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Comparison of direct mercury analyzer and FIA-CV-AAS in determination of methylmercury in fish

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Abstract. Methylmercury (MeHg) has been determined in fish reference materials by direct mercury analyzer (DMA 80) and FIA-CV-AAS. In order to evaluate accuracy, certified reference materials (Fish protein, NRCC - Dorm 4 and fish material, Ipen - Dourada 1) were analyzed after extraction and separation of mercury species. Good agreement of the results have been obtained (relative error of the determination between the methods varied from 1.5 % to 39 %). The repeatability of the results varied from 4 % to 26 %.

1. Introduction

Monomethylmercury (MeHg) is the most commonly occurring organo-mercury compound and one of the most toxic, and it is recognized as a major environmental pollution issue and health hazard for humans. Contaminated seafood is the major route of exposure for humans to MeHg. It represents, on average, 85 % of the total mercury present in fish [1].

Several methods for determining the concentration of inorganic mercury and organomercury species have been developed [2-6].

The wet digestion procedure generally is used, but it involves a number of reagents both for acidic digestion and mercury reduction and is therefore time-consuming and presents risks of mercury loss due to volatilization and significant manipulation of the samples. In contrast, the systems that combine sample combustion (thermal decomposition in the presence of O_2), Hg amalgamation, and atomic absorption spectrometry has already been proven to be an effective method to obtain reliable results [7-9].

Currently, we are investigating the MeHg concentration in fish materials. An important feature of these studies was that measurements were conducted by two different methods, direct mercury analyzer (DMA) and atomic absorption spectrophotometry with cold vapor generation and flow injection (FIA-CV-AAS), and its results were compared.

2. Experimental

2.1. Samples preparation

Two certified reference materials (fish protein, NRCC-Dorm 4, and fish material, Ipen-Dourada 1 [10]) were prepared and analyzed. The method is based on the acid leaching with hydrochloric acid solution, HCl 6 mol L^{-1} (by volume), and mercury separation of the organic and inorganic ion in exchange resin (Dowex 1×8 100–200 mesh). The methodology was based in Horvat and May [11,12].

Once separated, MeHg was decomposed to inorganic Hg^{2+} by ultraviolet (UV) irradiation and the final solution was diluted to approximately 30g with demineralised water. The solutions are ready to analyzed by both methods, FIA-CV-AAS and direct mercury analyzer.

2.2. FIA-CV-AAS

The samples solutions were inserted into the sample introduction system of an atomic absorption spectrophotometer (FS-SpectrAA220 Varian Australia Pty Ltd.) and methylmercury (such as mercury) is determined by the technique of atomic absorption spectrophotometry with cold vapour generation and flow injection (FIA-CV-AAS). A tin II chloride solution ($SnCl_2$ 25 % in HCl 25 % (by volume)) was used as reducer of the Hg. Argon was used as carrier gas at constant flow at 200 mL min^{-1}. Before analysis, the equipment was calibrated with Hg standard solutions in the range 2 to 12 µg kg^{-1} Hg.

2.3. Direct mercury analyzer

The same solutions analyzed by FIA-CV-AAS were introduced in the direct mercury analyzer (DMA-80, Milestone, Sorisole, Italy). An aliquot of the 300 µL each sample was added in the quartz boats. This equipment contains an automatic sampler, a quartz furnace, a cobalt-manganese oxide catalyst, a gold-coated sand amalgamator and an atomic absorption detection cell. The different steps of the analysis are controlled by software. Similarly, the equipment was calibrated with Hg standard solutions in the range 0.5 to 100 ηg Hg.

3. Results and discussion

Basic parameters obtained during validation of two analytical methods are presented in table 1.

Table 1. Quality assurance of both analytical procedures.

Parameter	DMA		FIA-CV-AAS	
	Dorm 4	Dou[a] 1	Dorm 4	Dou[a] 1
Repeatability, %	9	26	4	12
Recovery, %	61	88	70	98
Expanded uncertainty[b], %	23	46	28	48

[a]Dou 1 is Dourada 1
[b]Uncertainties expressed as 95% of level of confidence and k=2

The results indicate that both methods represents similar results. FIA-CV-AAS has a better repeatability of the results compared to DMA method. The recovery rates in both methods were at a similar level but to Dorm 4 was lower than Dourada 1. Probably it occurred due composition of the Dorm 4 (fish protein). To evaluated the measurement uncertainty, all possible sources of uncertainty, to both methods, were carefully identified. Afterwards, the uncertainty components were quantified and the combined standard uncertainty was calculated. Finally, using the equation $U = k.u_c$ where u_c is the combined standard uncertainty and k is a coverage factor equal to 2.

3.1. Comparison of methods with CRM values

The analytical performance of the methods was evaluated by the analysis of two certified reference materials (Dorm 4 and Dourada 1). The concentrations obtained are presented in table 2 and showed in the figures 1 and 2.

