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A study of thermal decomposition and combustion products of disposable polyethylene terephthalate (PET) plastic using the High Resolution Fourier Transform Infrared Spectroscopy, Selected Ion flow Tube Mass Spectrometry and Gas Chromatography Mass Spectrometry

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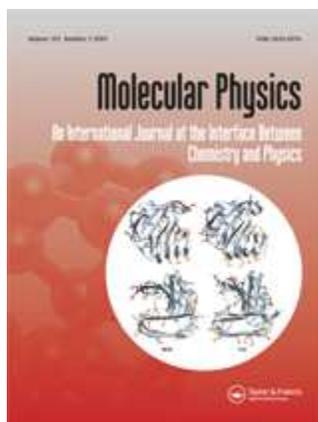
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A study of thermal decomposition and combustion products of disposable polyethylene terephthalate (PET) plastic using the High Resolution Fourier Transform Infrared Spectroscopy, Selected Ion flow Tube Mass Spectrometry and Gas Chromatography Mass Spectrometry

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3 **A study of thermal decomposition and combustion products of disposable**
4 **polyethylene terephthalate (PET) plastic using the High Resolution Fourier**
5 **Transform Infrared Spectroscopy, Selected Ion flow Tube Mass**
6 **Spectrometry and Gas Chromatography Mass Spectrometry**
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A study of thermal decomposition and combustion products of disposable polyethylene terephthalate (PET) plastic using the High Resolution Fourier Transform Infrared Spectroscopy, Selected Ion flow Tube Mass Spectrometry and Gas Chromatography Mass Spectrometry

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Abstract

The industrial production of poly (ethylene terephthalate), PET, continues to increase and thus it is important to understand the composition of fumes resulting from its disposal as a part of incinerated waste. In this study samples of PET material were combusted in a furnace corresponding to the German standard DIN 53 436 at the temperatures of 500 °C, 800 °C (in an air flow) and also uncontrolled burning in air. The gaseous products were then analysed using three different analytical methods: high resolution Fourier transform infrared spectroscopy (FTIR), selected ion flow tube mass spectrometry (SIFT-MS) and gas chromatography mass spectrometry (GC-MS). Carbon dioxide, methane, ethylene, acetylene, formaldehyde (methanal) and acetaldehyde (ethanal) were detected by FTIR. Water, methane, acetaldehyde, ethylene, formaldehyde, methanol, acetone, benzene, terephthalic acid, styrene (ethenylbenzene), ethanol, toluene (methylbenzene), xylene (dimethylbenzene), ethylbenzene, naphthalene, biphenyl and phenol concentrations were all quantified by both SIFT-MS and GC-MS. Additionally, the fumes resulting from uncontrolled combustion in air were analysed by FTIR which resolves the rotation-vibration structure of the absorption bands of formaldehyde (2779.90 and 2778.48 cm⁻¹) and propane, which was identified from characteristic vibrations of CH₃ groups at 2977.00 and 2962.00 cm⁻¹. The spectra were compared to the reference standards.

Keywords: Polyethylene terephthalate, PET, Combustion, High Resolution FTIR Spectroscopy, GC-MS, SIFT MS

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1. Introduction

The waste production is a fundamental problem from the environmental as well as the economic point of view. Approximately 15 million tonnes of the used plastic waste are generated every year across Europe. Of this volume, a mere 7% [1-3] is recycled and the remainder is deposited or incinerated [4]. Polyethylene terephthalate (PET, systematic name poly(oxy-1,2-ethanediyloxycarbonyl-1,4-phenylenecarbonyl)) is a highly thermally stable polymer with many uses, most frequently as packaging material for beverages [5] in the form of the well known PET bottles. The ideal way of dealing with PET waste is recycling. One of the possible recycling methods for PET is a controlled thermal degradation of PET into oligomers with olefin and carboxylic end-groups [6] including terephthalic acid whilst yielding minimal amounts of carbonaceous residue [3,7]. The terephthalic acid thus obtained together with other oligomers can subsequently be used in polymerisation for the production of recycled materials. Alternatively, there are two commercially available depolymerisation methods (methanolysis and glycolysis) available for PET recycling. Both of these methods reduce PET to either a monomer or the original raw materials which can be purified and subsequently re-reacted into “new” PET for use in a food-contact application, packing for detergents, cosmetics, high-quality carpets, foils, car spare parts or pillow filling for allergic persons [8].

It is worth noting that some polymers are not suitable for recycling, one example being polyethylene, PE, and sometimes for logistic and other reasons PET is not separated from the mixed communal waste. Thus the incineration of carbon-rich wastes is becoming an increasingly attractive alternative to the deposition in landfills, because as much as 90% reduction in volume [3,9] is achieved. There is a German standard DIN 53 436 [10] in place concerning the combustion of PET and any other plastic materials, which sets the maximum permitted amounts of the waste products in the fumes and also gives methods for the testing

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3 of their toxicity.

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6 Thermal stability and possible further applications of the degradation products of PET
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8 material have been widely-studied. Kinetic studies of PET combustion in the presence of
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10 various amounts of oxygen and with the temperatures ranging between 25 and 800 °C using
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12 TGA have recently been conducted [4,11,12]. Other studies have been carried out to identify
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14 the products of the thermal decomposition in the temperature range of 270-370 °C in a N₂
15
16 inert atmosphere using the MALDI, ¹H and ¹³C NMR methods [13]. Infrared spectroscopy
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18 has previously been used to study the products of PET thermal degradation [14] and also to
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20 study the hydro-thermal degradation under higher pressure [7,15]. Recently, PET degradation
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22 by the laser ablation was studied using AAS spectrometry, infrared spectroscopy, Gel
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24 Permeation Chromatography (GPC) and electron microscopy methods [16]. In one interesting
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26 experiment, PET material was also irradiated with Ar⁺ ions and studied using the Rutherford
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28 Backscattering (RBS) and Elastic Recoil Detection (ERD) techniques [17].

