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## Synthesis of hydrochloric acid solution for total mercury determination in natural waters

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### Abstract:

Total mercury ( $Hg_T$ ) determination requires the addition of concentrated hydrochloric acid solution ( $\geq 10 \text{ mol L}^{-1}$  HCl) in relatively high amounts to preserve the samples and to prepare reagent solutions. A method for the preparation of concentrated HCl with  $Hg_T$  concentration of lower than  $5 \text{ ng L}^{-1}$  is described in this article. It is based on the well-known chemical reaction:  $2 \text{ NH}_4\text{Cl} + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4 + 2 \text{ HCl}$ . This method is validated thanks to the US Environmental Protection Agency method 1631 and standard reference materials BCR-579 (mercury in coastal seawater).

**Keywords:** Synthesis – Hydrochloric acid – Mercury determination – Green analytical chemistry

## 1. Introduction

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Considering the very low concentrations of mercury (Hg) in natural waters (0.05-5.00 ng L<sup>-1</sup>), important loss and contamination problems can arise in sampling, sampling treatment and analysis processes [1-7]. The main mercury loss is due to Hg adsorption on bottle walls, but it is now recognized that the addition of acid (e.g. HCl) or oxidant (e.g. BrCl) allowed stabilisation of water samples for total dissolved Hg determination after filtration [4-7]. About contaminations, the routes are numerous and can lead to obtain erroneously high total mercury (Hg<sub>T</sub>) concentrations [8]. Such errors were common before the 80's and marine chemists have come to recognize that high concentrations were frequently reflecting contamination from sampling and analysis rather than ambient levels [5]. To overcome these analytical difficulties, a standardised sampling and analysis protocol has been proposed with the US Environmental Protection Agency (EPA) method 1631 [5]. During analysis, major problems might arise due to insufficient blank control. The total blank is composed of the system blank which is the total mercury coming from the analytical equipment (carrier gas argon, Teflon tubing, reaction vessel, gold quartz-sand trap, etc) and the reagent blank which is the total mercury coming from the reagent solutions (HCl, BrCl, NH<sub>2</sub>OH·HCl, SnCl<sub>2</sub>).

Repeated purging and analysis of pre-purged samples allow the determination of the system blank and its standard deviation. It should be stable and ≤ 10 pg, otherwise the system and/or operating variables must be changed.

Beside the system contamination, the reagent blank is determined by analyzing the reagent solutions and should not exceed 20 pg [5]. To preserve the samples and to prepare the reagent solutions, concentrated hydrochloric acid (HCl) solution is added in relatively high amounts to the samples and reagents; it must therefore be of superior quality [5, 9, 10]. High quality HCl solution is generally purchased at high cost [11-14], or may be obtained by repeated sub-boiling distillation of cheap analytical reagent grade HCl solution [1, 9, 15] or by purging analytical reagent grade HCl solution for at least 12h after adding a small quantity of reductant NaBH<sub>4</sub> to it [7]. The purpose of this article is to propose an alternative way synthesising high quality HCl solutions from low cost analytical reagent grade products. This quick and easy process presents advantages such as (i) a low cost production, (ii) controlled quantity and quality for 'fresh' solutions and (iii) cost and environmental gains if we consider the unused part of the commercial HCl solution because of the loss of quality due to a bottle which lasts a long time after opening. This environmental benefit is consistent with the green analytical chemistry (GAC) approach [16, 17]. Indeed, the diminution in the amount of reagents employed in the measurement step is a mean for reducing adverse environmental impact of analytical methodologies in the philosophy of GAC.

## 2. Experimental

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### Material

For each synthesised hydrochloric acid solution batch, the concentrations of HCl and Hg<sub>T</sub> were verified. With regard to the HCl concentration, a simple acid-base titration by a pH electrode (Mettler Toledo) and freshly prepared NaOH solutions was used. Hg<sub>T</sub> concentrations were measured using a Tekran 2500<sup>®</sup> cold vapor atomic fluorescence spectrometer (CVAFS) and gold quartz-sand traps for Hg pre-concentration.

