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THE DEVELOPMENT OF A TGA-MS BASED METHOD FOR DETERMINATION OF MICROPLASTIC IN SOILS

VÝVOJ METODY PRO SEMIKVANTITATIVNÍ STANOVENÍ MIKROPLASTŮ V PŮDÁCH METODOU TGA-MS

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ABSTRACT

The plastics, penetrating the environment unintentionally or deliberately, can be fragmented to form smaller particles in range of micrometre (so-called microplastics) and thus contaminate soil systems. Until now, the developed methods for determination of the microplastics in soil are mainly focused on qualitative analysis. Nevertheless, also their performance suffers with various problems. Moreover, almost all the analyses require a time-consuming sample pre-treatment. In this study, we focused on the development of a new analytical approach for quantitative determination of polyvinyl chloride (PVC) and polystyrene (PS) microplastics in soil using thermogravimetry-mass spectrometry (TGA-MS) without sample pre-treatment. Model sandy loam soil samples were spiked with microplastics to obtain final concentrations of 0.23–7 wt% PVC and PS, respectively. The samples were pyrolyzed with heating rate of 5 K min⁻¹ up to 1,000 °C. Subsequently, the evolved gases were analysed using MS. The obtained data were normalized with an external standard (calcium oxalate hydrate). Limits of detection depended on chosen *m/z* and were determined between 0.08–5.3 wt% for PVC and between 0.005–0.7 wt% for PS, respectively. Consequently, limits of quantification were between 0.3–17.7 wt% for PVC and between 0.002–2.2 wt% for PS. The results show that the coupling TGA-MS can be a complete semiquantitative approach for determination of micro-PVC and micro-PS in soil with low organic carbon content.

KEYWORDS

microplastics, PVC, polyvinyl chloride, PS, polystyrene, soil, TGA-MS, thermogravimetry-mass spectrometry

ABSTRAKT

Plasty, pronikající do životního prostředí ať už neúmyslně či záměrně, mohou být fragmentovány za vzniku částic v řádu mikrometrů (tzv. mikroplastů) a znečišťovat tak půdní systémy. Doposud vyvinuté analýzy pro stanovení mikroplastů v půdách jsou především zaměřeny na kvalitativní stanovení, nicméně i jejich provedení se zatím stále potýká s různými úskalími. Navíc, téměř všechny tyto analýzy vyžadují časově náročnou předúpravu vzorku. V této studii jsme se zaměřili na vývoj nové analytické metody pro kvantitativní stanovení mikroplastů polyvinylchloridu (PVC) a polystyrenu (PS) v půdách bez předchozí úpravy vzorku pomocí termogravimetrické analýzy spojené s hmotnostní spektrometrií (TGA-MS). Pro analýzu byly použity vzorky modelové půdy s nízkým obsahem organického uhlíku, které byly spikovány na výslednou koncentraci 0,23–7 hm% PVC či PS. Vzorky byly pyrolyzovány s teplotním krokem 5 K min⁻¹ až na teplotu 1000 °C. Pyrolýzní plynné produkty byly následně analyzovány s využitím hmotnostního spektrometru. Získaná data byla normalizována pomocí externího standardu (šřavelan vápenatý). Limity detekce se pohybovaly v rozmezí 0,08–5,3 hm% pro PVC a 0,005–0,7 hm% pro PS v závislosti na zvoleném *m/z*. Limity kvantifikace pak byly 0,3–17,7 hm% pro PVC a 0,002–2,2 hm% pro PS. Výsledky dokazují, že spojení TGA-MS může být konkurující semikvantitativní metodou pro stanovení mikro-PVC a mikro-PS v půdě s nízkým obsahem organického uhlíku.

KLÍČOVÁ SLOVA

mikroplasty, PVC, polyvinyl chlorid, PS, polystyren, půda, TGA-MS, termogravimetrie spojená s hmotnostní spektrometrií

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PROHLÁŠENÍ

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1. INTRODUCTION

The world population is rapidly increasing. To maintain the quality of life, the society should develop the sustainable strategies of environmental protection. One of the most effective way is smart use of resources and application of eco-friendly materials.

Plastics, materials with extraordinary properties, are an integral part of everyday life. They are versatile and therefore, used in virtually all sectors of human activity. When the plastics became the waste, it does not have to mean their end-life. The plastics waste can be reused in the same or different way as the original product. Despite many opportunities of reuse plastics, the huge amount of the plastic waste enters the environment. Currently, this issue is being lively discussed. There exist concerns mainly about plastic pollution of world oceans, but the interest is now focused also on terrestrial ecosystems.

Whether the people endeavour different ways to fight against the use plastics and even to avoid the plastic material in everyday life, they should be aware that nowadays, the plastics are still irreplaceable in many cases. In addition, they can save our life, protect the environment and reduce the increasing treat of global warming. Hence, the plastics should not be construed as enemies, as is sometimes claimed, but irreplaceable assistants.

2. THEORETICAL PART

2.1 PLASTICS

2.1.1 Definition

In general, the term plastic is used to describe various types of synthetic polymer materials. From the chemical point of view, they are substances composed of monomers (as a basic structural unit), which are connected together to form chain-like polymers. Typically, the most used plastics are consisted of 10,000 to 100,000,000 monomers per one chain [1].

Besides plastics of synthetic origin, there exist also polymers of natural origin. Most of both synthetic and natural polymers can be described by the following properties as a demonstration of their advantages: resistance to chemicals, various processing ways, very low thermal or/and electrical conductivity, lightweightness in comparison to metals, glasses and cotton textiles [2] and toughness [3]. In order to enhance such properties or facilitate the manufacturing process, there may also be used a variety of chemical additives into plastic compositions [1; 3].

Table 2.1 Main application fields of the most used plastics [4].

Name	Abbreviation	Application
Polypropylene	PP	food packaging, pipes, automotive accessories
Low-density polyethylene	LDPE	shopping bags, stretch wraps, mulching foils in agriculture
High-density polyethylene	HDPE	bottles for drugstore items, toys, houseware, pipes
Polyvinyl chloride	PVC	PVC floors, window frames, cable insulation, pipes, greenhouse and mulching foils for agriculture in China [5]
Polyurethane	PUR	building insulation, foams, furniture, mattresses, automotive, insulating foams for fridges
Polyethylene terephthalate	PET	beverage containers, sport clothes
Polystyrene	PS	disposable cups, dishes and cutlery, various packaging, building insulation

Broadening the usability of polymer materials causes the overall growing popularity of plastics. According to PlasticsEurope data¹ of 2015, the plastics demand main sectors represent packaging (39.9%), construction (19.7%), automotive (8.9%), and electronics (5.8%) or agriculture (3.3%), and further sectors including consumer and household goods, sport, health, safety, etc. Demand for polymer materials in EU amounted to 49 million tonnes in the same year. Demand for polypropylene (PP) exceeded 9 million tonnes, low-density polyethylene (LDPE) achieved the second place and the third highest demand was divided among high-density

¹ The data include information obtained in European Union (28 countries + Norway and Switzerland).

polyethylene (HDPE) and the other plastics including thermosets, adhesives, coatings and sealants. Polyvinyl chloride (PVC), polyurethane (PUR) as well as polystyrene (PS) then followed [4].

2.1.2 Plastic waste

Nowadays, the plastics are ubiquitous in everyday life. Owing to their properties and price, they have substituted various common materials, such as wood, glass, metals, paper or cotton textiles [1]. In 2015, there were 322 million tonnes of plastics produced all around the world [4]. Consequently, the amount of plastic waste has been increasing as well. Therefore, the question, how to handle the plastic waste, arises. There exist four main methods for the plastic waste management:

- mechanical recycling,
- chemical recycling,
- thermal recycling with an energy recovery,
- and landfilling [3; 6].

From the methods mentioned above, the mechanical recycling is highlighted as an environmentally friendliest approach [6]. Specifically, reducing of municipal solid waste volume through handling the plastic waste as a commodity belongs to one of the dominant advantages of recycling [7]. Some authors claim that most plastics are a kind of a renewable material source [6; 7].

However, there exist non-recycled plastics (NRPs), too. Their diverse physical properties are the main reasons for their accumulation in the environment. NRP contains a great deal of different additives which have an influence on material quality. In general, NRP is a material, which is a part of municipal solid waste, and cannot be redirected for recycling, or it can also be unusable residual waste after recycling [8]. Thus, new technologies for their thermal recycling are used and investigated and some case studies deal with NRPs issues, especially waste-to-energy and pyrolysis [8; 9].

Whether to recycle plastic waste or burn it, number of countries prefers landfill instead. Indeed, it is more advantageous in economical and practical point of view [1]. Nevertheless, landfill causes additional environmental issues. According to Verma et al. [10], incorrectly managed waste disposal could influence the environmental pollution. They specifically mention landfill leachate escape [10] or blown the light plastic material away [10; 11].

2.1.2.1 Plastic degradation

The stability of each plastic material is caused by its physicochemical properties and additives. Number of abiotic and biotic factors is included in potential deteriorating processes when the plastics are introduced in the environment. Three main basic groups of interactions between polymers and environment exist and include (i) plastics, designed as biodegradable materials, which may degrade faster (e.g. polylactic acid, whose biodegradation time can take from two weeks to two months depending on the specific environment), (ii) highly persistent materials with up to thousands of years of ongoing degradation and (iii) soft polymers ready to break apart [1].

Degradation of plastics is considered as an important issue both in material and environmental sciences. Generally, the degradation can be described as a breaking up of the

polymer into small debris. From the chemical point of view, it is a process during which the main polymer backbone chain is fragmented into shorter ones, while also the side groups can be simultaneously cleaved. As a result, molecular weight of newly-emerged degradation products decreases [1]. The resulting products are debris of different size (from macroparticles larger than 5 mm up to nanoplastics $\leq 0.1 \mu\text{m}$) plus various leached additives [11]. *Figure 2.1* summarizes the process and shows the fate of plastic fragments when especially abiotic factors act on them.

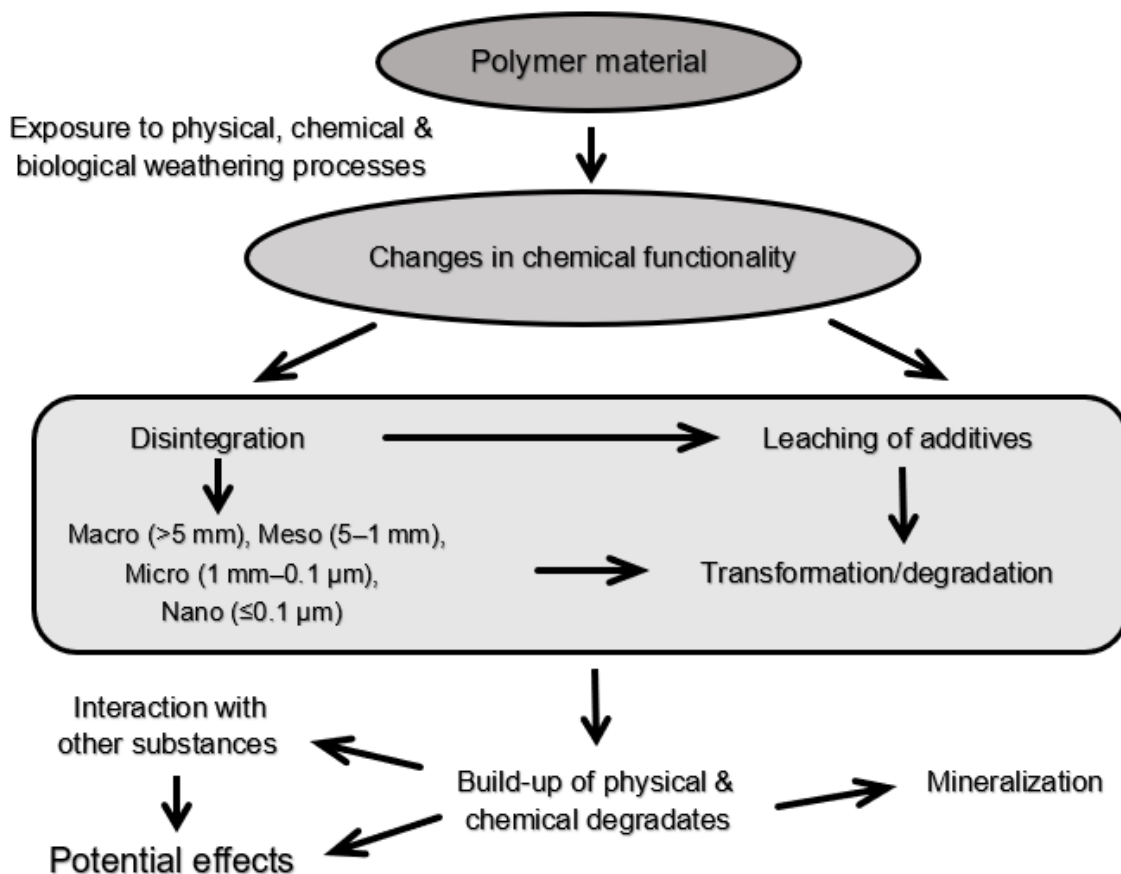


Figure 2.1 Conceptual model representing degradation pathways [11].

Biotic degradation

Biodegradation of plastics refers to the degradation process caused by decomposers [1], which produce simpler inorganic and organic compounds occurring commonly in nature. Depending on conditions, such as aerobic or anaerobic environment, mainly carbon dioxide or methane are produced, respectively. The other degradation products are biomass and water [12].

Occurrence of plastic material in diverse environment affects the degradation kinetics, while local conditions together with characteristics of surroundings and physicochemical properties of plastics play a major role [12; 13]. The most biochemical processes, affecting the plastic degradation, take place in cells of microorganism. Therefore, water solubility and transport of plastic particles into the cells are decisive factors [11]. To fragment the plastic waste into small segments, it needs to undergo the abiotic degradation at first. This includes many ways and conditions such as presence of oxygen, moisture or ultraviolet light. In addition, extracellular microbial enzymes, as a biotic factor, may enhance these processes [1].

The moment the plastics are chopped sufficiently, the small fragmented chains can penetrate into microorganism bodies. The carbon, as a main and basic building element, acts as a food and energy source for microorganisms [1]. In a simplified way, the biodegradation is an electron transfer, affected by chemical reactions and catalysed by enzymes [12].

Even though it seems that all bio-plastics undergo biodegradation, the reality is slightly different. The term bio-plastics refers to biodegradable plastics (made of fossil sources) or bio-based plastics (based on biomass or renewable sources), respectively. Therefore, there is no rule, that bio-based plastics must be completely biodegradable [13]. Although commonly used plastic carrier bags can be labelled as 100% degradable or compostable, this may not be always true in the real environment. Adamcová and Vavreková [14] studied degradability and biodegradability of four plastic samples, which were placed into municipal landfill for 12 months. The experiment showed that there were not any significant changes, except for slight colour changes.

Besides the benefits resulting from reducing the plastic waste, the biodegradable plastics also bring a lot of disadvantages such as higher price, worse mechanical properties and higher demands for storage [1].

Abiotic degradation

From the very beginning of using plastics, there was a problem with their long-time stability. This was mainly influenced by abiotic degradation, which posed many issues connecting with quality of plastics, such as tensile strength or rigidity. To enhance plastic material lifetime, various chemicals have been added to specific plastic materials (and according to their purposes) as stabilizers. The stabilizers are substances serving for increasing stability and durability of plastics and protecting them against adverse environmental influences [1]. Thermal stabilizers are another application, especially in manufacture. This is particularly common for PVC [3].

While the biotic degradation is biochemical process taking place due to enzymes, the abiotic degradation is affected by chemical reactions without organism influences. The abiotic degradation includes:

- *Photo-degradation* – is one of the common degradation processes of plastics and it is affected by light. The breakdown, observed as a chain scission or cross-linking, takes place when the plastic material is exposed to a radiation in ultraviolet (UV) or visible (VIS) range. The photo-sensitivity may be caused by presence of chromophores – photo-reactive groups, which absorb in UV or VIS range. Similar mechanism can also be observed in case of irregularity in the chemical structure of polymers. This may happen when either carbonyl or peroxy groups occur [1; 11].
Photons of UV/VIS light attack chemical bonding thereby initiate free radical reaction. The attack initiates chain reaction resulting in a decrease in the molecular weight [1; 11].
- *Thermal degradation* – temperature fluctuation represents another abiotic process, which may influence the polymer deterioration [11]. The consequence of increased temperature can cause: (i) softening of polymer until behaves more like a liquid, (ii) breakdown the polymeric structure without any chemical changes. When the breakdown is accompanied by changes in chemical constitution and usually emission

of low molecular weight products (e.g. water, hydrogen chloride, alcohol), destruction (iii) takes place there [3].

- *Oxidative and hydrolytic degradation* – oxygen occurring in atmosphere can attack the surface of polymer to form hydroxyl or carbonyl functional groups, which are more susceptible to naturally biotic processes [11]. Another way represents a catalytic process resulting in an elimination and formation of double bonds [1]. The hydrolytic degradation depends on chemical properties of the polymer and absorption of moisture into the structure [11].
- *Mechanical disintegration* – takes place when an external stress is applied. In a natural environment, various conditions occur such as weathering, freeze-thaw cycles, water flow and waves, pressure of soil or snow, abrasion, or influence of animals and plants [1; 11]. According to Kyrikou and Briassoulis [12] the fragmentation, especially in soil, can also be caused by earthworms, plants roots, insect or rodents. Due to mechanical nature of the stress, no chemical changes occur [1; 11].

2.1.3 What are microplastics

Some studies reported [14; 15; 16] degradation of plastics in various types of environment such as soil, marine, or alternatively abiotic conditions, involved in laboratory experiments. The results of these studies are primarily related to weight loss of material and other physical properties, however the degradable products themselves are not observed in detail. On the other hand, from the current reviews follow that most plastic materials yield more likely to disintegration than degradation [17] and small debris of different shapes are formed [18]. It is considered that amount of the debris gradually increases, and their size becomes even smaller [18].

According to several authors the term “microplastics” is referred to plastic particles <5 mm [1; 17; 18; 19]. Nevertheless, the term is considerably unclear, and it can be encountered with definitions particularizing mesoplastics as pieces between 1–5 mm, and then the microplastics <1 mm [11]. Another classification is shown in *Table 2.2*, where it is divided into three categories, and three subcategories [1].

Table 2.2 The size classification of plastic particles. The size of any pieces is meant as size along their longest dimension [1].

Category		Size
Macroplastics		≥25 mm
Mesoplastics		<25 mm–5 mm
Plastics	<i>Microplastics</i>	<5 mm–1 mm
	<i>Mini-microplastics</i>	<1 mm–1 μm
	<i>Nanoplastics</i>	<1 μm

In the real environment, there are two different ways how to produce microplastics. Besides the natural breakdown of large plastic items, the microplastics can be purposely manufactured, too. This group is called primary microplastics and are parts of everyday products. The second

mentioned category, secondary microplastics, is more likely result of weathering processes. However, its meaning within occurrence and environmental fate is equally important [1; 19; 20].

2.1.3.1 Primary microplastics

Primary microplastics as industry products have a lot of utilization. Since they have been intentionally manufactured, their relevance and impact are growing. As the first significant source, factories make small plastic pellets, a raw material, used in feedstock to form new plastic artefacts [19; 20]. For instance, only United Kingdom emits 105–1,054 tonnes of the pellets every year [1].

Another potential source is a mixing of the microplastics with cosmetics and care products which serve as glitters [19] or exfoliating agents [20]. The issue has been discussed around the world and several countries have already banned or planned to apply regulations related to using the microbeads in care products [21]. Based on current and available data, Duis and Coors [22] tried to hypothetically analyse real threat of the microbeads from liquid skin cleaners. They work on an assumption that around 6% of the products contain microplastics within EU, Norway and Switzerland. In addition, only 10% of all the mass is related to the microbeads. If the particles are washed down after application, they may travel and reach wastewater treatment plant (WWTP). The study works with assumption of 90% efficiency of WWTP in removing microplastics. Thus, only very small amount penetrates in aquatic environment [22]. Nevertheless, the question is what does happen with microplastics contained in sewage sludge afterwards.

Additional sources of the primary microplastics are also drilling fluids for oil and gas exploration and industrial abrasives, respectively [22].

2.1.3.2 Secondary microplastics

The secondary plastics are of similar importance as primary microplastics. As aforementioned, they are formed due to degradation processes of larger litter pieces. Nevertheless, the plastics are often applied to environment intentionally that increase the number of their potential sources. A typical example is a plastic mulching in agriculture [20; 23]. When required application period runs out, the mulches are supposed to be removed. Due to complicated and time-consuming removal, farmers rather incorporate mulching foils into soil using mechanical breakdown. Then, such plastic foils may remain in the soil for long time and gradually lose themselves physical properties until microplastic particles are formed [23].

Highly discussed problematical source has also been reported the washing of synthetic textiles [19; 24]. For instance, authors Sillanpää and Sainio [24] estimated a mean annual emission of plastic fibres from washing clothes to be 154,000 kg in Finland. Besides the textile materials, tyres or paint abrasions may also produce certain proportion of microplastic fragments [25].

There exists a hypothesis asserting that even if we could stop the emission of all plastic litter into the environment, the current plastic pollution and the degradation already affecting on would be sufficient for ongoing production and increasing microplastic mass for a long period [25].

2.1.3.3 Microplastic properties

Microplastics, occurring in environment, exist in manifold shapes and colours. Typically, primary microplastics gain spherical or fibrous shape since it is required by consumers, or

alternatively their shape is acceptable for industrial production, and not surprisingly resulting surface is more likely smooth [1; 25]. By contrast, secondary microplastics, undergoing natural weathering, tend to form random pieces giving rise to such a shape diversity. In fact, once both types of microplastics enter the environment, local conditions have a deciding impact on the resulting shape [1; 18]. Lambert and Wagner [18] further point out that for the investigation of formation of a new microplastic shape, the polymer origin and specific distribution of pore at the material surface should also be taken into consideration.

The concern about the appearance of microplastics may have an importance for further investigation. The findings can be applied in detection of plastic particles in environment thereby to trace potential sources of these pollutants [26; 27]. As stated by GESAMP [25], analysis of the microplastics, based only on their shape, may give rise to misleading some results though. Size and unlike appearance (namely of fibres) is more easily detected in comparison with the other types, and this may lead to overestimation of real ratio of the debris [25].

Size and shape may also have a biological impact. A study [28] investigated effect of regular shaped plastic microbeads and irregular shaped microplastic fragments on intake and output of *Daphnia magna*. Even though the ingestion rate was similar for both, the egestion was significantly slower for irregular shape. Almost 50% of organisms, fed with regular microbeads, could completely empty their guts whereas in case of microplastic fragments it was <1% of tested organisms. Thus, irregular microplastics might bioaccumulate in organisms with higher potential.

2.2 FATE OF MICROPLASTICS IN ENVIRONMENT

Microplastics are fundamentally of anthropogenic origin [17], which implies the tracing all sources primarily in area with human activity. A study [26], investigated concentration of different microplastics along Rhine River, claims the heterogeneous distribution across the river depending on population density and local industry as well as hydrological conditions. Indeed, the industry might have potentially high effect on the final pollution. Some authors confirm a significant influence of industrialized areas on resulting microplastic concentration, which is much higher in rivers close to these locations than in marine environment [17].

As mentioned above, WWTPs can be also considered to be a source of microplastics (*e.g.* washing of synthetic fibres and/or microbeads from personal care products) escaping into primarily aquatic environment through effluent. Moreover, if the wastewater flow exceeds proportioned limit, the sewage overflows directly into aquatic system without any treatment [19]. On the other hand, the efficiency of WWTPs is quite high in removing the microplastics and thus great amount is retained in the sludge [17; 19]. The sewage sludge is often required being spread on agricultural lands as a fertilizer, which can contain such persistent plastic particles [29]. Zubris and Richards [29] determined synthetic fibres from clothing in agricultural cultivated soil even up to 15 years after application the sewage sludge.

Importantly, environmental systems are very closely interlinked, which means that the plastic debris may pervade within them [19]. Several authors [17; 19; 20] have been attempting to describe these microplastic pathways between environmental compartments by diverse conceptual models (*Figure 2.2*). Their hypotheses reflect the dominant transport of plastic items

into marine environment, even though the reaching the ocean sinks might not mean the end of the route. High tides and storm events can help to transport microplastics back to shores as well as similar processes can take place in freshwater where flooding events may have the resemble effects [19].

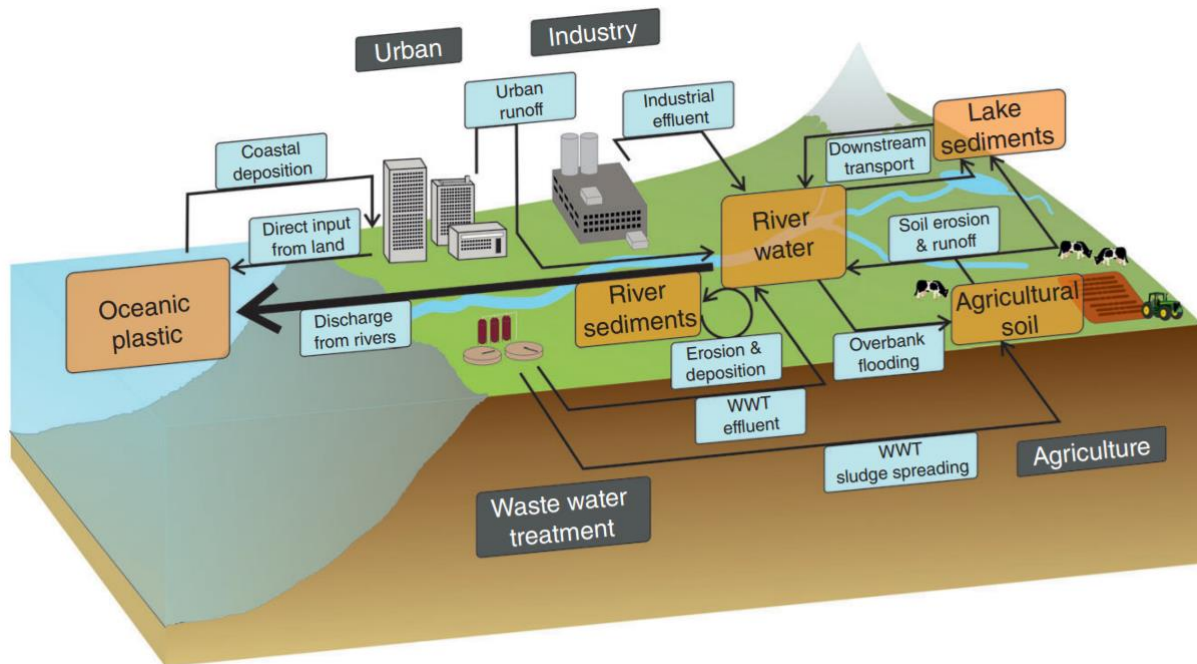


Figure 2.2 Conceptual model of the plastic cycle. The figure does not include atmospheric pathways [19].