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34 High-resolution Fourier Transform Infrared (FTIR) spectroscopy has not so far been
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36 exploited to study the products of PET thermal decomposition and combustion. Therefore,
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38 this paper presents the results of high-resolution FTIR characterisation of these products,
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40 paving the way for wider research into the degradation of other polymers. The same samples
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42 were also studied using selected ion flow tube mass spectrometry, SIFT-MS. This mass
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44 spectrometry method is based on the chemical ionisation in a flow tube and is chiefly suitable
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46 for absolute quantifications of trace amounts of volatile organic compounds in air in the
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48 presence of water vapour. SIFT-MS has been used in various fields of research [18] but this is
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50 the first time it has been utilised to study products of polymer combustion. The main objective
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52 of this study was to compare the products of thermal decomposition of PET at 500 °C,
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54 controlled combustion at 800 °C and fumes from uncontrolled flame in air as a simulation of a
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56 imperfect PET incineration.
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2. Experimental

2.1 The thermally uncontrolled combustion of PET

The material from a transparent PET bottle with a volume of 1.5 L was used for a combustion experiment mimicking burning of PET in stoves or home central heating boilers. The exact temperature of the combustion cannot be defined in this situation but it is worthy noting that the inflammation point of PET is 600 °C. A PET bottle was cut into strips of 1 x 2 cm in size and the weight of about 2 g. The gaseous products generated were pumped directly into a vacuum line and trapped in a liquid nitrogen trap and later released into the FTIR absorption cell.

2.2 The thermally controlled thermal decomposition and combustion

For the controlled thermal decomposition and combustion experiments a sample of a polyethylene terephthalate film (“TENOLAN”), from which PET bottles are made, was used. This time, the material was thermally decomposed and combusted at two temperature (500 °C and 800 °C) in the presence of air in an apparatus corresponding to the German standard DIN 53 436. The testing apparatus was set up according to DIN 53 436 (see diagram shown in Figure 1) and consisted of a quartz-glass combustion tube of 1 m length and 40 mm diameter, terminated with ball-and-socket ground joints, a quartz-glass boat of 400 mm length (15 + 1) mm diameter wall thickness 1.7 mm holding the sample and a circular furnace of 100 mm width encircling the tube. A motor with a helix gear moved the furnace along the tube at the speed of 1 cm/min. The temperature of the furnace was maintained by a regulation module which also controls the furnace motor. The glazed front wall enabled the direct observation of the flow of the fumes during the process. The compressed air from the laboratory mains passed through a pre-drying cartridge with crystalline CaCl₂ and a general-purpose flow meter, calibrated in the desired range of flows. The air flow was regulated using a needle

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3 valve to a flow of 150 L/hr. Note that this flow entered the tube in the opposite direction to
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5 the furnace movement and thus the sample was always exposed to a supply of clean air. The
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7 PET samples were supported inside the quartz glass combustion tube by a quartz glass boat,
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9 and heated to the preset temperatures 500 °C and 800 °C. Resulting fumes containing the
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11 thermal decomposition and combustion products were introduced via a connecting adapter
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13 into a 5 L mixing vessel (placed inside a box thermostat with forced circulation) in which they
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15 were kept at 130 °C.
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21 Two samples of PET foil of 0.15 mm thickness were cut into 400 x 20 mm strips and
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23 placed inside the combustion furnace boat always in five layers. The first sample of mass
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25 6.41 g was subjected to the flameless thermal decomposition at the temperature of 500 °C and
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27 the second sample of mass 6.28 g was combusted in flame at the temperature of 800 °C. As a
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29 part of the routine protocol elementary composition of the samples was determined as:
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31 C 62.86 % w/w; H 4.36 % w/w; N 0.12 % w/w and the stoichiometric ratio of weight of
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33 combusted oxygen to the weight of fuel calculated accordingly to ISO TR 9122 was $\Psi =$
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35 2.0928. Samples of fumes containing combustion products were taken directly from the
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37 mixing vessel into glass volumes with PTF stoppers. These glass volumes were transported
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39 and their content was analysed using FTIR, GC-MS and SIFT-MS.
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45 46 **2.3 FTIR spectroscopy**

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49 The gaseous products of the uncontrolled and controlled combustion of PET samples
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51 (at 500 °C, 800 °C) were released into a vacuum line and trapped in a liquid nitrogen trap. An
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53 absorption cell was filled to the pressure of 5.5 Torr by slow re-heating of this trap. The
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55 length of the absorption cell was 36.5 cm and the diameter was 5 cm. The spectra were
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57 obtained at an ambient temperature using the Bruker IFS 120 HR spectrometer in the spectral
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59 range of 500-7000 cm^{-1} . In order to cover the near-infrared (NIR) range a halogen lamp, a
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3 CaF₂ beam splitter and InSb detector were used and to cover the middle-IR (MIR) spectral
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5 region a glow bar source, KBr beam splitter and HgCdTe detector were applied. Fifty scans of
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7 the spectra were acquired at the resolution of 0.02 cm⁻¹ and 0.014 cm⁻¹ using the Blackmann-
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9 Harris apodisation function.
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12 13 14 **2.4 GC-MS**