Table 2. Results of MeHg (expressed in μg g^{-1} as Hg), with their uncertainties, in certified reference materials by different methods.

CRM	Certified value	DMA	FIA-CV-AAS
Dorm 4	0.354 ± 0.031	0.215 ± 0.049 (n = 5)	0.250 ± 0.070 (n = 5)
Dourada 1	0.245 ± 0.053	0.215 ± 0.099 (n = 15)	0.241 ± 0.115 (n = 15)

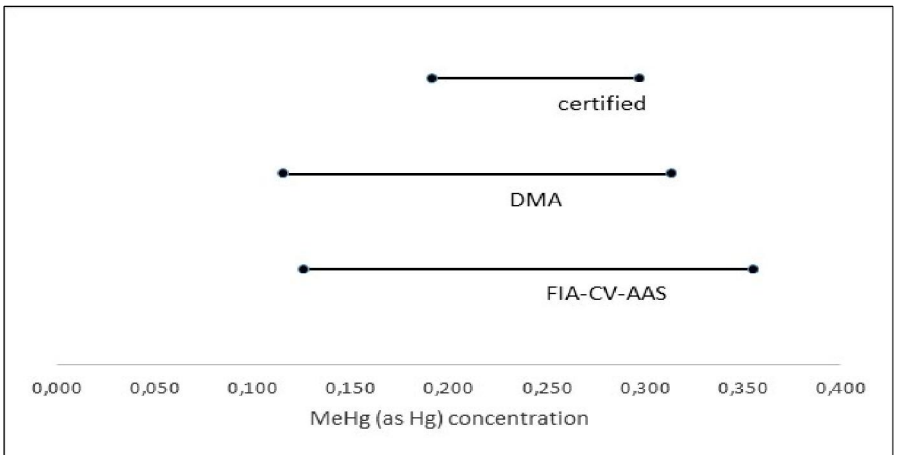

Figure 1. Results obtained by DMA and FIA-CV-AAS for MeHg (as Hg) in the Dourada 1.

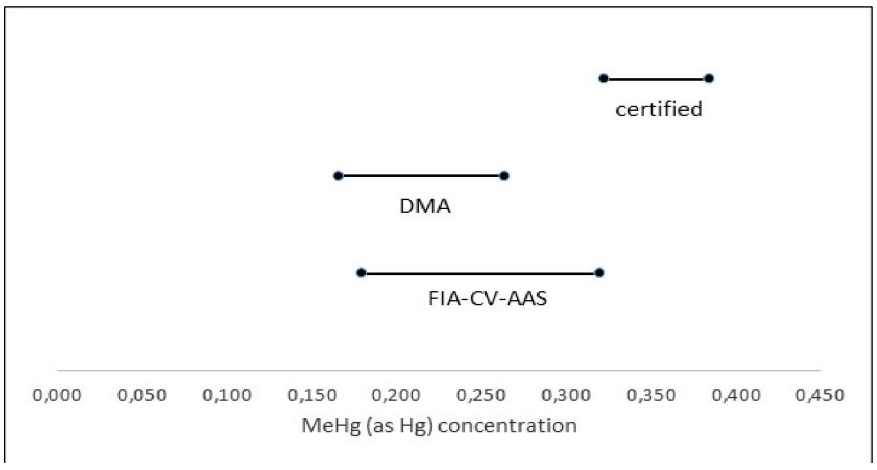

Figure 2. Results obtained by DMA and FIA-CV-AAS for MeHg (as Hg) in the Dorm 4.

The concentrations obtained show agreement in both methods, mainly by DMA method (showed in table 2 and figure 1). But the results obtained in the Dorm 4, when compared with the certified values were, on average, 34 % lower. Probably the composition of the Dorm 4 (fish protein) and the acid leaching method used, influenced the results obtained. Others studies has been necessary to improve this results for Dorm 4.

In the DMA method, relative error (R) of determination varied from 12 % to 39 % and in the FIA-CV-AAS method varied from 1.5 % to 29 %.

A paired Student's t-test, applied to compare the analytical results of the samples analyzed by both methods, showed that MeHg (as Hg) concentrations were not significantly different (t calculated < t tabulated, $\alpha = 1$ %) when used DMA or FIA-CV-AAS.

It should be noted that the DMA method is under development and the FIA-CV-AAS method is routine in our laboratory and accredited by CGCRE/INMETRO.

4. Conclusions

The analytical methods were characterized by good agreement of the results. Both methods showed sufficient sensitivity and considered to be robust. The good performance obtained with DMA method when compared with FIA-CV-AAS method encouraging with regards to application on a routine basis. The main inconvenience of the FIA-CV-AAS method, when compared with DMA method, is the quantity of the reagents and generated waste. The results obtained to Dorm 4, when compared with certified values, were not satisfactory. It will be studied, although the results obtained by DMA and FIA-CV-AAS confirmed the efficiency of the both methods. Finally, we concluded that the both methods can be used to determining methylmercury in fish materials.

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