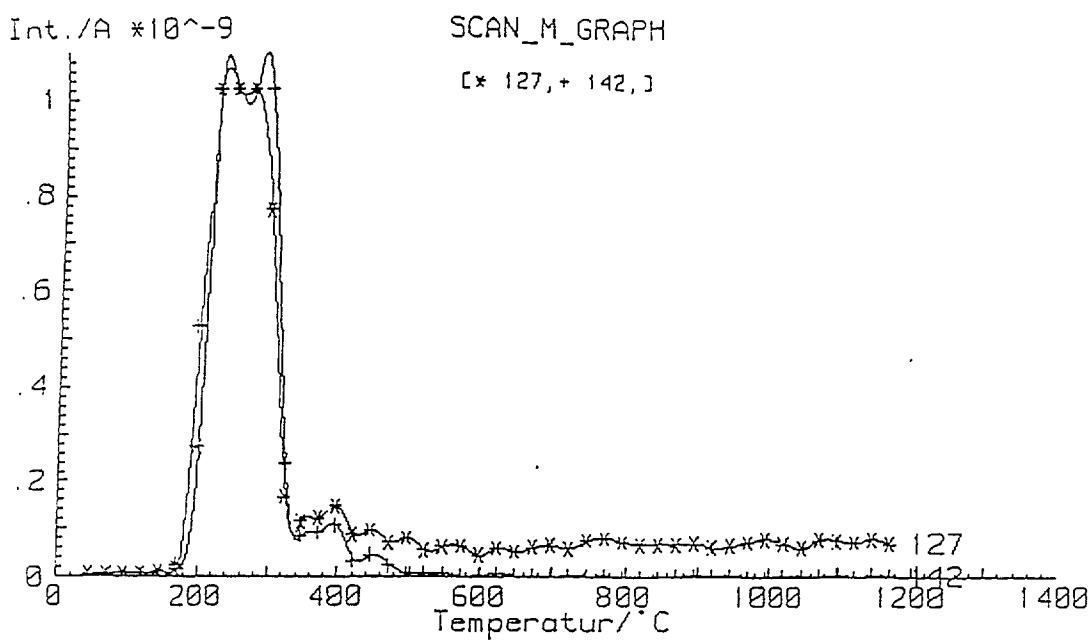
VERSUCHSNR.	M53-Tixosorb+BR	PROBE	Tixosorb+BR 25.2
DATUM	27 Aug 1996		
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/
OPERATEUR	CN		
NETZSCH	409/429-403	BEMERKUNG	S C A N



VERSUCHSNR.	M53-Tixosorb+BR	PROBE	Tixosorb+BR 25.2
DATUM	27 Aug 1996		
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/
OPERATEUR	CN		
NETZSCH	409/429-403	BEMERKUNG	S C A N

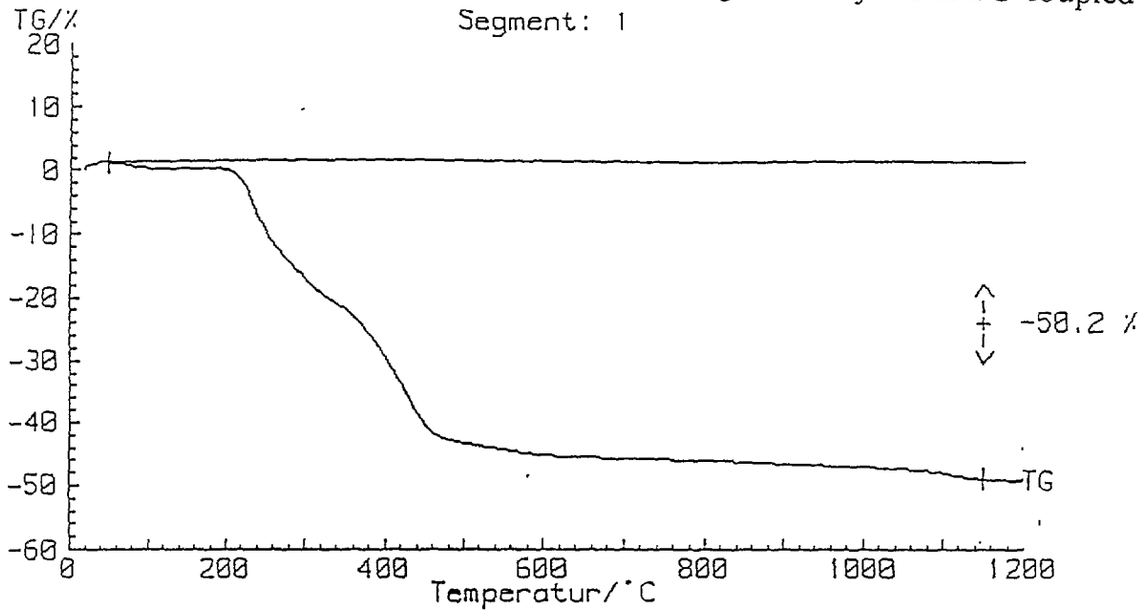


VERSUCHSNR.	M53-Tixosorb+BR	PROBE	Tixosorb+BR	25.2
DATUM	27 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	

