

TECHNICAL NOTE

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Removal of traces of mercury from a carrier gas for analytical purpose

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Abstract

Background: The analysis of mercury by cold vapor requires a gas, usually argon or helium, to transport elementary mercury to the gold trap or directly to the detector. When analyzing mercury in environmental matrices, a gas with a metal concentration as low as a few picograms per cubic meter is needed. Different sorbents have been used to purify the gas for a long time, but little information is available about them, mainly considering the analytical purpose. This paper presents results of the absorption capacity for solids and hypochlorite solutions that usually are used as mercury sorbents, giving technical information to the analyst to decide the best gas cleaning process to be used.

Findings: The absorption capacities of different sorbents were tested using atomic fluorescence spectrometry. Among the tested solids, platinum presented the highest absorption capacity (13.04 pg Hg per gram of Pt). Interaction between sodium hypochlorite, sodium chloride, and EDTA in the absorption capacity was investigated by a 2³ factorial design. Results showed a significant interaction between hypochlorite and chloride.

Conclusions: A solution of 1.26 mmol L⁻¹ sodium hypochlorite, 0.48 mol L⁻¹ sodium chloride, and 0.6 mmol L⁻¹ EDTA shows the highest absorption capacity (167.3 pg Hg) among the tested compositions. That solution has eliminated even traces of mercury from gases, resulting in a carrier free of mercury, what cannot be achieved using the solid sorbents tested, despite the use of solutions which is more tedious than the use of solids to clean gas. Anyway, the hypochlorite solution shows to be a good option to clean gases that have to be used in the analysis of mercury in samples with very low concentration.

Keywords: Environmental sample; Sodium hypochlorite; Absorption capacity

Introduction

The determination of the concentration of metals in environmental samples has drawn the attention of researchers over the years, and the chemical speciation analyses of metals have received particular attention (Borges et al. 2012; Wotter et al. 2011). The impact of mercury in the environment concerning its toxicity, mobility, bioaccumulation, and biomagnification is responsible for a continuous interest to investigate the fate of this metal (Santos et al. 2008; Stergarsek et al. 2013; Emili et al. 2012). The development of analytical methods and lower limits of quantification have allowed increasing the understanding of biogeochemical processes involving mercury and other metals. Among the most popular analytical methods to

analyze mercury is the cold vapor atomic fluorescence spectrometry (CVAFS) (Santos et al. 2008; Leermakers et al. 2005), whose main advantage is separation of the analyte from the matrix by purging the volatile mercury with an inert gas to the detector, with a net result of high sensitivity and selectivity and lower limit of quantification. However, the success of the determination by CVAFS is closely related to the quality of the gas used to purge the analyte, since it is often necessary to make determinations of a few picograms of mercury (Liang et al. 1996).

Concentrations of dissolved gaseous mercury in surface water or dimethylmercury in environmental matrices, for example, are extremely low, and therefore, the need for extremely low blank values is essential (Emili et al. 2012; Hines et al. 2012). The care with cleaning materials, purification of reagents, and nature of the materials to be used in the mercury analyses are perfectly defined (MESL 1997).

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However, if the mercury concentration in the gas is not low enough, one should purify it.

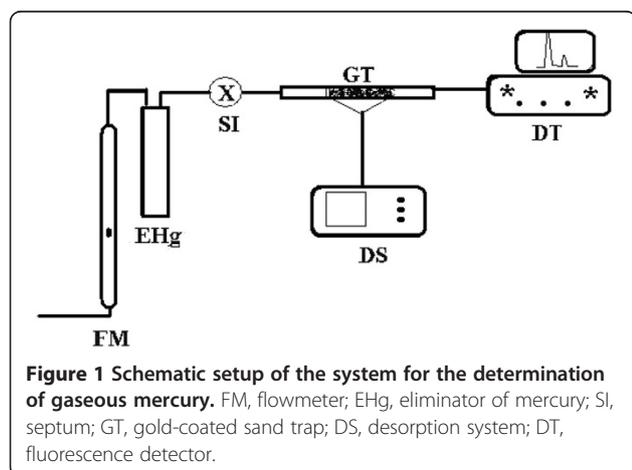
The gas purification can be achieved by different ways. Solid sorbents, as traps containing particles of gold, platinum, or active carbon, usually are used by the analyst due to their operational facility (Liang et al. 1996). Solutions also can be used to remove mercury from gaseous streams. The mercury can be oxidized by hypochlorite solutions, producing Hg^{2+} (Sizeneva et al. 2005), but the importance of the physical states during the reaction must be remembered. Thus, the dissolution of one drop of metallic mercury in a hypochlorite solution is a heterogeneous reaction which takes place on the surface, depending on the area and the surface state. Sizeneva et al. (2005) established that the reaction of mercury dissolution in hypochlorite solution is first order. If mercury is considered to be in the gaseous state reacting with the hypochlorite solution, then the reaction is second order (Zhao and Rochelle 1999).

