Extending the potential of ICP-MS as analytical tool for evaluating the safety of food nanomaterials

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INTRODUCTION

Engineered inorganic nanomaterials (iENMs) are being manufactured in ever increasing quantities and finding a wide range of food-related applications, including food ingredients, additives, supplements and contact materials. Assessing the potential risk of iENMs requires methods of analysis that can be successfully employed in experimental studies addressing their interaction with biological systems. Characteristics of iENMs that affect their behaviour and toxicity include size, shape, surface properties, aggregation state, solubility, mass concentration and elemental composition.

Among the analytical tools used to determine relevant properties in nanotoxicological studies, ICP-MS plays a major role. It can be used as a detector of unparalleled sensitivity for the measurement of the mass concentration of iENMs in biodistribution studies, whereas hyphenated ICP-MS based techniques have a tremendous potential as characterisation tools. So far, ICP-MS has been used primarily for the detection and characterisation of iENMs based on such elements as selenium and noble metals. Application to oxide nanomaterials, such as SiO_2, has been hampered by analytical challenges, i.e., high background and substantial spectral interferences.

EXPERIMENTAL CONDITIONS

Sample introduction system: lowering Si background

The problem of Si release from the quartz used in the spectrometer sample introduction system has been solved by completely eliminating quartz. For this purpose, the entire sample introduction system of the ICP mass spectrometer has been substituted with non-quartz components. This entailed using a ceramic D-torch instead of the quartz torch, a sapphire injector instead of the quartz injector, a cyclonic spray chamber in PFA instead of the quartz spray chamber, and a PFA concentric nebulizer instead of the quartz nebulizer. The use of quartz has also been avoided during sample preparation.

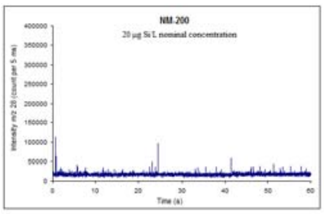
Si detection by DRC-ICP-MS

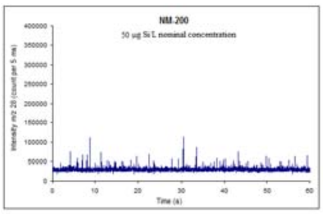
Si has three naturally occurring isotopes - i.e., ^{28}Si (abundance 92.2%), ^{29}Si (4.7%), and ^{30}Si (3.1%) - which suffer from severe interferences in ICP-MS due to C- and N-containing polyatomic ions (CO, COH, N_2, N_2H, NO). Several different reaction gases were investigated for the reduction of polyatomic interferences on Si isotopes by DRC-ICP-MS and satisfactory results were obtained with methane on ^{28}Si.

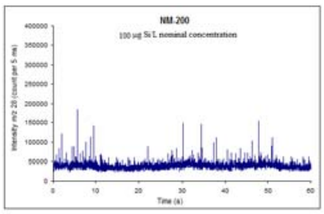
Detection of silica nanoparticles by DRC-ICP-MS in time resolved mode

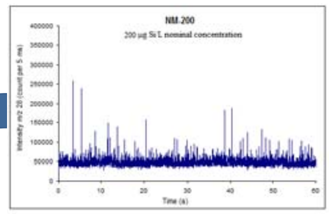
Commercial nanosized SiO2 materials employed in the food sector and for a variety of other applications have been provided by the JRC (IHCP, Ispra) in pre-scored glass ampoules. They consisted in amorphous nanosilica obtained by different production systems, i.e., precipitated (NM-200, NM-201, NM-204) and thermal (NM-203). Silica nanoparticles were suspended in ultrapure water by sonication with a TT13 Bandelin probe at 150 W for 20 min in ice bath. DRC-ICP-MS in time resolved mode was used to detect averaged signals arising from several individual NPs in each time slot (dwell time 5 ms) and study the behaviour of their dispersions.

RESULTS

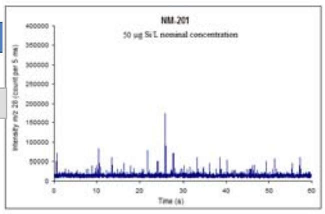


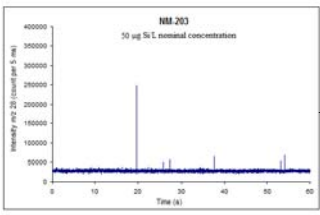


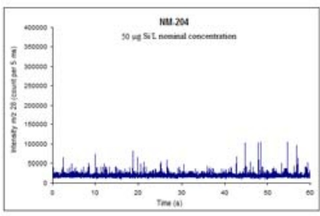




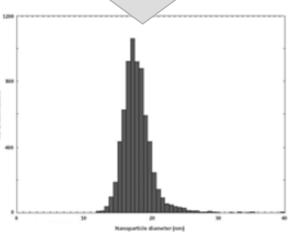
Same nanomaterial (NM-200), dispersions with increasing mass concentration

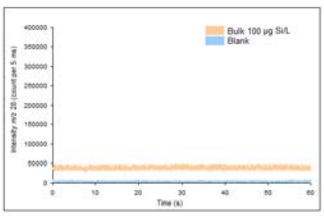






ERM-FD100 was used as calibrant to convert signal distributions into size distributions. Primaries were found to have diameters in the 10-20 nm range as found by SEM.





NM-200

Large aggregates are formed. About 20% of the detected Si pass the 0.22 µm filter and it is mainly soluble Si.

NM-201

Large aggregates are formed. Only 4% of the detected Si pass the 0.22 µm filter and there is no soluble Si.

NM-203

Particles are smaller compared to the other NMs and 66% of the detected Si pass the 0.22 µm filter, with some soluble Si.

NM-204

Large aggregates are formed. Only 7% of the detected Si pass the 0.22 µm filter and it consists in soluble Si.

***In vivo* experiments**

Particle size distribution matches results obtained by SEM/TEM

Membrane filtration

● *0.22 µm membrane* separates small particles from large aggregates. ● *Amicon 10KDa cut-off* separates primaries (about 10 nm as determined by SEM) from soluble Si. ● *Soluble Si* is detected by this approach. Is important to distinguish it from NPs due to differences in toxicity.

CONCLUSIONS

Dynamic reaction cell inductively coupled plasma-mass spectrometry was used to detect unlabeled silicon dioxide nanoparticles by time resolved analysis. Dramatic differences in aggregation were observed for materials such as NM-200 and NM-203, which exhibited different behaviours in terms of bioaccumulation in target organs in *in vivo* toxicokinetic experiments carried out in the context of the NANOGENOTOX Joint Action.

NANOGENOTOX

The NANOGENOTOX Joint Action is co-funded by the Executive Agency for Health and Consumers (Grant Agreement 2009 21 01). This document arises from the NANOGENOTOX Joint Action which has received funding from the European Union, in the framework of the Health Programme. This publication reflects only the authors' views and the Executive Agency for Health and Consumers is not liable for any use that may be made of the information contained therein.

4th International IUPAC Symposium for Trace Elements in Food (TEF-4), Aberdeen 19-22 June 2011