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A macro STA-system for environmental samples

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Abstract

A new Thermal Analyser was developed for solving environmental problems with TA–MS. The sample volume of 170 ml and the balance capacity of 500 g allow a real upscaling, i.e. representative amount of waste can be tested. The furnace is designed for a homogeneous heating of this large sample volume and the gas flow system guarantees a direct interaction between the purge gas (up to $1000\ \mathrm{ml\ min^{-1}}$) and the sample. Simultaneous thermogravimetry and differential thermal analysis are possible up to 1200°C. Because of the ecological importance of the evolved volatiles during waste incineration, this Macro-STA 419, is equipped with an on line mass spectrometer coupling by a double orifice system, heatable up to 350°C as well as a GC–MS system. All construction parts which come in contact with the sample and the decomposition products are resistant to corrosion. The new developed system is introduced, some specific technical requirements are discussed together with their solutions, and applications will be presented. © 1997 Elsevier Science B.V.

Keywords: Thermal analyser; TA–MS; STA-system

1. Introduction

In the field of waste-, soil- and contaminated site analysis as well as risk assessment of hazardous compounds there are considerable research deficits, especially regarding the thermal disposal or reconstruction. In principle, these problems can be solved by the methods of thermal analysis as differential thermal analysis (DTA) and thermogravimetry (TG), especially with direct coupling to high sensitive gas analysis techniques, like mass spectrometry (MS) [1]. With these analytical capacities thermal processes can be investigated or simulated under selectable atmospheric conditions whereby all necessary informations can be won [2–29].

In the past, the development of these thermoanalytical methods by highly sensitive and precise analytical techniques, resulted in a miniaturisation of the measuring cells which led to the minimisation of the sample quantities. So, today only few milligrams of the sample material are necessary and possible.

Nevertheless, the samples developed from the problems mentioned above, e.g. garbage or contaminated soil, are normally heterogeneous materials with varying composition. So the results, taken from a few milligram of the sample are neither representative nor meaningful and the conclusions drawn from a transfer relationship of about $1 : 10^{10}$ are no reliable bases for the judgement and risk assessment. Further problems arise from the available mass spectrometric coupling systems. In most cases, the efficiency of the MS is limited so that a detection of trace hazards is not possible and due to the complex nature of the sample, the on line measured mass spectra result from complex gas mixtures. This complicates the interpretation or

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even makes it impossible. So, the goals of further development were:

- enlarging of the sample capacity,
- simultaneous coupling of thermal analysis with MS and GC–MS,
- identification of trace hazards,
- separation of complex gas mixtures.

2. Device

A more favourable transfer relationship can only be realised by a larger dimensioned measuring cell. This "scaling up" however could happen not only by a linear enlargement of the assembly groups of an usual thermoanalytical device. First of all, the measuring cell (sample container) needs to be constructed for the special requirements arising from the great sample amount. Due to thermal diffusivity and the dimensions of the sample, temperature gradients within the sample as well as mass transport problems have to be taken into account. For the avoidance of condensation and diffusion processes, a special gas suppliance has to be developed.

Further, the special requirements of the oven system, temperature registration, gas flow and interfacing analysis techniques like mass spectrometry and gas chromatography have to be solved.

Based on this considerations, the "Macro STA 419" -Apparatus, which is shown in Fig. 1 in principle