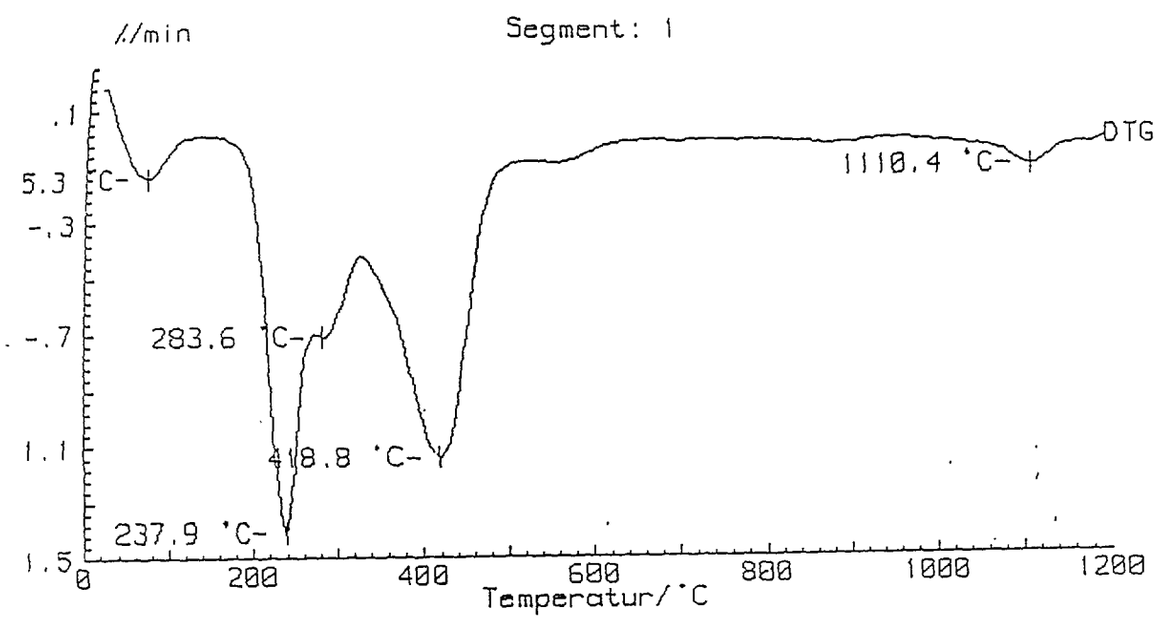


VERSUCHSNR.	M53-Tixosorb+BR	PROBE	Tixosorb+BR	25.2
DATUM	27 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	

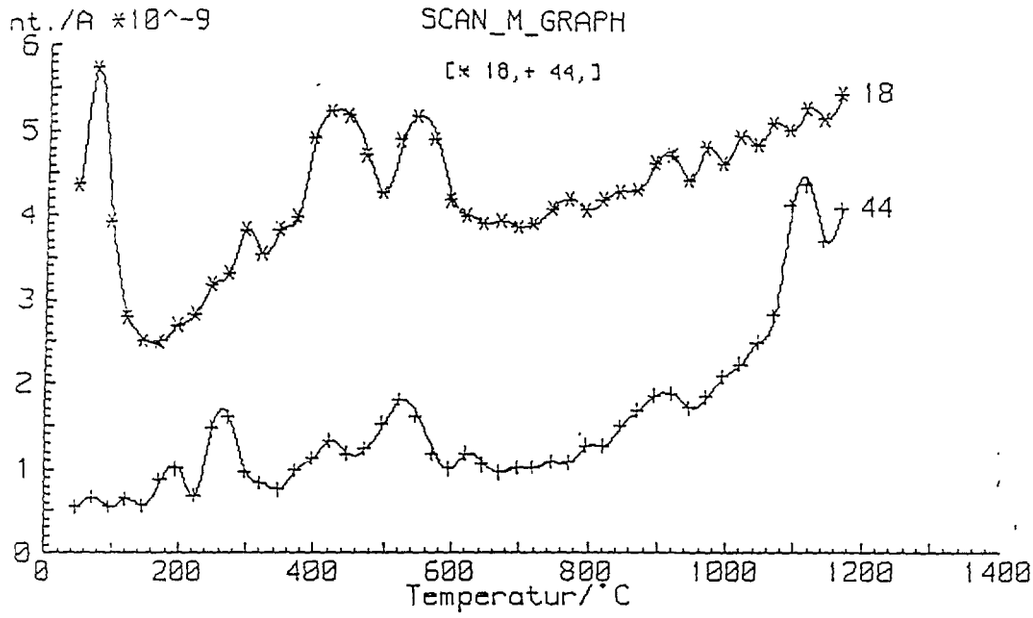
Fig. 20. Thermal stability of BR treated orgahophilic bentonite products characterized during heating in nitrogen by thermogravimetry TG/DTG coupled with MS