Up to now, the interaction between aquatic and terrestrial compartments is mostly highlighted. However, another possible way not yet deeply investigated, is the transport via atmosphere with a consequent deposition. For instance, in Parisian agglomeration the average daily fallout was observed at 110 ± 96 fibres $m^{-2} day^{-1}$, and thus the annual atmospheric deposition was estimated between 3–10 tons of fibres for the area. From this amount, 29% belong either to fibres of plastic or mixture of plastic and natural origin while the size range of the most detected fibres was between 200–600 μm [30]. Cai et al. [31] analysed microplastic pollution in air of Dongguan city in China. They determined the same order of magnitude which gave in average 36 ± 7 plastic particles $m^{-2} day^{-1}$. The study also included films, fragments and foam but the microplastics were almost exclusively fibres [31]. The air contamination seems to enable the microplastics redistribution on a large distance [17], and furthermore contaminate unpopulated area. Therefore, more attention should be paid to the atmosphere transport of microplastics.

2.2.1 Microplastics in terrestrial environment

Most of studies focus on presence and effect of microplastics mainly in aquatic compartments. However, in fact the dominant production, utilization, and usually disposal of microplastics or their precursors take place on land, and it can be assumed that the debris first undergo biogeochemical interactions [17].

2.2.1.1 Soil – function, properties and interaction with microplastics

An importance of soil for the environment and sustainability is essential. It is a matrix for plant growth and food production, plays a crucial role in water retention and filtering, and it is a nutrient supply and a habitat for a diverse number of organisms [32].

Nevertheless, the soil can also retain a great amount of pollutants. It is namely caused by continual cultivation and agriculture. During these interventions, various fertilizers and pesticides are applied. Such substances can contain a variety of pollutants [29; 32; 33]. Focusing on microplastic pollution, Nizzetto et al. [33] hypothesize that agriculture soil may be considered as one of the largest sinks. In general, interaction between soil and the other compartments (*i.e.* air and water) tends to chemical circulation within environment, and soil itself can convert to pollutant [32].

Constituent organisms can participate in the incorporation of microplastics after their emission into soil. A scientific research [34] presented that earthworms (*Lumbricus terrestris L.*) transport small plastic particles down the soil (*Figure 2.3*). The observation showed the smaller the items, the deeper in the soil profile.



Figure 2.3 Microplastic items (polyethylene of 1.18–1.4 mm size) incorporated into soil via earthworm transport [34].

Overall, these arguments lead to opinion that presence of microplastics affects changes in physical, chemical and biological processes. In dependency on concentration of dissolved organic matter (DOM) the soil quality is influenced. DOM is even low proportion of the total soil organic matter (SOM), representing <0.25 wt%. Nevertheless, the pivotal function resides in biogeochemistry where among the other things, the cycle of soil organic carbon and nutrient

transport are directed. However, it is very little known about the interaction between plastic particles and DOM. Owing to that the impact of microplastics on DOM has been studied. The microplastic presence encourages enzyme activities in soil (*i.e.* higher microbial activity), and thus they might accumulate in soil. Further, higher releasing of nutrients into soil was observed [35].

2.2.1.2 Important potential sources

China, chiefly its inhospitable areas, is well-known for using plastic-film mulches in agriculture (*Figure 2.4*). Since 1982, the plastic utilization in agriculture branch has been rapidly increasing; in 2011 China applied 1.2 Mt of plastic-films on farmland [36]. So far, the most plentifully used polymer is PE [23]. Only China, Japan and South Korea employ annually 700,000 tons of LDPE for mulching, and together hold the first place with 80% of global plastic mulching [36]. On the contrary, Liu et al. [5] assert PVC as the most commonly used polymer for mulching in China. Farmers choose PVC foils instead of PE material to decrease costs of planting. In addition, PVC renewable films have also become popular. Nevertheless, the situation may amend soon and usage of PVC material in agriculture would be regulated by National Soil Pollution Prevention [37]. In several countries such as United States, plastic mulches with PVC content have been already banned [36].



Figure 2.4 Plastic mulching in China [5].

Even though the technique widespread around the world² evinces many advantages such as higher yield, better crop quality, protection of seedlings, keeping up or slightly increasing

² European area, covered with plastic mulches, comprises of 4,270 km², and thus it ranks among the largest proportion of agriculture surface. On a worldwide scale, the utilization was estimated being 5.7% per year until 2019 [39].

temperature and humidity of soil, protection of soil against erosion, or reduction of used herbicides and fertilisers [23], there exist certain concerns. Disintegrated microplastics persist in soil [29; 38], and thus can accumulate there [23; 35; 38]. Moreover, variety of contaminants occurring in surrounding environment can be sorbed on their surface [23; 33; 35; 38]. Microplastics themselves can leach additives into soil [23] or volatile chemicals can be desorbed, respectively [36].

Compost processing as a fertilizer on farmland can be another source of microplastics. Especially the compost of bio-waste origin has been found it contains a lot of residual plastic waste, even the compost undergoes a treatment. Annual estimation of visible plastics spread out together with compost on field could be up to 6.3 kg ha⁻¹. However, smaller plastic particles were not considered in the study though [39].

Similar study [33] was performed for estimation microplastic pollution from sewage sludge applied on agricultural sites. Accordingly, using rough data and their extrapolation the authors assessed an annual microplastic input on agricultural field of 63,000–430,000 and 44,000–300,000 tons to EU and North America, respectively.

2.2.2 Microplastics as an environmental hazard

Plastic materials, employed in everyday life, are usually supplemented with various additives and plasticisers enhancing their properties [1; 3]. However, some of the added chemicals have been recognized as toxic or endocrine disruptors [20]. Among the most discussed are phthalates, bisphenol-A, polybrominated diphenyl ethers (PBDE) and metals [20; 23; 33]. Even though some of these compounds are strictly regulated [40], polymers can contain up to 3% by weight [33].

The additives very often bound to polymeric structure by physical interactions. Consequently, they can leach out and contaminate surrounding compartments [17; 20]. PVC, the most common polymer used as mulching foil in China [5], was studied for its undesirable effects in soil. The soil was treated with PVC mulching film residues for 30 and 60 days, respectively. After exposure, phthalate acid esters were analysed in soil as released plasticisers from PVC film. Although the increasing amount of foil interrelated with concentration of phthalates determined in soil, the longer period of incorporated film had decreasing effect on resulting concentration of phthalates [41]. A real example of leaching harmful compounds into soil was observed close to industrial estate and roads around Sydney. Determined concentrations of PVC in soil of 0.03–6.7 wt% correlated with amount of found non-volatile organic chlorine compounds [42].

Released pollutants can subsequently contaminate aquatic environment or be uptaken by growing plants [20]. Du et al. [43] documented the uptake of di-(2-ethylhexyl) phthalate (DEHP), a sort of commonly used phthalate ester, from plastic mulches by 10 types of vegetable plants. They investigated plastic mulch foil, which is widely available and applied in China regions. The observation confirmed the uptake of DEHP by all 10 species of vegetable. In some cases, the determined concentrations in plants reached up to 736 µg g⁻¹ (dry weight), while the daily limit of DEHP is 1,200 µg for a 60 kg person. Noteworthy, DEHP is considered as a potential hazardous for human health, regarded as an endocrine disruptor, toxic, teratogenic and carcinogenic [43].

The environmental hazard may also be caused by adsorption of pollutants on the surface of microplastics [20; 38] and furthermore, be ingested by biota, which means transport such chemicals into their bodies [27]. The adsorption together with leaching contaminants are dependent on surface area, *i.e.* the larger the surface of particles per unit of mass, the higher the potential for sorption interactions. Therefore, microplastics or even nanoplastics may uptake greater concentration from surroundings [17; 20; 25]. Accordingly, the possibility of adsorption on microplastics and nanoplastics has been studied. Napper et al. [44] examined PE microbeads extracted from cosmetics, which were exposed to mixture of phenanthrene and dichlorodiphenyltrichloroethane (DDT) in seawater. The results demonstrated sorption both pollutants [44]. Another evidence of adsorption was showed in a study [45], where micro-PE and even nano-PS were able to sorb polychlorinated biphenyls (PCBs) from freshwater and seawater.

Up to now the enrichment effect of small-sized plastics within terrestrial environment was very poorly researched. Hodson et al. [46] performed an experiment with Zn. The research shows that there is a potential for accumulation of metals from soil to microplastics and even the enriched particles may be considered to be the source for soil fauna.

As we already mentioned microplastics can represent a vector for transport pollutants into organisms [1; 46], and even increase bioavailability of toxicants. That was discovered, for example, in guts of earthworms. The microplastics desorbed 3–30 times more Zn than enriched soil [46]. Notwithstanding this finding, some studies were criticized for overestimation the microplastic concentration which does not respond with real amount founded in nature, and thus the bioaccumulation might not be so high [1; 20].

Particle size in combination with particular organism species may have fundamental impact on ingestion the particle [20; 28]. The large plastic items evince low toxicity while the decreasing size might increase risk of toxicity due to easier intake. Such concerns have primarily come with plastic debris in nano-scale. Nanoplastics might pass through body tissues and selective membranes, and furthermore migrate along with bloodstream. Behavioural changes were observed in fish, where nanoparticles occurred in their brain [17].

Albeit the nanoplastics and their effect have become very discussed, the documentation in real environment is lacking. So far, there exists only one study [47] proving their presence in real environment. The nanoplastics, such as PE, PS, PVC, and PET, were determined in the North Atlantic subtropical gyre. The presence of nano-PVC and nano-PET, the material denser than seawater, shows likely different properties and behaviour than larger debris [47].

However, not only sorbed chemicals, even microplastics themselves can cause physical damage in organism. On the contrary, the harmful threat by physical way usually increases with larger plastic [20]. Ingestion of microplastics may replace a real food of organisms and thus reduce food intake which lead to unwanted diet. Besides, the intestinal tract can be blocked with microplastic. Additionally, sharped and pointed items damage inner tissues and intestinal tract [22].

2.3 MICROPLASTIC ANALYSIS

The increasing interest in the microplastics in environment has also brought an increasing interest in the analysis of microplastics. However, currently many questions, regarding the problematic of the microplastic analysis and developed standardisations, are still open. The problems regard to the determination of size of microplastics, their appearance, sampled environmental compartment, and others. Indeed, some of studies³ have been addressing such issues and concluded that some results might be erroneous [48].

2.3.1 Sampling and pre-treatment

To begin with all analysis of microplastics occurred in environment, the first step includes sample collection. Since the microplastics cover various appearances, they consist of different polymers (and thus they vary in such properties, *e.g.* density), and are globally widespread in environmental compartments, the sample collection deserves a special attention. Depending on appropriate sampling strategy, it can be obtained unfailling and representative sample adequate for further analysis [1].

Most studies have concerned to aquatic systems, shorelines and sediments; however, soil and atmosphere investigation are lacking. The reason is that the soil is a very complex nonhomogeneous medium, composed of mixture of organic and mineral parts, therefore the representative sampling as well as extraction of microplastic require more effort [1].

Usually, the first step is a removal of coarse impurities (*e.g.* animal and plant residues, stones and anthropogenic waste) from the sample. This visual control can lead to misinterpretation because distinguishing the plastic material from the others is not always easy [49]. Accordingly, most scientific researches avoid this kind of microplastic separation from the samples. Nevertheless, the authors have to carry out sample pre-treatment another way because their analysis usually requires it [48].

To obtain homogeneous sample, the material is sometimes grinded. This can cause formation of secondary microplastics. The problem is that these fine particles might be better incorporated into the matrix thereby a subsequent extraction and/or direct analysis may have more difficulties with quantification and characterization [42].

Flotation, a procedure applicable for recovering microplastics from sediment, is likely less efficient due to presence variety kind of microplastic [17]. In other words, dissimilar densities of plastic material prevent comprehensive separation [50]. Another pre-treatment can be a chemical degradation, which is used for removing organic matter (*e.g.* hydrogen peroxide treatment). However, this purification might result in degradation of mass of plastic items [17].

Fuller and Gautam [42] tried to extract microplastics from municipal waste and soil using pressurized fluid extraction (PFE). PFE works in a mode, where a solvent is at subcritical temperature and high pressure through which the solvent changes itself properties. PFE is typically applied for extraction the semivolatile organic compounds from solid matter. The authors claim the technique can quantitatively separate microplastics from diverse and even complex matrix and so the instrument is likely to be universally applicable. In addition, particles <30 μm can be extracted which is in contrast to other physical treatment processes [42].

³ Microplastic residues were determined in 24 German beer brands [74], in honey and sugar [75], although later this statement was falsified with assertion that the authors had used inadequate analytical procedure [76].

Overall, although microplastics can occur in various concentrations in environment, sample concentration and purification are often necessary to obtain sufficient measurable mass for subsequent analysis [27]. Additionally, matrix effect can play a crucial role, especially an amount of SOM [39]. On the other hand, the less the analytical steps, the less such errors may set in. Moreover, the analytical effort tends to cheaper and faster determination [27].

2.3.2 Analysis

In order to choose appropriate analysis for microplastics, many aspects must be considered. The most common assertion is a fact that the analytical set up is dependent on particle size, *i.e.* with decreasing dimension of the particle the analysis is more demanding. Thus, visual methods, mentioned below, are inappropriate in case of real microplastics or even nanoplastics [48].

2.3.2.1 Visual methods

Renner et al. [48] made a review of scientific papers published between 2015 and 2017 to summarize the most used techniques for microplastic determination. They found out that the visual detection took the first place with 79% of all studied researches. The high number of utilization is not so surprising because the method is characterized by one big advantage – it is very simple [1]. However, it should be noted that in half cases, visual methods were used as supporting tool for further identification [48].

Visual examination is usually performed with human eye and often accompanied by an optical microscopy [17; 48]. Hence, the effectiveness is quite low with error being 20%–70% [1] or more⁴, and recommended application is down to 500 μm [1; 48] or alternatively 100 μm [1]. The main discussed issue has been overestimation of fibres and contrarily underestimation of fragmented microplastics [1]. Renner et al. [48] alert that although there exists a protocol related to right methodology to avoid the errors using visual determination for microplastics, only one quarter of the all papers mentioned it. In addition, the recommendation also reports some criteria for polymer identification [1]. Additionally, if a laboratory does not apply the quality criteria for high cleanliness, the samples may easily be contaminated and show false positive results [51]. Therefore, Crawford and Quinn [1] also present a contamination prevention protocol in their publication.

In addition to the above-mentioned issues, another drawback can take place when large volume of samples is supposed to be analysed via this technique, and thus it is more time consuming. Consequently, a smaller and representative sample is randomly chosen [1].

Scanning electron microscopy

Scanning electron microscopy (SEM) is a technique, providing a scanning of a small surface of a sample to create an image. It can be used for smaller plastic fragments due to resolution lower than 0.5 nm with magnification of 2,000,000 times [1], and thereby brings more information about sample surface [48]. The technique helps to distinguish plastics from another material, although the preference is normally given to the other devices, such as infrared spectroscopy [48].

⁴ In study of atmospheric fallout in China [31] only 27% from all collected fibres which were considered as microplastics, were truly plastic origin and the remnant was eventually cellulose. In this case, microscopic determination served more likely for primarily estimation, which was carried out further identification with an infrared microscopy.

In addition, the special application is an investigation biofilm growing onto the surface of microplastics *Figure 2.5*. This may be advantageous for understanding disintegration and degradation taking place in nature [1].

Despite such benefits, SEM ranks among costly analytical optical methods with demanding operation requires a lot of experiences, and relatively high demands for place [1].

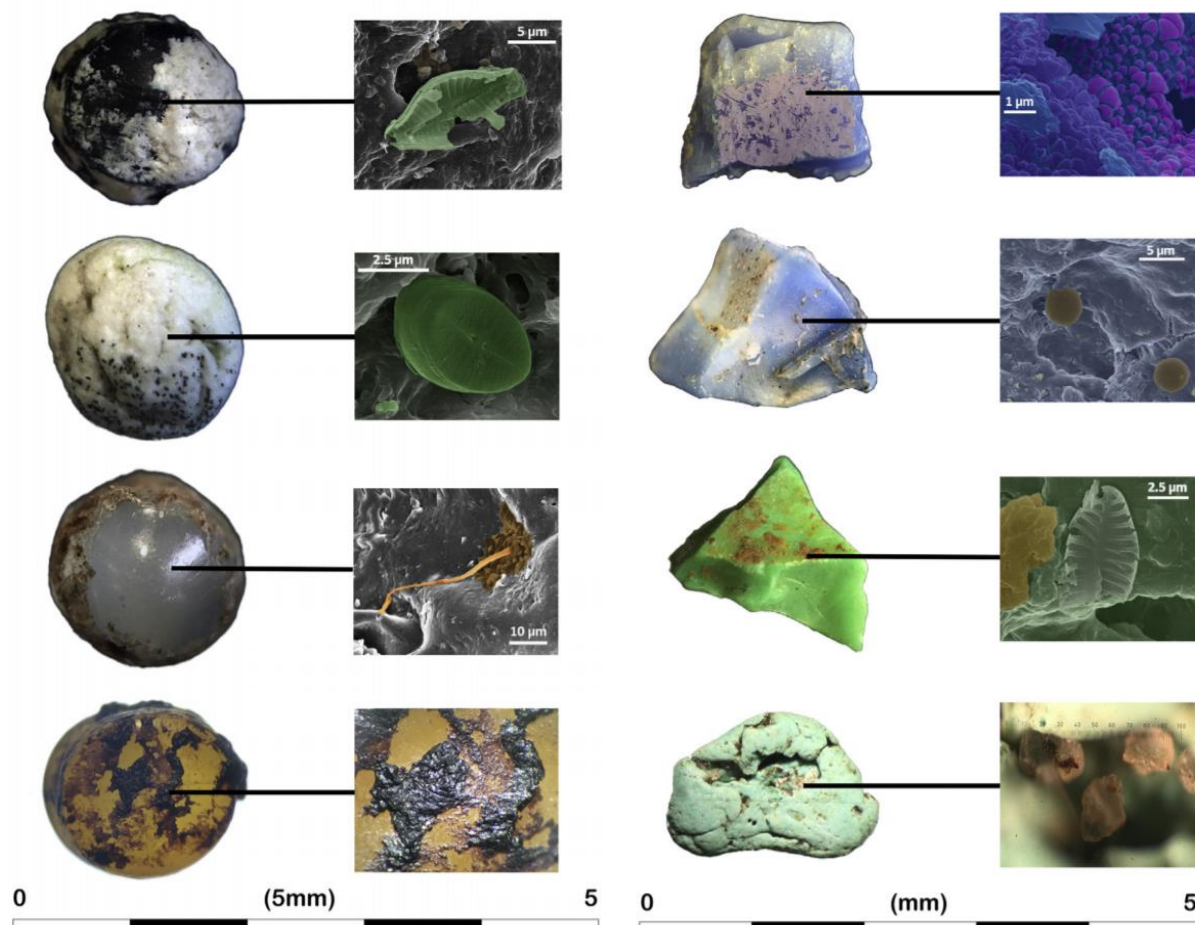


Figure 2.5 Detection of biofilm settled upon the surface of primary (left) and secondary (right) microplastics using scanning electron microscopy (SEM) [1].

2.3.2.2 Fourier transform infrared spectroscopy, Raman spectroscopy

Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy have become increasingly popular for characterization of microplastics [1; 48; 50; 52; 53]. Both techniques are characterized with comparatively simple operation and provide high accuracy [1; 50; 52], require low sample amount and additionally, no special preparation for measurement. Therefore, it can also be recommended for soil samples [53]. This is in contradiction to David et al. [51] who claim that soil sample, due to its complex structure, should undergo pre-treatment process to eliminate strong matrix effect owing to presence SOM. Such SOM can hide microplastics and furthermore, exhibit itself random signals which are results of SOM autofluorescence. This is confirmed by Elert et al. [52] who observed a significant fluorescence of contaminants and agree with essentiality of sample pre-treatment. Nevertheless, FTIR was

successfully applied for soil samples contaminated with microplastics and extracted using PFE [42].

FTIR is a technique where an infrared light interacts with a sample. If the light is absorbed and molecules in the sample can change their dipole moment, the molecules will begin to vibrate with characteristic frequency. In the contrary, Raman spectroscopy obtains spectra by scattered light of specific frequency. All process starts with generation a laser beam which can cause vibrations in molecules again and thereby, changes in polarizability of the molecule take place. Such vibrations subsequently cause the scattering [1]. Indeed, the characteristic signals of plastic polymers can be identified using these methods and additionally, the instruments can provide information about size distribution of microplastics [50; 52].

In conclusion, it can be highlighted as the advantage being non-destructive methods [50] suitable down to 20 μm (FTIR) and 1 μm (Raman spectroscopy), respectively [39]. Both spectroscopic methods provide satisfying results of microplastic identification [48], however additional effort should be spent for elimination such drawbacks.

2.3.2.3 Challenges in new approaches

Among more frequent methods for identification and quantification microplastics, a new analytical approach is gaining gradual interest. Typically, it is gas chromatography coupled with mass spectrometry (GC/MS) preceded by methods based on thermal decomposition, such as pyrolysis (*py*) and/or thermal extraction and desorption (TED) [48; 51]. The approach finds its application and its limits are also gradually recognized.

Thermal decomposition-gas chromatography/mass spectrometry

Py-GC/MS is a destructive method. Sample is thermally decomposed in an inert atmosphere or in vacuum to produce compounds, which are characteristic for each initial material. Typically, the temperature reaches 200–600 $^{\circ}\text{C}$. Then, chromatographic column separates the products that are subsequently analysed via determination mass-to-charge ratio (m/z) using mass spectrometry [1; 53].

Only a small amount of sample is needed, without pre-treatment and additionally, the instrumentation does not require any homogenization which may be advantageous for complex matrix such as soil [53]. Contrarily, some authors [48] point out the importance of sample treatment before measurement due to high matrix effect. There is also potential for misinterpretation when simultaneously analysed polymers degrade into the same products [48].

Fries et al. [54] tested *Py*-GC/MS as an analytical tool for determination of microplastics in marine sediment from Norderney (Germany). After extraction, based on density separation, the particles were sorted using SEM and subsequently separately analysed. Nevertheless, the particle selection is time consuming and studied particles cannot be identified together.

First publication about using TED-GC/MS for determination and quantification microplastics in soil was documented by Dümichen et al. [50]. The study focused only on PE, however, obtained calibration curves served for the first quantifiable evaluation. The benefits proceed from the combination both: (*i*) pyrolysis where high mass of the sample can be used (up to 100 mg [52]) thereby it provides a representative sample composition, and (*ii*) GC/MS, a method convenient for terminal detection with high resolution. Such advantages lead to a new opportunity for identification and even quantification microplastics in heterogeneous and

complex sample and avoid time consuming pre-preparation. Besides, the approach guarantees acceptable experimental efforts together with obtained results [50].

Both techniques are still at the beginning, hence more investigations are needed, especially, the mixture more plastic polymers and soil with different content of SOM [50]. The research group has been working on determination the other plastic materials, such as PP, PE, PS, PET, and their mixture to obtain suitable results for further quantification measurement [55].

Thermogravimetry-mass spectrometry

Alternatively, David et al. [51] have been coming with a thermogravimetry-mass spectrometry (TGA-MS) approach to develop a new method for quantification micro-PET in soil without pre-treatment.

Coupling TGA with MS via heated capillary enables to transfer evolved gases for further analysis in mass spectrometer [51]. TGA provides information about the dependency of the mass on the programmed temperature [56]. The sample is thermally decomposed either in an aerobic or in an anoxic inert atmosphere with constant increasing temperature rate, which can reach up to 1,100–1,500 °C [51; 56].

Subsequently, the gases are analysed by MS. The principle of MS is an ionization of an investigated analyte, sorting generated ions based on m/z and their detection [57]. The first step, the ionization, strongly depends on physicochemical properties of analyte [57; 58]. Due to producing gas phase in TGA furnace, the electron ionization (EI) is commonly used [51; 56]. The EI source emits electrons from heated filament, which are accelerated by electron potential towards an anode. During this trajectory, the electron beam collides with molecules of the sample and ionization takes place. The new formed molecular ion (so-called radical cation) can subsequently fragment two pathways into: (i) a radical and an ion, or (ii) a molecule and a new radical cation (*Figure 2.6*), and thus molecular ion can miss in mass spectrum [58].

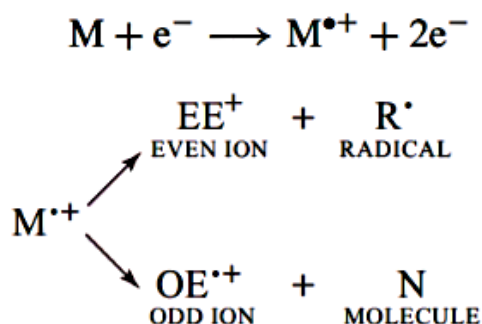


Figure 2.6 Electron ionization of a molecule with electron to form a radical cation and subsequent fragmentation to form radicals or a molecule and a new radical cation [58].

Afterwards, the new formed and accelerated ions pass through mass analyser and are separated according to their m/z ratio. There exist a great number of analysers working different principles with different limitations and advantages. Then, sorted ions are detected using detector transforming ions into measurable signal [58].

David's et al. approach [51] also became an inspiration for this thesis. The advantage of TGA is that it could be used for distinguishing plastics and soil with the similar pyrolytic products because they can degrade at different temperatures. However, the authors [51] alert that results may be influenced with SOM content as well as a sort of microplastic material and

thus it can have a negative effect on achieved limit of detection (LOD) and limit of quantification (LOQ) so further investigation is needed.

Also, the atmosphere conditions and/or the temperature rate can affect the pyrolytic products and their stoichiometry. For example, it was observed for pyrolysis of PVC [59]. *Figure 2.7* shows dependency of weight (TGA curve) and weight loss (first derivative TGA curve; dTGA) of PVC on heating rate. It can be seen that increasing heating rate increases temperature of degradation.

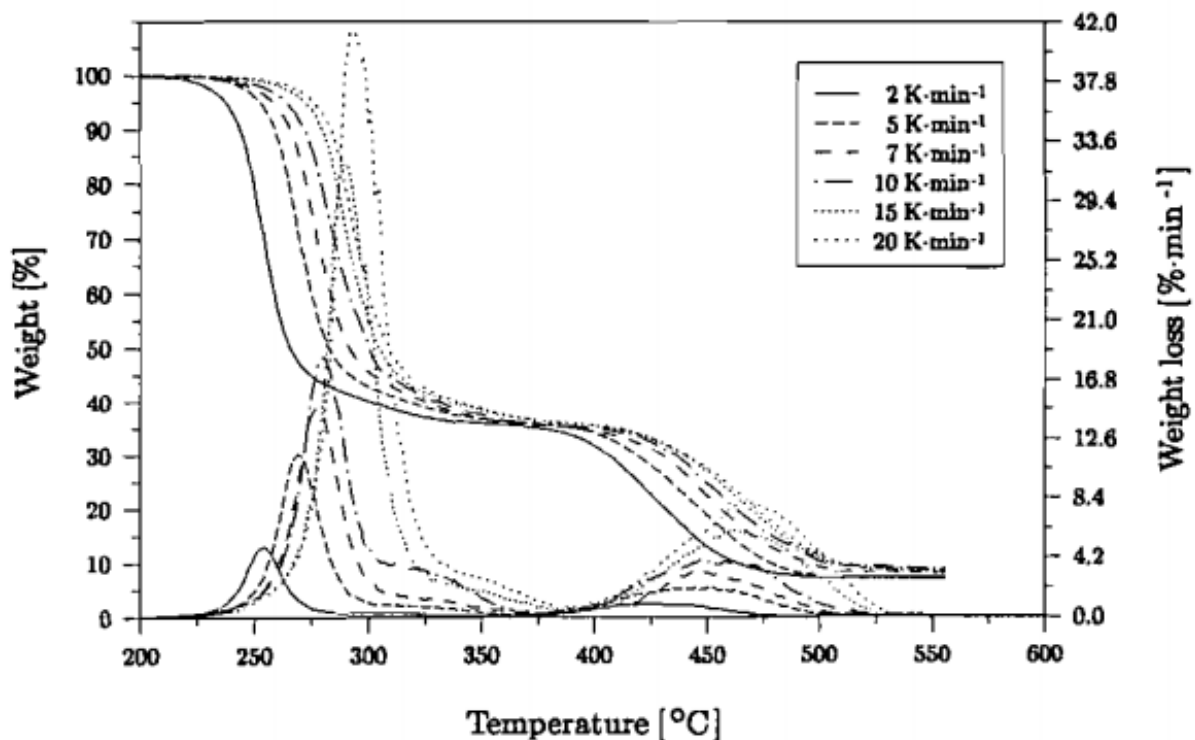


Figure 2.7 TGA and dTGA curves of PVC degradation under helium atmosphere in dependency on heating rate [59].

