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Towards a future screening method for nanoparticles in seafood
–For surveillance and risk assessment of food safety

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Need for analytical method for determination of NPs in marine samples

Engineered nanoparticles (NPs) are used worldwide, due to their unique, useful characteristics. NPs have been shown to be taken up by organisms and into cells, where they influence these organisms negatively, e.g. by increasing oxidative stress. NPs can also be produced unintentionally, e.g. through grinding processes related to mining. Norway is one of very few countries using the sea for dumping mining waste, and recently, mining companies have received new permissions to deposit large amounts of mining waste in the Repparfjord and Førdefjord. This emphasizes the need for an analytical platform applicable for surveillance and screening of NPs of unknown compositions in seafood organisms and indicators of environmental status.

⇨ The aim of this project is to develop a generic analytical screening method for metal containing nanoparticles (NPs) in seafood using single particle inductively coupled plasma mass spectrometry (sp-ICP-MS), and here the preliminary results from the project are presented.

Determination of particle size by sp-ICP-MS

Particle size plays a role in the toxicity of elements or metals. Hence, this new analytical dimension of size needs to be added to the already established total and species specific determination of metals and elements to aid in the future risk assessments of food safety. Single particle inductively coupled plasma mass spectrometry (sp-ICP-MS) has been shown to be a powerful analytical technique for the determination of the size distribution of NPs [1]. For the determination of nanoparticles, however, the sample needs to be in suspension, and decomposition of the matrix by acids, bases and enzymes is necessary to extract NPs into solution [2, 3].

To evaluate the effect of the extraction procedure on the NPs, different types of marine samples, including mussel tissue (blue mussel), oyster tissue (Oyster tissue, CRM, NIST 1566b), fish muscle tissue and fish feed were extracted with various extraction procedures. The samples analysed were spiked with reference material (30nm and 60nm Au), and extracted with water (1), acidic digestion (2), basic digestion (3) (TMAH), and by enzymatic digestion (protamex and proteinase K, (4, 5)). Spiked and non-spiked samples were then analysed by sp-ICP-MS, with detection of ^{197}Au. Selected samples were also analysed for ^{56}Fe and ^{66}Zn.

Experimental outline

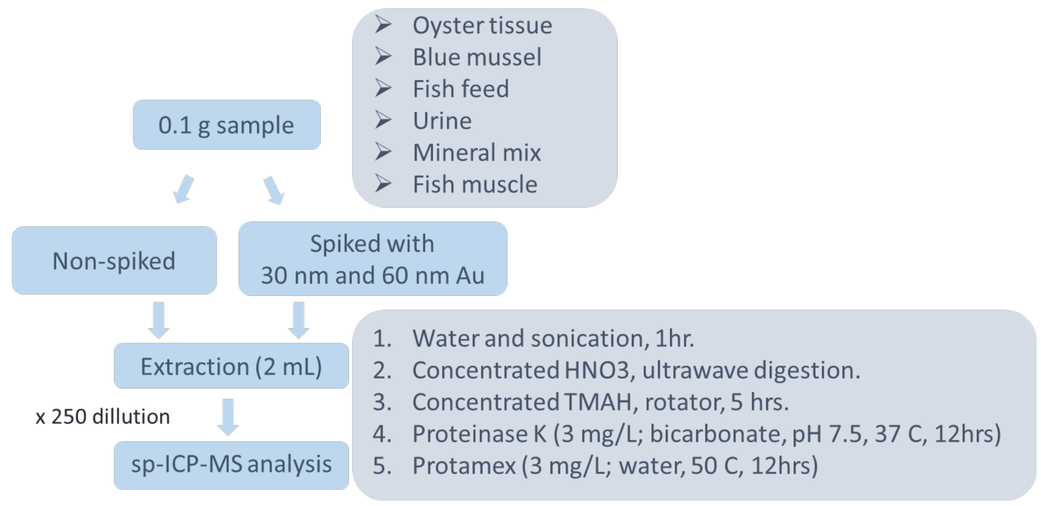

Table 1. Instrumental settings for sp-ICP-MS (7900, Agilent Technologies) and autosampler (Agilent Technologies)

