



Evaluation of thermoanalytical methods equipped with evolved gas analysis for the detection of microplastic in environmental samples

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ABSTRACT

Microplastic particles are currently detected in almost all environmental compartments. The results of detection vary widely, as a multitude of very different methods are used with very different requirements for analytical validity.

In this work four thermoanalytical methods are compared and their advantages and limitations are discussed. One of them is thermal extraction-desorption gas chromatography mass spectrometry (TED-GC/MS), an analysis method for microplastic detection that has become established in recent years. In addition, thermogravimetric analysis coupled with Fourier-transform infrared spectroscopy (TGA-FTIR) and mass spectrometry (TGA-MS) were applied, two methods that are less common in this field but are still used in other research areas. Finally, microscale combustion calorimeter (MCC) was applied, a method not yet used for microplastic detection.

The presented results are taken from a recently published interlaboratory comparison test by Becker et al. (2020). Here a reference material consisting of suspended matter and specified added polymer masses was examined, and only the results of the recoveries were presented. In the present paper, however, the results for the individual polymers are discussed in detail and individual perspectives for all instruments are shown.

It was found that TED-GC/MS is the most suitable method for samples with unknown matrix and unknown, variable kinds and contents of microplastic. TGA-FTIR is a robust method for samples with known matrix and with defined kinds of microplastic. TGA-MS may offer a solution for the detection of PVC particles in the future. MCC can be used as a very fast and simple screening method for the identification of a potential microplastic load of standard polymers in unknown samples.

1. Introduction

Since the introduction of thermoplastic as industrial products, their use in such sectors as packaging, the automotive industry, and construction has increased constantly, amounting to a value of 65 million tons in Europe in 2017 [2]. Although proper waste management is supposed to include correct disposal and recycling as well, plastic is often leaked to the environment unintentionally. When thermoplastic products or materials are exposed to complex conditions, such as UV radiation, oxidation, hydrolysis, microbial degradation, higher temperatures and mechanical stress, they can fragment into smaller particles. This process is due to the degradation or scission of polymeric chains and can be observed macroscopically as embrittlement of the material

[3]. Such small particles 1 – 1000 µm in size are called microplastic [4]. They are observed almost everywhere in the environment and the risks or effects these particles present are still unclear. It is for example estimated that amounts of 108.9 ± 40.1 tons of macroplastic and 14.7 ± 9.0 tons of microplastic are ending up in Swiss fresh waters each year [5]. The amount of plastic waste flowing from rivers into global oceans, which serve as a final sink, is estimated at 1.15–2.41 million tons per year [6]. There are only few data available on the fate of plastic in terrestrial ecosystems, which could be anywhere from 4 to 23 times higher than in aquatic ecosystems [7]. The contribution of air, or better transport through air, is obvious, but its effects are still not understood and have yet to be quantified [8,9].

Since there are no standardized or harmonized methods for the

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analysis of microplastic, a wide variety of different methods is applied. The application of different analytical tools with specific advantages and disadvantages is not only confusing for newcomers, but also for users from practical application (monitoring laboratories, regulatory authorities) and for stakeholders involved with this work (politicians, environmental organizations). When in peer reviewed articles analytical tools or results are presented often the scientific applicability of a single analytical tool is in the focus. Little attention is paid to the evaluation of the different methods in terms of their practical application, e.g. the time spent per measurement, possible complications through contamination, the need for user knowledge, as well as the complexity of the information obtained and the potential suitability of a given method for specific applications.

In most cases, spectroscopic methods are used for the analysis of microplastic particles, such as mid-infrared or Raman spectroscopy [10]. These methods allow the unambiguous identification of polymers in environmental samples by their specific absorption spectra. If the spectroscopic methods are linked with an imaging technique, additional information about the size, shape and number of particles is obtained. Automated data processing and correlation to reference spectra or classification in characteristic clusters accelerate the evaluation of the data [11,12]. But the greatest limitation of these methods is that complex and time-consuming sample preparation is needed in practice. Using such spectroscopic measurements yields particle numbers as the result.

Thermoanalytical methods like pyrolysis gas chromatography coupled with mass spectrometry (Py-GC/MS) or thermal extraction-desorption gas chromatography mass spectrometry (TED-GC/MS) can be used for the determination of mass fractions. These methods are already in use for the analysis of microplastic in complex environmental samples with a minimum of sample preparation [13–15]. However, interpreting the complex information those measurements contain still requires a high level of expertise.

But there are also simpler, less complex thermoanalytical methods. The coupling of thermogravimetry (TGA) with evolved gas analysis, e.g. Fourier-transform infrared spectroscopy (FTIR) or mass spectrometry (MS), is well established in research fields of polymer characterization such as processing stability and fire retardancy. Such analytical tools have been commercially available for decades. However, such methods have been used only sporadically in the field of environmental analysis. TGA-FTIR and TGA-MS have been used for the characterization and assessment of the volatile thermal degradation products of wood waste, refuse-derived fuel, waste plastic and waste tires [16,17] as well as for the characterization of activated sludge interacting with activated carbon [18]. In the recent past, these methods have also been used to quantify microplastic. Yu et al. [19] proposed TGA-FTIR for the characterization and quantification of microplastic in mussels, seawater and soil. The polymers polyvinyl chloride (PVC), polyamide (PA) and polystyrene (PS) can be quantified by their method, but the detection of polypropylene (PP), polyethylene (PE) and polyethylene terephthalate (PET) was not possible. David et al. [20] successfully used TGA-MS for the direct quantitative analysis of PET in soil samples spiked with microplastic recycle from PET bottles. Two reviews about application of thermoanalytical techniques can be found in literature [21,22].

All of the existing thermoanalytical methods discussed above are based on structural information about the polymer-specific decomposition products. This is also meaningful because the chemical structure of a synthetic polymer is different from the chemical structure of the organic environmental matrix. However, these two components differ in terms of other characteristics as well, for instance, in their heat of combustion. In the area of waste management and fire retardancy the high heat of combustion or fire load of most common plastics like PE, PP or PS is well known. This is because those polymers pyrolyze completely into volatile hydrocarbons. Afterwards these gaseous pyrolysis products can be totally combusted into carbon dioxide and water. This thorough exothermic oxidation provides a maximum of heat release. In contrast to

this, the environmental matrix pyrolyzes into volatiles, char and ash. Their volatile decomposition produces particular hetero-functionalities, including esters, ethers, hydroxyl groups, and amides. In consequence, the heat released by those components is clearly lower. The thermal analytical tool most suitable for measuring the heat released is called a microscale combustion calorimeter (MCC) and is well known from fire retardancy research [23,24]. The functionality, application and the existing limitations of the method are presented and discussed as a potential new screening method for the analysis of microplastic in environmental samples. Very promising is that a single measurement using this method takes only 10–20 min and allows very simple evaluation of the data collected.

The aim of this paper is to compare TED-GC/MS with the more common, well established thermoanalytical methods TGA-FTIR and TGA-MS for the analysis of microplastic in environmental samples, and also with the promising alternative method MCC. The comparison is made on a defined sample of polymers in a suspended matter matrix prepared for an interlaboratory test, which was recently published by Becker et al. [1]. Fig. 1 and Table 1 show the results of the interlaboratory test samples of the individual polymers. The best results for PE and PP were achieved with TED-GC/MS. PS was detected with acceptable results using TED-GC/MS and TGA-FTIR. Only TED-GC/MS determined PET within an acceptable range. The lowest standard deviation was achieved by TGA-FTIR, and the highest observed for TGA-MS, which also exhibited the worst accuracy. In contrast to Becker's paper [1], this paper is more about the advantages and disadvantages of the individual methods and will highlight the possible application of the methods TGA-FTIR and TGA-MS, and also evaluate a new thermoanalytical method, MCC. In addition, the determination of PVC in environmental samples which cannot be detected by TED-GC/MS yet will be demonstrated as successful with TGA-MS.