3. THE AIM OF THE EXPERIMENT

The presented thesis deals with an analytical determination and quantification of micro-PVC and micro-PS in soil. These plastic materials rank among the most demanded and used plastics [4], therefore, they are potential environmental contaminants.

Formerly, PVC was very popular plastic material due to its properties. Nevertheless, several issues have been found, *e.g.* concerning PVC recycling, waste management, and leaching toxic additives from PVC materials. Currently, PVC popularity increases again. In case of PS, the environmental pollution is mainly caused by drifting of the material from construction sites and landfills. The formed plastic particles and even leaching additives are considered to be potential environmental pollutants.

The aim of the experiment is the application of the pilot findings reported in the study of David et al. [51]. They dealt with quantitative determination of micro-PET in soil using TGA-MS. Based on the study, the goal is to develop a method for the direct quantitative analysis of micro-PVC and micro-PS in soil.

TGA-MS is a new approach for the microplastic quantification in soil. However, the development is in a stage of a pilot study so far. Due to the soil complexity and non-homogeneity, the analysis of microplastics cannot be usually performed without a sample pre-treatment. The TGA-MS method represents a new potential in this issue and accordingly, the analysis seems to be possible without the time consuming and demanding sample purification and/or pre-treatment.

We suppose that the TGA-MS approach may play a crucial role in the field of microplastic analysis in the future, even though there exist some limits currently. Hence, it is a necessity to focus on the others soil types with various SOM content as well as testing the method for quantification microplastics in a mixture.

4. EXPERIMENTAL PART

4.1 INSTRUMENTS AND TOOLS

Thermogravimetry coupled with mass spectrometry via capillary

- TGA analyser STA 449 F3 Jupiter (NETZSCH, Germany)
- TGA crucibles (Netzsch, Selb, Germany)
 - 85 μ L alumina crucibles (NETZSCH, Germany)
 - Inert gas argon Ar: purity 5.0 (Tyczka Industrie-Gase GmbH, Germany)
 - Synthetic air special (N₂/O₂); purity 4.5 (Tyczka Industrie-Gase GmbH, Germany)
- Mass spectrometer QMS 403 C Aëolos (NETZSCH, Germany)
 - Ion source: cross-beam electron ionization
 - Mass filter: quadrupole with hyperbolic rods and pre-filter
 - Detector: secondary electron multiplier
- capillary (SGE Analytical Science, Australia)
 - 75 μ m fused silica capillary; controlled heating to 300 °C

Others

- Analytical balance AX105DR (Mettler Toledo, Switzerland)
- Electronic analytical microbalance SE 02-OCE (Sartorius, Germany)

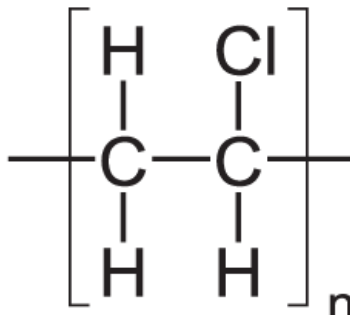
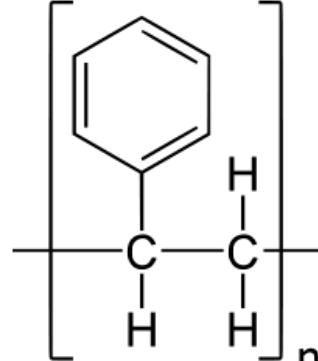
4.2 CHEMICALS AND STANDARDS

- Poly(vinyl chloride) – low molecular weight, powder (Sigma-Aldrich, Germany)
- Poly(styrene) – powder (GoodFellow, England)
 - Mean particle size: 250 μ m
- LUFA sandy loam soil; type 2.2 (LUFA Speyer, Germany)
 - Organic carbon content 1.61 \pm 0.15%
 - Dominant particle size 0.02 \pm 0.63 mm
- Calcium oxalate hydrate CaC₂O₄·H₂O (Sigma-Aldrich, Germany)

4.3 MICROPLASTIC ANALYTES

Two sorts of plastic were chosen for microplastic analysis in soil. We took into consideration the main market demand for the plastic materials as well as a potential for soil pollution. Another criterium was an assumption of a formation of characteristic pyrolytic products which would vary from soil pyrolytic products. Based on that, we chose PVC and PS for further investigation (*Table 4.1*).

Table 4.1 Basic information about PVC and PS.

	Polyvinyl chloride	Polystyrene
Abbreviation	PVC	PS
Chemical formula	$(C_2H_3Cl)_n$	$(C_8H_8)_n$
Structure		
Application	PVC floors, window frames, cable insulation, pipes, greenhouse and mulching foils for agriculture in China	disposable cups, dishes and cutlery, various packaging, building insulation

4.4 METHOD

4.4.1 Preparation of samples

One calibration set was prepared for each microplastic. The model sandy loam soil was individually spiked with 0.23 to 7 wt% of micro-PVC or micro-PS. As a result, it was prepared seven and eight different concentrations of micro-PVC and micro-PS, respectively. The samples were weighed into glass vials (volume 20 mL) and the total weigh was between 4,988.23 and 6,082.18 mg. Subsequently, the prepared samples were thoroughly mixed. Samples were stored in dark place with constant room temperature.

4.4.2 Thermogravimetry-mass spectrometry analysis

We weighed between 20–40 g of sample into 85 μ L alumina crucibles. The analysis of microplastics in soil was performed with TGA-MS (NETZSCH, Germany). The TGA was coupled with MS via 75 μ m fused silica capillary (SGE Analytical Science, Australia). The TGA chamber was twice evacuated and filled with argon 5.0 as an inert gas. The pre-selected m/z was varied in dependency on analysed microplastics. The set parameters are shown in *Table 4.2*.

Table 4.2 TGA-MS settings.

Temperature range	40–1,000 °C
Heating rate	5 K min ⁻¹
Carrier gas	Argon 5.0
Gas flow	20 mL min ⁻¹
Capillary temperature	300 °C
<i>m/z</i>	PVC: 35, 91, 104, 112, 128, 18, 28, 44
	PS: 51, 91, 103, 117, 132, 18, 28, 44
Detector settings	For <i>m/z</i> 18, 28 and 44 <ul style="list-style-type: none">▪ secondary electron multiplier: 1,400 V▪ dwell time: 1 s▪ resolution: 50 a.u.
	For <i>m/z</i> 35, 51–132 <ul style="list-style-type: none">▪ secondary electron multiplier: 2,400 V▪ dwell time: 5 s▪ resolution: 250 a.u.

4.4.3 Transfer capillary control experiments

The coupling TGA-MS can be done via a capillary-less orifice or a heated capillary. The latter can theoretically cause partial blockage issues. The gaseous products might condensate during the capillary transfer since the capillary is heated at 300 °C whereas the temperature reaches up to 1,000 °C in the TGA chamber. Consequently, there is a risk that the evolved gases block the capillary [51]. Owing to the argument, every microplastic analysis was followed with cleaning run; an empty crucible was heated with rate 10 K min⁻¹. Synthetic air was used to oxidize all the residual material in capillary instead of argon. The settings for cleaning run are shown in *Table 4.3*. In order to control potential residues and working capillary, we performed a pyrolysis of calcium oxalate hydrate afterwards. Used parameters for calcium oxalate hydrate are similar to analysis of microplastics and are shown in *Table 4.2*.

Calcium oxalate hydrate also served as an external calibration for samples.

Table 4.3 Settings for clean run.

Temperature range	40–1,000 °C
Heating rate	10 K min ⁻¹
Carrier gas	Synthetic air
Gas flow	50 mL min ⁻¹
Capillary temperature	300 °C

5. RESULTS AND DISCUSSION

5.1 PREPARATION OF SAMPLES

Generally, spiked samples can be prepared in two ways:

- a) weighing soil and microplastics directly into the TGA crucibles, or
- b) preparation of a greater amount of the spiked samples into glass vials.

David et al. [51] carried out the first option when they weighed micro-PET and soil directly into the crucibles. The advantage lies in accurate weighing out both constituents thereby the result mass concentration is precisely known. On the other hand, the soil cannot be so perfectly mixed with microplastics and consequently, the sample is not homogeneous. Additionally, this method is comparatively time consuming.

Accordingly, we chose the second option to prepare spiked soil samples prior to the analysis and store them into glass vials. The procedure is quicker than in the first case. Even though we obtained better mixed sample, its representativeness is not entirely guaranteed. In other words, the accurate mass concentration is not guaranteed in whole volume. Such drawback may have an impact on calibration curves.

5.2 A GENERAL THERMOGRAVIMETRY-MASS SPECTROMETRY RECORD

The TGA curve shows the dependency of the mass on the programmed temperature. If the mass of a sample does not change, there is a plateau on TGA curve. It means that the material is thermostable in the temperature interval. Contrarily, if the temperature causes physical and/or chemical changes (*e.g.* thermal decomposition), the resulting curve shows mass changes. For example, there is shown the highest mass loss in range of 380–460 °C in *Figure 5.1*.

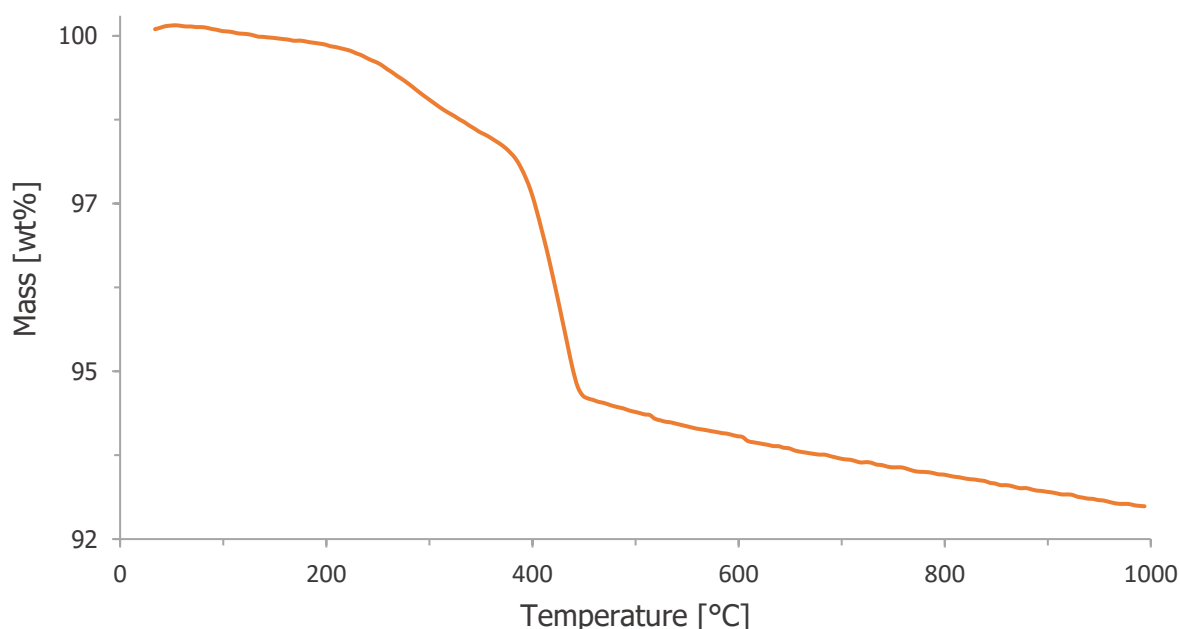


Figure 5.1 An exemplary TGA curve of PS in soil.

The TGA-MS record can be completed with MS curves. The MS curves show a signal response of observed masses in dependency on temperature. In *Figure 5.2*, there is seen that the

observed masses were detected in range between 248–488 °C with the highest intensity at 438 °C. Hence the signal response correlates with amount of evolved pyrolytic gases (*Figure 5.1*).

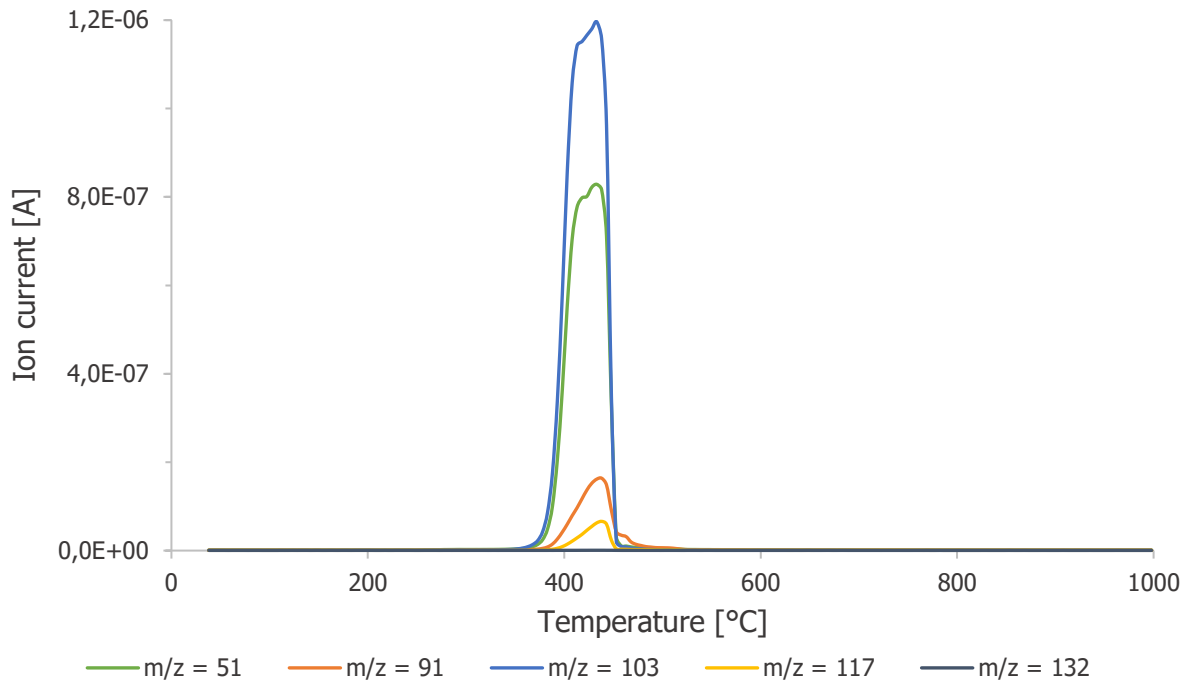


Figure 5.2 An exemplary MS curves of PS in soil obtained from TGA-MS record.

5.2.1 Thermal degradation of model sandy loam soil

For further study, it was necessary to perform the TGA analysis of LUFA sandy loam soil. *Figure 5.3* shows resulting TGA and dTGA curves. Two mass losses were observed. The first

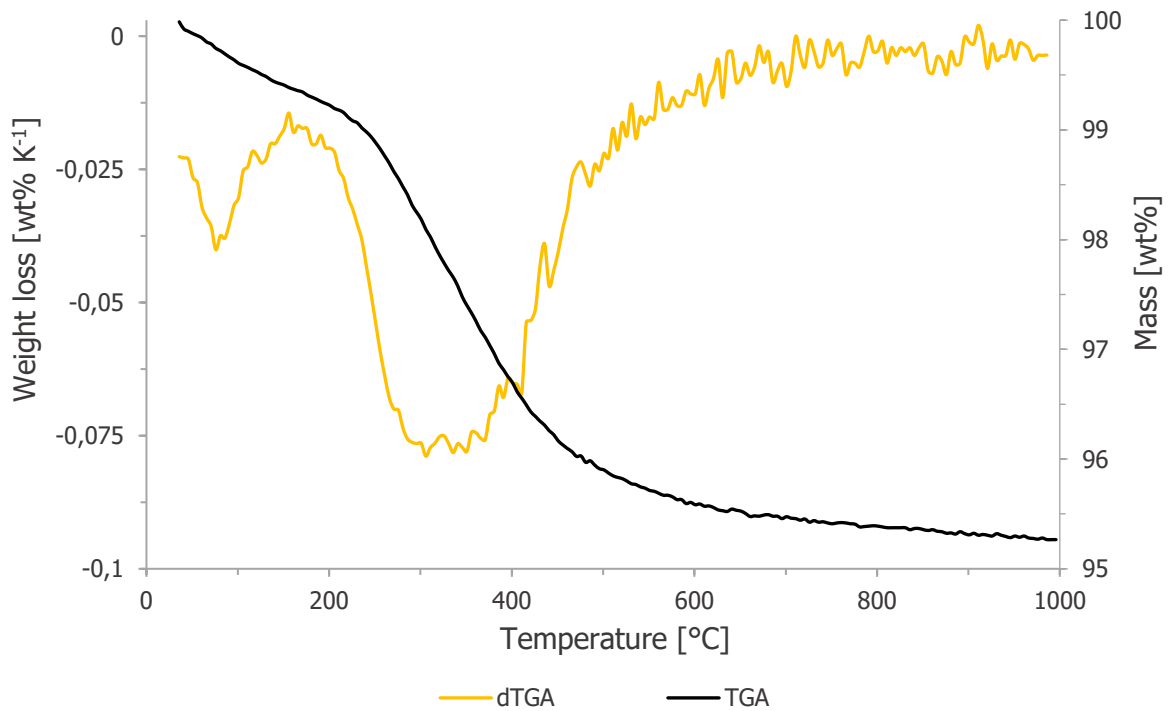


Figure 5.3 TGA and dTGA curve of model sandy loam soil.

mass loss takes place up to 200 °C. That is characteristic for loss of water, which can occur in various forms [60]. The second peak of dTGA curve starts around 200 °C and terminates around 600 °C. This step corresponds to degradation of thermolabile SOM (200–450 °C) and stable SOM (>450 °C) [60].

5.2.2 Thermal degradation of polyvinyl chloride

Thermal degradation of PVC was already comprehensively described [59; 61]. However, the pyrolytic products and their stoichiometry can change depending on used conditions [59]. To understand thermal degradation processes, the TGA analysis was carried out under conditions chosen in this work. The aim of study was a research on pyrolytic behaviour of pure PVC and PVC spiked in soil. The TGA and dTGA graphs are shown in *Figure 5.4* a *Figure 5.5*, respectively. For comparison, in the graphs are also records of soil thermal degradation.

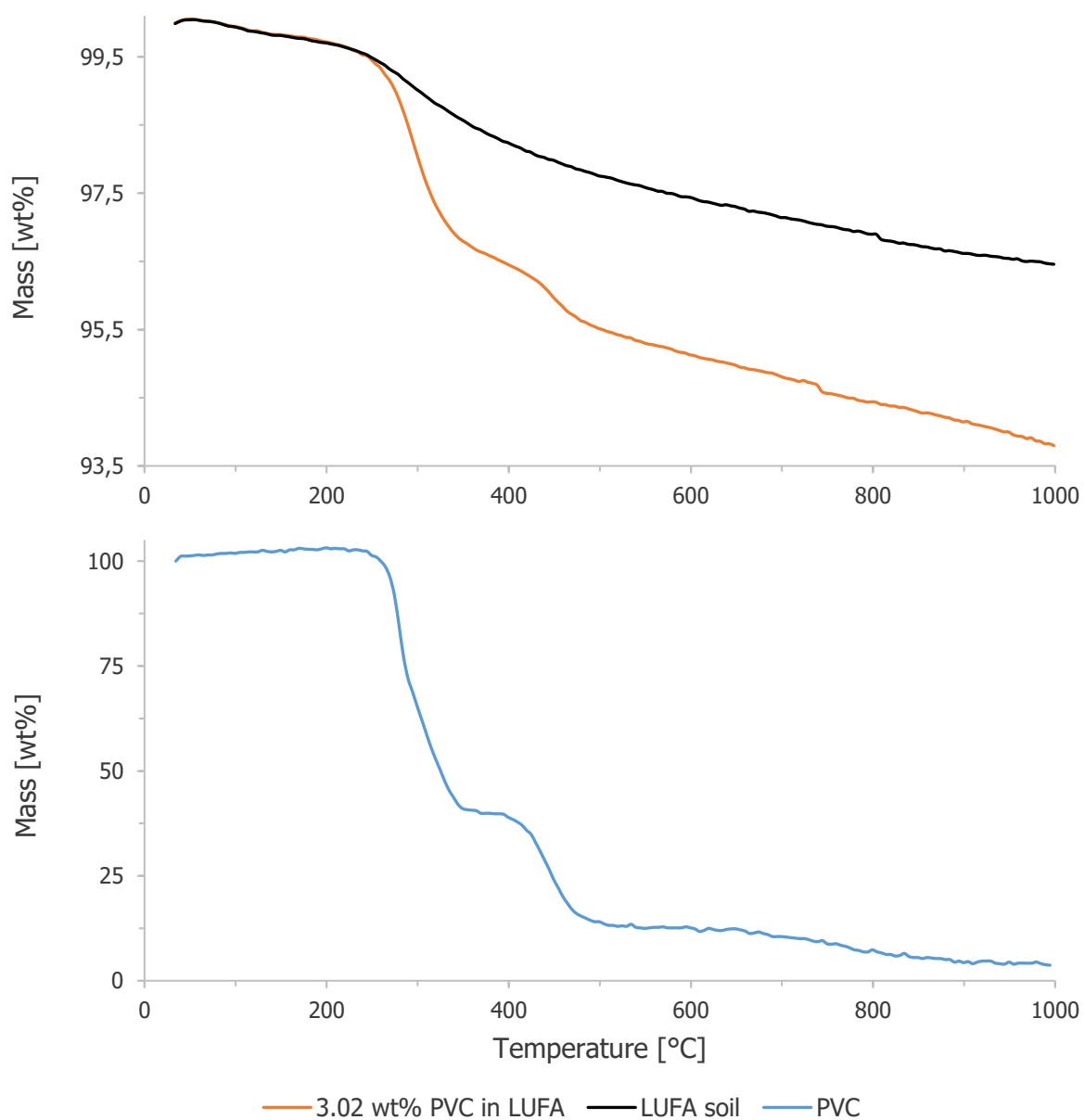


Figure 5.4 TGA curves of spiked soil with 3.02 wt% PVC, LUFA soil (upper) and pure PVC (lower).

Also, in our study we observed two degradation steps of pure PVC, which occurred in the range between 232–359 °C and 383–495 °C. The two-step degradation process was also described in literature [62], although both temperature intervals may slightly vary in dependence on TGA conditions [59; 62]. We noticed that the main mass loss took place in the first step and it was significantly higher than in the second step. It is caused primarily by evolving of hydrogen chloride [59; 61; 62].

The influence of soil on PVC thermal degradation was observed (*Figure 5.4 a Figure 5.5*). The dTGA peaks of PVC in soil, corresponding to the first and second decomposition step, were about 5–10 °C towards higher temperature (*Figure 5.5*). It indicates that the soil slightly increases the thermal stability of PVC. For instance, similar results were observed in mixture of PVC with commonly used plasticiser, where the effect was even more significant [62].

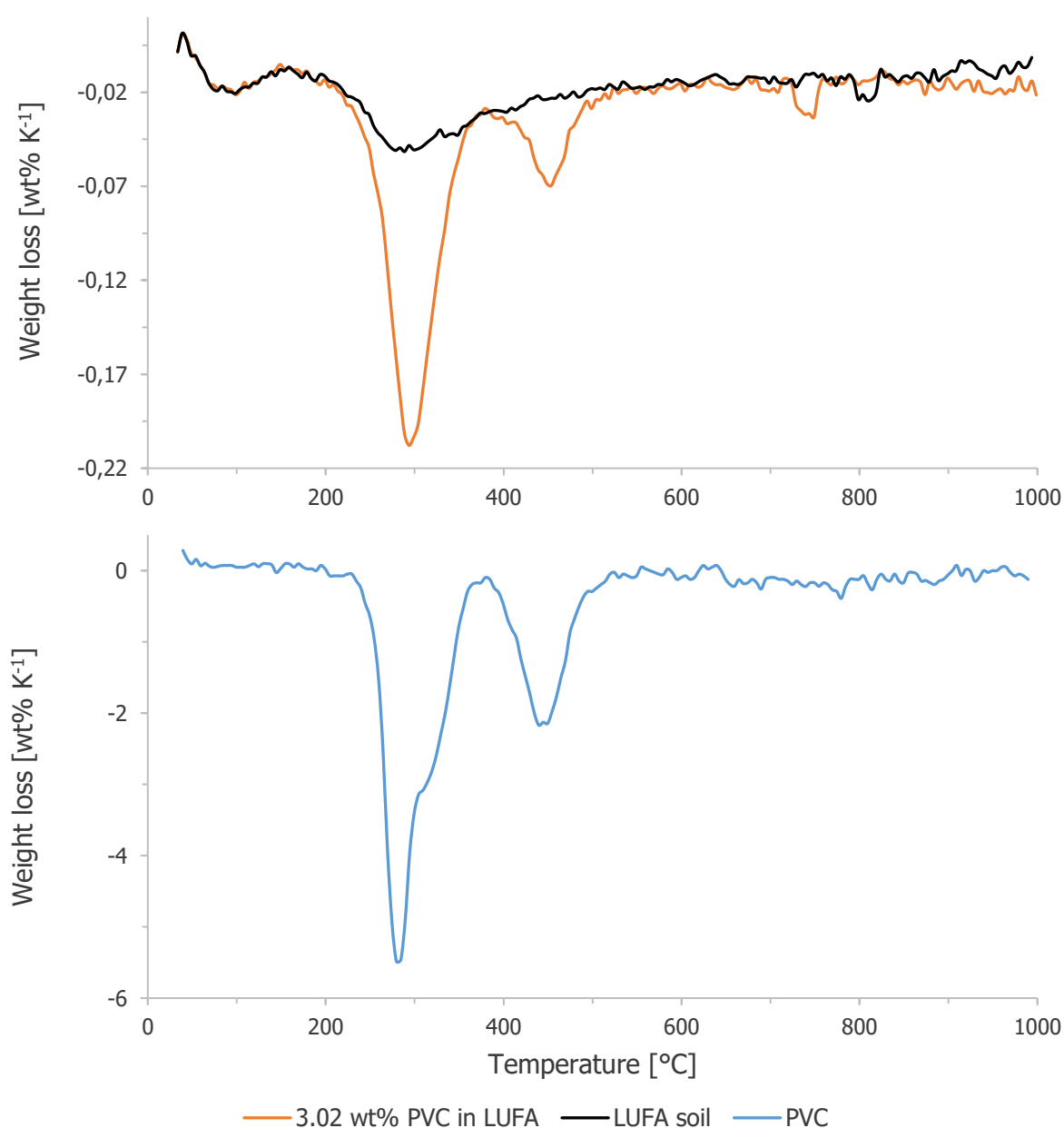


Figure 5.5 dTGA curves spiked soil with 3.02 wt% PVC, LUFA soil (upper) and pure PVC (lower).

