Analysis of butyltin compounds in sediments by means of GC-AED

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Summary

Organotin compounds are variously used industrial chemicals. One of the most toxicological relevant compounds is tributyltin (TBT). TBT has been used as an effective component in antifouling paints for decades. Thus, it is set free into the water column in considerable amounts and affects also non-target organismens in very low concentrations. Molluscs like snails and mussels are particularly sensitive and reproduction can be influenced significantly thereby. Once released into the water column, TBT accumulates in sediments and will remain there beyond years due to its high persistence. Several guideline values, target levels and quality standards were specified for TBT, its degradation products monobutyltin (MBT) and dibutyltin (DBT) as well as for other organotin compounds in sediments.

To verify these requirements a powerful analytical procedure for the determination of butyltin compounds in sediments is necessary. For these purposes an analytical method, existing for the analysis of aqueous samples, was enhanced and optimised to be suitable for the determination of these compounds in sediments. Aims of this optimisation were:

- High extraction efficiency of all butyltin compounds, including the highly polar analyte MBT
- Good accuracy and reproducibility
- Sufficient sensitivity

Within the development of the analytical procedure the methodology of design of experiments was used as a tool, thus offering the advantage of obtaining a multitude of information by minimised effort. This means, not only the optimal conditions for several factors but also knowledge about the behaviour of the analytes in case of deviations from these settings could be received with small effort at the same time. Thus critical steps of sample preparation and measurement could be determined as well.

It turned out to be of particular importance and necessity for the optimisation of the measurement by means of gaschromatography and atomic emission detection to check the sample introduction by means of splitless-injection. Additionally tetrapentyltin was used as quantification internal standard to compensate for variations of detections response. This application lead to a satisfying precision of the measurement at good sensitivity.

For the extraction of butyltin compounds from the matrix an approach was chosen that seems to be most suited to achieve an as far as possible release of the polar MBT. For this purpose use of hydrochloric acid and sonication of the sample were selected. A simultaneous transfer into an organic phase (mixture of hexane and ethyl acetate) immiscible with water lead to the possibility of using a high acid concentration, which is necessary for the leaching of MBT. Thus, a negative influence on the subsequent derivatisation using sodium tetraethylborate could be excluded. The polarity of the mixture of hexane and ethyl acetate appeared to be significant for the transfer of MBT into this organic phase. It would have been an improvement to use complexing agents, had not tropolone – used for this purpose – led to a poorly reproducibility of results.

A comprehensive validation completed the development of the analytical procedure and proved the performance of this analytical method. By analysis of certified reference materials PACS-2 and BCR-646 available at present the good accuracy and reproducibility could be

confirmed for the determination of all butyltin compounds. Specified limits of detection and quantification proved to be more than sufficient for the verification of actual guideline values and target levels.

Due to references from literature, information from organotin analysts and professionals making use of determined butyltin concentrations as well as due to the insufficient precision of an individual sediment sample observed during validating a second main focus was discovered for this investigation. Therefore also the susceptibility of the analytical method for the determination of the butyltin compounds in sediments to interferences in relation to matrix influences was systematically examined both regarding the accuracy and the reproducibility. This aim could be achieved by the investigation of sediment, into which selected components were incorporated. The components examined in these model experiments were selected due to references from the literature. However, comprehensive studies for these compounds as studied in this work have not been performed for the derivatisation by means of sodium tetraethylborate and measurement by means of GC-AED so far.

In presence of elemental sulphur the quantification of butyltin concentrations by means of an external calibration higher concentrations than in the same sample without elemental sulphur could be noticed specific for DBT only. When applying the standard addition method this effect could not be proven. Aldrich humic acid was selected as model substance for the organic matter in sediments. For this substance influences on the accuracy of the determination could be detected when applying both of the two mentioned quantification procedures. However, one can assume that the observed behaviour of the butytin compounds towards humic acid will not be of such relelvance with regard to the usual concentrations of humic substances in sediments.

In presence of petroleum-derived hydrocarbons and lead influences on the accuracy and reproducibility of the butyltin-determination could not be noticed using the model experiments. However, by means of analysis of correlation an influence on the reproducibility could be proven for other metals than lead, especially for chromium and nickel.

The comparison of the coefficients of variation calculated of repeated investigations of real samples with the recommendations of the Association of Analytical Communities, AOAC, showed that the predominant number of samples could be analysed with sufficient reproducibility. However, further not determined influences on the reproducibility and/or accuracy could not be excluded completely despite application of the standard addition method. But the developed and optimised analytical procedure for the determination of the butyltin compounds still turned out to be sufficient for routine analysis. Due to the increased demand of chemicals and time when applying the standard addition method, the principle use of this analytical procedure is assumed to be for confirmation of results, which were received with less extensive, but also more trouble-prone analytical methods – like simultaneous extraction and derivatisation – and which lie in the range of the guideline values and target levels. The field of the environmental monitoring could represent a further area of application of the developed analytical method, using extraction with hydrochloric acid, hexane and ethyl acetate, derivatisation with sodium tetraethylborate and measurement by means of GC-AED. The efficiency of this determination of butyltin compounds in sediments could be proven in this study with regard to accuracy, reproducibility and senisitivity.