

## Evolution of gases in the primary pyrolysis of different sewage sludges

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### Abstract

Thermogravimetry/mass spectrometry (TG/MS) was applied to eight different sewage sludge samples digested anaerobically and aerobically. The samples were thermally degraded in a nitrogen atmosphere using a heating rate of 20°C/min. The mass loss and the evolution profiles of the thermal decomposition products of molecular mass less than 100 Da were monitored. The thermal loss occurs in three stages, centered around 250°C, 350°C and 550°C, producing high quantities of gases, as hydrogen, water, hydrocarbons (C<sub>1</sub>–C<sub>4</sub>, both saturated and unsaturated), methanol, chloromethane, carbon dioxide and acetic acid. The production of acetic acid during aerobic treatment is much higher than during anaerobic treatment. On the other hand, the organic matter that is biodegraded in the aerobic process produces a series of compounds that, when pyrolyzing, does not form char. © 1998 Elsevier Science B.V.

*Keywords:* Sewage sludge; Pyrolysis; Mass spectrometry

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### 1. Introduction

According to the more and more restrictive legislation on the discharge of residual waters to the environment, the number of waste water treatment plants (WWTPs) and the volume of waste that should be treated increase day by day. The generation of water of sufficient quality involves the appearance of the sewage sludge as a byproduct, where most of the pollutants of the initial water are concentrated.

According to data of the Water Research Centre (Medmenham, UK), the amount of sewage sludge produced in the European Community (EC) in 1984 was around 5.56 millions of tons of dry residue with a 33% increase predicted for 1994 [1]. These sludges are

usually subjected to different processes of stabilization (anaerobic treatment, aerobic treatment, composting, etc.). The different methods of stabilization and the final disposal of these sludges in the EC (data as percentage) are described in [2].

The pyrolysis of these sludges might be a feasible alternative to the disposal in landfills and to their incineration. The pyrolysis process involves the heating of the sludge in an inert atmosphere, which leads to the production of carbon, tar, and gases. In the last few years, the thermochemical processes have been considered as one of the most promising ways in order to get valuable products from residues.

The pyrolysis of organic materials (lignocellulose, plastics, municipal solid wastes, etc.) has received renewed attention due to the possibility of converting these wastes into useful energetic products or into valuable chemicals. Moreover, the pyrolysis of

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the sewage sludges presents the advantage of concentrating the heavy metals (except mercury and cadmium) present in the final residue [3–5]. The lixiviation of these metals is minor in the case of the ashes of pyrolysis in contrast to the ashes of incineration [3]. In this way, the final disposal in landfills of these sludges is most secure.

The yields of the products obtained from a pyrolysis process are determined by the raw material decomposition (primary reactions) and to the reactions suffered by the primary volatiles (secondary reactions). The extent of the secondary reactions depends on the experimental equipment as well as the operating conditions. It is well known that high residence times and high temperatures favor the secondary reactions.

In the case of equipment such as a thermobalance, in which the heating rate is low, the cracking of primary products is negligible. Therefore, thermogravimetry is one of the techniques used to study the primary reactions of the thermal decomposition of solids, which has been widely used to study the thermal decomposition of polymers and other materials. The interpretation of the experimental data can provide information on the composition of the material, order of reaction, number of different processes that take place in the reaction, and the corresponding kinetic constants.

For the pyrolysis of sewage sludges, where different reactions are being examined, a kinetic model has been proposed [2]. The model assumes that three organic fractions are decomposed each one according to the scheme:



The model was validated with the TG data obtained for an anaerobically digested and a non-digested sludge [2]. The decomposition of the three fractions follows different paths, the third fraction being the most char-forming fraction, which has been assigned to non-biodegradable compounds. The first and second fractions correspond to biodegradable organic matter and dead bacteria. Comparing the results obtained with the digested and the non-digested sludge, the relative initial amount of fraction 3 increases after the anaerobic treatment.

The products of sludge pyrolysis have also been studied. Kasakura and Hiraoka [6] studied the pyrolysis in a pilot plant, obtaining yields of H<sub>2</sub> as high as 5.5 vol%. Other compounds obtained by these authors were CO (near 3.65 vol%), methane (1.48 vol%), ethylene (0.58 vol%), and others in minor yields. Other products of interest were HCN, nitrogen oxides, hydrogen chloride, and sulfur oxides. Piskorz et al. [7] and Konar et al. [8] showed that the more important compounds in the sludge pyrolysis are carbon oxides, water and hydrocarbons up to C<sub>4</sub>. Bellmann et al. [3] pyrolyzed the sludge in a fluidized bed reactor, obtaining yields of gases near 40 wt% at 750°C. Konar et al. [8] carried out the pyrolysis over activated alumina, reducing the quantity of carbonyl groups in the liquid hydrocarbons. Kaminsky and Kummer [9] pyrolyzed the sludge in a fluidized bed reactor, remarking on the variation of the composition of the oil fraction with temperature. Koch and Kaminsky [5] studied the pyrolysis of a refinery sludge in the fluidized bed, showing that this method enables a refinery to reduce waste disposal. The products obtained by primary and secondary pyrolysis of sewage sludges were studied by Caballero et al. [10]. The primary pyrolysis was performed in a Pyroprobe 1000 analytical apparatus, connected in series to a secondary reactor and a gas chromatograph. The products analyzed were carbon oxides, water and several hydrocarbons, and the authors conclude that with this technique, a total gas yield as high as 46 wt% can be obtained, and that the pyrolysis is an adequate way of characterizing of this type of materials.

