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A portable kit for on-site mercury determination and speciation

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Fish is considered one of the best sources of important substances for the human diet, providing, for instance, omega 6, useful against hypertension, coronary heart diseases and cancer, as well as high-quality proteins and nutrients, such as selenium and antioxidants. However, the accumulation of methylmercury (CH_3Hg) in fish tissues results in the incorporation of mercury into the food chain[1]. In the European Legislation, a maximum limit of CH_3Hg in food has not been established yet. Provisional Tolerable Weekly Intake (PTWI) values of 1.3 mg kg^{-1} CH_3Hg and 4 mg kg^{-1} Hg body weight were set (EFSA, 2012), while the maximum levels of total mercury (Hg_{TOT}) admitted by the European legislation are 0.5 mg kg^{-1} in small and medium fishes, mussels and most of seafood and 1 mg kg^{-1} in predatory fish respectively (2006/1881/EC, s.d.). For all these reasons it is very important to be able to discriminate between the inorganic and organic forms of mercury in food. Several techniques have been used for Hg determination. The application of these techniques for monitoring mercury concentration in food (fish, in particular) presents several drawbacks: some methods require very expensive instruments and/or highly specialized personnel and they either do not allow to perform on-site real time measurements or they not allow speciation studies[2].

The aim of this work is to report the development and validation of a simple analytical method (patent pending) that allows to overcome the problems previously exposed; the method is coupled to a kit for on-site analysis, e.g. on boats or in ports, suitable to provide a quick quantification of both Hg_{IN} and CH_3Hg content in fresh caught fish.

A portable sample pretreatment was optimized to determine total mercury content. An aliquot of fish tissue was added with 6 M HCl and heated at 60±5 °C in a food warmer. A new home-made sorbent (CYXAD, Amberlite XAD modified with CHYPOS 101, a negatively charged ionic liquid), was prepared to separate inorganic mercury (Hg_{IN}) and CH_3Hg. (Figure 1)

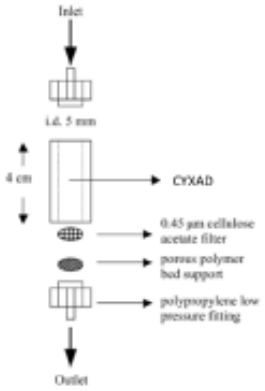

Figure 1. The support column contained the cartridge filled with CYXAD

The latter is not retained onto the resin, whereas Hg_{IN} is bound to the sorbent and subsequently eluted with HCl. After separation, mercury species were determined using square wave anodic stripping voltammetry (SW-ASV) with a solid gold electrode (SGE), using a portable potentiostat.

A certified reference material (BCR 627 Tuna Fish), freeze-dried samples and fresh samples were analysed, to check the reliability of the procedure. The results obtained with a benchtop voltammetric analyzer, after dissolution of the samples in microwave oven, were compared with those found with a portable potentiostat afterheating in the food warmer.

The quantification with the portable method is comparable to that obtained with the Direct Mercury Analyzer (DMA), an automated instrument, based on atomic spectroscopy, routinely used for mercury determination in many laboratories. The proposed procedure demonstrates good accuracy both for Hg_{IN} and

CH_3Hg even in presence of a high fat content, it is faster than the DMA in speciation studies, it does not require the use of organic solvent, it allows accurate and precise measurements to be made without the use of expensive and large instruments, making it possible to analyze the samples directly on the fishing site or in the port. [3]

This portable procedure can have many applications, such as monitoring of fish products for the protection of consumer health, on site screening analysis and environmental monitoring (i.e. determination of Hg species in fish and seabirds as water pollution indicator).

[1] E. de Paiva et al. 2017. Food Control 80, 104.
[2] A. Giacomino et al., 2017. Food Chem. 221, 737.
[3] A. Giacomino et al., 2021. Food Chem. 342, 128347.