Preparation of internal standard operating procedures for the methods using UV-PVG-µCCP-OES and implementation within the accredited laboratory of the partner

(CO-UBB, P1-ICIA)

Procedure1.

Determination of total Hg in water by photochemical cold vapor generation and detection by optical emission spectrometry in a capacitively coupled plasma microtorch (UV-PVG-µCCP-OES)

The procedure complies with drinking water legislation (Law 458/2002).

The present standard operational procedure refers to determination of total Hg in water after photochemical cold vapor generation under UV exposure and detection by optical emission spectrometry in a capacitively coupled plasma microtorch (UV-PVG-µCCP-OES). The procedure sets out sample preparation, description and operation of the related instrumentation, evaluation of the analytical performances and criteria for the internal quality control.

The schematic diagram of the procedure is presented in Figure 1.

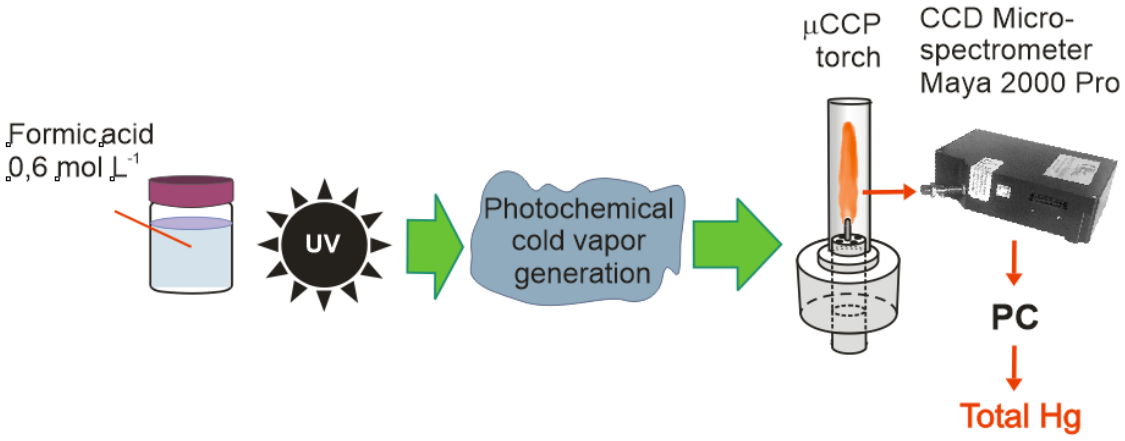

Figure 1. Schematic diagram of the procedure for the determination of total Hg in water by UV-PVG-µCCP-OES

The procedure is based on the determination of total Hg by photo-induced cold vapor generation under UV exposure that has the same efficiency for CH_3Hg^+ and Hg^{2+} species in 0.6 mol l^{-1} HCOOH and measurement by optical emission spectrometry in the capacitively coupled plasma microtorch (UV-PVG-µCCP-OES). The method is applicable to the analysis of surface water, well, tap drinking and bottled water (still or gaseous), groundwater and waste water.

A volume of 565 µl 98-100% HCOOH is added to an aliquot of up to 20 ml water and further a final dilution to 25 ml is achieved with ultrapure water. In this solution total Hg is determined by UV-PVG-µCCP-OES after preconcentration on a gold filament microcollector. Calibration is achieved against Hg^{2+} standards in the range 0-0.1 ng ml^{-1} containing 0.6 mol l^{-1} HCOOH. Plasma microtorch is operated at 15 W and 100 ml min^{-1} Ar and the emission signal is measured with the Maya2000 Pro microspectrometer at 253.652 nm. The method provides detection/quantification limits of 0.1/0.3 ng l^{-1} Hg, recovery in certified reference materials (ERM-CA713 Waste water and ERM-CA615 Groundwater) of 97±12% total Hg and precision in the range 4.4-12.4%. Details on the proposed procedure are available in the reference Covaci et al., JAAS 2018.