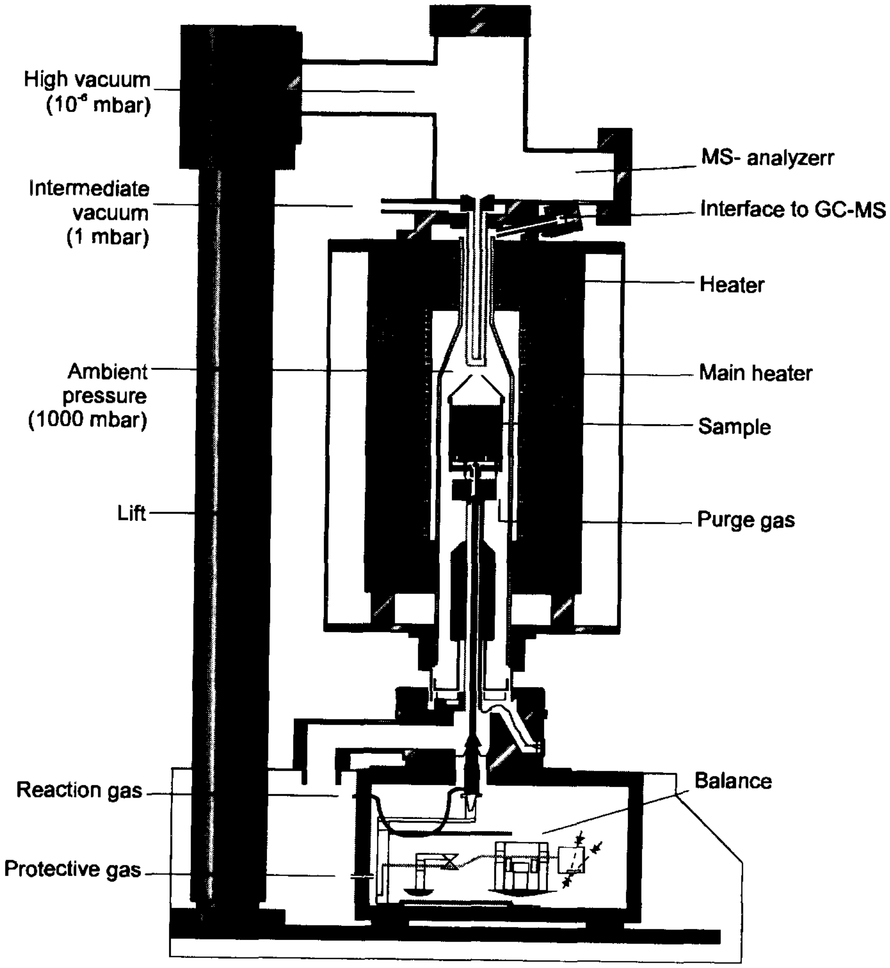

Fig. 1. Scheme of the "Macro STA 419" device

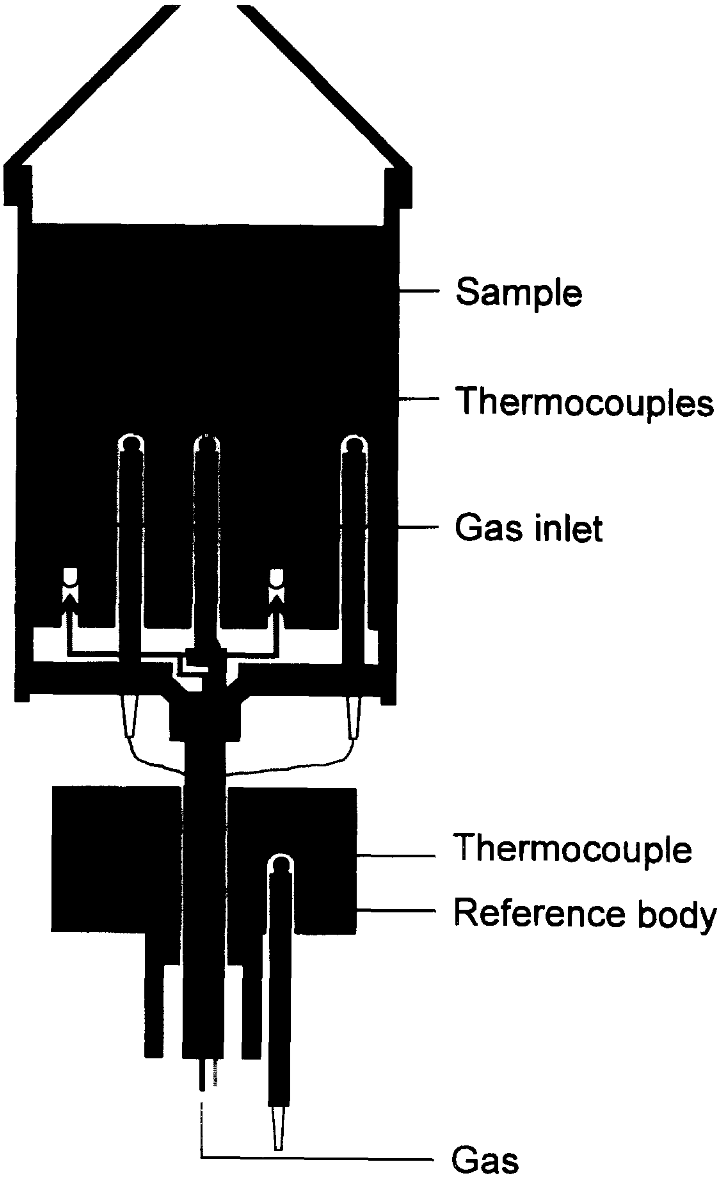

Fig. 2. Measuring cell.

was developed as a joint project in cooperation with the Netzsch- Gerätebau company.

Within the oven system, which allows a maximum temperature of 1200°C, the special measuring cell build from alumina oxide is arranged. The measuring cell, which has a volume of 170 cm^3, is placed on an evacuable analytical balance. Over the diameter of the measuring cell, shown in Fig. 2, three DTA sensors are arranged to allow an overview over the energetic processes in the sample during the heating process. The reference thermocouple is placed in a reference body outside the sample. The DTA sensors are protected by ceramic sheaths from corrosive substances.

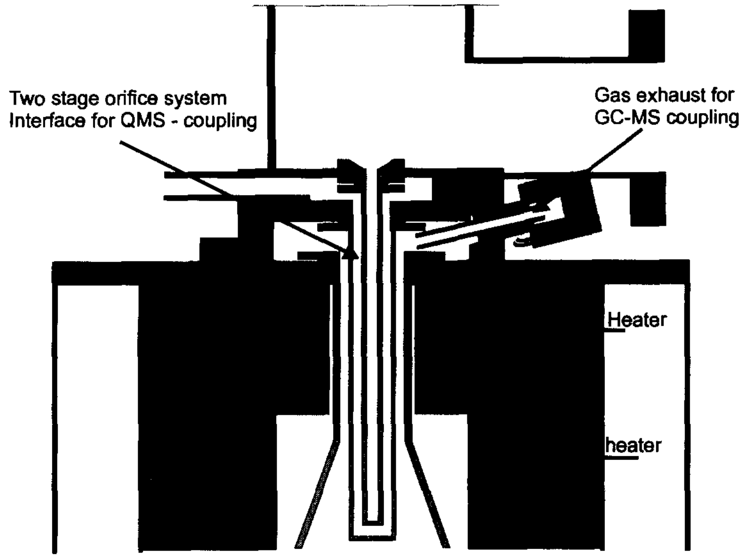

Fig. 3. Interface system for the on line coupling with QMS and GC–MS systems.

