Extending the capabilities of field flow fractionation online with ICP-MS for the determination of particulate carbon in latex and charcoal

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Abstract

There is a broad range of carbon based engineered particles including polymer latex particles and carbon black. Also in environmental systems particulate carbon such as humic acids and soot or coal (the latter two summarized as black carbon) is of great importance and is involved in nutrient storage and (re)cycling. Therefore, detailed characterisation of the size distribution and elemental composition of such particles is required to understand the material properties and their environmental relevance. Field flow fractionation (FFF) online with inductively coupled plasma mass spectrometry (ICP-MS) is routinely applied for the characterisation of metal containing particles. However, the far majority of FFF studies relies on UV detection for organic carbon while elemental detection of carbon has hardly been used. Our previous work demonstrated the capability of FFF-ICP-MS for the determination of carbon in fine particulate matter, focusing on humic acid in water samples. The current work investigates the feasibility of carbon detection and quantification in larger particles with sizes up to about 750 nm. For this purpose, latex particle size standards of 21 nm, 100 nm, 250 nm and 740 nm were analysed as well as extracts of charcoal spiked soil. Elemental analysis using combustion techniques was employed as reference for the total carbon content of the samples to establish a mass balance. Recoveries for FFF separation of latex particle standards were in the range from 69% to 83% and in the range from 78% to 104% in flow injection mode. Carbon mass balance calculated from FFF fractionation, ultrafiltration and total content for the extracts from soil and charcoal spiked soil achieved 76% to 105%. Variation of the sampling depth was investigated to check if increased dwell time of the particles in the plasma affects the carbon ionisation and quantification. No significant change of carbon recoveries was observed, yet the signal to noise ratio improved 3-fold. This study provides a method for the analyses of carbon containing particles via FFF-ICP-MS, which allows for the first time the simultaneous measurement of carbon and other nutrients and is hence more timesaving than other methods.

Introduction

Engineered carbon containing particles from the nanometer to micrometer size range are employed in a variety of applications. For example, latex suspensions of a broad range of compositions are used for coating, painting, papermaking, cosmetics, biomedical and pharmaceutical purposes.[1,2] Frequently, inorganic nanoparticles are modified with an organic surface coating leading to core-shell particles with improved properties.[3] Carbon black, i.e. the reaction product obtained from incomplete combustion of oil or similar materials, is applied in large scale as pigment in inks, paints, printer toner and for improving the stability of automobile tyres.[4,5] In addition, black carbon, i.e. soot or coal particles are released from many sources into the environment including automobile exhaust, commercial or household combustion processes, smoking and forest fires.[6-9] In environmental water samples, inorganic particles with organic coating are present along with organic macromolecules ranging from humic acids up to cells or micro-algae.[10,11] In all these cases reliable characterisation of particle size, size distribution and elemental composition is of interest and of need to improve knowledge and understanding of both the properties of engineered materials and environmental colloids.

Field flow fractionation (FFF) is generally recognised as a widely applicable technique for particle separation in various matrices with minimum requirement for sample preparation prior to injection onto the channel. The majority of applications is targeting engineered metal or metal oxide particles as well as metal contents in environmental nanoparticles and colloids.[12] In this case, online detection with inductively coupled plasma mass spectrometry (ICP-MS) provides sensitive, isotope selective multi-element detection next to complementary UV/VIS and light scattering detection. Regarding carbon based particles, several studies applied flow, sedimentation or thermal FFF separation with UV detection at 254 nm and/or light scattering detection for various suspended polymer latexes as well as carbon black in ink or industrial preparations.[2,4,5,13,14] Element selective detection was not applied in these studies. Commercially available monodisperse latex particles are frequently used for size calibration of FFF separation methods based on UV detection and light scattering.

In spite of the vital role of carbon in both environmental science and industry, hardly any attempt was made so far to apply carbon specific detection techniques online with FFF for elemental characterisation of latex and black carbon particles. Recently, we investigated the potential of FFF online with ICP-MS for the detection and quantification of particulate carbon in aqueous samples focusing on humic acids and proteins.[15] The few applications and the challenges of carbon detection with ICP-MS are summarised in this previous work. Validation was performed by parallel FFF runs online with an organic carbon detector (OCD) which is based on a thin film UV-reactor to oxidise organic carbon and detect as CO_2 by infrared. In case of organic macromolecules in the low nm size range it is expected that both, the inductively coupled plasma and the UV-reactor are sufficient to decompose the organic structures entirely and thus provide full quantification of the particulate carbon eluting from FFF. This could be demonstrated by matching results from FFF-ICP-MS and FFF-OCD for citric acid and humic acid standard solutions and environmental water samples as well as for bovine serum albumin.[15]