Procedure 2.

Determination of methylmercury in seafood by photochemical cold vapor generation and detection by optical emission spectrometry in capacitively coupled plasma microtorch (UV-PVG-μCCP-OES)

This procedure is in compliance with the below mentioned legislation:

1. Commission Regulation 2006/1881/EC setting maximum levels for certain contaminants in foodstuffs. Official J. EU (2006) L364/5.
2. CODEX STAN 193-1995. Codex general standard for contaminants and toxins in food and feed (2009) 1-44.
3. Decision 2002/657/EC implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results, Official J. Eur. Communities, 2002, L221, 8–36.
4. Decision 2007/333/EC laying down the methods of sampling and analysis for the official control of the levels of lead, cadmium, mercury, inorganic tin, 3-MCPD and benzo(a)pyrene in foodstuffs, Official J. Eur. Communities, 2007, L88, 29–38.
5. Decision 2011/836/EC of 19 August 2011 amending Regulation (EC) No 333/2007 laying down the methods of sampling and analysis for the official control of the levels of lead, cadmium, mercury, inorganic tin, 3-MCPD and benzo(a)pyrene in foodstuffs, Official J. Eur. Communities, 2011, L215, 9–16.

The present standard operational procedure refers to determination of methylmercury in seafood by photochemical cold vapor generation capacitively coupled plasma microtorch optical emission spectrometry (UV-PVG-μCCP-OES). The procedure sets out sample preparation, description and operation of the related instrumentation, evaluation of the analytical performances and criteria for the internal quality control.

The schematic diagram of the procedure is presented in Figure 2.

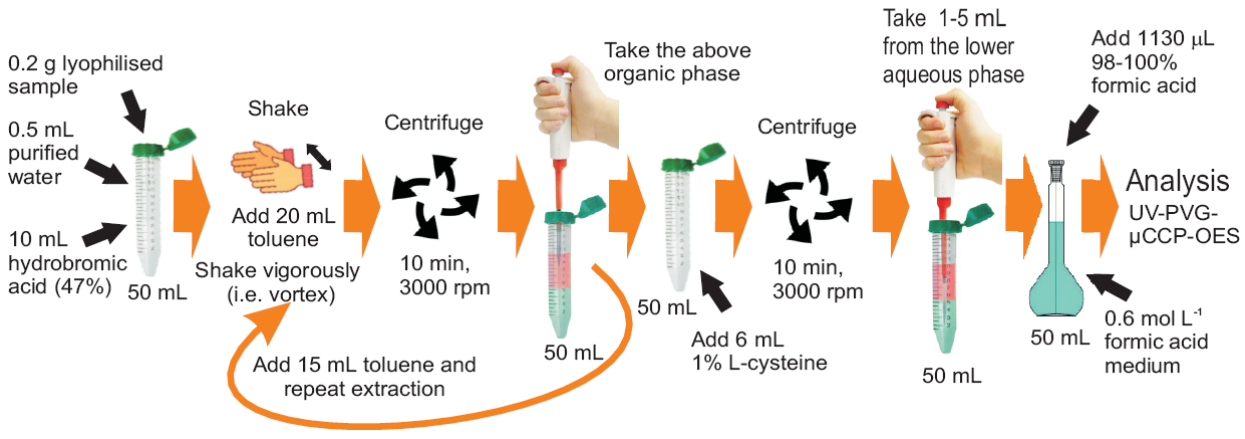

Figure 2. Schematic diagram of the procedure for the determination of methylmercury in seafood by UV-PVG-μCCP-OES