2. Material and methods

2.1. Material

The interlaboratory test materials used to compare the methods were: suspended matter without polymers and suspended matter spiked with the polymers PE, PP, PS and PET. The ultrahigh-molecular-weight polyethylene PE was received from Celanese Corporation. The polymers PP, PS and PET were kindly provided as granules by PlasticEurope and their partners. The granules were cryo milled using a sieve mill (ultra-centrifugal mill ZM 200, Retsch, Haan, Germany) equipped with a ring sieve of 1 mm trapezoid holes. The polymeric materials contain a minimum of additives and are standard qualities for food packaging. The suspended matter was taken from the upper Danube River, sampled by a sedimentation box. The preparation of and detailed information on the interlaboratory test material are elaborated in Becker et al. [1].

The PVC powder (average particle size, $D_{50} = 156 \mu\text{m}$) was received from Vestolit (Marl, Germany). The other PVCs were basic commodities. We used two hard PVC materials which hereafter are called bar 1 and bar 2 (practical application: construction object, drainage pipe) and one soft PVC (PVC tube for medical applications). The matrices used for the PVC method development of TGA-MS were obtained from the Environmental Specimen Bank (Umweltbundesamt, Berlin, Germany). These matrices (suspended matter, sediments, plant material, soil, different kind of fish and honey) are not presented in detail here, because they only represent selected, representative matrices from different environmental media (aquatic, terrestrial and biological samples).

2.2. TED-GC/MS

Thermal extraction-desorption gas chromatography mass spectrometry (TED-GC/MS) is a two-step analytical approach. First, the sample is pyrolyzed under a gentle flow of nitrogen using a thermobalance (TGA2, Mettler Toledo, Columbus, USA) and the decomposition products are

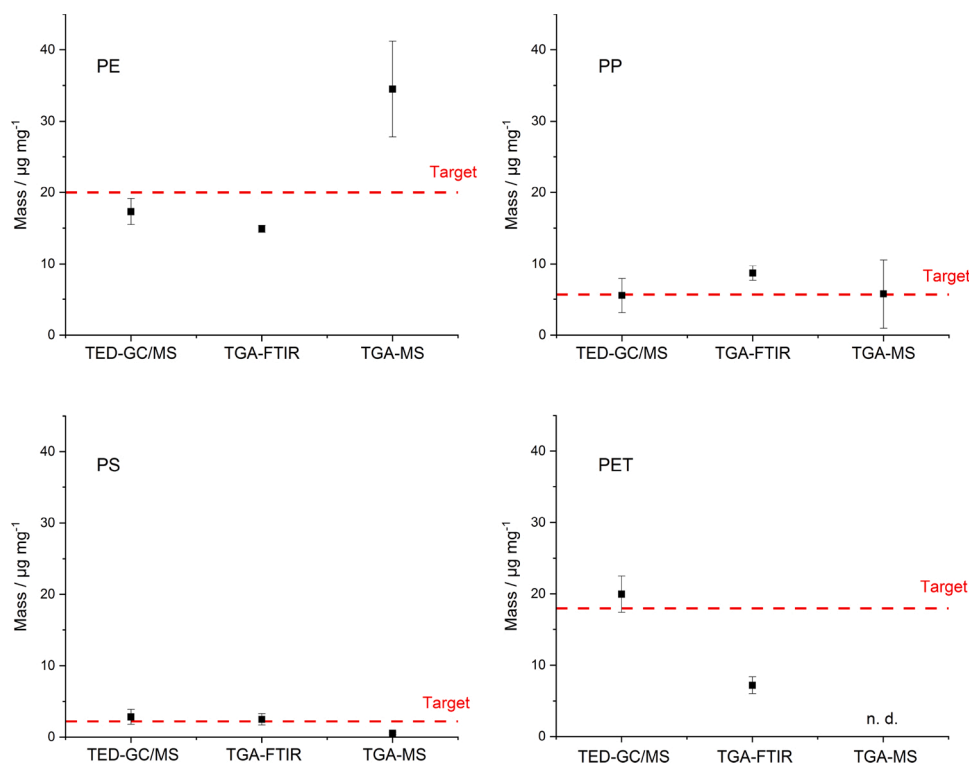


Fig. 1. Results of the interlaboratory test samples for the investigated polymers PE, PP, PS and PET by the three TGA methods; n.d.: not detectable.

Table 1

Target values and results of the interlaboratory test samples using the three TGA methods in $\mu\text{g mg}^{-1}$; n.d.: not detectable.

Polymers	Target	TED-GC/MS	TGA-FTIR	TGA-MS
PE	20.00	17.33 ± 1.83	14.92 ± 0.48	34.51 ± 6.71
PP	5.70	5.56 ± 2.41	8.72 ± 1.02	5.78 ± 4.78
PS	2.20	2.84 ± 1.05	2.48 ± 0.81	0.54 ± 0.16
PET	18.00	19.95 ± 2.55	7.19 ± 1.17	n. d.

collected through a solid phase extraction (SorbStar, Mercury Instruments GmbH, Karlsruhe, Germany). Afterwards, the samples are desorbed and analyzed using a thermal desorption unit of a GC/MS system (TDU and CIS4, Gerstel, Mülheim an der Ruhr, Germany; gas chromatograph 7890B + mass spectrometer 5977B, Agilent, Palo Alto, USA). The qualification and quantification of the polymers in the environmental sample are based on specific decomposition products. Further information on the method and parameters are reported in the publications by Eisentraut et al. [14] and Duemichen et al. [15].

For the TED-GC/MS measurements, 150 μL aluminum oxide crucibles were used, with 15 mg of the interlaboratory test material with polymers and 20 mg of the interlaboratory test material without polymers. A heating rate of 10 K min^{-1} was applied. The decomposition products were collected between 25 and 600 $^{\circ}\text{C}$ for both sample types. For the quality control of the measurement, deuterated polystyrene was used as an internal standard (d5PS: fully deuterated aromatic ring, Polymer Source, Dorval, Canada). The interlaboratory test materials with and without polymers were each measured six times. Using the interlaboratory test material without polymers as matrix, an external calibration was recorded for the quantification. This spiking was realized using a micro balance with a reading accuracy of 5 μg . 15 mg of matrix material each were spiked with a constant amount of deuterated PS and with defined amounts of PE (0.04, 0.09, 0.17, 0.33, 0.40, 0.49 mg as particles), PP (0.05, 0.11, 0.16, 0.19, 0.24, 0.31 mg as particles), PS (0.01, 0.02, 0.03, 0.04, 0.05, 0.06 mg as solution in toluene) and PET (0.04, 0.14, 0.17, 0.27, 0.31, 0.21 mg as particles) at six mass content

levels. In practice, this was done by first dosing and carefully detect the particles masses of the polymers and then adding the matrix.

Results of a preceding blank measurement and of the pure matrix were included in the calibration curve as the zero level.

2.3. TGA-FTIR

The TGA-FTIR measurements were performed using a TGA/DSC3+ thermobalance (Mettler Toledo, Columbus, USA) coupled with an FTIR spectrometer (Nicolet iS50 Advanced FT-IR, Thermo Fisher Scientific, Waltham, USA) equipped with a gas measuring cell (260 $^{\circ}\text{C}$). The transfer line used (inner diameter: 1 mm) was maintained at 250 $^{\circ}\text{C}$. The FTIR measurements were performed over a range of 4000 – 400 cm^{-1} with a resolution of 4 cm^{-1} and a scan rate of 16 scans per spectrum.