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17 The gas chromatograph with a mass spectrometer detector, GC-MS, an instrument
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19 used for this study was “Trace GC Ultra-DSQ II” (Thermo Electron Corporation). The
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21 parameters of the Rxi™ 5 ms (manufactured by Restek) chromatographic column were: 30 m
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23 x 0.25 mm x 0.25 μm. The temperature of the SL/S injector was 235 °C, the liner diameter
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25 was 5 mm and the achieved temperature range was 37-300 °C.
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29 Samples of gases originating from the controlled thermal decomposition and
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31 combustion in the quartz combustion furnace were taken directly from its exhaust at the end
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33 of the combustion tube. The sampling method used a 500 μL gas-tight syringe preheated to
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35 60 °C. The standard method of the direct Head Space analysis was applied. The samples were
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37 dosed at 60 °C. The volume of the sample dose was always 500 μL for both temperatures
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39 (500 °C and 800 °C). The individual peak assignments seen in the chromatographs were
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41 based on the measurements of standards and their comparison with NIST '05 Mass Spectral
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43 Libraries for Xcalibur [18].
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49 50 **2.5 SIFT-MS**

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52 Selected ion flow tube mass spectrometry, (SIFT-MS), is a technique for a
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54 simultaneous real-time quantification of several trace gases in air and exhaled breath. It relies
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56 on the chemical ionization of the trace gas molecules in air/breath samples introduced into
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58 helium carrier gas, using H₃O⁺, NO⁺ and O₂⁺ reagent (precursor). Reactions between the
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60 precursor ions and the trace gas molecules proceed for an accurately defined time, the

precursor and product ions being detected and counted by a downstream mass spectrometer. The absolute concentrations of trace gases in single breath exhalation can be determined by SIFT-MS down to parts-per-billion (ppb) levels, obviating sample collection into bags or onto traps [19]. The calibration using chemical standards is not routinely required, as the concentrations are calculated using the known reaction rate constants and the measured flow rates and pressures [20]. For this study samples of the gaseous products of controlled decomposition and combustion were collected in 6 L glass vessels at the atmospheric pressure, kept at an ambient temperature of 20 °C and introduced into the Profile 3 SIFT-MS instrument (manufactured by Instrument Science Limited, Crewe, UK) via a heated calibrated capillary and full scan mass spectra were obtained by repeated full scans for all three precursor ions. The concentrations of main compounds identified on the mass spectra were calculated from the precursor and product ion count rates, the known carrier gas and sample flow rates and flow tube pressure, according to the general method for the calculation of absolute trace gas concentrations in air from selected ion flow tube mass spectrometry data [20]. The rate coefficients were taken from the kinetic library supplied with the SIFT-MS instrument where available or estimated theoretically [19]. The accuracy of quantification in this complex mixture is estimated to be a factor of about two, +100% -50% of estimated absolute error. The relative precision of the measurement, however, is better estimated at about +/- 30%. Thus the results provide an order of magnitude of information about the concentrations of the main components of the thermal decomposition and combustion products in the sampled fumes.

3. Results and Discussion

3.1 FTIR spectroscopy

In the NIR and MIR spectra of fumes from the uncontrolled combustion (Figure 2), we

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3 successfully identified a homologous series of saturated hydrocarbons, which were assigned
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5 on the basis of stretching vibrational and rotational modes of C-H groups of methane
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7 (3019 cm^{-1}), ethane (2985, 2969 and 2954 cm^{-1}) and propane (2977 and 2962 cm^{-1}); the
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9 unsaturated hydrocarbon ethene, which was verified by the existence of vibrational and
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11 rotational bands of the rocking modes of the C-H group at 949 cm^{-1} , and acetylene, whose
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13 stretching vibrational and rotational modes of the C-H group were observed at 3374 and
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15 3289 cm^{-1} and deformation vibrational and rotational bands of the same group at 730 cm^{-1} .
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17 The group of aldehydes was represented by acetaldehyde and formaldehyde, whose stretching
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19 vibrational and rotational modes of C-H groups lay in the FTIR spectrum at 2715 cm^{-1}
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21 (acetaldehyde) and 2780 and 2778 cm^{-1} (formaldehyde). The above-listed analysis of the IR
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23 spectra was performed using the individual vibrational and rotational lines listed in the
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25 HITRAN database [21] and using our database in a Bruker OPUS computer program.
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32 Spectra and the analyses of the products of thermal decomposition of PET in a quartz
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34 furnace corresponding to the DIN standard, at the temperature of 500 °C (see Figure 3a) were
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36 similar to uncontrolled combustion. Thus in the FTIR spectra of products of PET decomposed
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38 at 500 °C, we have identified methane, ethane, ethyne, formaldehyde, carbon dioxide, carbon
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40 monoxide and water. Figure 3b shows that the PET combustion at 800 °C (i.e. above the
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42 inflammation point) is a process of more efficient burning and the main combustion products
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44 are carbon oxides and water. Carbohydrates and aldehydes appear only in concentrations that
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46 are lower than the detection limit of our FTIR method.
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51 The main advantage of using the high-resolution FTIR method in comparison to the
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53 more commonly used low resolution FTIR spectroscopy (resolution 1-5 cm^{-1}) is that it allows
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55 resolving the detailed structure of the vibrational bands, which often overlap in the spectra of
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57 complicated gaseous mixtures. With our high-resolution method, we can for example
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59 differentiate the stretching rotation-vibration lines of C-H bonds in propane from the
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3 stretching rotation-vibration lines of C-H in methane (see Figure 4).
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6 7 **3.2 GC-MS**