RF power	1550
Nebulizing gas	1.05
Nebulizer	Micromist
Nebulizer pump	0.1
Torch	1.5 mm
Tubing ID	1.02 mm
Integration time	0.1 msec (peak integration mode)
Isotopes monitored	^{197}Au, ^{56}Fe, ^{66}Zn
Analysis time	60 sec
Probe rinse	60 sec
Reference material	Au (100ppt, 200ppt)
Ion standards	Au, Zn, Fe (1ppb, 10ppb, 100ppb)

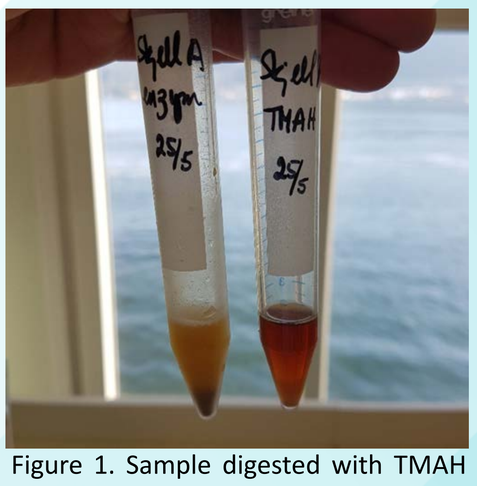

Figure 1. Sample digested with TMAH and enzyme (protamex). The TMAH extract was clearer compared to the enzymatic digest.

Results and discussion

1 Transport/nebulization efficiency

Transport/nebulization efficiency (TE/NE) is one of the most important parameters in sp-ICP-MS.

TE/NE was determined using (1) the particle size, (2) the particle concentration and by (3) manual uptake. Approach (3) gave the highest value of the TE/NE; varying from 7-11 % (n = 4) when measured on a daily basis. The TE/NE measured by (1) and (2) gave an estimate of around 5 and 4 %, respectively.

⇨ Only minor differences were seen in the results for particle size distribution when applying the different TE/NE determination approaches.

2 Effect of particle number

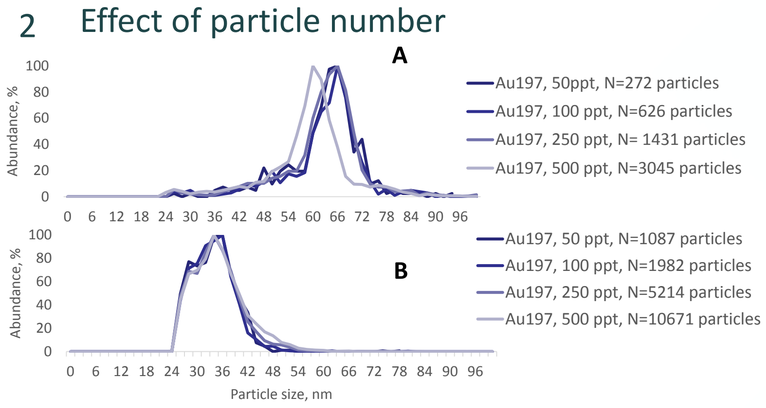

Figure 2. Particle size distribution measured for NP solutions of 60 nm Au (A) and 30 nm Au (B) with concentrations from 50 ppt to 500 ppt.

⇨ A slight shift in size is seen for the most concentrated solution of 60 nm NPs . This is not seen for 30 nm NPs solutions.

