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PYROLYSIS STUDY OF SEWAGE SLUDGE BY TG-MS AND TG-GC-MS COUPLED ANALYSES

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The pyrolysis of an urban plant sewage sludge carried out under He atmosphere was studied by thermogravimetric-mass spectrometric (TG-MS) and thermogravimetric-gas chromatographic-mass spectrometric (TG-GC-MS) analyses. The sludge was thermally degraded with a heating rate of 10°C min^{-1} in the 20–1000°C interval; its mass loss is 51.8% up to 600°C and 61.4% up to 1000°C. Gas chromatographic analyses of the gas released during major thermogravimetric events allow the identification of various chemical species. Water, carbon mono- and di-oxide, several hydrocarbons (up to C5, both saturated and unsaturated) were the major detected species. Minor amount of pollutant species, such as cyano-compounds, were also detected. Among the released species hydrocarbons constituted the major fraction (53%), thus suggesting their immediate exploitation as fuel gas. The pyrolysis behaviour of this sample was then compared with other sewage sludge arising from wastewater treatment plants subjected to anaerobic digestion as found in literature data.

Keywords: *pyrolysis study, sewage sludge, thermogravimetric-mass spectrometric-gas chromatographic analyses*

Introduction

The storage and degradation of wastewater sludge is a topical problem of great importance and complexity owing to both the European Urban Wastewater Treatment Directive (91/17/EEC), and the trend of the sludge production, which reached 10 Mton year^{-1} in 2005 [1].

The high concentration of heavy metals, and the bacteria and viruses content do prevent the use of sewage sludge as fertilizer. Landfill disposal of wastewater sludge should be avoided, because it involves the subtraction of soil from agriculture use. In this case the sludge requires expensive pre-treatments in order to eliminate organic pollutants. Moreover this choice implies the loss of sludge energy content [2–4]. Incineration appears a useful method, even if the cost of scrubbing of gaseous by-product up to acceptable limits cannot be disregarded [1]. Pyrolysis with gasification of organic compounds may be a plausible and viable option in view of an ecological disposal of sludge, along with the exploitation of produced gas as an alternative energy source [2–9].

In this regard, the characterization of the gas phase evolved from a thermal treatment is required in order to define its heat of combustion. TG-MS analysis allows the detection in real time of the gaseous species released during the thermal decomposition of the solid sample. When gaseous species are simultaneously released their correct identification may be difficult, because the recorded mass spectrum shows the fragmentation pattern sum of all the species. TG-MS was also used to characterize the gas phase evolved from sludge thermal treatment under inert or air atmospheres [10–13].

Here we report a TG-MS study of sewage sludge pyrolysis, using samples furnishes by a civil plant of urban wastewater treatment in our city. Our lab-assembled instrumental apparatus, with the TG-MS and TG-GC-MS configurations, allows, beside the real time monitoring of the process, the accurate qualitative and semi-quantitative gas phase analysis of released compounds, sampled in correspondence with the most significant thermogravimetric events [14–18].

Experimental

Samples

A sewage sludge sample was furnished by the urban wastewater plant of Trento (population about 100,000). The sludge was previously dehydrated in the sewage plant, milled and dried at 120°C for 5 h.

Instrumentation

Thermogravimetric (TG) and differential thermal analyses (DTA) were performed on a LabSys Setaram thermobalance operating in the 20–1000°C range, with a heating rate of 10°C min^{-1}, under 100 cm^3 min^{-1} He

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flow. Samples were analysed by using a 0.1 cm^3 alumina crucible and α-Al_2O_3 as reference.

Gas chromatographic (GC) analyses were carried out on an HRGC Carlo Erba Instruments chromatograph, equipped with a GR8 Bimatic thermostatted micro-valve for gas sampling, and a VG-QMD-1000 Carlo Erba Instruments quadrupole mass spectrometer as detector. Chromatographic elutions were performed by using OV1 Mega (15 m, 0.32 mm) and poraPLOT Q Chrompack (25 m, 0.32 mm) capillary columns with a temperature program of 30°C for 5 min, followed by 10°C min^{-1} heating rate up to 200°C, held for 15 min. Helium was used as carrier gas with 15 kPa inlet pressure.