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9 Table 1 contains the analytic comparison of gaseous components obtained from the
10 thermal decomposition at a temperature of 500 °C with the combustion products obtained at
11 800 °C. Twenty three organic molecules were identified at 500 °C, and at 800 °C, there were
12 twenty one different compounds. The characteristic groups of GC-MS analysis were aromatic
13 compounds, derivates of benzoic acid, group of phthalates, biphenyles and others. Common
14 products such as styrene, toluene and naphthalene were found in both samples. From the
15 relative abundance of each identified compound in the chromatograms (see Figure 5 and 6) it
16 is evident that their abundance at the temperature of 800 °C is lower than in the case of
17 500 °C. This trend was confirmed also by SIFT-MS analysis (see the next section and Table 2
18 there). Exceptions were biphenyle (peak number 17) and naphthalene (peak number 13), their
19 relative abundance was higher in the 800 °C sample.
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36 37 **3.3 SIFT-MS**

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39 An analysis of the gaseous products originating from the controlled decomposition and
40 combustion at 500 °C and 800 °C was carried out using three precursor reagent ions H_3O^+ ,
41 NO^+ and O_2^+ . Several compounds were identified from the characteristic ions present in the
42 H_3O^+ spectra (see Figure 7). Additionally, the spectra obtained with NO^+ and O_2^+ precursors
43 were used to quantify those compounds which do not react with the H_3O^+ precursors. The O_2^+
44 spectra were only of a limited value because of the complexity of the mixture and overlap of
45 multiple fragmentation patterns. This has prevented unambiguous identification of more
46 complex organic compounds, however quantification of several hydrocarbons was possible.
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The compounds identified on the SIFT-MS spectra are listed in Table 2 together with the
characteristic product ions and their concentrations calculated for the two temperatures. SIFT-

MS can be also used to quantify the concentration of water vapour in the fumes [22] and the results are given in Table 2.

To illustrate how the ions observed on the spectra are related to the compounds present in the analysed gaseous mixture, we will outline the main features of ion chemistry which are involved. The H_3O^+ precursor ions are known to react with unsaturated hydrocarbon alkenes (C_nH_{2n}) and alkynes (C_nH_{2n-2}) [22] and with aromatic hydrocarbons by proton transfer leading to the formation of the MH^+ product ions.



Such proton transfer also occurs with aldehydes, ketones, small alcohols and many other compounds, as is known from many previous studies [22]. However for styrene and biphenyl, (identified by GC-MS, see Section 3.2) there was so far no knowledge of the SIFT-MS product ions. Thus, we have carried out a quick study of the ion chemistry of these two compounds and found that proton transfer is indeed the only process occurring for both styrene and biphenyl and no fragmentation occurs. In fact all products of H_3O^+ reactions identified in table 2 are protonated molecules MH^+ . The aromatic hydrocarbons were responsible for the following ions in the H_3O^+ mass spectra: m/z 79 (benzene), 93 (toluene) and 107 (xylene, ethylbenzene) and for the ions at m/z 78, 92 and 106 in the NO^+ spectra. The ions in the H_3O^+ mass spectra at m/z 31 and 49 ($MH^+ \cdot H_2O$) are due to the presence of formaldehyde and the ions at m/z 45 and 89 are characteristic of acetaldehyde. The ions at m/z 89 are proton bound acetaldehyde dimers ($MH^+ \cdot M$). The ions at m/z 33 and 47 are protonated methanol and ethanol, the ions at m/z 59 and 77 correspond to acetone as is confirmed by the presence of ions at m/z 88 ($NO^+ \cdot M$) in the NO^+ spectrum.

However, it must be noted that H_3O^+ ions do not transfer protons to saturated alkanes and O_2^+ precursors may be used for their identification. This is exemplified in the case of methane:



This reaction is unusually slow, the rate coefficient being only $5.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ [23]. Thus the product ions of the reaction (2) are seen in O_2^+ spectra at m/z 47 as characteristic product ions of methane. Ethylene reacts with O_2^+ by the charge transfer, thus forming product ion at m/z 28.

Aromatic hydrocarbons undergo charge transfer with both NO^+ and O_2^+ precursors, thus forming molecular ions M^+ . Using a combination of H_3O^+ and NO^+ ions was thus appropriate for the reliable quantification of aromatic hydrocarbons in the fume gas samples.

The inspection of Table 2 reveals that in general concentrations of organic products are lower at the higher combustion temperature of $800 \text{ }^\circ\text{C}$ than at decomposition temperature of $500 \text{ }^\circ\text{C}$. This conforms to the results of previous studies [4,9]. The exception to this trend is the behaviour of naphthalene and biphenyl, which are seen to be more concentrated in the products of higher temperature combustion. Also there is significantly more water vapour present in the mixture obtained at $800 \text{ }^\circ\text{C}$. In the present study it was not possible to quantify CO_2 using SIFT-MS because the characteristic ion $\text{CO}_2 \cdot \text{H}_3\text{O}^+$ overlaps hydrated protonated acetaldehyde at m/z 63, thus exclusion of CO_2 from table 2 does not imply its absence.

