Sorption effects interfering with the analysis of polycyclic aromatic hydrocarbons (PAH) in aqueous samples

Oliver Krüger [a,*], Ute Kalbe [a,1], Kerstin Meißner [a,1], Sebastian Sobottka [b,2]

[a] BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany
[b] Gartenstr. 1, 14169 Berlin, Germany

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) are severe environmental pollutants that are analyzed frequently. The risk assessment of PAH impact to groundwater can be performed using leaching tests. Therby a liquid–solid separation step including centrifugation may be required, which in turn might lead to loss of analytes due to sorption on the equipment. Thus we determined the PAH recoveries from various container materials (polyethylene (PE), polypropylene (PP), polytetraflourethylene (PTFE), stainless steel (ES), and perflouroalkoxy (PFA)) and compared them to selected PAH properties. We found the best recoveries for PFA (68%) and PTFE (65%) containers. We found good negative correlations (-0.93 and better) between PAH recovery and log partition coefficient organic carbon–water (log K_{OC}) for PFA, PTFE, and ES containers.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are hydrophobic organic compounds consiting of two or more fused aromatic rings. They emerge from incomplete combustion of organic material and are thus ubiquitous in the environment [1,2]. The main emissions of PAH are from anthropogenic sources like fossil fuel combustion and petrochemical production, refineries, power plants, asphalt, and tire wear debris [3,4]. Due to the toxicity and partial carcinogenicity of these compounds [5], the United States Environmental Protection Agency listed 16 of them as pollutants of high priority (EPA PAH), that are thus monitored very frequently.

The analysis of PAHs in environmental samples can be hampered due to their sorption on equipment walls during sample collection, transportation, and preparation. This can lead to loss of analytes and thus to low recoveries [6,7] which is especially important for aqueous environmental samples, where the PAH concentrations are usually low (< 1 mg/L) [6]. Sorption of PAHs to various plastic compounds is well known, especially to polyethylene (PE) [8], polypropylene (PP) [9], ethylvinylacetate [10], and silicone [11]. One option to overcome the problem of loss of PAH due to sorption is to use these materials for passive sampling of PAH directly from aquatic environments, without any sample preparation [11–13]. In doing so, possible interaction of PAH to humic substances and sorption to dissolved organic matter (DOM) has to be taken into account, as researched for instance by Simal-Gándara et al. [14,15]. Whereas this approach is very useful and established for the direct determination of PAH in water, it is not suitable for all the cases. Its application might not be possible due to complex matrices or lack of adequate passive samplers. Furthermore sometimes the respective standards or legislation do not allow for passive sampling.

Leaching tests, for instance, are important tools for the risk assessment of contaminated materials, particularly with regard to contaminant release to groundwater [16,17]. Several procedures have been developed and standardized for the investigation of organic contaminants in solid compartments, including column [18] and batch tests [19,20]. Additional particles can emerge during the experiments, especially in the case of batch tests. Since these particles hamper the analysis, a liquid–solid separation step is necessary to reduce their amount to a level similar to that in groundwater. The respective standards thus stipulate centrifugation followed by filtration (glass fibre filter) since filtration alone is known to be critical regarding sorption effects on common membrane filter materials. The centrifugation step might lead to significant loss of analytes due to sorption on container walls, since the sample is exposed to high acceleration. Since centrifugation is required by the standards and it is difficult to find container materials suitable for high accelerations apart from plastic or stainless steel it is necessary to know about the respective sorption properties.

So far, little is known about the sorption of PAH to centrifuge containers. Rawa-Adkonis et al. investigated the loss of PAH in

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Table 1
Selected properties of 15 EPA PAH [25,26].

Compound	Abbr.	No. of rings	Molecular mass [g/mol]	Solubility in water [mg/L]	Partition coefficient log K_{OC}
Naphthalene	Nap	2	128	31.7	2.97
Acenaphthene	Ace	3	154	1.93	3.66
Fluorene	Flu	3	166	1.68–1.98	3.86
Phenantrene	Phe	3	178	1.20	4.15
Anthracene	Ant	3	178	0.076	4.15
Fluoranthene	FlAnt	4	202	0.20–0.26	4.58
Pyrene	Pyr	4	202	0.077	4.58
Benzo[a]anthracene	BaA	4	228	0.01	5.30
Chrysene	Chr	4	228	2.8×10^{-3}	5.30
Benzo[b]fluoranthene	BbF	5	252	1.2×10^{-3}	5.74
Benzo[k]fluoranthene	BkF	5	252	7.6×10^{-4}	5.74
Benzo[a]pyrene	BaP	5	252	2.3×10^{-3}	6.74
Dibenz[a,h]anthracene	DahA	5	278	5×10^{-4}	6.52
Benzo[g,h,i]perylene	BghiP	6	276	2.6×10^{-4}	6.20
Indeno[1,2,3]pyrene	Ind	6	276	0.062	6.20