To ensure, that all parts of the sample are equal facing the chosen atmosphere and on the other hand, all evaporation or degradation products are transported actively from the measuring cell to the subsequent analytical units, the reaction gas will be supplied directly into the sample via a special bell floor. Thereby an intensive contact of the sample with the reaction gas as well as a fast detection, not hindered by diffusion phenomena is realised. The conical cover of the measuring cell focus the gases from the measuring cell on the interface system, shown in Fig. 3. Through an additional heating of the oven head a condensation of the released products is avoided and the introduction of the gases to the subsequent analytical systems results without change of their composition.

2.1. *Temperature-homogeneity*

Due to the enlargement of the measuring cell and the sample size, problems of heat transfer within the sample will occur. For this reason, a temperature gradient within the sample will be established and can be measured by the difference of the three DTA sensors (Fig. 4). It depends on the heating rate applied, the atmosphere and the sample heat capacity. To avoid or to minimise these temperature gradients, a special ceramic insert from aluminium nitrite is introduced into the measuring cell (Fig. 5).

The effects can be seen in Fig. 6. Within the TA-curves of the degradation of calcium oxalatehydrate, the degradation steps are much better separated from each other and the individual mass losses are much better in accordance to the theoretical values. The mass spectrometric detection of the degradation products (H_2O, CO and CO_2) becomes more sensitive since the same amount of calcium oxalate yields higher intensities of the individual masses.

2.2. *Gas flow and interface system*

2.2.1. *Mass spectrometric detection.*

For the subsequent gas analytical devices, it is necessary to have an active transport of the degradation or evaporation product out of the sample. For this purpose, as mentioned above, we constructed a special measuring cell with a bell shaped floor for gas supply directly through the sample. In Fig. 7 the investigation of 100 g inert material (Al_2O_3 powder), contaminated with 100 ppm naphthalene and phenanthrene is shown. The ion current intensities for each molecular ion (*m/e* 128 naphthalene and *m/e* 178 phenanthrene)

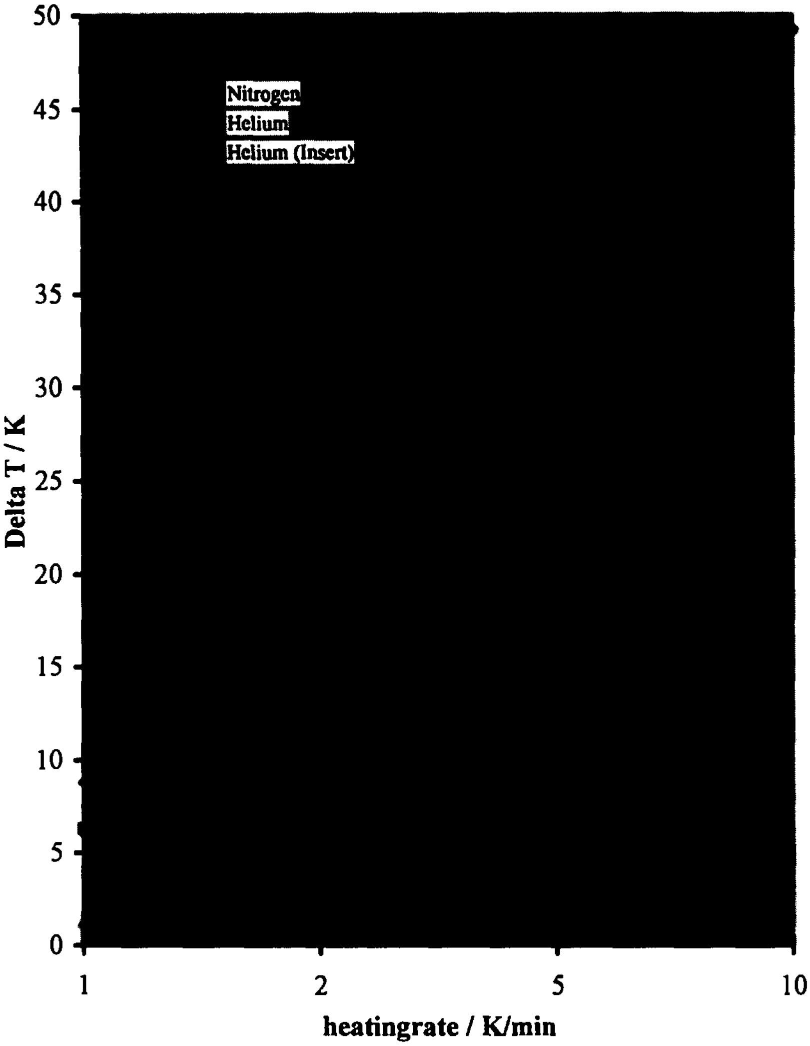

Fig. 4. Temperature differences between DTA sensors 1 and 3 at 300°C.

show significant peaks at the boiling point temperatures of each substance with a very short tailing. This indicates, that the mass spectrometric detection of these materials follows the real course of the concentration in the gas phase, and is not disturbed by diffusion processes.

2.3. GC–MS analysis

The interface system for the direct GC–MS coupling consists of a heatable valve at the top of the oven (Fig. 3). The test of the interface system was done again with a defined contaminated inert material. In this case we used 100 g alumina contaminated with 10 ppm naphthalene and phenanthrene. As it can be seen from the chromatogram in Fig. 8 both substances can be detected. Even phenanthrene with a boiling temperature of 338°C will not be lost by condensation at cold spots.

