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# MONITORING THE MASS OF MICROPLASTICS USING A SIMPLE THERMOANALYTICAL METHOD

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**ABSTRACT:** All national economies and human activities along the rivers contribute to the accumulation of plastics in the oceans. This is due to seemingly unavoidable entries from, e.g., car tire abrasions, littering, industrial facilities or producing businesses. The presented study is part of the process to detect and quantify relevant (micro)plastic entries into the environment. Only by quantifying and characterising the microplastic emissions, reduction measures can be derived and surveyed. A simple, and thus cost-efficient thermoanalytical method for determining the biomass content of refuse dericed fuel was developed and tested at TU Wien (Elemental Analysis combined with Overdetermined Equation Method – EA-OEM). Within the last five years, the EA-OEM method has been further applied and specifically adapted for the regular observation of microplastics in an industrial effluent. Four different monitoring phases, including some development and validation work, have been carried out so far. Additional conducted spiking tests revealed a recovery rate of >93%. Moreover, the agreement with comparative radiocarbon measurments is high. A size range of 10 µm to 5 mm could be covered on a mass basis (mg/L). By repeated measurements, the microplastic containment measures could be proven to be successful. Further monitoring campaigns will be conducted at the site and further effluents and environmental samples are subject to future investigations with this method (e.g. wastewater, detection of tire abrasions).

*Keywords: microplastic, thermoanalytical method, elemental analysis, industrial effluent, monitoring, balance method, EA-OEM*

## 1. INTRODUCTION

Latest studies show that considerable amounts of (micro)plastics are transported into the ocean by rivers. All national economies and human activities along the rivers – even if there are high environmental standards in force – contribute to the accumulation of plastics in the oceans. This is due to seemingly unavoidable entries from, e.g. car tire abrasions, littering, dissipative use of consumer products, industrial facilities or producing businesses. The presented study is part of the process to detect and quantify relevant masses of microplastic entries into the environment.

Microplastic analysis is mostly done by means of light microscopy techniques, delivering detailed information about number, size, shape and sometimes polymer type of the detected microplastic particles (Pimpke et al., 2020). This information are essential parameters for assessing the overall microplastic pollution and assessing ecotoxicological risks. However, the particles in the environment range from 1 µm up to 5 mm and even at nanoscale (Mintenig et al., 2018). Thus, from plain information on particle

numbers, no conclusion on the overall microplastic load can be derived and techniques suitable to analyse the mass of microplastics are needed. Thereto, thermoanalytical methods and spectrometers are applied (Goedecke et al., 2020). However, rather high investment costs for mass spectrometers, elaborate operation skills and high labor input reduce the applicability of these methods.

A new cost-efficient method was introduced by Mallow et al., 2020, which allows the total amount of microplastic to be determined. This method is based on organic Elemental Analysis (EA), combined with an Overdetermined Equation Model (OEM).

This method was further validated and tested by the authors for different kinds of samples. Within this study, investigations of samples from an industrial effluent are presented. The objective is to develop an appropriate sampling and analysis procedure for the monitoring of the microplastic load in the effluent. Further, the practicability for regular monitoring is assessed.

## 2. METHOD

### 2.1 Elemental Analysis combined with an Overdetermined Equation Method (EA-OEM)

The applied method – the Elemental Analysis, combined with an Overdetermined Equation Model (EA-OEM) – is based on the principle of solving a set of overdetermined equations, containing the mass shares of fossil and biogenic matter and the respective elemental composition of these matters. Thus, it relies on the same principle as the so-called Adapted Balance Method, which was developed for the detection of biomass in waste samples and refuse-derived fuels (Fellner et al., 2011, Schwarzböck et al., 2018). The Adapted Balance Method was again adapted for the application of microplastic in different environmental samples. General steps of the EA-OEAM are as follows:

- Theoretical division of the sample into three fractions: biogenic, plastics and inert material. Whereby the biogenic matter and the plastics need be significantly different in their macro-elemental composition.
- Determination of the macro-elemental composition of the water-free sample (C, H, N, S, O determinations). ( $Tx$ )
- Determination of the ash content in the sample ( $A$ ) and subsequently, determination of the elemental composition of the water-free ash ( $TIx$ )
- Calculation of the water- and ash-free elemental composition  $TOx$  ( $x = C, H, N, S, O$ ). According to the equation:  $TOx = \frac{Tx - TIx * A}{1 - A}$  (equation 1)
- One-time determination of the sample-specific  $TOx$  values of the biogenic fraction and the plastics fraction ( $TOx_B$  and  $TOx_P$ - elemental composition of the biogenic fraction and elemental composition of the polymers prevailing in the sample)
- Set up balance equations, where the determined  $TOx$  values of the sample are on one side of the equations (per element) and the  $TOx_B$  and  $TOx_P$  values, multiplied by the mass shares of biogenic and plastics are on the other side of the equations.
- Calculation of the unknown mass shares of the biogenic and plastics fraction by means of a non-linear data reconciliation (see also Fellner et al., 2011 and Mallow et al. 2020). The result is the mass fraction of biogenic matter and of plastics in the sample (as sum parameter).

### 2.2 Validation of the EA-OEM

In order to initially validate the method for the respective samples and their matrix, spiking experiments have been conducted. Additional PE/PP (ratio of 1:1) in concentrations between 0.5 % and 50% were added to samples collected at the industrial effluent (see also Spacek et al., 2020).

A further examination of the EA-OEM was done by participating in a round robin test, conducted by the German Federal Institute for Materials Research and Testing (BAM) (Becker et al., 2020). Synthetic

environmental samples with defined micrplastic content were distributed to 11 different laboratories, applying different analysis methods. Goal was to collect experience with thermoanalytical methods for the detection of microplastics. The sample contained a polymer-free matrix and the four polymers PE, PP, PS and PET. The polymer types were known to the participating laboratories, but not the respective shares or the total share of plastics (Spacek et al., 2020).

The radiocarbon method ( $^{14}\text{C}$ -method), a method well-established to detect the biomass in environmental samples was applied as comparative method to the EA-OEM approach. This analysis (accelerator mass spectrometry) was applied to selected samples, collected at the industrial effluent and compared to results from the EA-OEM.

### 2.3 Application of EA-OEM to industrial effluent

The EA-OEM has been applied and specifically tested for samples from an industrial effluent, so that a continuous monitoring can be done. Four phases of method testing and monitoring have been done so far (see Table 1).

Table 1. Phase of testing and monitoring of microplastic determination in an industrial effluent (sampling campaigns)

Phase (Year)	Goal of investigation	Focus of analysis
1 (2015)	Exploration, development and validation of analysis method	Plastic in raw effluent (> 250 $\mu\text{m}$ ), spiking experiments
2 (2017)	Development of sampling method and validation of analysis method	Plastic in raw effluent (> 12 $\mu\text{m}$ ), comparison to radiocarbon method
3 (2020)	Application of developed procedure	Plastic in effluent after containment measures (> 10 $\mu\text{m}$ ), microscopic pictures
4 (2020)	Application of developed procedure and characterization of particles	Plastic in effluent after containment measures (> 10 $\mu\text{m}$ ), microscopic pictures, first estimation on particle size distribution
5 (to be done)	Application of developed procedure and characterization of particles	Plastic in effluent after further improvement of containment measures (> 10 $\mu\text{m}$ ), microscopic pictures, determination of particle size distribution

### 2.4 Sampling and sample preparation

First sampling was conducted with nets, thus only large particles >250 $\mu\text{m}$  could be detected. To cover also small-sized particles, an own sampling procedure was developed and applied in following campaigns. A defined volume of effluent was drawn by means of an automatic sampling device equipped with a peristaltic pump every hour over a period of 24 hours. Thereby, 100-240 L effluent were collected per sample (with a total of 7-16 samples per sampling campaign).

The collected samples were transferred to the laboratory and filtered through a metal mesh filter with 10  $\mu\text{m}$  mesh size (in phase 2 cellulose filters were used with 12  $\mu\text{m}$ ). The filters were treated in an ultrasonic bath to remove all particles from the filter. Thereby around 0,5 – 5 g of material was collected.

The filtered material was treated over night with 30%  $\text{H}_2\text{O}_2$  and afterwards dried at 90°C. If necessary the material was comminuted by means of a ball mill or ultracentrifugal mill to obtain a homogenous sample (<500  $\mu\text{m}$ ).