It has been established that TG/MS is well suited for the characterization of gaseous thermal degradation products of different materials [11–16]. As opposed to flash pyrolysis (with heating rates higher than 1000°C/s), TG applies low heating rates (1–200°C/min) and permits the monitoring of the evolution profiles of products as a function of temperature. In addition, the mass loss curve (TG) and the mass loss rate curve (DTG) provide quantitative and highly reproducible data, useful for studying the thermal conversion [11].

The objective of this work is to study the thermal behavior of eight different sewage sludge samples in order to compare the products obtained in the different pyrolysis processes and apply the previously suggested kinetic model to confirm the presence of three stages of decomposition.

## 2. Experimental

The sludges produced at eight different WWTPs situated in the southeast of Spain have been studied. Four of the WWTPs use an anaerobic treatment of the sludge and the others use an aerobic treatment. Table 1 lists the characteristics and location of each of the treatment plants.

For the eight WWTPs studied, and during seven days, three daily samples of sludge were taken at the selected points of sampling and dried in an oven of natural convection at 105°C. These 21 dry samples were mixed, producing two integrated samples representative of the flow of each sludge. To assure the homogeneity of the experimental samples, eight aliquots of this solid were milled in an agate mortar. These samples were used for elemental analysis and thermogravimetry. The process of sampling was repeated on four different dates (November 1993, February 1994, May 1994 and August 1994) giving a total number of 32 samples to be pyrolyzed.

The determination of the total content of oxidizable carbon was performed by titration of the  $\text{Cr}_2\text{O}_7^{2-}$  remaining after the reaction of the sludge with this reagent [17]. The organic nitrogen was measured by the Kjeldahl method [18], the potassium content by flame emission spectrometry [19] and the phosphorus by colorimetry [20].

Thermogravimetric runs were performed in a Perkin–Elmer Thermobalance, model TGA7, controlled by a PC AT compatible system. The atmosphere used was nitrogen with a flow rate of  $60 \text{ cm}^3 \text{ min}^{-1}$ . The experiments were carried out at a heating rate of  $20^\circ\text{C}/\text{min}$ . The initial sample mass was between 15 and 20 mg. These conditions were selected in order to get an adequate signal in the MS equipment.

The mass spectrometer consists of a Balzers MSCube-2000 with an ion source of electron impact at 70 eV. The connection between the thermobalance and the mass spectrometer is done by means of a quartz capillary of 0.220 mm internal diameter, maintained at 190°C. The mass spectrometer incorporates a quadrupole axis, model QMG 421-C, with a turbomolecular pump TSH 055, that selects or sorts the ions. The intensity of twenty-eight selected ions was monitored, together with the thermogravimetric parameters (temperature, mass) at different times. The ion intensities were normalized to the sample mass as well as to the intensity of the  $^{28}\text{N}_2$  isotope of the carrier gas, in order to eliminate errors caused by a shift in the mass spectrometer sensitivity. The intensity data must not be compared between the different compounds due to the different sensitivities of the mass spectrometer. However, the intensity values of a given ion are comparable between the samples because they were normalized to the carrier gas and the sample mass.

To ensure that the equipment gives the actual temperature of the sample, a calibration of the temperature has been done in each run, by introducing two metals in the sample and surrounding the oven and the sample by a magnet. These two metals (alumel and nickel in our case) lose their magnetic properties at a definite temperature (Curie-point transition, at 163°C and 365°C, respectively), yielding the mass loss curve as shown in Fig. 1. The curve is then corrected in the temperature and in the mass axis according to the thermal loss of the metals, giving the corrected curve of Fig. 1. In this figure, the mass loss of a sample without the two metals is also shown, in order to show that no catalytic effect is present. This method for correcting the temperature has been applied to all the TG runs, thus assuring the reliability of the tempera-

Table 1  
Characteristics of the treatment plant, elemental analysis and the ash content of the sample selected