20 mg of the interlaboratory test material with and without polymers were measured six times each using 150 μL aluminum oxide crucibles. Heating rates of 10 K min^{-1} were applied and a nitrogen flow of 30 mL min^{-1} passes through the TGA and FTIR system. External calibration with about 0.5 and 2 mg of the pure polymers was used to calibrate the measurements. This is not enough for a basic validation of the method, but it is sufficient for the assessment of the method on the question.

Data from the evolved gas analyses were examined by creating release rates. This means that selected absorption bands or regions of the spectra were integrated, and their changes plotted over time or temperature, respectively. The software OMNIC 9 (Thermo Fisher Scientific, Waltham, USA) was used.

2.4. TGA-MS

The TGA-MS measurements were performed using a thermobalance (STA7200, Hitachi High-Tech Analytical Science, Oxford, UK) connected with a mass spectrometer (GSD 320 Thermostat TM, Pfeiffer-Vacuum, Asslar, Germany) by a coupling device (280 $^{\circ}\text{C}$, REDshift, San Giorgio in Bosco, Italy).

The samples were weighed into a 65 μL aluminum oxide crucible (about 20 mg for the polymers in matrix or the pure matrix) and

pyrolyzed in the TGA at a heating rate of 10 K min^{-1} under a flow of nitrogen of about 200 mL min^{-1} . During measurement, part of the decomposition products were passed via a heated transfer capillary (deactivated fused silica tubing, outer diameter: 0.22 mm, inner diameter: 0.15 mm, maintained at $280 \text{ }^\circ\text{C}$, split of 1:200) and the coupling into the inlet ($150 \text{ }^\circ\text{C}$) of the mass spectrometer. The mass spectrometer was operated in electron ionization (EI) mode at 70 eV . The measurements were performed in the single ion mode. Each of the interlaboratory test materials with and without polymers was measured six times. An external one-point calibration with about 1 mg of the pure polymers was used to calibrate the measurements. In this case, no major efforts were made to validate the method because the result of the TGA-MS measurements was not satisfactory for other reasons. However, this is explained in the results section.

Data from the evolved gas analyses were examined by creating mass traces. This means that the change in selected mass fragments is plotted over time or temperature, respectively. The PVC experiments were performed in $25 \text{ }\mu\text{L}$ aluminum oxide crucibles containing about 5 mg of the PVC samples or 10 mg of matrix spiked with PVC.

2.5. MCC

The MCC measurements were performed using a FAA Microcalorimeter (Fire Testing Technology, East Grinstead, UK) in accordance with ASTM D 7309 [25]. Samples of $5.00 \pm 0.05 \text{ mg}$ were measured. The pyrolyzer temperature ranged from 150 to $800 \text{ }^\circ\text{C}$ at a heating rate of 1 K s^{-1} , and the combustor was set to a temperature of $900 \text{ }^\circ\text{C}$. MCC takes advantage of the oxygen consumption method, with 1 g of consumed oxygen equating $13.1 \pm 0.7 \text{ kJ}$ of heat production [26]. The MCC measurements were not evaluated in the usual way, by determining heat release capacity and the total heat release per sample mass, but instead by determining the heat release in the typical decomposition range of the pure hydrocarbon polymers, such as PP, PE and PS. Thus, environmental matrices deliver heat release rate (HRR) curves rather like a background consisting of very broad and flat humps over temperature, whereas polymers become visible in sharp HRR peaks in temperature ranges well defined by their decomposition.

3. Results and discussion

For pyrolysis a thermobalance is used in TED-GC/MS, TGA-FTIR and

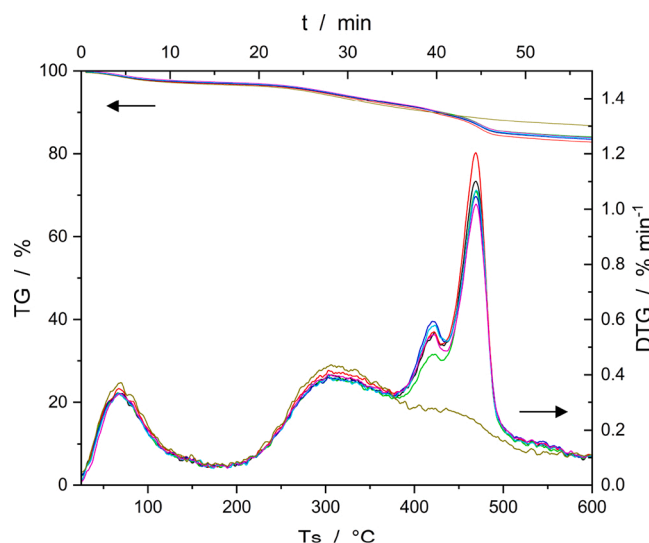


Fig. 2. Thermogravimetry results of six measurements of the interlaboratory test material with polymers, and one measurement without polymers for comparison. Left axis: relative sample mass as TG curves; Right axis: corresponding DTG curves (first deviation of TG curves).

TGA-MS. Fig. 2 shows exemplary TGA measurements of the interlaboratory test materials as they were obtained by all presented methods. The graph consists of the sample's relative mass loss (TG) and the mass loss rate (DTG) to facilitate visual interpretation. The trend of the TG curves is similar up to $400 \text{ }^\circ\text{C}$ (mass loss approx. 10 %). Between 400 and $500 \text{ }^\circ\text{C}$, the decomposition of the polymers takes place, which is recognizable by two peaks in the DTG curves. Overall, up to $600 \text{ }^\circ\text{C}$, a pyrolytic mass loss of about 12 % can be observed for the interlaboratory test material without polymers, and 16 % for the sample with polymers. Therefore, for all TGA methods the mass loss of $\sim 4\%$ can be taken as an indicator for the maximum polymer content in the sample. This maximum value should not be exceeded even if the polymer content in the sample is evaluated by evolved gas analysis. Additionally, the homogeneity of the analyzed samples can be assessed. The reproducible curve pattern of plotted curves indicates that a sample of 20 mg is in first approximation homogeneous.

3.1. TED-GC/MS: the most powerful method

With TED-GC/MS, the polymers PE, PP, PS and PET are clearly identified by their specific decomposition products, which are well known [26]. Using gas chromatography, the resulting decomposition products of each polymer are separated and individually detected. This allows the identification of the decomposition products using the NIST database. An overview of the qualifiers and quantifiers used is presented in Table 2. More detailed information on the used marker substances has been published by Duemichen et al. [27]. All evaluated decomposition product peaks areas were normalized for the peak area of the monomeric decomposition product of the internal standard deuterated PS. A preceding analytical blank measurement was considered.

The best results for the determination of PE and PP were achieved with TED-GC/MS. PET was determined with satisfactory results solely by this method. The determination of PS was also successful. The standard deviations were low (see Fig. 1 and Table 1). These results of TED-GC/MS measurements confirm that this is the method most suitable for microplastic detection in unknown samples (matrix, kind of polymer und content) with a minimum of evaluation expense, but it does require user knowledge for technical handling. However, this will become clearer in the following parts of the work.

3.2. TGA-FTIR: a very robust routine method

For the evaluation of TGA-FTIR, measurements of the pure polymers were carried out first. Characteristic bands were selected for all four polymers (Fig. 3). An overview of those characteristic vibrations is given in Table 3. More detailed information about evolved gas analyses of the

Table 2

List of qualifier and quantifier substances used for the PE, PP, PS and PET detection by TED-GC/MS.