4. Conclusions

In this study, high resolution FTIR spectroscopy was used for the first time to analyse products of PET thermal decomposition and combustion. The spectra of a series of these obtained products were measured even under the conditions where their spectral rotation-vibration bands overlap. The results show that high resolution FTIR spectroscopy can hardly compete with methods based on mass detection in cases where trace amounts of heavier organic molecules are to be identified. This is because the rotation-vibration spectra of heavy molecules in their gas phase at room temperature are unresolved and their measuring requires the use of sub-Doppler techniques. On the other hand, the advantage of the FTIR

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3 spectroscopy is that it allows observation of a very broad spectral range and that the
4
5 intensities of the vibrational bands, mainly of the light molecules (water, carbon monoxide,
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7 carbon dioxide, methane, formaldehyde etc.), provide a broad view of the thermal
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9 decomposition and combustion of PET and its degree of conversion into the final combustion
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11 products (CO₂ and H₂O). Although only a single-pass absorption arrangement (36.5 cm) was
12
13 used, we were able to detect small concentrations of some organic substances, such as
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15 formaldehyde and propane, in the fumes.
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20 The main aim of this work was to compare the products resulting from uncontrolled
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22 combustion of PET (burning in stoves and home boilers) to the processes in which the
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24 physical conditions of the thermal decomposition (500 °C) or combustion (800 °C) are
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26 exactly defined and controlled. The results of this study show that uncontrolled burning in air
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28 leads to products which are similar to those from thermal decomposition in a quartz furnace at
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30 the temperature of 500 °C, i.e. below the PET inflammation point of 600 °C. In comparison,
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32 the products of PET combustion at 800 °C contain mainly carbon oxides, water and the
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34 heavier hydrocarbons in significantly lower concentrations. The only two cases where
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36 concentration increased at the higher temperature were biphenyle and naphthalene. This was
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38 independently indicated by both GC-MS and SIFT-MS results.
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43 From the point of view of the analysis of volatile substances, the gas chromatography
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45 method remains the best. The combination of gas chromatography with the mass detection
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47 represents a very effective combination of separation and a highly sensitive detection
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49 technique. A wide range of aromatic and polyaromatic substances such as the group of
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51 phthalates [23] was identified using gas chromatography. Concentrations of these compounds
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53 were quantified also using SIFT-MS and the precision of this technique was sufficiently high
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55 to observe significant differences in the composition of the fumes originating from different
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57 temperatures of decomposition and combustion.
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3 Finally it is worth to mention that FTIR was found to complement mass spectrometry
4 based techniques in identification of methane and C₂ hydrocarbons which were not accessible
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6 to the GC-MS and SIFT-MS methods used in this study.
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10 This study confirms the utility of the above mentioned combined analysis in providing
11 important information both for an incineration purpose as for certain assessment of fire
12 effluents danger effects on persons a and the environment.
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15 16 17 18 19 20 **Acknowledgement**

21
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Figure captions

Figure 1: Tube furnace decomposition and sampling apparatus according to DIN 53 436 [10,25]: 1-furnace tube; 2-connecting adapter; 3-heating thermostat; 4-fume outlet; 5-mixing and measurement vessel; 6-diluent secondary air inlet (not used in the present study); 7-sampling line; 8-particle filters; 9-metering gas pump; 10-refrigerator; 11-CO, CO₂ and O₂ analyzers; 12-NO₂/NO converter; 13-SO₂, NO_x and moisture analyzer; 14-exhaust outlet.

Figure 2: MIR and NIR spectra of the fumes from uncontrolled combustion of PET.

Figure 3: Comparison of the MIR and NIR spectra of fumes from controlled decomposition and combustion of PET at 500 °C and 800 °C

Figure 4: Rotational-vibrational structure in methane and propane (stretching bands of C-H bonds)

Figure 5: The chromatogram of fumes from controlled decomposition of PET at 500 °C

Figure 6: The chromatogram of fumes from controlled combustion of PET at 800 °C

Figure 7: SIFT-MS spectrum obtained for fumes from controlled decomposition of PET at 500 °C using the H₃O⁺ reagent ion. The ion signal intensities are shown on a logarithmic scale in counts per second (c/s) as a function of the mass-to-charge ratios (m/z) of the ions.

Table 1: The assignment of peaks from the gas chromatography

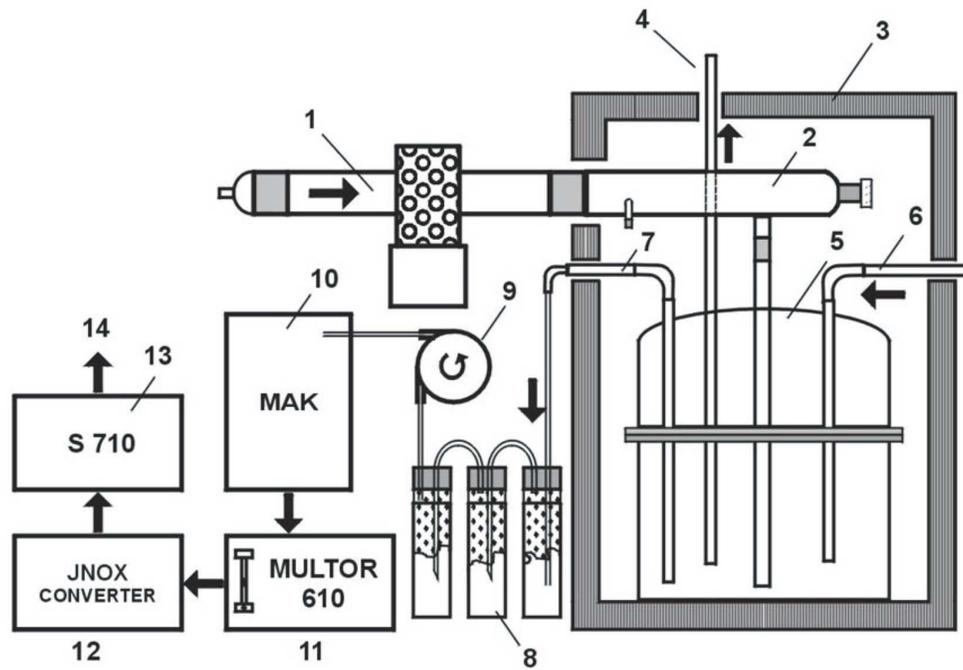
PET film – composition of fumes:		500 °C		800 °C	
Assig n.	Name	Area	Ratio	Area	Ratio
1	Phenyl ethyne			32.9	2.59
2	Xylene	76.5	0.50		
3	Styrene	157	1.03	21.6	1.70
4	Benzaldehyde	103	0.67	18.2	1.43
5	Phenol	44	0.29	19	1.50
6	Indene			22	1.73
7	Indane	16	0.10		
8	Phenylacetaldehyde	20.3	0.13		
9	Acetophenone	44	0.29	29.8	2.35
10	Methylbenzoate	24	0.16	6.5	0.51
11	Vinylbenzoate	962	6.29	169	13.32
12	Benzoic acid	4789	31.30	192	15.14
13	Naphthalene	12,4	0.08	63.8	5.03
14	4-methyl-benzoic acid	343	2.24		
15	4-ethyl-benzoic acid, phenyl ester	53.2	0.35		
16	4-ethyl-benzoic acid	323	2.11		
17	Biphenyl	334	2.18	268	21.13
18	3,4-dimethyl acetophenone	350	2.29		
19	Diphenylmethane			14.9	1.17
20	Biphenylene			23	1.81
21	Dibenzofurane			7.1	0.56
22	6-methoxyquinoline-N-oxide	553	3.61	18.4	1.45
23	Phthalates (group of esters of phthalic and terephthalic acids)	5864	38.33	259	20.42
24	Terephthalic acids	353	2.31		
25	9-fluorenone	83	0.54		
26	Anthracene			40.2	3.17
27	4-biphenyl carboxylic acid	540	3.53	42.1	3.32
28	Pyrene			3.8	0.30
29	Ethylene dibenzoate	199	1.30	13.2	1.04
30	1,4-triphenyl	55	0.36	4	0.32
	Footing:	15298.4	100.00	1268.5	100.00

