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Short communication

Rapid and accurate determination of Thallium in seawater using SF-ICP-MS

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ABSTRACT

We present a method for the rapid and direct determination of dissolved Thallium (Tl) using high resolution sector field inductively coupled mass spectrometry (SF-ICP-MS) suitable for the measurement of large time series (e.g. during monitoring). Thallium data are presented for a series of natural sea water samples, which were validated with sea water standards CASS-4 and NASS-5. The sea water samples and standards were diluted 10 times prior to measurement with SF-ICP-MS in low resolution mode (R = 300, LR). For both CASS-4 and NASS-5 (salinity of 30.5) we calculated a concentration of about 11 ng L^{-1} when using Tl values of 14 ± 2 ng L^{-1} (at salinity of 35 ± 1) published by Flegal and Patterson [1] for Atlantic and Pacific sea water. For CASS-4 we report a Tl value of 10.6 ± 0.7 ng L^{-1} ($n = 70$), for NASS-5 a Tl value of 10.3 ± 0.8 ng L^{-1} ($n = 11$). For Tl in both CASS-4 and NASS-5, the overall error in accuracy and precision is less than 4% and 8% (2 s), respectively. Further, values of 7.7 ± 0.3 and 6.7 ± 0.2 ng L^{-1} Tl were found for the estuarine standard SLEW-3 (salinity of 15) and the river water standard SLRS-4, respectively, for which no certified value exists so far. The detection and quantification limits of our method are 0.1 and 0.3 ng L^{-1}, respectively. Slight differences in the accuracy of our method and other published methods for the determination of Tl in sea water are discussed. Time-series of natural coastal water samples gave Tl values (6–12 ng L^{-1}), which correspond to determined salinities, and hence, appear realistic and oceanographically consistent.

1. Introduction and objectives

Thallium (Tl) has an extremely low concentration level in the oceanic environment, in the range of 8–20 ng L^{-1} [1–4]. This low concentration level may explain why Tl only receives little attention regarding its environmental distribution and behaviour, although it is as toxic as Cd and Hg, which are considered priority substances under the European Water Framework Directive [5]. Thallium use in society has become important due to a growing demand in high-technology industries and increasing reliance on fossil fuels for energy. In general, Tl is released to the environment from coal and ore combustion, cement manufacture and metal smelting [6].

Typically, the concentration of Tl in ocean water samples is determined by isotope dilution (ID) ICP-MS or TIMS after preconcentration with or without hydride generation or ICP-MS after cloud point extraction [2–4,7–9]. These methods are highly accurate and highly precise, albeit time-consuming in contrast to our method: here, the sample is only diluted 10 times and measured directly using SF-ICP-MS according to the method of Rodushkin and Ruth [10]. This method also served in previous works [11,12] where Mo, Mn, U and V were routinely determined for sea water samples of large time-series. Here, we simply add Tl to the measuring protocol, the details of which are outlined below. We further report on Tl values for standards CASS-4 (coastal sea water), NASS-5 (open sea water), SLEW-3 (estuarine water) and SLRS-4 (fresh water).

2. Material and methods

2.1. Samples

All plasticware (bottles of PE and PFA) used for sampling, sample processing and sample storage was soaked in 2% (v/v) HNO_3 (subboiling quality) for at least 24 h before being rinsed in ultra pure Milli-Q water. Sea water samples were taken carefully with a small PE bucket by hand. Onboard, sea water samples and blanks (Milli-Q water) were rinsed through 0.45 μm SFCA syringe filters, stored in pre-cleaned PE recipients (see above) and acidified to 1% (v/v) with distilled HNO_3.

2.2. Instrumental analysis and operating conditions

Samples were analyzed for ^{205}Tl by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo Finnigan Element II mass spectrometer on separate days during separate months in 2010. Prior to analyses, the samples were diluted 10 times to avoid

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Table 1
Tl data for reference materials.