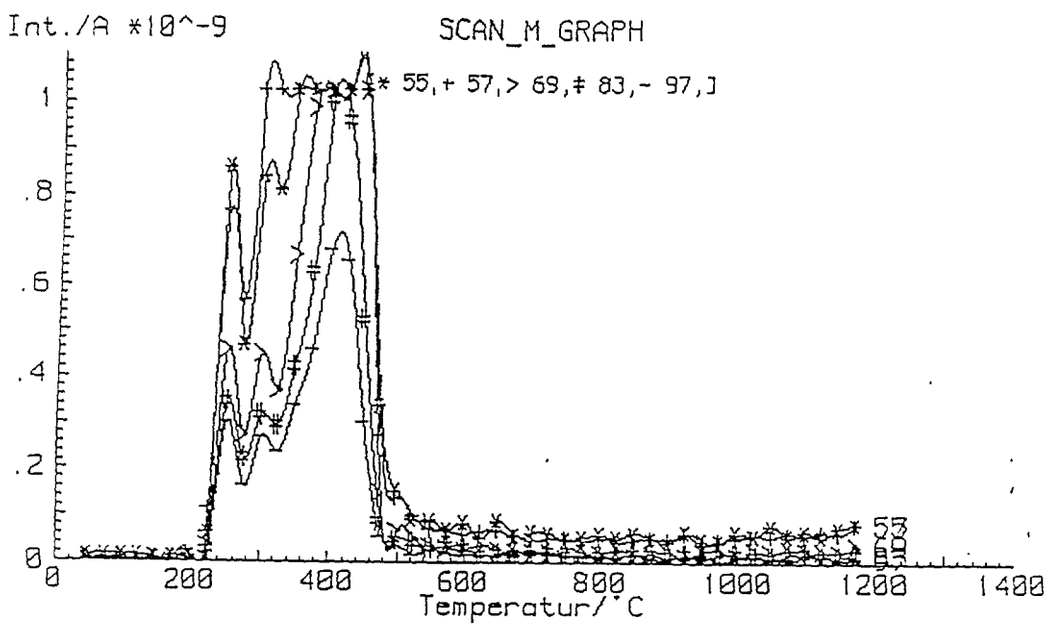
VERSUCHSNR.	M45-TIXOGEL+BR	PROBE	TIXOGEL+BR	25.2
DATUM	14 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