The procedure is based on double liquid-liquid extraction in the HBr-toluene-1% L-cysteine solution, photo-induced Hg cold vapor generation in 0.6 mol l^{-1} HCOOH and emission measurement in the capacitively coupled plasma microtorch. Sample preparation is carried out according to the protocol recommended by Joint Research Center, Institute for Reference Materials and Measurements, Geel, Belgium, initially developed for methylmercury determination in seafood by thermal decomposition atomic

absorption spectrometry. An amount of 0.2 g lyophilized sample is moistened in a tube with 0.5 ml ultrapure water, then 10 ml HBr 47% and further 20 ml toluene are added and the tube is vigorously shaken in a vortex system for 2 min. Supernatant is separated by centrifugation at 3000 rpm for 15 min. Extraction is repeated with another volume of 15 ml toluene. The collected organic phase is mixed with 6 ml 1% L-cysteine solution, shaken and centrifuged at 3000 rpm for 10 min. An aliquot volume of 1 – 5 ml of the aqueous extract is diluted to 50 ml in 0.6 mol l^{-1} HCOOH. Quantification of methylmercury is achieved by photo-induced cold vapor generation optical emission spectrometry at 253.652 nm in capacitively coupled plasma microtorch against Hg^{2+} standards in the range 0 – 5 ng ml^{-1} in 0.6 mol l^{-1} HCOOH. The method provides quantification of 6 µg kg^{-1} CH_3Hg^+ expressed as Hg in dry mass, precision of 2.7-9.4% assessed from 12 measurements of lyophilized fish samples containing 0.044 – 0.208 mg kg^{-1} Hg and accuracy of 99±8% (95% confidence interval) assessed from CRMs analysis (BCR-463 Tuna Fish, ERM-CE464 Tuna Fish, DOLT-4 Dogfish liver and TORT-2 Lobster Hepatopancreas). Details on the procedure are available in the reference Covaci et al., Talanta 2017.

Procedure 3.

Speciation of mercury as CH_3Hg^+ and Hg^{2+} in seafood by cold vapor generation in HCOOH and $SnCl_2$ medium and detection by optical emission spectrometry in capacitively coupled plasma microtorch ($SnCl_2$-CV-µCCP-OES/UV-PVG-µCCP-OES)

This procedure is in compliance with the European legislation mentioned above.

The present standard operational procedure refers to speciation of mercury as monomethylmercury (CH_3Hg^+) and Hg^{2+} in seafood by chemical cold vapor generation with formic acid under UV exposure and $SnCl_2$ respectively, and detection by capacitively coupled plasma microtorch optical emission spectrometry (UV-PVG-µCCP-OES/$SnCl_2$-CV-µCCP-OES). The procedure sets out sample preparation, description and operation of the related instrumentation, evaluation of the analytical performances and criteria for the internal quality control.

The schematic diagram of the procedure is presented in Figure 3.

