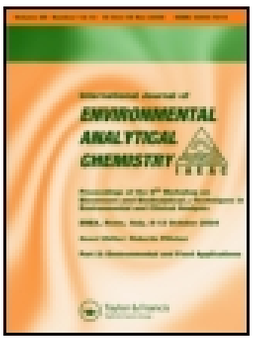

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ARTICLE

Facilitating local analysis in northern regions: microwave plasma-atomic emission spectrometry for mercury determination in wild Atlantic salmon

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ABSTRACT

An analytical procedure was developed to quantify mercury concentration in wild Atlantic salmon (*Salmo salar*) muscle tissue by cold-vapour microwave plasma-atomic emission spectrometry (CV-MP-AES) with microwave-assisted acid digestion. Muscle samples were collected from the Atlantic salmon Food, Social, and Ceremonial fisheries in Lake Melville, Labrador (Canada). Muscle samples were digested with nitric acid and hydrogen peroxide, mercury was stabilised with thiourea, reduced with $NaBH_4$, and quantified by CV-MP-AES. Analysis of fish protein certified reference material (CRM, DORM-3) by CV-MP-AES was used to assess the accuracy and precision of the procedure. CRM recovery averaged 88% with a relative standard deviation of less than 8%. The limits of detection were as low as 0.22 $\mu g \cdot L^{-1}$ in solution which translate to 0.02 $\mu g \cdot g^{-1}$. Mercury concentrations in salmon muscle tissue quantified by CV-MP-AES were not significantly different from results obtained by cold vapour-atomic fluorescence spectrometry (CV-AFS) from an accredited laboratory. Our results indicated that the CV-MP-AES procedure is appropriate for the quantification of mercury at background levels (range 0.15–0.29 $\mu g \cdot g^{-1}$ dry weight) in wild fish of Labrador.

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Mercury; Microwave Plasma-Atomic Emission Spectrometry; atomic fluorescence spectrometry; cold-vapour; fish muscle

1. Introduction

Northern regions (Arctic and subarctic) are exposed to increasing mercury concentrations, mostly produced and released by anthropogenic sources at lower latitudes and then transported to northern regions [1–3] or locally by hydroelectric development [4,5]. Inorganic mercury, which also occurs naturally, is methylated by bacteria in aquatic environments to its most toxic form (methylmercury) [6]. Methylmercury is readily bioaccumulated and biomagnified through the aquatic food chain [7], which results in increased mercury concentrations in fish including the traditional food sources of indigenous communities [2]. Mercury has a wide range of adverse effects on human health and monitoring mercury concentrations in food sources is critical [2,8].

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Lake Melville is a large (3 000 km^2) subarctic estuarine fjord in Labrador that supports important Food, Social, and Ceremonial (FSC) fisheries. In Lake Melville, total mercury concentrations in muscle tissue of anadromous Arctic char (*Salvelinus alpinus*), Atlantic salmon, and brook trout (*Salvelinus fontinalis*) averaging 0.062 ± 0.042 $\mu g \cdot g^{-1}$ wet weight (ww), 0.073 ± 0.020 $\mu g \cdot g^{-1}$ ww, and 0.10 ± 0.034 $\mu g \cdot g^{-1}$ ww, respectively [9]. Total mercury concentration averaged 0.04 $\mu g \cdot g^{-1}$ ww in anadromous arctic char collected along the coast of Labrador [10]. In the Canadian Arctic, mercury concentrations were below 0.05 $\mu g \cdot g^{-1}$ ww in anadromous arctic char [11] and ranged from 0.015 to 0.25 $\mu g \cdot g^{-1}$ ww in Northern Dolly Varden (*Salvelinus malma*) [12]. Svalbard arctic char mercury concentrations ranged from 0.039 to 0.44 $\mu g \cdot g^{-1}$ ww [13]. Health Canada assumes that 100% of mercury in fish muscle is in the most toxic form (methylmercury) [14], therefore total mercury is used as a conservative estimate of methylmercury concentrations.