Polymer	Qualifier	Quantifier
PE	1,12-tridecadiene	1,11-dodecadiene
	1,13-tetradecadiene	
	1,14-pentadecadiene	
	1,15-hexadecadiene	
	2,4-dimethylhept-1-ene	
PP	2,4,6-trimethylnon-1-ene (isomer 1)	2,4,6,8-tetramethylundec-1-ene (isomer 1)
	2,4,6-trimethylnon-1-ene (isomer 2)	
	2,4,6,8-tetramethylundec-1-ene (isomer 2)	
	2,4,6,8-tetramethylundec-1-ene (isomer 3)	
PS	2,4-diphenyl-1-butene	styrene
	2,4,6-triphenyl-1-hexen	
PET	vinyl benzoate	ethyl benzoate
	benzoic acid	

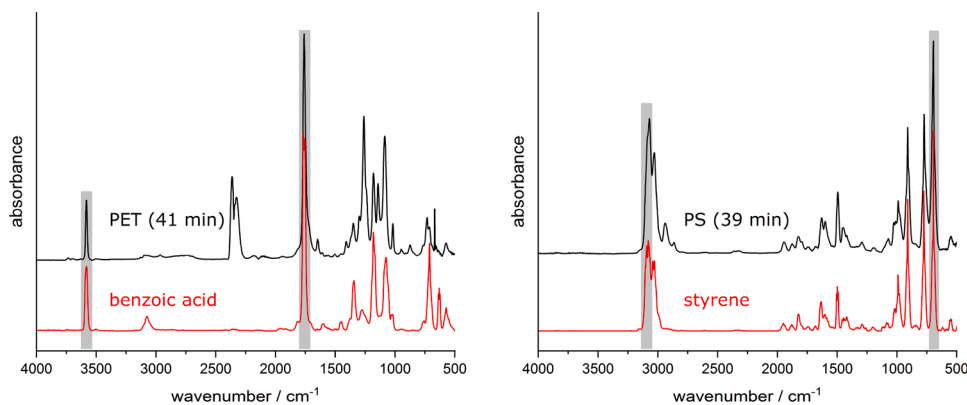


Fig. 3. Gas phase IR spectra of the decomposition gases of PET and PS and the reference spectra of benzoic acid and styrene.

Table 3

Selected wave numbers for the detection of the polymers PE, PP, PS and PET using TGA-FTIR.

Polymer	Characteristic band	Description
PE + PP	2990 – 2945 cm^{-1}	CH_3 groups
	2885 – 2801 cm^{-1}	CH_2 groups
PS	700 – 695 cm^{-1}	Mono substituted ring
	3128 – 3052 cm^{-1}	– C-H at aromatic rings
PET	3582 cm^{-1}	– O-H of free carboxylic acid
	1826 – 1704 cm^{-1}	= C=O of free carboxylic acid

investigated polymers can be found in works published by Braun and Schartel [28–30].

The C=O stretching vibration band (1826 – 1707 cm^{-1}) was used for the quantification of PET; in addition, the O–H stretching vibration (3582 cm^{-1}) qualifies the characteristic decomposition product benzoic acid. For PS, the vibration band —from plane deformation of the

monosubstituted ring system (700 – 695 cm^{-1}) was used for quantification, and the CH— stretching vibration (3128 – 3052 cm^{-1}) was used to qualify the characteristic styrene. These two bands (one for quantification, one for verification) were selected for each kind of polymer to ensure unambiguous identification of the polymers in complex matrices, since the bands individually might not be specific.

For the TGA-FTIR measurements of interlaboratory test samples with polymers, the decomposition products of PET and PS, benzoic acid and styrene, respectively, are clearly identified by gas phase FTIR. To determine the masses of PS and PET with TGA-FTIR, the release rates of the previously selected vibrational bands (Table 3) were integrated. The bands of these specific decomposition products of PS do not overlap with the signals of the environmental matrix. For PET, a small, interfering signal from the environmental matrix without polymer was observed; therefore, the integrated signal of the interlaboratory test material without polymers was then subtracted.

For PE and PP (see Fig. 4 left), the intense symmetric C–H stretching vibration of CH_2 (2885 – 2801 cm^{-1}) as well as the symmetric CH—

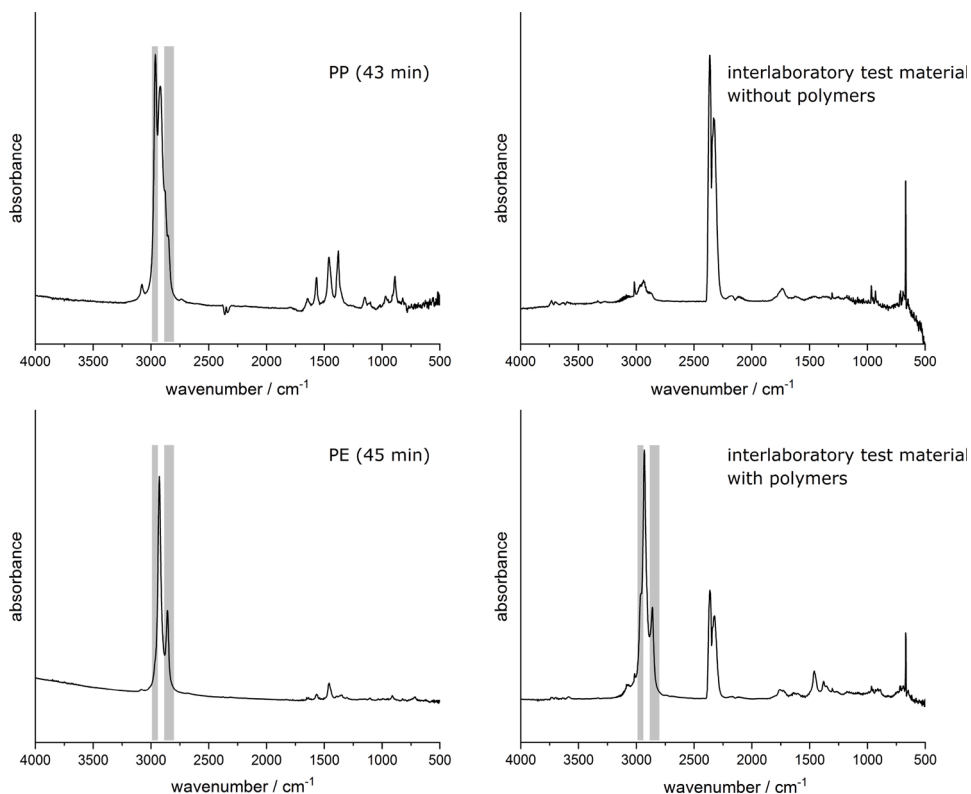


Fig. 4. Gas phase IR spectra of the decomposition gases of polypropylene (PP), polyethylene (PE) and the interlaboratory test materials with and without polymers.

stretching vibration of CH_3 bands ($2990 - 2945 \text{ cm}^{-1}$) in the aliphatic decomposition products interfere with each other, and the decomposition of the two polymers occurs at the same temperatures. However, the measurements of the pure polymers showed that the relative share of the band intensities differ in CH_2 and CH_3 . This fact should be used to analyze the polymer mix in matrix to quantify both PE and PP in the samples. Unfortunately, the environmental matrix alone also shows low intensities of CH_2 and CH_3 vibrations (wavelength range $3000 - 2800 \text{ cm}^{-1}$), which may be caused by e.g. content of humic substances.

Fig. 5 provides examples for TGA data (5a) corresponding with the release rates for PE and PP (5c) and for PS (5e). For quantification, related release rates were integrated. While the results were used directly for PET and PS, further calculations are required for PE and PP since they are not distinguished by individual bands. This was done as follows.