City	Code of the sample	Treatment	Organic content (%)	C/N	N (%)	P (%)	K (%)	Ash (%)
Alcoy	ALC	Anaerobic	21.66	5.61	3.86	2.25	0.15	45.45
Alicante	ALI	Anaerobic	22.03	5.56	3.96	2.39	0.17	55.53
Benidorm	BEN	Anaerobic	39.00	14.01	2.77	0.78	0.19	25.87
Elche	ELC	Anaerobic	30.04	5.81	5.17	1.73	0.14	34.86
Altea	ALT	Aerobic	27.46	4.74	5.79	1.84	0.22	30.77
Crevillente	CRE	Aerobic	21.57	4.14	5.21	2.42	0.27	41.27
Elda	ELD	Aerobic	24.66	5.05	4.88	2.49	0.21	46.48
Torrevieja	TOR	Aerobic	21.19	4.60	4.61	2.52	0.13	50.27

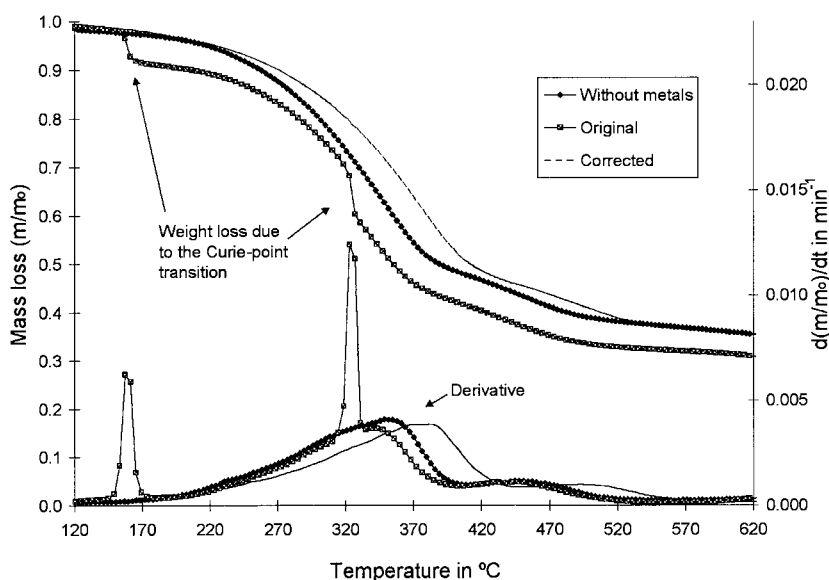


Fig. 1. Correction of the temperature in the TG curves by the Curie transition of alumel and nickel.

ture measurements and assuring a very good reproducibility.

### 3. Results and discussion

#### 3.1. TG/DTG curves

Fig. 2 shows the mass loss curve obtained for the four samples, taken at different dates, coming from Alcoy, as representative of the other's sludge. The differences between the curves are due to the different organic content of the samples. If the curve is normalized to the total mass loss, the differences are much smaller. The differences in the organic content are more apparent when considering the others WWTP. The curve corresponding to each WWTPs obtained in November 1993 has been selected as representative of each station (a code for each sample has also been selected). Table 1 shows, together with the characteristics of the treatment, the elemental analysis and the ash content of the sample selected. These figures are similar to those of the same WWTP taken at a different date.

Fig. 3 shows the TG and DTG curves for the eight samples coming from each WWTP, clearly showing

the presence of, at least, two processes in the sample mass loss. According to the previous work [5] the decomposition takes place in three different processes. Fig. 3 also shows that the curves for the samples ALC and ALT are slightly displaced to higher temperatures. On the other hand, samples ALI and TOR undergo an important mass loss at temperatures lower than 220°C. The form of the DTG curve for sample ALC is quite different, being wider than the other ones. The curve BEN has a marked process centered at 470°C.

Table 2 shows the contribution of each fraction to the initial mass ( $w_{10}$ ,  $w_{20}$  and  $w_{30}$ , as percentage of the organic matter). This table also shows the contribution to the mass at time infinity of each fraction ( $w_{1\infty}$ ,  $w_{2\infty}$  and  $w_{3\infty}$ , as percentage of the total mass at time infinity due to the organic matter, i.e., the total mass loss) for each sample. This table reveals that the mass at time infinity is almost completely due to fractions 2 and 3, but in the samples coming from WWTPs with an aerobic treatment, the mass loss of fraction 2 is near 100%, not contributing to the mass residue at time infinity.

This fact reveals an important feature: the organic matter that is biodegraded in the aerobic process produces a series of compounds that, when pyrolyzing, does not form char. This can be explained by