3. Application measurement

The above described device was constructed for the examination of heterogenous materials as waste-, soil-

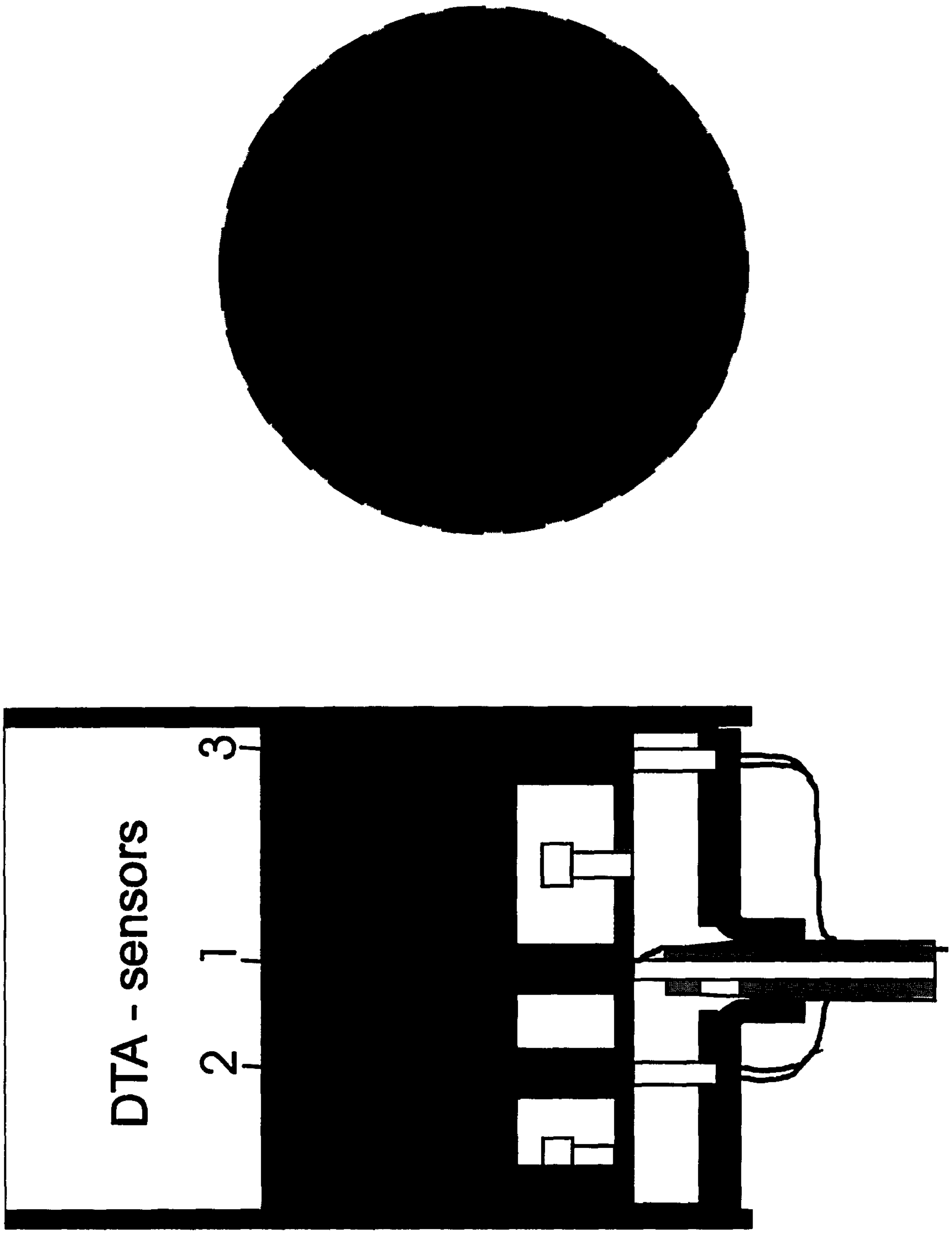

Fig. 5. Measuring cell with ceramic insert.