The proportion of PE or PP in the interlaboratory test material was calculated based on the ratio of the CH_3/CH_2 areas of the pure polymers. In a second step, the mass, as the sum of PE and PP (see Fig. 5c), was determined by the external calibrations with the known ratio. Then the

ratio was used to determine the masses of the individual polymers PE and PP in the sample. The results show that the sum of PE and PP was determined very well with $23.6 \mu\text{g mg}^{-1}$ (target: $25.7 \mu\text{g mg}^{-1}$), while the proportion of the individual polymer was underestimated for PE with $14.9 \mu\text{g mg}^{-1}$ (target: $20 \mu\text{g mg}^{-1}$) and overestimated for PP with $8.7 \mu\text{g mg}^{-1}$ (target: $5.7 \mu\text{g mg}^{-1}$). These deviations may be due to scattering effects leading to spectroscopic base line shifts for pure PE and PP (Fig. 4, left). However, no baseline shift was observed for the measurements of the interlaboratory test materials (Fig. 4, right).

In sum, the TGA-FTIR measurements achieved the lowest standard deviations and show the smallest deviations from the target value after TED-GC/MS (see Fig. 1). This simple, cost-efficient and a fully automated combination of devices is one of the routine methods in the field of polymer chemistry. The coupling between the thermobalance and the FTIR is realized via a heated transfer line with an inner diameter of 1 mm, which means that the risk of clogging and the cleaning effort are very low. The complete system can be heated out with synthetic air or even pure oxygen, and possible organic contamination will be easily oxidized.

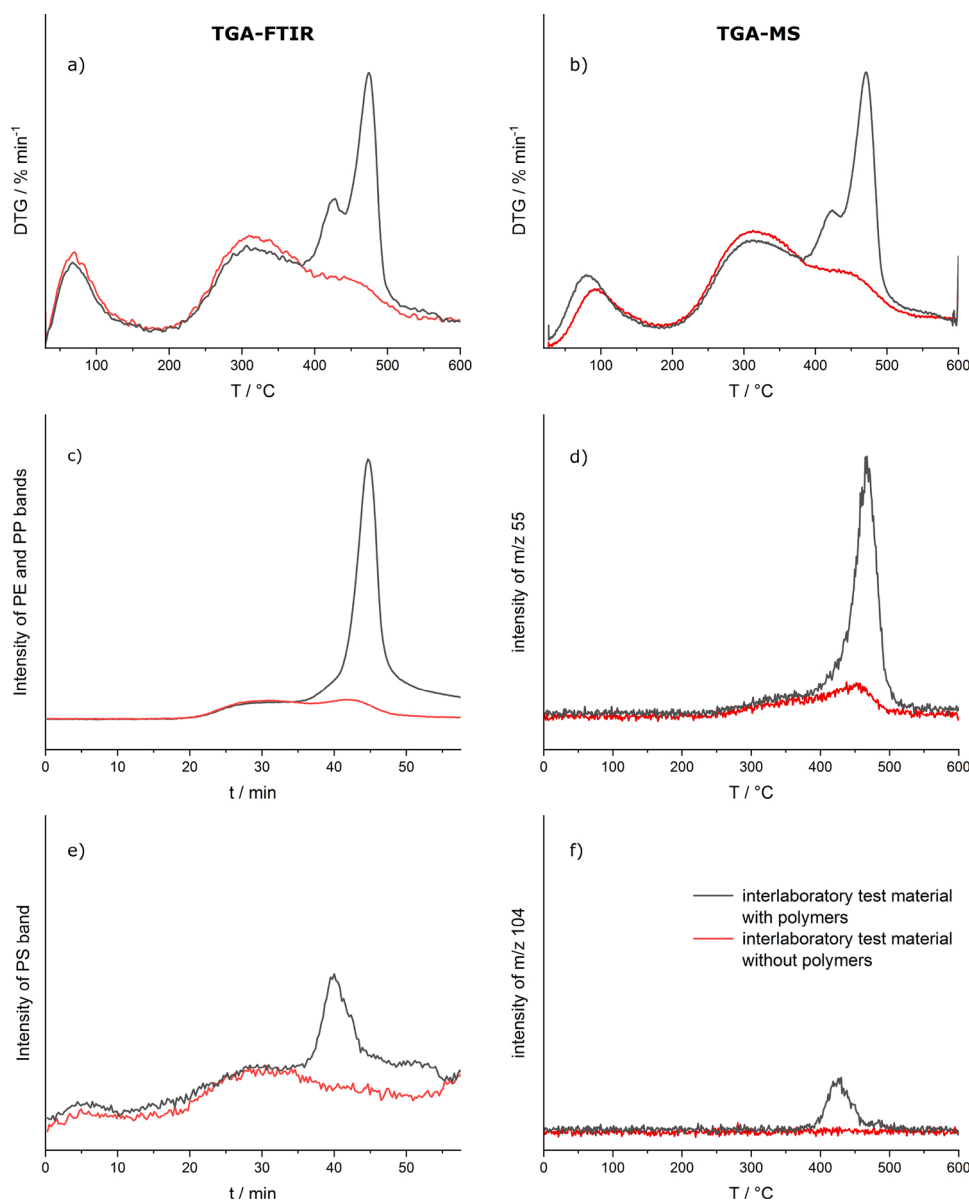


Fig. 5. Results of TGA-FTIR (left) and TGA-MS (right) measurements of the interlaboratory test material with and without polymers; a) and b) thermogravimetric DTG curves, c) release rates for PE and PP, d) corresponding mass traces of m/z 55, e) release rates for PS and f) corresponding mass traces m/z 104.

The qualification and quantification of the polymers with TGA-FTIR may be restricted by knowledge of the pure matrix, since the selected IR bands may not allow unambiguous identification of the polymers in unknown environmental matrices.

3.3. TGA-MS: a possible alternative for detection of PVC

First, specific mass fragments representing the individual polymers were identified from the decomposition gases of the pure polymers. An overview of the detected mass to charge ratios is given in Table 4.

PS was identified and quantified in the interlaboratory test materials without further difficulties by the mass traces of the m/z ratios shown in Table 4. However, the measurements by TGA-MS led to an underestimation of the polystyrene. By means of TED-GC/MS and TGA-FTIR, PS values were determined that were significantly closer to the target value (see Fig. 1 and Table 1).

The detected masses for PE and PP are almost identical. Only the aliphatic ratios of m/z 84 were found for PE, in contrast to m/z 72 for PP. In addition, some mass to charge ratios are more dominant for PP than for PE (m/z 55, 56, 57, 68, 69, 70, 71), while some signals (m/z 54) are almost equally intense in PE and PP.

The masses selected for PET (m/z 90, 105, 154) were not detected even in the pure polymer. This was due to the different setup of the TGA-MS coupling compared to David et al. [20]. The decomposition products are passed from the TGA to the MS through a heated transfer capillary (diameter: 150 μm). Due to the diameter of the capillary, a cut-off occurs for fragments with m/z above approx. 110. In addition, the decomposition of PET results in a mixture of monomeric terephthalic acid and vinyl ester oligomers in a first stage, and the loss of low molecular weight and volatile substances in a second stage [31]. Since the sublimation point of terephthalic acid is at 402 °C, it can resublime during the transition through the transfer capillary ($T = 280$ °C). The resublimation of terephthalic acid can lead to clogging of the transfer capillary. Therefore, the identification of PET is not possible with the present TGA-MS device. The effect of a blocked transfer capillary due to condensation effects or further reactions in the capillary has been discussed by Duemichen et al. [32].

Fig. 5d and f show examples of the mass traces of m/z 55 (5d) and m/z 104 (5f) in the interlaboratory test material with and without polymers. The major part of the signal is caused by the polymers, since the

Table 4

Selected m/z ratios for the detection of the polymers PE, PP and PS with TGA-MS.