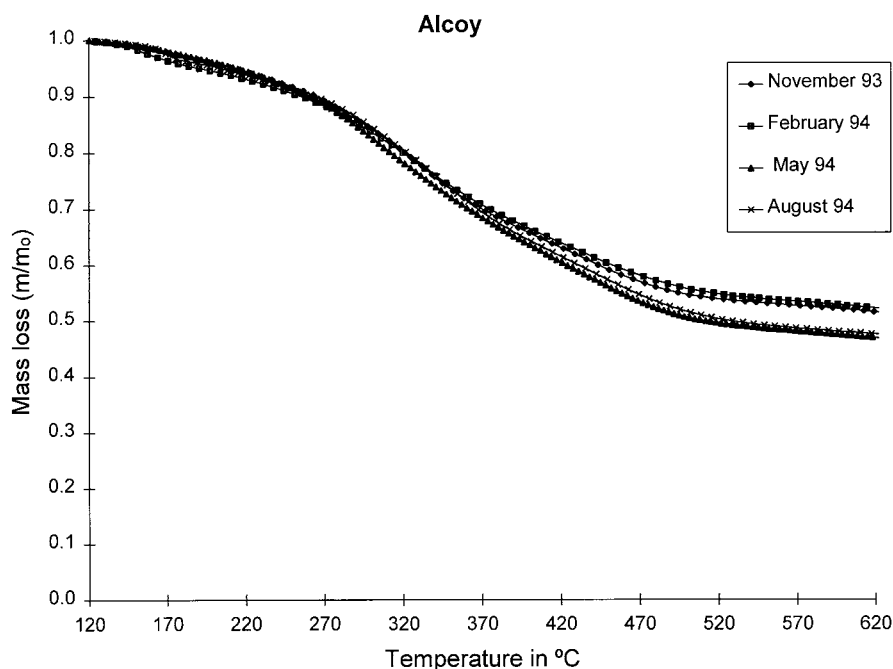


Fig. 2. Mass loss of four samples from Alcoy.

Table 2

Contribution of each fraction to the initial mass and contribution to the mass at time infinity of each fraction

Sample	ALC	ALI	BEN	ELC	ALT	CRE	ELD	TOR
$W_{inert}$	45.45	55.53	25.87	34.86	30.77	41.27	46.48	50.27
$w_{10}$	0.51	0.65	5.70	2.09	5.89	0.36	0.03	5.83
$w_{20}$	64.20	12.77	7.55	24.27	62.56	24.59	32.60	69.27
$w_{30}$	35.29	86.59	86.75	73.64	31.55	75.05	67.38	24.89
$w_{1\infty}$	0.02	0.03	0.10	0.11	3.70	0.04	0.00	0.35
$w_{2\infty}$	<b>36.83</b>	<b>9.00</b>	<b>8.09</b>	<b>14.81</b>	2.45	0.00	0.00	1.07
$w_{3\infty}$	63.15	90.97	91.81	85.08	93.85	99.96	100.00	98.57

considering that the aerobic process is more energetic, producing highly degraded compounds that are easy to volatilize, producing lower pyrolysis char.

### 3.2. Production of each compound analyzed

The evolution profiles of  $m/z=2, 15, 18, 26, 39, 42, 43, 44, 45, 50, 55$  and  $60$  have been monitored. Table 3 shows the assignments of each signal to the different compounds. This assignment has been done according to the literature and takes into account the ions of the compounds expected from the pyrolysis [2,4,6–10].

Figs. 4–6 show some of the most relevant peaks obtained in the  $20^\circ\text{C}/\text{min}$  runs for the aerobic and the anaerobic WWTPs. In these figures, for each ion the y-axis represents a relative intensity (RI) of the mass with respect to the carrier gas.

Table 4 shows the integrated intensity data for the products analyzed. As has been pointed out in Section 2, the intensity data must not be compared between the different compounds. This table shows that the differences between the integral MS signals of the different sludges are not significant, except for acetic acid, where the production during aerobic