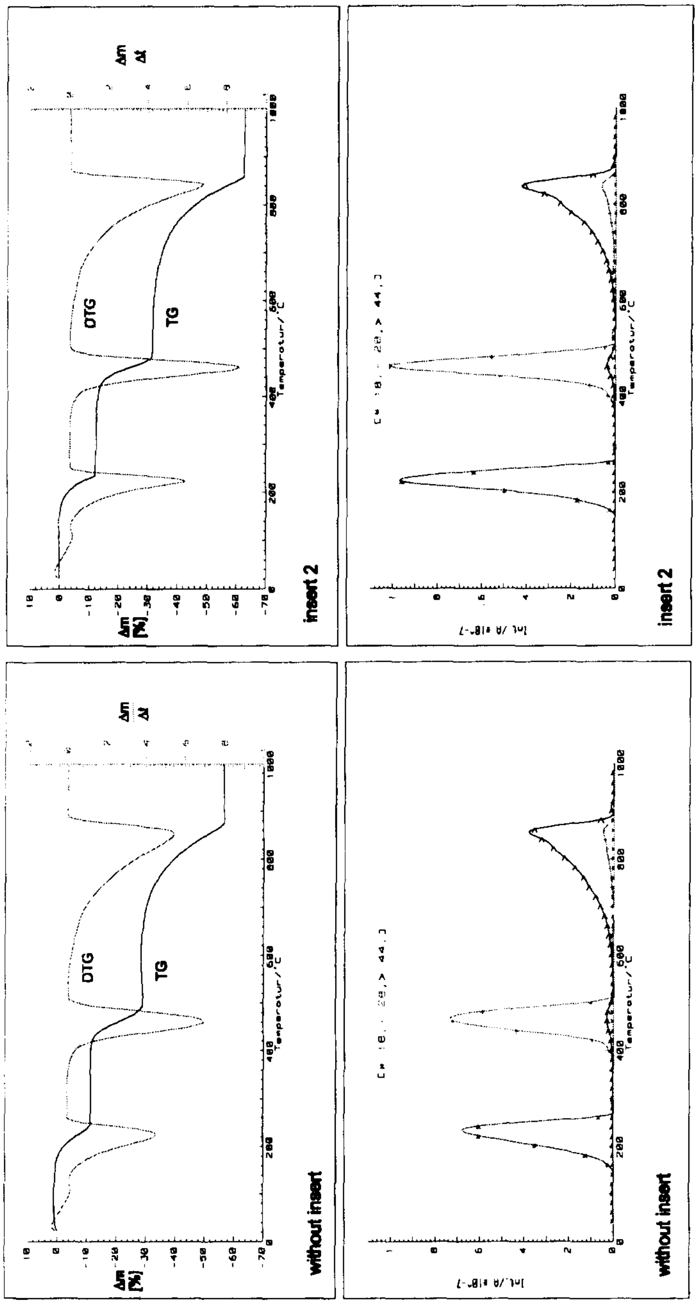

Fig. 6. TA- and MS- curves from calcium oxalate with(right) and without (left) insert.

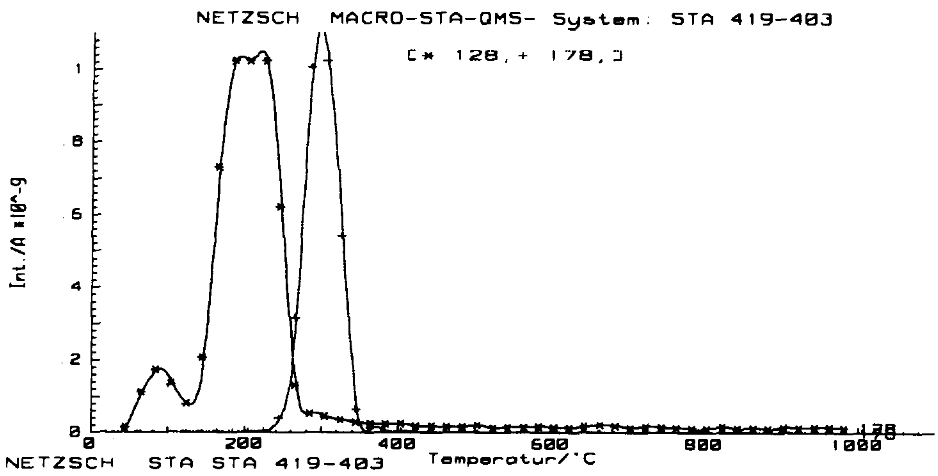

Fig. 7. Ion current intensities of naphthalene and phenanthrene.

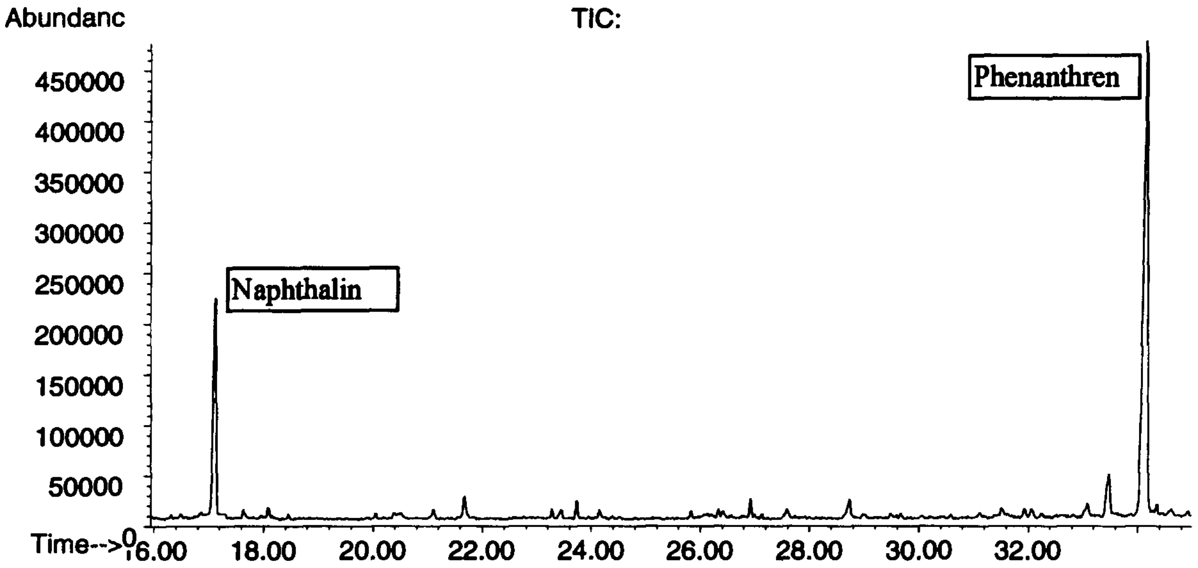

Fig. 8. Total Ion Chromatogram from 10 ppm naphthalene and phenanthrene.