Electron impact mass spectra (70 eV) were continuously registered and stored with frequency of 1 scan s^{-1} ranging from 2 to 500 amu.

The TG-MS and TG-GC-MS instrumental interfaces, experimental procedure, and data processing adopted in this study was described elsewhere [14].

The elemental analysis of the dried sludge was carried out through an E.A. 1108 Fisons analyzer by the Analytical Chemistry Laboratory, Department of Chemistry, University of Padua, Italy. The analyses of metals, contained in the dried sludge, were carried out on a Ciros^{CCD} ICP-OES Spectro spectrometer.

Calorific value of the dried sewage sludge sample was measured with an adiabatic oxygen bomb calorimeter [19].

Results and discussion

Elemental analysis (C, H, N and S) and content of metals in the dried sewage sludge are reported in Table 1.

The high heating value (HHV) of the dried sludge, measured by means of a bomb calorimeter, results in 20.0 kJ g^{-1}. This parameter is also determined by using the modified Dulong formula and the mass% of the elements obtained by our TG-MS and TG-GC-MS measurements [20]. The calculations gives the result of 20.5 kJ g^{-1}, in good agreement with the experimental value.

The thermal treatment of the sewage sludge, under inert atmosphere, shows a continuous mass loss (61.4%) up to 1000°C. The TG curve (Fig. 1) presents a first event in the 100–600°C range, with intensity of 51.8%, followed by a second modest mass loss (9.6%) in the 600–1000°C range. For the first event, DTG curve shows an intense peak at 320°C, with a pronounced shoulder at 460°C. The second event at higher temperatures is characterised by two small overlapped bands centred at 705 and 770°C, respectively.

The mass spectrometric analysis of the released species (TG-MS measurement) shows the total ion current (TIC) curve reported in Fig. 2, which is characterised by two intense overlapping peaks at 325 and 470°C, followed by a small band at 700°C. Mass spectra, at the most significant TIC peaks, indicate main evolution of CO_2 and H_2O at 325°C (Fig. 2, in-

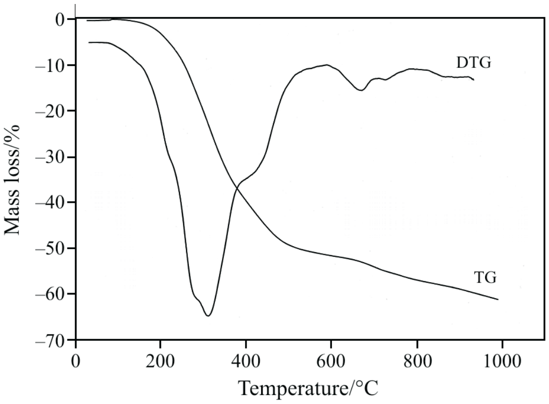

Fig. 1 Thermal analysis of the dried sewage sludge. TG and DTG curves recorded in the TG-MS measurement

Table 1 Elemental analysis and content of metals in the dried (120°C) sewage sludge

Element or species	Amount/	
	mass%	mg kg^{-1}
C	36.0	
H	4.5	
N	5.6	
S	0.5	
SiO_2	10	
Al		$6.7\cdot10^3$
B		62
Ba		460
Bi		6
Ca		$52.2\cdot10^3$
Cd		<4
Co		4
Cr		130
Cu		240
Fe		$43.4\cdot10^3$
Ga		4
In		2.2
K		940
Li		$1.34\cdot10^3$
Mg		$3.88\cdot10^3$
Mn		128
Na		780
Ni		24
Pb		16
Zn		540

