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DESIGN CONSIDERATIONS AND AN EXAMPLE OF APPLICATION OF AN IN-HOUSE MADE TG-MS INTERFACE

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Abstract

The design, the abilities and a characteristic application of an in-house made interface for combining thermogravimetry (TG) with mass spectrometry (MS) are presented. The TG-MS interface consists mainly of three co-axial tubes. The position of the intermediate tube was determined after calculation of the temperature profile at the TG furnace exit tube. The inner tube position was determined taking into consideration its protection against condensation of heavy molecules and the time delay for the transfer of the evolved gases. This interface allows either continuous sampling and transferring of the evolved gases from the TG to the MS or repetitive introduction of short sampling pulses of TG evolved gases to MS. The interface is capable of coupling various commercial instruments. In the present work two configurations of this interface are demonstrated. Finally an example of application of this interface on forest fuel pyrolysis is presented.

Keywords: design, engineering computations, hyphenated methods, pine-needles, pyrolysis, TG-MS interface

Introduction

The study of compound degradation by thermogravimetry (TG) can be greatly enhanced when evolved-gas analysis is used. It appears that the most popular technique used in combination with TG is mass spectrometry (MS) on account of its sensitivity, versatility and fast analysis time [1–6].

The TG-MS coupling system (TG-MS interface) should meet several specifications such as: rapid evolved-gas transfer from the sample pan of the TG to the MS; no condensation of evolved gases in the TG furnace and re-evolution in the next experiment (memory effects); no degradation or condensation of evolved gases, no disturbances with TG and MS performance; no air insertion during TG furnace opening; simplicity in construction; easy system decoupling and cleaning; low cost; and continuous monitoring and versatility with respect to TG and/or MS [7]. Finally, an

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intergraded TG-MS system should include software for resolving possible overlapping mass spectra of co-eluting substances [8–10].

In this work an in-house made TG-MS interface is presented. The interface was developed according to the before mentioned specifications. The interface works in inert or oxidative atmosphere. Its versatility is based mainly to the ability to couple with minor modifications any type of TG with any type of MS (e.g. Hewlett–Packard, Balzers). This interface allows either continuous sampling and transferring of the evolved gases from the TG to the MS (continuous sampling) or repetitive introduction of short sampling pulses of TG evolved gases to the MS (repetitive pulsed sampling).

A procedure for the evaluation of the performance of the in-house made TG-MS system has been proposed in a previous work [7]. This procedure includes tests for monitoring the mass-flow stability, the gas transfer delay, the evolved-gas condensation effect and the interferences of the coupling system on TG and MS performance. The proposed evaluation procedure can be used in general for monitoring the performance of a TG-MS system and can also be a basis for design improvements. In addition, it may be used for comparing the results of different TG-MS systems or for interlaboratory comparisons. A number of tests have also been reported for evaluating the performance of the TG-MS interface when operating in repetitive pulsed sampling mode [11]. When the interface operates in repetitive pulsed sampling mode the results of the TG-MS analysis (TG and MS signals) might be different compared to the results produced when the interface works in continuous sampling mode. This is due to pressure variation in the interface when changing from sampling interval to no sampling interval. So it is essential to ensure that such a repetitive pulsed sampling system is not introducing any qualitative or quantitative errors in the results of the TG-MS analysis. In addition the proposed tests evaluate the system repeatability of sampling duration, sampling period and sampling quantity.

The purpose of this work is to present and discuss the basic design considerations and the engineering computations of the TG-MS interface. As an example of application of the TG-MS interface, the pyrolysis of pine needles and the effect of various chemicals upon it, is presented. This pyrolysis is a complicated phenomenon to cope with only thermal methods [12–14]. The TG-MS method applied to *Pinus halepensis* pine needles is presented and discussed.

