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TG-MS AS A TECHNIQUE FOR A BETTER MONITORING OF THE PYROLYSIS, GASIFICATION AND COMBUSTION OF TWO KINDS OF SEWAGE SLUDGE

L. F. Calvo, M. E. Sánchez, A. Morán and A. I. García[*]

Chemical Engineering Department, University of León, IRENA-ESTIA, Avda. Portugal 41,
León 24071, Spain

Abstract

Sewage sludge disposal is a difficult task owing to increasingly restrictive re-use policies. Its final destination will obviously depend on its nature and composition but the generation of energy is a significant option. The thermochemical conversion requires exhaustive gas emission controls. In this regard, this paper offers the results of the use of mass spectrometry together with a thermogravimetric analysis system used to study the thermal conversion processes of two kinds of sewage sludge under different atmospheres simulating pyrolysis, gasification and combustion. This TG-MS combination indicates that gasification is the best process for one kind of sludge while a co-combustion process is more suitable for the other.

Keywords: sewage sludge, TG-MS, thermochemical conversion

Introduction

Wastewater treatment entails the generation of a by-product, sewage sludge, which is difficult to dispose of, owing to both increased production and more restrictive policies concerning re-use. In Europe, the implementation of Urban Wastewater Treatment Directive 91/17/EEC will bring about a major increase in sewage sludge production, expected to be around 9.4 million tonnes in 2005 [1], as it requires treatment of all waste water from towns with population equivalents of over 2000 [2]. The final destination of sewage sludge obviously depends on its nature, whence the importance of its characterization [3]. The most traditional option for disposal is its use as a fertilizer, but more and more restrictions are appearing for both political and economic reasons.

Regarding the second difficulty of disposal, the latest trends in EU policies show two major types of restriction: exhaustive monitoring prior to disposal, and the special importance of the evolution of soil parameters in the case of landfill applications [4]. Another possibility for sewage disposal is its conversion into useful materi-

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[*] Author for correspondence: E-mail: dfqagp@unileon.es

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als, such as activated carbon or building materials, an option which could utilize all the expected production of sludge in the short term [5].

If energy production is to be considered, care must be taken not to diminish its power capacity, as it has a high carbon and hydrogen content. For this option, sludge has to pre-treated to dry out its high moisture content [6].

As the process of thermochemical conversion of sewage sludge requires exhaustive gas emission controls, its composition should be determined before any industrial application, which can be done by means of mass spectrometry (MS) as a gas analysis technique, together with a thermogravimetric analysis system.

To study the thermal degradation of wastes, many TA techniques have been used, for instance, TG in the study of the degradation of tyres by Díez [7] and TG-DSC, by Napoli [8], and others [9]. Other authors have also studied this subject [10]. However, deriving knowledge of the thermal degradation process from TG mass loss data is rather complicated owing to generally complex kinetics [11]. In this regard, mass spectrometry is a useful tool for the investigation of thermal decomposition of wastes, as information is not only obtained on mass loss, but also on substances generated. Coupled with TG, this technique is becoming increasingly common:

The combination of MS and a thermogravimetric analysis system offers several advantages in thermal gas emission determination such as real-time analysis and qualitative and quantitative analysis [12].

Many authors have published research into gas emissions in combustion or co-combustion process of different materials, such as medical waste [13], biomass [14], poultry litter [15], while others have examined the emissions from gasification [16]. Several have also worked on determining emissions from pyrolysis [17, 18]. No studies exist, however, of gas emissions from the three different thermal conversion process (combustion, gasification and pyrolysis) of sewage sludge.

This paper analyses gas emissions in the process of heating sewage sludge under different atmospheres of helium and oxygen simulating pyrolysis, gasification and combustion. There are two objectives: to study the thermal conversion processes themselves and to compare the gas emissions of these two kinds of sludge when they are heated under different atmospheres with different oxidative properties. It will thus be possible to determine the best treatment method for disposal of each material as far as energy is concerned.