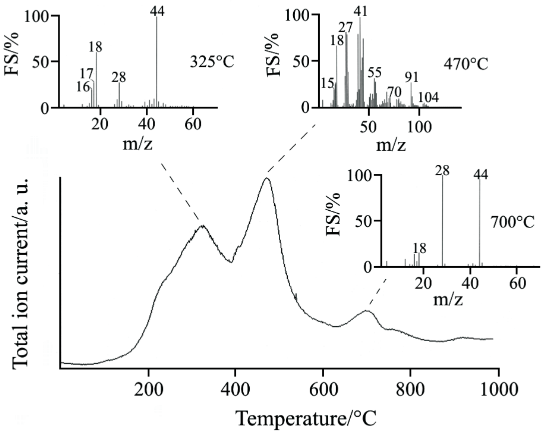

Fig. 2 Total ion current (TIC) curve of the evolved gas phase in the TG-MS analysis of the dried sewage sludge. In the insets mass spectra recorded corresponding to selected pyrolysis temperatures

set 325°C: *m*/*z* signal at 44, 28 and 18, 17, 16, respectively), whereas at 470°C the simultaneous release of different compounds (Fig. 2, inset 470°C: *m*/*z* signal at 26–29, 39–44, 45–57, 63–70, 69–83, 91–98, 103–105) is observed. Finally, spectra recorded at 700°C show the evolution of CO, CO_2 and small amounts of H_2O.

TG-GC-MS analyses were carried out sampling the gas phase evolved at the maximum intensities of mass losses, using the PoraPlot Q and the OV1 capillary columns for a better identification of released compounds. Gas chromatographic elutions at 320°C confirm the presence of CO_2 and H_2O, with small amounts of acetaldehyde, acetonitrile, acetone and traces of other unidentified species. Gas sampling at 460°C indicates the evolution of several compounds. With the PoraPlot Q column, CO, CO_2, H_2O, alkanes and alkenes up to C5, are observed (Fig. 3). The chromatogram of the elution in OV1 column shows a first peak which corresponds to the unresolved mixture of the compounds identified in the previous analysis (PoraPlot Q elution), followed by other chromatographic peaks corresponding to water, toluene, and minor amounts of styrene and C8 and C9 hydrocarbons. Chemical species detected and identified by the 460°C sampling are listed in Table 2. Their amounts were calculated taking into account the area of the chromatogram peaks, in view of considering the mass spectrometer as a detector presenting the same sensibility in revealing all different chemical species. Gas sampling at 705°C confirms evolution of CO and CO_2, with very small amounts of H_2O.

As observed by other authors [2], CO and CO_2 arise from pyrolytic decomposition of partially oxygenated organic compounds (lipids, carbohydrates, cellulose, lignin) and, to a lesser extent, from decomposition of inorganic salts such as carbonates. In an analogous way, acetaldehyde and acetone derive from oxygenated organic compounds. Cyano compounds may derive from proteins, nucleic acids and dead micro-organisms present in sewage sludge; they could be formed by dehydrogenation of amino groups [2].

Table 2 Chemical composition of the gas phase evolved at 460°C in the pyrolysis of the urban plant sewage sludge. Percent values are calculated from peak areas of gas chromatographic elutions (TG-GC-MS analyses)

Evolved species	Gas phase composition/mol%
CH_4	2.4
CO	1.7
CO_2	12.9
C_2H_4	1.0
C_2H_6	4.3
C_3H_6	6.3
C_3H_8	5.1
H_2O	14.7
HCN	1.9
C_4H_8	11.0
C_4H_{10}	4.7
CH_3CN	4.5
C_5H_{10}	5.5
C_5H_{12}	3.6
toluene	7.0
C_8H_{16}	3.0
C_8H_{18}	2.2
styrene	4.5
C_9H_{18}	1.8
C_9H_{20}	1.9

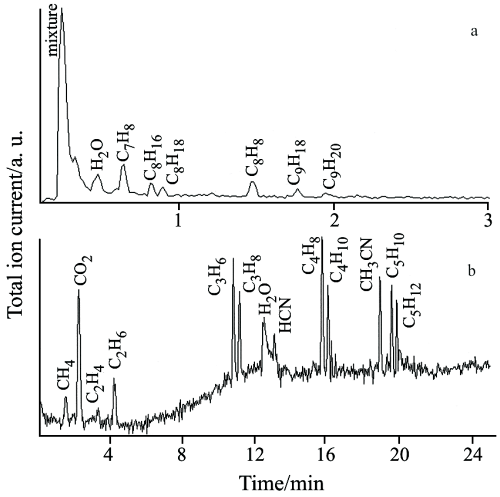

Fig. 3 Gas chromatographic elutions of the gas phase evolved and sampled at 460°C, during the pyrolysis of the sewage sludge. a – OV1 and b – PoraPlot Q capillary column, respectively