### 2.4 Analyses

The application of the EA-OAM requires the macro-elemental composition (C, H, N, S, O) in the sample to be determined.

Elemental analyses were conducted using an elemental analyzer (Elementar Vario Macro for CHNS-determination) at temperatures of > 1000°C. The combustion gases are adsorbed and desorbed before being detected by heat conductivity sensors. The measurement of oxygen is similar (Elementar Vario El) but is conducted in an oxygen-free atmosphere.

The elemental composition is additionally determined in the anorganic part of the sample (in the ash). Thus, the organic elemental composition can be calculated based on an ash- and water free basis (see section 2.1).

Radiocarbon analyses (as comparative method) were conducted by the LARA, the Laboratory for the Analysis of Radiocarbon with Accelerator Mass Spectrometry (AMS) at the University of Bern.

### 3. RESULTS

#### 3.1 Results of recovery tests

##### 3.1.1 Results of spiking experiments

Figure 1 shows the results of the spiking experiments. It can be seen that there is very good correlation of the EA-OEM-measured values with the theoretical values, throughout the whole range of microplastic contents. A recovery rate of 93% to 110% could be determined at >1% microplastic content. At 1% of microplastic content, the recovery rate reduced to 80%. Thus, a first estimation on the detection limit could be obtained (around 1%). However, changing conditions can shift the detection limit up, e.g. changes in the plastic composition. The accurate determination of the initial values  $TOX_B$  and  $TOX_P$  is decisive. See details in Spacek et al., 2020.

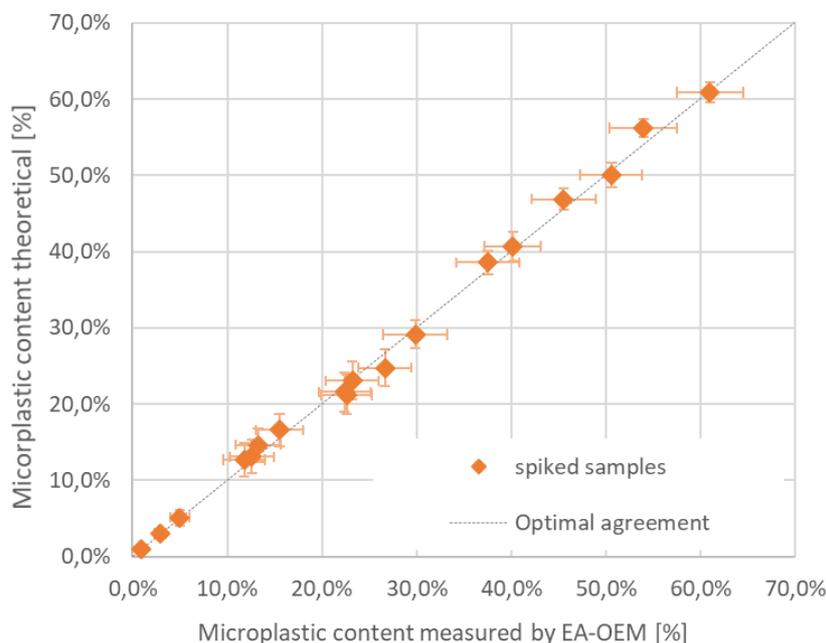


Figure 1: Results of recovery test with samples spiked with PE+PP

##### 3.1.2 Results of round-robin test

Figure 2 shows the measurement results when EA-OEM was applied to the sample provided during the round-robin test of BAM (Becker et al., 2020). The total microplastic content was estimated as well as the shares of PE+PP, PET, and PS (PE+PP can only be detected as a sum by EA-OEM because of their similar elemental composition). Thus, this was the first try to distinguish the different polymers by the EA-OEM by adapting the balance equations in the calculation model. Until now, only the sum of all

polymers was detected by EA-OEM. From Figure 2, one can see a very good correlation of theoretical values with the measured values. A recovery rate of 97% is observable for the total plastic content. The mean recovery rate over all participating laboratories was 78% (Becker et al., 2020). Even pure polymers (PE+PP, PET) could be detected at very high recovery rates (104% and 99%). For PS, the recovery was only 6%. It is assumed that parts of the PS share was assigned to the PE+PP share by EA-OEM due to the similar macro-elemental composition. The PS is very likely to be covered by the EA-OEM as it is also decomposed fully when combustion furnace of the elemental analyzer. The low recovery rate for PS points to difficulties of EA-OEM to detect polymers at low concentrations (Spacek et al., 2020).

