New analytical methods for quantification of Hg species in soft water using HPLC-ICP-MS technique

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Introduction

Mercury is a highly toxic element with negative effects on the environment and human health due to its bio accumulative properties. Although ecological impact assessment and health risk evaluations typically consider only the total Hg content, it is crucial to distinguish between the highly toxic alkylated mercury compounds (primarily methylmercury, MeHg) and the less toxic inorganic forms of mercury.

The total mercury content is used to assess ecological impact and health risk. It is very important to distinguish between the toxic forms of alkylated compounds (mainly methyl-Hg) and the less toxic forms, such as the inorganic forms of Hg. Once formed, methyl-Hg bioaccumulates in the aquatic food chain (with bioaccumulation factors up to 10^6), leading to an increase in exposure levels and thus resulting in a high toxicity risk. The organic forms of mercury include: methyl-Hg (MeHg), ethyl-Hg (EtHg), dimethyl-Hg (Me2Hg), and phenylmercury (PhHg).

Materials and methods

For the development of the mercury speciation method in water samples, a calibration curve was made in the range of 0.1 µg/L to 1.0 µg/L. For Hg2+, a certified reference material (CRM) of 1000 mg/L Hg, made from $Hg(NO_3)_2$ in 2 mol/L HNO_3, produced by Supelco was used. For methylmercury (MeHg), methylmercury chloride with 95% purity, produced by LGC, was used as the CRM. From the 1000 mg/L stock solutions of Hg2+ and MeHg, an intermediate stock solution containing both compounds (Stock Solution 1) was prepared with a concentration of 1 mg/L in ultrapure water.

From the 1 mg/L stock solution, a working stock solution (Stock Solution 2) with a concentration of 10 µg/L in ultrapure water was prepared. For both organic and inorganic mercury, measurements were taken for 199, 200, 201, and 202 isotopes. Table 1 presents the optimal parameters of the HPLC-ICP-MS system for the detection and quantification of Hg species.

Table 1. Optimal parameters of HPLC-ICP-MS equipment for the detection of Hg species

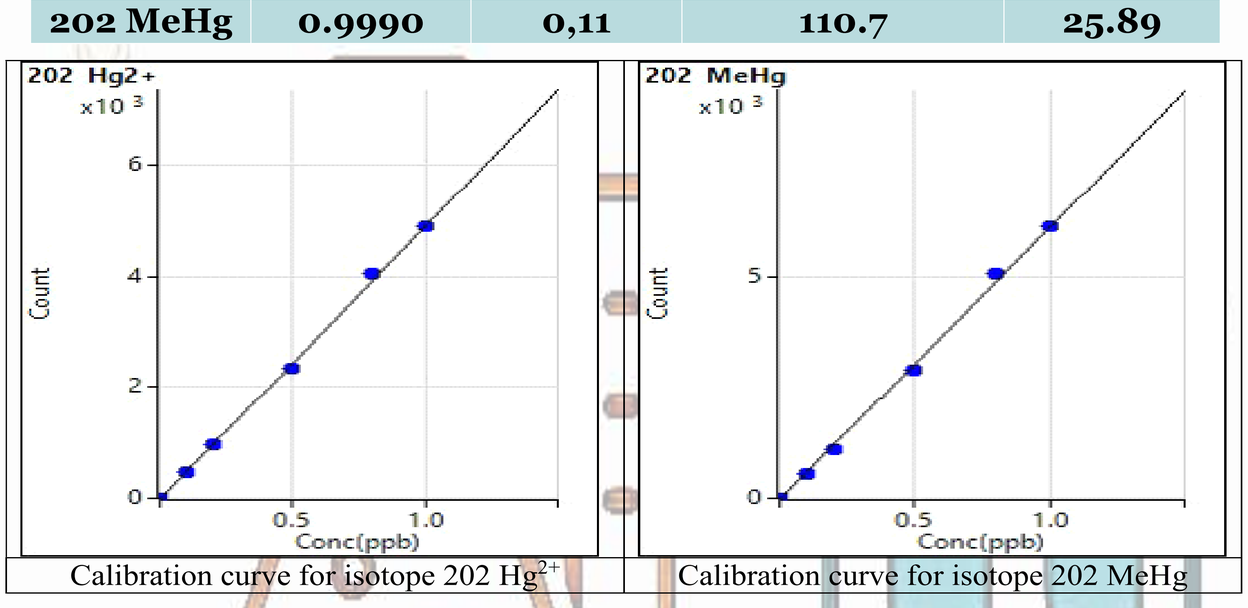
HPLC parameters	ICP-MS parameters
➢ Column: Thermoscientific Hypersil GOLD, 150mm x 4.6 mm ➢ Column temperature: ambient temperature ➢ Injected volume: 75 µL ➢ Mobile phase: 1 g/L L-cysteine ➢ Mobile phase flow rate: 1.0 mL/min ➢ Elution: Gradient | ➢ Sample run time: 7 min	➢ RF Power: 1550 W ➢ Nebulizer pump: 0.4 rps ➢ Nebulizer gas flow: 1.10 L/min ➢ Internal system temperature: 35.1°C ➢ Plasma gas flow rate: 15 L/min ➢ Auxiliary gas flow rate: 0.9 L/min ➢ He gas flow rate: 4.3 mL/min

Results and discussion

The performance parameters evaluated for the developed method were: linearity, LOQ, recovery and measurement uncertainty of the method. The solutions used to plot the calibration curve with concentrations of 0.1 µg/L, 0.2 µg/L, 0.5 µg/L, 0.8 µg/L, and 1.0 µg/L were obtained from the 10 µg/L stock solution 2, with dilution performed using a 1 g/L L-cysteine solution (mobile phase). The values obtained for the monitored performance parameters are presented in Table 2.