Materials and methods

Materials

Representative samples of two kinds of urban sewage sludge were used for this study, designated SLA and SLB. The former was obtained from the treatment of waste waters from a large city (population about 1.5 million) and the latter from a smaller one (population about 150.000). Both were subjected to stabilization by the same kind of anaerobic digestion as at their original sewage treatment plants and were dehydrated by centrifugation. The sludges were then ground to pass through a 0.2 mm screen for feeding to the thermobalance. For the analysis of some properties the material had to be ground to pass through a 420 μm screen.

Fuel analysis

The sludges were analysed to determine the main properties affecting emissions. Moisture content was determined gravimetrically by the oven drying method. The highest heating value at constant volume (HHV) was measured with an adiabatic oxygen bomb calorimeter. Fuel was previously sampled in 1 g amounts, pelletized in a hand press to 12.7 mm diameter, and oven-dried to a constant mass at 377±3 K prior to analysis.

Proximate determination was carried out according to modified procedures ASTM D 3172-D 3175 (Standard Practice for Proximate Analysis of Coal and Coke); E 870 (Standard Methods for Analysis of Wood Fuels), D 1102 (ash in wood), and E 872 (volatile matter in wood); and the methods for refuse-derived fuel (RDF)-E 830 (ash), and E 897 (volatile matter). Ash concentration was determined at 848 K for 2 h in an atmospheric pressure air muffle furnace. This temperature is that specified by ASTM, and is slightly below the minimum temperature specified for wood. Volatile matter concentration was determined under inert conditions using a modified method for sparking fuels, in which samples in covered nichrome crucibles were placed in the front part of an open muffle furnace preheated to 1223 K for 6 min to dispel volatiles over a period of more gradual heating. The process was brought to completion in a closed furnace over an additional 6 min, the crucibles removed, and cooled under desiccant while still covered, and weighed immediately.

To ascertain the elemental composition, sludge samples were sent to a commercial laboratory where standard methods were used.

Thermogravimetry and mass spectrometry analysis

Thermogravimetric analysis was carried out using a TA Instruments SDT2960, which is able to provide a continuous measurement of sample mass as a function of time or temperature and also give a DTG signal (rate of mass loss) when used with the appropriate software.

Samples weighing 6–8 mg were placed in a pottery crucible and heated at 50 K min^{-1} from ambient to 923 K. To simulate combustion, gasification and pyrolysis, five different atmospheres were used, all with a flow of 100 mL min^{-1}: 100% helium, 97% helium/3% oxygen, 95% helium/5% oxygen, 90% helium/10% oxygen and 100 % oxygen, respectively, designated He100, He97, He95, He90 and He0.

Gases emitted during the thermal conversion process were monitored with a Balzers GSD 300 mass spectrometry apparatus in line with the thermal analysis equipment. The coupling of the TG via the capillary to the MS was made at the exit of the thermogravimetric analyser. Several authors have studied the optimal connection between TA-MS, such as Hatton [19]. Such coupling allows relative concentration of the gas emitted to be determined at near-equilibrium conditions, although it length-

Table 1 Relation between mass number (*m*/*z*), fragment and probable parent molecule

m/*z*	key fragment	probable parent molecule
2	H_2^+	H_2
15	CH_3^+	CH_4
28	CO^+	CO
30	$C_2H_6^+$, NO^+	C_2H_6, NO
44	CO_2^+	CO_2
46	NO_2^+	NO_2
64	SO_2^+	SO_2

ens the response time of the MS signals, so our thermal and spectrometric analyses were not exactly synchronised [20].

M/*z* signals reported by MS were 2, 15, 28, 30, 44, 46 and 64. All of them are gaseous species of especial interest in the heating process. They can be observed in Table 1. Although a quantitative analysis is not performed, a comparison of the intensity of the emission peaks between the different runs was made, for which data had to be standardized. These gas emissions were important from two points of view, energy value and environmental damage [21].

Instead of nitrogen, helium was used for the inert atmosphere, as N_2 has the same molecular mass as CO, making CO determination possible by mass spectrometry. No appreciable differences were detected in TG profiles.