Design of the TG-MS interface

Description and general considerations

A rough diagram of the TG-MS interface is shown in Fig. 1. It is based on the concept of the vapour sampling device developed by Arnold *et al*. [15]. It consists of: (1) a Pulsed Sampling System (PSS) which allows sampling of evolved gases from a TG furnace and (2) a transfer line which transfers a small portion of the evolved gases from the TG to the MS [7, 11]. The transfer line consists of a capillary uncoated, deactivated column which is inside a heating thermomantle. The heating thermomantle is a thermal resistance wrapped around a flexible tube made of stainless steel. The

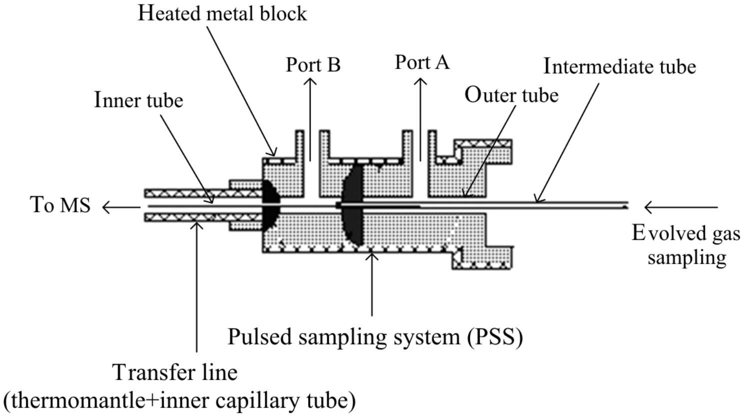

Fig. 1 Schematic diagram of the TG-MS interface

PSS consists of three coaxial tubes and is heated by a metal block. The inner tube is the transfer line capillary column connected to the MS ion source. The outer tube is connected to a vacuum source, through port A. It allows the exit of the TG evolved gases to the atmosphere and produces stable laminar flow conditions in the PSS. The flow through the intermediate tube has two modes of operation: (1) the idle mode, when the intermediate tube is flushed with an inert gas, entering from port B, in order to prevent evolved gases from reaching the capillary and prevent air entrance during TG furnace opening and (2) the sampling mode, when the intermediate tube is connected to vacuum, through port B, in order to direct the evolved gases to the head of the capillary. Important parameters in the design of the TG-MS interface are: the presence of cold spots, dead volumes, TG furnace orientation, way of heating and length of transfer line, type of capillary column and relative position of the intermediate and the inner tube.

The interface can operate either in continuous sampling mode or in repetitive pulsed sampling mode. An electronically controlled solenoid valve adjusts sampling period and duration. When the sampling duration is adjusted to be infinite, then the system operates in a continuous sampling mode. This mode is used in conventional TG-MS analysis. Repetitive pulsed sampling mode is used for controlling the amount of a substance introduced to the MS and is a requirement for extending the use of the interface to on-line thermogravimetry-gas chromatography-mass spectrometry (TG-GC-MS) [16]. For that purpose, the capillary, uncoated column of the interface must be substituted by a short capillary chromatographic column. Small pulses of the TG evolved gases are introduced repetitively into the chromatographic column in repetitive pulsed sampling mode. Partial chromatographic separation is taking place in the chromatographic column in the short time interval between two pulses. The partially separated evolved gases are then entered into the MS. If the chromatographic resolution is not sufficient, then chemometric curve resolution techniques can be applied.

Figures 2 and 3 present two configurations for the analysis of evolved gases that have been set-up in order to develop a TG-MS system. In Fig. 2, the TG-MS interface

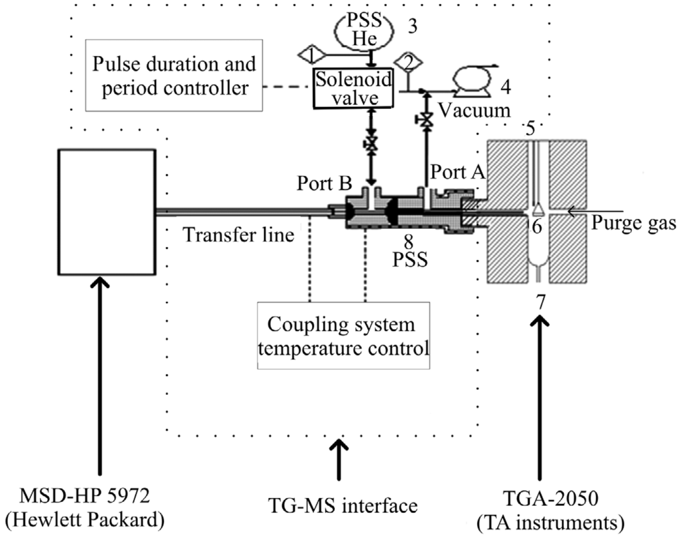

Fig. 2 Schematic diagram of the TG-MS interface coupling a thermogravimetric analyser (TA Instruments, TGA 2050) with a Mass Selective Detector, MSD (Hewlett Packard, 5972): 1 – idle mode, 2 – sampling mode, 3 – He inlet at idle mode, 4 – vacuum pump, 5 – TG thermocouple, 6 – sample pan, 7 – TG furnace quartz tube, 8 – pulsed sampling system