## Mercury measurements

Hg<sub>T</sub> determination for freshwater samples is well documented and a large majority of researchers use the US Environmental Protection Agency (EPA) method 1631 [5]. Prior to analysis, all Hg in a sample aliquot is oxidized to labile Hg<sup>2+</sup> with bromine monochloride (BrCl) solution. After oxidation, the sample is sequentially reduced with hydroxylaminehydrochloride (NH<sub>2</sub>OH·HCl) solution to neutralize free halogens which can destroy the gold traps, then reduced with an excess of stannous chloride (SnCl<sub>2</sub>) solution to convert Hg<sup>2+</sup> to volatile Hg<sup>0</sup>. Elemental Hg is purged from solution with Hg-free argon and collected onto a collection gold trap by amalgamation. Hg is thermally desorbed from this trap into an argon stream that drives the released Hg<sup>0</sup> to the analytical gold trap. The Hg is thermally desorbed from the analytical trap into an argon stream that carries Hg<sup>0</sup> vapor into the cell of an atomic fluorescence spectrometer. The analytical procedure used both for analysis of the synthesised HCl solution and the reference material has followed the method described here and detailed by Cossa et al. [14].

## Reagent solutions

The argon used as a carrier gas is Argon Instrument 5.0 (99.999%, Linde Gas) which has been Hg purified by passing through a gold quartz-sand trap. All the Teflon material used for the synthesis of hydrochloric solutions was perfluoroalkoxy (PFA) Teflon.

At first, to test the Hg<sub>T</sub> concentration in the synthesised HCl solution and validate our method, concentrated HCl (30%) Suprapur<sup>®</sup> solution (Merck) was used for the reagents preparation. Moreover the Hg<sub>T</sub> concentration was measured in this commercial solution to compare to our synthesized HCl solution.

Hg<sub>T</sub> determination requires the preparation of the stannous chloride (SnCl<sub>2</sub>), hydroxylaminehydrochloride (NH<sub>2</sub>OH·HCl) and bromine monochloride (BrCl) solutions. These reagent solutions were carried out as described by Cossa *et al.* [14].

After preparation, the solutions were stored in Teflon bottles tightly capped, double-bagged in new polyethylene zip-type bags and stored in a cold ( $\leq 4$  °C) and dark place in a plastic box until use.

## Cleaning

The Teflon material used for the synthesis of HCl solution was cleaned by heating to 60-70 °C in 4 M HCl for at least 12 h. The material was cooled, rinsed ten times with deionised water, and dried in a Hg-free clean bench just before use.

## Synthesis of hydrochloric acid solution

The HCl solution was synthesised using the well known industrial process:  $2 \text{NH}_4\text{Cl} + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4 + 2 \text{HCl}$ , with an extreme care to avoid Hg contamination. The best way is to minimize exposure to ambient contamination including: (i) the use of a laminar flow hood equipped with a charcoal filter, (ii) wearing gloves and (iii) the use of metal-free and well cleaned material.

In the process, 20 mL H<sub>2</sub>SO<sub>4</sub> (MM = 98.07 g mol<sup>-1</sup>; d = 1.83; 95% for analysis, Fisher Scientific) react with 20 g NH<sub>4</sub>Cl (MM = 53.49 g mol<sup>-1</sup>; 99.5% for analysis, Fisher Scientific) to produce HCl gas which is dissolved in 20 mL of deionised water. The H<sub>2</sub>SO<sub>4</sub> was put in a Teflon recipient (30 mL, Savillex<sup>®</sup>) and brought to the Teflon reaction flask (120 mL, Savillex<sup>®</sup>) containing the NH<sub>4</sub>Cl thanks to a peristaltic pump (Gilson<sup>®</sup>) (Fig. 1). The Teflon reaction flask was equipped with a

two ports transfer cap; one port was connected to the H<sub>2</sub>SO<sub>4</sub> flask via the peristaltic pump, the other to the Teflon recipient (30 mL, Savillex<sup>®</sup>) containing the deionised water which received the HCl vapour. To avoid over pressure, this Teflon recipient was not hermetically closed but protected with a Parafilm<sup>®</sup> sheet and a polyethylene zip-type bag. Connections consisted of PFA Teflon tubings and a Viton<sup>®</sup> tubing for the peristaltic pump. The H<sub>2</sub>SO<sub>4</sub> flow was adjusted to 0.1 mL min<sup>-1</sup>. This low flow was required to carry out a correct dissolution of the HCl gas into the deionised water in order to give a concentrated HCl solution. These process conditions allow obtaining about 27 mL HCl within 4 hours with a yield going from 82% to 87% depending on the batches.