5.2.3 Thermal degradation of polystyrene

The mechanism of PS thermal degradation is considered to be complicated due to radical reactions, which are additionally dependent on reaction conditions [63]. Accordingly, we investigated pyrolytic behaviour of pure PS and the results were compared with pyrolysis of PS spiked in soil. The TGA and dTGA graphs are shown in *Figure 5.6* and *Figure 5.7* respectively. For comparison, in the graphs are also soil thermal degradation records.

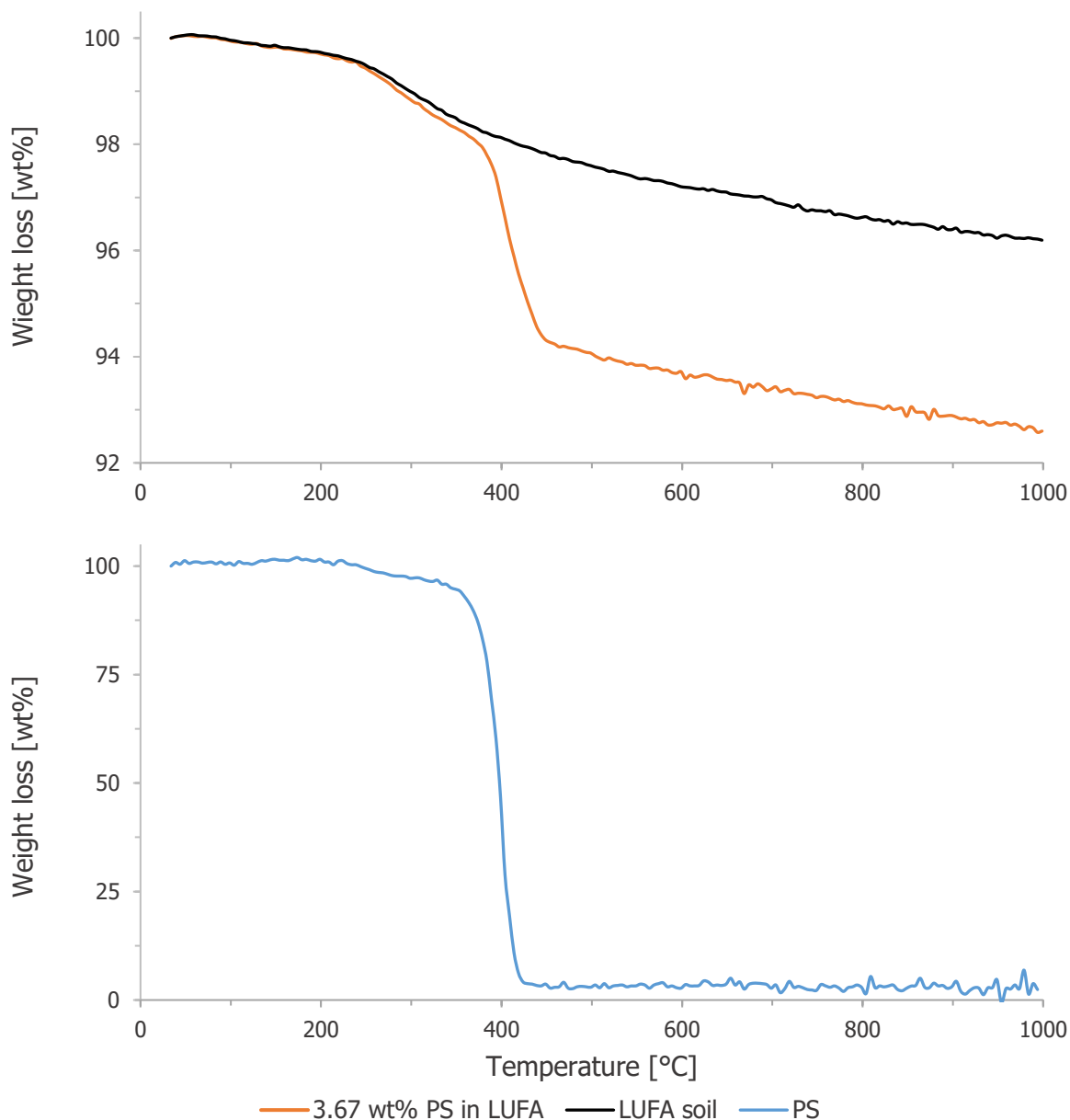


Figure 5.6 TGA curves of spiked soil with 3.67 wt% PS, LUFA soil (upper) and pure PS (lower).

It was found out that PS thermally degrades in a narrow range of temperature (344–436 °C), which is in line with previous researches [64; 65]. The degradation has characteristic fast weight loss, which can be caused by its homogeneous structure [64].

The effect of soil presence on resulting degradation process was recorded. In particular, the peak minimum corresponding to PS degradation takes place at around 30 °C higher temperature

in case of spiked soil (*Figure 5.7*). In addition, the intensity of dTGA peak of pure PS is higher, which means that the degradation is faster.

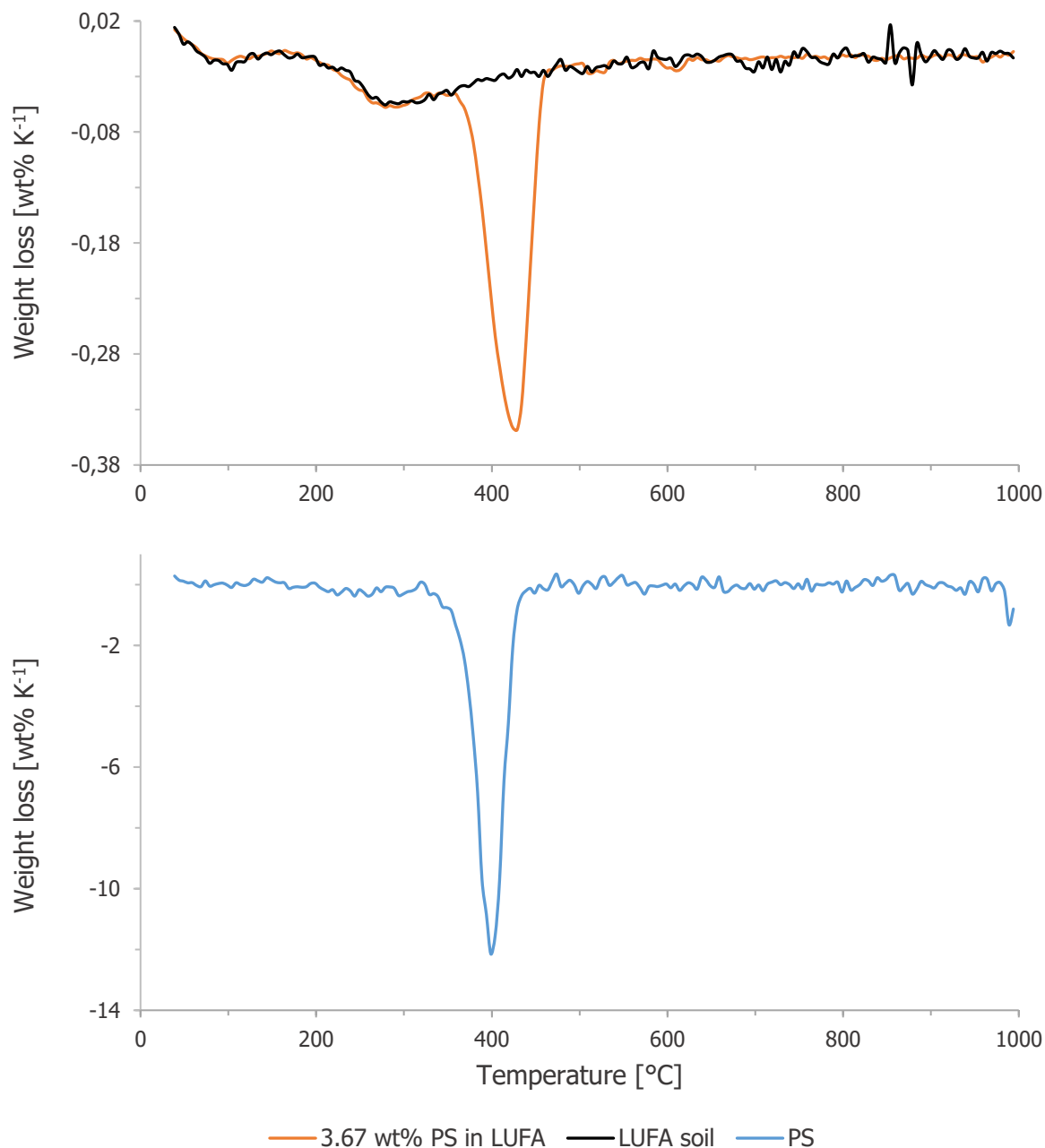


Figure 5.7 dTGA curves spiked soil with 3.67 wt% PS, LUFA soil (upper) and pure PS (lower).

5.3 QUALITATIVE ANALYSIS OF EVOLVED GASES

The coupling TGA-MS serves for studying degradation processes and analysis of products. First, scanning all masses in Scan-Bargraph mode can be used for identification of pyrolytic products. Even though the Scan-Bargraph scan in a range between 1–300 amu is available at quadrupole MS 403 C Aëolos (NETZSCH, Germany), the obtained data would not provide any useful information, due to:

1. The more m/z are supposed to be scanned, the less the data can be obtained for each m/z .
2. The less the data for each m/z are recorded, the less sensitive the analysis is.

Hence, only the most frequent m/z should be detected and the mass with low molecular weight would have much higher intensity than the characteristic mass of polymers.

Due to aforementioned issues, the selection of masses was necessary to carry out prior to the measurement. The masses were chosen based on the previous studies, where the authors reported the degradation products of PVC and PS. Then, it was necessary to take into account several facts to choose correct masses.

1. The reactions, taking place during the pyrolysis of mixture of soil and microplastics, have not been satisfactorily explained yet. There is an inert atmosphere and the temperature reaching high values in the TGA chamber. These parameters create a very reactive environment, which may cause non-specified interactions and reactions among material and evolved gases. Moreover, the products can vary in different conditions [63].
2. There may also be an effect of SOM. The SOM content may catalyse and/or react via radical reactions with the microplastics at high temperature and the terminal products can be affected similarly as in case of pyrolysis biomass with PS [65] or lignin with PS [66].
3. The pyrolytic products subsequently undergo electron ionization in MS, hence the m/z of their characteristic fragments are also formed and should be taken into account.

5.3.1 Selection mass-to-charge ratio for polyvinyl chloride pyrolytic products detection

Since the PVC pyrolysis takes place in two steps, we focused on products which are characteristic for each phase. In the first phase, hydrogen chloride is evolved, while the crosslinked polyene is decomposed in the second step. Overall, the PVC pyrolysis products can be categorized into five groups:

1. hydrogen chloride,
2. aliphatic hydrocarbons,
3. aromatic hydrocarbons,
4. chlorinated aliphatic hydrocarbons,
5. chlorinated aromatic hydrocarbons, such as chlorobenzene [62].

We perused several scientific researches [62; 59; 67] and based on that, we summarized the most common pyrolytic products of PVC, which are shown in *Table 5.1*. Accordingly, the most intensive m/z were found out using on-line libraries [68; 69].

Even though the literature [62; 59] suggests that the most pronounced PVC pyrolytic product is hydrogen chloride, we detected even higher intensity of signal $m/z = 35$. Since dehydrochlorination can occur in radical reaction [62], chlorine radical is also formed during the reaction [59]. The TGA-MS reactive environment, such as high temperature in the TGA chamber and heated capillary might have an influence on whole reaction course. The mentioned conditions might atomize chlorine or form chlorine molecule and therefore, the signal response of $m/z = 35$ is more intensive than $m/z = 36$.

We eventually chose these m/z : 35, 91, 104, 112 and 128 for further analysis, although we also detected such masses in trace concentrations in blank soil sample. *Figure 5.8* shows dependency of dTGA curve and chosen m/z curves on temperature for 7 wt% PVC in LUFA.

Table 5.1 Pyrolytic products of PVC and their m/z of the highest peaks.

Name	m/z highest peaks
α -Methylstyrene	77, 78, 103, 117, 118
Benzene	50, 51, 77, 78
Chlorobenzene	112, 114
Chlorine (Cl)	35, 37
Chlorine (Cl ₂)	35, 70, 72
Chlorophenyl	127, 162, 164
Cumene	91, 105, 120
Hydrogen chloride	35, 36, 38
Naphthalene	128
Octene	27, 28, 41, 43, 55, 56, 69, 70, 112
Styrene	51, 78, 103, 104
Toluene	91, 92
Xylene	51, 91, 105, 106

The dTGA curve has minimum at lower temperature than MS peaks (*Figure 5.8*). This is caused by transfer the gases via capillary and detector delay. We also observed that the MS peaks did not start at the same temperature for each m/z and their peak maximum differed as well. It could be caused by the adsorption on the wall of silica fused capillary [61]. Nevertheless, the chlorine peak ($m/z = 35$) starts and reaches the maximum at slightly higher temperature than the masses corresponding to aromatic structure of analyte. However, this is in contrast to observation of Czégény et al. [61], who observed this chromatographic effect for hydrogen chloride during pyrolysis of PVC. Hydrogen chloride is a polar molecule whereas chlorine, detected in our study, is non-polar. Thus, we should detect $m/z = 35$ at lower temperature than masses of aromatic compounds.

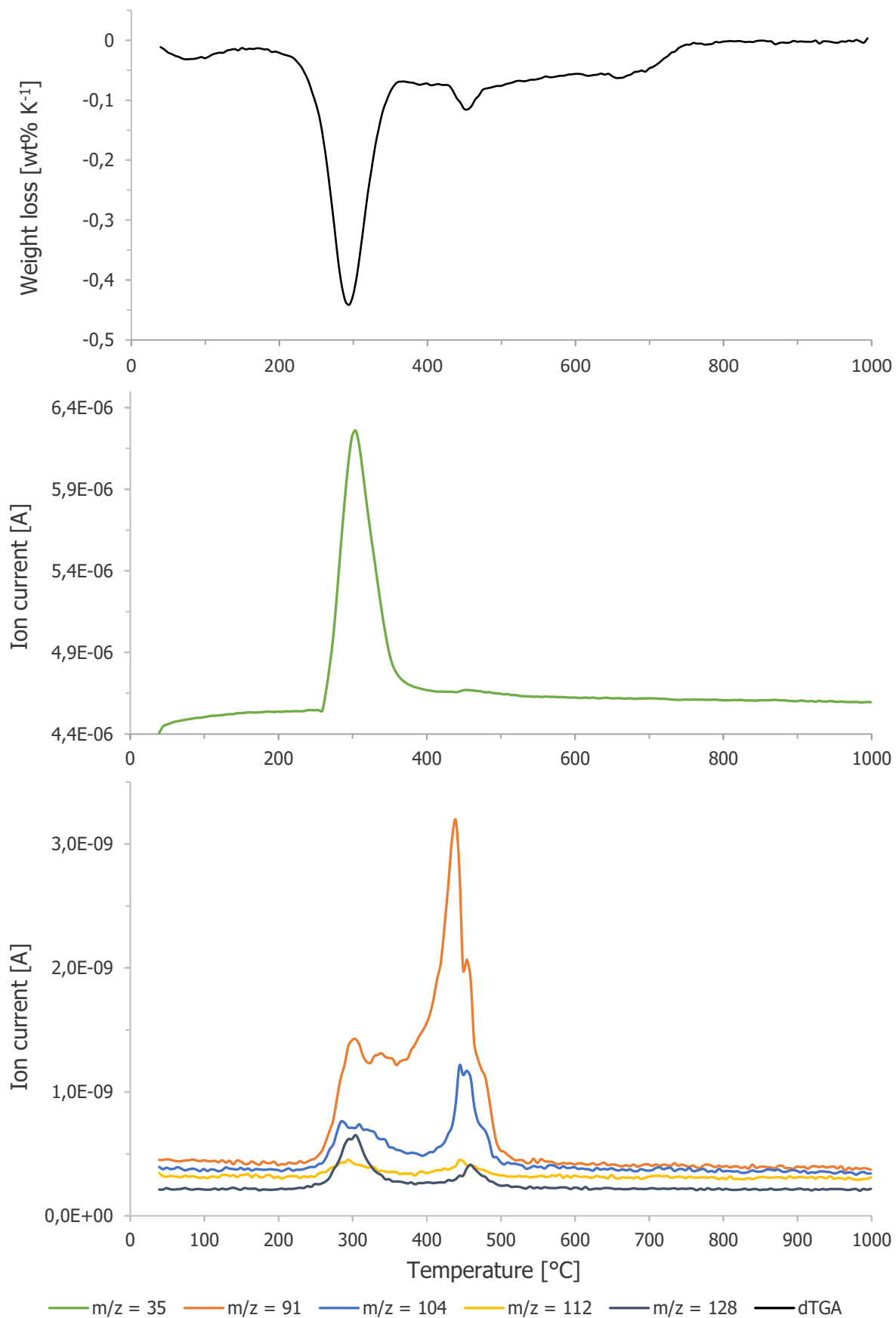


Figure 5.8 An exemplary dTGA and MS curves related to selected m/z signals (35, 91, 104, 112, 128) of 7 wt% PVC in LUFA.

5.3.2 Selection mass-to-charge ratio for polystyrene pyrolytic products detection

The thermal degradation of PS in an inert atmosphere is one-step process [65] and takes place mainly due to radical chain reaction mechanisms [63; 64; 65; 70]. Therefore, various products are formed. We reviewed several scientific researches [63; 64; 65; 66; 70] and based on that, we summarized the most common pyrolytic products of PS, which are shown in *Table 5.2*. Accordingly, the most intensive m/z were investigated using on-line libraries [68; 69].

Table 5.2 Pyrolytic products of PS and their m/z highest peaks.

Name	m/z highest peaks
1-Ethenyl-3-ethylbenzene	115, 117, 132
2-Phenyltetralin	91, 104, 208
2,4-Diphenyl-1-butene	91, 117, 193
2,4,6-Triphenyl-1-hexene	91, 103, 117, 193, 195
α -Methylstyrene	77, 78, 103, 117, 118
Ethylbenzene	91, 106
Styrene	51, 78, 103, 104
Toluene	91, 92

As reported by Özsın and Pütün [65], the major product of PS pyrolysis is styrene monomer. This is mainly caused by produced short-chain radicals. Accordingly, we expected the highest signal response for $m/z = 104$ (*i.e.* the highest peak of styrene). Surprisingly, even higher signal was observed for $m/z = 103$.

We eventually selected these m/z : 35, 91, 104, 112 and 128 for further analysis. *Figure 5.9* shows dependency of dTGA curve and chosen m/z curves on temperature for 7 wt% PS in LUFA.

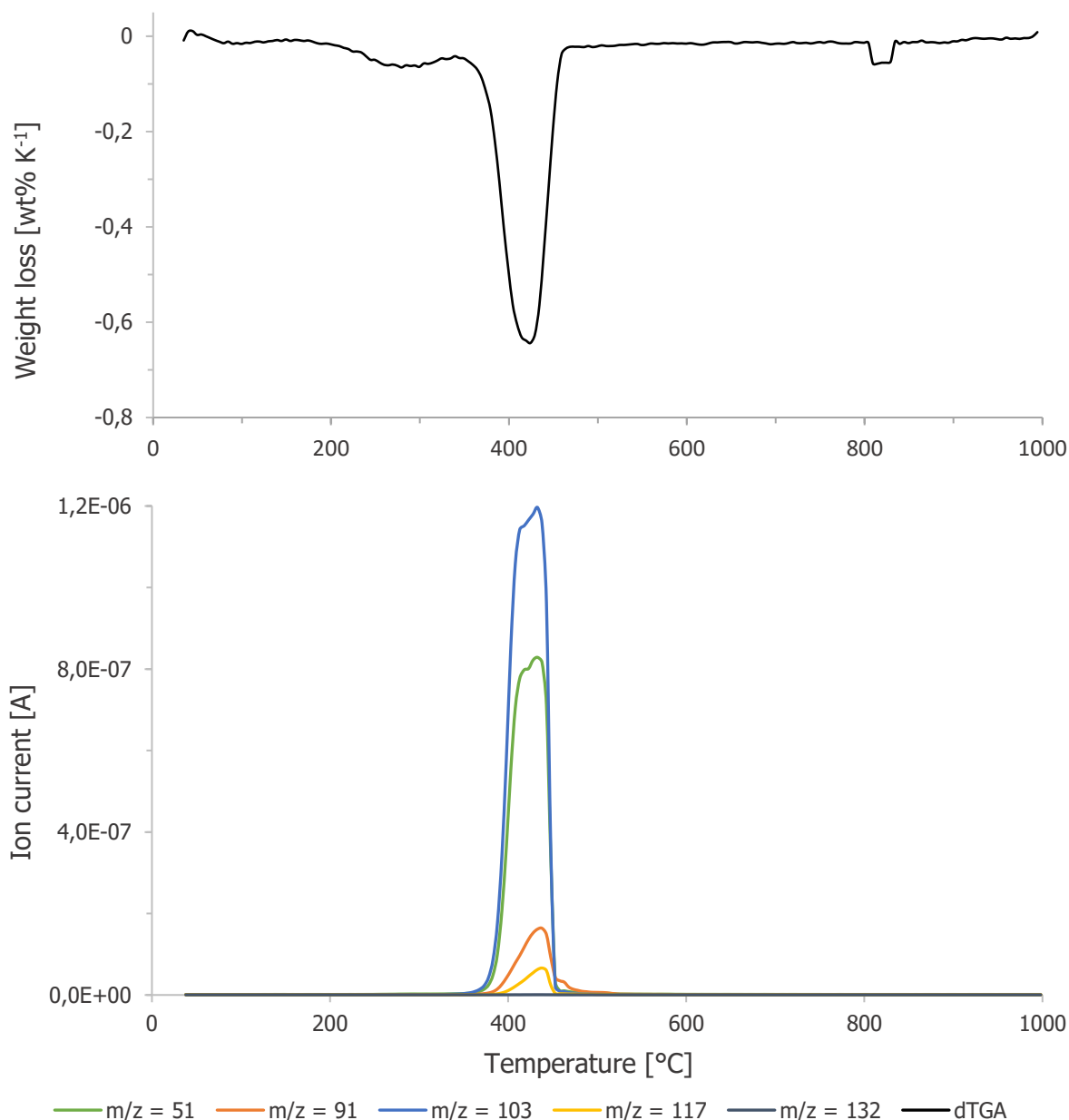


Figure 5.9 An exemplary dTGA and MS curves related to selected m/z signals (51, 91, 103, 117, 132) of 7 wt% PS in LUFA.

5.4 MATRIX EFFECT

Matrix effect was studied, because soil may interact with microplastics during the pyrolysis and therefore to affect the signal response. The study was performed by comparing the signal intensities of MS curves for soil, polymer and mixture of plastic with soil. Since MS provides an absolute value, the curves were normalized by original weight of polymer in sample. The investigation of mixtures was carried out only for one concentration of each microplastic (*i.e.* 3.02 wt% PVC and 3.67 wt% PS in LUFA soil).

Figure 5.10 shows normalized MS signals of PVC, soil and spiked PVC in soil for $m/z = 35$. It can be seen that the peak shape of pure PVC varies from mixture of PVC with soil and the maximum is at higher temperature. The matrix effect may be caused by unknown reactions

between SOM and microplastic. Such dehydrochlorination step of PVC can be also modified by inorganic salts [61] which occur in soil.

The MS signals of PVC for the other masses (91, 104, 112 and 128) are summarized in APPENDIX (Figure 9.2–Figure 9.5).

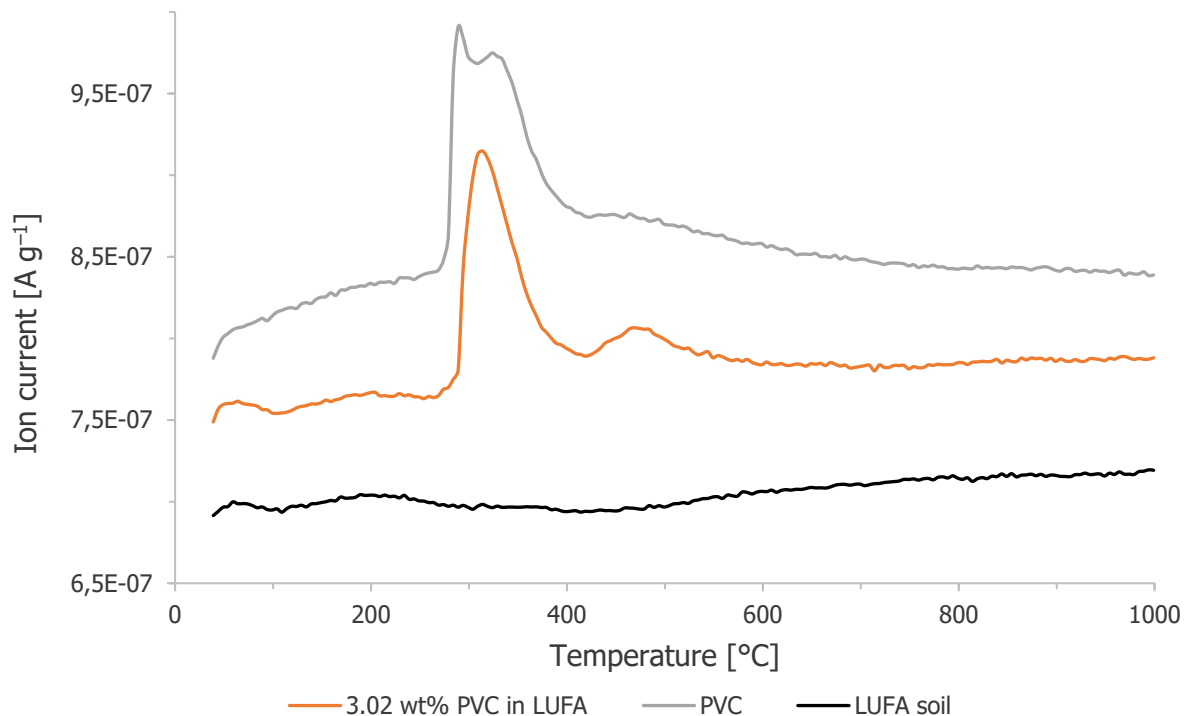


Figure 5.10 Normalized MS curves of PVC, soil and 3.02 wt% PVC in soil for $m/z = 35$.