water samples during sampling, transportation and storage in glass containers and found considerable losses [7]. López García et al. researched sorption of PAH to PE, glass, and polytetrafluoroethylene (PTFE) and ways to decrease sorption by means of micelle formation [6]. The addition of acetonitrile, surfactants, or aliphatic alcohols [21] is known to reduce sorption of PAH. However, this option is not feasible for the preparation of environmental samples. Surfactants are known to alter the affinity of PAH to soil particles [22], which would most probably falsify the analysis. Anyway, the respective standards do not allow to add any additives during sample preparation. Schults et al. tested fluoranthene sorption to stainless stell and PTFE centrifuge containers and found 40% lower concentrations after 10 min centrifugation at 3000g [23].

Few is known about the sorption properties of PAH to sampling equipment. Yates et al. determined log partition coefficients for silicone rubber water to examine the sorption process of PAHs to silicone rubber during passive sampling [24].

In addition, irregularities of the surface texture of the centrifuge containers like rills, roughness, or scrapes, might influence the sorption of PAHs to the container walls.

Thus we determined the PAH recovery after centrifugation in five different container materials (PE, PP, PTFE, stainless steel (ES), and perflouroalkoxy (PFA)). We examined the sum of 15 EPA PAHs as well as the single PAHs. We performed six repetitions each to determine possible memory effects. We compared the respective recoveries with selected PAH properties to determine whether there are correlations. The log partition coefficient organic carbon–water (log K_{OC}), for instance, might be a meaningful parameter to describe PAH distribution between water and container materials. Furthermore, we made a microscopic analysis of the surface texture of the containers to determine possible irregularities. The selected PAH properties as well as the abbreviations used in this work are given in Table 1.

2. Materials and methods

2.1. PAH analysis and chemicals

PAH concentrations were determined directly from 10 mL of the respective aqueous solution with stir bar sorptive extraction (SBSE), as described recently [27]. It is an equilibrium method with no further sample preparation and we use only particle-free water for the standard solutions as well as the actual samples. Thus we expect no interfering effects on the analysis other than from the centrifugation containers. Additionally, we checked a PAH reference solution (PAH concentration 11.0 μg L^{-1}) with both SBSE and liquid–liquid extraction and found similar results (13.4 and 10.4 μg L^{-1}, respectively). The higher concentration determined with SBSE is probably due to losses of analytes during the liquid–liquid extraction [27]. The HPLC system was an Agilent 1200 Series with fluorescence detector and a Zorbax Eclipse PAH column of 4.6×100 mm^2 with 1.8 μm particle size. Since acenaphthylene shows no fluorescence, we did not measure or discuss it in this work. Ultrapure acetonitrile and water for HPLC separation were purchased from Liquid Chromatography Systems. We obtained NIST Standard Reference Material 1647e from the U.S. National Institute of Standards and Technology as PAH standard, consisting of a mixture of 16 EPA-PAH in acetonitrile. This standard was also used for the preparation of the test solutions. We took water for the test solutions from a Siemens Ultraclear UV high-purity water system.

2.2. Centrifugation equipment

For the centrifugation of the test solutions we used a Beckmann Coulter Avanti J-E centrifuge with JA-14 fixed angle rotor. We used screw capped centrifuge containers of 250 mL volume each. Stainless stell containers (ES) were obtained from Beckmann Coulter, Krefeld, Germany and polytetrafluoroethylene containers (PTFE) from Bohlender GmbH, Grünsfeld, Germany. Perfluoroalkoxy (PFA), polyethylene (PE), and polypropylene (PP) containers were provided by courtesy of Vitlab GmbH, Großostheim, Germany.