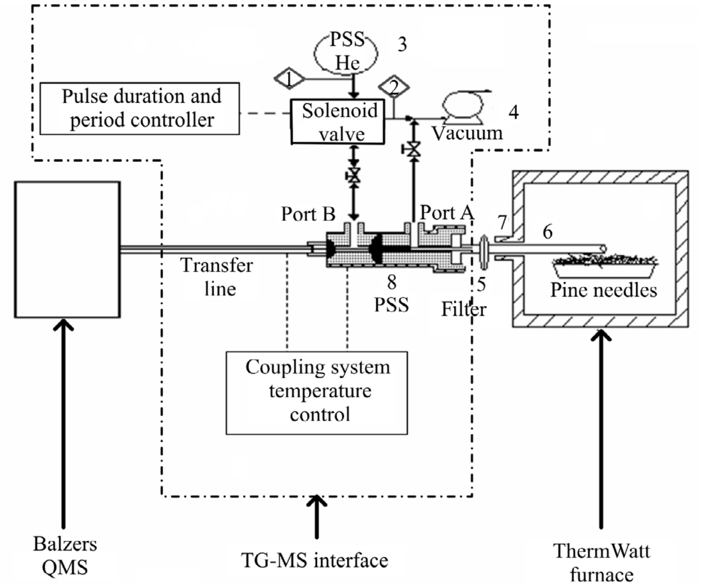

Fig. 3 Schematic diagram of the TG-MS interface in conjunction with Thermawatt furnace and Balzers Quadrupole Mass Spectrometer (QMS): 1 – idle mode, 2 – sampling mode, 3 – He inlet at idle mode, 4 – vacuum pump, 5 – glass fiber filter, ∅=92 mm, 6 – glass sampling tube 50 cm, 7 – vent hole, 8 – pulsed sampling system

is coupling a thermogravimetric analyzer (TA Instruments TGA 2050) with a mass spectrometric detector (Hewlett Packard 5972). In Fig. 3, the TG-MS interface transfers the evolved gases from a Thermawatt furnace (inner dimensions $24\times17.5\times10$ cm^3) to a Balzers quadrupole mass spectrometer (QMS) [17].

Estimation of the relative position of the intermediate tube

The relative position of the intermediate tube of the PSS, strongly, affects the response of the MS. It is important that the inlet of the intermediate tube is at constant temperature; otherwise the evolved gases concentration at sampling point would be temperature dependent and the response of the MS would be affected by the furnace temperature. In the following an example of the estimation of the position of the intermediate tube is given.

In Fig. 4, the exit tube of the TG (TA Instruments TGA 2050) furnace (half-cut) is presented. According to the scheme, the exit tube is surrounded by thermal resistances along part AB and insulation and water-cooled housing along part BC. In order to estimate the position of the intermediate tube of the TG-MS interface inside the furnace exit tube, the temperature profile along part BC of the furnace exit tube was calculated. The equation used was:

$$T_x = T_s - (T_s - T_B)\exp\left(-\frac{4hx}{\rho u c_p d}\right) \qquad (1)$$

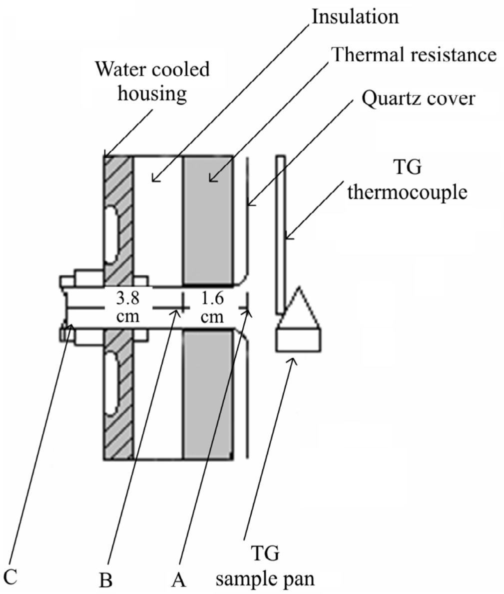

Fig. 4 Exit tube of TG (TA Instruments, TGA 2050) furnace (half-cut). Part AB of the exit tube is in contact with thermal resistance. BC is the rest part of the exit tube which is not in contact with thermal resistance

where T_x (in K) is the temperature at distance x downstream point B, T_s (in K) is the exit tube wall temperature, T_B (in K) is the temperature at point B, h (in W m^{-2} K^{-1}) is the convection heat transfer coefficient, c_p (in J kg^{-1} K^{-1}) is the gas specific heat, x (in m) is the distance from point B towards the exit, u (in m s^{-1}) is the gas velocity, d (in m) is the inner diameter of the furnace exit tube and ρ (in kg m^{-3}) is the gas density.

In Table 1, the parameters and the equations used for the calculation of the temperature profile are given. For the calculations it was assumed that the gas flow consisted of He, T_s was constant at 40°C (313 K) and the TG furnace temperature was 700 K, which represents a mean temperature in TG analysis. Part AB of the exit tube

Table 1 Parameters and equations for the calculation of the temperature profile inside the furnace exit tube

Parameter	Symbol	Reference or Equation	Value
He density at 700 K	$\rho_{\mathrm{He\,(700\,K)}}$	[18]	0.06969 kg m^{-3}
He density at 500 K	$\rho_{\mathrm{He\,(500\,K)}}$	[18]	0.09754 kg m^{-3}
He viscosity at 700 K	$\mu_{\mathrm{He\,(700\,K)}}$	[18]	$350\cdot10^{-7}$ N s m^{-2}
He viscosity at 500 K	$\mu_{\mathrm{He\,(500\,K)}}$	[18]	$283\cdot10^{-7}$ N s m^{-2}
Prandl number at 700 K	$Pr_{\mathrm{(700\,K)}}$	[18]	0.654
He thermal conductivity at 500 K	$\lambda_{\mathrm{He\,(500\,K)}}$	[18]	$220\cdot10^{-3}$ W m^{-1} K^{-1}
He heat capacity at 500 K	$Cp_{\mathrm{He\,(500\,K)}}$	[18]	$5.193\cdot10^{3}$ J kg^{-1} K^{-1}
Exit tube BC wall temperature	T_s		313 K
Exit tube AB temperature	T_B		700 K
He mass flow	$\dot{m}_{\mathrm{He}}$		$22.7\cdot10^{-6}$ kg s^{-1}
Exit tube inner diameter	d		$3.2\cdot10^{-3}$ m
Length of part AB of the exit tube	l_{AB}		$16.000\cdot10^{-3}$ m
He mean velocity at 700 K	$u_{\mathrm{He(700\,K)}}$	$u_{\mathrm{He(700\,K)}}=\dfrac{4m}{\rho_{\mathrm{He(700\,K)}}\pi d^2}$	7.75 m s^{-1}
He mean velocity at 500 K	$u_{\mathrm{He(500\,K)}}$	$u_{\mathrm{He(500\,K)}}=\dfrac{4m}{\rho_{\mathrm{He(500\,K)}}\pi d^2}$	5.53 m s^{-1}
Reynolds number at 700 K	$Re_{\mathrm{(700\,K)}}$	$Re_{\mathrm{(700K)}}=\dfrac{\rho_{\mathrm{He(700\,K)}}u_{\mathrm{He(700\,K)}}d}{\mu_{\mathrm{He(700\,K)}}}$	50
Length of developed thermal boundary layer at 700 K	$l_{\mathrm{e,T}}$	$l_{\mathrm{e,T}}=0.05d\,Re_{(700K)}Pr_{(700K)}$	$5.232\cdot10^{-3}$ m
Convection heat transfer coefficient at 500 K	h	$Nu=\dfrac{hd}{\lambda_{\mathrm{He(500\,K)}}}=3.66$	251.6 W m^{-2} K^{-1}