Tabel 2. Performance parameters obtained following validation of the analytical method

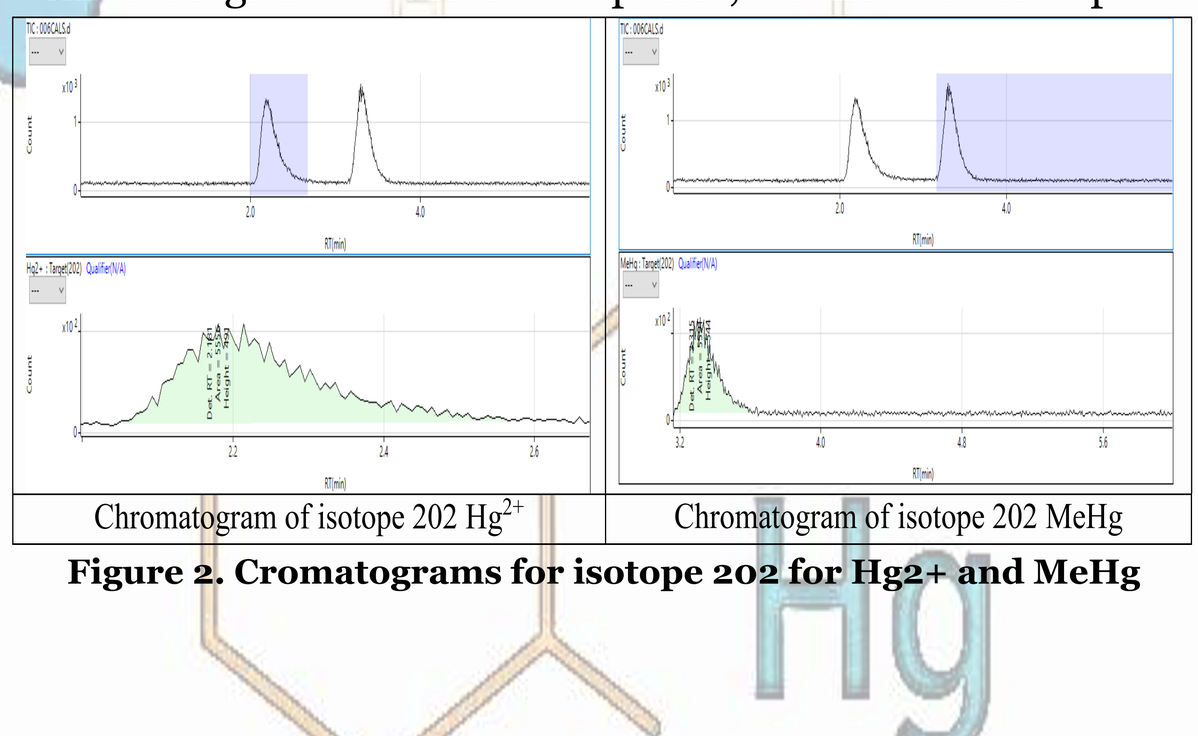
Hg species isotope	Linearity, R	LOQ, µg/L	Recovery (drinking water), %	Uex, %
199 Hg^{2+}	0.9981	0,11	99.5	26.30
200 Hg^{2+}	0.9978	0,24	103	32.03
201 Hg^{2+}	0.9990	0,42	102.4	32.77
202 Hg^{2+}	**0.9992**	**0,17**	**102.8**	**26.26**
199 MeHg	0.9995	0,18	105.3	30.94
200 MeHg	0.9997	0,10	102.4	27.01
201 MeHg	0.9970	0,20	106.8	35.79
202 MeHg	**0.9990**	**0,11**	**110.7**	**25.89**



Calibration curve for isotope 202 Hg^{2+} | Calibration curve for isotope 202 MeHg

Figure 1. Calibration curve for isotope 202 for Hg2+ and MeHg

According to the experimental data and considering the recommendations from the relative isotope abundance table, the isotope 202 from both species is the most suitable for quantification. Figure 1 shows the linear regression lines for the 202 isotope of the two mercury species monitored, and Figure 2 shows the chromatograms of these two species, for the same isotope.



Chromatogram of isotope 202 Hg^{2+} | Chromatogram of isotope 202 MeHg

Figure 2. Cromatograms for isotope 202 for Hg2+ and MeHg

Conclusion

The developed method is suitable for the detection and quantification of mercury species. The data obtained from the method validation showed that isotope 202 is the most suitable for the two species monitored.

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