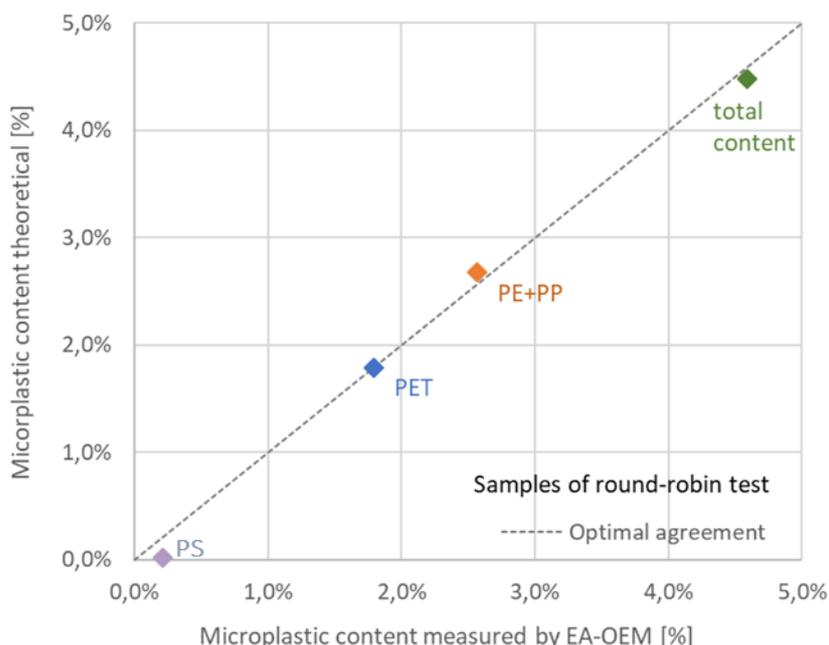


Figure 2: Results of recovery test with samples from round robin test

### 3.1.3 Comparison to radiocarbon method ( $^{14}\text{C}$ method)

The radiocarbon method ( $^{14}\text{C}$  method) which determines the fossil share of the sample on the basis of the contained carbon isotope  $^{14}\text{C}$  was used as a comparative method. Accelerator Mass Spectrometry (AMS) according to DIN EN ISO 21644:2021 was applied.

From Figure 3 it can be seen that the results from EA-OEM are comparable to the one by  $^{14}\text{C}$  method (agreement of 76 %). However, for some samples the agreement is rather low (<60%). The reason for this could be found in the biogenic matrix. It could be observed the  $^{14}\text{C}$ -method detects also some plastics in the pure biogenic matrix, which is assumed to be caused by a changed carbon-isotope ratio in the biogenic fraction. This distorts the results slightly and leads to overestimations of the microplastic content. The reason for the changed carbon-isotope ratio could not be found yet. Thus, for the regarded samples, the two methods are comparable when the biogenic matrix in the samples is low (e.g. algae).