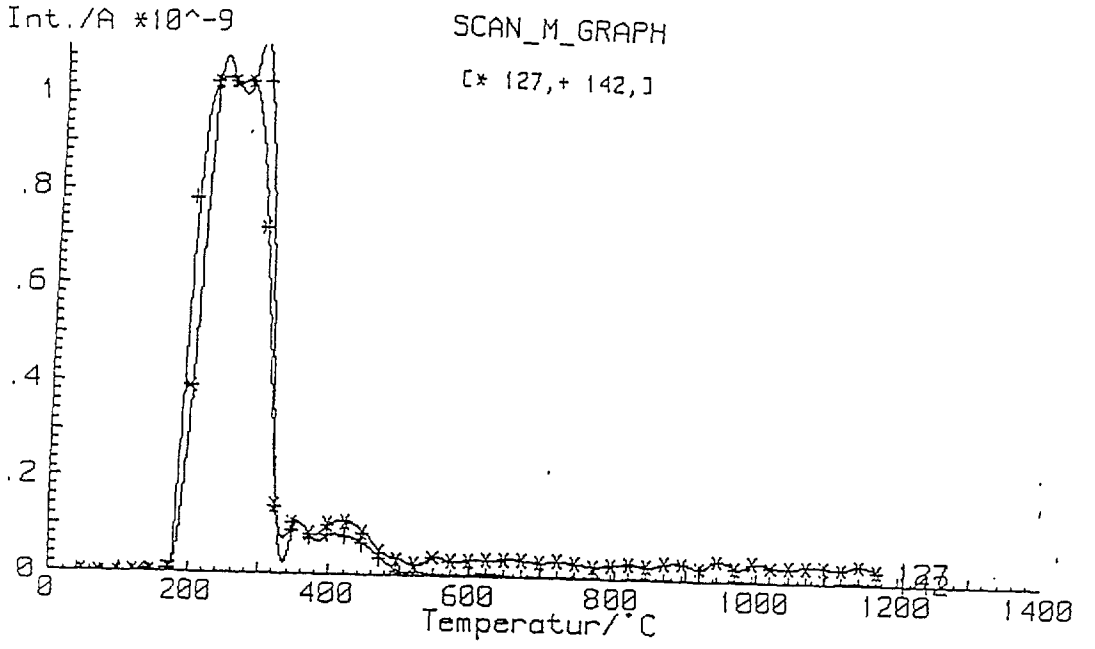
)ERSUCHSNR.	M45-TIXOGEL+BR	PROBE	TIXOGEL+BR	25.2
)ATUM	14 Aug 1996			
.ABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
)PERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



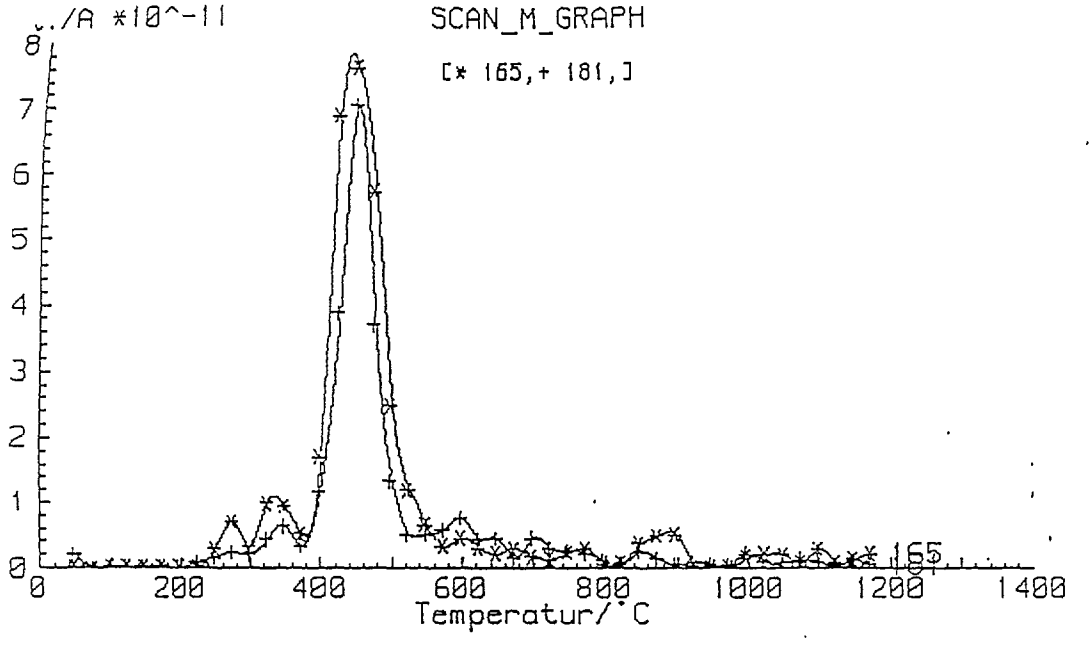
ERSUCHSNR.	M45-TIXOGEL+BR	PROBE	TIXOGEL+BR	25.2
ATUM	14 Aug 1996			
ABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
PERATEUR	CN			
ETZSCH	409/429-403	BEMERKUNG	S C A N	



VERSUCHSNR.	M45-TIXOGEL+BR	PROBE	TIXOGEL+BR	25.2
DATUM	14 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



VERSUCHSNR.	M45-TIXOGEL+BR	PROBE	TIXOGEL+BR	25.2
DATUM	14 Aug 1996			
LABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
OPERATEUR	CN			
NETZSCH	409/429-403	BEMERKUNG	S C A N	