Northern regions have limited analytical capacity and mercury quantification is usually not performed locally. Local analytical capacity could benefit northing communities by making community based research more feasible and in turn help communities define, prioritize and address their scientific. Increasing mercury research capacity at research stations located in northern regions is now being facilitated by the commercialisation of the microwave plasma-atomic emission spectrometry (MP-AES) system [15]. Although the microwave-induced plasma technology has existed since the 1950s, it was not until the 1990s that the microwave-induced plasma torch was developed [16], and in 2011 a system using the microwave-induced plasma torch coupled to an atomic emission spectrometer was commercialised (MP-AES by Agilent Technologies). This analytical system operates using a nitrogen generator, therefore, reducing costs and challenges related to transportation and supply of other gases (e.g. argon and acetylene) [15,17]. MP-AES is a cost-effective analytical system compared to inductively coupled plasma systems (ICP-MS and ICP-AES) and the multi-elemental capability offer more possibilities than the traditional atomic absorption spectrometry (AAS). Since the commercialisation of the MP-AES, a wide range of elements have been quantified using this system in geological materials [15,18], inorganic fertiliser [19], water, soil, and sediment [20], crude oil [21], sunflower [22], agricultural materials [23], wine [24], and leather and fur [25]. Overall, the analytical performance of the MP-AES was reported superior to AAS [18,19,23] and comparable to ICP-AES [17,23,25].

Cold vapour is a well-established technique that enables mercury determination with analytical systems that require volatile compounds (AAS or AES) [26,27]. A reducing agent (sodium borohydride, $NaBH_4$ or tin chloride, $SnCl_2$) in an acid matrix is used for the generation of mercury cold vapour, transforming mercury in solution (Hg^{2+}) to its volatile form (Hg°). Both reducing agents have been successfully applied for mercury determination by CV-MP-AES [19,25]. A common problem linked to mercury determination is the memory effect caused by the adsorption of mercury on the surfaces of the sample introduction system, which leads to an increase in signal strength during the analysis and results in long wash-out time, poor accuracy, and reliability between analyses even at relatively low concentration (1–5 $\mu g \cdot L^{-1}$) [28–30]. A number of different procedures have been proposed to solve this problem such as the addition of gold [29], a sulphur-containing compound (e.g. 2-mercaptoethanol, L-cysteine, thiourea) [29–31], or a mix of Triton X-100, ammonia, and ethylene_diaminetetra_acetic acid (EDTA) [32,33]. For cost, toxicity, and simplicity-related reasons, analytical procedures using gold, 2-mercaptoethanol, and Triton X-100 should be excluded when working in northern regions.

To the best of our knowledge, there have been no studies that have assessed the accuracy and precision of mercury determination in fish tissue with a MP-AES analytical system. This study aims to evaluate the potential of using thiourea to stabilise mercury in sample solution after digestion and $NaBH_4$ as reducing agent to accurately and precisely quantify total mercury in wild Atlantic salmon from Lake Melville by CV-MP-AES. The capacity of CV-MP-AES for measuring total mercury at concentrations below the consumption limit (maximum concentration) for mercury in fish recommended by Health Canada for subsistence fishery (0.2 $\mu g \cdot g^{-1}$ ww) [34] is investigated. The proposed procedure has been developed for quantifying total mercury concentration.

2. Experimental

2.1 *CRM and reagents*

The certified reference materials (CRM), DORM-3 (fish protein), were purchased from the National Research Council Canada, NRCC.