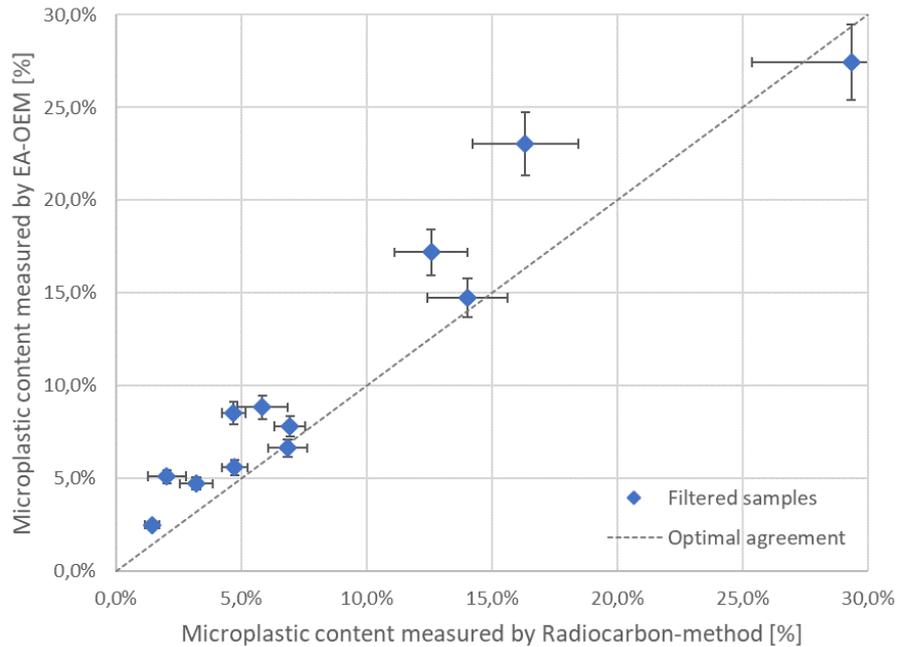


Figure 3: Comparison of detected microplastic content by EA-OEM with comparative method

### 3.2 Results of microplastic detection in industrial effluent

Figure 4 and Figure 5 present monitoring results during different monitoring campaigns at the industrial effluent. The microplastic content (in mg/L) could be determined with at least double determinations at different sampling points. Figure 4 shows that an installed containment measure was successful in reducing the microplastic load (reduction of 98%). Also over time a significant reduction of microplastic in the samples could be observed (Figure 5). A visual impression of the particles gives the microscopic image in Figure 6, showing roughly the size range of the plastic particles (a range of 10  $\mu\text{m}$  to 5 mm was covered by the measurements). Further characterization of the particles will be done (e.g. particle size distribution), in order to specifically increase the effectivity of the containment measure at the site.

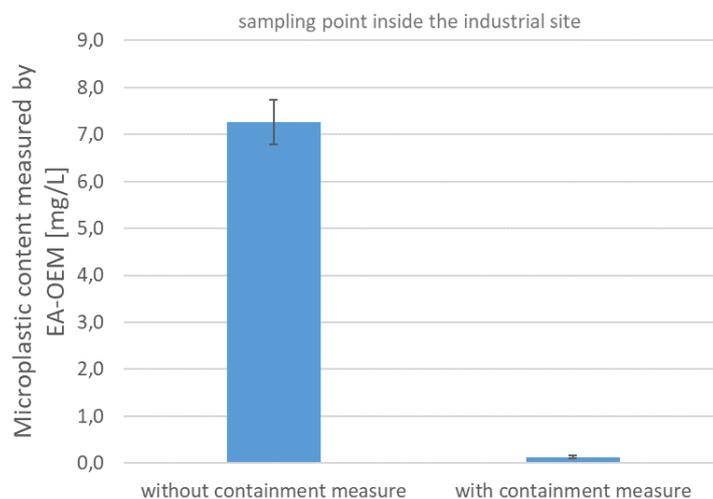


Figure 4: Measured microplastic content by EA-OEM in industrial effluent (measurement at same day at different sampling points)

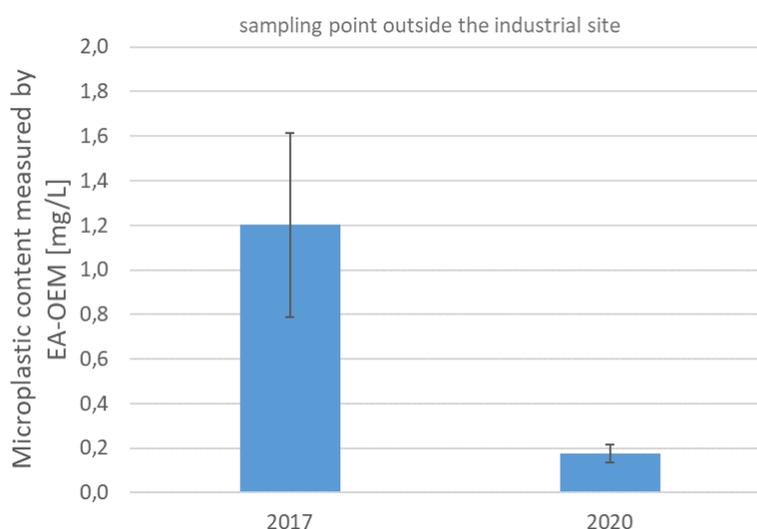


Figure 5: Measured microplastic content by EA-OEM in industrial effluent during two different monitoring campaigns (year 2017 and year 2020)