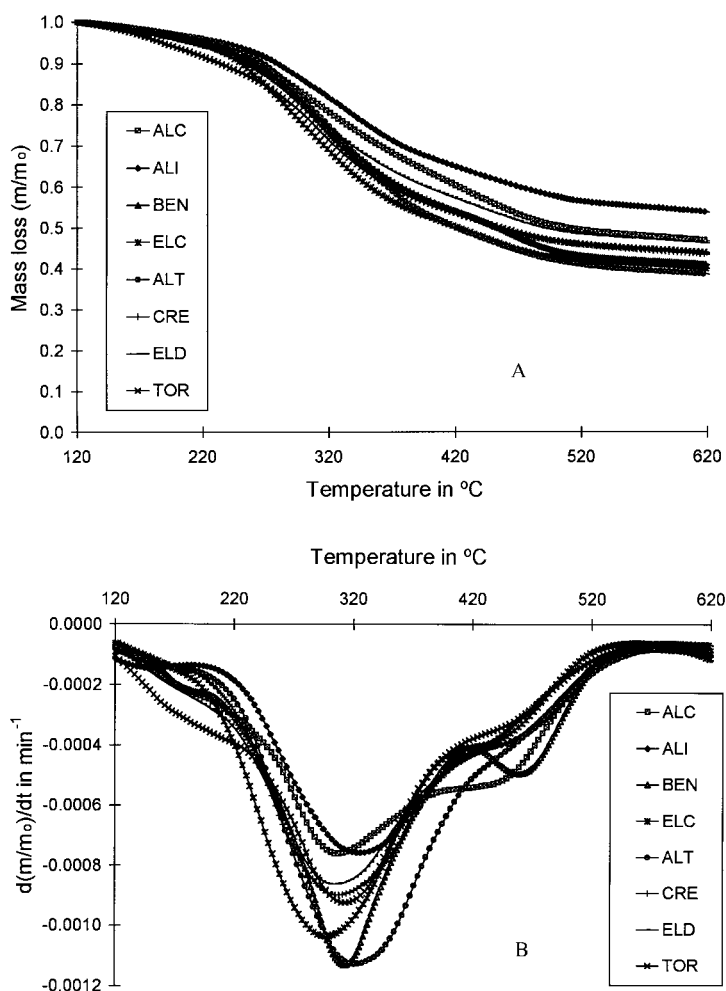


Fig. 3. TG curves and DTG curves of samples from the eight WWTP studied. (a) TG, (b) DTG.

Table 3  
Assignments of each signal of the Mass Spectrometer

$m/z$	Ion	Mainly due to:
2	$H_2^+$	Hydrogen
15	$CH_3^+$	Methane
18	$H_2O^+$	Water
26	$HCN^+$ , $C_2H_2^+$	HCN, ethylene
39	$C_3H_3^+$	Propylene
42	$CH_2CO^+$ , $C_3H_6^+$	Aldehyde, propane
43	$CH_3CO^+$ , $C_3H_7^+$	Carboxylic acid, propane
44	$CO_2^+$	Carbon dioxide
45	$CH_3CHOH^+$	Ether, alcohol
50	$CH_3Cl^+$	Chloromethane
55	$C_4H_7^+$	Butane
60	$CH_3COOH^+$	Acetic acid

treatment is much higher than during anaerobic treatment (except in the WWTP placed at Elche (code ELC)).

In the anaerobic digestion, the initial production of acetic acid (by the acetogenesis process) is continued by methanogenesis, producing a series of highly degraded compounds. Furthermore, in the aerobic digestion, the bacteria responsible for the methanogenesis process cannot exist, so many of the compounds remaining contribute to the production of acetic acid, which is not true for anaerobic treatment. The high acetic acid production from the sludge ELC may reveal that the WWTP is not running very well (since the second process does not take place). This