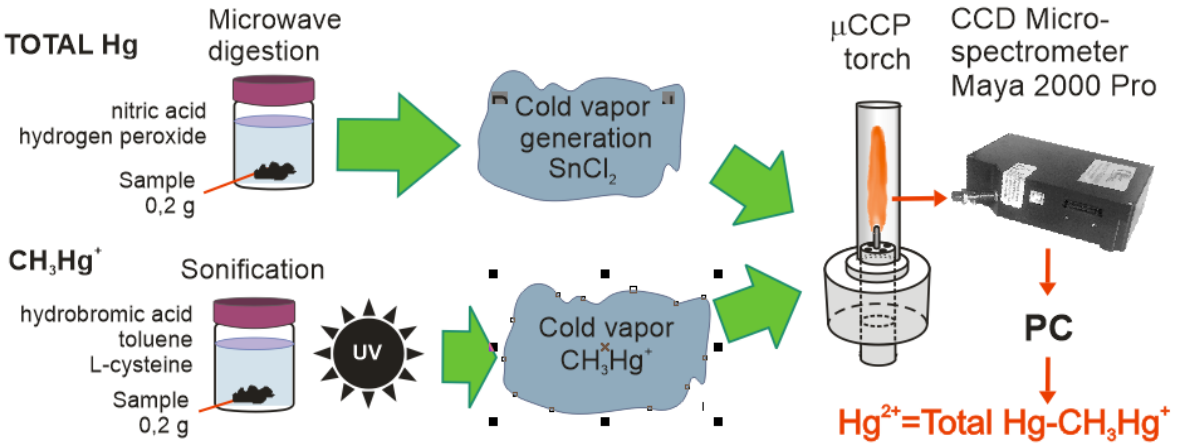

Figure 3. Schematic diagram of the procedure for the speciation of Hg in seafood by $SnCl_2$-CV-µCCP-OES/UV-PVG-µCCP-OES

The procedure is based on the determination of total Hg and CH_3Hg^+, than calculus of Hg^{2+} content by subtracting. Total Hg is quantified after digestion of 0.2 g sample in 60% nitric acid (8 ml)- 30% hydrogen peroxide (2 ml) mixture, derivatization to cold vapor with 20% $SnCl_2$ in 15% HCl medium and detection by capacitively coupled plasma torch optical emission spectrometry ($SnCl_2$-CV-µCCP-OES). Determination of CH_3Hg^+ is based on double liquid-liquid extraction in the HBr-toluene-1% L-cysteine solution, photo-induced Hg cold vapor generation in 0.6 mol l^{-1} HCOOH and emission measurement in the capacitively coupled plasma microtorch (UVCV-µCCP-OES). The sample preparation protocol is that recommended by Joint Research Center, Institute for Reference Materials and Measurements, Geel, Belgium, initially developed for the determination of methylmercury in seafood by thermal decomposition atomic absorption spectrometry. Am amount of 0.2 g lyophilized sample is moisturized in a centrifuge tube with 0.5 ml ultrapure water, then 10 ml HBr 47% and further 20 ml toluene are added and the tube is vigorously shaken in a vortex system for 2 min. Supernatant is separated by centrifugation at 3000 rpm for 15 min. Extraction is repeated with another volume of 15 ml toluene. The collected organic phase is mixed with 6 ml 1% L-cysteine solution, shaken and centrifuged at 3000 rpm for 10 min. An aliquot volume of 1 – 5 ml of the aqueous extract is diluted to 50 ml in 0.6 mol l^{-1} HCOOH. Quantification is made by capacitively coupled plasma microtorch optical emission spectrometry at 253.652 nm

against Hg^{2+} standard solutions in the range 0 – 1 ng ml^{-1} in 5% HCl medium for total Hg and 0.6 mol l^{-1} HCOOH for CH_3Hg^+. Plasma microtorch is operated at 15 W and 100 ml min^{-1} Ar, while the emission is measured with Maya2000 Pro microspectrometer. The method provides limits of detection/quantification of 3/9 µg kg^{-1} total Hg and 2/6 µg kg^{-1} CH_3Hg^+, recovery of 100±10% total Hg, 100±8% CH_3Hg^+ and 102±13% Hg^{2+} in CRMs (BCR-463 Tuna Fish, ERM-CE464 Tuna Fish, DOLT-4 Dogfish liver and TORT-2 Lobster Hepatopancreas) and precision of 2.4-7.8%, 2.4-11.9% and 3.8-14.0% respectively. Details on the procedure are available in the reference Covaci et al., Food Control, 2017.

Procedure 4.

Mercury speciation as CH_3Hg^+ and Hg^{2+} in seafood by photochemical cold vapor generation in the presence and absence of UV irradiation and detection by capacitively coupled plasma microtorch optical emission spectrometry (UV–Vis-PVG-μCCP-OES)

This procedure is in compliance with the European legislation mentioned above.

The present standard operational procedure refers to speciation of mercury as monomethylmercury (CH_3Hg^+) and Hg^{2+} in seafood by photochemical cold vapor generation in the presence/absence of UV irradiation and detection by capacitively coupled plasma microtorch optical emission spectrometry (UV–Vis-PVG-μCCP-OES). The procedure sets out sample preparation, description and operation of the related instrumentation, evaluation of the analytical performances and criteria for the internal quality control.