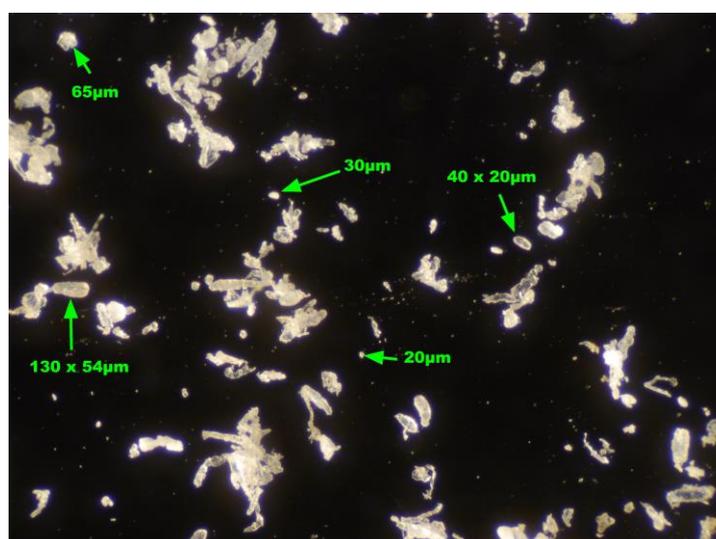


Figure 6: Microscopic image of one of the microplastic samples

### 3.4 Assessment of effort for EA-OEM when used for monitoring

An initial assessment of  $TOX_B$  and  $TOX_P$  values is crucial for the reliability of the EA-OEM ( $TOX_B$  – elemental composition of the biogenic fraction prevailing in the sample,  $TOX_P$  – elemental composition of the polymers prevailing in the sample). The polymer composition and the composition of the biogenic fraction have to be determined or estimated as precise as possible as the calculation result of EA-OEM depends on their precision. Thus, this (initial) step has the highest workload and is best defined for each sample type. However, investigations over the last years showed that the polymer composition in the environmental samples is mostly dominated by PE.

Within the presented monitoring study, the following net workloads can be estimated for one sample:

- Sampling: <30min (setup of the sampling station) + transport time
- Sample preparation: <60min (filtering,  $H_2O_2$  treatment, drying, comminution)
- Analysis: <30min (ash content determination, CHNSO analyses)
- Calculation: <30min (data preparation and data entry)

## 4. CONCLUSIONS

Through the application of the EA-OEM method, the microplastic content as a sum parameter can be determined on a mass basis. The study shows that the method is practicable for the quantification of microplastic in filtered effluent samples. Adaptations of the method for this application were necessary, particularly due to usually small sample mass. The recovery tests confirm the reliability of the method over a wide measurement range. A first estimation on the detection limit could be obtained.

The method was applied to monitor an industrial effluent over period of three years (three comparable sampling campaigns). Initial more intense work had to be done in the first phase to develop a specific sampling and analysis procedure and to collect the site-specific data on the elemental composition of polymers and biogenic materials. After this phase, the EA-OEM method was easily applicable and could be used to monitor the success of microplastic containment measures. Also repeated sampling and analysis campaigns can now be conducted relatively easily. Compared to other methods (like radiocarbon method, spectrometry) the EA-OEM does not require special skills and the equipment necessary is easy to handle. Elemental analyses (CHNSO) are necessary, but these are less costly than other analytical methods.

Thus, the EA-OEM will be tested also for the microplastic quantification in other environmental samples, such as wastewater or tire abrasion.

Further work will be done to improve the process of sampling and analysis. One major focus will also be on a better and more accurate determination of the elemental composition of polymers in (unknown) samples. This is regarded as a critical parameter for the reliability of the EA-OEM method. A combination with other methods (such as Pyrolysis-GC-MS) seems reasonable for this initial stage of EA-OEM.

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