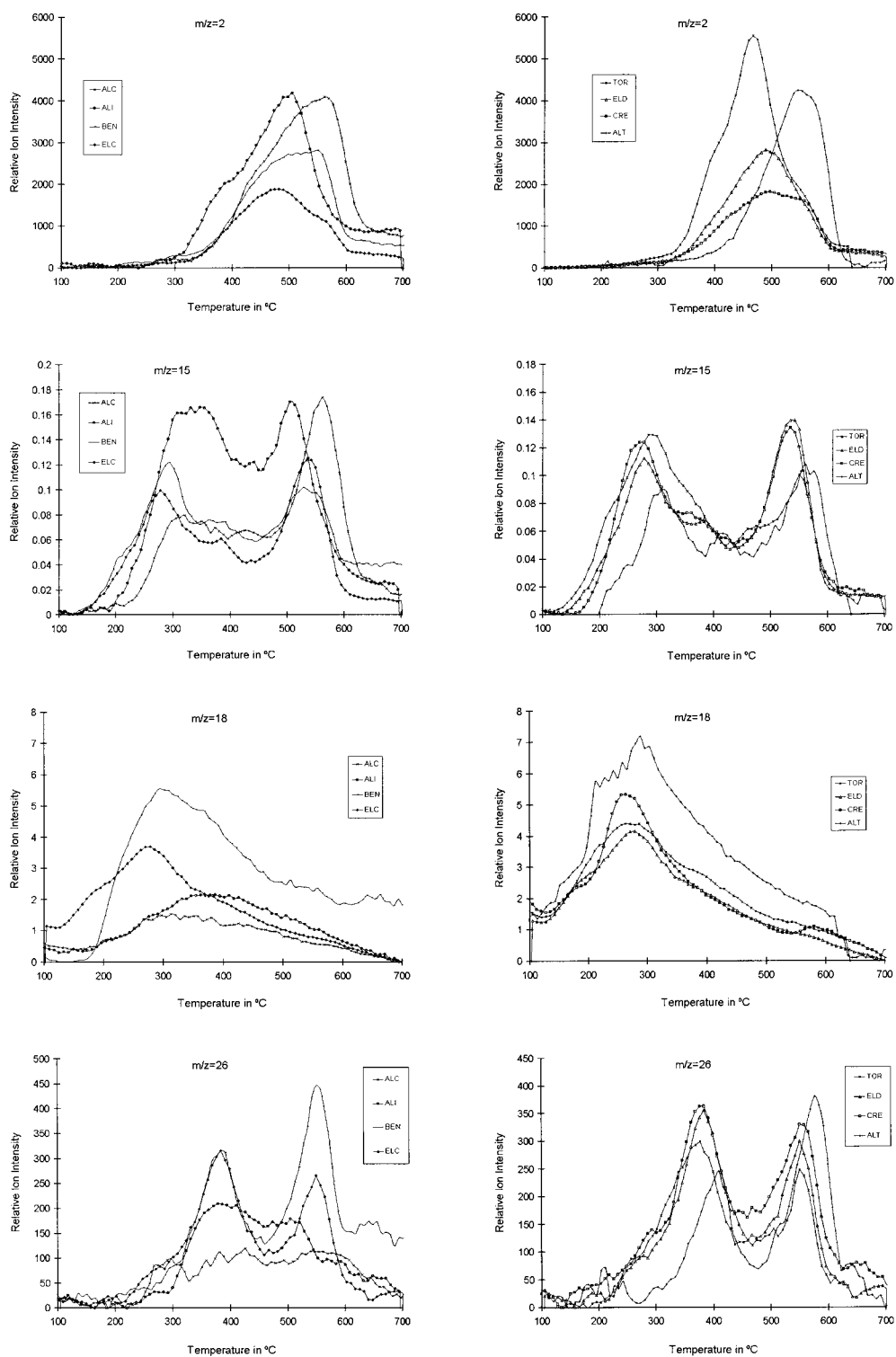


Fig. 4. Evolution profiles of the pyrolysis products at 20 °C/min,  $m/z=2, 15, 18, 26$ .

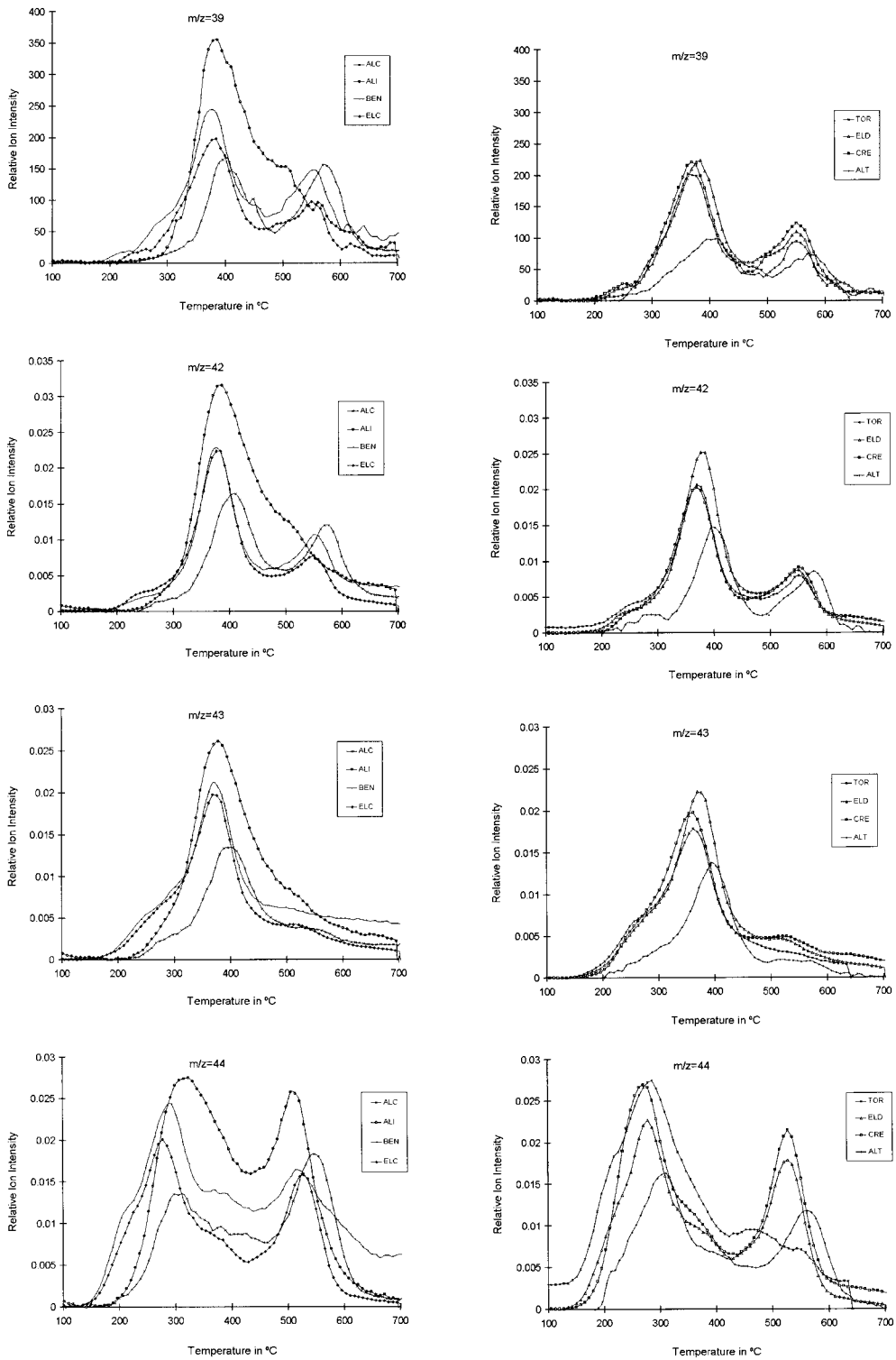


Fig. 5. Evolution profiles of the pyrolysis products at 20°C/min,  $m/z=39, 42, 43, 44$ .