However, latex particles and soot or charcoal particles constitute much larger and more robust carbon based structures.[16,17] Therefore, the aim of the current study is to evaluate the performance of ICP-MS detection online with FFF for the quantification of carbon in latex particles up to a size of 740 nm and charcoal spiked soil particles up to a size of 450 nm. Compared to the humic acids with a diameter in the low nm range the 740 nm latex particles are about 50-fold larger in diameter and thus $50^3 = 125000$-fold larger in volume assuming spherical shape. This estimation clearly demonstrates the challenge of introducing latex particles of this size directly into the plasma. Quantitative metal recovery from (nano)-particles in the inductively coupled plasma is reported for particle sizes up to about 500 nm for silica.[18] For particles below this size limit the residence time in the plasma is expected to be sufficient for the full decomposition of the particles in order to achieve the same ionisation efficiency for the particle bound metals compared to a dissolved metal standard. Additional limitation for the upper particle size for unbiased elemental detection by ICP-MS is the selective removal of droplets larger than approximately 10 µm in the spray chamber which affects also particles larger than about 2 µm.[18] Offline combustion analysis of the samples was used as reference for the total carbon concentration to calculate recoveries. In addition, the effect of sampling depth on the recovery of particulate carbon in latex samples by ICP-MS was investigated. The optimisation of FFF separation conditions and relation of the particulate carbon to particulate metal or phosphorus concentrations are not within the scope of the work presented here but will be addressed in future applications.

Experimental

Chemicals, calibration standards and samples

Sodium chloride (EMSURE for analysis), citric acid (p.a.) and Certipur TOC calibration standard were supplied from Merck, Darmstadt, Germany. Deionised water was prepared using a Millipore purification system. Polystyrene latex particle standards with nominal size of 21 nm, 100 nm, 250 nm and 740 nm were obtained from Postnova Analytics, Landsberg, Germany with concentration of 8.0%, 8.2%, 8.0% and 8.1%, respectively, in water. Soil material with a carbon mass fraction of approximately 13 g/kg was collected from topsoil (0-25 cm) of a Haplic Phaeozem from Halle, Germany.[19] Charcoal was prepared by heating maize (*Zea mays* L.) in stainless steel containers up to 350°C using a muffle furnace and maintaining this temperature for 2 h. After cooling the charcoal was ground. Carbon mass fraction in this charcoal is approximately 664 g/kg.

Sample preparation

The latex standards were 200-fold diluted in deionised water in triplicate prior to analysis. Aliquots of soil were spiked with charcoal and extracted in duplicate (referred to as A and B) according to an established protocol for dissolved organic carbon analysis following Kalbitz et al..[20] In detail, 9 g of soil was mixed with 1 g of charcoal; thereafter 100 mL of deionized water were added. The mixture was shaken end over end for 2 h, left to stand for 24 h at room temperature and was passed through a glass microfiber filter with pore size of 450 nm (GF6 125; Hahnemühle, Dassel; Germany). The non-spiked soil (9 g) was extracted in duplicate (referred to as A and B) according to the same procedure using the same soil to water ratio. The obtained filtrates were directly used for FFF-ICP-MS analyses without further treatment.

Asymmetric flow field flow fractionation online with ICP-MS

A metal-free AF2000 system (Postnova Analytics, Landsberg, Germany) was coupled online with UV detection and an Agilent 7500 Quadrupol-ICP-MS system (Agilent Technologies, Japan). Particle separation was performed using 1 kDa PES membrane, 500 µm spacer thickness and 25 µmol L^{-1} NaCl in deionised water as carrier. An internal standard solution (Rh and Y in 0.5% HCl) was mixed with the FFF eluate through a tee-piece between the FFF and the ICP-MS. In case of the latex suspensions the injection volume was 250 µL with a focus time of 6 min at 0.2 mL min^{-1} tip flow; the initial cross flow was 1 mL min^{-1} for 4 min followed by a power gradient down to 0 mL min^{-1} within 40 min and finally 30 min constant cross flow at 0 mL min^{-1}. In case of the soil samples a volume of 500 µL was injected at a tip flow of 0.2 mL min^{-1} and focused for 15 min. Thereafter, a linear cross-flow gradient from 2.5 mL min^{-1} down to 0 mL min^{-1} within 30 min was applied followed by 50 min constant cross flow at 0 mL min^{-1}. Detector flow rate was 0.5 mL min^{-1}. The FFF method used here for the charcoal spiked soil samples was not optimised, yet, regarding peak resolution of the particulate carbon fraction. The emphasis was on reliable elution and recovery of the particulate carbon fraction to study the performance of ICP-MS for the carbon quantification of this fraction. Please note that a direct comparison of the elution times of the latex particles and those of the particles in soil extracts is not possible due to differences in the FFF fractionation methods.