Results and discussion

Before thermogravimetric and spectrometric analyses the sludges were analysed to determine the main properties affecting gas emissions during thermal conversion. Results are shown in Table 2. SLB has a higher ash content than SLA owing to a more complete digestion process [22], implying that it has a lower maximum heating

Table 2 Sewage sludge properties

	Elemental analysis/%						Proximate analysis/%			
Sludge	C	H	N	S	Cl	O	Moisture	Ash	Volatiles	HHV[1]/ MJ kg^{-1}
SLA	36.2	4.5	5.6	1.1	0.1	14.7	7.9	37.9	55.0	15.4
SLB	22.7	3.3	3.1	0.9	0.1	16.1	3.9	53.8	42.9	9.5

[1] HHV: High heating value

All values dry basis except moisture

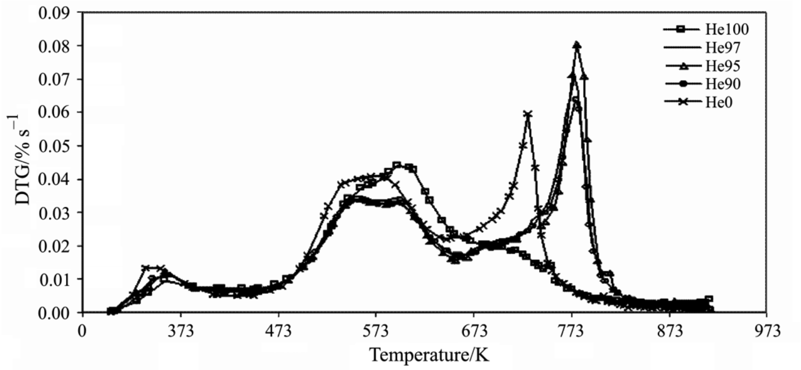

Fig. 1 SLA heating profiles

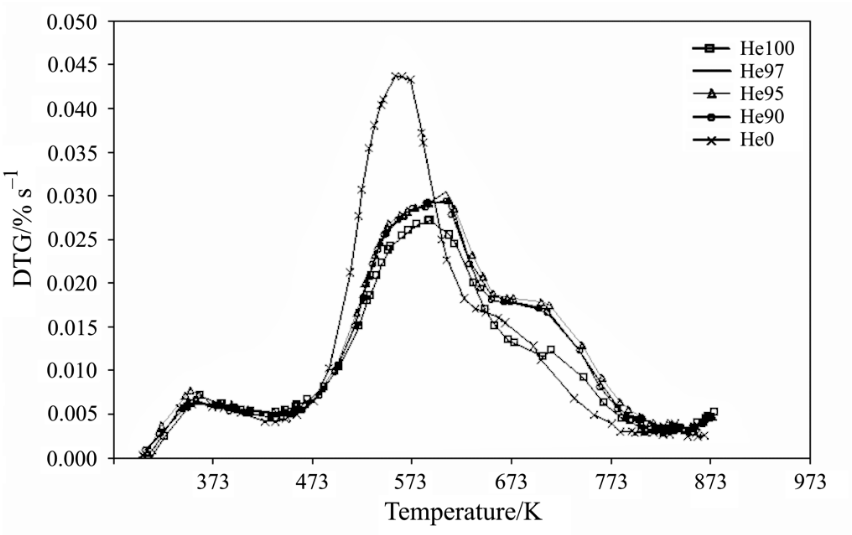

Fig. 2 SLB heating profiles

value than SLA, and would be less efficient as a fuel. It will also be observed that SLA has a higher C content than SLB.

