

Head-space solid phase-microextraction of butyl- and phenyltin compounds in human urine after derivatisation with sodium tetraethylborate and subsequent determination by capillary gas chromatography with microwave-induced plasma atomic emission and mass spectrometric detectors

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Organotin compounds have been extensively monitored in various environmental compartments including water, soil, sediments and marine biota [1,2]. Reports on the monitoring of organotin compounds concentration in human have, however, remained scarce and have been the subject of intensive debate [3,4]. This may at least in part be due to the fact that analytical methods specifically targeted at measuring organotin compounds in human tissue or liquors have not been reported so far.

In order to fill this gap, a head-space solid phase-microextraction (HS-SPME) method was developed and optimized for the gas chromatographic separation and determination of the most commonly found organotin compounds in cases of human exposure. Non volatile ionic organotin compounds (butyltin- and phenyltin compounds) were in-situ derivatised to their ethylated derivatives by sodium tetraethylborate (NaBEt₄) directly in urine matrix. Various parameters affecting the yield of the integrated derivatisation/extraction procedure with SPME were examined, while using tetrabutyl tin as standard. The method was optimized for direct use in the analysis of undiluted human urine samples and six compounds could be determined after a 15 min head-space equilibration time at room temperature. The selectivity of the microwave-induced plasma atomic emission detector (MIP-AED) used here as an element specific detector for chromatography allowed the interference-free detection of tin signals in all cases. GC with quadrupole mass spectrometric detection (GC/MS) was used in parallel for identification of the molecular structure of the eluted compounds in the urine samples. The performance characteristics of the developed method are given both for the determination of mixtures of these compounds, as well as for the individual determination of each compound. Detection limits at the low ng Sn /L level for all organotin compounds (on a 25 ml sample) can be achieved which makes the technique suitable for sensitive routine analysis of human urine samples, with minimum sample preparation. Finally the feasibility of the proposed method was demonstrated by applying this technique to the analysis of several human urine samples.

References:

- [1] M. Hoch, *Appl. Geochem.*, 16 (2001) 719-743.
- [2] E. Rosenberg, *Speciation of Tin*. in: *Handbook of Elemental Speciation* (eds. R. Cornelis, K. Heumann, H. Crews, J. Caruso) Wiley, Chichester, 422-463 (2005).
- [3] J.B. Nielsen, J. Strand, *Environm. Res.* 88 (2002) 129-133.
- [4] K.E. Appel, *Drug Metabol. Rev.* 36 (2004) 763-86.