	CASS-4	NASS-5	SLEW-3	SLRS-4
Precision				
Ave. value (ng L^{-1})	10.6	10.3	7.71	6.68
SD (ng L^{-1})	±0.7	±0.8	±0.3	±0.2
RSD (%)	6.6	8.1	3.5	2.8
#	75	11	4	7
Min (ng L^{-1})	8.92	9.08	7.34	6.55
Max (ng L^{-1})	11.7	11.5	7.90	6.88
Accuracy[a]				
Ave. value (ng L^{-1})	10.8	10.7		
SD (ng L^{-1})	±0.3	±0.5		
RSD (%)	2.6	4.4		

[a] When adopting 11 ng L^{-1} as a reference value, see text for details.

ICP-MS sampler clogging, which allowed a high sample throughput per day. Usually, we measured Tl together with a suite of other metals (Ba, Mn, Mo, U, V, Co), hence, the number of sea water samples were 40 per day. If Tl was to be measured alone, the sample number would rise to 120 per day.

The ICP-MS operating conditions were as follows: power = 1.4 kW; plasma gas flow = 14 L min^{-1}; auxiliary gas flow = 0.8 L min^{-1}; nebulizer gas flow = 0.8–0.9 L min^{-1} (nebulizer gas daily tuned), no guard electrode, low oxide formation (<1% UO^+). Measurements were done in low resolution mode (R = 300, LR; which meet quadrupole instrument characteristics). Linear calibrations in the range of 0.25–25 ng L^{-1} Tl were achieved using calibration standards prepared by dilution of single standard solution of 1000 ppm Tl (MERCK) in 2% (v/v) distilled HNO_3. Procedural blanks (filter blanks during field work, laboratory solutions of distilled HNO_3) showed negligible counts (less than 30 cts s^{-1}, which roughly translates to ~0.1 ppt). The instrument was daily tuned to show best agreement in intensity and sensitivity when switching from fresh water matrix (instrument calibration) to salt water matrix (samples, standards).

Drift in instrument sensitivity was accounted for by the addition of 8 μg L^{-1} of the internal standard ^{175}Lu to all samples and standards. CASS-4 was analyzed as a check after every five samples. This was necessary to monitor a possible drift during the course of a daily run since ^{175}Lu and ^{205}Tl differ by 30 amu. However, the effect of a drift was undetectable since it was within the precision of single measurements during a period of 6–8 h. The standard NASS-5 was measured once during a daily run. The standards SLEW-3 (estuarine water) and SLRS-4 (freshwater) were also determined for the concentration of Tl, for which so far no published Tl values exist to our knowledge.

To check whether the salt matrix load constitutes a problem on the accurate detection of Tl (signal attenuation) we determined Tl for both CASS-4 and NASS-5 by standard addition measured with ICP-MS. The spikes were equidistant at 10, 20 and 30 ng L^{-1} Tl, and all solutions were spiked with Lu as well (8 μg L^{-1}).

3. Results and discussion

3.1. *Tl data for CASS-4, NASS-5, SLEW-3 and SLRS-4*

The detection and quantification limits of our method (which are 3 and 10 times the standard deviation of the blank level, respectively) are 0.1 and 0.3 ng L^{-1}, respectively. Thallium data for CASS-4, NASS-5, SLEW-3 and SLRS-4 are summarized in Table 1. The overall error in accuracy and precision for Tl in both CASS-4 and NASS-5 was less than 4% and 8% (2 s), respectively. The error in precision of multiple runs of randomly chosen sea water samples was also less than 7%.