Heating profiles at programmed temperatures for the five atmospheres tested are shown in Fig. 1 (SLA) and Fig. 2 (SLB). He100 is representative of a pyrolysis process, He0 of combustion and the others of gasification. The curves show four stages in the thermal conversion process of sludge for which four different temperature zones can be interpreted if oxygen is present in the atmosphere during the heating process. They can be identified by the presence of the shoulders in the curve. Analysis of these different stages (drying, devolatilization, a heterogeneous stage and the ignition-and-burning stage) and a model for describing overall decomposition can be found in Calvo *et al*. [6]. Without oxygen (pyrolysis) only the first three stages can be differentiated, as the fourth one does not take place. Mass loss during heating is higher for SLA, and SLB ignites at temperature 100 K lower than SLA.

Mass spectrometry analysis was used to monitor gas emissions which are identified with these molecular masses giving these m/z signals: 2, 15, 28, 30, 44, 46, 64, which were identified for both kinds of sludge in the five different heating atmospheres. Results are shown in Figs 3–9 but only for He100, He95 and He0, as showing all the atmospheres would obscure the clarity of the curves. The representation of these three atmospheres in the figures obviously allows to the same conclusions to be drawn.

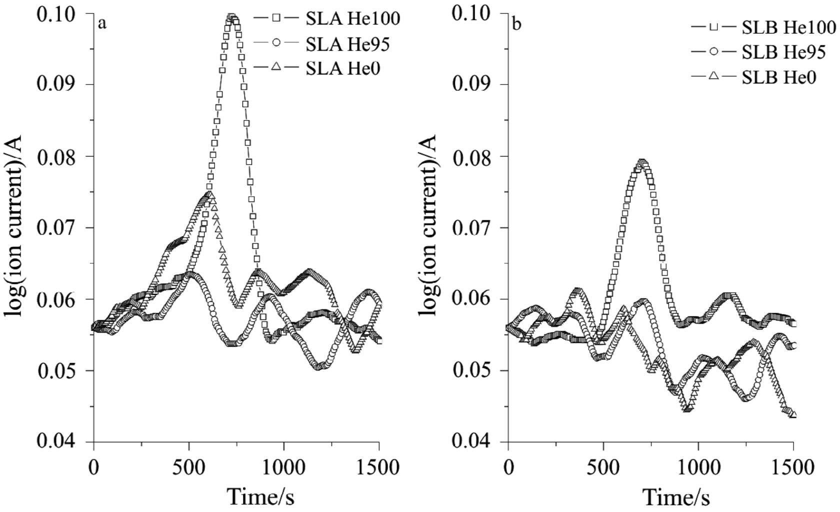

Fig. 3 m/z=2 emission a – for SLA and b – for SLB in Atm100, Atm95 and Atm0

a) m/z=2

This value of m/z is associated with the emission of hydrogen (Table 1), which is an important gas from the point of view of energy owing to its high calorific value, 41.22 MJ Nm^{-3}. The highest emission of hydrogen for both sludges occurred when the heating atmosphere is totally inert (He100), more being emitted by SLA than SLB, probably because of its higher hydrogen content. Less hydrogen is emitted in gasification atmospheres, and no emission occurs if the heating atmosphere is totally oxidant (He0).

b) m/z=15

This value is associated with methane (Table 1), an important gas for its energy value with a high calorific value of 12.99 MJ Nm^{-3}. It will be observed that the highest methane emission for both sludges was produced in a totally inert atmosphere (100% helium), when the process simulated was pyrolysis. Methane emission decreased as atmospheric oxygen content increases, falling to zero in He0 (100% oxygen).