and contaminated site samples. For a test of the total device we investigated a contaminated soil sample from an industrial ground. The sample was prepared, using 150 g quartz sand and 10 g of the soil sample. The inert quartz material was used to fill up the measuring cell for positioning the soil sample around the DTA sensors and to cover the sample. The sample was investigated in an argon atmosphere from ambient temperature up to 1000°C using a 2 K min^{-1} heating rate. The TA- curves in Fig. 9 show a three step weight loss in this temperature range. The first step with its DTG- peak maximum indicates the loss of moisture which is also indicated by the on line mass spectrometric detection of H_2O (*m*/*e* 18). The evolution of CO and CO_2 can be detected during the second and third degradation step (Fig. 10). Also in the second step, an evolution of organic material can be detected. As it can be seen from the mass spectrometry in Fig. 11 a lot of peaks in the range $m/e > 50$ occur. This evolution of organic

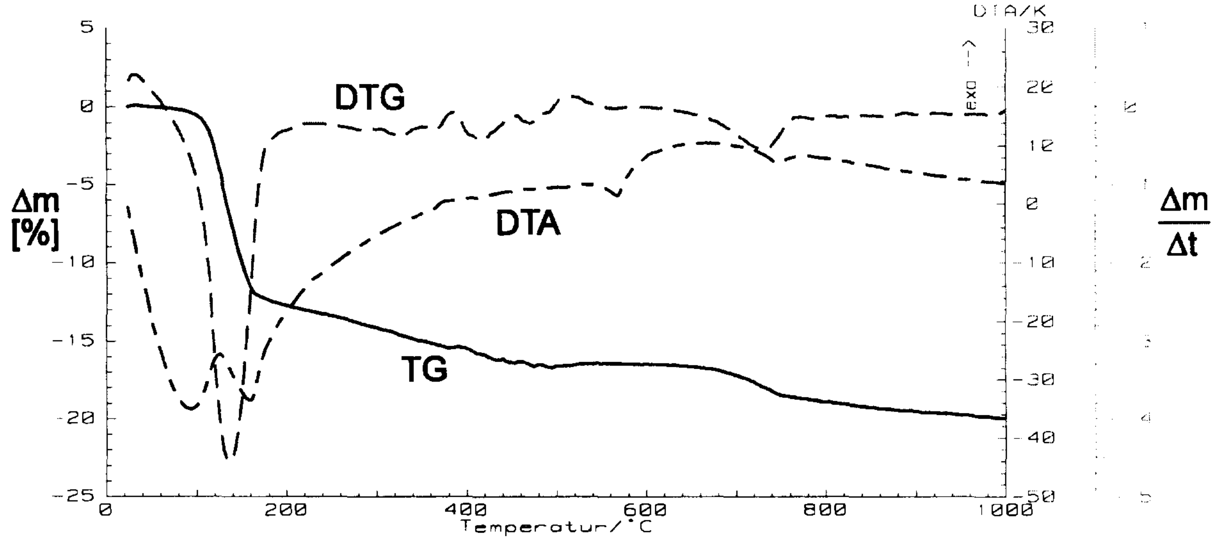

Fig. 9. TA- curves of a contaminated soil sample.

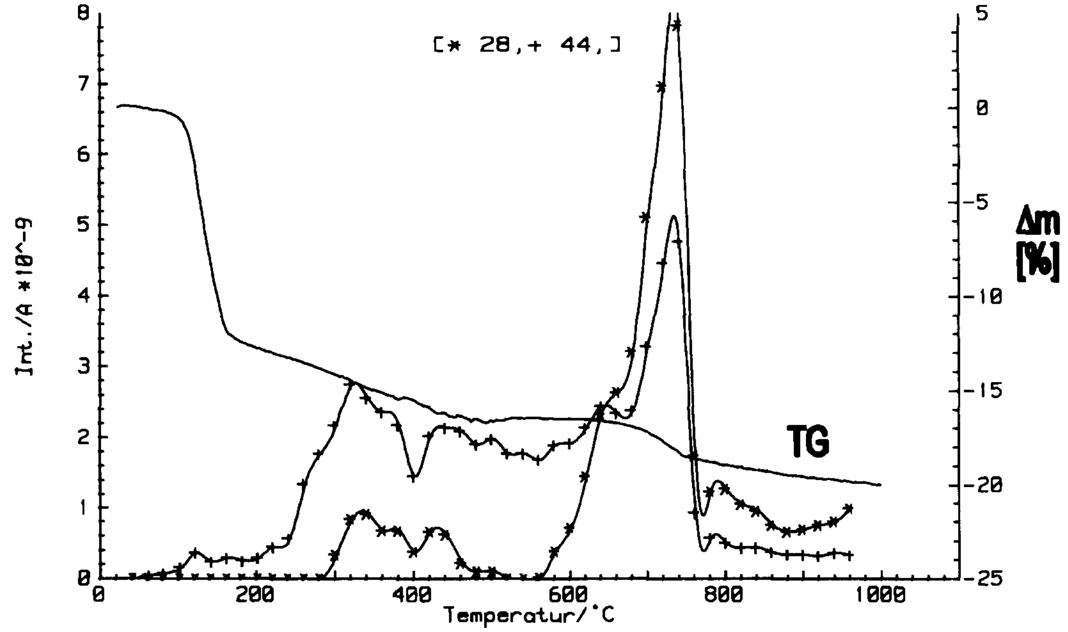

Fig. 10. Evolution of CO and CO_2 from a contaminated soil sample.

material is finished at about 600°C. The third degradation step accompanied by the evolution of CO and CO_2 is due to the degradation of the inorganic soil compounds.