The qualitative analysis of species evolved throughout the pyrolysis up to 1000°C, can be obtained by selecting an appropriate *m*/*z* signal (Fig. 4), recalled from TG-MS data, suitable to monitor a specific compound among the various released species [14]. Unfortunately, some compounds observed in TG-GC-MS analyses present a similar pattern of signals, with common *m*/*z* ions. Water evolution trend (easily monitored by its *m*/*z* molecular ion, *m*/*z* 18) shows a broad asymmetric curve in the 80–750°C range, with a maximum at 310°C and a shoulder at 470°C. Aromatic hydrocarbons such as styrene (*m*/*z* 104) and toluene (*m*/*z* 91) evolve showing intense peaks around the 470°C. The *m*/*z* 44 ion is present in the mass spectrum of different species (acetaldehyde, acetone, propane, butane, pentane and toluene [21]). However, the intensity of *m*/*z* 44 ion in the fragmentation pattern of these compounds is quite low. Moreover, the amounts of these released compounds (estimated by the integration of their elution peaks in TG-GC-MS analyses) are also very low, so that it may be reasonably concluded that the contribution of *m*/*z* 44 ion current due to these species is negligible in comparison with the CO_2 contribution. Accordingly, the CO_2 evolution trend presents two overlapping peaks at 240 and 320°C, followed by a shoulder at 430°C and by less intense peaks at 610 and 700°C. The trend of the *m*/*z* 28 signal monitors the evolution of CO and/or N_2. Nevertheless, this signal is also present in the mass spectrum of CO_2 and even in the fragmentation pattern of other species, which are here released in a lower amount. This ion current presents two overlapping bands at 240 and 325°C (in agreement with the CO_2 release) followed both by a broad peak at 470°C (in correspondence with the evolution of the hydrocarbon mixture) and by two more intense peaks at 710 and 760°C, which characterize the TIC curve at high temperatures. The release of hydrocarbons occurs mainly in the 350–550°C interval and gives rise to the most intense peak of the TIC curve. This fact may be highlighted by directly observing the trend of the *m*/*z* 15 ion current (Fig. 4), that represents the CH_3^+ ion commonly formed in the fragmentation process of every methyl containing organic compound. This current shows an intense peak centred at 475°C preceded by a smaller broad band at 325°C. Moreover, hydrocarbon release can also be deduced by comparing the trend of the TIC curve with the trend of the curve obtained from the sum of the *m*/*z* 18, 28 and 44 ion currents (Fig. 5), used to monitor the release of inorganic species H_2O, CO (N_2) and CO_2 throughout the pyrolysis. From this comparison the absence of the intense peak at 470°C is observed. Finally, the trend of this peak is formed again by the curve obtained through summing the main *m*/*z* ion signals of hydrocarbon species, which were detected in TG-GC-MS analyses (*m*/*z* 15, 27, 39, 41, 43, 55, 56, 70, 91, 104).

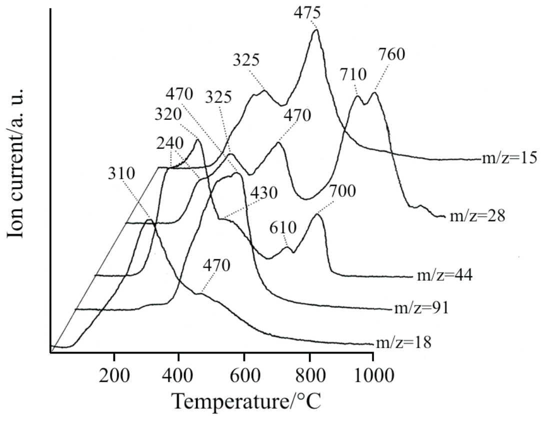

Fig. 4 Ion currents of selected *m*/*z* values, recalled from TG-MS analysis, used to monitor the release of selected species