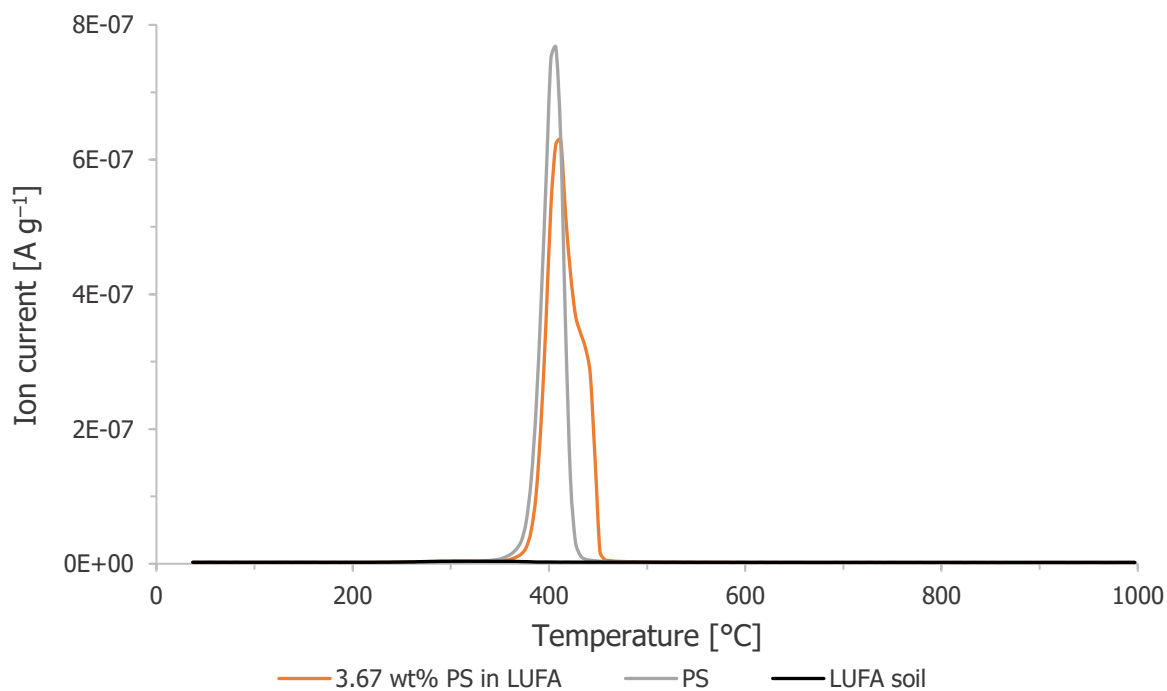


Figure 5.11 Normalized MS curves of PS, soil and 3.67 wt% PS in soil for $m/z = 51$.

Figure 5.11 reports normalized curves of MS signals for PS, soil and PS spiked in soil for $m/z = 51$. The intensity of PS in soil is significantly lower and the degradation has slower progress with termination at higher temperature. Due to high signal response, Figure 5.12 shows a detailed view of baseline. It can be seen that the $m/z = 51$ was also detected in soil sample, although the intensity of signal response was considerably lower.

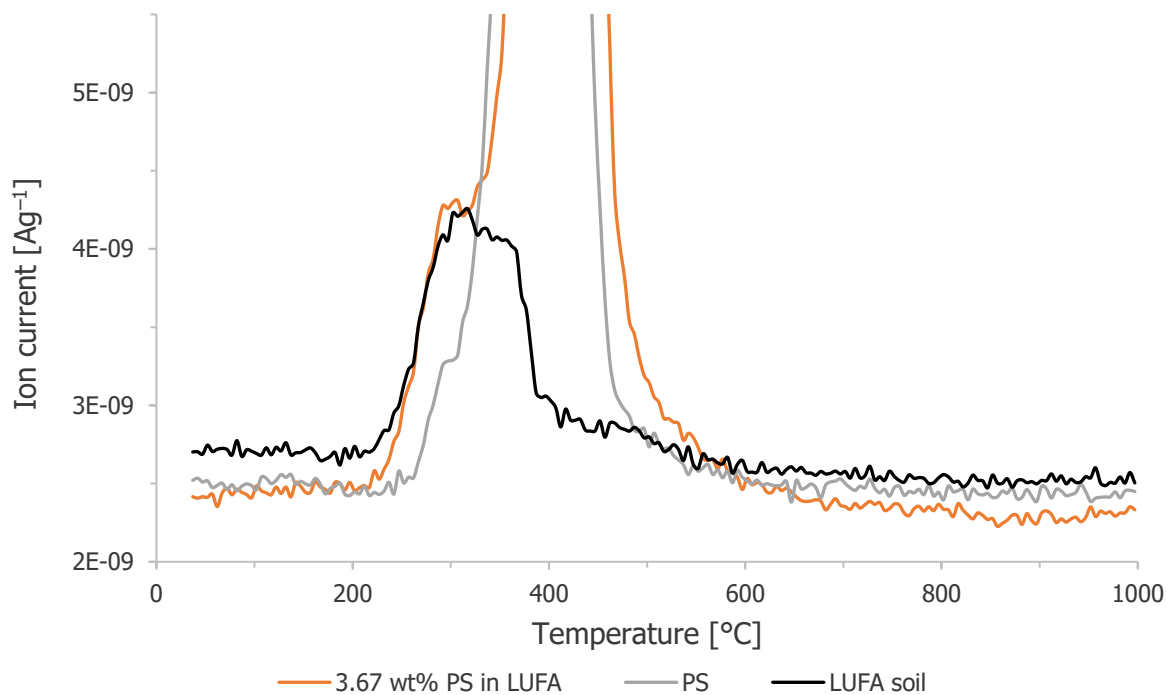


Figure 5.12 Detailed view of normalized MS curves of PS, soil and 3.67 wt% PS in soil for $m/z = 51$.

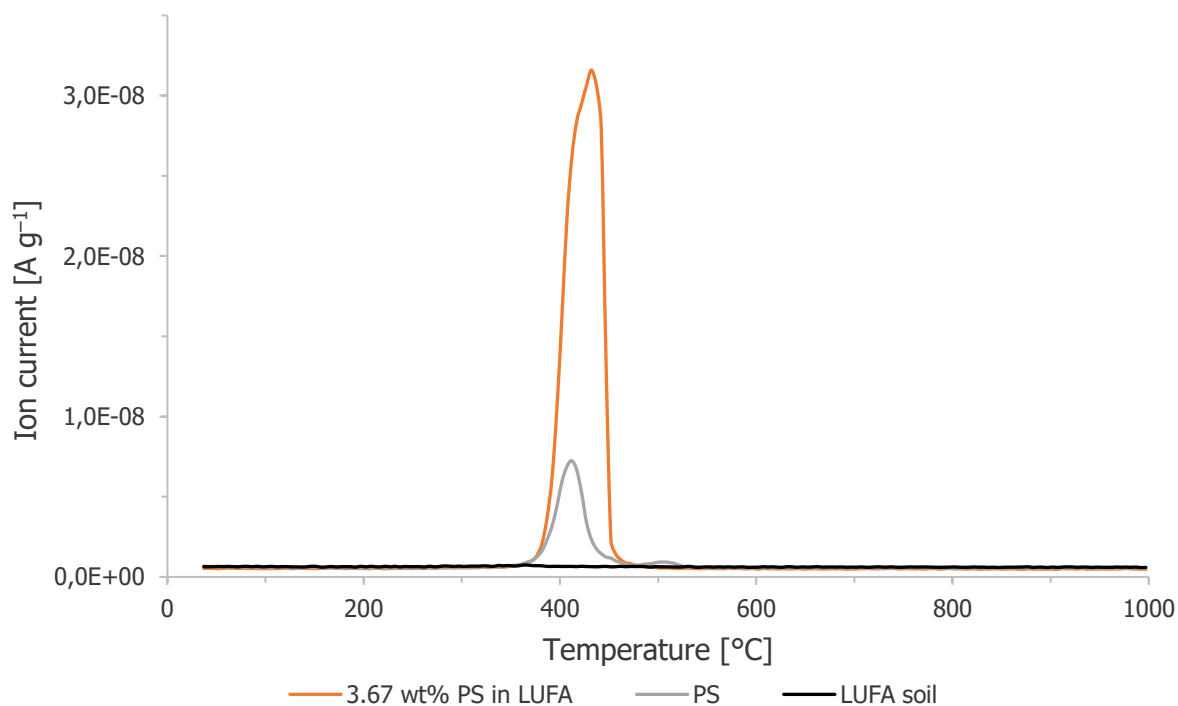


Figure 5.13 Normalized MS curves of PS, soil and 3.67 wt% PS in soil for $m/z = 117$.

Even though we expected the signal response of PS spiked in soil may have lower signal than pure PS for all masses, in some cases we observed the opposite effect. For instance, *Figure 5.13* shows the most extreme example, where the MS signal response for $m/z = 117$ has more than five times higher intensity for PS in soil than pure PS. The graph also shows signal response of blank. The detailed view of baseline is shown in *Figure 5.14* where it can be seen that $m/z = 117$ was detected in soil only in trace amount. The synergetic effect was also observed in pyrolysis of PS with chestnut shell [65]. This effect showed the higher MS signal of some evolved gases compared to the MS signals of blank. Such results indicate the changes in reaction mechanism [65]. Furthermore, the pyrolysis of plastic mixture with other compounds can lead even to new products formation [62].

The MS signals of PS for the other masses (91, 103, and 132) are reported in *APPENDIX (Figure 9.6–Figure 9.10)*.

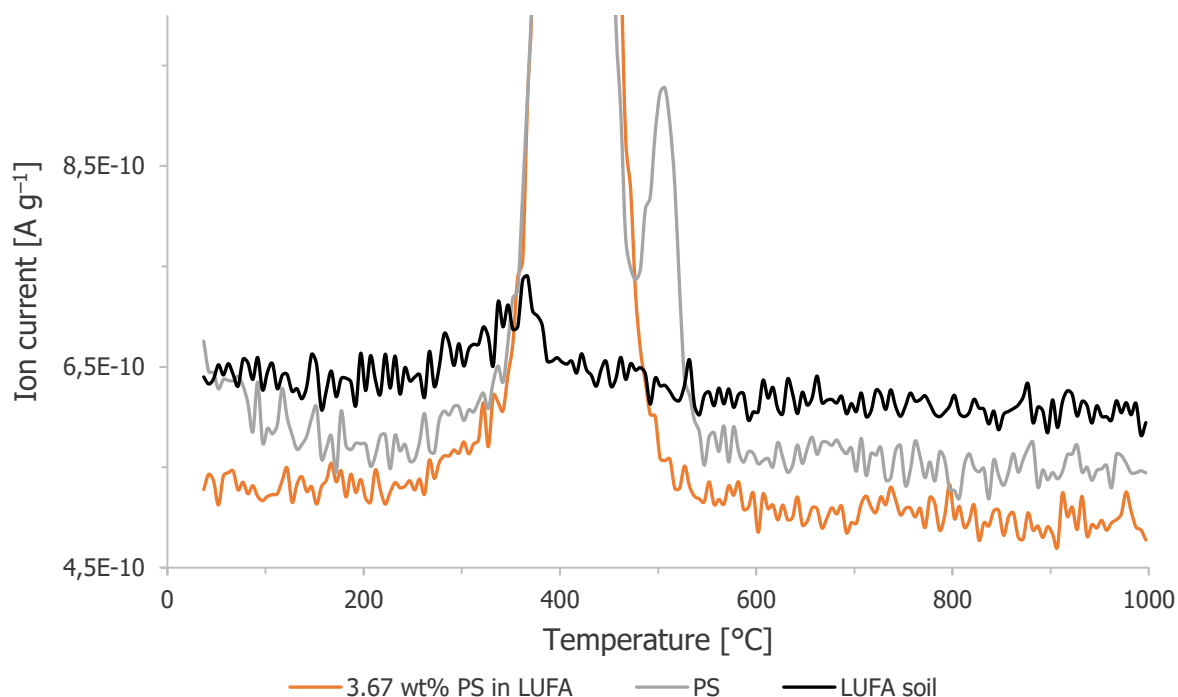


Figure 5.14 Detailed view of normalized MS curves of PS, soil and 3.67 wt% PS in soil for $m/z = 117$.

5.5 QUANTITATIVE ANALYSIS OF EVOLVED GASES

To obtain calibration curve plots, the experiments of quantitative analysis of microplastics were carried out with respect to chosen m/z . The spiked soil samples were prepared at concentrations of 0.23–7 wt%. The measurements were performed in duplicates. Then, the calibration curve plots were made from obtained data as a dependency of peak area on microplastic concentration in soil. Calculated linear regressions from calibration curve plots may serve for quantitative determination of unknown micro-PVC and micro-PS concentration in sandy loam soil.

5.5.1 Calibration curves

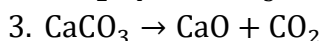
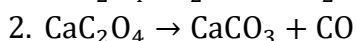
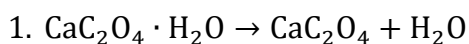
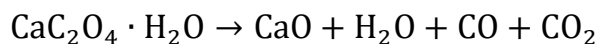
The calibration curve plots were created from integration of signal responses of each m/z in dependency on concentration (wt%) of spiked model LUFA soil with micro-PVC and micro-PS, respectively. A zero point of the plots is a signal response of blank; *i.e.* LUFA soil without spiked microplastics. Since MS provided an absolute value, the peak areas were normalized by original sample weight.

The samples were prepared prior to the analysis; hence the sample representativeness was not guaranteed in whole volume. Accordingly, some points were excluded from the calibration plots.

The quantitative interpretation is generally problematic in TGA-MS system [71]. To ensure issues connected with changes of working conditions (*e.g.* the detector state), an internal standard is widely used [51]. The internal standard serves for more accurate analyte quantification. One of the requirements for the internal standard is its inertness within all components of a sample. Two methods exist and include: (*i*) calibration using solid with well-known and defined stoichiometric reaction of thermal decomposition, and (*ii*) injection of defined amount of calibration gas which flows together with carrier gas through the TGA-MS device [71].

David et al. [51] applied cysteine as the internal standard for analysis micro-PET in soil. Due to the unknown thermally-induced reactions of microplastics with soil during pyrolysis, we decided to carry out the normalization using external standard method. Accordingly, the obtained data of analytes were normalized by calcium oxalate hydrate, which was measured prior to the sample analysis.

Calcium oxalate hydrate decomposes in three steps:



and its stoichiometric weight loss is well described. An exemplary TGA-MS record of calcium oxalate hydrate, obtained from our measurement, is shown in *Figure 5.15*.

Consequently, the data from calibration curve plot were normalized with peak area of $m/z = 18$ from calcium oxalate hydrate. The resulted values obtained from calibration curves for PVC and PS are shown in *Table 5.3* and *Table 5.4*, respectively. An exemplary calibration curve plots without normalization on the external standard are shown in *Figure 5.16*, whereas *Figure 5.17* represents an exemplary calibration curve plot with the normalization on calcium oxalate hydrate. The final exemplary calibration curve with excluded some points is shown in *Figure 5.18*. All calibration curves of PVC and PS are attached in *APPENDIX (Figure 9.11–Figure 9.19)*.

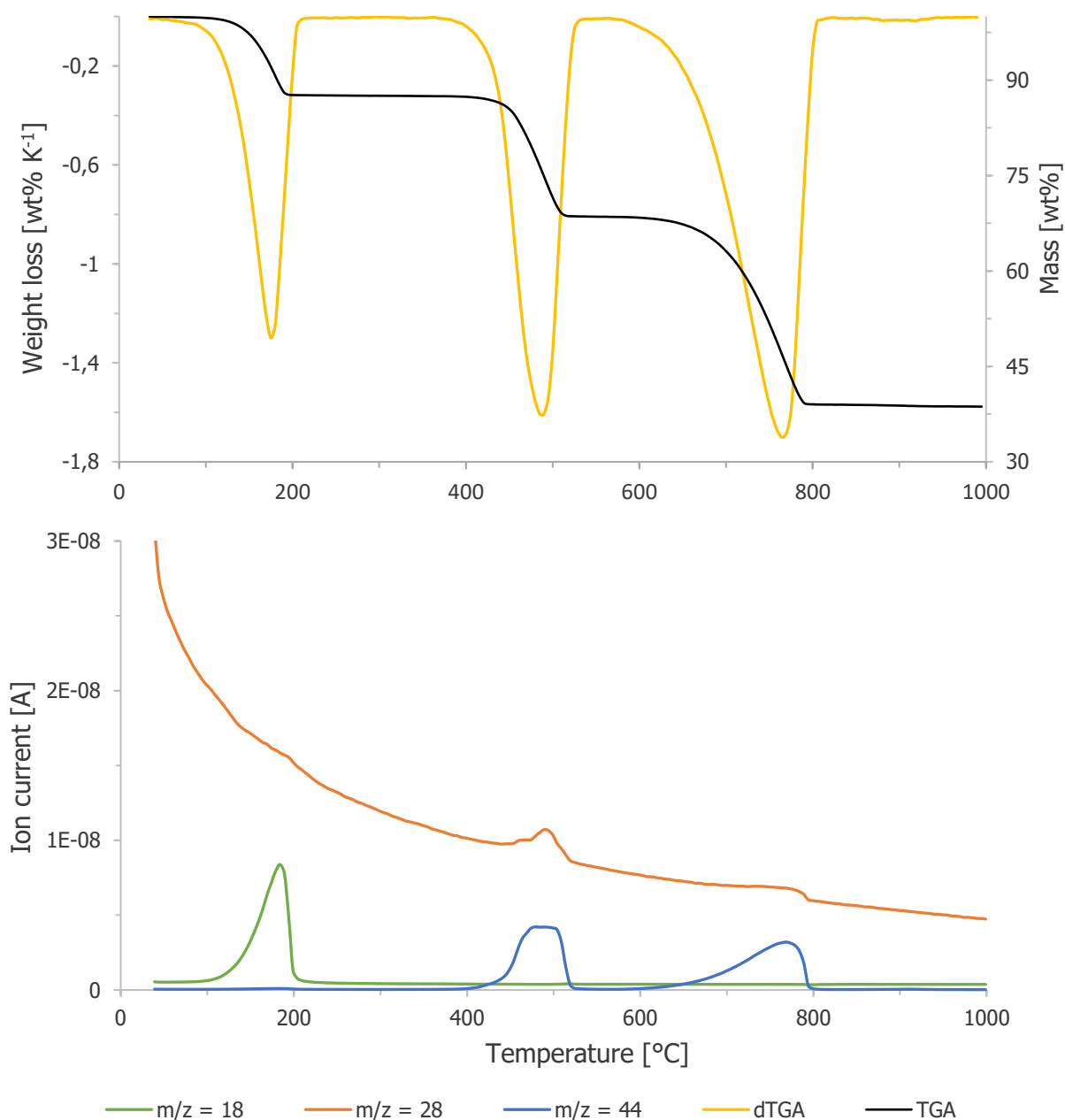


Figure 5.15 An exemplary TGA-MS record of calcium oxalate hydrate.

Table 5.3 Coefficients of determination obtained from calibration curve plot of LUFA soil spiked with micro-PVC for each m/z : a) without normalization on the external standard, b) with normalization on the external standard, and c) adjusted with normalization on the external standard.

m/z	R^2	R^2 (normalized)	R^2 (normalized, adjusted)
35	0.9349	0.9125	0.9432
91	0.9007	0.9305	0.9671
104	0.8765	0.9267	0.9626
112	0.4851	0.6419	0.9175
128	0.9275	0.8936	0.9561

Table 5.4 Coefficients of determination obtained from calibration curve plot of LUFA soil spiked with micro-PS for each m/z : a) without normalization on the external standard, b) with normalization on the external standard, and c) adjusted with normalization on the external standard.

m/z	R^2	R^2 (normalized)	R^2 (normalized, adjusted)
51	0.8884	0.9050	0.9609
91	0.8465	0.9588	0.9824
103	0.8861	0.9017	0.9598
117	0.8551	0.9546	0.9797
132	0.7338	0.9036	0.9415

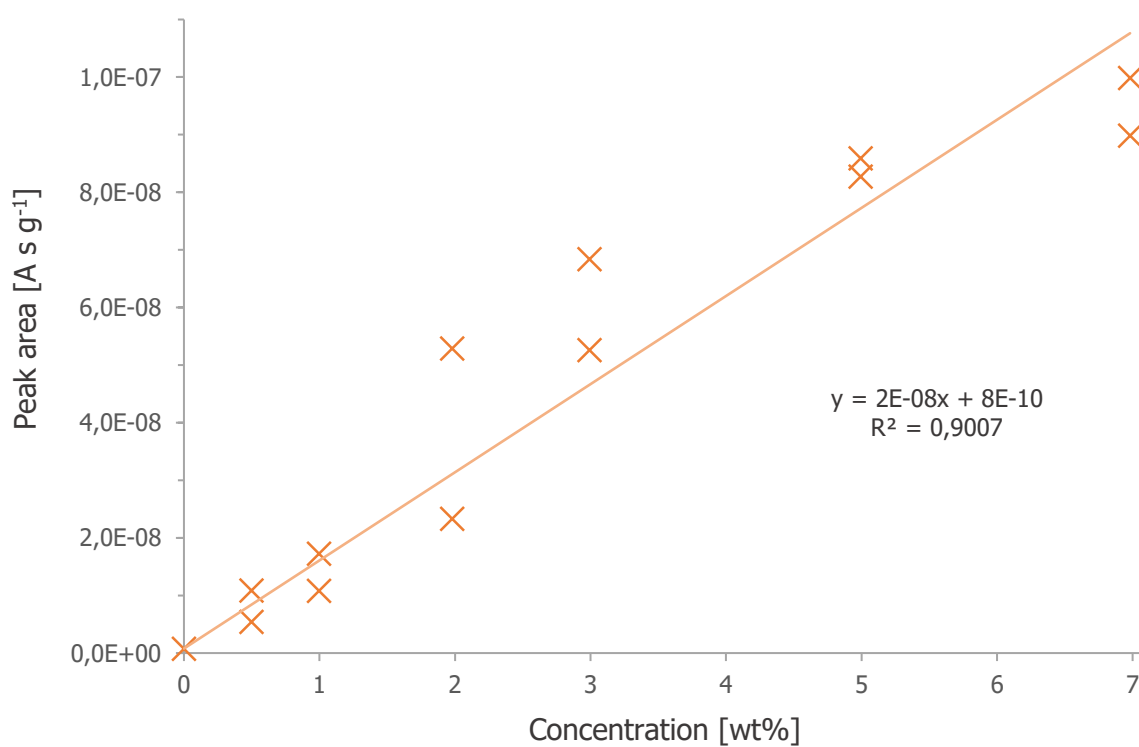


Figure 5.16 An exemplary calibration curve plot (PVC in LUFA, $m/z = 91$) without normalization on calcium oxalate hydrate.

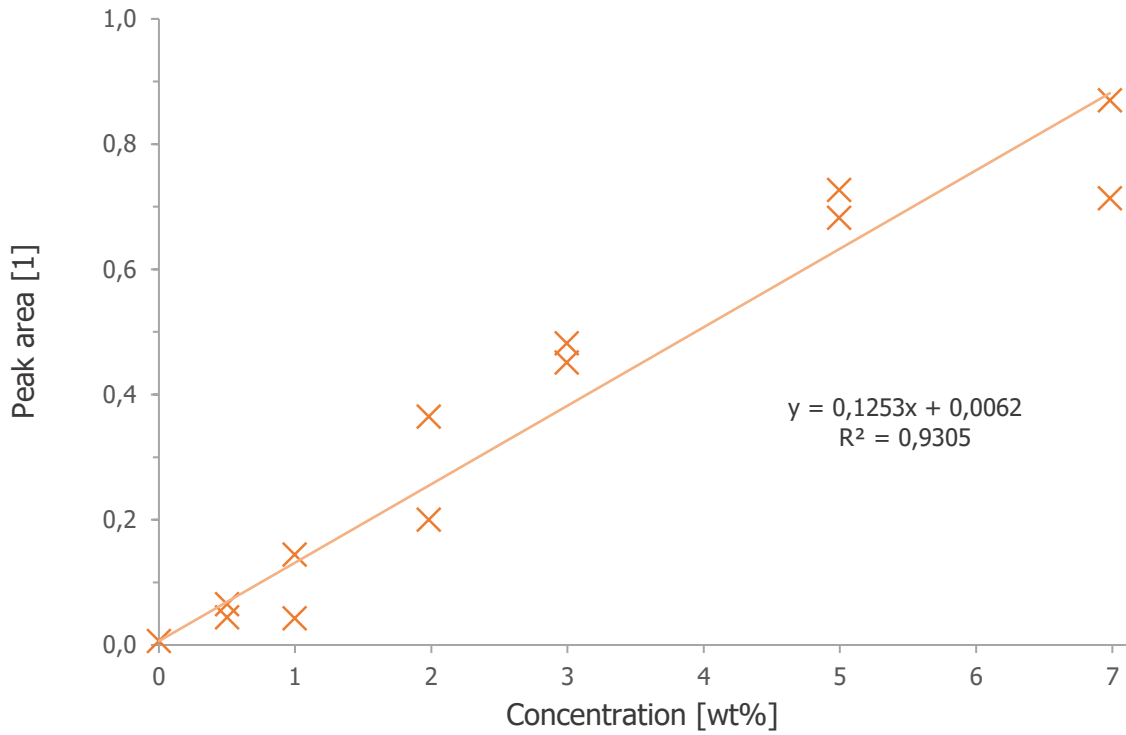


Figure 5.17 An exemplary calibration curve plot (PVC in LUFA, $m/z = 91$) with normalization on calcium oxalate hydrate.

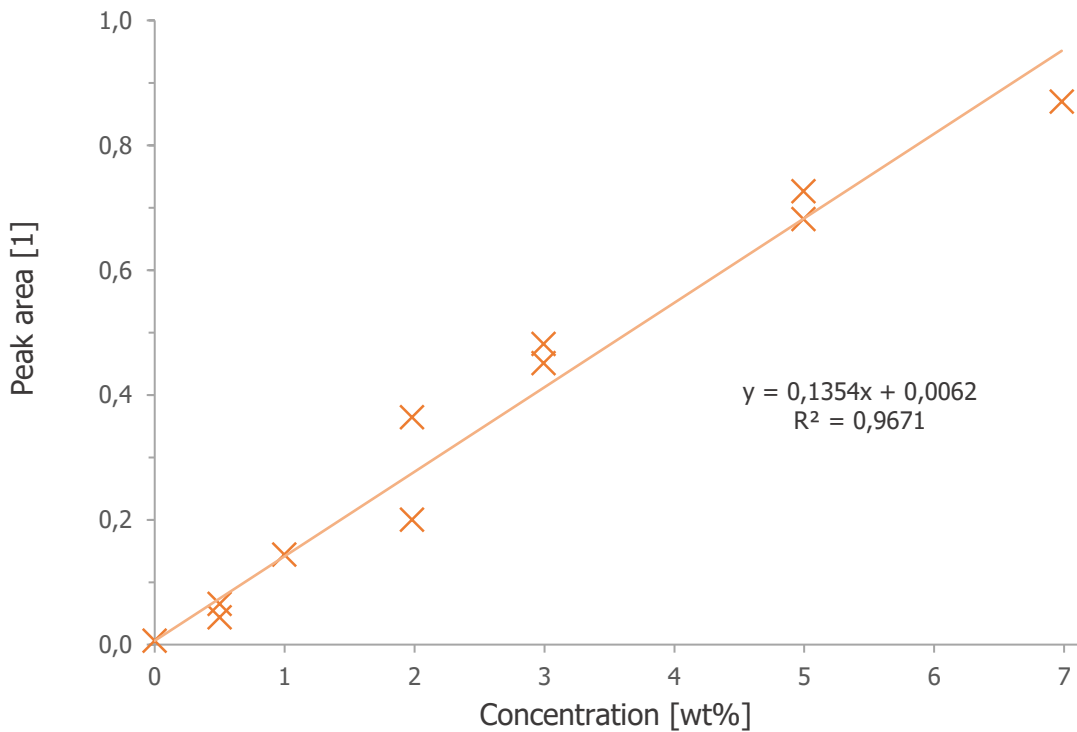


Figure 5.18 The calibration curve plot (PVC in LUFA, $m/z = 91$) with normalization on calcium oxalate hydrate

5.5.2 Limit of detection and limit of quantification

Limit of detection (LOD) and limit of quantification (LOQ) were calculated according to equations (1) and (2), respectively:

$$\text{LOD} = \frac{3 \cdot h_n}{m} \quad (1)$$

$$\text{LOQ} = \frac{10 \cdot h_n}{m} \quad (2)$$

where h_n is a noise on a baseline whereas m is a slope of a calibration curve plot obtained from function of peak height on its concentration, *i.e.* $h = f(c)$ [72].

