Evaluation of Ti levels in water samples exposed to different concentrations of TiO$_2$ nanoparticles by Portable XRF and TXRF.

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Many nanomaterials based on metallic particles, such as titanium dioxide nanoparticles (TiO$_2$NPs), are used in the preparation of new materials and processes. Thus, toxicology has become a very important and growing field in nanoscience. It refers to the study of the interactions of these composites with biological systems, proposing the development of reliable protocols for risk assessment for humans and the environment.

This study aimed to apply X-Ray Fluorescence in nanomaterials experiments, showing its potential in the chemical determination of metallic nanoparticles and possible assistance in data collection for future studies of environmental toxicity. Thus, two experiments were simulated: a) acute toxicity; three water samples were taken in duplicate from 200 L tanks to compare different treatments. These treatments were water without TiO$_2$NPs (control) and water exposed to 500.0 and 1000.0 mg.L$^{-1}$ TiO$_2$ nanoparticles (TiO$_2$NPs) for 48 hours; b) chronic toxicity; water samples from five treatments were taken in duplicate: control samples and samples exposed to 1.0; 5.0; 10.0 and 50.0 mg l$^{-1}$ of TiO$_2$ nanoparticles for 14 days, simulating an environmental and non-accidental exposure.

Water samples from the acute toxicity experiment (48 hours) were collected and placed in acidified vials of approximately 300 ml. All samples were subjected to an ultrasound bath (sonicated) for 15 minutes and 2 ml subsamples (aliquots) were collected for PXRF measurements. The 2 ml aliquots were placed directly into the sample holder and measured in the XRF portable system without any kind of sample preparation.

Standard water samples were prepared with the following concentrations 1.0; 5.0; 10.0; 50.0; 100.0; 500.0 and 1000.0 mg.L$^{-1}$. They were used for the quantitative determination of Ti that is part of the TiO$_2$ nanoparticles compound (TiO$_2$NPS) in the water samples from acute exposure experiments (48 hours). The results showed concentrations of Ti very close to TiO$_2$NPs concentrations in the tanks from where the samples were obtained, indicating that the employed PXRF system is able to determine amounts of Ti quite close to exposure values.

The water samples for the chronic toxicity experiment were analyzed by a Total Reflection X-ray Fluorescence system (TXRF), the S2PICOFOX - Bruker benchtop, with a data acquisition system connected via serial interface to a laptop. In this case, the chronic exposure of water samples showed smaller values than the nominal value of TiO$_2$NPs exposure. However, a correlation between the amount of the Ti element in the samples and the exposure concentration of TiO$_2$NPs was obtained.

The presence of many other elements such as Si, P, S, Cl, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn and Sr was observed in some samples and the variation of these elements for different samples was analyzed. The presence of Br and Pb in some water samples was also detected.