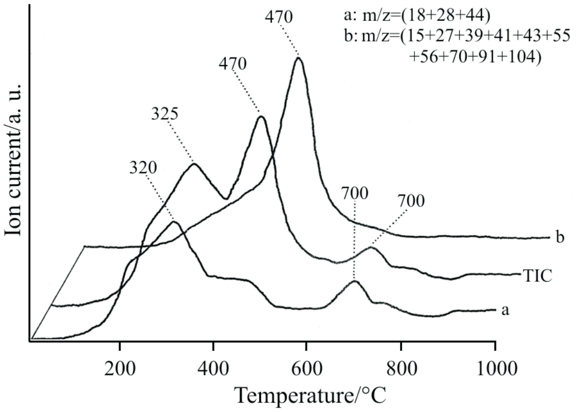

Fig. 5 Comparison among the total ion curve (TIC) and the curves obtained from the sum of selected fragment ions used to monitor the evolution of specific compounds. a – *m*/*z*=18+28+44 curve for H_2O+CO+CO_2 release; b – *m*/*z*=15+27+39+41+43+55+56+70+91+104 curve for hydrocarbon mixture release

A semi-quantitative evaluation of the pyrolysis process is here proposed by the comparison of experimental data concerning: (*i*) the chemical composition of the gas phase released at 460°C (TG-GC-MS analysis); (*ii*) the values obtained from the integration of appropriate *m*/*z* ion currents (TG-MS analysis); (*iii*) the elemental analysis of dried and pyrolyzed sludge samples.

An estimated value of released H_2O, CO and CO_2 species are first calculated by considering the integrated values of their representative *m*/*z* ion current curves. These species are the 47% of the evolved gas phase, as shown in Table 3 (details of data processing procedure here adopted are reported in previous studies of the authors [14–17]). The released hydrocarbon amount was obtained through subtracting from the

Table 3 Mass balance of the main elements present in the sewage sludge and in the compounds released during the pyrolysis process

Species		Gas phase composition						
		Compounds			Elements			
		from TG-MS anal./mol%	from TG-GC-MS anal./mol%	mass%	mass%			
					C	H	N	O
CO		15.4		8.8	3.8			5.0
CO_2		17.3		15.5	4.2			11.3
H_2O		14.5		5.3		0.6		4.7
hydrocarbon mixture	CH_4	52.8	1.8	0.6	0.45	0.15		
	C_2H_4		0.7	0.4	0.34	0.06		
	C_2H_6		3.2	2.0	1.6	0.4		
	C_3H_6		4.7	4.0	3.4	0.6		
	C_3H_8		3.8	3.4	2.8	0.6		
	HCN		1.4	0.8	0.36	0.03	0.41	
	C_4H_8		8.3	9.5	8.1	1.4		
	C_4H_{10}		3.5	4.1	3.4	0.7		
	CH_3CN		3.4	2.8	1.7	0.1	1.0	
	C_5H_{10}		4.1	5.9	5.1	0.8		
	C_5H_{12}		2.7	4.0	3.3	0.7		
	toluene		5.3	10.0	9.1	0.9		
	C_8H_{16}		2.2	5.0	4.3	0.7		
	C_8H_{18}		1.6	3.7	3.1	0.6		
	styrene		3.4	7.2	6.6	0.6		
	C_9H_{18}		1.3	3.3	2.8	0.5		
	C_9H_{20}		1.4	3.7	3.1	0.6		
element percentages		in the total evolved gas phase			67.55	10.04	1.41	21.0
		content in the initial dried sludge			41.5	6.2	0.9	12.9
		differences with the elemnetal analysis			+5.5	+1.7	–4.7	

value of the TIC curve area the value of the curve used to monitor the H_2O, CO and CO_2 release; that amount was 53%. Taking into account the chemical composition of the hydrocarbon mixture released around 460°C, as calculated from the TG-GC-MS analysis (Table 2), the amount of each evolved hydrocarbon was determined. The molar percentages of all the released species were then converted to mass percentages. From these data, the mass percentages of C, H, N and O were determined for each released compound, along with their sums. Finally, by considering the mass loss of the pyrolyzed sample, the percentages of C, H, N and O in the initial sludge was determined and compared with the values obtained from the elemental analysis. Experimental data reported in Table 3 show that C% is overestimated by a value of +5.5%, while N% is underestimated by a similar value, that is –4.7%. This discrepancy may be justified by considering that in this data processing the *m/z* 28 signal, used to monitor and quantify the CO species, also includes the contribution arising from the possible presence of released N_2. Indeed, the very close molecular mass of these two species (m.m. CO=28.010 amu, m.m. N_2=28.014 amu) cannot be discriminated by our mass spectrometer.