2.3. Test procedure

For the preparation of the test solutions, we diluted 1 mL of the PAH standard, which contained 98.32 mg/L PAH (sum of 15 EPA PAH, without acenaphthylene), in 10 mL acetonitrile. 1 mL of this solution was then diluted in 2 L high-purity water, resulting in a calculated PAH concentration of the actual test solutions of 4.69 μg/L. The acetonitrile content in these solutions is 0.05%, thus we consider there is no influence of acetonitrile on the sorption and analysis of PAH. Significant effects are to be expected only at acetonitrile contents of 10% or higher [28].

Blank values were determined for all containers prior to the experiments. Therefore, we put 200 mL high-purity water in each container, centrifuged them for 2 h at 3000g and determined the PAH concentrations. Those were low, especially compared to the test concentrations (PFA: 0.04 μg/L; PTFE: 0.10 μg/L; ES: 0.10 μg/L; PE: 0.05 μg/L; and PP: 0.03 μg/L), thus we expected no influence of the blank values on our experiments.
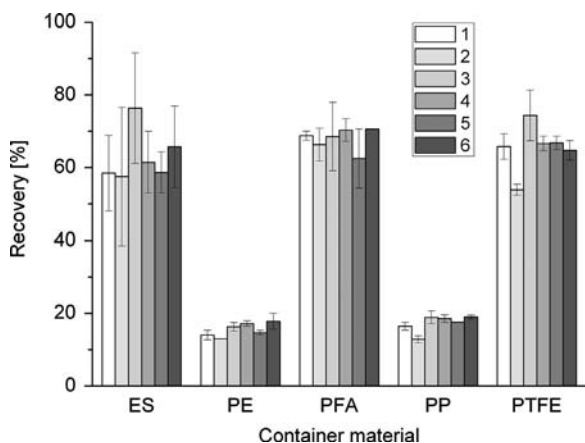
Fig. 1. Overall PAH recovery from centrifuge containers.

Fig. 2. Single PAH recovery from PFA containers.

The actual PAH content of each batch of the test solution was determined to allow for the calculation of PAH recoveries after the centrifugation procedure. Each container was filled with 200 mL of the test solution, then centrifuged for 2 h at 3000g, as stipulated by the standard. The PAH concentration was then determined again and the recoveries (stated in %) calculated for the sum of PAH as well as each compound individually. The containers were cleaned first in a laboratory washer, then filled with 20 mL acetonitrile and agitated in an horizontal shaker for 10 min and finally dried in a drying cabinet at 90 °C. The whole experimental procedure was conducted six times altogether. All experiments were carried out in duplicates.

In the case of the sixth repetition with the PFA containers (see Figs. 1 and 2) we observed significantly higher recoveries for every PAH from one of the containers (up to 170%). We presume an error during the experiment and/or the SBSE analysis and considered this results as an outlier. Thus we excluded the respective data from the evaluation.

2.4. Microscopic analysis

Images of the internal container surfaces were taken using a Keyence digital microscope VHX-600 combined with VH-Z20 lens and VHX-1000 with VH-Z250 lens (magnification 50–500-fold).

3. Results and discussion

3.1. Sorption to container materials

Fig. 1 shows the recovery rates of the sum of PAH after each of the six consecutive experiments. A high recovery rate implies a low sorption to the container surface. The overall mean recoveries were the highest for PFA, PTFE, and ES (68%, 65%, and 63% respectively) and the lowest for PP and PE (17% and 16%). The recoveries from the ES container material showed the highest relative standard deviations (RSD) from 6% to 19%, compared to 0.1% to 9% with the other materials. Whereas the recovery rates from PP and PE container increased slightly with the number of experiments, we observed no distinct trend with the other materials.