In case of PVC, we applied this procedure. As above-mentioned, PVC degrades in two steps, while the first one is accompanied with more intense weight loss. However, the intensities of peaks of m/z in *Figure 5.8* show mixed results. That means that the intensity of the first and second peak varied in dependency on m/z . This would complicate the correct determination of LOD. For this reason, we chose the peaks corresponding to the highest concentration (7 wt% PC in soil) and based on this selection, we determined the LOD. Therefore, we intentionally ignored the mutual ration of peaks intensities, which changed with decreasing concentration.

The calculated values for PVC and PS are shown in *Table 5.5* and *Table 5.6*, respectively.

Table 5.5 Limit of detection (LOD) and limit of quantification (LOQ) calculated for micro-PVC spiked in LUFA soil.

m/z	LOD [wt%]	LOQ [wt%]
35	0.08	0.3
91	0.3	0.9
104	0.6	1.9
112	5.3	17.7
128	1.2	4.1

There is shown significantly higher LOD and LOQ of PVC for $m/z = 128$ and even for $m/z = 112$ in *Table 5.5*. We cannot reject that other m/z would give higher intensities than $m/z = 112$ and $m/z = 128$ in concentration range of 0.25 to 7 wt% micro-PVC in sandy loam soil.

In *Table 5.5*, it can be seen that the lowest value of LOD was obtained for $m/z = 35$ and was 0.08 wt%. However, to measure lower PVC concentrations, the sample should be pre-concentrated prior to the analysis. Nevertheless, the aim of this study was to avoid pre-treatment to simplify the analysis. Thus, the LOD and LOQ for $m/z = 35$, 91 and 104 gave acceptable results for quantification via TGA-MS for 0.5–7 wt% PVC in soil with low organic carbon content.

The LOD and LOQ of PS for chosen m/z show very low values, except the $m/z = 132$, which has also acceptable LOD and LOQ (*Table 5.6*). Overall, we can conclude that the selected masses can be used for quantification via TGA-MS for micro-PS in sandy loam soil with low organic carbon content.

Table 5.6 Limit of detection (LOD) and limit of quantification (LOQ) calculated for micro-PS spiked in LUFA soil.

<i>m/z</i>	LOD [wt%]	LOQ [wt%]
51	0.002	0.006
91	0.004	0.01
103	0.0005	0.002
117	0.01	0.03
132	0.7	2.2

It should be noted that calculated LOD and LOQ values relate to pure micro-PS and micro-PVC without added additives. They were analysed separately in sandy loam soil with low organic carbon content. However, the study is still at the beginning and the results may vary if another soil type is analysed. The purity of used plastics and plastic mixture analysis should be taken into account as well.

5.6 TRANSFER CAPILLARY CONTROL EXPERIMENTS

The capillary between TGA and MS might affect the quality of results. For instance, the evolved gases might adsorb on the capillary surface and thus the false errors could be obtained. To verify that the evolved gases were not influenced during the transfer through the capillary, we carried out the transfer capillary control experiment. The test was always performed after the measurement of the sample with PVC or PS content.

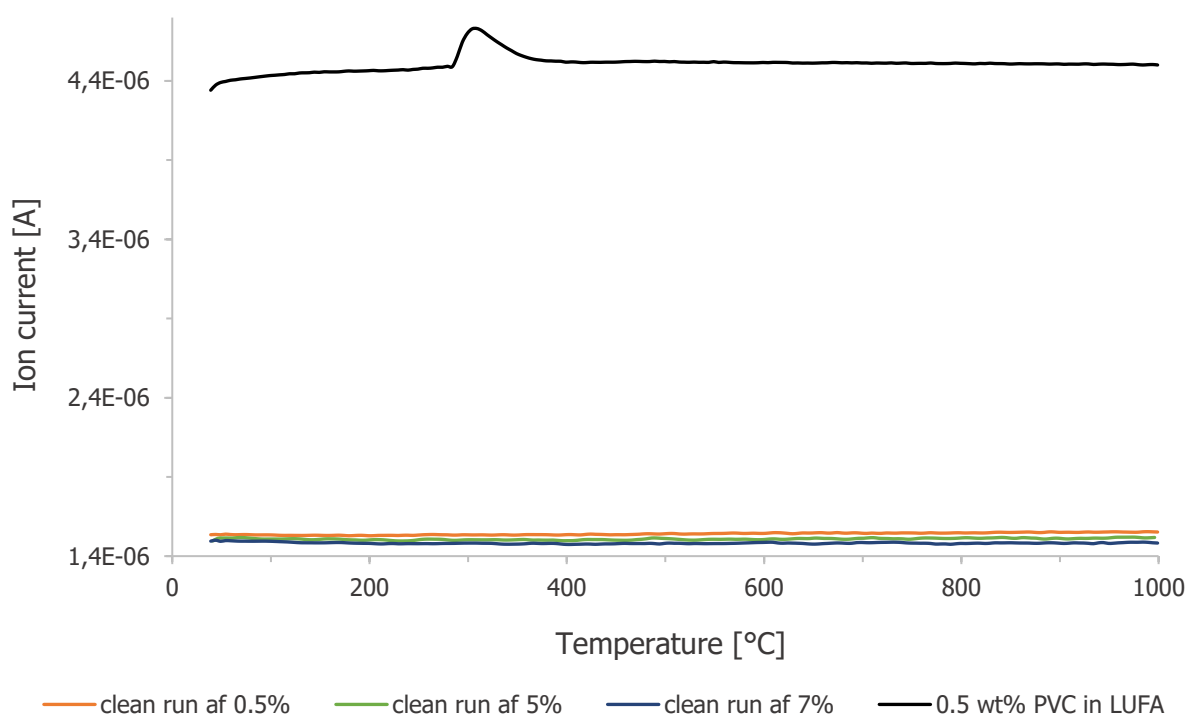


Figure 5.19 An exemplary MS records for $m/z = 35$ signals of cleaning runs after pyrolysis of PVC in soil. The signals are selected for cleaning runs after the least concentrated PVC sample (0.5 wt%) and the highly concentrated PVC samples (5 and 7 wt%). In the record is also $m/z = 35$ signal of 0.5 wt% PVC in soil.

We assumed that if the evolved gases adsorb on the capillary surface during the sample measurement, they should desorb during the consequent cleaning run. Therefore, the MS record of the cleaning run should show the change in its intensity. *Figure 5.19* shows the comparison of the MS signal responses during the cleaning runs after PVC in soil with different concentration. Moreover, in *Figure 5.19* is also the MS signal of the least concentrated PVC in soil. Therefore, we compared the cleaning runs of the least concentrated PVC sample with the most concentrated PVC samples to see differences.

In case of all cleaning runs for each polymer and each m/z , no signal was detected (even in zoomed detail).

The same process was performed for calcium oxalate hydrate, which followed the cleaning run. *Figure 5.20* shows the comparison of the selected MS signal responses during the oxalate tests. The selection was carried out for the oxalate after the least concentrated PVC sample and the most concentrated PVC samples. Moreover, *Figure 5.20* also shows MS curve of the least concentrated PVC in soil.

In *Figure 5.20* it can be seen that $m/z = 35$ was also detected during the oxalate pyrolysis. As above-mentioned, calcium oxalate hydrate thermally degrades in three steps, which are well-described. Therefore, the degradation should not evolve any gases which would correspond with $m/z = 35$. However, the intensity of peaks does not change if we compare MS curves of the same m/z for oxalates after samples with different PVC content.

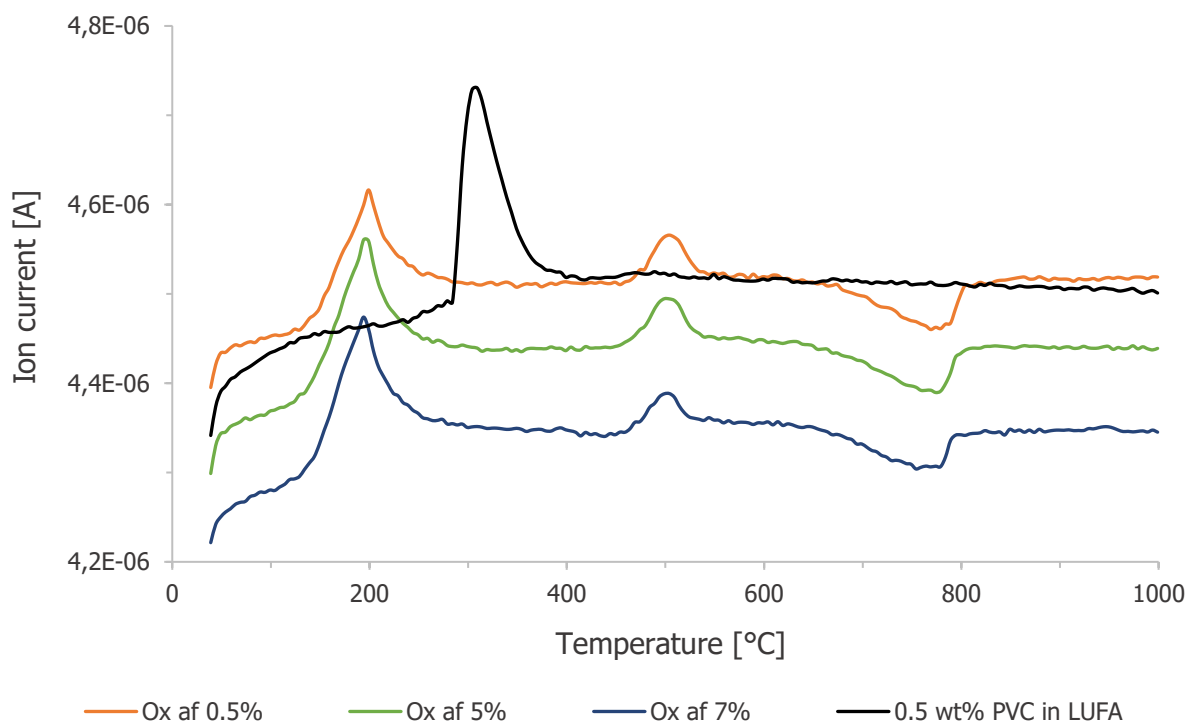


Figure 5.20 An exemplary MS records for $m/z = 35$ signals of calcium oxalate hydrate (Ox) after pyrolysis of PVC in soil. The signals are selected for pyrolysis of calcium oxalate hydrate after the least concentrated PVC sample (0.5 wt%) and the highly concentrated PVC samples (5 and 7 wt%). In the record is also $m/z = 35$ signal of 0.5 wt% PVC in soil.

The signals occur only at temperature intervals in which oxalate degrades (*Figure 5.15*). Nevertheless, this effect was observed only for $m/z = 35$. The other masses (PVC: 91, 104, 112 and 128; PS: 51, 91, 103, 117 and 132) showed only one peak, which always occurred at the first degradation step of oxalate. An example can be seen in *Figure 5.21*, where are shown the MS records of $m/z = 91$ for oxalates after pyrolysis of sample with PVC content. Again, in the record is also the MS signal obtained from pyrolysis of 0.5 wt% PVC in soil.

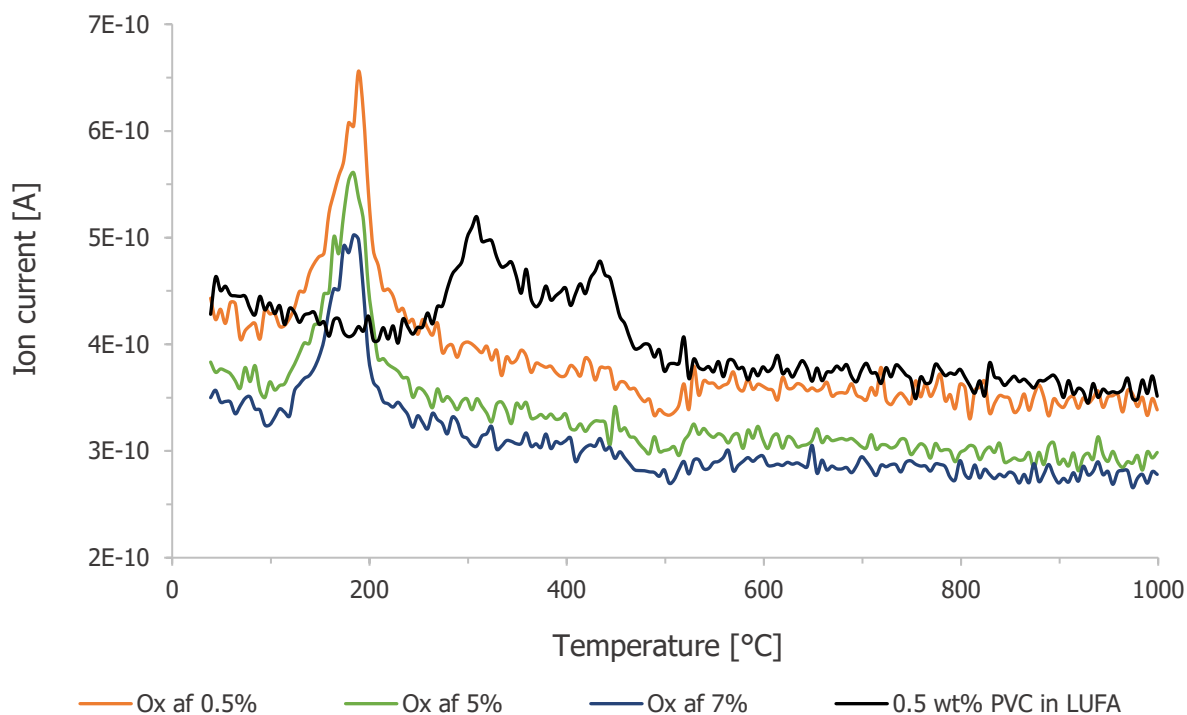


Figure 5.21 An exemplary MS records for $m/z = 91$ signals of calcium oxalate hydrate (Ox) after pyrolysis of PVC in soil. The signals are selected for pyrolysis of calcium oxalate hydrate after the least concentrated PVC sample (0.5 wt%) and the highly concentrated PVC samples (5 and 7 wt%). In the record is also $m/z = 91$ signal of 0.5 wt% PVC in soil.

Based on the results, we suppose that the evolved gases are adsorbed on the capillary surface during the gas transfer. However, the cleaning runs are performed under different condition (the carrier gas is air, *Table 4.3*) than the pyrolysis of the sample and calcium oxalate hydrate (in argon atmosphere, *Table 4.2*). Therefore, the air used for cleaning might not desorb the compounds from the capillary surface, but it desorbs, when the argon is used again. This hypothesis could explain, why no signal is seen during the cleaning run. This reminds a chromatographic effect in the capillary, *i.e.* desorption is influenced by mobile phase. By contrast, the oxalate pyrolysis evolves gases (such as water, carbon oxide and carbon dioxide) which might increase the furnace and capillary pressure and subsequently cause desorption of various compounds. As a result, they are detected during the oxalate degradation.

6. CONCLUSION

In this study, a new analytical approach was developed for quantitative determination of PVC and PS microplastic in soil using TGA-MS. The main advantage of this technique results from avoiding the time-consuming sample pre-treatment.

The linear dependency was observed between the MS signal response and concentration of the microplastics. To take into account the issues connected with changes of working conditions, calcium oxalate hydrate was used as an external standard.

From the obtained data, LOD and LOQ were calculated for each polymer. The values of LOD and LOQ varied in dependency on chosen m/z . LOD was determined in range between 0.08–5.3 wt% for PVC and 0.005–0.7 wt% for PS, respectively. Consequently, LOQ was between 0.3–17.7 wt% for PVC and between 0.002–2.2 wt% for PS. Thus, in most of chosen m/z , the obtained values of LOD and LOQ gave acceptable results for determination of 0.5–7 wt% micro-PVC and 0.23–7 wt% micro-PS in soil with low organic carbon content via TGA-MS. However, noteworthy, this approach is still being developed and we cannot reject that the results may change if another soil type and/or mixture of microplastics is used. Also, the plastics enhanced with additives may affect the determination.

Potentially, the evolved gas analysis consisting of TGA-MS technique may be applied for the analysis of a plastic material with characteristic pyrolytic products, which differ and are unique compared to the soil pyrolytic products. Due to this reason, analysis of PE and PP (the plastics with the greatest worldwide demand) may be very complicated if the sample is not pre-treated. In that case, we would recommend an extraction of the microplastics or removal SOM using, *e.g.* hydrogen peroxide.

The further challenges should focus on using another sort of standardization (*e.g.* an internal solid standard of injection of a calibration gas) and to analyse the soil with plastic mixture.

We assume that the TGA-MS method could compete with the other analyses for determination of microplastics in soil. Nevertheless, more attention should be paid on the issues with the adsorption evolved gases on the capillary surface, which couples TGA and MS. Overall, the coupling TGA-MS can be applied for semiquantitative analysis of micro-PVC and micro-PS in mineral soils with low organic carbon content.

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8. LIST OF ABBREVIATIONS

DDT	dichlorodiphenyltrichloroethane
DEHP	di-(2-ethylhexyl) phthalate
DOM	dissolved organic matter
dTGA	the first derivative of thermogravimetric curve
EI	electron ionization
EU	European Union
FTIR	Fourier transform infrared spectroscopy
GC	gas chromatography
HDPE	high density polyethylene
LDPE	low density polyethylene
LOD	limit of detection
LOQ	limit of quantification
<i>m/z</i>	mass-to-charge ratio
MS	mass spectrometry
NRP	non-recycled plastic
PBDE	polybrominated diphenyl ether
PCB	polychlorinated biphenyl
PET	polyethylene terephthalate
PFE	pressurized fluid extraction
PP	polypropylene
PS	polystyrene
PUR	polyurethane
PVC	polyvinylchloride
SEM	scanning electron microscopy
SOM	soil organic matter
TED	thermal extraction and desorption
TGA	thermogravimetry
WWTP	wastewater treatment plant
<i>py</i>	pyrolysis

9. APPENDIX



Figure 9.1 Coupling TGA-MS via capillary; TGA analyser STA 449 F3 Jupiter and mass spectrometer QMS 403 C Aëolos (NETZSCH, Germany) [73].

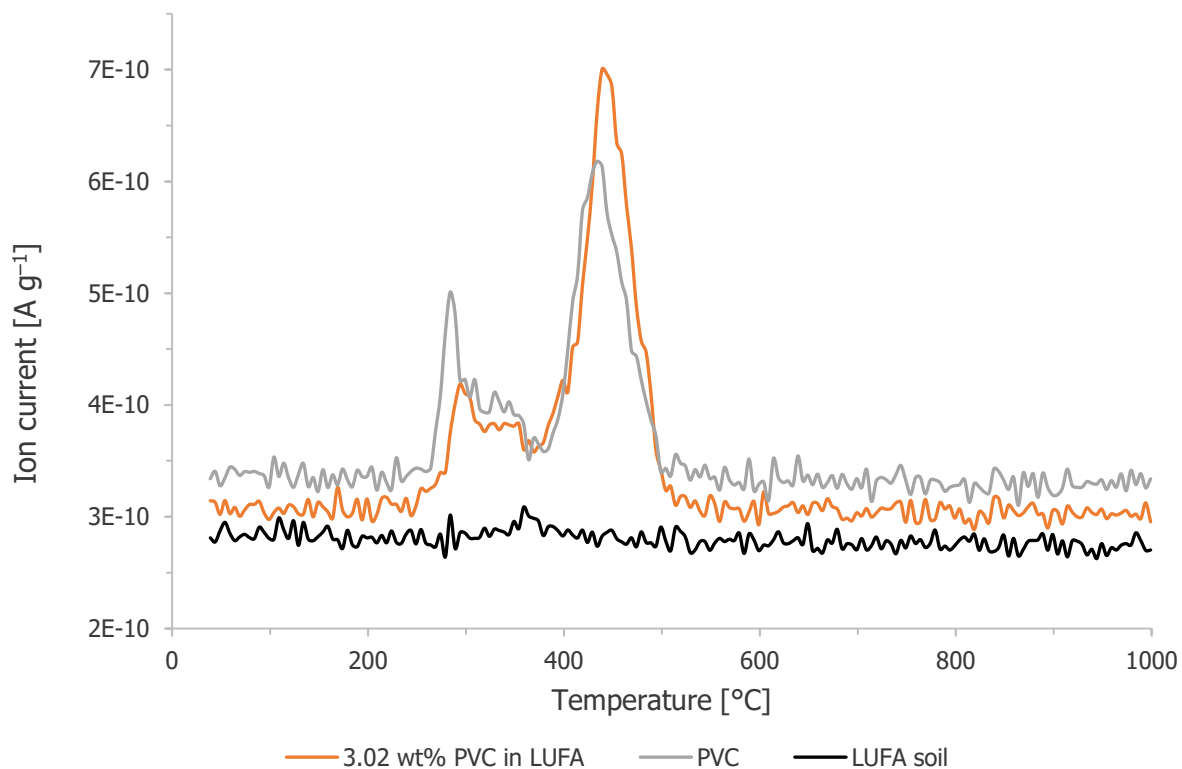


Figure 9.2 Normalized MS curves of PVC, soil and 3.02 wt% PVC in soil for $m/z = 91$.

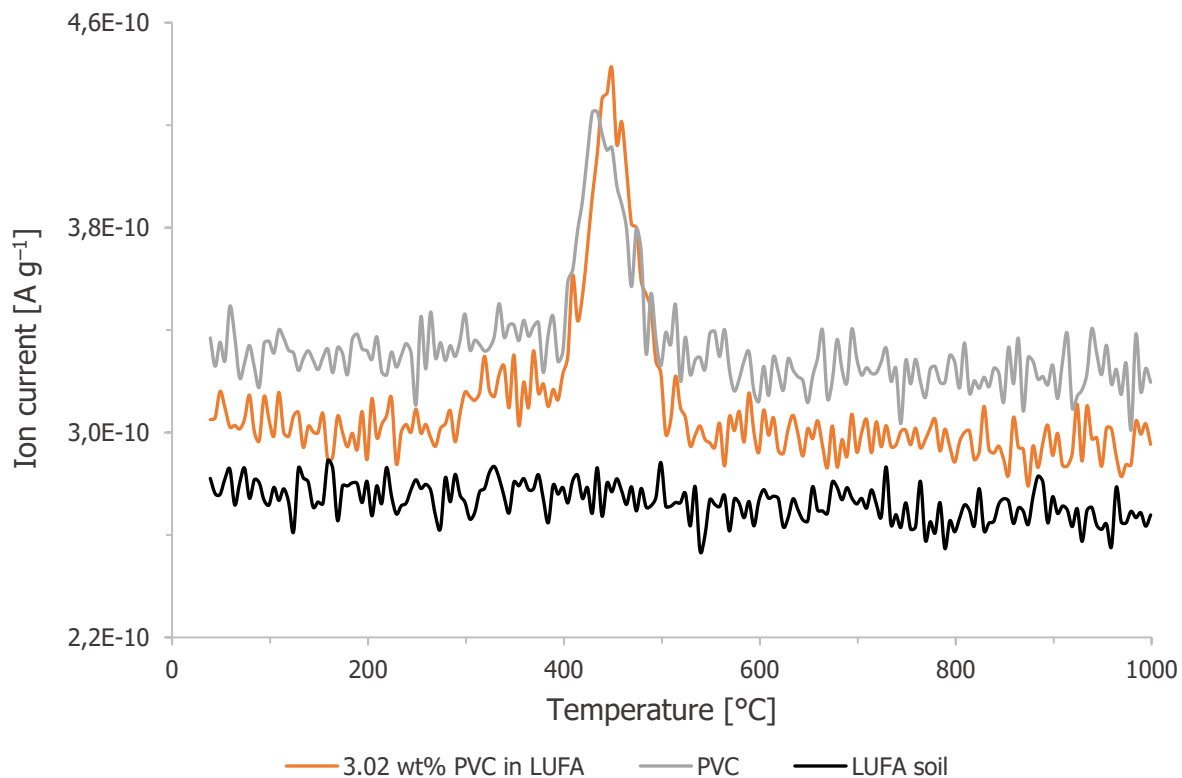


Figure 9.3 Normalized MS curves of PVC, soil and 3.02 wt% PVC in soil for $m/z = 104$.

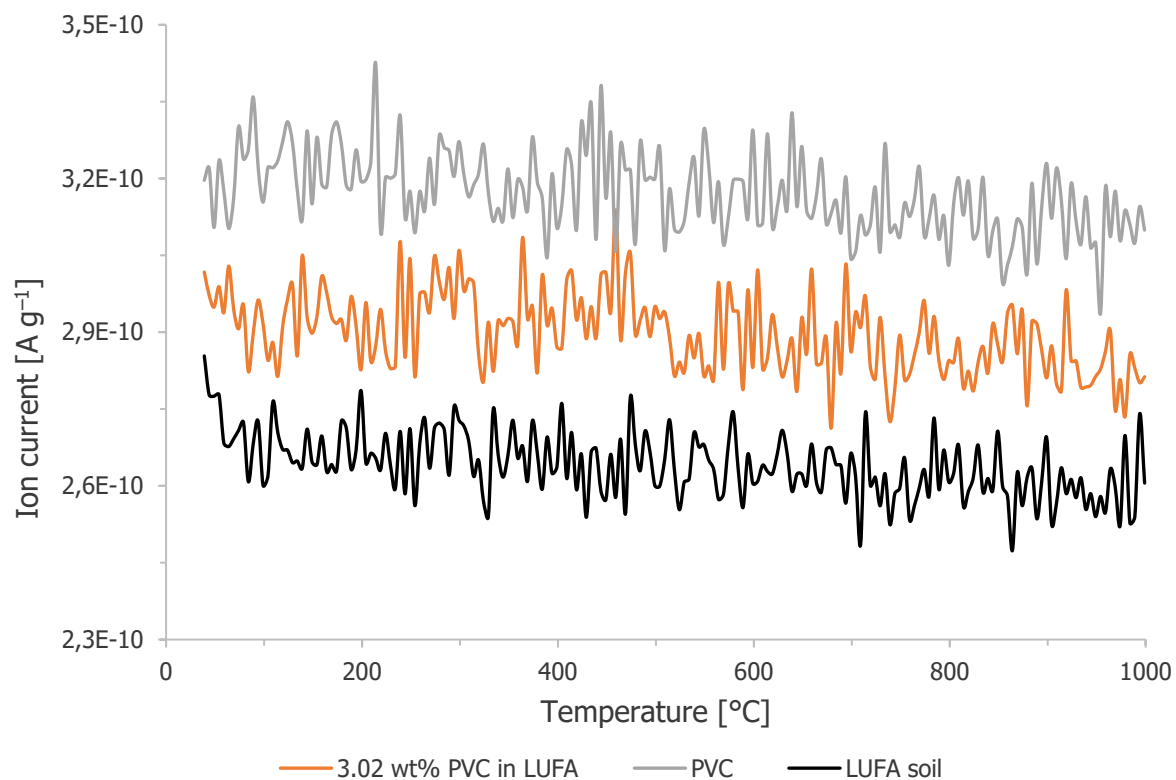


Figure 9.4 Normalized MS curves of PVC, soil and 3.02 wt% PVC in soil for $m/z = 112$.