Table 2. Main compounds identified in the SIFT-MS spectra of fumes of PET thermal decomposition and combustion at 500 °C and 800 °C. For each compound, the stoichiometric formula is given together with its approximate molecular weight in g/mol, the precursor ions used for chemical ionization, the corresponding mass to charge ratio of the characteristic product ions and their concentrations in fumes analysed at atmospheric pressure in units of parts per million ppm.

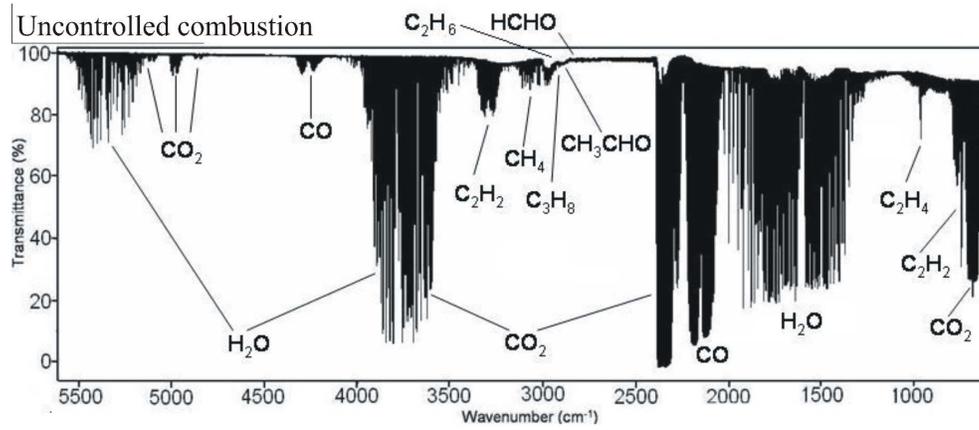
Name	Formula	Molecular weight g/mol	Precursor Ions	m/z of product ions	ppm 500 °C	ppm 800 °C
Water	H ₂ O	18	H ₃ O ⁺	19-37-55	700	9000
Methane	CH ₄	16	O ₂ ⁺	47	600	15
Acetaldehyde	C ₂ H ₄ O	44	H ₃ O ⁺	45	90	8
Ethylene	C ₂ H ₄	28	O ₂ ⁺	28	11	3
Formaldehyde	CH ₂ O	30	H ₃ O ⁺	31	7	4
Methanol	CH ₄ O	32	H ₃ O ⁺	33-51	4	0.3
Acetone	C ₃ H ₆ O	58	H ₃ O ⁺ NO ⁺ O ₂ ⁺	59-77 88 43-58	5	0.03
Benzene	C ₆ H ₆	78	H ₃ O ⁺ NO ⁺ O ₂ ⁺	79 78 78	4	2
Phthalates and terephthalic acid	C ₈ H ₆ O ₄	166	H ₃ O ⁺ NO ⁺ O ₂ ⁺	149 149 149	1.4	0.7
Styrene	C ₈ H ₈	104	H ₃ O ⁺ NO ⁺ O ₂ ⁺	105 104 104	0.8	0.5
Ethanol	C ₂ H ₆ O	46	H ₃ O ⁺	47	0.6	0.3
Toluene	C ₇ H ₈	92	H ₃ O ⁺ NO ⁺ O ₂ ⁺	93 92 92	0.5	0.1
Xylene, ethylbenzene	C ₈ H ₁₀	106	H ₃ O ⁺ NO ⁺ O ₂ ⁺	107 106 106	0.5	0.2
Naphthalene	C ₁₀ H ₈	128	H ₃ O ⁺ NO ⁺ O ₂ ⁺	129 128 128	0.2	0.4
Biphenyl	C ₁₂ H ₁₀	154	H ₃ O ⁺ NO ⁺ O ₂ ⁺	155 154 154	0.05	0.08
Phenol	C ₆ H ₆ O	94	H ₃ O ⁺	95	0	0.7