Figs. 2–6 show the recovery of each of the 15 EPA PAH from the investigated container materials over six repetitions. For PFA, the recoveries decrease with increasing molecular mass of PAH (Fig. 2). We found the highest recovery rate for Ace (93%; mean value of all six repetitions) and the lowest for DahA (24%). In case of PTFE containers, the findings are similar (Fig. 3), with slightly lower recovery rates (Ace 90%; DahA 21%). We found comparable
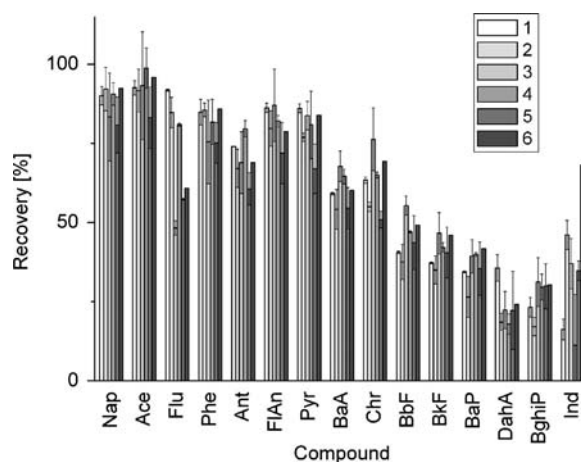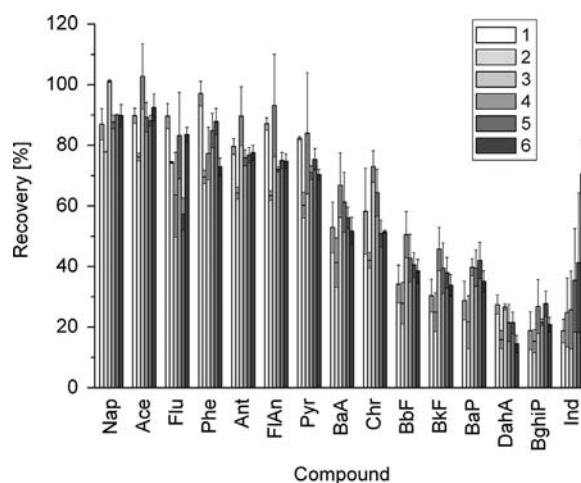

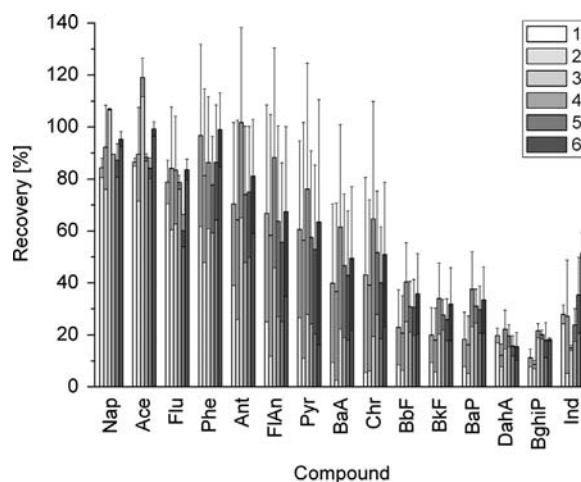Fig. 3. Single PAH recovery from PTFE containers.

Fig. 4. Single PAH recovery from ES containers.

results for ES containers (Fig. 4) with the highest recovery rate for Ace (95%) and the lowest for BghiP (16%). The relative standard deviations of the recovery rates for ES containers were significantly higher than those for all other container types, especially for the small to medium-sized PAHs i.e. Phe, Ant, FlAn, Pyr, BaA, and Chr (19–48%).
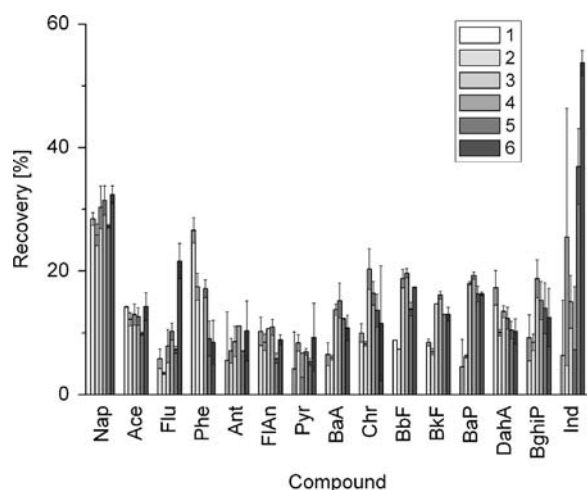
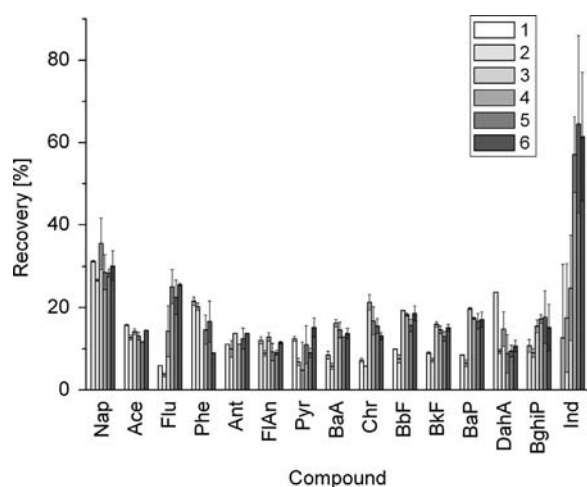**Fig. 5.** Single PAH recovery from PE containers.