The same samples were also analysed using flow injection through the FFF channel at constant tip flow of 0.5 mL min^{-1} and cross flow of 0 mL min^{-1} to determine the total carbon concentration in the samples for calculation of the recovery of the eluted and quantified particulate carbon.

The isotopes ^{12}C and ^{13}C were monitored by ICP-MS in addition to the internal standards ^{89}Y and ^{103}Rh and further elements of interest such as ^{27}Al, ^{31}P and ^{57}Fe (see fractogram of soil extracts in Figure S1 of the Supplementary Information). The instrument was operated in helium collision cell mode to minimise spectral interferences by cluster ions and to suppress the ^{12}C signal to a suitable intensity range. The future aim of this work is to monitor carbon in parallel to metals and phosphorus in the eluting particulate fractions from FFF by ICP-MS. Therefore, no carbon specific optimisation of gas flows or RF power was performed but conditions were kept at the optimum tune values for multi-element analysis. Only variation of the sampling depth was investigated as described below. In all cases calibration was performed using the post-channel (PC) approach.[15] Briefly, calibration standards were introduced via the internal standard line to establish a calibration which allowed conversion of the intensity based fractograms into mass flow fractograms. The absolute amount of eluting carbon was determined by peak integration and the concentration was calculated as ratio with the injection volume. In addition, an aqueous citric acid standard was analysed in flow injection mode (no cross flow) via the FFF autosampler to verify stability of the FFF-ICP-MS system, for drift correction of the carbon quantification and to cross-check the PC calibration.

Ultrafiltration of soil extracts to determine the low molecular weight fraction

Amicon filtration units (4 mL capacity, Merck-Millipore, Germany) with 3 kDa regenerated cellulose membrane, the closest commercially available cut-off matching the 1 kDa membrane used for FFF separation, were pre-cleaned by adding 4 mL of deionised water and centrifuging at a speed of 4000 g for 10 minutes; the permeate (approximately 2 mL) and the remaining water were decanted. The cleaning procedure was repeated and the permeate was kept as filter blank sample. Subsequently, 4 mL of the soil extracts were processed in the same way and the permeate kept for carbon analysis by ICP-MS.

Carbon determination by elemental analyser (EA)

An aliquot of 10 µL of each latex stock solution was pipetted in tin capsules in triplicate. The aqueous solvent was evaporated on a hot plate at about 60°C until constant weight. The capsules were then closed and analysed with a Vario EL cube (Elementar, Langenselbold, Germany) for carbon. Calibration was performed with solid sulfanilic acid.

Carbon determination by combustion analyser CS600

As independent comparison, the total carbon concentration in the diluted latex samples and the spiked as well as non-spiked soil extracts was determined using a Leco CS600 instrument. Ceramic crucibles were cleaned by heating at 1000 °C for at least 2 h. Subsequently, aliquots of 300 µL or 500 µL of the liquid particle suspensions were pipetted into the crucible. The aqueous solvent was evaporated on a hot plate at about 70°C. 1 g iron and 1.5 g tungsten were added to the crucibles prior to analysis. Calibration was performed with carbon containing steel standards. Two to five replicate analyses of each sample were performed across different days to study the repeatability of the drying and measurement process.

Total carbon determination by ICP-MS

Carbon determination in permeates from ultrafiltration and in the corresponding non-filtered soil extracts and extracts from coal spiked soil was performed as previously reported using an Agilent 7500 ICP-MS with collision cell in He-Mode (Agilent Technologies, Japan).[15] One set of dilutions was acidified with 1% HCl and purged with Argon to remove inorganic carbon. Replicate dilutions were prepared with acidification but omitting the Ar purging. When using the solvent blank to correct for carbon background both sets of dilution provided matching results indicating that the carbonate fraction of the soil was either not relevant or removed to sufficient extent by acidification.