The Tl value of 10.3 ± 0.8 ng L^{-1} for NASS-5 is higher than the Tl value of 9.37 ± 0.02 ng L^{-1} determined by Nielsen et al. [2] using ID-ICP-MS after matrix separation, but closer to 9.82 ± 0.12 ng L^{-1} Tl determined by Meeravali and Jiang [8] with ICP-MS after microwave assisted mixed-micelle cloud point extraction. Indeed, ID-ICP-MS should yield the most reliable results in terms of accuracy. However, we assume that our method is nevertheless accurate due to the following reasons: both CASS-4 and NASS-5 Tl values are ± identical and closer to the assumed value of ~11 ng L^{-1} Tl than the value determined with ID-ICP-MS. Our assumed value of 11 ng L^{-1} Tl is oceanographically consistent based on Flegal and Patterson's [1] findings of 14 ± 2 ng L^{-1} Tl for a salinity of 35 ± 1 and conservative behaviour of Tl. Even if we use 12 ng L^{-1} Tl for a salinity of 35 we still get 10.5 ng L^{-1} Tl for NASS-5. Based on the assumption of an oceanographically consistent behaviour of Tl the value of 9.37 ng L^{-1} Tl for NASS-5 [2] appears a bit low (but may be correct nevertheless).

Further, the results for Tl using standard addition were 11.5 ± 0.8 ng L^{-1} Tl for both CASS-4 and NASS-5. This is in good agreement with the determined value of Tl using 10 times dilution (Table 1). If there is a considerable matrix effect on the determination of Tl then we should expect a Tl value lower than the obtained values for NASS-5 and CASS-4. Further, if the salt matrix causes any signal attenuation then this is only within the precision of the measurements during a daily run.

We admit that the error in precision of our method is large in comparison to the error in precision of the ID-ICP-MS method [2]. However, we would like to stress that our method is suitable for a large number of samples, which is certainly too time-consuming to be measured with ID-ICP-MS.

The reliability of our measurements was further assessed using measurements of Mn, Mo, U and V, for which CASS-4 and NASS-5 are certified. The error for accuracy and precision for these elements were less than 7% (for details see [11,12]).

For the estuarine standard SLEW-3 (salinity of 15) and the river water standard SLRS-4, values of 7.7 ± 0.3 ng L^{-1} and 6.7 ± 0.2 ng L^{-1} Tl were found, respectively (Table 1). Assuming a conservative behaviour of Tl we should expect a slightly lower Tl value, such as 6 ng L^{-1} for SLEW-3. The Tl value for SLRS-4 is indeed high since we should expect very low values from conservative mixing. For example, pristine rivers (unaffected by human activity) have just 1–2 ng L^{-1} Tl [3]. Maybe there were already anthropogenic contributions of Tl to the river and the estuary at the time of sampling of these standard materials.

3.2. *Variations of dissolved Tl in coastal seawater samples*

We measured Tl concentrations at a fixed station in the southern Jade Bay, a large tidal inlet in NW Germany in January 2010 (Fig. 1). We sampled every hour, and after 48 h we started a transect at low tide to the North covering 11 stations, whereas the last station was reached at local high tide.

For the time series, Tl concentration and salinity range from 6 to 10 ng L^{-1}, and 26.5 to 28.5‰, respectively (Fig. 1b). A clear reproducible pattern becomes obvious, with low values during low tide and high values during high tide (Fig. 1b). During high tide, at salinity around 28–28.5‰, Tl concentrations vary between 9 and 10 ng L^{-1}. This is in good agreement with an expected Tl salinity relationship when a conservative behaviour of Tl is assumed. For the transect, the concentrations of Tl as well as salinity increase from 8.2 to 12 ng L^{-1} and 27.5 to 30.2‰, respectively (Fig. 1c). Again, assuming a conservative behaviour of Tl, this is still in good agreement. The very low Tl at the fixed station during low tide may hint at non-conservative processes, the interpretation of which will be part of another publication.