3 Matrix effects

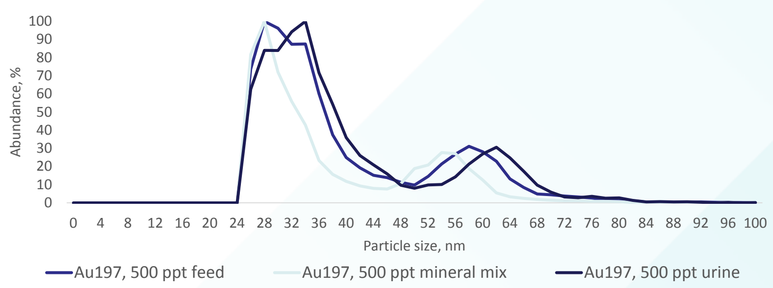

Figure 3. A mixture of 30 nm and 60 nm Au NPs spiked into water extracts of feed, mineral mix and urine.

⇨ Further work needs to be conducted to verify that the matrix effects also applies to NPs analysis by sp-ICP-MS.

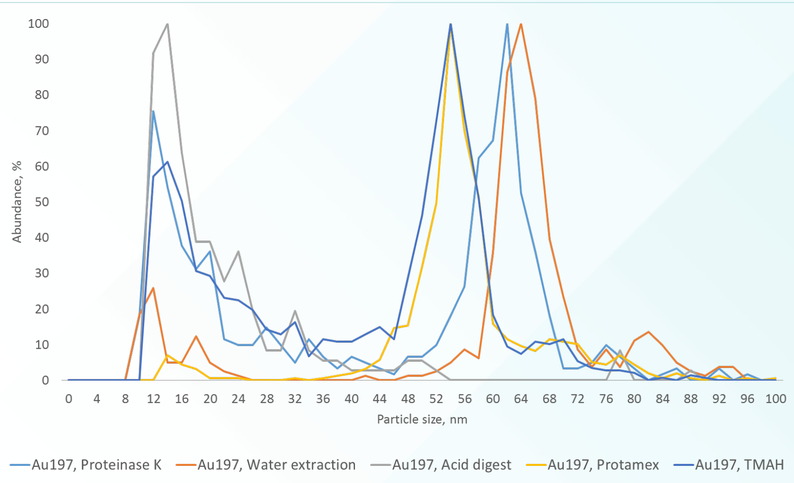

Figure 4. Particle size distribution of 60nm NPs spiked in Oyster tissue (SRM-1566b) and extracted using protocol 1-5.

⇨ Acid digestion completely digests the NPs, whereas water extraction, enzymatic and TMAH digestion results in signals for NPs in the 60 nm region. Extraction with water and protamex gives a lower signal in the low nm particle size region (10-40 nm) compared to the other protocols.

Table 2. Measured and certified/reported concentration (mg/kg) of iron (^{56}Fe) and zinc (^{66}Zn) in Oyster tissue (CRM 1566b) and in fish feed when extracted with acid digestion.

	^{56}Fe		^{66}Zn	
	Measured concentration (mg/kg)	Certified/ reported concentration (mg/kg)	Measured concentration (mg/kg)	Certified/ reported concentration (mg/kg)
Oyster tissue	233	205.8 ± 6.8	1424	1424 ± 46
Fish feed	270	220 ± 34	137	140 ± 3

⇨ Total concentration of other elements such as Fe and Zn in oyster tissue and fish feed could also be determined simultaneously with particle size in sp-ICP-MS-mode.
NPs of Fe and Zn were not detected in the acid digest or in the water extracts of oyster tissue and fish feed.

Conclusion and future work

- The preliminary data indicate that milder extraction conditions such as enzymes and water could be used for Au NP extraction in marine samples. While TMAH dissolves the samples more completely.
- The aim for future work is to establish a screening method for NPs in seafood using sp-ICP-MS.
- Furture work will focus on determining titanium (Ti) and copper (Cu) as these are the main elements of interest regarding mining activities in Norway.
- Also NPs of other elements, e.g. zinc (Zn), iron (Fe), mercury (Hg), selenium (Se), are of interest to study in marine samples.
- Complementary techniques, e.g. transmission electron microscopy (TEM) and asymmetric flow field flow fractionation (AF4), will be require to obtain more specific information on the nanoparticles.

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