was assumed to have the same temperature as the TG furnace due to direct contact with thermal resistances. The parameters needed for the calculation of T_x, were calculated in a mean temperature of $(T_B+T_s)/2\approx 500$ K. For the calculation of h (in W m^{-2} K^{-1}) the following equation was used:

$$Nu=\frac{hd}{\lambda}=3.66 \tag{2}$$

where Nu is the Nusselt number, d (in m) is the exit tube inner diameter and λ (in W m^{-1} K^{-1}) is the thermal conductivity coefficient of the gas. Nusselt number was given the value of 3.66 because the gas flow along BC was found to be laminar ($Re<2100$) and the thermal boundary layer was fully developed ($l_{e,T}<l_{AB}$).

After substitution, Eq. (1) results in:

$$T_x=313-(313-700)\exp(-112.28\,x) \tag{3}$$

Equation (3) shows that temperature decreases very fast downstream point B and it becomes almost equal to T_s. So, the intermediate tube can be placed a few millimeters downstream point B. At this point the temperature is not affected by the changes of furnace temperature. Moreover, the intermediate tube can act as a condensation stage for the heavier evolved gases. This can be also used for protecting the inner tube against contamination.

Estimation of the relative position of the inner tube

The relative position of the inner tube is determined by two criteria. The first one is that the time delay for the gas transfer from the inlet of the intermediate tube to the inlet of the inner tube should be as small as possible. Assuming that the gas flow through the intermediate tube is plug type, the time delay t_d (in s) is calculated from:

$$t_d=\frac{\pi\frac{d_{int}^2}{4}l}{Q} \tag{4}$$

where d_{int} (in m) is the inner diameter of the intermediate tube, l (in m) is the distance between the inlets of the inner and the intermediate tube and Q (in m^3 s^{-1}) is the volumetric flow through the intermediate tube. According to Eq. (4), t_d is increasing with l. At a constant volumetric flow of 40 mL min^{-1}, t_d was found to be less than 0.2 s for various positions of the inner tube. According to the first criterion the optimum position of the inner tube would be immediately after the intermediate tube inlet. However, this position is not suitable for the idle mode, when the intermediate tube is flushed with inert gas.

The second criterion concerns the protection of the inner tube. According to it, the inner tube inlet should be away from the intermediate tube region where condensation of the heavier molecules is taking place. This region can be determined experimentally by using an intermediate tube made from glass. In this way, the condensation region is visible. In our TG-MS experiments with forest fuels, condensates were observed along the first 2.2 cm of the intermediate tube.

Taking the two criteria into account, the inner tube was placed immediately after the condensation region, which is approximately 2.2 cm from the intermediate tube inlet.

An example of application of the TG-MS interface: Pyrolysis of pine needles in the presence of chemical retardants.

Experimental

Instrument

The configuration shown in Fig. 2 was used for the TG-MS analysis. The TG instrument was a TA Instruments, TGA 2050 and the MS was a Hewlett–Packard 5972. The transfer line of the TG-MS interface was a deactivated 2.17 m×0.15 mm i.d. Chrompack capillary column.

Materials

The chemicals $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$, active substances of various commercial fire retardants, were both p.a. grade and BDH and Carlo Erba reagents respectively. Pine needles (*Pinus halepensis*) were collected from a forest near an urban area, during the fall period. They were washed with deionized water for dirt removing, dried at room temperature for 5 days and then, they were cut at suitable size (3 mm).

Samples

Pine-needles 3 mm at length was used as sample, as the closest approach to the realistic conditions during a forest fire. Three types of sample were prepared: untreated needles (a), mixtures of needles with 10% *w*/*w* $(NH_4)_2HPO_4$ (b), mixtures of needles with 10% *w*/*w* $(NH_4)_2SO_4$ (c). A stock aqueous solution of known concentration of the chemical was added to a preweighted sample of pine-needles, to obtain a final concentration of 10% *w*/*w* (mass of chemical to mass of pine-needles). The volume of the mixture was completed with distilled water up to 10 mL. After mixing, the samples were dried in an oven at 40°C for 48 h. The same procedure was followed for preparing untreated samples in the absence of fire retardants.