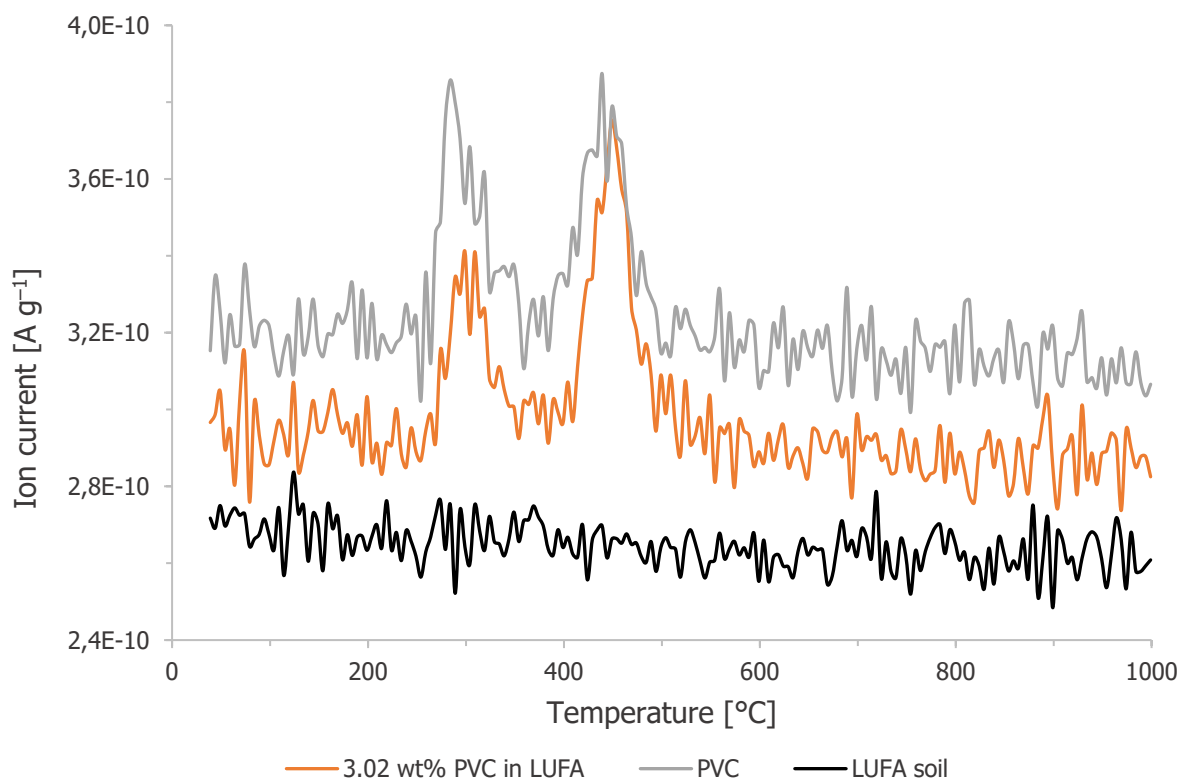


Figure 9.5 Normalized MS curves of PVC, soil and 3.02 wt% PVC in soil for $m/z = 128$.

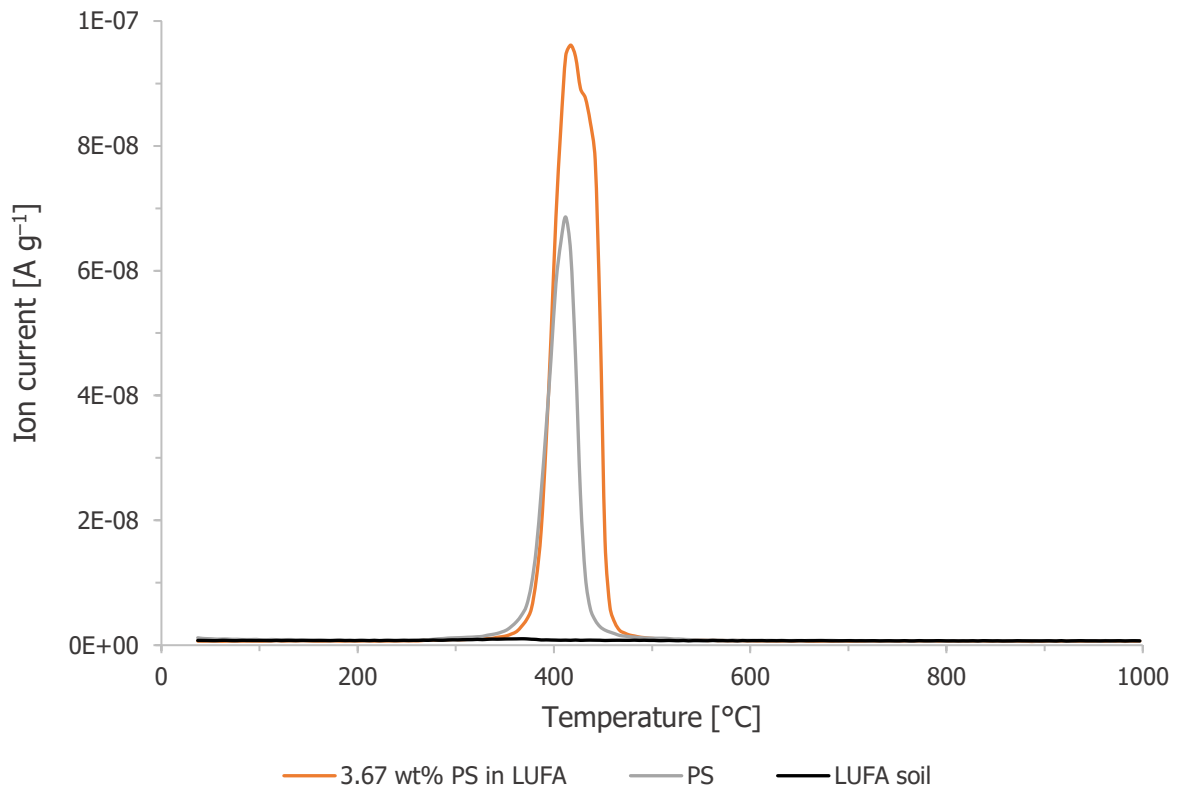


Figure 9.6 Normalized MS curves of PS, soil and 3.67 wt% PS in soil for $m/z = 91$.

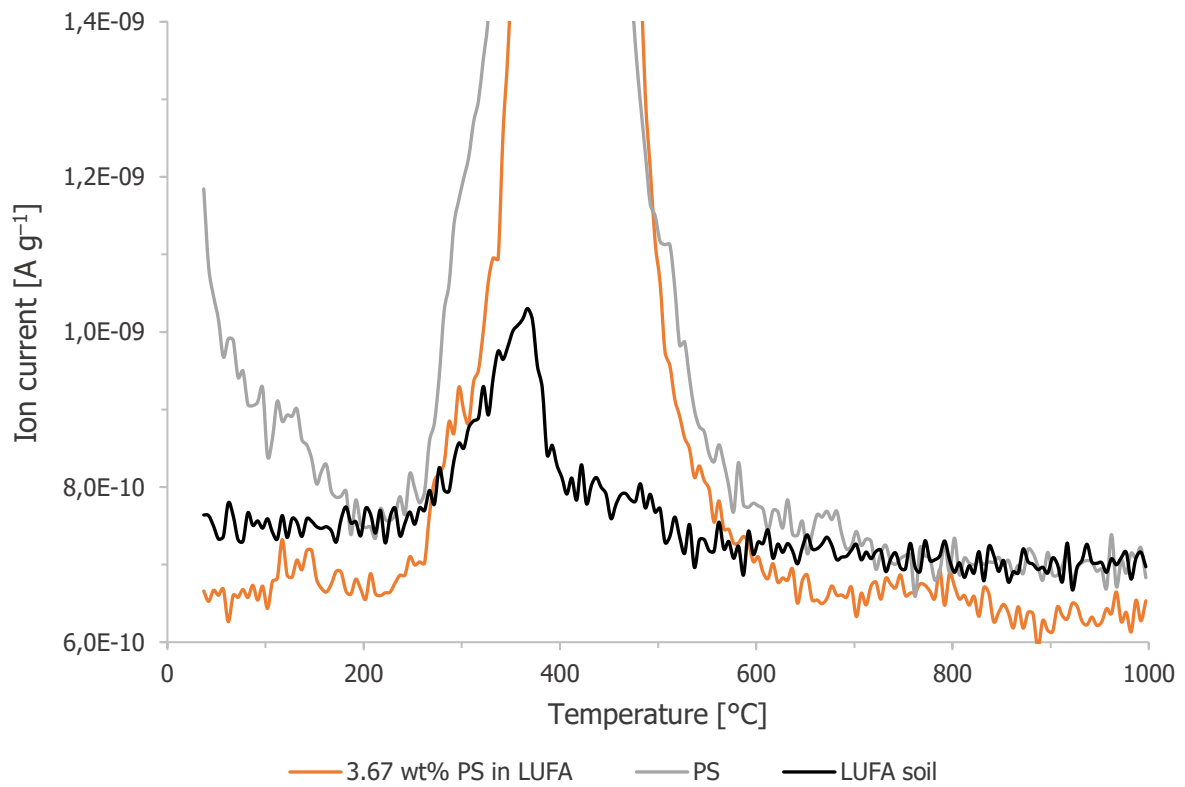


Figure 9.7 Detailed view of normalized MS curves of PS, soil and 3.67 wt% PS in soil for $m/z = 91$.

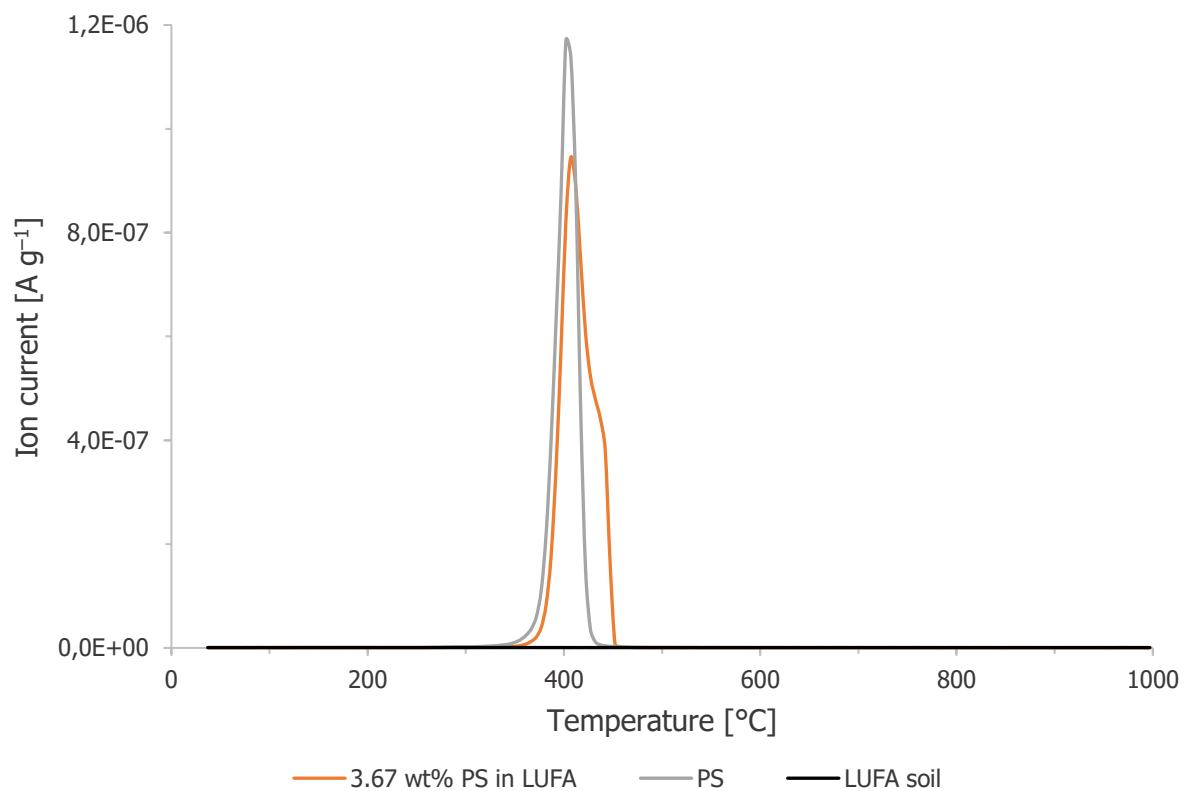


Figure 9.8 Normalized MS curves of PS, soil and 3.67 wt% PS in soil for $m/z = 103$.

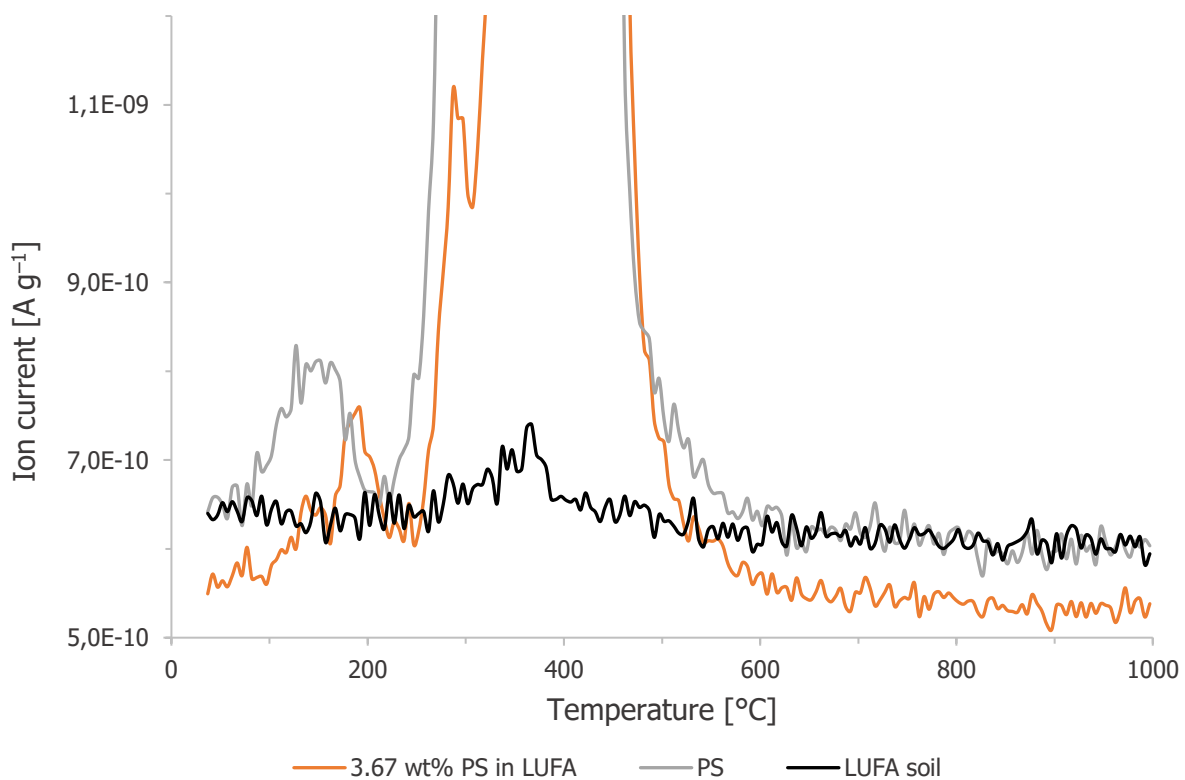


Figure 9.9 Detailed view of normalized MS curves of PS, soil and 3.67 wt% PS in soil for $m/z = 103$.

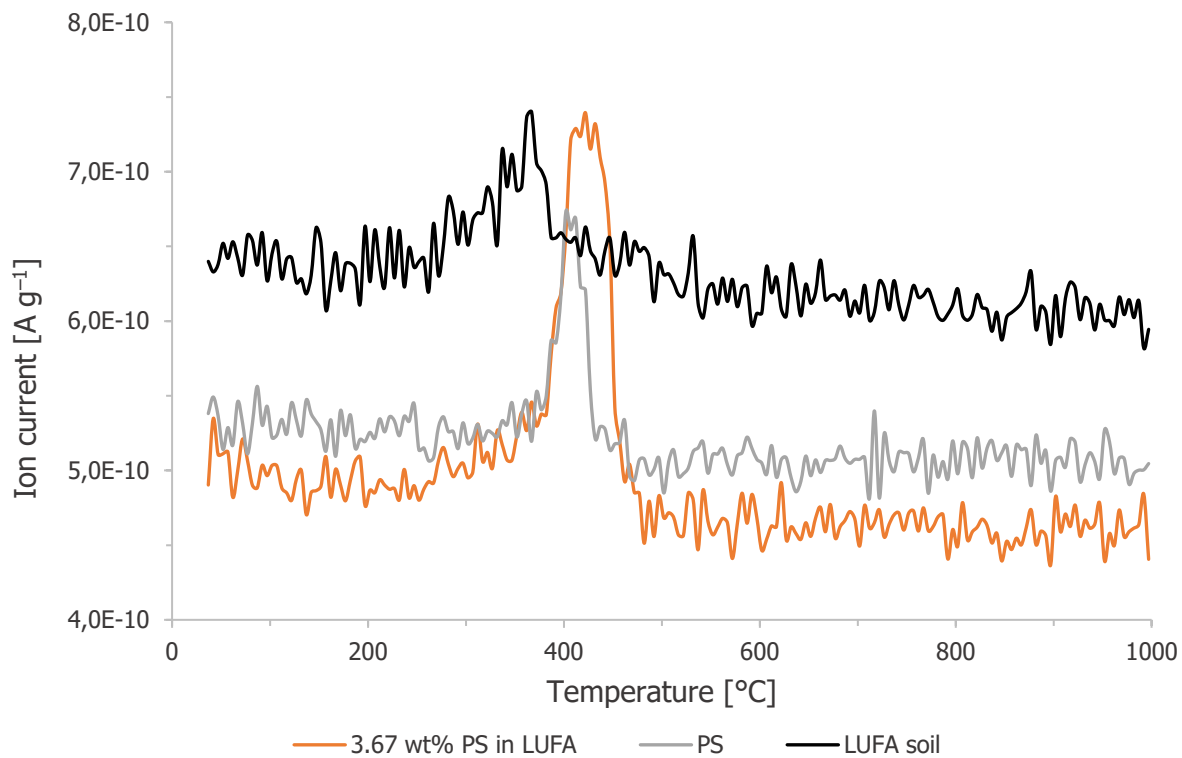


Figure 9.10 Normalized MS curves of PS, soil and 3.67 wt% PS in soil for $m/z = 132$.

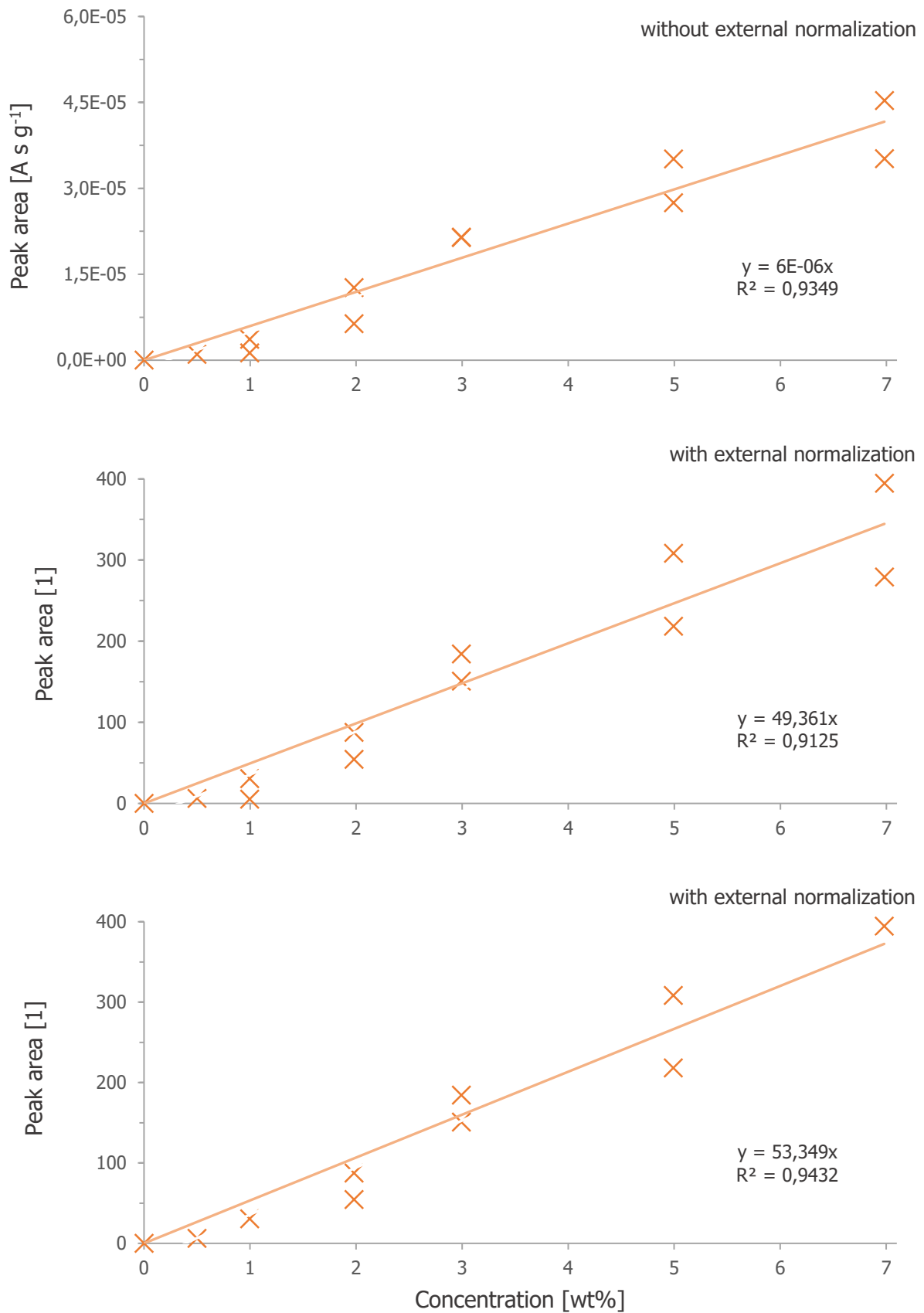


Figure 9.11 Calibration curve plot (PVC in LUFA, $m/z = 35$); a) without normalization (upper), b) with normalization on calcium oxalate hydrate (middle), c) with normalization and selected points (lower).

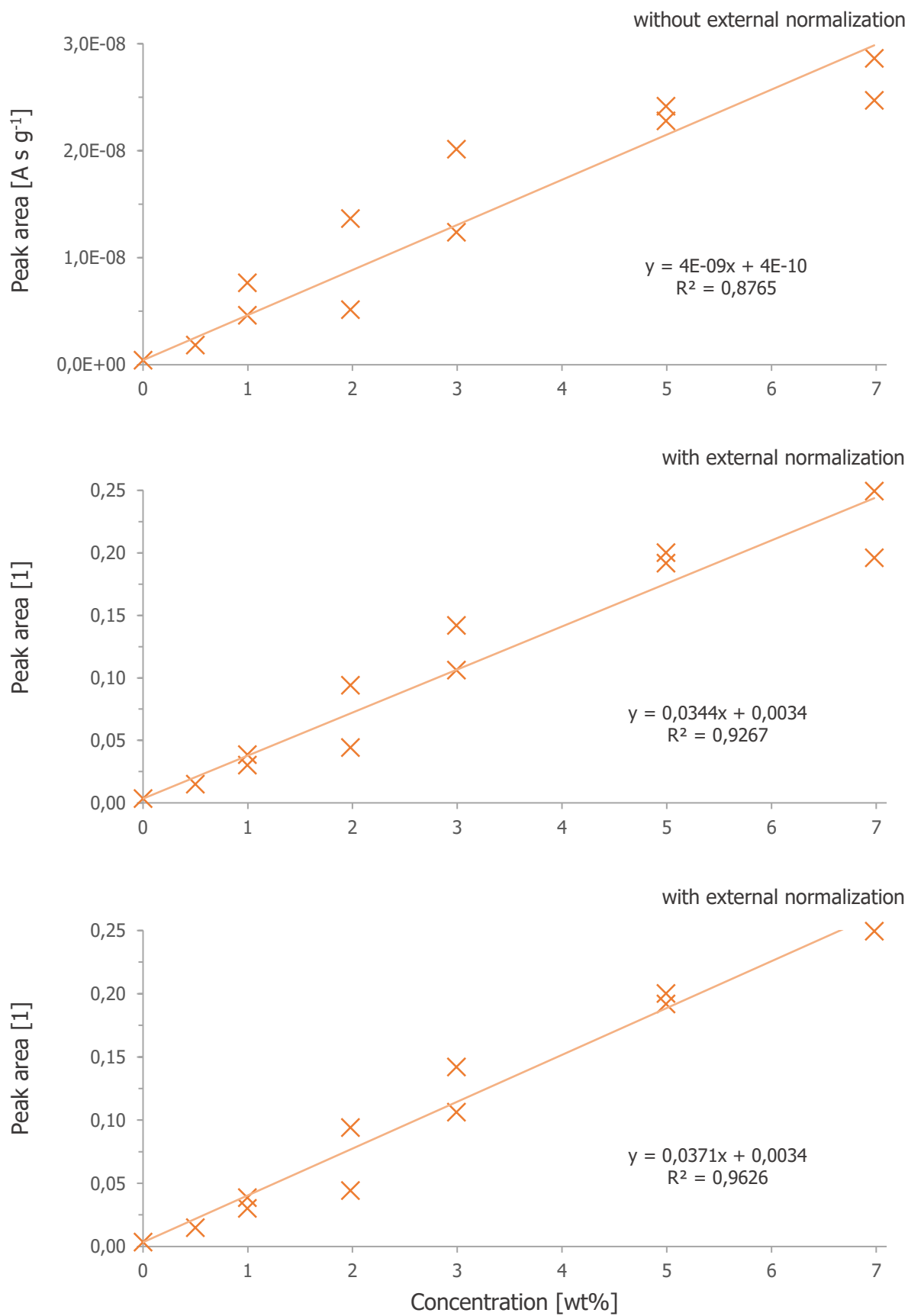


Figure 9.12 Calibration curve plot (PVC in LUFA, $m/z = 104$); a) without normalization (upper), b) with normalization on calcium oxalate hydrate (middle), c) with normalization and selected points (lower).