Fig. 6. Single PAH recovery from PP containers.

The recoveries from PE (Fig. 5) and PP (Fig. 6) are generally low. Mean values for PE ranged between 8% and 13% with the exception of Nap (29%) and Ind (24%). For PP the recoveries were between 10% and 16% for the majority of PAHs, 30% for Nap, and 40% for Ind. We observed no distinct trends of recovery rates of the single PAHs. The only exception for PFA, PTFE and ES was Ind, whose recoveries increased in the course of the repetitions. In the case of PE and PP, we observed an increase of recoveries for Flu and Ind.

In the case of ES, PFA, and PTFE container materials, possible accumulation of PAHs over six consecutive centrifugation runs does not seem to have an influence on their respective recoveries. Although the recoveries indicate that sorption occurred, either the cleaning procedure between the runs is sufficient to remove the sorbed PAH thus making the sorption sites available again or the number of sites is large enough for the PAH sorbed in six consecutive runs. The only exception is Ind that shows increasing recovery rates. The effect seems to be substance specific, since it occurs with all tested materials. The reason for this remains unclear since molecular mass and log K_{OC} are comparable to the other 5- and 6-membered ring PAHs. On the other hand, its water solubility is higher, which might indicate a different sorption behaviour.

Albeit PE and PP containers showed only slight or rather negligible memory effects, the recovery rates are low for all tested PAH, which would lead to a significant loss of analytes during the

Table 2
Linear correlation coefficients (r) between PAH recoveries and selected PAH properties.

Container material	Correlation coefficients (r) of PAH recoveries vs.		
	Molecular mass	Solubility in water	Partition coefficient log K_{OC}
PFA	−0.93	0.39	−0.93
PTFE	−0.96	0.40	−0.95
ES	−0.97	0.44	−0.96
PE	−0.07	0.73	−0.08
PP	0.02	0.48	−0.02

sample preparation process. That would lead to false low results, thus making both not suitable for use as container materials for centrifugation of aqueous samples containing PAHs. Whereas the recovery rates from ES container are significantly higher, the relative standard deviations (RSD) are high, the highest for all tested materials. Scratched or otherwise damaged surface, as indicated by microscopic analysis (see Section 3.2) might lead to additional sorption capacity. ES is presumably more prone to scratches during the cleaning process than plastic materials. Scratches might lead to increased sorption of analytes, thus hampering the cleaning process and consecutively lead to higher RSDs.

PFA and PTFE container materials show recoveries comparable to ES but lower RSDs. Furthermore, we observed no memory effects during the six consecutive experiments. Thus PFA or PTFE seems to be the best option for centrifuge containers.

Table 2 shows the linear correlation coefficients between the recoveries PAH from the different container and selected PAH properties. PFA, PTFE, and ES show good negative correlations of the recovery vs. molecular mass and log K_{OC} and no correlations vs. solubility in water. Since the former parameters are related to sorption processes, these correlations might indicate that recovery rates of PAH depend more on sorption effects than on their solubility in water. Further research on these effects might be useful to estimate the loss of PAH during sample preparation. These tests should take into account actual environmental samples with particles and colloids that are prone to sorb PAHs. For PE and PP materials we observed no correlations at all.