Polymer	m/z	Description (possible mol peak)
PE	54	C ₄ H ₆
	55	C ₄ H ₇
	56	C ₄ H ₈
	57	C ₄ H ₉
	68	C ₅ H ₈
	69	C ₅ H ₉
	70	C ₅ H ₁₀
	71	C ₅ H ₁₁
	84	C ₆ H ₁₂ (hexene)
	54	C ₄ H ₆
PP	55	C ₄ H ₇
	56	C ₄ H ₈
	57	C ₄ H ₉
	68	C ₅ H ₈
	69	C ₅ H ₉
	70	C ₅ H ₁₀
	71	C ₅ H ₁₁
	72	C ₆ H ₁₂ (2-methyl-butane)
	77	C ₆ H ₅
	78	C ₆ H ₆ (benzene)
PS	92	C ₇ H ₈
	103	C ₈ H ₇
	104	C ₈ H ₈ (styrene)
	118	C ₉ H ₁₀ (α -methylstyrene)

traces are much more intense in the measurements with polymers. In addition, the signal reaches its maximum during the decomposition temperatures of the pure polymers PE and PP, as can be seen in the DTG curve (5b), which already indicates relatively large amounts of these materials.

To quantify the polymers PE, PP and PS, the mass traces of the characteristic m/z ratios were integrated, and the blank values determined in the measurement of the interlaboratory test material without polymers were subtracted where necessary (see Fig. 5). PE and PP cannot be distinguished based on the m/z ratios, since the distinguishing masses (m/z 72, 84) in the pure polymers had low intensities and were not detected in the interlaboratory test materials.

Since PP and PE cannot be separated by specific m/z ratios or decomposition temperatures, quantification was achieved using the mass traces of the m/z ratios 54 and 55. m/z 54 was observed in the pure substances in both polymers in approx. equal intensities, while the release of m/z 55 was more intense in PP. The different release intensities of the mass fragments are needed to distinguish between PE and PP. Since both polymers contribute to the measured peak areas for the release of m/z 54 ($a_{54,PE}$ and $a_{54,PP}$ as response factor or area per mass pure polymer, respectively) and m/z 55 ($a_{55,PE}$ and $a_{55,PP}$ as response factor or area per mass pure polymer, respectively), the following set of linear equations can be assumed for the resulting peak areas:

$$a_{54, \text{sample}} = a_{54, PE} \cdot m_{PE} + a_{54, PP} \cdot m_{PP} \quad (\text{I})$$

$$a_{55, \text{sample}} = a_{55, PE} \cdot m_{PE} + a_{55, PP} \cdot m_{PP} \quad (\text{II})$$

Unravel the Eqs. (I) and (II) to the mass of PE (m_{PE}), then put both equations on a par and unravel to the mass of PP (m_{PP}) results in:

$$m_{PP} = \frac{a_{54, PE} \cdot a_{55, \text{sample}} - a_{55, PE} \cdot a_{54, \text{sample}}}{a_{54, PE} \cdot a_{55, PP} - a_{55, PE} \cdot a_{54, PP}} \quad (\text{III})$$

To determine the mass of PE (m_{PE}), analogous to this (I) and (II) are unraveled to the mass of PP (m_{PP}) and the two formulas are equated, resulting in:

$$m_{PE} = \frac{a_{54, PP} \cdot a_{55, \text{sample}} - a_{55, PP} \cdot a_{54, \text{sample}}}{a_{54, PP} \cdot a_{55, PE} - a_{55, PP} \cdot a_{54, PE}} \quad (\text{IV})$$

The response factors are known from the measurements of pure PE and pure PP. Accordingly, PE and PP were distinguished and quantified in the interlaboratory test material with polymers using TGA-MS, even though the mass fragmentation patterns of the unseparated decomposition products were very similar. In addition, a 50:50 mixture of the two polymers was prepared and measured. This measurement confirmed the theoretical approach described above.

The TGA-MS measurements show the largest standard deviations in terms of PE and PP. This was because fewer measurements were analyzed, since only three of the six determinations were suitable for use. In the other three measurements, clogging of the capillary (probably related due to terephthalic acid formation, but also other molecules larger than 150 g mol⁻¹) resulted in strongly reduced MS signals of all masses. The m/z ratios for the determination of PE and PP are non-specific and may also be found in aliphatic matrix constituents like fatty acids, proteins or waxes. In addition, Fig. 1 shows that the mass of PP determined by TGA-MS are very close to the target value, but PE and PS are clearly over- or underestimated, respectively. Even though TGA-MS is also a cost-efficient and a fully automated combination of devices, TGA-FTIR is more advantageous in practical use. In contrast to TGA-FTIR, the complete TGA-MS system cannot be heated out with air or oxygen. The MS is sensitive to oxygen; therefore a limiting factor is the clogging of the capillary connecting the TGA to the MS.

Although TGA-MS does not appear to be a worthwhile alternative for microplastic analysis compared to TED-GC/MS and TGA-FTIR, we were able to identify a real advantage of using TGA-MS. TED-GC/MS allows the detection of PE, PP, PS and PET, but so far PVC is the only one of the mass-relevant polymers that cannot be detected. TGA-FTIR and TGA-MS

should be suitable methods to detect PVC in environmental samples. PVC decomposes in two decomposition stages. According to the literature [33], hydrochloric acid and benzene are evolved as main products in the first decomposition process. In the second decomposition process mainly saturated and unsaturated aliphatic compounds are formed. Using the TED-GC/MS, hydrochloric acid is not detectable, benzene from PVC is not, without further measures, distinguishable from benzene evolved by PET, PS or other sources and for the aliphatic compounds during the second step no specific markers were identified.

Hydrochloric acid is known to be analyzed sensitively by TGA-FTIR. However, ammonia released from environmental samples can react with hydrochloric acid to yield ammonium chloride, which may precipitate and interfering with quantification. Benzene shows a low sensitivity in infrared spectroscopy, because the only intense signal overlaps with the CO₂ signal between 680 and 665 cm⁻¹. Therefore, TGA-FTIR is unsuitable for the analysis of PVC in environmental samples.

Using TGA-MS, the decomposition product benzene can be detected with a high sensitivity. Benzene is also formed during the decomposition of PS and PET. However, it can be clearly attributed to PVC due to the decomposition temperature (400 °C for PS and 280 °C for PVC) and continuous evolved gas analysis, which is not provided by TED-GC/MS.

In order to identify specific *m/z* ratios by which PVC can be clearly detected, various types of PVC were measured with the TGA-MS. The TGA curves and the associated DTG profiles are shown in Fig. 6. The TG curves show a decomposition process at approx. 280 °C and another at approx. 450 °C for all PVC samples. The three hard PVC samples showed a mass residue of approx. 21 %, and the soft PVC sample (PVC tube) of approx. 6%. At the beginning of the first decomposition process of the soft PVC, an additional mass loss process occurs, which is probably attributable to plasticizers. The TG curve of the second PVC bar shows an additional decomposition process at the end of the first stage, which is probably caused by additives. No chlorinated decomposition products were detected, but *m/z* 77 of benzene was clearly recognized (Fig. 6c).

A suspended matter matrix was spiked with PVC to assess the specificity of the decomposition products, determined during the measurements of the pure PVC samples. Benzene was the only decomposition product that was detected. Fig. 7 shows the intensity of benzene (*m/z* 77) over the temperature, normalized to the sample mass. At the first decomposition stage of the PVC, a signal with *m/z* 77 can clearly be seen, which also has a higher intensity when the amount of PVC is increased.