### 3. Results and discussion

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The total mercury background concentration in ocean water is around 0.05-2.00 ng L<sup>-1</sup> [2, 4], which represents, for a 100 mL sample usually collected for Hg<sub>T</sub> determination, a Hg<sub>T</sub> amount of 5-200 pg. The Hg<sub>T</sub> contamination due to the necessary use of HCl solution (sample preservation and reagent preparation) is estimated as follows. It has already been shown that Hg<sub>T</sub> is stable for long-term storage when samples are kept in the dark and acidified with 0.4-0.5% HCl (v/v) [4, 5, 13, 14]. With a superior quality HCl solution having a 5 ng L<sup>-1</sup> Hg<sub>T</sub> concentration, as recommended [5], such an add represents a 2-3 pg Hg<sub>T</sub> amount for a 100 mL sample. When using the same HCl solution to prepare the reagent solutions, the Hg<sub>T</sub> contaminations coming from the HCl solution are 0.5 ng L<sup>-1</sup>, 0.1 pg L<sup>-1</sup> and 4 ng L<sup>-1</sup> for SnCl<sub>2</sub>, (NH<sub>2</sub>OH·HCl) and BrCl solutions respectively. To carry out the Hg<sub>T</sub> determination, 0.5% (v/v) bromine monochloride solution, 0.2% (v/v) hydroxylamine hydrochloric solution and 0.5% (v/v) stannous chloride solution must be added to the sample [5, 14]. Therefore, considering a 100 mL sample, the amount of Hg<sub>T</sub> coming from a 5 ng Hg L<sup>-1</sup> HCl solution, represents around 20 pg. If the purging of reducing reagent solutions, SnCl<sub>2</sub> and (NH<sub>2</sub>OH·HCl) with Hg-free argon can reduce Hg<sub>T</sub> to acceptable levels, it is not the case for BrCl because it is an oxidant solution. However, the KBrO<sub>3</sub> and KBr can be purified by heating them to 250 °C for a minimum of 12 h [14]. Hence, it is obvious that one of the main keys to avoid Hg contamination during the preservation and the analysis processes is to use the mostly Hg-purified HCl solution.

The HCl concentrations and total mercury concentrations were measured for (i) a concentrated HCl (30%) Suprapur<sup>®</sup> solution (Merck) issued from a just-opened bottle and (ii) the here synthesised HCl solutions. Results are shown in Table 1. The results regarding Hg<sub>T</sub> concentrations were validated by investigation of the standard reference material BCR-579. This sample with a certified mercury value of 1.9 ± 0.5 ng Hg kg<sup>-1</sup> (n = 6) consists of acidified coastal seawater. It was analysed with the described method and a mean value of 2.0 ± 0.5 ng Hg kg<sup>-1</sup> (n = 5) was obtained.

This study shows the following results: (i) both types of HCl solutions (commercial and synthesised) are concentrated acid solutions; (ii) it confirms that the concentrated HCl (30%) Suprapur<sup>®</sup> solution (Merck) is a high purity grade; (iii) it proves that the HCl solution synthesised by the proposed method is almost Hg-free even when prepared with low grade products which are potentially Hg contaminated. Reaction between NH<sub>4</sub>Cl and H<sub>2</sub>SO<sub>4</sub> occurs in a non-reducing environment making the presence of volatile reduced Hg species unlikely. The lower volatility of the oxidized Hg species limits its transfer within the HCl gas stream produced by the reaction, even with low grade reagents.