Investigating the effect of sampling depth on carbon detection by ICP-MS

FFF was operated in flow-injection mode online with ICP-MS as described above for the latex particle standards. The sampling depth in the ICP-MS tune file was changed in steps of 0.5 mm starting from the value 7.0 mm (recommended by the manufacturer) used in previous experiments up to 10.0 mm, which is the maximum suitable value according to the instrument manual. For each setting of the sampling depth, a volume of 250 µL of the following three test solutions was sequentially injected: aqueous citric acid solution, 100 nm and 740 nm latex standard. Both latex particle standards were prepared at 200 fold-dilution in deionised water. Afterwards, the analysis of the three test solutions was repeated for most of the sampling depth settings, but in different order (7.0 mm, 8.5 mm, 10.0 mm, 9.5 mm and 8.0 mm) to exclude artefacts from system drift and to check for repeatability. The obtained ^{12}C signals were normalised to the post-channel added internal standard Rh and the peaks were numerically integrated using EXCEL® software (Microsoft Corporation, USA). The carbon concentration in the citric acid test solution was determined by ICP-MS against the Certipur TOC standard resulting in 455 mg L^{-1} ± 8 mg L^{-1} (mean ± SD). Based on this standard a single-point calibration was established for each analysis of the three test solutions and carbon in the latex samples was quantified. In analogy to the first set of measurements the recovery was calculated based on the results from elemental analysis of the respective latex stock suspensions. In addition, the signal-to-noise ratio was determined for each flow-injection-run as ratio of the peak height and three times the standard deviation of the baseline (before peak elution). Another set of measurements was performed with the same instrumental setup to check for potential influence of the carbon concentration in the plasma on the optimum sampling depth. For this purpose the injection volume of the 100 nm latex suspension was varied (125 µL, 250 µL, 375 µL, 500 µL and 625 µL) (n=1) to generate increasing carbon concentrations in the plasma during elution of the flow injection peak at sampling depths of 7, 7.5, 8.5 and 10 mm.

Results and discussion

Carbon specific detection of latex particles using FFF-ICP-MS

Commercially available particle size standards of polystyrene latex are frequently used to establish size calibration for FFF-UV systems. We injected the latex standards (21 nm, 100 nm, 250 nm and 740 nm) into the FFF-ICP-MS setup and monitored ^{12}C. The overlayed fractograms of the sequentially analysed standards are shown in Figure 1. The applied cross flow gradient provides adequate differences in the elution times according to increasing particle size of the latex standards. Similar peak height and peak shape was obtained for the four standards, which agrees with the equal concentration for all stock solutions as provided by the manufacturer. From qualitative and semi-quantitative perspective all standards are well detected by ICP-MS without obvious size dependent signal loss or suppression.

For more detailed investigation, all latex standards were analysed in triplicate and quantified based on the post channel carbon calibration. After each replicate analysis of the four latex samples a standard of citric acid was analysed in flow injection mode. The resulting carbon concentration was converted into mass-% and recoveries were calculated based on the polystyrene mass fraction given by the manufacturer (Table 1). The results indicate good recovery around 75% for the FFF separation of the latex particles with exception of the 21 nm standard with only 58% recovery. Flow injection analysis of the standards provided significantly higher recoveries ranging from 69% (21 nm) to 93% (100 nm). The difference of 10% to 18% between both recoveries represents particulate carbon (latex) which is not recovered during the FFF separation due to interaction with the membrane and potentially present low molecular mass carbon compounds which are lost with the cross flow through the membrane during FFF separation. The dissolved carbon fraction is expected to provide minor contribution considering that the latex particles are diluted in deionised water only.

For quality control, independent total carbon analysis of the stock suspensions of the latex samples was performed by combustion as routinely applied for elemental analysis (EA) of organic compounds to check for potential changes due to aging. The recoveries based on the EA results instead of the concentration given by the supplier (Table 1) are summarised in Figure 2. EA confirms the lower carbon concentration observed in the 21 nm latex standard using FFF-ICP-MS. Thus the recoveries for the 21 nm, 100 nm and 250 nm latex suspensions are in similar range of 76% to 83% in FFF separation mode (with cross flow) and 90% to 104% in flow injection mode (without cross flow). This indicates adequate quantification of particulate carbon in the latex samples up to 250 nm particle size. In case of the suspension with the largest particle size of 740 nm, EA provides a carbon concentration 11% higher than the concentration given by the manufacturer. Consequently, the recovery of FFF-ICP-MS quantification of the 740 nm latex standard is lower than the recovery for the latex suspensions with smaller particle size when using the carbon concentration from EA as reference. In spite of this the recoveries of 69% in separation mode and 78% in flow injection mode (Figure 2) are still in an acceptable range considering that the 740 nm particles are nearly 3-times larger in diameter compared to the 250 nm particles, which equals an approximately 27-fold increase in volume assuming spherical shape.

