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LABORATORY AND FIELD PROCEDURES FOR THE DETERMINATION AND SPECIATION OF MERCURY BY ANODIC STRIPPING VOLTAMMETRY

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The availability of reliable and sensitive procedures for the determination and speciation of mercury is of great interest in several fields, such as environmental monitoring, food safety and clinical toxicology, owing to the potential toxicity of this metal, even at low concentrations. The most common analytical techniques for mercury quantification are cold vapour or fluorescence atomic absorption spectrometry and inductively coupled plasma mass spectrometry. Furthermore, direct mercury analysis can be carried out with devices able to automatically perform both sample decomposition and analyte detection by AAS [1]. An alternative approach for mercury determination is the use of electrochemical techniques, which are sensitive, versatile, inexpensive and suitable for on-site measurements with portable instrumentation. Most procedures rely on anodic stripping voltammetry (ASV), but also stripping chronopotentiometry, potentiometry and pulsed amperometry coupled with high performance liquid chromatography (HPLC) have been adopted. As to ASV, the most suitable working electrode (WE) material for mercury determination is gold, in different forms: solid, microwire, fiber, ultramicroband array, film (deposited on conventional or screen printed carbon substrates), nanoparticles. Gold WEs are used without modification or modified with different reagents, such as ligands or thiols. Other electrode materials used for mercury are glassy carbon, carbon paste, boron-doped diamond, platinum, modified with organic molecules, polymers or other modifiers [2].
The knowledge of mercury speciation is important, since organometallic forms, deriving from methylation of inorganic mercury, are more toxic than the latter. Speciation techniques for mercury are usually based on extraction or chromatographic separation coupled with spectrometric or (less commonly) electrochemical detection.
Our research group has been studying mercury determination and speciation since 2008. We have developed analytical methods for quantifying the total concentration of this element by ASV with a commercial solid gold electrode (SGE) and with a home-made nanoparticle-modified glassy carbon electrode (AuNPs-GCE). The advantages of AuNPs are their electrocatalytic properties, their large surface area, which ensures better mercury preconcentration and lower detection limits, and the renewable surface. The AuNPs-GCE has been applied to the determination of mercury in different matrices, such as drinking waters, sediments, food and pharmaceuticals.

Finally, we have focused our attention on fish [3], which accumulate relevant concentrations of mercury in their tissues and thus, can represent a major dietary source of this element for humans (Figure 1). We have developed a determination and speciation protocol able to distinguish between inorganic mercury (HgIN) and methylmercury (MeHg), the most commonly occurring methylated form of this element in natural waters. The protocol consists of the following steps: i) digestion of an aliquot of fresh fish with a mixture of HNO_3 and H_2O_2, followed by determination of total mercury (HgTOT) by ASV; ii) extraction of another sample aliquot with HCl, and treatment of the extract in a cartridge packed with a commercial resin modified with a ionic liquid (Patent Pending), which selectively retains HgIN; iii) elution of HgIN and analysis of the eluate by ASV; iv) calculation of MeHg by difference.

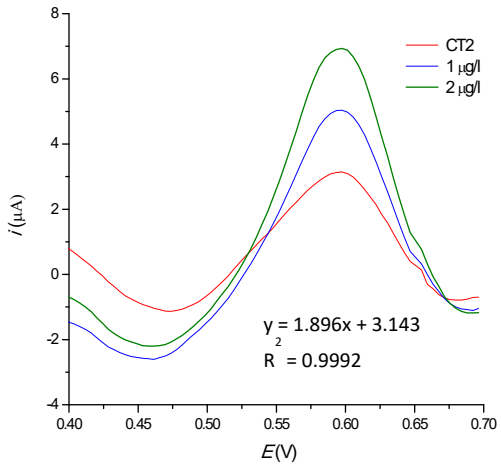

Figure 1. Voltammograms obtained for Hg quantification in a sample of canned tuna fish (CT2) with AuNPs-GCE

The protocol was tested on a certified reference material, Tuna Fish BCR 463 (98% recovery) and applied to the analysis of fish samples (canned tuna, swordfish, mussels, etc.) with two different approaches: i) microwave oven digestion and benchtop voltammetric analyzer; ii) digestion with a commercial food warmer and portable analyzer (Palmsens3), in view of on-site measurements. The LOQs in the fish-matrix were 0.5 μgL^{-1} for SGE and 0.1 μgL^{-1} for AuNPs-GCE, corresponding to 0.30 and 0.06 $mgkg^{-1}$ in the fresh sample. The samples were analyzed in parallel using direct mercury analyser (DMA) at the IZPLV: consistent results were obtained with the two voltammetric approaches and the DMA.
The proposed protocol is simple, inexpensive, and suitable for on-site analysis, allowing for the increase of controls on fish batches, thus reducing the risks to consumer health.

References

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