Method

About 2 mg of sample were heated from ambient temperature up to 650°C with a heating rate 50°C min^{-1} at helium atmosphere (purge gas) in the TG furnace. The TG-MS interface was heated at 180°C and was operated in continuous sampling mode. The MS signal, ranging from 10 to 200 amu, was monitored with scan frequency 6.1 scans s^{-1}. The quantitative calibration of MS signal for H_2O (m/z 18) and CO_2 (m/z 44) was based upon the thermal degradation of $KHCO_3$ [19].

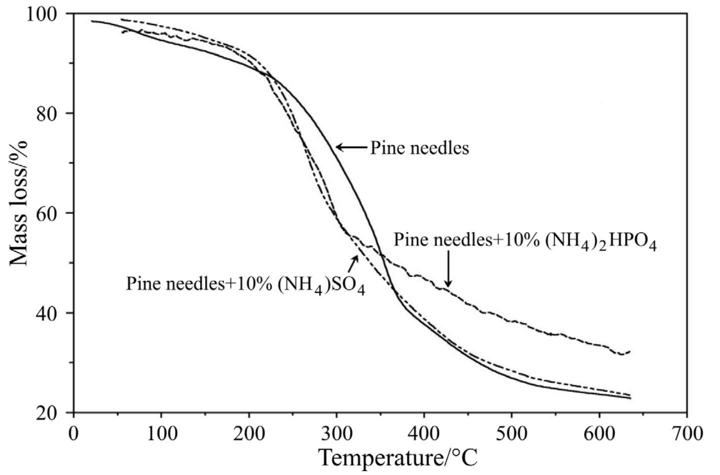

Fig. 5 TG curves of untreated pine needles and pine needles treated with $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$

Results and discussion

In Fig. 5 the TG curves of the treated and untreated pine needles are presented. $(NH_4)_2HPO_4$ seems to increase significantly the char residue.

In Figs 6–8 the average spectra in the temperature range of 40–500°C of the untreated pine needles (Fig. 6) and the pine needles treated with $(NH_4)_2HPO_4$ (Fig. 7) and $(NH_4)_2SO_4$ (Fig. 8), are presented. The mass peaks at *m*/*z* 96, 68, 110 are attributed to the furan derivatives (cellulose origin). In the presence of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ an increase of intensity at *m*/*z* 94 is observed, which is attributed to the phenol derivatives.

CO_2 and H_2O were quantified based on the peak areas of the MS signals of mass peaks at *m*/*z* 44 and 18 respectively. Calibration curves for CO_2 and H_2O were produced based upon the thermal treatment of various quantities of $KHCO_3$ [18]. The

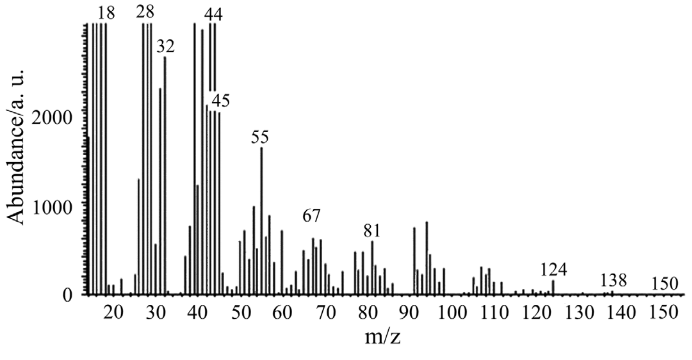

Fig. 6 Average mass spectrum of TG-MS analysis of untreated pine needles

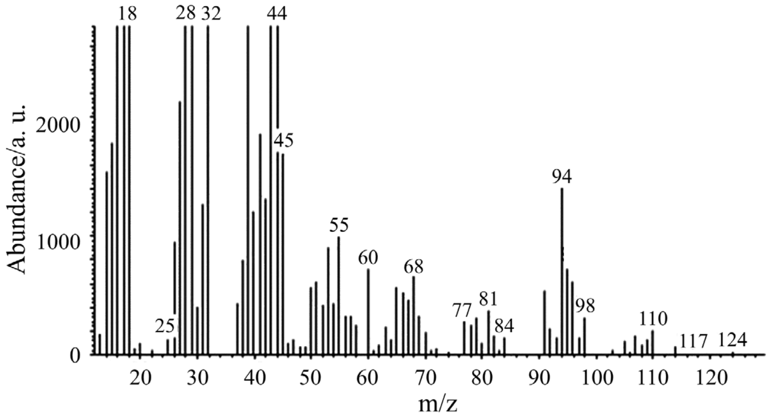

Fig. 7 Average mass spectrum of TG-MS analysis of pine needles+10%*w*/*w* $(NH_4)_2HPO_4$