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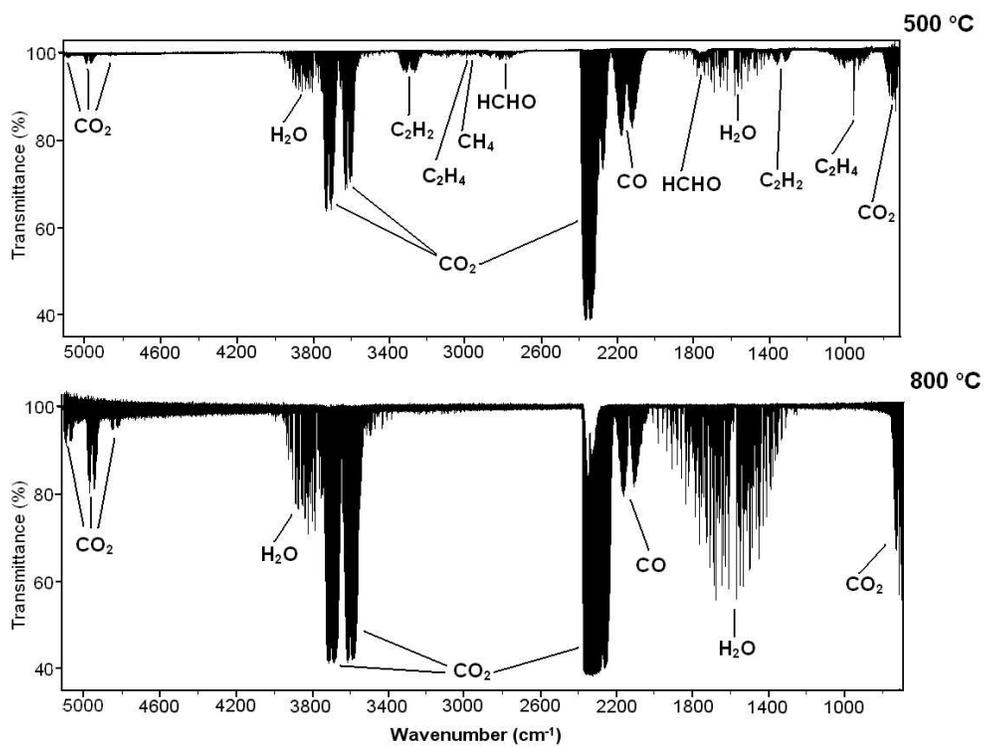
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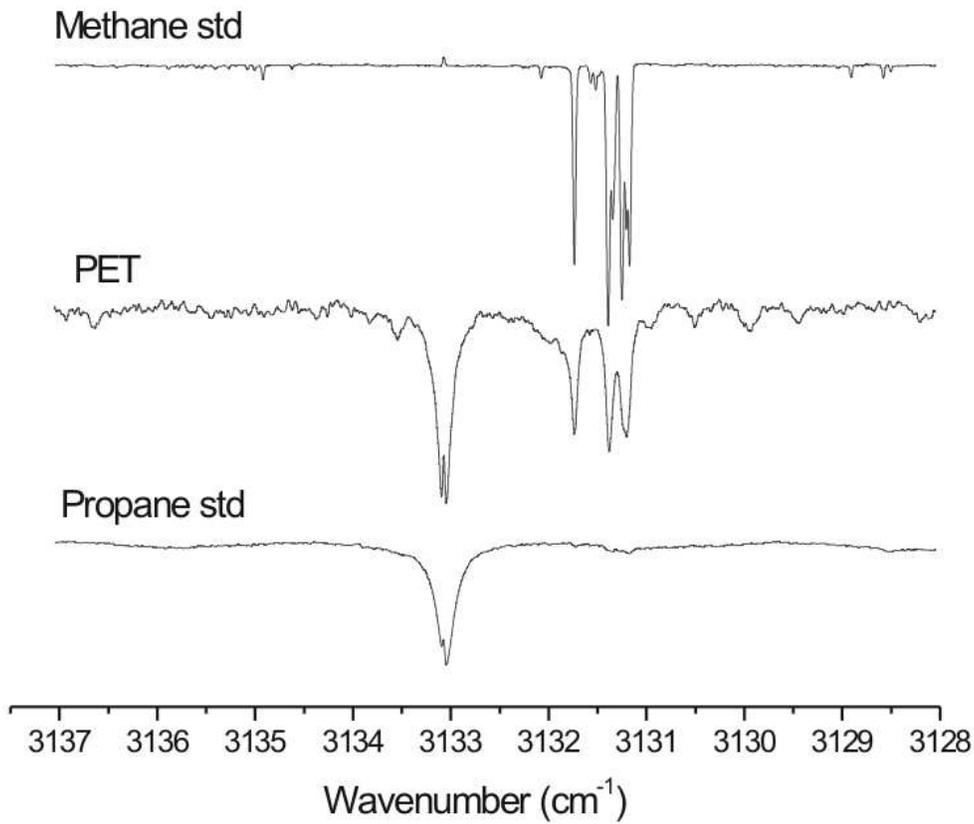
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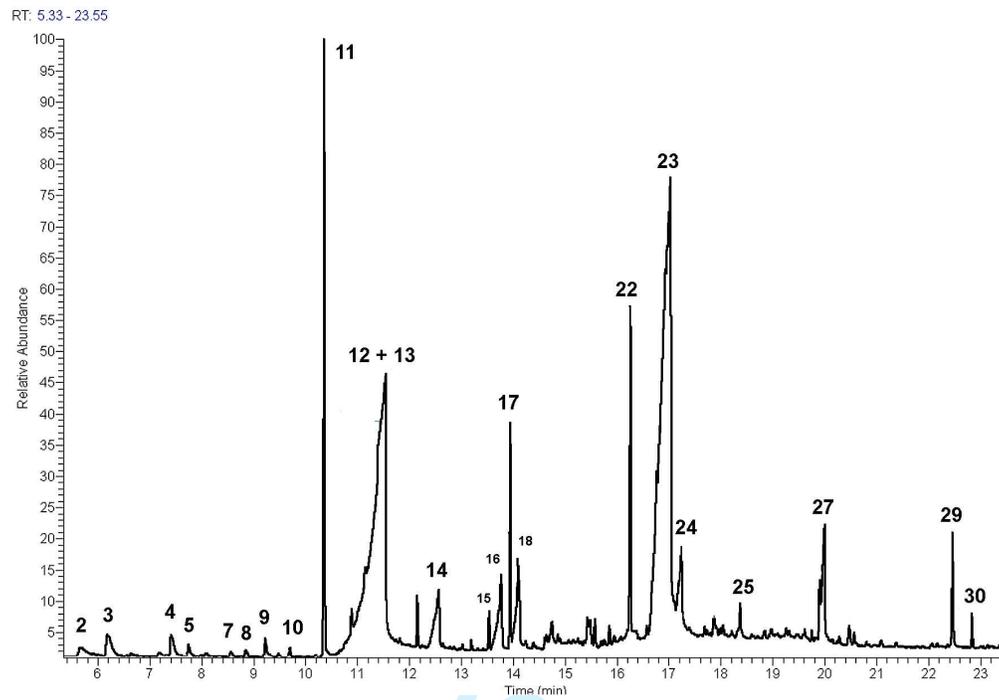