Taking into account the complex process of injection and separation of a particle suspension and subsequent analysis of the carbon concentration by ICP-MS these recoveries are certainly not optimum, but in an acceptable range. Improvement is possible by minimising the interaction of the particles with the membrane by modifying the carrier composition and/or the membrane material. However, monitoring of carbon requires a carrier without carbon-containing modifiers. The current conditions (PES membrane, 25 μmol L^{-1} NaCl in water) are derived from the gentle separation of natural colloids in environmental water samples and focusing on maintaining the particle size distribution originally present in the sample instead of maximising recovery.

Total carbon determination in the same dilutions of the latex samples used for FFF-ICP-MS measurements by a CS instrument operating combustion at higher temperatures and allowing the analysis of larger sample volumes confirmed the results from elemental analysis for the relevant size range from 100 nm to 740 nm however with an offset of about 20% (recoveries (mean ± standard deviation) range from 74% ± 7% to 85% ± 8%). This offset might be due to the calibration based on carbon containing steel samples. The recovery for the 21 nm sample is much lower (51% ± 8%). In general, this standard was found to be less stable than the larger investigated latex particles due to higher rate of aggregate formation leading to partial precipitation which could be visually observed. Increased aggregate formation with decreasing latex particle size was also reported in a previous study.[21] Based on the total carbon quantification by elemental combustion analysis, Figure 2 indicates that the lower recovery for the 21 nm latex standard is not due to an FFF-ICP-MS related bias and therefore this was not studied in further detail.

More relevant for validation of the carbon detection by ICP-MS is the slight decrease in carbon quantification recoveries from the 250 nm latex sample to the 740 nm latex. Additional investigations are required to verify whether this is an artefact of the elemental analysis via combustion (supported by the fact that the determined carbon concentration is higher than the concentration given by the manufacturer) or whether recovery from FFF is lower for the large particles or whether the ICP-MS quantification is suffering from systematic bias in this particle size range.

Particulate carbon determination in soil-charcoal extracts

Encouraged by the promising results for the monodisperse latex standards in simple aqueous matrix, particulate carbon detection and quantification was also investigated in a more complex environmentally relevant matrix. For this purpose, we selected a soil sample and spiked this sample with charcoal to create a model for black carbon particles in the terrestrial environment. The original soil and the spiked soil were extracted leading to aqueous suspensions of coal and soil particles. Considering that charcoal particles and their aggregates may cover a broad particle size range, the upper size was limited to about 450 nm by filtration prior to analysis by FFF-ICP-MS, according to the definition of "dissolved organic carbon" in environmental science.[20] Therefore, the charcoal derived particulate carbon in these extracts is expected to be present within the size range up to 750 nm previously investigated by the latex particles. In addition the extracts contain organo-macromolecules (e.g. humic acids) as well as inorganic particles such as ferrihydrit in the low nanometer size range and larger mostly inorganic particles with organic coating (e.g. clay) naturally present in the soil. Figure 3 summarises the fractograms of the extracts of a soil sample with and without charcoal spiking. The corresponding fractograms for phosphorus and selected metals are shown in the Supplementary Information (Figure S1). For details on fractionation of soil nanoparticles and colloids please refer to our previous work.[22, 23] For example, it was shown that the natural soil organic matter in soil leachates is to large proportions associated to inorganic colloids.

The Rh-normalised signal from triplicate analysis (Figure 3) is matching well, indicating stable and repeatable fractionation conditions for the natural soil particles as well as the spiked charcoal particles. The peak with maximum at 55 minutes elution time is clearly increased for the charcoal spiked soil demonstrating that the charcoal particles are eluting from the FFF channel and that the carbon in charcoal is successfully monitored by ICP-MS.