A nominal calorific value of the released gas mixture was calculated taking into account both the chemical composition of the gas phase (determined by TG-MS and TG-GC-MS measurements), and the ΔH^0 values of the combustion reactions of evolved compounds. Actually, only the species which are gasses at standard conditions (C1–C4 hydrocarbons+CO, CO_2, H_2O and HCN) were considered to form the nominal released gas mixture. For these species their molar percentages were recalculated by considering data of Table 3. A calorific value of 35.5 MJ m^{-3} was obtained.

These results show that pyrolysis of this sewage sludge sample may represent a viable process option for its environmental treatment. The residual mass of pyrolyzed sludge (addressed to landfill) is considerably reduced and the enthalpy content of the released hydrocarbons may be recovered as fuel gas.

Comparison with literature data

A direct comparison among the results of thermal treatments of different sewage sludge could be very difficult and ambiguous, due to the parameter variety, which influences this kind of study. Indeed, the source of the sewage sludge, the kind of treatment undergone in original plant, the thermal study carried out inside analytical instrumentations or lab-scale reactors, the inert or reactive atmosphere of the annealing process, must all be considered. Moreover, in order to compare the results obtained in the pyrolysis of our sewage sludge sample with those studied by other authors, the bibliographic research was addressed to the topics concerning: the urban plant sewage sludge; the chemical analysis of the gas phase evolved from waste; the TG-MS coupled applications.

The first discriminating parameter is the type of sludge, deriving from urban or industrial wastewater plant. For an urban plant the dimension of the city may also be an important factor to be considered, as shown by Calvo *et al.* [13]. Moreover, the digestion process in the wastewater plant can be carried out either in aerobic or anaerobic conditions. The choice of the treatment atmosphere influences the chemical features of the final sludge, that yields a particular pattern of its pyrolysis products. So, for example, sludge aerobic digestion inhibits the presence of bacteria responsible for methane-genesis, so that in the subsequent pyrolysis process an increasing amounts of released oxygenated compounds and minor amounts of released hydrocarbons are formed. These facts, in turn, are responsible for a minor char output, as shown by Conesa *et al.* [10]. Finally, the kind of drying process carried out on the sewage sludge could strongly influence the amount of residual water present in the solid, that directly affects the oxygen content in the sludge, leading to a definite chemical composition of the released gas phase, as observed by Arenillas *et al*. in the case of rank coals [22]. Table 4 shows a comparison among elemental analyses of urban sewage sludge samples which underwent anaerobic digestion.

A second aspect concerns the operative conditions used in the study of thermal treatment of sewage sludge. Typical parameters are: the different kind of thermal conversion process (pyrolysis, gasification, combustion) obtained by varying the inert/oxygen chemical composition of the purge gas (Calvo *et al.* [13, 23]); the analysis of pure sewage sludge or of samples mixed with combustible materials, such as coal, (Otero *et al.* [12]); the type of reactor used, either continuous or batch (Fullana *et al.* [2]); the kind of heating process carried out in conventional electrically-heated furnace or microwave oven (Menéndez *et al.* [24]). On the other hand, the pyrolysis process can be studied either on very small amounts of sludge samples, directly analysed inside thermobalance [10, 13], or on major amounts of samples by using lab-scale cylindrical reactors ([2], Inguanzo *et al.* [25]). Nevertheless, the final pyrolysis temperature and the heating rate could widely influence the yields of fractions of gas, of liquid and solid residue, as well as their calorific values [25].

