

Abstract

Microorganisms have the characteristic peculiarity to attach to surfaces, and to cover them with a film of extracellular polymeric substances (EPS). Together with the EPS, they are called biofilms. These are able to adsorb metal ions from the surrounding medium. Therefore, the analysis of biofilms can be used as environmental analytical monitoring procedure for metal ions. Usually, the metal contents in biofilms are determined after isolation from their natural surfaces, drying and acid decomposition, and then related to the dry weight of the biofilms. However, this procedure includes the risk of elemental loss or contamination, and it is also very laborious and time-consuming.

Thus an analytical procedure for the *in situ* growth of biofilms on the surface of sample holders was developed for the total reflection X-ray fluorescence analysis (TXRF) by hanging them directly into the river. After drying and adding an internal standard, the biofilms can be directly measured by the TXRF spectrometer, without any further treatment. For the quantification of the accumulated metal contents, the dry weight and the carbohydrate contents of the biofilms were used as reference parameters. For this purpose, a procedure has been developed in which the biofilms are removed from the sample holders by an ultrasonic microprobe and afterwards hydrolysed by hydrochloric acid. The carbohydrate contents in the obtained solutions were determined by the photometric method of Dubois. Furthermore, the contents of sulphur and phosphorus of the biofilms, which were also determined by direct measurement with the TXRF spectrometer, were verified for their use as reference parameters for the quantification of metal ions contents.

An analysis of variance as well as an analysis of correlation showed that the contents of sulphur, phosphorus and carbohydrate are suitable as reference parameters for the quantification of the contents of metal ions, which are accumulated in the measured biofilms. The reproducibility varies between 6 and 22 %. Whereas the often used dry weight of biofilms is unsuitable as reference parameter. Using sulphur and phosphorus as reference parameters, the decisive advantage of the developed analytical procedure consists in the omission of any treatment of the biofilms.

The results show that sulphur and phosphorus are mainly part of the bioorganic matrix, and nearly do not exist as free anions in the analysed biofilms. Like the metal ions and the carbohydrates, they are integrated in the metabolic processes.

An analysis of correlation showed a significant correlation between the respective contents of metal ions in the compartments biofilm, water sample, suspended matter as well as sum of water sample and suspended matter, for all analysed elements, except titanium and copper. This indicates that, instead of water samples, suspended matter or rather mixed samples, biofilms can also be used for the characterization of the contamination of aquatic systems.

The observed correlations demonstrated that the biofilms accumulated the metal ions from the medium, specific to the element, and included them into the metabolism. The metal contents determined in the biofilms showed a time-dependent, sigmoid gradient. First, a high accumulation for all elements was detected, which in most cases approached a limit afterwards. The relative patterns of element distribution of biofilms originating from the same sample point were nearly the same, even after different periods of growth.

The suitability of the developed analytical procedure was demonstrated prototypically on biofilms originating from the rivers Odra and Elbe.