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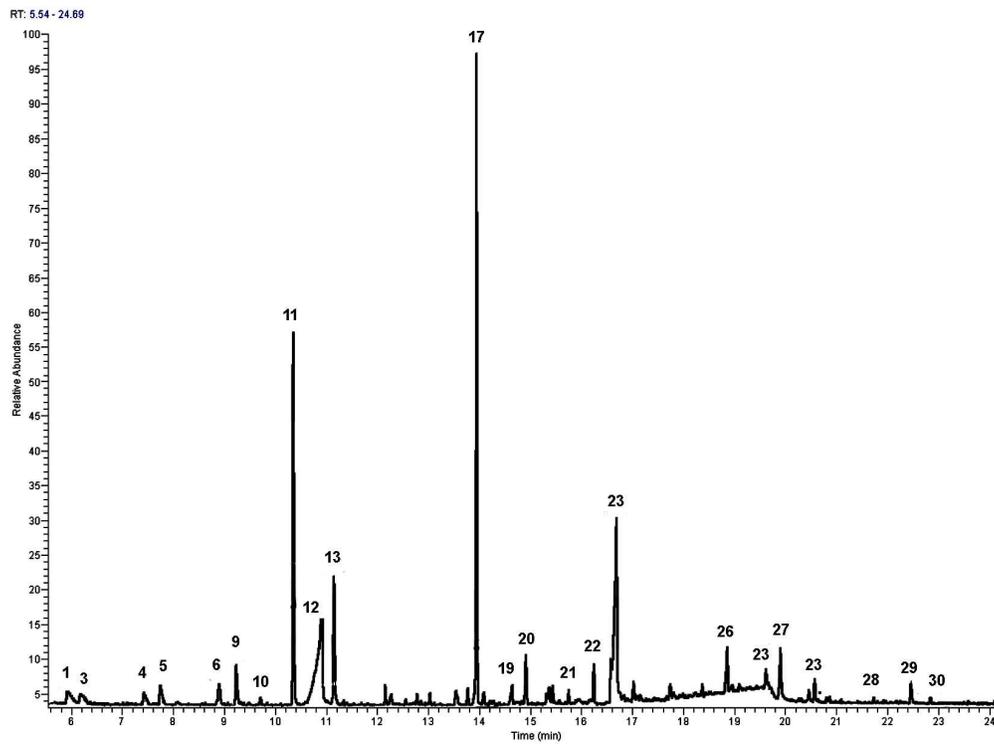


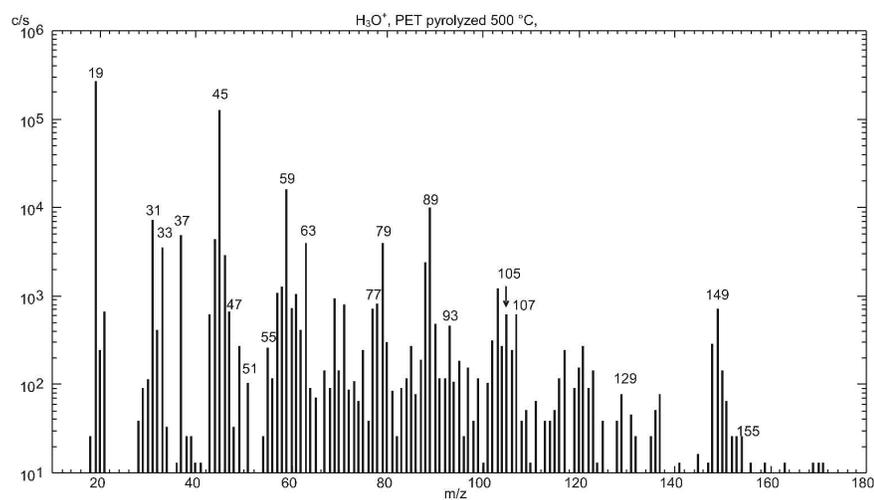
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