Regarding the chemical analysis of species evolved in gas phase during the pyrolysis of sludge samples, thermal analyses were, in the past, associated with the use of cold traps, where released compounds were first condensed and subsequently analyzed by using gas chromatographs equipped with thermo-conductivity or flame-ionization detectors. Recently, however, the applications of coupled TG-MS instrumentation, although differently assembled, enable a real time monitoring of the evolved gas phase both during the process time and with the pyrolysis temperature increasing [22, 26]. Standard TG-MS instrumentation usually utilizes quadrupole mass spectrometer able to collect specific *m/z* ion signals, when operating by electron impact ionization mode. This operative approach 'selected ion monitoring' requires a preventive attribution of detectable *m/z* signals to pre-definite compounds. Indeed, some of these attributions could be inaccurate, taking into account that the same *m/z* signal could detect ions, having the same mass/charge ratio, which are generated from wholly different chemical species simultaneously evolved. To this concern, typical examples are: the attribution of m/z=15 signal to CH_4 release, even if the CH_3^+ ion is commonly formed in the ionic fragmentation process of each hydrocarbon com-

Table 4 Selected chemical characteristics of dried sewage sludge samples arising from urban waste water plants with anaerobic digestion, reported in literature data

	Sample							
	our	SLB Calvo [13]	SLA Calvo [13]	LLE Otero [12]	N° 3 Fullana and Font [2, 3]	L Menéndez [24]	S Inguanzo [25]	BEN Conesa [10]
C/mass%	36.0	22.7	36.2	38.1	30.6	49.1	35.7	38.8
H/mass%	4.5	3.3	4.5	5.2	4.9	7.3	5.2	–
N/mass%	5.6	3.1	5.6	4.5	3.0	8.1	3.5	2.8
S/mass%	0.5	0.9	1.1	0.9	<1	1.5	0.7	–
HHV/kJ g^{-1}	20.0	9.5	15.4	16.8	9.9[a]	–	16.6	–
HHV/MJ m^{-3}	35.5[b]	–	–	–	–	6.9[b]	–	–

[a]net calorific value; [b]referred to the released gas phase

pound containing a methyl group; *m/z*=28, to monitor the release of CO, could also detect releases of CO_2 (being this value present in CO_2 mass spectrum with minor intensity), unsaturated hydrocarbons (C_2H_4), and N_2, particularly in the case of sewage sludge pyrolysis. On the other hand, in literature few papers report the use of TG-MS coupling where the mass detector works in 'scan mode' [26]. Actually, only the continuous recording of mass spectra of evolved gas phase could give an idea of the abundance of the compounds simultaneously released, looking to the variety and complexity of the detected signals. In particular, for an ultimate identification of the effective number of species simultaneously released, a further gas chromatographic separation of the gas mixture is required, like the TG-GC-MS analysis obtainable with our lab-assembled instrumental interface.

Among the samples reported in Table 4, the sewage sludge sample SLA, studied by Calvo *et al.* [13], shows the chemical composition more similar to that of our sample, which only presents a halved S content. Both samples underwent anaerobic digestion in the original plants, although SLA sludge had arisen from an urban plant of a large city with a population one order of magnitude higher than our case. In the same paper, a second sample SLB arose from an urban plant of a city with a population closer in number to ours, but this latter sludge had undergone a more complete digestion process (differently from what had occurred to our specimen). Although subsequent values were obtained with different kinds of analyses, SLA sample showed an ash content of 37.9% (at 575°C) close to the value 38.6% found for solid residue recovered after inert thermal treatment on our sludge (at 1000°C). More difficult was the comparison between their evolved gas phases, due to the different instrumental-analytical approaches used in the analyses. The 7.9% of moisture and 55.0% of volatiles, found for SLA sample, slightly differed from the 3.2% of H_2O release and the total 58.2% of CO, CO_2, hydrocarbons and N-compounds release, which were calculated from the integration of the mass spectrometric data during the entire pyrolysis of our sludge sample.