Subsequently, a couple of matrices (suspended matter, sediments, plant material, soil, different kind of fish, honey) were screened with the TGA-MS to rule out that benzene was produced during the pyrolysis of natural substances. None of these matrices showed any release of benzene that might interfere with the detection of PVC.

Although TGA-MS showed the poorest performance in the interlaboratory comparison test compared to TED-GC/MS and TGA-FTIR, the identification of benzene as decomposition product marker for PVC is promising for the use of TGA-MS.

MCC: possible alternative thermoanalytical screening tool?

In the interlaboratory comparison test by Becker et al. [1], further, less known methods were used. One of them was MCC. While evolved gas analysis with MS and FTIR uses structure related information on the polymeric decomposition products, MCC can use another polymer specific property: the formation of pyrolysis products with a very high effective heat of combustion.

This method determines the heat release rate (HRR) and total heat release (THR) per sample mass of a milligram sample based on the oxygen consumption method. A milligram sample is pyrolyzed in inert atmosphere flow under constant heating rates of typically 1 K s⁻¹. Thus, the method corresponds closely with TGA measurements at high heating rates and can be classified as a thermoanalytical method. The formed decomposition gases are oxidized in a locally separated oven at 900 °C that adds an oxygen flow. The oxygen consumption is used to calculate the heat release rate versus the pyrolysis temperature. For hydrocarbon polymers like PE, PP, and PS, THR values of 38.8 – 41.6 kJ g⁻¹ can be

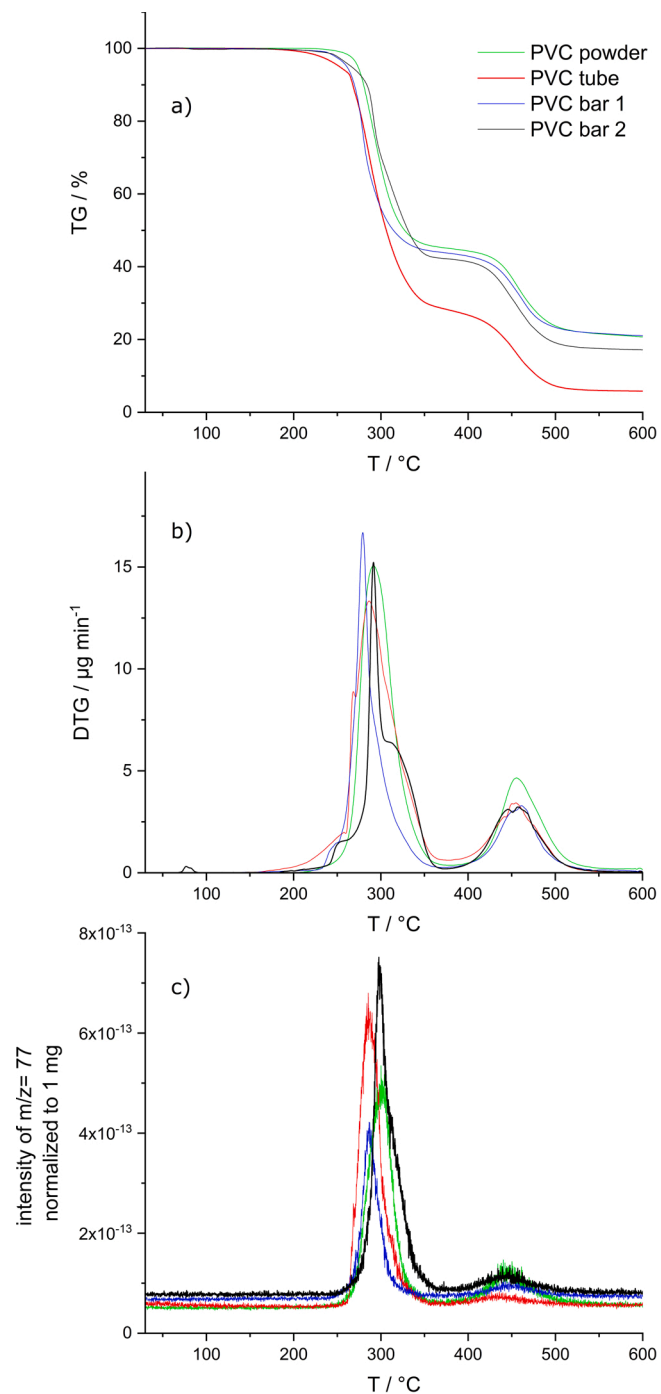


Fig. 6. Results of the TGA-MS measurements of different PVCs; a) relative sample mass as TG curves; b) corresponding DTG curves (first deviation of TG-curves), c) *m/z* 77 plotted over temperature.

observed, whereas the value of PET is distinctly lower (15.3 kJ g⁻¹) [23]. As the THR of environmental matrices is typically below 1 kJ g⁻¹, and the heat release is rather evenly spread over the entire temperature range, the polymer content in the sample can be estimated in the temperature range of polymer decomposition. Here we used an estimated value of 40 kJ g⁻¹ to evaluate the polymer combustion of polymers, consisting of mainly polyolefins and 31.13 kJ g⁻¹, as the target mixture of PE, PP, PS and PET was known.

Because of the limited sample mass load of 5 mg in the current equipment, the measurements were repeated 5 times for the matrix and 10 times for the interlaboratory test material with polymers (Fig. 8). The

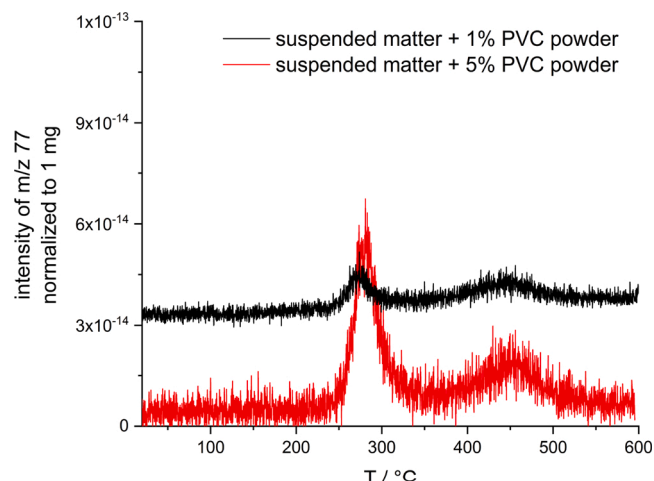


Fig. 7. Results of the TGA-MS measurements of suspended matter spiked with 1% and 5% of PVC, respectively; m/z 77 is plotted over temperature.