ERSUCHSNR.	M45-TIXOGEL+BR	PROBE	TIXOGEL+BR	25.2
ATUM	14 Aug 1996			
ABOR	IOEC TA-LABOR	ATMOSPHÄRE	Stickstoff/ca.100 ml/	
PERATEUR	CN			
ETZSCH	409/429-403	BEMERKUNG	S C A N	

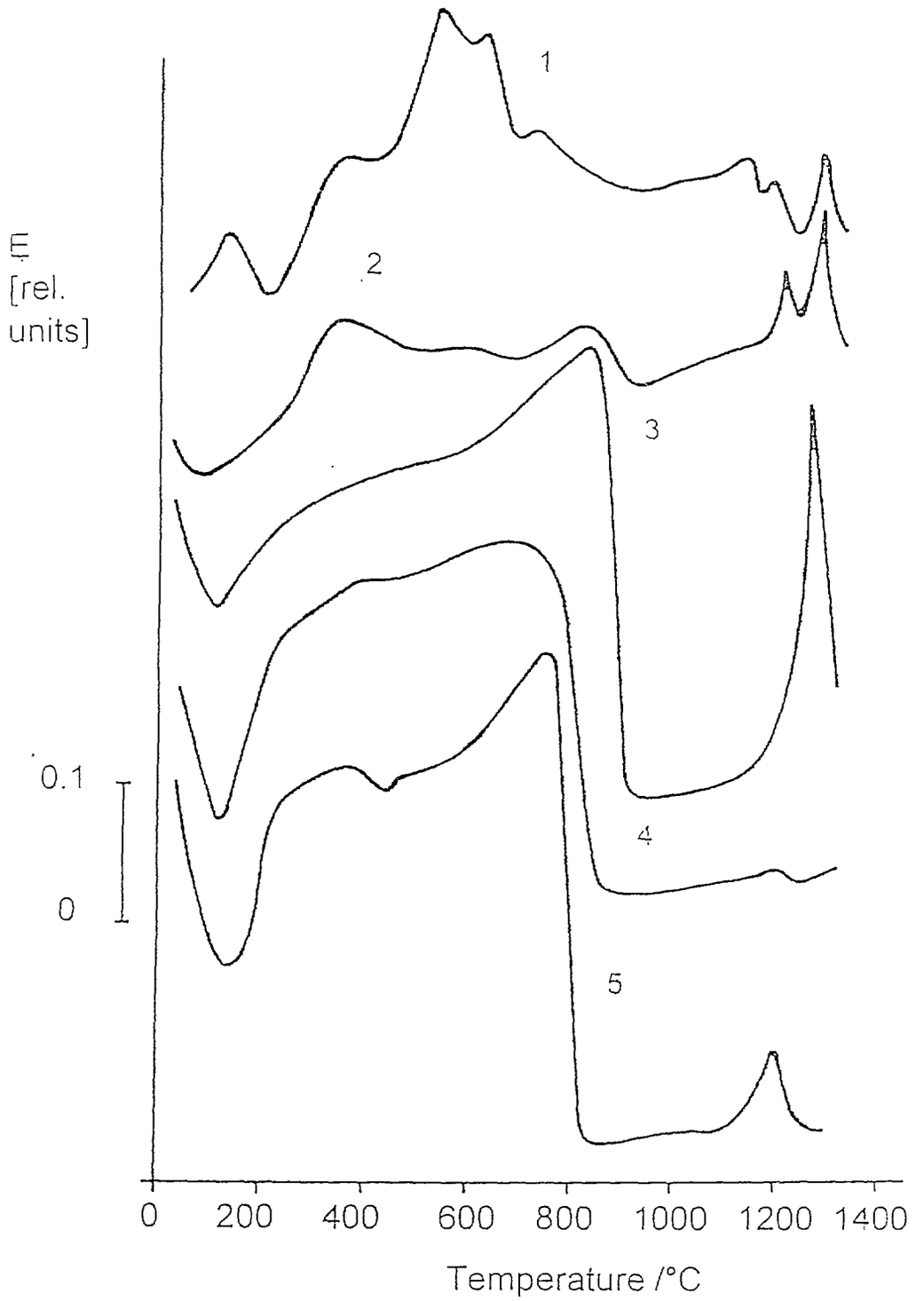


Fig. 21. Results of emanation thermal analysis characterizing microstructure changes taking place during heating argon of TIXOTON product before and after treatment with different organic compounds

curve1: TIXOTON – non treated, curves 2–5: TIXOTON treated with diethylamine, acetic acid, n-heptan and ethylenglycol, respectively