Reducing agent solution of 0.1M sodium hydroxide (NaOH, Anachemia, VWR, Radnor, USA) and 1% w/v sodium borohydride ($NaBH_4$, Fisher Scientific, Hampton, USA) was freshly (<1 h) prepared before CV-MP-AES analysis. A solution of 10% w/v thiourea (CH_4N_2S, Fisher Scientific, Hampton, USA) was used to stabilise mercury in sample solutions. A stock standard solution of Hg ($1000 mg \cdot L^{-1}$) for ICP-MS analytic grade was purchased from Fluka Analytical (Sigma-Aldrich, St. Louis, USA). Trace metal grade nitric acid trace metal grade (15.9M HNO_3, Ultrex II, J.T. Baker, Center Valley, USA) and hydrogen peroxide trace metal grade (≥30% H_2O_2, TraceSELECT®, Sigma-Aldrich, St. Louis, USA) were used as reagents in microwave digestion.

2.2 *Apparatus*

Samples were digested with an MARSXpress microwave digestion system (CEM Corporation, Matthews, USA). Digested samples were analysed with an Agilent Technologies 4200 MP-AES (Santa Clara, USA) equipped with a multi-mode sample introduction system (MSIS) and an autosampler (Thermo Fisher Scientific, CETAC, ASX-520, Waltham, USA). The sample and reducing agent solutions were pumped separately with the MSIS, mixed after the peristaltic pump with a mixing tee, and then connected to the spray chamber (Figure 1). The unused sample lines to the nebuliser and MSIS were capped to prevent nebuliser gas from escaping. The MP-AES operating conditions following manufacturer recommendations are listed in Table 1. The rinse, sample uptake, stabilisation, and read times were increased to ensure accurate and precise quantification. Viewing position and nebuliser flow were optimised automatically by the software instrument before each calibration. The nitrogen plasma gas was supplied by a 4107 Nitrogen generator (Agilent Technologies). Data were acquired using MP Expert version 1.5.0.6545 software provided by Agilent Technologies.

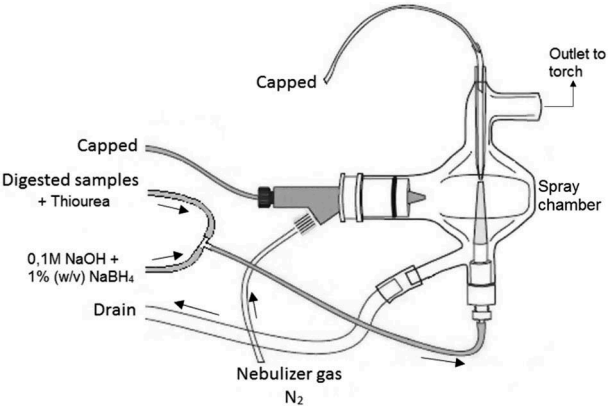

Figure 1. Schematic diagram of the MSIS for cold-vapour mercury analysis with MP-AES. The digested samples with 1% thiourea solution and reducing agent solutions are pumped separately, mixed at the mixing tee, and then enter the spray chamber. Volatile Hg° is transported by the nebuliser gas to the torch.

Table 1. MP-AES operating conditions for mercury analysis.

Instrument parameter	
Nebuliser	Concentric
Spray chamber	MSIS
Nebuliser flow rate (L/min)	0.50–0.55
Nitrogen consumption (L/min)	20
Read-time (s)	10
Number of replicates	3
Rinse time (s)	60
Sample uptake delay (s)	45
Stabilisation time (s)	30
Pump speed (rpm)	15
Sample flow rate (mL/min)	~2.0
Reducing agent flow rate (mL/min)	~2.0
Viewing position	0–10
Hg wavelength (nm)	253.652

2.3 *Samples and sample preparation*

Muscle tissue samples from 15 adult Atlantic salmon were obtained from the FSC fisheries in Lake Melville near the town of North West River (Labrador) during summer 2014. Salmon were measured (fork length, cm), sampled for muscle tissue on the dorsal area behind the head, stored in a clean Nalgene bottle (50 mL), kept on ice during sampling period (2–3 h), and stored at −20°C. At the end of the field season, frozen samples were sent to the chemistry laboratory of the biology, chemistry, and geography department at the Université du Québec à Rimouski.