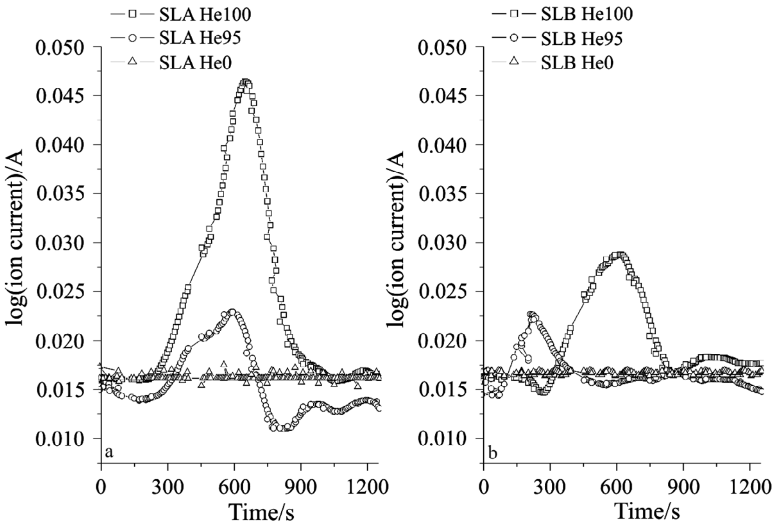

Fig. 4 *m*/*z*=15 emission a – for SLA and b – for SLB in Atm100, Atm95 and Atm0

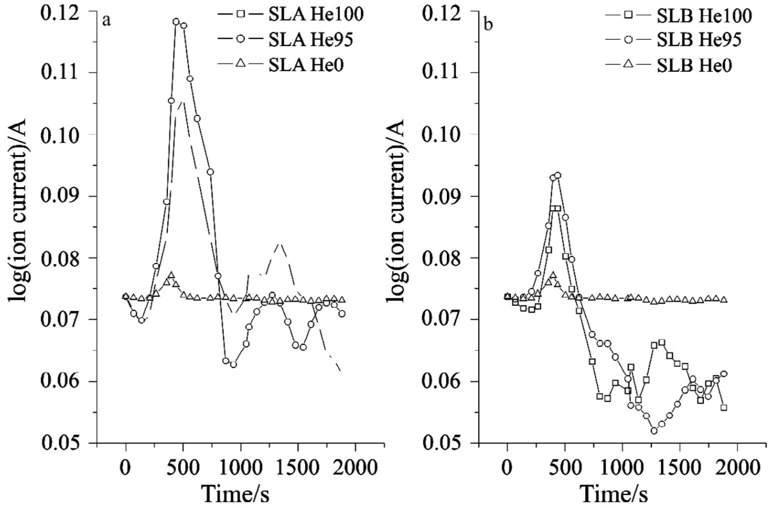

Fig. 5 *m*/*z*=28 emission a – for SLA and b – for SLB in Atm100, Atm95 and Atm0

Of the two sludges, SLA gives off more methane than SLB, probably owing to its higher carbon and hydrogen content. This difference is better observed in the case of heating atmospheres simulating the gasification process. In any event, for both SLA and SLB, the greatest methane emission occurs at the second shoulder of the devolatilization stage [6], as organic polymers were emitted during this stage [23, 24].

c) *m*/*z*=28

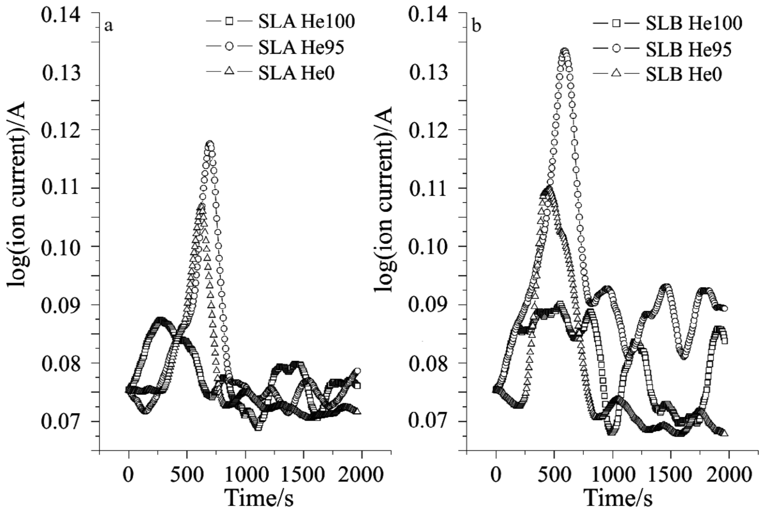

Fig. 6 m/z=46 emission a – for SLA and b – for SLB in Atm100, Atm95 and Atm0

CO emission is indicated by this m/z value (Table 1), which is significant for energy production because of its high calorific value, 12.87 MJ Nm^{-3}. Release of this compound was observed only when the heating atmosphere contained helium, so none was emitted when it was 100% oxygen. The highest emission was observed at the second shoulder of the devolatilization stage and in gasification heating atmospheres.

