Implementation of the new eco-scale methods by UV-PVG-µCCP-OES validated on real samples

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Implementation of the new methods for the determination of total mercury

The new eco-scale methods for the determination and speciation of Hg were implemented for the analysis of various real samples, such as seafood (fish filet), food of animal or vegetal origin and water. Results are presented in Tables 1 – 3.

Table 1. Results for total Hg (mg kg^{-1}, mean±CI, n=5 and 95% confidence level) in fish filet and mushrooms by UV-PVG-µCCP-OES without preconcentration compared to other spectrometric methods (Covaci et al., JAAS, 2018)

Sample	UV-PVG-µCCP-OES	$SnCl_2$-CV-µCCP-OES	$SnCl_2$-CV-ICP-OES	$SnCl_2$-CV-AFS
Tuna	0.212±0.017	0.191±0.013	0.226±0.008	0.211±0.008
Trout	0.110±0.004	0.095±0.010	0.094±0.006	0.096±0.006
Salmon	0.108±0.007	0.111±0.005	0.109±0.014	0.099±0.007
Hake	0.216±0.007	0.216±0.08	0.219±0.008	0.218±0.009
Carp	0.089±0.006	0.086±0.004	0.100±0.003	0.086±0.004
Mackerel	0.198±0.025	0.211±0.014	0.197±0.009	0.206±0.009
Cod	0.372±0.014	0.368±0.006	0.359±0.007	0.387±0.013
Cod	0.305±0.048	0.317±0.033	0.306±0.031	0.309±0.017
Mushroom	0.268±0.038	0.258±0.021	0.254±0.028	0.268±0.018
Mushroom	4.48±0.25	4.26±0.33	4.51±0.40	4.33±0.21

Table 2. Results for total Hg by UV-PVG-µCCP-OES with preconcentration in vegetables, fruits, food supplements, meat and meat organs (Covaci et al., JAAS, 2018)

Sample	Total Hg (µg kg^{-1}), mean±CI
Apple	5.2±0.4
Cabbage	11.6±0.8
Potatoes	64.2±3.8
Carrot	54.0±5.9
Onion	89.4±10.0
Celery	36.7±3.3
Parsley	122±7
Rice	37.8±2.8
Wheat bran	3.3±0.4
Brown bread	1.0±0.1
Maize	52.1±3.6
Pork meat	46.4±3.6
Chicken meat	59.8±5.7
Chicken liver	123±9
Supplement for athletes	65.6±5.2
Multimineral supplements	1.1±0.2

Table 3. Results for total Hg in water analyzed by UV-PVG-μCCP-OES with preconcentration (Covaci et al., JAAS, 2018)

Sample	Total Hg (ng l^{-1}), mean±CI
River water	10.0±0.8
River water	11.6±0.8
Tap water	9.2±0.9
Hard drinking water	5.7±0.9
Well water	68.7±2.6
Well water	75.7±4.3
Well water	40.2±2.2
Bottled water (still)	13.8±1.2
Bottled water (still)	1.2±0.2
Bottled water (still)	3.1±0.4
Bottled water (still)	8.4±0.7
Bottled water (still)	68.9±3.9
Bottled water (sparkling)	24.6±2.7
Bottled water (sparkling)	26.1±2.3
Bottled water (sparkling)	33.1±2.5
Bottled water (sparkling)	61.8±4.5

[a] CI is confidence interval for n=5 and 95% confidence level

No significant differences were identified between UV-PVG-μCCP-OES and reference methods related to results for Hg content in fish muscle and mushroom. Concentrations of 0.089 – 0.372 mg kg^{-1} Hg in fish fillet and up to 4.48 mg kg^{-1} in mushrooms were determined with a precision of 2.6-12.7%. When using Hg preconcentration, precision of measurements was 3.0 - 12.8% for food and food supplements containing 1.0 – 123 μg kg^{-1} Hg and 4.4 – 12.4% in various water samples with concentrations of 1.2 – 75.7 ng l^{-1} Hg. In this way the applicability of the solubilization in formic acid for Hg determination was extended as it was found to be suitable for food of animal and vegetable origin and food supplements in addition to fish samples as reported till now.

Implementation of the method for Hg speciation using UV–Vis-PVG-µCCP-OES

The results obtained for Hg speciation in real samples of fish muscle are presented in Table 4.

Concentrations of 0.089 – 0.305 mg kg^{-1} total Hg and 0.018 – 0.120 mg kg^{-1} Hg^{2+} were measured with a precision of 2.6 – 10.2% and 2.0 – 13.4% respectively. The pooled precision for the determination of CH_3Hg^+ calculated as the difference between total Hg and Hg^{2+} were in the range 5.3 – 14.5% and took into account the individual variability. Our results were similar to those provided by TD-AAS as reference method. The method proposed by us for Hg speciation fulfills the recommendation of AOAC in terms of precision to be in the range 3 – 15%. The method also complies with the demand in Commission Regulation (EC) No 333/2007 related to the RSD value estimated from the Horvitz's equation to be lower than 19% for contaminant levels similar to those of total Hg and its species found in our test samples.

Table 4. Results for Hg speciation (mg kg^{-1}, mean±CI, n=5 and 95% confidence level) in fish muscle (Covaci, et al., Microchem J., 2018)

Sample	UV–Vis-PVG-µCCP-OES			TD-AAS		
	Total Hg	Hg^{2+}	CH_3Hg^+	Total Hg	Hg^{2+}	CH_3Hg^+
Tuna	0.212±0.017	0.022±0.002	0.190±0.023	0.215±0.012	0.013±0.002	0.202±0.022
Trout	0.110±0.004	0.079±0.007	0.031±0.003	0.104±0.006	0.063±0.008	0.041±0.005
Salmon	0.126±0.007	0.018±0.003	0.108±0.019	0.125±0.004	0.028±0.003	0.097±0.008
Hake	0.216±0.007	0.035±0.002	0.181±0.012	0.216±0.010	0.047±0.007	0.169±0.025
Carp	0.089±0.006	0.019±0.002	0.070±0.009	0.099±0.008	0.010±0.002	0.089±0.019
Mackerel	0.198±0.025	0.031±0.004	0.167±0.030	0.190±0.019	0.025±0.005	0.165±0.025
Cod	0.305±0.032	0.120±0.003	0.185±0.020	0.308±0.023	0.110±0.014	0.198±0.021
RSD (%)	2.6 – 10.2	2.0 – 13.4	5.3 – 14.5	2.6 – 8.1	7.1 – 18.4	6.6 – 17.0

Results:

- Methods implemented in the laboratory for the determination of total Hg and speciation as Hg^{2+} and CH_3Hg^+ in real water and food samples
- 3 papers published in ISI journals (Covaci et. al., JAAS, 2018, Covaci et al., Microchem. J., 2018 and Senila et al., Chem. Pap., 2018)
- 1 participation in international event *(The 45nd International Conference of the Slovak Society of Chemical Engineering, Tatranske Matliare, May 2018)*