3.2. Influence of the condition of container surfaces

Rills and a general roughness of the container surface imply a larger surface area compared to smooth and even container walls. Scratches are disruptions of the surface that might lead to a higher sorption capacity. Fig. 7 shows microscopic images of the inner surfaces of the tested containers which are in contact with the solutions (or eluates). ES reveals significant scratches (ES 500×), some of them even rusty (ES 50×) – indicating a relatively rough-textured surface. PTFE and PFA show smooth surfaces, although PFA exhibits some tiny bumps (2.5 μm height). PE and PP have a more textured surface with significant rills, elevations and rough-ness. The rough-textured surface of the ES containers might be a reason for the higher RSDs we observed for the PAH recovery. The PTFE and PFA surfaces seem to be undamaged by usage. Even the rills of the PFA surface obviously did not lead to higher RSDs. The textured surface of PE and PP containers – even though not affecting the RSDs significantly – might indicate a larger surface area, and thus increasing the sorption capacity. This might lead – together with the less water repellant properties of PE and PP compared to PTFE and PFA – to the observed lower recoveries.
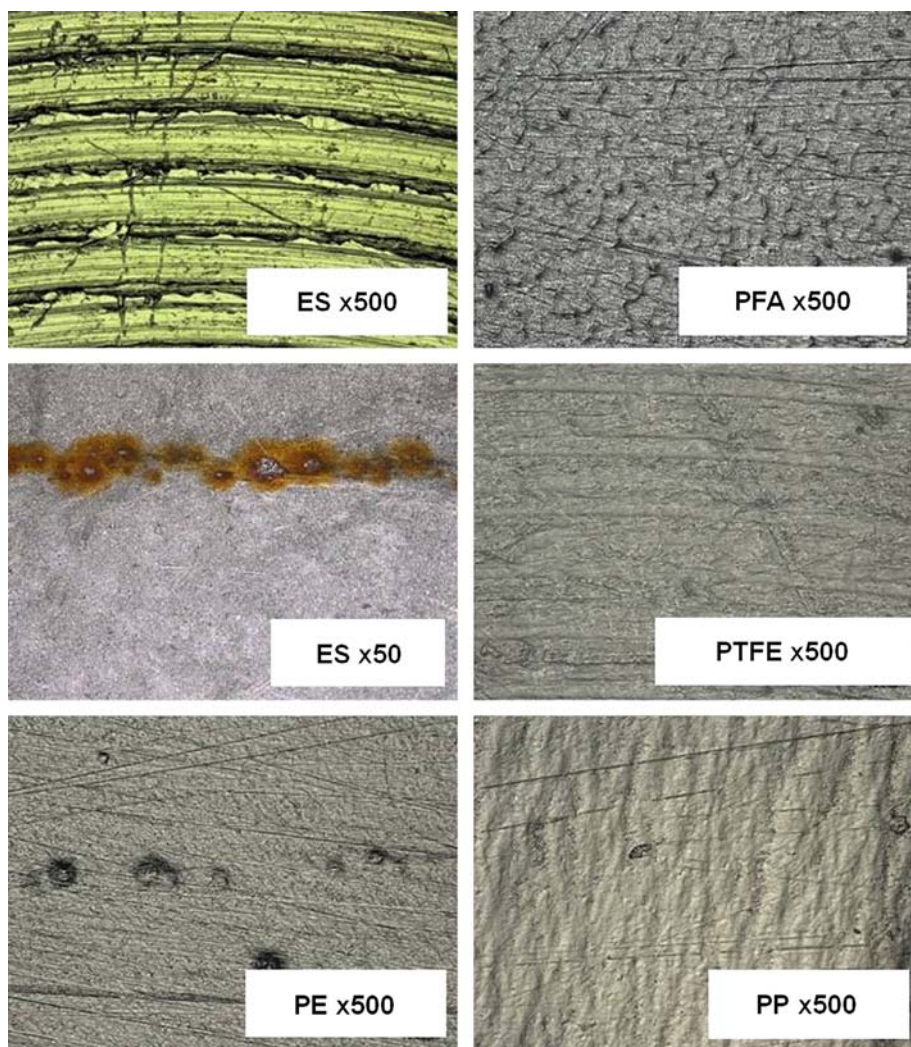
Fig. 7. Microscopic images of internal centrifuge container surfaces (magnification 50–500 ×).

4. Conclusions

PFA and PTFE showed the best performance of all tested materials concerning recovery rates of PAH, repeatability and memory effects and are thus probably the best suited for use as container materials for centrifugation of aqueous samples containing PAH. Whereas ES showed similar recoveries, the RSDs were considerably higher and cannot be preferably recommended. PE, PP are not suitable for usage as centrifugation containers due to their low recoveries. Further research on the sorption phenomena during the sample preparation of actual environmental samples might help to estimate the loss of PAH prior to analysis. Further research is recommended to determine the possible influence of particles and organic matter on the analysis of PAH in actual field samples.

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