The results in Figure 3 show that monitoring of charcoal particles in soil extracts is possible by FFF-ICP-MS. Quantification of particulate carbon in fraction 1 (15 minutes to 44 minutes elution time) and in fraction 2 (44 minutes to 70 minutes elution time) was performed in analogy to the latex samples for two replicate extracts A and B of the same soil and two corresponding extracts A and B of this soil spiked with charcoal. All 4 extracts were analysed in triplicate in FFF-ICP-MS separation mode. Flow injection analysis was also performed in triplicate using the same injection volume as in separation mode. However, the soil matrix concentration and the carbon signal in the charcoal spiked soil were too high during the narrow flow injection peak for reliable carbon quantification. Therefore, total carbon quantification in this case was performed by offline ICP-MS analysis of acidified 10-fold diluted soil extracts. The results are summarised in Table 2. Total carbon concentrations (mean ± standard deviation) in the non-spiked soil extracts are 66.5 ± 5.4 mg L^{-1} for soil extract A and 55.4 ± 5.3 mg L^{-1} for soil extract B while the concentrations in the extracts of charcoal spiked soil were nearly 4-fold higher with 191.6 ± 10.4 mg L^{-1} for extract A and 199.1 ± 10.6 mg L^{-1} for extract B. These results were confirmed by combustion analysis using the CS instrument resulting in carbon recoveries (mean ± standard deviation) of 91 ± 15% and 95 ± 10%, respectively, for the non-spiked soil extracts as well as 80 ± 23% and 82 ± 6%, respectively, for the extracts of charcoal spiked soil compared to ICP-MS. Based on these results only approximately 2% of the spiked total charcoal-carbon was found in the fraction < 450 nm. This may indicate that the majority of charcoal particles is retained in the solid residue due to its hydrophobic nature and interaction with soil components decreasing the water extractable fraction. However, since charcoal particles are in the size range of hundred nm up to several µm it is more likely that a major portion of charcoal particles is larger than 450 nm and consequently excluded from this analysis.[8, 24]

About one third of the total carbon concentration in the filtered soil extracts (<450 nm) is recovered in the second fraction of the FFF-ICP-MS fractogram both for the untreated and the charcoal spiked soil. This indicates that the recovery of the natural carbon containing particles from the FFF channel is matching the recovery of the spiked charcoal particles in the soil extract in this fraction. The first fraction provides a minor contribution of about 6-8%. The recoveries for soil extract B are generally higher due to the lower total carbon concentration obtained by offline ICP-MS compared to soil extract A.

Establishment of a carbon mass balance for the soil extracts and the extracts from charcoal spiked soil is required to derive conclusions on the recovery for quantification of coal particles by ICP-MS. Compared to the synthetic monodisperse aqueous latex suspensions this is more difficult because the soil extracts also contain significant amounts of low molecular weight organic compounds which are passing the FFF membrane and are thus not detected by FFF-ICP-MS. In addition, fraction 2 of the FFF separation contains both natural soil carbon containing particles and charcoal particles, either independently co-migrating with the soil particles or through adherence to soil particles. The carbon concentration in the low molecular weight fraction passing through the FFF membrane and thus escaping detection was estimated by ultrafiltration using devices with a molecular weight cut off as close as possible to the cut off of the FFF membrane. The permeate was analysed by ICP-MS and percentage recovery of total carbon concentration was calculated. Also in this case the results for untreated and spiked soil extracts are very similar apart from the above mentioned exception of soil extract B (Table 2). In summary, the fractions 1 and 2 and the low molecular weight fraction reach about 75-80% of total carbon. In analogy to the latex particles (Figure 1) it is likely that the major part of the gap in the mass balance is due to incomplete recovery of carbon containing particles from the FFF channel. Thus the contribution of inadequate quantification by ICP-MS can be considered of minor relevance.

Are latex particles fully decomposed in the plasma? – Effect of sampling depth

The graphical summary of particulate carbon recovery by FFF-ICP-MS as a function of latex particle size (light and dark grey, Figure 2) generally demonstrates a satisfactory value above 70%. However, there is a slight decreasing tendency from 100 nm over 250 nm to 740 nm. Most of the decrease is still within the standard deviation of replicate measurements, but there might be a slight systematic bias in ICP-MS detection and quantification. According to previous studies on slurry analysis, significant particle size dependent changes in the efficiency of the sample introduction via nebuliser and spray chamber is not expected below 2 µm.[25] Therefore, we did not investigate this possibility in more detail. Another concern about the direct introduction of particles into the ICP-MS is the question whether those particles are fully decomposed in the plasma and thus generate the same ion intensity as a low molecular weight dissolved standard of the same element at the same concentration. Studies have shown that this works for example for 500 nm silica particles [18], but it was also shown that the maximum suitable particle size for full quantification is dependent on the chemical composition of the particle.[25]