Easier is the comparison with the thermal behaviour of sludge sample N° 3, in Fullana's work [2], taking into account the accurate qualitative and quantitative chemical analyses carried out on the volatiles. These were first collected by means of bags and adsorbed on resins, and then analysed by GC and GC-MS techniques. Conversely, with our TG-MS apparatus, the released compounds are analyzed in real time during the whole pyrolysis process, with the constraint to detect and identify only the most abundant species. Apart from the comparison between the amounts of the same released compounds, no other conclusion could be drawn as regards the temperature intervals of their evolutions. A second aspect, which diversifies the two samples, concerns the different kind of heating process, being sludge N° 3 directly pyrolyzed at 850°C in a horizontal reactor, whereas our sample underwent a linear increase of the temperature in a thermobalance. Nevertheless, the release of CO and CO_2 are similar: 4.6 and 6.3%, for sludge N° 3 *vs*. 5.4 and 9.5% for our sample, respectively. According to the classification adopted in Fullana's paper, light hydrocarbons (C1–C6 species plus benzene and toluene) account for a 9.4% in sludge N° 3 *vs*. our 26.9%. The different chemical composition of the organic fraction released from the two samples is also focused by comparing the mixture of semi-volatile compounds and the relative nitrogen-derived species, which are respectively: 1.8 and 0.3% for sludge N° 3, 14.1 and 2.2% for our sample. Actually, our sewage sludge releases an important fraction of organic combustible species, which justifies both the high calorific value found for the solid sample and the one calculated for the evolved gas mixture. These calorific values, though comparable with those of literature data [25], agree with the high organic content of our sludge and with its low digestion undergone in the original plant. Finally, a comparison of the trends of some released compounds can be proposed by considering the sludge sample BEN in the work of Conesa *et al.* [10]. Water is released with the same mono-modal trend that shows the same maximum (at ca. 300°C) and a tailing effect; this fact could indicate that the two samples present a similar content of moisture. The *m/z* 15 ion current shows the same bi-modal trend with a first band at the same temperature (around 300°C), and a most intense second band at 575°C for sample BEN and at 100°C less for our specimen. Actually, on the basis of the TG-GC-MS gas chromatographic elution, the gas phase sampled at 475°C shows only the 1.8% of methane, so that the trend of this signal monitors the total evolution of hydrocarbon mixture and not only the CH_4 species. Indeed, sludge BEN presents the same bi-modal trend, with the latter peak at ca. 575°C, for other signals (*m/z* 26, 39, 42) which were used to follow the release of both saturated and unsaturated C2, C3 hydrocarbons. CO_2 release appears more complex in both samples, because it is sprayed in several overlapped events up to 700°C for our sludge and up to 520°C for sample BEN. For BEN sludge, hydrogen evolution, usually well detected by mass spectrometer working in SIM mode, is depicted by a broad flat band in the 400–580°C interval. Unfortunately, up to date, H_2 release can not be error-free monitored with our spectrometer, due to the difficulty to optimize the tuning conditions at the lower limit of the scan region. Nevertheless, preliminary results seem to indicate that H_2 evolves together with hydrocarbons, around 470°C, when the C–C and C–H bond breaking reactions are thermally activated.

Conclusions

The pyrolysis of the sewage sludge sample, previously dried at 120°C, was carried out under inert atmosphere and it was studied by TG-MS and TG-GC-MS analyses. A detailed identification of gaseous species, evolved during the thermal treatment up to 1000°C, was obtained. The loss of sludge mass resulted 61.4%, while the evolved gas phase consisted of hydrocarbons for 53%. Sewage sludge features and chemical species released during pyrolysis were compared with samples, arising from similar wastewater urban plants, analysed by other authors.

These data show that the pyrolysis process carried out on our sludge sample halves the amount of material addressed to landfill disposal. Moreover, the pyrolysis process yields an evolved gas mixture which can be exploited as fuel gas in neighbouring power plants.

The results obtained in the pyrolysis study of this sewage sludge sample indicate the analytical potentiality of our TG-MS, TG-GC-MS apparatus, which was suitably customized for the characterization of inorganic materials synthesized by sol–gel method. The complementary information acquired by analysing both TG-MS and TG-GC-MS measurement data allows real time monitoring of released gas species during pyrolysis. This is possible only after the safe identification of main evolved compounds, which is performed by quick recordings of successive mass spectra. On the other hand, the species identification is not performable with the use of the only ion currents. A useful qualitative and semi-quantitative chemical analysis is thus obtained by means of the two instrumental interfaces, that efficiently contribute to the description of pyrolysis behaviour of even such complex substance mixtures as those released from wastewater sewage sludge.

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