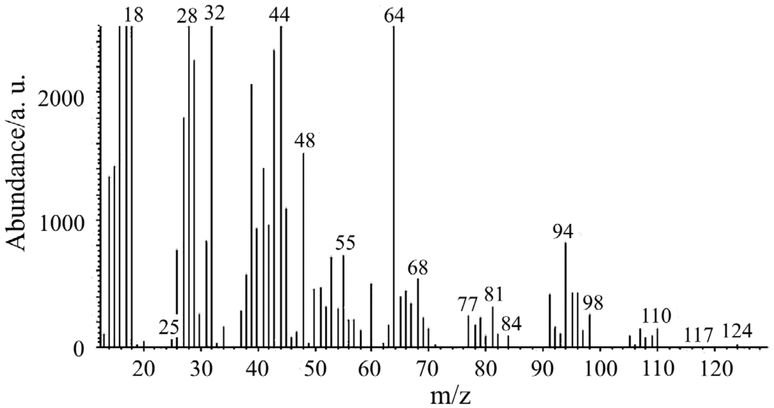

Fig. 8 Average mass spectrum of TG-MS analysis of pine needles+10%*w*/*w* $(NH_4)_2SO_4$

w/*w* percentage of H_2O, CO_2, char residue and combustible volatiles at 580°C from the pyrolysis of pine-needles in the presence and absence of chemical retardants is presented in Fig. 9. The percentage of the combustible volatiles was calculated after the subtraction of water and carbon dioxide percentage from the total mass loss recorded in the TG% mass loss curve. It appears that the presence of chemical retardants does not significantly decrease the evolution of H_2O and CO_2. However, the char residue is increased significantly in the presence of $(NH_4)_2HPO_4$, whereas, the evolution of combustible volatiles is decreased, when the pyrolysis is over (580°C). It seems that $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ do not favor the dehydration pathway of needles degradation, but they affect the pyrolysis mechanism after the depolymerisation process has been started [12].

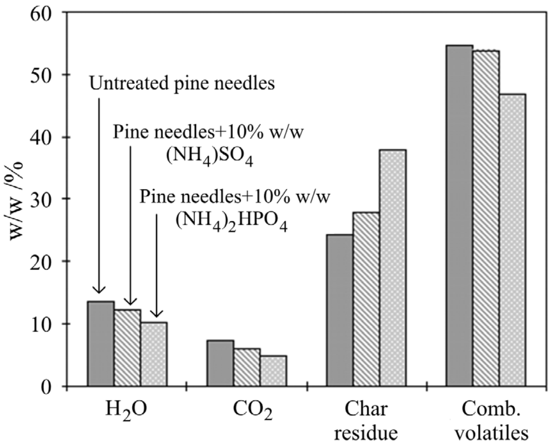

Fig. 9 Composition of pyrolysis products originated from treated and untreated pine needles pyrolysis, measured by quantitative TG-MS analysis

Conclusions

The hyphenated technique of TG-MS appears to significantly contribute to a deeper insight of thermal degradation retaining its basic characteristic; a quantitative analysis of evolved gases. Application of TG-MS analysis for studying the effect of fire retardants on the pyrolysis of pine needles indicated the effectiveness of $(NH_4)_2HPO_4$ as it increases the char residue and decrease the evolution of combustible volatiles. However it is still under investigation the complex way in which the fire retardants affect the pyrolysis mechanism.

Improvements in design and development of the TG-MS interface are carried out for improving sensitivity, selectivity and increased range of molecular masses that the technique can monitor. To improve the identification of pyrolysis products various types of transfer line will be tested to enhance the separation of the evolved gases when the system works as a TG-GC-MS one. In addition software with chemometric methods will be used to help in resolving overlapping peaks.

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