In particular for large particles it is expected that an increase of the dwell time in the plasma supports particle decomposition and ionisation and thus the probability of full quantification. Variation of the sampling depth, that means the distance between plasma torch and sampling cone, is an option to achieve such higher dwell time. Few studies report optimisation of the sampling depth for nanoparticle detection by ICP-MS. For example, Kalomista et al. found significant improvement of Au and Ag nanoparticle detection in single particle mode by ICP-MS when optimising the sampling depth.[26] Ho et al. found a shift of the optimum sampling depth for single-particle detection of 250 nm Au particles compared to 150 nm Au particles and also for refractory 80 nm ZrO_2 particles compared to a Zr solution to slightly higher position.[27]

Therefore, we studied the effect of increasing sampling depth from 7.0 mm up to the 10.0 mm for latex particles using FFF-ICP-MS in flow injection mode. For each sampling depth a citric acid standard was first analysed and used as single point calibration to correct for changes in sensitivity. Afterwards a sample of 100 nm latex particles and a sample of 740 nm latex particles (at 200-fold dilution in analogy to Figure 2) were analysed. When increasing the sampling depth a linear increase in ^{12}C peak areas was observed both for the citric acid and the latex particles (correlation coefficients from 0.976 to 0.998). Replicate analysis was performed in different order of sampling depth settings to exclude any artefact from instrumental drift. The relative standard deviations from duplicate analysis were <5.5% indicating high stability and repeatability of this experiment. Based on the citric acid standard the carbon concentrations of the latex samples were calculated for each sampling depth and their recoveries were calculated based on the carbon concentration determined by elemental analysis of the latex stock solutions via combustion. The results summarised in Figure 4 indicate no significant change in particulate carbon concentration depending on sampling depth. This suggests that both the 100 nm latex particles and the 740 nm latex particles were already fully decomposed in the plasma at the previously used sampling depth of 7.0 mm and increase of the dwell time in the plasma does not improve recoveries for carbon quantification. The mean recoveries from all measurements in this experiment were 104.5% ± 3.3% for the 100 nm latex particles and 94.0% ± 2.5% for the 740 nm latex particles (mean ± SD). These recoveries are improved compared to the first data set shown in Figure 2 demonstrating that the initially obtained slightly decreased recoveries for the 740 nm particles are not due to a systematic bias of ICP-MS detection in this size range.

Moreover, it was investigated whether the carbon concentration in the plasma has an effect on the optimum sampling depth. Using the example of the 100 nm latex particle suspension the injection volume during flow-injection FFF-ICP-MS was varied. The results show similar increase of the carbon peak area with increasing sampling depth for all investigated injection volumes (see Figure S2 of the Supplementary Information). Calibration curves constructed from the increasing injection volumes at different sampling depths showed very good linearity (correlation coefficients of 0.9949 at sampling depth of 7; 0.9997 at sampling depth of 8.5 and 1.0000 at sampling depth of 10; example shown in Figure S3 of the Supplementary Information). From these results it can be concluded that the optimum sampling depth is independent of the carbon concentration in the plasma.

Although the recovery did not change, another interesting effect was observed from this optimisation experiment. When checking the flow-injection peaks in more detail it was found that the signal stability improved significantly for sampling depths above 8.0 mm. This is clearly demonstrated by overlaying the signals from duplicate analysis at 7.0 mm and 10.0 mm sampling depth for citric acid, 100 nm latex particles and 740 nm latex particles in Figure 5. Considering that also the signal intensity increased with increasing sampling depth it is likely that this is also the case for the signal to noise (S/N) ratio. Figure 6 proves the correlation of S/N ratio and sampling depth for the 100 nm latex particles achieving a correlation coefficient of 0.91. Similar results were found for citric acid and the 740 nm latex particles with slightly lower correlation coefficients of 0.73 and 0.75, respectively. About 3-fold improvement of S/N ratios was found when increasing the sampling depth from 7.0 mm to 10.0 mm. This indicates a potential for improving the performance of particulate carbon monitoring by FFF-ICP-MS in future studies.