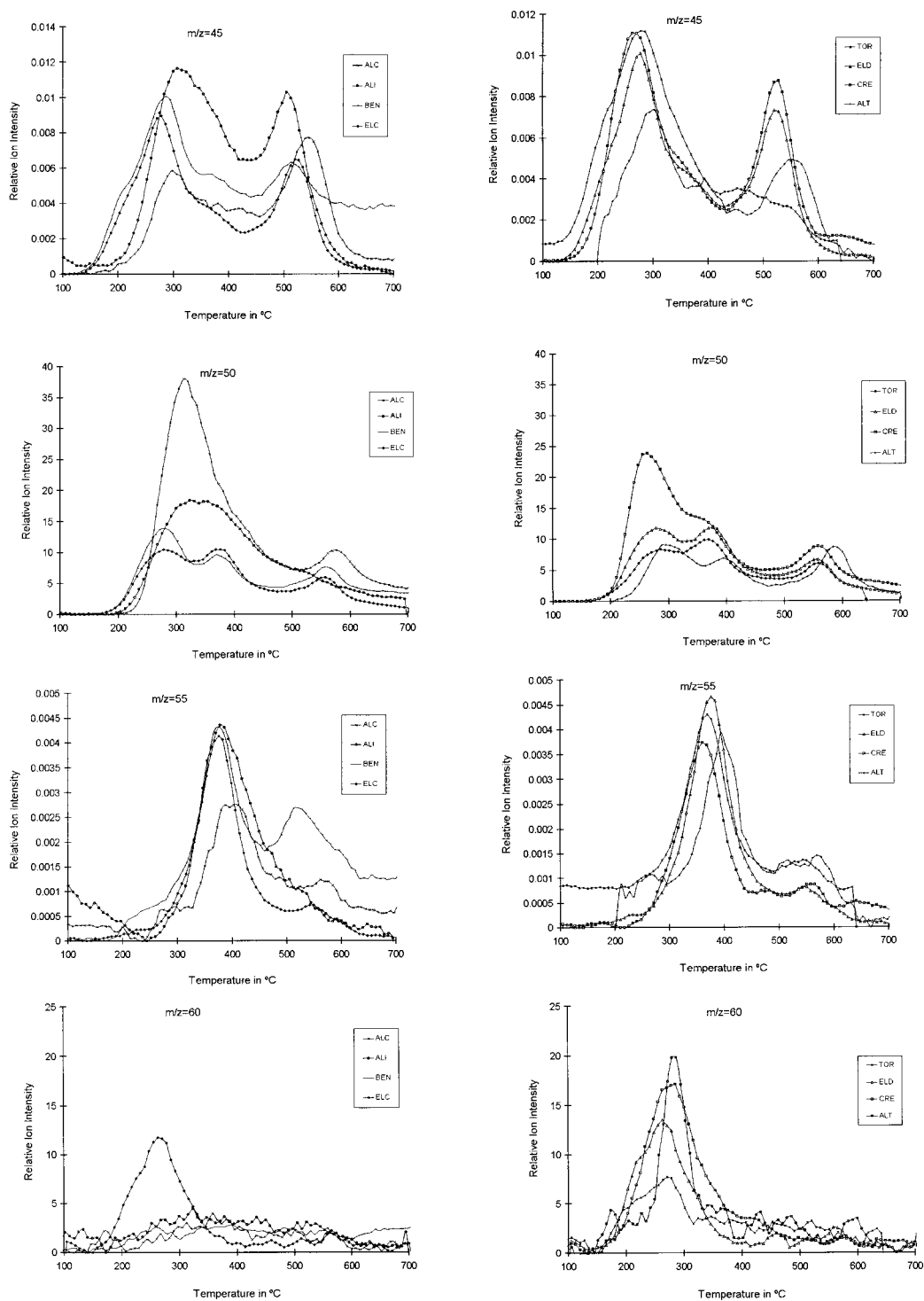


Fig. 6. Evolution profiles of the pyrolysis products at 20°C/min,  $m/z=45, 50, 55, 60$ .