d) m/z=46

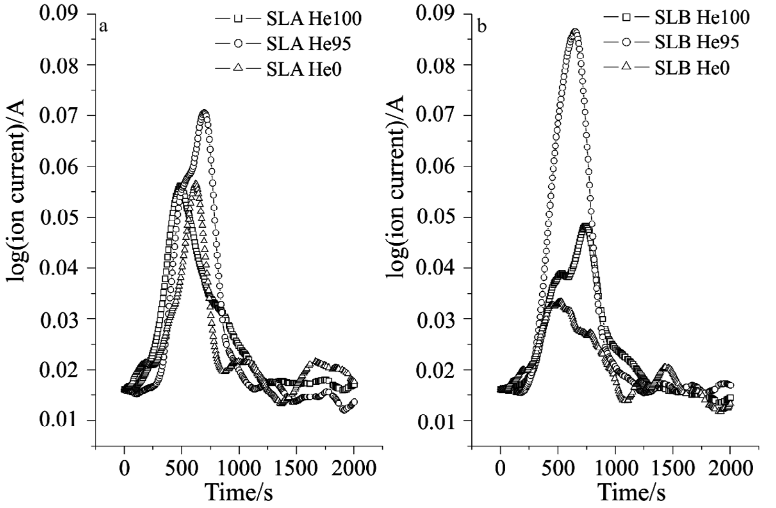

Fig. 7 m/z=30 emission a – for SLA and b – for SLB in Atm100, Atm95 and Atm0

Nitrogen dioxide is associated with this value (Table 1). Nitrogen compounds are one of a group of chemical species that can harm the environment and compromise human health as NO_x is a primary component of photochemical smog, being partially responsible for corroding metals and causing acid rain [25].

Nitrogen dioxide was released during the ignition stage in gasification heating atmospheres, but not in the previous devolatilization stage, which does happen in a combustion atmosphere. In He100, NO_2 emission is impossible owing to the lack of oxygen.

e) *m*/*z*=30

Two species are identified with this *m*/*z* value: ethane and nitrogen monoxide (Table 1). The former is important for its calorific value, while the latter is a nitrogenous species with similar properties to nitrogen dioxide. NO emission is also detected from *m*/*z*=46, so it may be determined which shoulders of the curves are associated with ethane and which ones with NO.