In laboratory, samples were rinsed with ultrapure water, frozen at −80°C, freeze-dried (Labconco, Kansas, USA), homogenised (VirTis model '45'), and stored at −20°C.

For CV-MP-AES analyses, salmon sub-samples (approximately 0.5 g) were accurately (± 0.1 mg) weighted into 55 mL TFM® vessels (CEM Corporation, MARSXpress). To each sub-sample, 10 mL of nitric acid and 1 mL of hydrogen peroxide were added before being tightly capped. The sub-samples were then digested at high temperature and

under pressure with a microwave digestion system for a total of 30 min in two different steps with the power set at 800W. The first step was a ramp temperature for 20 min to 160°C. Temperature was maintained at 160°C for 10 min during step 2. Once cooled to room temperature, digested samples were transferred into cleaned (10% HNO_3 and ultrapure water) 50 mL polypropylene conical centrifuge tubes. Sample volumes were then adjusted to 40 mL with ultrapure water and stored in a refrigerator until analysis. For quality control, a procedural blank (HNO_3 and H_2O_2) was included in each digestion run. Also, for assessing accuracy and precision, five sub-samples of the CRM were digested as previously described for salmon muscle samples.

Before CV-MP-AES analyses, 1 mL of the 10% w/v thiourea solution was added to each digested salmon, CRM, and procedural blanks (9 mL) and allowed to react for 30 min. The thiourea reacted with the digested sub-samples and formed a white precipitate. However, preliminary tests showed that the precipitation process did not affect the mercury concentrations in solution. After precipitation (~30 min), the solutions were filtered with a 25 mm diameter 0.45 µm PTFE membrane syringe filter (VWR, Radnor, USA).

Sub-samples of our 15 salmon freeze-dried and homogenised muscle samples were sent to the Lakehead University Environmental Laboratory (LUEL; Thunder Bay, Ontario), accredited by the Canadian Association for Laboratory Accreditation Inc. (CALA) to ISO 17,025 for result comparison and validation. The LUEL determined total mercury concentrations in salmon muscles using the EPA method 1631 with cold vapour-atomic fluorescence spectrometry (CV-AFS). The results obtained were compared to the CV-MP-AES results with a paired t-test.

2.4 *MP-AES analysis*

Before analyses, the MP-AES system was purged with nitrogen for a period of 3 h and mercury quantifications were performed under nitrogen atmosphere. Seven levels of calibration ranging from 0 to 10 µg·L^{-1} were selected to match the expected concentrations. Calibration solutions contained ~2.8M HNO_3 and 1% w/v thiourea to mimic the sample matrix. To assess accuracy and precision of the procedure, the CRM digested sub-samples were analysed first, followed by the salmon digested sub-samples and the procedural blanks. The system was rinsed for 1 min with 10% HNO_3 ultra trace grade between each analysis.

The calibration solution of 10 µg·L^{-1} was the highest mercury concentration entering the system. To assess if memory effect was occurring at this mercury concentration, the mercury emission signal was monitored during and after the injection of the calibration solution (10 µg·L^{-1}), followed by the rinsing solution. The signal rapidly decreased after the beginning of the system rinsing and after 60 s the intensity had stabilised to the background noise level, indicating that thiourea was successfully stabilising mercury and rinsing solution and time are sufficient to eliminate mercury in the system. The limits of detection (LOD) was calculated from the regression line of the calibration as described in Miller and Miller [35]. Accuracy and precision of the procedure were verified using t-tests on CRM certified value and the experimental mean value of mercury obtained by CV-MP-AES.

Table 2. Limits of detection (LOD) calculated from the calibration curves. The experiments were performed in June 2015 (JN2015) and August 2016 (AU2016).