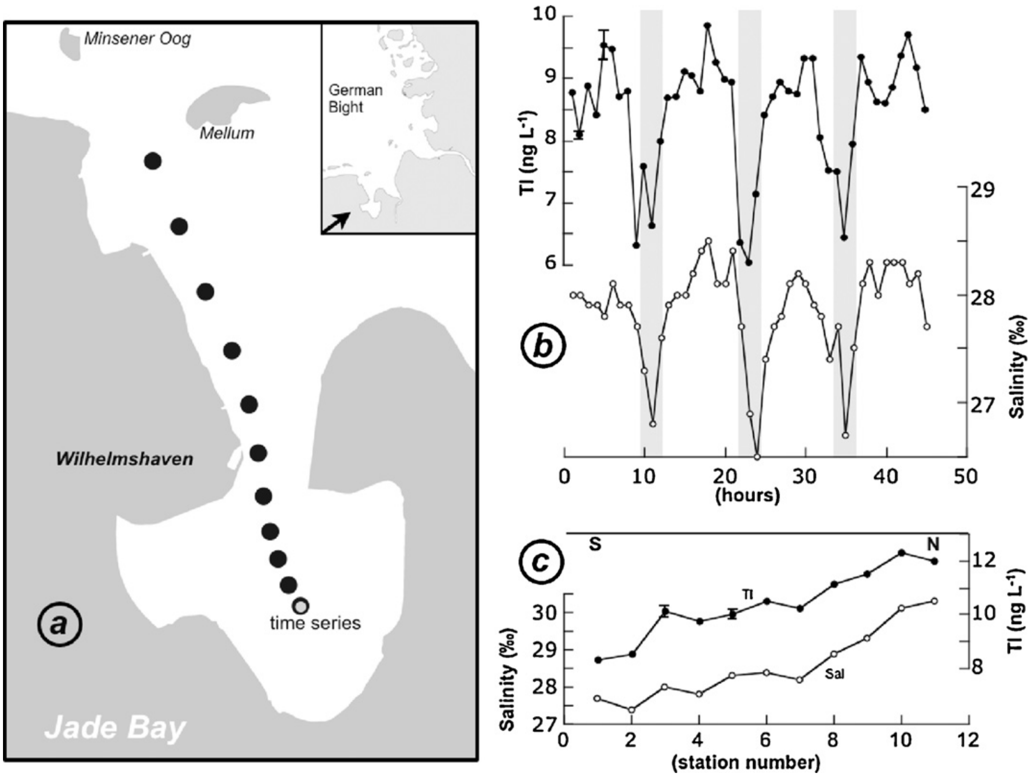

Fig. 1. (a) Map showing the tidal inlet Jade bay (NW Germany) with sampling stations. (b) Concentrations of dissolved Tl and salinity measured every hour in January 2010 at the time series station. Grey vertical bars indicate low tide. (c) Concentrations of dissolved Tl and salinity measured on a S–N transect starting right after time series at low tide with no time lag. Error bars in (b) and (c) indicate double measurements.

4. Conclusions

We present here a quick and reliable (accurate and precise) method to measure Tl concentrations in large numbers of sea water samples using sector field ICP-MS. We also present for the first time tidal variations in the concentration of Tl in coastal waters. The Tl concentrations are oceanographically consistent and reproducible. According to expected salinities the sea water standards CASS-4, NASS-5 and the estuarine water standard SLEW-3 yield realistic Tl values (10.6, 10.3 and 7.71 ng L^{-1}, respectively). By contrast, the freshwater standard SLRS-4 shows an elevated Tl concentration (6.68 ng L^{-1}) compared to river waters unaffected by anthropogenic Tl contributions.

We admit that the error in precision for the method presented here is larger than that for isotope dilution ICP-MS. However, the error in precision is substantially low enough to detect an apparent non-conservative behaviour of Tl in coastal waters, which is the most important objective for our research. For future measurements of open North Sea water (salinity of 33‰) we expect Tl concentrations of about 12–13 ng L^{-1} according to its conservative behaviour. Further, our method is highly suitable for the determination of Tl in freshwater samples (no salt matrix; dilution is not necessary).

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