Conclusion and outlook

The examples investigated in this study clearly indicate the capability of FFF-ICP-MS to provide adequate quantitative carbon determination also for large polymer particles up to a size of 740 nm and colloidal sized (<450 nm) charcoal-soil associations. This opens several new applications of this instrumental setup both for engineered and for natural particles enabling the determination of metal or phosphorus to carbon ratios without the need for another detection system. Moreover, for the first time element selective detection of carbon in latex and charcoal particles was performed online with FFF separation. In particular for complex environmental sample matrices this approach provides quantitative determination of carbon in stable particulate structures such as black carbon. Due to the hydrophobic nature of black carbon, direct analysis of black carbon suspensions without stabilising soil matrix was not investigated in this study. Therefore, black carbon quantification could only be checked via the carbon mass balance. This could be improved in future studies by suitable carbon-free reagents in the carrier to enable analysis of purely aqueous black carbon suspensions and thus direct calculation of the quantification recovery by FFF-ICP-MS in analogy to latex. Further optimisation is required to fine-tune the particulate carbon detection by ICP-MS with special focus on improved baseline stability and limit of detection. The variation of ICP-MS sampling depth was identified as promising option for this purpose.

Conflicts of interest

There are no conflicts of interest to declare.

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Table 1 Recoveries [%] for particulate carbon concentrations (mean and standard deviation, n=3) determined by FFF-ICP-MS in four polystyrene latex standards based on the concentration given by the manufacturer. In addition, flow injection through the channel without cross flow was performed to determine total carbon concentration in the latex samples for comparison.

Polystyrene latex	**FFF fractionation**		**Flow injection mode**	
	Mean	**SD**	**Mean**	**SD**
21 nm	57.7	1.4	68.9	0.4
100 nm	74.5	5.4	92.9	3.6
250 nm	77.4	0.8	91.5	3.0
740 nm	76.8	1.5	86.6	3.6

Table 2 Quantification of particulate carbon in two replicate (A and B) soil extracts and extracts of charcoal spiked soil (mean and standard deviation, n=3) determined by FFF-ICP-MS. Fraction 1 (elution time 15 min to 44 min) and fraction 2 (elution time 44 min to 70 min) were quantified. The obtained results are given as percentage ratio to the total carbon concentration as determined by offline ICP-MS. In addition, results from ultrafiltration through 3 kDa membrane are included (n=1).

	Fraction 1 [% of total]		**Fraction 2 [% of total]**		**Ultrafiltration [% of total]**	**Sum [% of total]**
	Mean	**SD**	**Mean**	**SD**		
Soil A	8.6	0.4	36.0	2.4	34.3	78.9
Soil B	14.9	4.3	44.6	2.3	45.7	105.3
Soil A spiked	6.3	0.4	35.6	0.6	36.8	78.6
Soil B spiked	5.8	0.7	33.0	0.5	36.9	75.7

Figure captions

Figure 1 Overlayed FFF-ICP-MS fractograms for latex standards of size 21 nm, 100 nm, 250 nm and 740 nm monitoring ^{12}C.

Figure 2 Recoveries for the quantification of carbon in latex suspensions analysed by FFF-ICP-MS (n=3) in separation mode (with cross flow) as well as in flow injection mode (FI, without cross flow). Carbon quantification by combustion analysis (CS600 instrument, n=5) is provided for comparison. All recoveries are based on carbon determination by elemental analysis (n=3) as reference.

Figure 3 Overlayed FFF-ICP-MS fractograms monitoring ^{12}C (normalised to the internal standard Rh) for the triplicate analysis of a soil extract and an extract of the same soil spiked with charcoal.

Figure 4 Recoveries of carbon quantification for 100 nm and 740 nm latex standards (based on results from elemental analysis) for variation of the sampling depth. Measurements were performed using flow-injection FFF-ICP-MS. Mean and standard deviation for n=2 with exception of 7.5 mm and 9.0 mm with n=1 (the standard deviation in these cases was calculated as mean of the standard deviations of the other data points).

Figure 5 Flow-injection peak shapes for duplicate injection of citric acid (a), 100 nm latex particles (b) and 740 nm latex particles (c) at sampling depth of 7.0 mm and 10.0 mm using FFF-ICP-MS.

Figure 6 Signal-to-noise ratios (S/N) calculated from the peak height and the threefold standard deviation of the baseline as a function of the sampling depth for the example of 100 nm latex particles analysed by flow-injection FFF-ICP-MS.