The schematic diagram of the procedure is presented in Figure 4.

The procedure is based on the determination of total Hg (CH_3Hg^+ and Hg^{2+}) by UV photo-induced cold vapor generation in 0.6 mol l^{-1} HCOOH and selective derivatization of Hg^{2+} in 0.6 mol l^{-1} HCOOH under Vis exposure (UV lamp turned off) then optical emission measurement in capacitively coupled plasma microtorch (UV–Vis-PVG-μCCP-OES). Concentration of CH_3Hg^+ results by subtraction.

An amount of 0.2 g lyophilized sample is subjected to ultrasound-assisted extraction in 10 ml HCOOH 98-100% for 3 h for 50 °C. The supernatant is separated by centrifugation at 3000 rpm for 15 min. Two aliquot volumes up to 1 ml are diluted to 50 ml with ultrapure water to contain 0.6 mol l^{-1} HCOOH. One sample is used for the determination of total Hg by UV-PVG-μCCP-OES, while the other for Hg^{2+} quantification by Vis-PVG-μCCP-OES after preconcentration from 25 ml sample on a gold filament microcollector. Calibration is carried out with Hg^{2+} solutions in the range 0-1 ng ml^{-1} in both cases. Plasma microtorch is operated at 15 W and 100 ml min^{-1} Ar, while the emission is measured with Maya2000 Pro microspectrometer at 253.652 nm. The method provides limits of detection/quantification of 9/27 μg kg^{-1} total Hg and 4.8/14.4 μg kg^{-1} Hg^{2+}, recovery of 99±6% total Hg, 99±9% Hg^{2+} and 99±10% CH_3Hg^+ in CRMs (BCR-463 Tuna Fish, ERM-CE464 Tuna Fish, DOLT-4 Dogfish liver and TORT-2 Lobster Hepatopancreas) and precision of 2.6-10.2%, 2.0-13.4% and 5.3-14.5% respectively. Details on the procedure are available in the reference Covaci et al., Microchem. J., 2018.

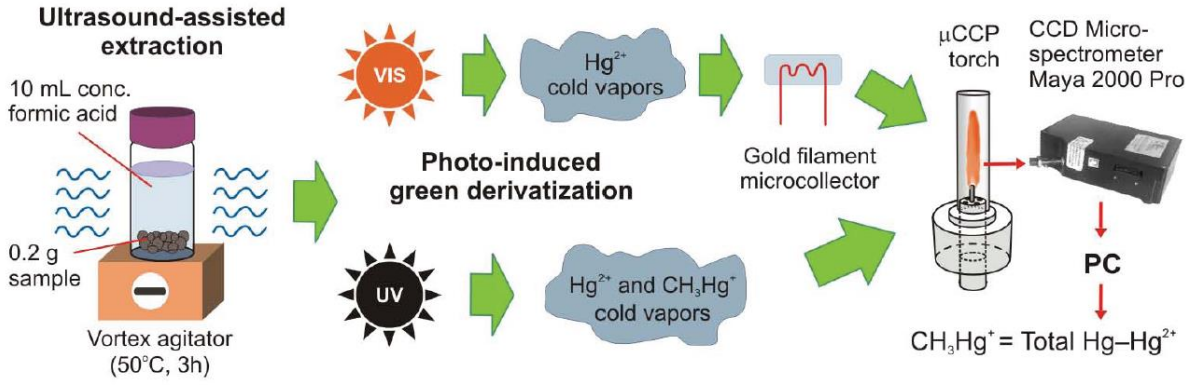

Figure 4. Schematic diagram of the procedure for the speciation of Hg in seafood by UV–Vis-PVG-μCCP-OES

Results: 4 analytical procedures implemented in laboratory