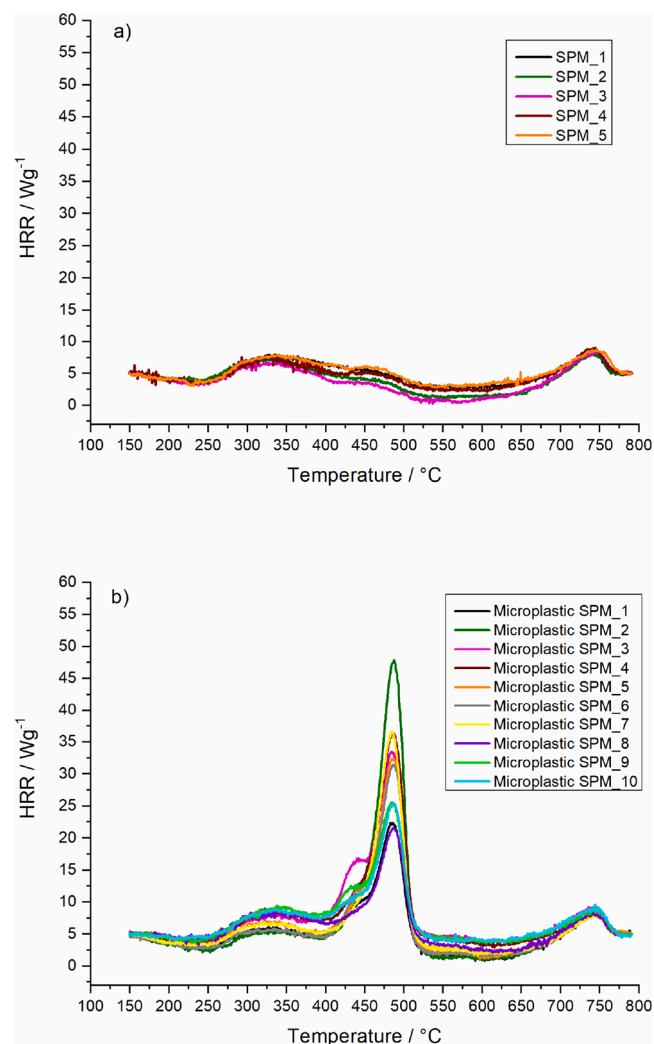


Fig. 8. MCC results, heat release versus temperature, of a) the suspended matter matrix (SPM) and b) the suspended matter spiked with PE/PP/PS/PET mixture (Microplastic SPM).

HRR curve of the environmental matrix is characterized by the expected very low HRR spread in broad humps over the whole temperature range of the measurement. Only a minor fraction of the mass is released; the effective heat of combustion of the volatiles is low. The HRR was always in the same order of magnitude as the background that is usually subtracted in the standard evaluation. All HRR curves of the interlaboratory test material with polymers show a clear peak around 475 °C with variations in the formation of a main HRR peak at 450 and 525 °C, with a distinctive shoulder between 400 and 450 °C. Related to the analysis sample, this indicates a clear inhomogeneity of the added polymers in the samples. However, the shoulder is assumed to relate to the PS and PET content in the sample, and the main peak to PE and PP. To integrate the HRR of the polymers, a line shift of about 5 W g^{-1} was done and a zero line correction performed (point 1: 150 °C and point 2: 800 °C). The integration of the peak, assuming an effective heat of combustion of 40 kJ g^{-1} and subtracting the matrix by a straight line between 370 and 550 °C before integration, yielded $35.0 \pm 7.6 \mu\text{g mg}^{-1}$; subtracting the matrix and additionally using the averaged heat of combustion for the target mixture yielded $45.0 \pm 9.8 \mu\text{g mg}^{-1}$. The target value of all polymers in the interlaboratory test material is $45.9 \mu\text{g mg}^{-1}$, hence the result of MCC investigation is promising.

Because a single analysis takes only 10–20 min and the evaluation of data is very simple, applying MCC is promising for a fast screening method to detect the fulfillment of a critical limit value. However, the commercial MCCs available were obviously not designed to determine the content of polymer in a matrix. The current setup of MCC defines the limits for determining polymer content. Simultaneous determination of the mass loss rate would enable the data to be evaluated based on the real effective heats of combustion of different plastics instead of an estimated averaged value, increasing accuracy and selectivity. Reducing the heat release rate and increasing the mass of the investigated specimen would deliver more representative results, and also reduce the number of measurements needed.

4. Conclusion

For the first time, the three thermoanalytical methods TED-GC/MS, TGA-MS and TGA-FTIR were systematically investigated and discussed for their ability to detect microplastic in environmental samples. A new method, MCC, was also applied. For the comparison of the methods, an interlaboratory test material was used without and with defined, added polymer masses of PE, PP, PS and PET. All polymers were used in unaged form; however, due to the detection of the bulk property of polymers in those thermoanalytical methods, the partial aging of the polymers, which is observed in real samples, will not affect the results significantly [27].

A summary is given about the advantages and limitation of the different tools in Table 5.

The TED-GC/MS is the only method that allows the unambiguous identification of specific decomposition products for the tested polymers PE, PP, PS and PET. In general TED-GC/MS is independent of the matrix composition and can determine microplastic load without knowledge of the matrix composition. However, it is a complex trace analysis that requires extensive user knowledge, and it is sensitive to contamination, for example, when the sample contains large amounts of plastic contents. In addition, the analysis of PVC is not possible with this method, because for this polymer no specific markers are yet known. But in the framework of the comparison of methods in the present work, TED-GC/MS is the only solution for samples with unknown matrix and unknown, variable kinds and amounts of microplastic content.

TGA-FTIR and TGA-MS are technically simpler, since a transfer line or capillary, respectively, links the TGA directly with the evolved gas analysis. However, the unambiguous evaluation of the occurring vibration bands or m/z ratios is not possible if the matrix composition of the sample is not known. Here the matrix's contribution to the signals must always be considered or known. In practice this means that a

Table 5
Overview of the advantages and limitation of the different methods.

	Advantages	Limitation	Suitable method for ...
TED-GC/MS	Almost matrix independent Clear differentiation between various polymers Less technically complex method	Complex method—high user knowledge needed Detection of PVC currently not possible Matrix contribution to the signal needed (background value)	... unknown matrix samples with unknown variable kinds of microplastic and content
TGA-FTIR	Easy to clean against organic contamination Less technical complex method	Differentiation between PE and PP only by calculation Matrix contribution to the signal needed (background value)	... known matrix samples with defined kinds of microplastic
TGA-MS	Detection of PVC is possible	Differentiation between PE and PP only by calculation No detection of marker compounds with molecular mass > 150 g mol ⁻¹ (PET) Matrix contribution to the signal needed (background value)	... detection of PVC
MCC	Very fast measurement	No differentiation between different polymers: only PE, PP, PS contribute significantly to the signal Limited to only 5 mg of sample mass	...very fast and simple screening campaigns for the identification of a potential microplastic load of standard polymers in unknown samples

background value is needed. Both TGA-FTIR and TGA-MS allow differentiation between PE and PP by using a model calculation. TGA-MS does not allow the analysis of PET, because no specific marker can pass the capillary due to its high molecular weight. In addition, the deviations from the target value for the quantification of PS were also greater for TGA-MS than for TGA-FTIR. A major advantage of TGA-FTIR is that it can be cleaned simply by running heat through it when organic residues contaminate the device. Based on the investigations carried out in this paper, TGA-FTIR would be preferable for analysis of microplastic as a simpler technique for screening samples with well-known or constant matrix composition. Hence, TGA-FTIR is suitable for samples with known matrix composition and with defined kinds of microplastic.

But TGA-MS showed a high potential to detect PVC. Benzene evolved at 280 °C was therefore used as a marker molecule with *m/z* 77. TED-GC/MS and TGA-FTIR do not have this potential.

MCC, as it is established in the ASTM standard [25], does not effectively differentiate between the different polymers. Sensitivity increases by up to a factor of 10 with decreasing char yield and increasing effective heat of combustion. Nevertheless, the principle of the method is very promising as a fast screening method to detect the main standard polymers like PE, PP, PS that are found in the environment, and it shows clear development potential. Hence, MCC as a fast analysis tool is suitable for the first identification of a potential microplastic load of standard polymers in unknown samples.

Author statement

CG, DD, PE and UB planned the study and designed the experiments. CG and DD carried out the TGA-FTIR and TGA-MS experiments and interpreted the results. PE performed and interpreted the TED-GC/MS measurements. BS and PK carried out and interpreted the MCC measurements. YW was significantly involved in evaluating the TGA-MS data. CG and DD wrote the initial draft. All authors contributed to the final manuscript.

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Data statement

The generated data are available on request from the corresponding author.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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