

DETERMINATION OF MERCURY CONTENT IN A SHALLOW FIRN CORE FROM GREENLAND BY ISOTOPE DILUTION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Abstract. The total mercury content was determined in 6 cm sections of a shallow 7 m firn core and in surrounding surface snow from Summit, Greenland (elevation: 3238 m, 72.58°N, 38.53°W) collected in May 2001 by isotope dilution cold-vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS). The focus of this research was to evaluate the capability of the ID-CV-ICP-MS technique for measuring trace levels of Hg typical of polar snow and firn. Highly enriched ²⁰¹Hg isotopic spike is added to approximately 10 mL melted core and thoroughly mixed. The Hg²⁺ in the sample is reduced on line with tin(II) chloride (SnCl₂) and the elemental Hg (Hg⁰) vapor pre-concentrated onto gold gauze using a commercial amalgam system. The Hg is then thermally desorbed and introduced into a quadrupole ICP-MS. The blank-corrected Hg concentrations determined for all samples ranged from 0.25 to 1.74 ng/L (ppt) (average 0.59 ± 0.28 ng/L (1σ)) and fall within the range of those previously determined by Boutron *et al.* [Geophys. Res. Lett. 25, 1998, 3315–3318] (≤0.05–2.0 ng/L) for the Summit site. The average blank value was 0.19 ± 0.045 ng/L (*n* = 6, 1σ) and the method detection limit was 0.14 ng/L. The Hg values specifically for the firn core range from 0.25 to 0.87 ng/L (average 0.51 ± 0.13 ng/L (1σ)) and show both values declining with time and larger variability in concentration in the top 1.8 m.

Keywords: firn core, Greenland, isotope dilution, mercury, trace

1. Introduction

The trace metal mercury is a pollutant of global concern because of its relatively long atmospheric residence time (approximately 1 year) and its potential to form highly toxic methylmercury which bioaccumulates in the aquatic food chain. Hg in the environment is derived from both natural and anthropogenic sources with natural sources contributing an estimated 9 Mmol per year (e.g. land surface (soil degassing) and oceanic evasion) and anthropogenic contributing roughly 13 Mmol/year (combustion sources (fossil fuels, medical waste incineration)) (Lamborg *et al.*, 2002, p. 1116). The dominant species of Hg in the atmosphere is elemental mercury (Hg⁰) (at a concentration of 1.6 ng/m³) (Lindqvist, 1991; Schroeder *et al.*, 1998) and this relatively inert Hg⁰ can be transported long distances prior to chemical transformation and consequently has global environmental influence. Once the mercury is chemically or photochemically oxidized to reactive gaseous mercury (RGM) and/or particle-associated mercury (PM) (Lindberg *et al.*, 2001) it is highly water soluble resulting in enhanced deposition via wet and dry processes. In the Arctic, oxidized mercury accumulates in the snowpack to be later released via snowmelt in the summer season where it can be transformed to methylmercury and becomes available to the terrestrial ecosystem. The principal route of human exposure to methylmercury compounds is via fish and shellfish consumption (EPA, 1997). Ingestion of methylmercury by humans can cause central nervous system damage and endocrine system disruption (NRC, 2000). High levels of Hg have been found in Arctic food supplies and elevated levels have been observed in the native people (approximately 80% of the Greenland population has levels in blood that exceed 50 μg/L) of the circumpolar countries including Greenland whose populations consume large amounts of fish and piscivorous species (AMAP, 1998; UNEP, 2002, p. 62).

Low concentrations of oxidized mercury play an important role in the biogeochemical cycling of this metal because of the increased solubility and enhanced deposition to the environment. The mercury concentrations in certain regions of the Arctic (e.g. elevated sites in Greenland) are low and require measurement techniques capable of high precision and accuracy for understanding mercury cycling within these environments. Typical concentrations in natural waters (rainfall, snow, and ice) are non-detectable to 0.5 $\mu\text{g/L}$ range, which presents a challenge to many of the analytical techniques available for Hg determination (ATSDR, 1999; Mann *et al.*, 2003). Cold-vapor atomic absorption spectrometry (CVAAS) and cold-vapor atomic fluorescence spectrometry (CVAFS) have very low limits of detection (sub- ng/L range) and have been used successfully in the measurement of Hg in snow and ice, where concentrations can be in the ng/L (ppt) range (Boutron *et al.*, 1998; Ferrari *et al.*, 2000; Schuster *et al.*, 2002; Shanley *et al.*, 2002). Recently, inductively coupled plasma mass spectrometry (ICP-MS) has been used for the determination of Hg in various matrices such as bovine blood, fish tissue, coal and other fossil fuels, and bottled water (Christopher *et al.*, 2001; Long and Kelly, 2002; Kelly *et al.*, 2003; Mann *et al.*, 2003). The very high sensitivity (instrument detection limit $<0.1 \text{ ng/L}$, 3σ) of this method combined with the inherently accurate isotope dilution method allowed for the ultra trace (parts per trillion, ppt) levels of Hg encountered in bottled waters to be determined with relatively high accuracy and precision (Mann *et al.*, 2003). Using isotope dilution obviates the need to perform yield studies since 100% yields are unnecessary for accurate quantification. In the present work, the method has been employed for the determination of trace levels of Hg in a shallow firn core and surface snow samples obtained from Summit, Greenland to evaluate the capability of the isotope dilution cold-vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS) technique for measuring the trace levels of Hg of polar snow and firn. The Summit site was chosen because of the documented low Hg levels ($\leq 0.05\text{--}2.0 \text{ ng/L}$) previously measured by CVAFS (Boutron *et al.*, 1998, p. 3315).

5. Summary and Conclusions

The primary focus of this research was to test the capability of the ID-CV-ICP-MS technique for measuring ultra-trace levels of Hg typical of polar snow and firn. Cold-vapor generation coupled with the inherently accurate and precise isotope dilution method of analysis provides the sensitivity and reliability required for trace-level Hg quantitation. The low detection limit (0.14 ng/L) and small blank values (average: $0.19 \pm 0.045 \text{ ng/L}$ (1σ)) make this technique competitive with CVAAS and CVAFS with the added advantage of intrinsic accuracy of isotope dilution and is much improved over other methods for Hg analysis in waters (Al-Saleh *et al.*, 1998; Manzoori *et al.*, 1998; Allibone *et al.*, 1999; Misund *et al.*, 1999; De la Riva *et al.*, 2002; De Wuilloud *et al.*, 2002; Manganiello *et al.*, 2002). The data suggest: (1) Hg content has decreased during the past 11 years and (2) Hg exhibits a seasonal signal near the surface (top 1.8 m) of the core. The decreasing trend observed is likely caused by the combination of decreased anthropogenic Hg emission and inadequate sampling resolution. Based on the dates of the core, the variability observed in the top 1.8 m may correspond with seasonal polar sunrise chemistry; however, higher sampling resolution is needed to determine this relationship. The demonstrated capability of this technique to measure low-level (ng/L) quantities of Hg in snow and firn strongly suggests the technique would be useful for this and other applications requiring high sensitivity such as urban atmospheric pollution. In addition newer generations of ICP-MS instruments are a factor of 5–10 more sensitive which may allow the determination of lower concentrations if blanks are sufficiently reduced. For example, from Figures 2 and 4, a factor of 2 reduction in error bars and higher resolution sampling would allow the Hg trends observed to be better constrained.