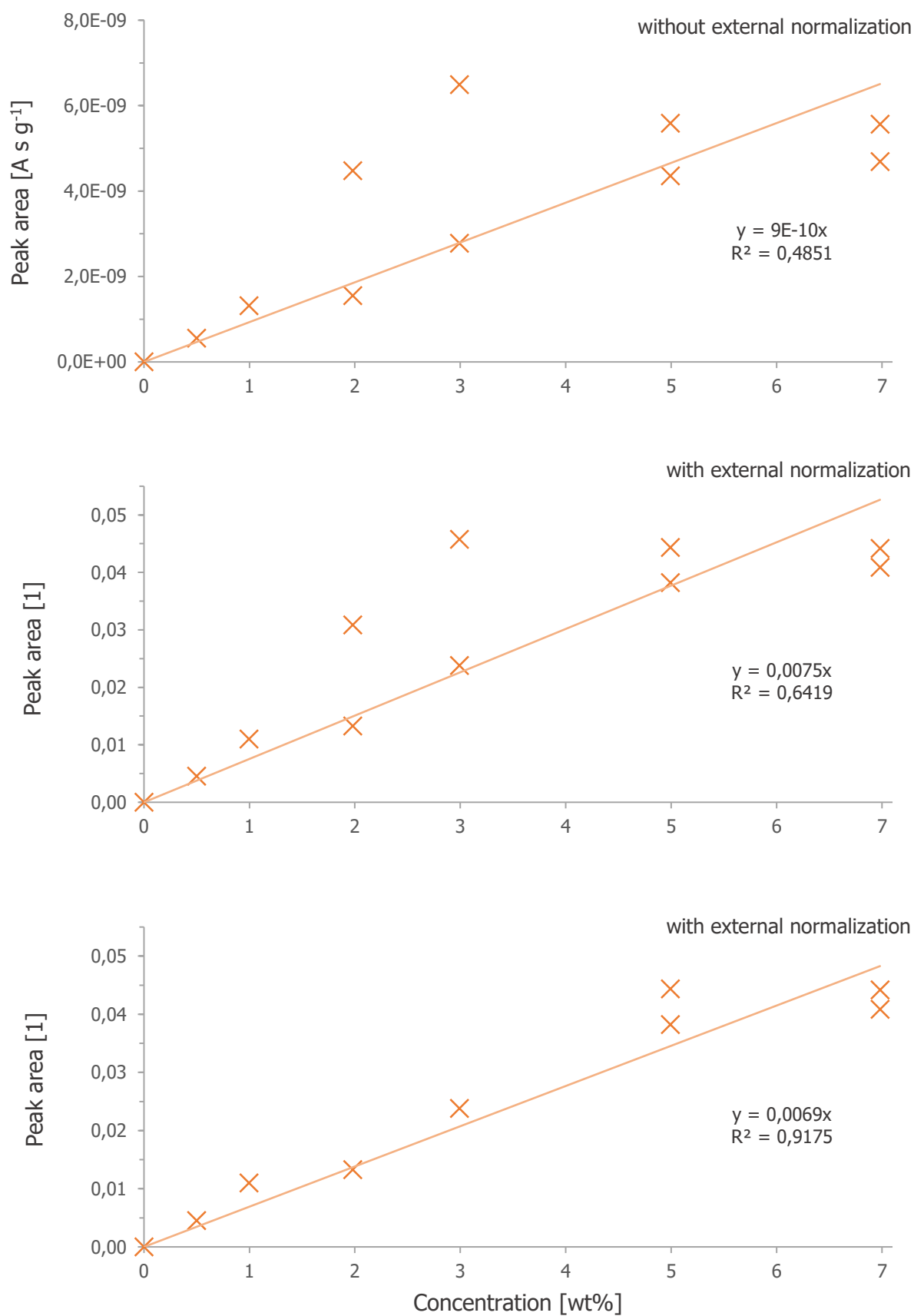


Figure 9.13 Calibration curve plot (PVC in LUFA, $m/z = 112$); a) without normalization (upper), b) with normalization on calcium oxalate hydrate (middle), c) with normalization and selected points (lower).

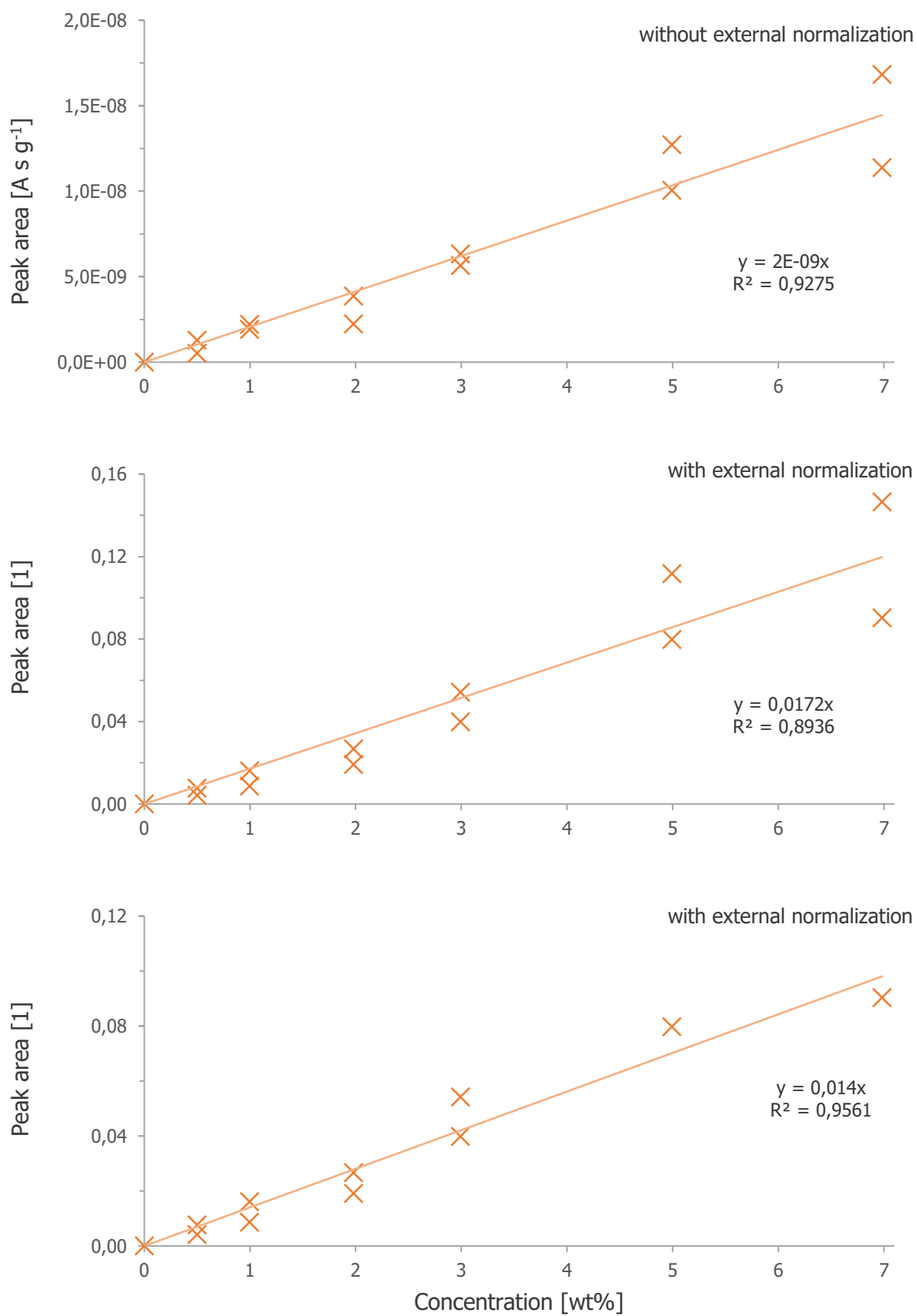


Figure 9.14 Calibration curve plot (PVC in LUFA, $m/z = 128$); a) without normalization (upper), b) with normalization on calcium oxalate hydrate (middle), c) with normalization and selected points (lower).

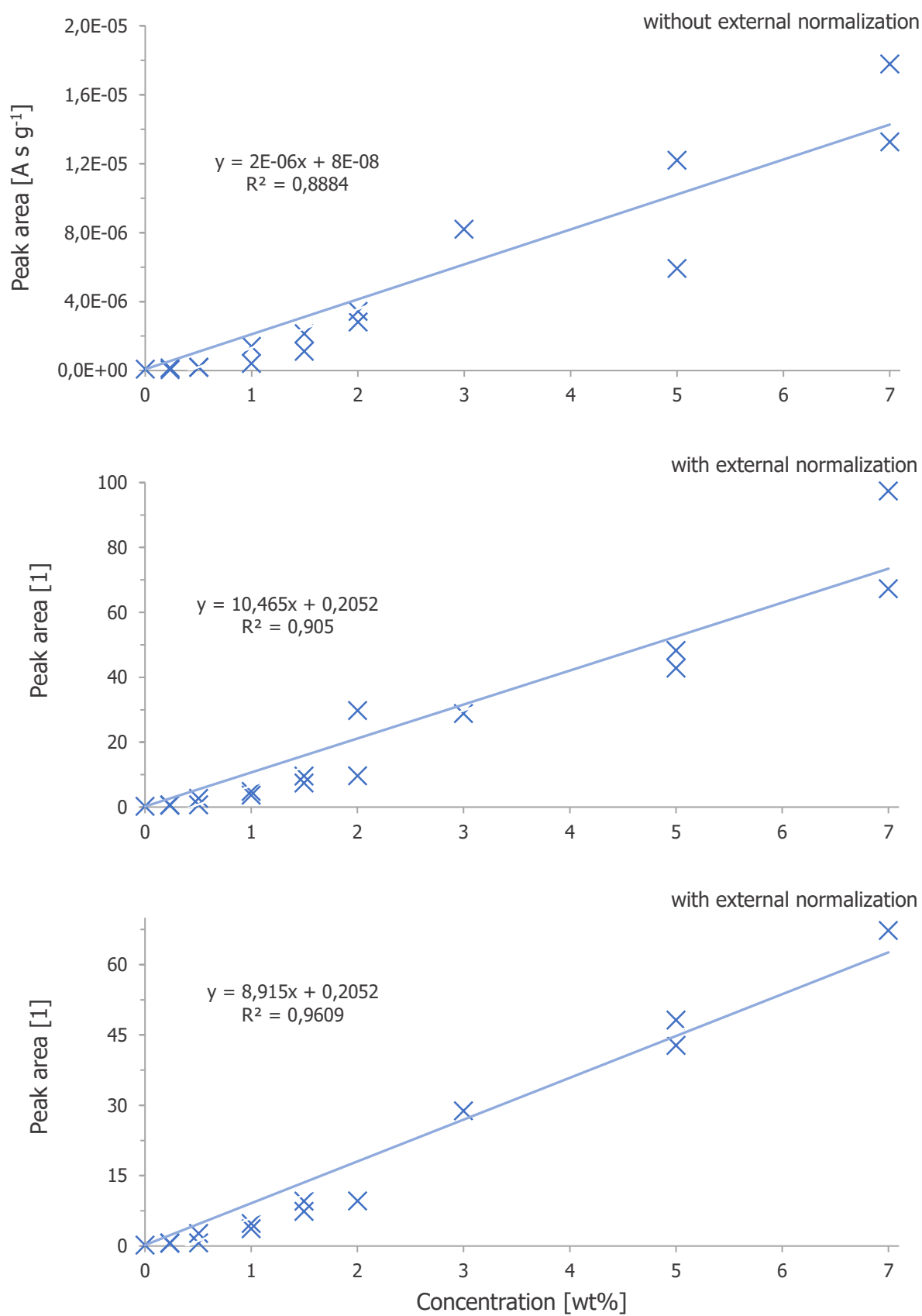


Figure 9.15 Calibration curve plot (PS in LUFA, $m/z = 51$); a) without normalization (upper), b) with normalization on calcium oxalate hydrate (middle), c) with normalization and selected points (lower).

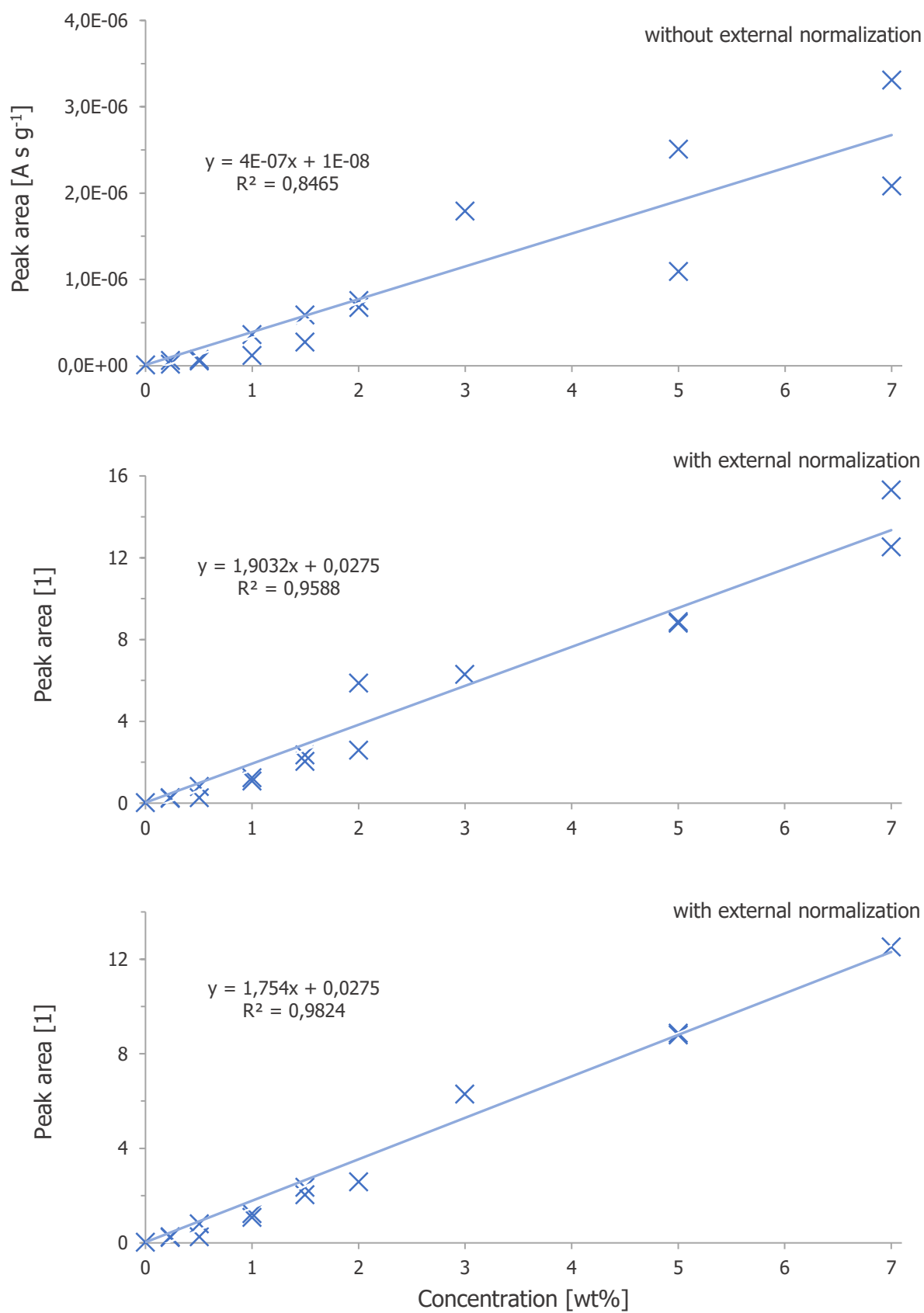


Figure 9.16 Calibration curve plot (PS in LUFA, $m/z = 91$); a) without normalization (upper), b) with normalization on calcium oxalate hydrate (middle), c) with normalization and selected points (lower).

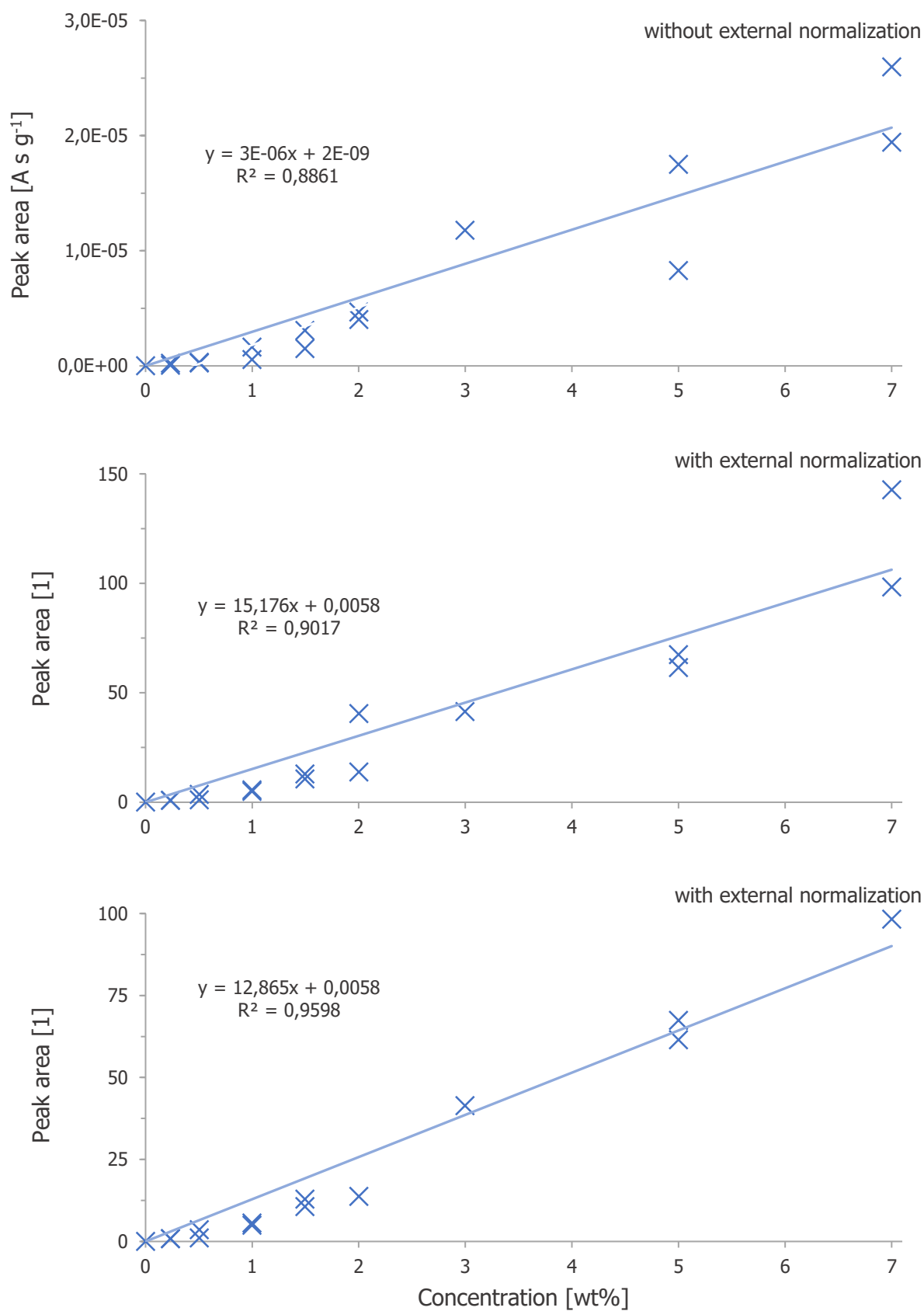


Figure 9.17 Calibration curve plot (PS in LUFA, $m/z = 103$); a) without normalization (upper), b) with normalization on calcium oxalate hydrate (middle), c) with normalization and selected points (lower).

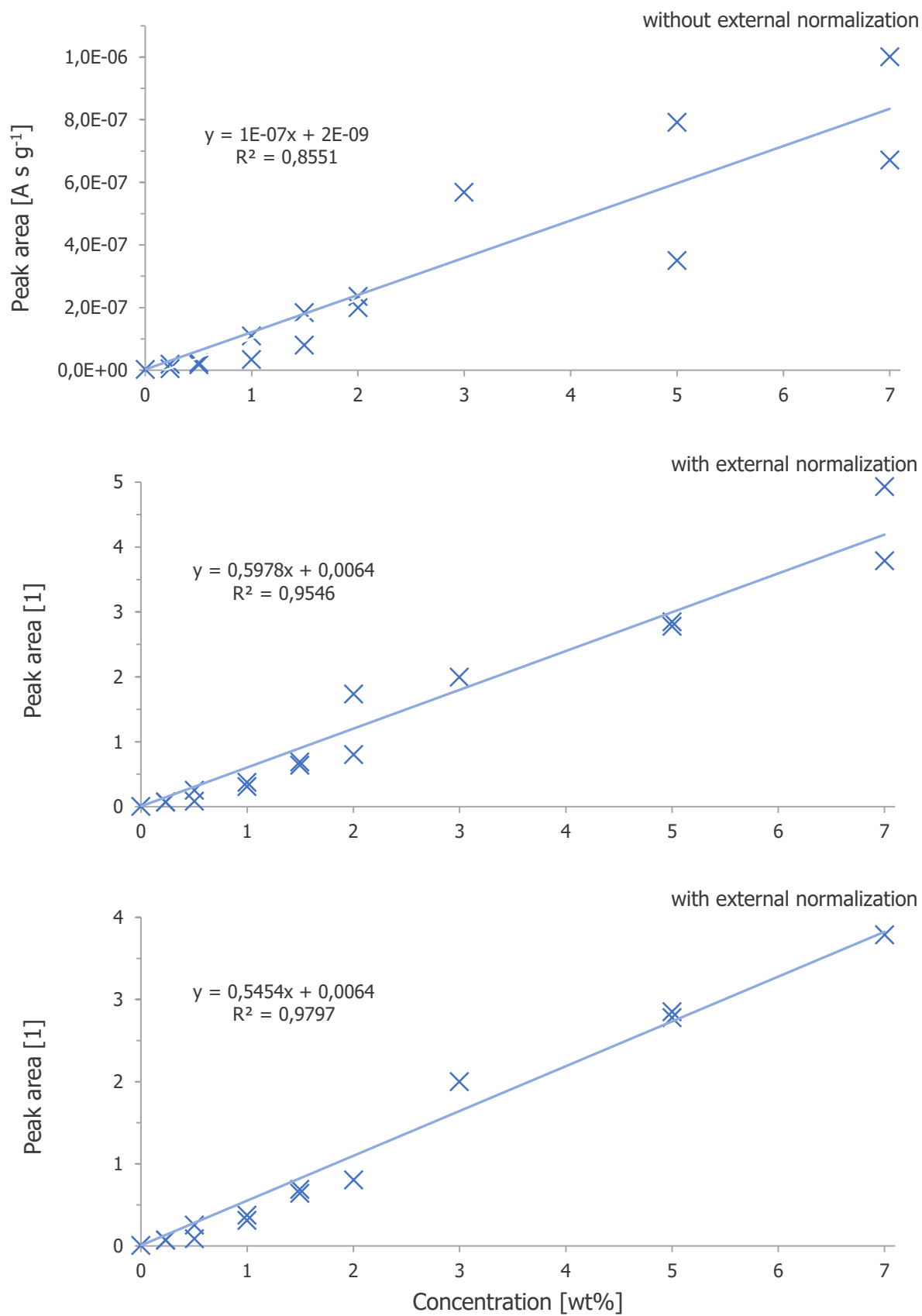


Figure 9.18 Calibration curve plot (PS in LUFA, $m/z = 117$); a) without normalization (upper), b) with normalization on calcium oxalate hydrate (middle), c) with normalization and selected points (lower).

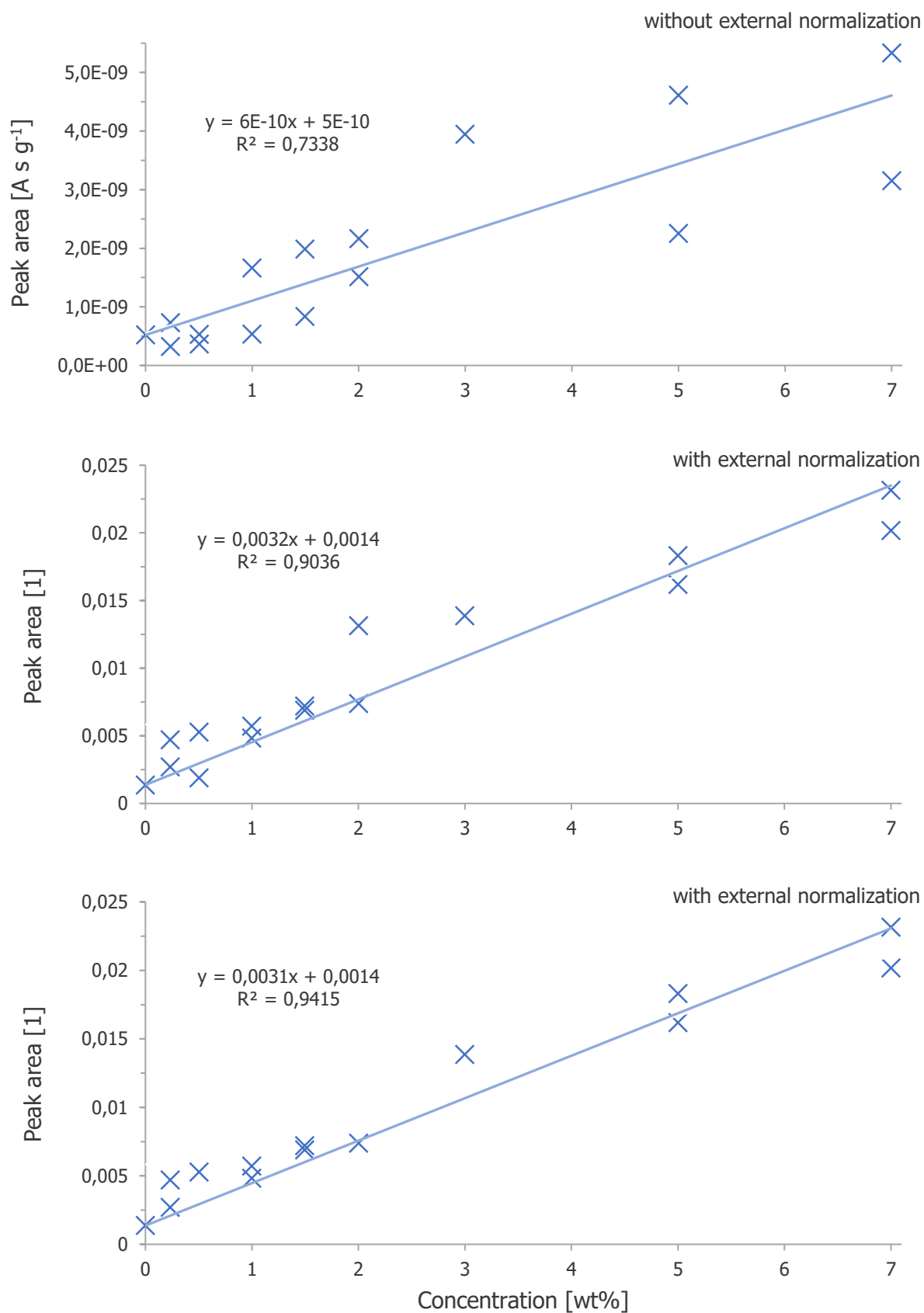


Figure 9.19 Calibration curve plot (PS in LUFA, $m/z = 132$); a) without normalization (upper), b) with normalization on calcium oxalate hydrate (middle), c) with normalization and selected points (lower).