Calibration curve (conc. range $\mu g \cdot L^{-1}$)	Correlation coefficient	Intercept (b)	Slope (m)	SD ($S_{y/x}$)	LOD (y_1) ($\mu g \cdot L^{-1}$)	LOD* ($\mu g \cdot g^{-1}$)
JN2015 (0–10)	0.99986	−22.29	239.29	17.86	0.22	0.018
AU2016 (0–10)	0.99978	−11.74	215.73	19.60	0.27	0.022
$y_1 = 3S_{y/x} + b$						

* Based on a 0.50 g sample mass

3. Results and discussion

3.1 *LOD*

The LODs obtained for the analysis of total mercury with the MP-AES is similar or lower than the limit of detection reported for AAS [19] or ICP-AES [25]. Laboratory work lasted for more than 1 year, during that time period high reproducibility was achieved by performing calibration curves and obtaining excellent linearity with correlation coefficients of at least 0.999 (Table 2). LOD was as low as 0.22 $\mu g \cdot L^{-1}$ and is similar to what Lima et al. [19] found (LOD: 0.3 $\mu g \cdot L^{-1}$) when measuring mercury in inorganic fertiliser with CV-MP-AES using $SnCl_2$ as reducing agent. The lowest LOD obtained in this study translated to 0.018 $\mu g \cdot g^{-1}$ dw with a freeze-dried muscle tissue mass of 0.50 g. The LOD of this study is lower to what was previously found (LOD of 2.0 $\mu g \cdot g^{-1}$ dw) by Zhao et al. [25] when measuring mercury in leather and fur with CV-MP-AES using $NaBH_4$ as reducing agent.

Since samples were freeze-dried for conservation purposes, the concentration in dry weight obtained had to be converted to wet weight to compare with the Health Canada standard for mercury in fish. Based on an estimated 75% water content for fish muscle [36], the highest mercury concentration observed in salmon muscle was 0.071 $\mu g \cdot g^{-1}$ ww, which is well under the Canadian consumption limit for mercury in fish (0.2 $\mu g \cdot g^{-1}$ ww) set by Health Canada for subsistence fishery [34]. Furthermore, when the LOD (0.02 $\mu g \cdot g^{-1}$ dw) is converted to wet weight (0.005 $\mu g \cdot g^{-1}$ ww), the developed CV-MP-AES procedure is able to detect mercury at a level well below the Canadian consumption limit for mercury in fish.

3.2 *Accuracy and precision*

Results obtained for both CRM and salmon muscle analyses show that MP-AES can accurately and precisely quantify mercury concentrations with the analytical procedure used. Total mercury concentrations in CRM and salmon muscle tissue measured with CV-MP-AES were well above the LOD determined (Tables 3 and 4). The CV-MP-AES procedure showed high accuracy and precision with a recovery percentage averaging 88% ± 8.6% and a relative standard deviation (RSD) of 7.8% for the five CRM sub-samples (Table 3). These results indicate that variability in the measurements is more related to sample treatment than system variability. Procedures using CV-MP-AES have been reported to have 95–101% recovery with RSD of 1.6–3.8% with certified reference materials [19,25]. Although the recovery percentage was lower in this study, no significant difference ($t_{10} = 2.23$, $p > 0.05$) was observed between the CRM certified value and CV-MP-AES experimental values. Furthermore, recovery percentage and the RSD

Table 3. Accuracy and precision of the developed CV-MP-AES procedure for mercury quantification in five CRM (DORM-3, fish protein, certified value 0.382 ± 0.060 μg·g^{-1} dry weight) sub-samples by three repeated measurements. [a] The 95% confidence interval (CI) was calculated on the five replicate mean values and for the mean recovery value. The relative standard deviation (RSD) is based on the standard deviation of the mean values of the five replicates.

Replicates	Mean mercury ± CI (μg·g^{-1} dw)	Recovery (%)	RSD (%)
CRM-1	0.315 ± 0.010	82	1.0
CRM-2	0.356 ± 0.007	93	0.7
CRM-3	0.347 ± 0.010	91	0.0
CRM-4	0.360 ± 0.010	94	1.4
CRM-5	0.301 ± 0.025	79	3.6
Mean[a]	0.336 ± 0.032	88 ± 8.6	7.8

Table 4. Mercury concentrations (μg·g^{-1} dry weight) in 15 different wild Atlantic salmon muscle samples analysed by CV-AFS (accredited laboratory) and CV-MP-AES. The relative error (%) was calculated from the MP-AES compared to the accredited laboratory results.