A further interpretation of the mass spectral data taken on line during the evolution of organic materials is not possible without additional knowledge about individual compounds in this mixture. These informa-

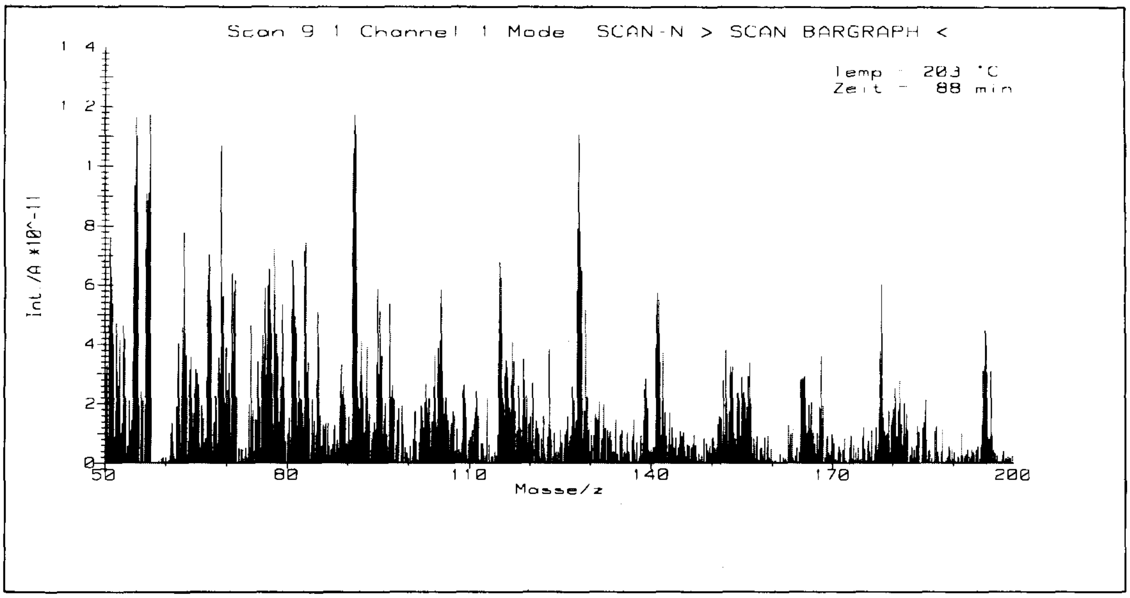

Fig. 11. Mass spectrum at 203°C (evolution of organic materials).

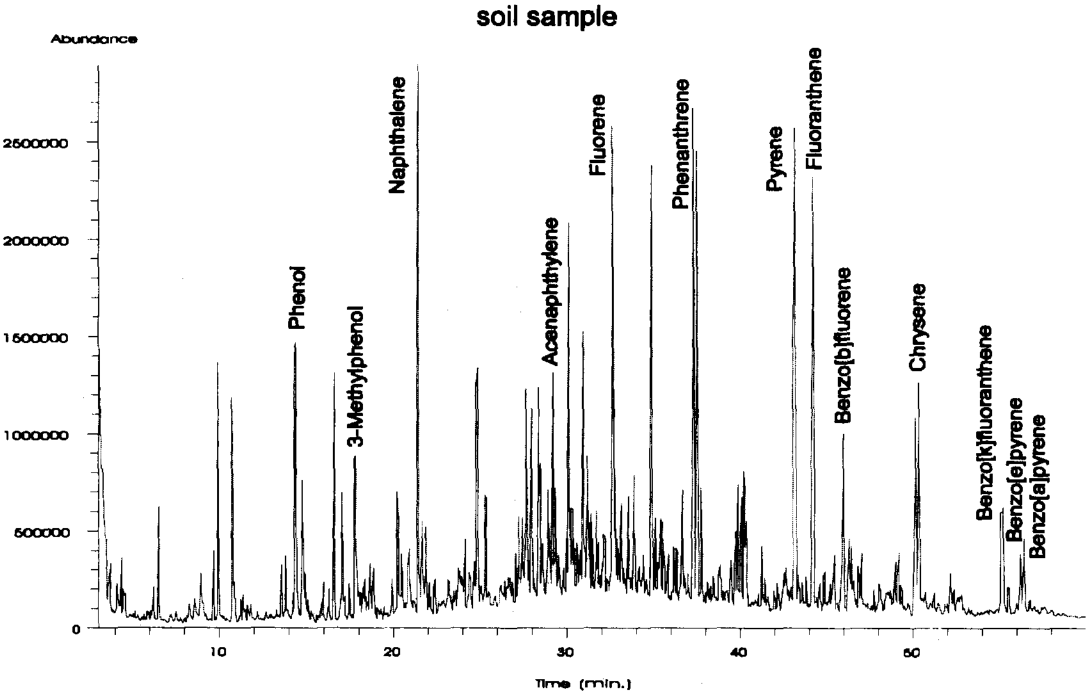

Fig. 12. Total Ion Chromatogram of the overall collected evolved substances of a contaminated soil sample.

tion can be achieved from the over all GC–MS analysis. All gases, evolved during the heating process were collected on XAD-4 resin and then investigated by GC–MS. In Fig. 12 the total ion chromatogram with some selected identified substances of this investigation is shown. As it can be seen, more then 100 substances, even with very high boiling points can be detected and quantified after calibration with standard reference materials.