Table 4  
Integrated MS intensities (arbitrary units) of the most important products detected by TG/MS

<i>m/z</i>	ALC	ALI	BEN	ELC	ALT	CRE	ELD	TOR
2 Hydrogen	2	2.16	0.608	0.685	2.232	0.62	1.27	1.54
15 Methane	7.15	10.8	4.125	4.448	6.383	5.43	6.22	6.35
18 Water	3.4	4.6	2.318	2.719	4.503	3.62	3.61	3.22
26 Ethylene	4.08	3.48	0.891	2.153	3.569	1.43	4.15	4.09
39 Propylene	0.54	0.9	0.527	0.481	0.303	0.56	0.57	0.49
43 Propane	0.67	1.15	0.45	0.503	0.767	0.53	0.69	0.57
44 CO <sub>2</sub>	1.37	1.98	0.799	0.909	1.253	0.93	1.33	1.25
45 Methanol	0.61	0.97	0.32	0.353	0.741	0.38	0.48	0.45
50 Chloromethane	1.17	0.94	0.375	0.465	0.496	0.7	0.66	0.5
55 Butane	3.88	5.31	1.423	1.441	5.591	0.87	2.4	2.11
60 Acetic acid	0.24	0.79	0.839	3.111	4.239	4.72	4.36	3.67

indicator may thus provide valuable information about the operating performance of a plant.

### 3.3. Evolution of each mass with temperature

From Figs. 4–6, three main processes occur in the decomposition and evolution of gases are present in all the samples. The first process is centered (more or less, depending on the sample) at 250°C, the second at 350°C and the third at 550°C.

In the first stage, the main products evolved are methane, carbon dioxide, water, chloromethane and acetic acid. In the second stage the main products are hydrocarbons ( $m/z=26, 39, 42, 43, 55$ ), alcohols ( $m/z=45$ ) and chloromethane ( $m/z=50$ ). The third process produces mainly hydrogen ( $m/z=2$ ), methane ( $m/z=15$ ), carbon dioxide ( $m/z=44$ ) and also hydrocarbons ( $m/z=26, 39, 42$ ) alcohols ( $m/z=45$ ) and chloromethane ( $m/z=50$ ).

Methane evolution takes place at a slightly lower temperature than the rest of the hydrocarbons, and in the third process methane and the majority of the other hydrocarbons are produced.

The main water evolution in the pyrolysis of materials such as almond shells is observed at a low temperature (<200°C) [16], but when pyrolyzing other materials it is produced over a wide range of temperatures [11]. This is the case for the sludges studied in this paper, water being produced at temperatures as high as 600°C. The production of water at high temperature cannot be explained by volatilization of the water that the sample contains. Fig. 4 shows that hydrogen evolution takes place over a broad range of

temperatures, between 350°C and 600°C. The production of hydrogen in the samples TOR and ALI is advanced. Production takes place at lower temperature if the treatment is aerobic, except for the case of ALC.

There are differences between the different samples considered. For example, ethylene evolution ( $m/z=26$ ) occurs in two processes exists for all the samples, but for samples ALI and ALC the process centered at 550°C is very low. Another example is that of  $m/z=42$ : the second process is quite different for sample ALI, where this process practically does not exist.

The evolution of acetic acid is more pronounced in the aerobically treated sludges, as discussed above and can be seen in Fig. 6.

Chloromethane evolution is the only one that takes place in the three stages of the decomposition. Three processes are also present in the chloromethane evolution from almond shells impregnated with CoCl<sub>2</sub> [16].

The kinetic model proposed for this type of material [2] considers three different decomposing fractions, each one of which can be correlated with the stages of gas evolution, confirming (together with the DTG curves) that the kinetic model has a physical sense.

## 4. Conclusions

An important conclusion of the above experimental results and the analysis of the data, is that the reproducibility of the experiments is enhanced when the runs are performed together with a Curie-point calibration process.

The primary pyrolysis of the sewage sludges produces a high quantity of chemicals (around 45 wt%), which are principally hydrogen, water, hydrocarbons ( $C_1$ – $C_4$ , both saturated and unsaturated), methanol, chloromethane, carbon dioxide and acetic acid.

The decomposition occurs in three stages (centered on 250°C, 350°C and 550°C). In the first, the main products evolved are methane, carbon dioxide, water and acetic acid; in the second the main products are hydrocarbons and alcohols; the third process produces mainly hydrogen, methane, carbon dioxide and also hydrocarbons and alcohols. Chloromethane is the unique compound that is produced during the three stages. Water evolution takes place over a wide temperature range. The previously proposed kinetic model, which considers three different decomposing fractions, is supported by the analyses of the evolved gases.

Two principal differences between anaerobic and aerobic sludges have been found: (a) the production of acetic acid during aerobic treatment is much higher than during anaerobic treatment, and (b) the organic matter that is biodegraded in the aerobic process produces a series of compounds that, when pyrolyzing, does not form char. These two facts may provide valuable information about the operating performance of the plant.

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