Salmon	Length (cm)	CV-AFS Hg (μg·g^{-1})	CV-MP-AES Hg (μg·g^{-1})	Relative error (%)
A	51	0.168	0.2	19.0
B	55	0.189	0.204	7.94
C	56	0.157	0.172	9.55
D	56	0.174	0.186	6.90
E	56	0.229	0.206	10.0
F	57	0.196	0.215	9.69
G	57	0.171	0.187	9.36
H	57	0.172	0.185	7.56
I	59	0.225	0.199	11.6
J	61	0.159	0.174	9.43
K	64	0.21	0.214	1.90
L	75	0.163	0.15	7.98
M	82	0.191	0.221	15.7
N	83	0.253	0.256	1.19
O	85	0.246	0.285	15.9
Mean				7.97

values meet the recommendation (75–120% recovery percentage and 8–15% for repeatability precision) for analysis in trace amount (μg·g^{-1}) as described in AOAC [37].

The 15 salmon sampled had lengths ranging from 51 to 85 cm (Table 4). The mercury concentrations in salmon muscle samples quantified by CV-MP-AES and CV-AFS (accredited laboratory) ranged from 0.15 to 0.29 μg·g^{-1} dw and from 0.16 to 0.25 μg·g^{-1} dw, respectively (Table 4). In comparison to mercury concentrations obtained by CV-AFS, the relative error of the mercury concentration in salmon muscle determined by CV- MP-AES vary from 1.19 to 19.0% with an average of 7.97% (Table 4) and no significant difference was observed between mercury concentrations quantified by both procedures (t_{14} = 2.06, $p > 0.05$). Although relative errors were as high as 19% for one sample, our procedure was compared to two standardised procedure and no significant difference was observed which indicates that our procedure is suitable for accurately and precisely quantifying mercury at low concentration.

Total mercury concentrations in Atlantic salmon, Arctic char, and Brook trout in Lake Melville have been reported to vary between 0.062 and 0.105 μg·g^{-1} ww [9]. The accuracy, precision and detection limit obtained indicate that our procedure is appropriate to quantify mercury background concentrations in salmonids in Lake Melville.

Mercury concentrations found in Arctic salmonids vary from 0.001 to 0.6 μg·g^{-1} ww [11–13]. With the parameters used, the LOD is slightly higher than what can be found in some of the fish muscle in the Arctic. However, it is possible to simply increase the muscle quantity digested or to dilute less after digestion to ensure that the concentration in the digested sample is higher than the LOD. Thus, with the high sensitivity, accuracy, and precision demonstrated in this study, the CV-MP-AES is an appropriate procedure to quantify mercury for northern regions.

4. Conclusions

An analytical procedure for mercury quantification in Atlantic salmon muscle using CV-MP-AES was developed and its performance was evaluated. Analysis of CRM and salmon muscle demonstrated that the procedure developed can accurately and precisely quantify mercury in fish samples. No significant difference was found between mercury concentrations in wild Atlantic salmon determined by CV-AFS (accredited laboratory) and by CV-MP-AES; indicating that the procedure developed can be used to quantify accurately mercury at background level in northern regions. As shown in this study, due to the low operating cost, use of nitrogen for plasma, and sensitivity, accuracy, and precision, MP-AES analytical systems could be implemented in northern regions more easily than other analytical systems (e.g. ICP-AES, AAS). It also represents a rapid, economical, and safe technique to assess mercury concentrations in biological matrices similar to Atlantic salmon muscle tissue. This analytical strategy could facilitate data gathering for northern regions by reducing analytical cost and easing and enhancing communication between scientists and northern communities.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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