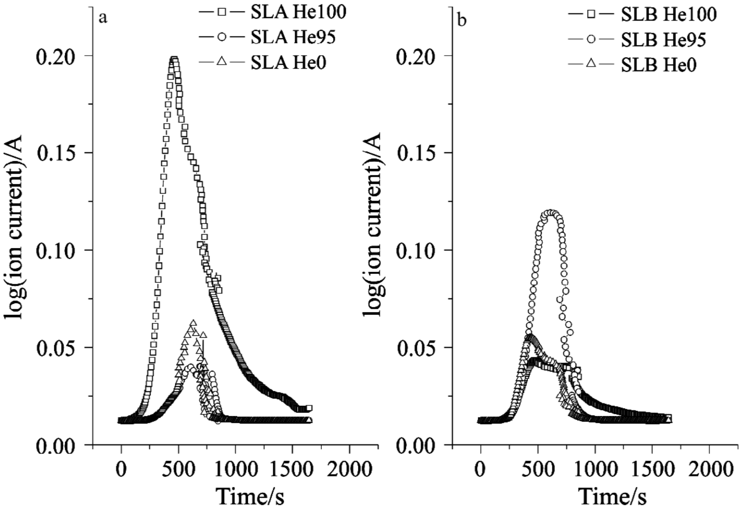

Fig. 8 *m*/*z*=44 emission a – for SLA and b – for SLB in Atm100, Atm95 and Atm0

Comparing curve *m*/*z*=30 with curve *m*/*z*=46 shows that NO emission may be associated with the ignition-and-burning stage, although in the case of He0 this emission occurred at the end of the volatilization phase as the atmosphere is totally reactive. Similar considerations to nitrogen dioxide can be observed, ethane being released during the devolatilization stage. Therefore, in He100, no ignition occurred, so *m*/*z*=30 must only have been associated with ethane, whose emission was at its highest. Ethane emission is higher for SLA than for SLB, probably owing to a higher carbon content.

f) *m*/*z*=44

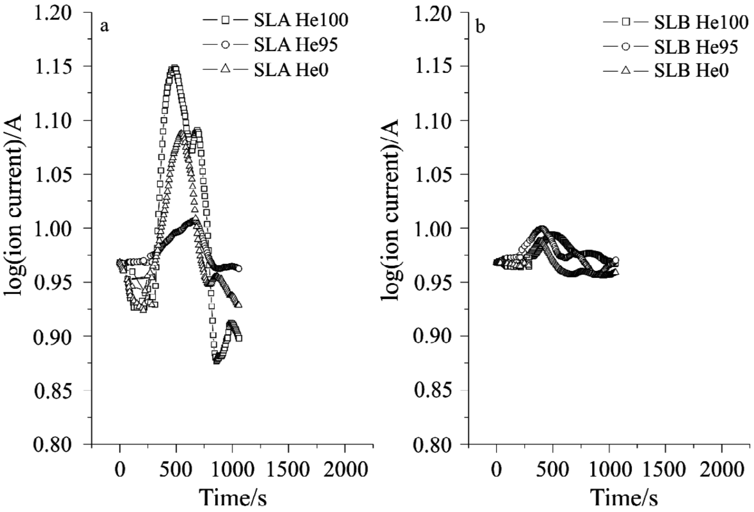

Fig. 9 *m*/*z*=64 emission a – for SLA and b – for SLB in Atm100, Atm95 and Atm0

CO_2 and N_2O emissions are associated with *m*/*z*=44 (Table 1). Like nitrogen monoxide, N_2O was emitted during the ignition-and-burning stage, although some was released in the devolatilization stage for SLB in He100.

As has been said, CO_2 emission was observed in all the heating atmospheres for both SLA and SLB, but it should be pointed out that the lowest emissions took place in gasification atmospheres (He97, He95 and He90).

g) *m*/*z*=64

SO_2 is associated with this value of *m*/*z* (Table 1). Emission of this compound was noted in all heating atmospheres for both SLA and SLB, more so for SLA, owing to its higher S content in elemental analysis, 1.1% of dry matter for SLA as opposed to 0.9% for SLB.

SO_2 may be also observed for He100, when no oxygen was present in the heating atmosphere, because of the oxygen content in elemental analysis.

A study of the mass spectrometry results reveals a major emission of energy-producing gases (hydrogen, methane, carbon dioxide and ethane) in pyrolysis and gasification, although fewer pollutants are emitted by the latter process than the former.

Conclusions

The joint use of mass spectrometry and the thermogravimetric system can be used to ascertain the heating performance of sewage sludge as fuels, so it is possible to determine the best heating disposal method for a given kind of sludge. For this paper, two kinds of sludge were studied, designated SLA and SLB. Mass spectrometry results showed gasification to be the most efficient process for the former as more energy-rich compounds are produced, while this process generates the fewest pollutants. The high calorific value of SLB, together with the value of its gas emissions, suggests that a co-combustion process would be recommendable.

This conclusion is also borne out by DTG profiles. During heating, mass loss is greater for SLA sludge, making it better suited for gasification or pyrolysis, although the latter process produces more pollutants. A combustion or co-combustion process would be more appropriate for SLB sludge as it ignites at a temperature 100 K lower than SLA sludge.

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