With this additional information, the temperature resolved evolution of individual compounds can be measured by the on line coupled quadrupole mass

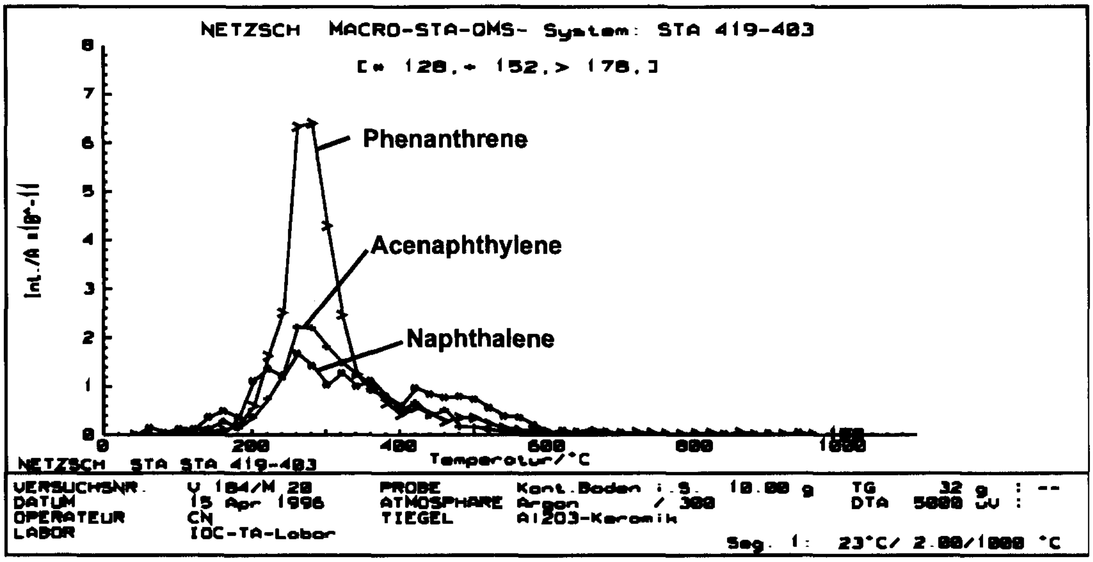

Fig. 13. Temperature resolved evolution of Naphthalene, Phenantrene and Acenaphthylene.

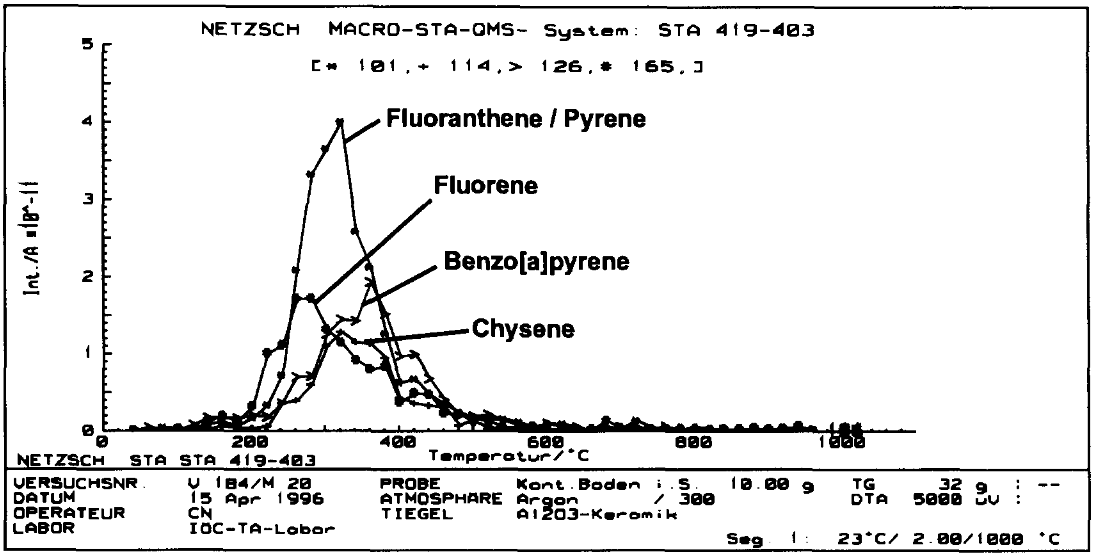

Fig. 14. Temperature resolved evolution of Fluoranthene/ Pyrene, Benzo[a]pyrene, Fluorene and Chrysene.

spectrometer. This can be done either in the so called mid (multiple ion detection) - mode where up to 64 fragments can be monitored simultaneously over the total temperature range or from the recalculation of the ion intensities of the selected fragments from the mass spectra series taken during the heating of the sample. In Figs. 13 and 14, the temperature resolved evolution of Naphthalene (*m/z* 128), Phenanthrene (*m/z* 178) and Acenaphthylene (*m/z* 152) as well as Fluoranthene / Pyrene (*m/z* 101), Benzo[a]pyrene (*m/z* 126), Fluorene (*m/z* 165) and Chrysene (*m/z* 114) is shown.

4. Conclusions

The use of thermal methods for the investigation of heterogeneous samples is restricted by the very small amount of sample material. Nevertheless, samples arising from the problems in the field of ecological science, as waste, contaminated soil, etc. are very heterogenic samples. From these substances, sample amounts in the mg range could never be representative and the achieved results are meaningless. The new device, the Macro STA 419, was built to overcome these initiations and is, as it could be shown, very successful.

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