## Conclusion

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The synthesis described in this article allows quick, cheap and easy obtaining of concentrated HCl solutions having  $Hg_T$  concentration  $< 5 \text{ ng L}^{-1}$ , value which corresponds to the grade concentration recommended by the literature for total mercury analysis. Key advantages of this alternative way to have HCl solutions of superior quality are the following. First, costs for a given quantity are at least 2 times less than the purchase of a Suprapur<sup>®</sup> grade HCl solution. It can even cost 25 times less if highly pure commercial solutions are considered. Secondly, this synthesis allows always having 'fresh' solutions with controlled qualities (HCl concentration and almost Hg-free) and quantities. The usual minimum amount of commercial concentrated Suprapur<sup>®</sup> grade HCl solution is 250 mL when the required quantities for total mercury analysis are small, so that a given bottle lasts a long time after opening, increasing the risks of HCl concentration loss and Hg contamination. Thirdly, if we consider the unused part of a commercial HCl solution, because of the loss of quality once the container is opened, the synthesis of the exact required quantity increases the cost gain but also becomes an environmental benefit. It corresponds to the philosophy of GAC by decreasing the amounts of consumed reagents.

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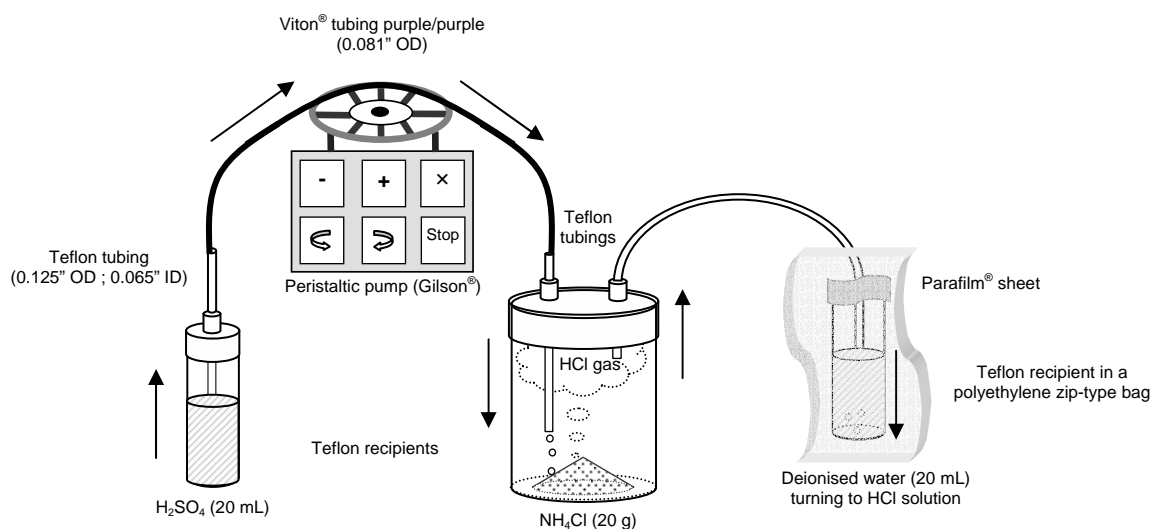
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## Figures

**Fig. 1** Schematic of the experimental protocol for the HCl synthesis



## Tables

**Table 1** HCl and total mercury concentrations for commercial and synthesised HCl solutions

HCl solution	[HCl] (mol L <sup>-1</sup> ) <sup>1)</sup>	[Hg <sub>T</sub> ] range (ng L <sup>-1</sup> )	[Hg <sub>T</sub> ] mean (ng L <sup>-1</sup> )	Standard deviation (ng L <sup>-1</sup> )	Number of determination
Suprapur®	10.0	1.32 - 1.44	1.38	0.05	5
Synthesised batch 1	12.2	0.57 - 0.68	0.64	0.04	5
Synthesised batch 2	11.9	0.18 - 0.31	0.24	0.05	5
Synthesised batch 3	11.8	0.60 - 0.73	0.66	0.04	5
Synthesised batch 4	12.0	0.46 - 0.56	0.51	0.05	5
Synthesised batch 5	11.8	0.22 - 0.31	0.27	0.05	5