This paper presents a study comparing the capacity of well-known sorbents to remove gaseous mercury and the mercury concentration obtained after a helium stream passed through those sorbents.

Materials and methods

The tests were carried out with helium gas 5.0 in which the mercury concentration was determined by atomic fluorescence spectrometry after absorption on a gold-coated sand trap (MESL 1997; Horvat et al. 1993) to be equal to 6.35 ng m^{-3} ($n = 5$). The concentration of a commercial sodium hypochlorite (0.21 mol L^{-1}) was determined by iodometric titration (Lagowski 1995). Sodium chloride and EDTA were pro-analysis (Merck, Whitehouse Station, NJ, USA). Ultrapure water (resistivity $18.2 \text{ M}\Omega \text{ cm}$, Milli-Q, Millipore Co., Billerica, MA, USA) was used to prepare all the solutions.

Figure 1 shows a schematic of the system used to perform the experiments. Briefly, the gas flow was set at



200 mL min^{-1} using a flowmeter (FM) (model PMR5-010005, Cole Parmer, Vernon Hills, IL, USA). The gas flows through the eliminator of mercury (EHg), which can be a column containing a solid or a bubbler with a specific solution. A septum (SI) was placed in line for injecting the gaseous mercury standard. The mercury is absorbed on a gold-coated sand trap (GT) (Tekran Instruments Corporation, Toronto, Ontario, Canada) during sometime and, soon after, is desorbed under temperature control by a desorption system (DS) (QMS multifunction controller, Slovenia). A fluorescence detector (DT) (Brooks Rand model III, Brooks Rand Labs, Seattle, WA, USA) records the intensity of the analytical signal (Mercury Guru Software version 4.7).

In the experiments which aim to compare the performance of solid sorbents, glass columns of 124-mm length and 9-mm diameter containing the solid to be evaluated were used and placed in the EHg position (Figure 1). The gas flows through the system for 3 min, and mercury not adsorbed by EHg is the pre-concentrate; at the end of the experiment, the signal is recorded. The experiment is repeated five times for each solid, and the means of absorption capacities are compared using Duncan's post hoc test at a significance level of 5%. The absorption capacity (AC) is calculated as follows:

$$AC = W1 - W2,$$

where $W1$ is the total mass of mercury that flows through the system during the experiment time, calculated by multiplying the time of the experiment, mercury concentration in the gas, and the gas flow rate; $W2$ is the mass of mercury not retained in EHg ($W2$) calculated using the peak height.

Four different solid sorbents are tested, namely (a) coal taken from a chemical cartridge mask of a multi-gas personal protection with a bed height of 65 mm, here referred to as C1; (b) coal taken from a chemical cartridge to be used against mercury vapors or chlorine gas from an individual protective mask with a bed height of 60 mm, here referred to as C2; (c) metallic gold particles with an average diameter of 0.1 mm and bed height of 15 mm, referred to as A1; and (d) platinum wire coil with a bed height of 10 mm, referred to as A2. The solids are packed into columns, with quartz wool used to seal the ends of the column.

When solutions are evaluated to sorb mercury, the system is assembled as shown in Figure 1, and a 150-mL glass flask is used, containing 50 mL of the solution to be tested, in EHg position. The gas flows through the system during a period (TPC) determining the pre-concentration of mercury. Then, the metal is desorbed by heating, and the fluorescence is measured. If the TPC is low and no peak appears, the procedure has to be repeated until a peak is recorded. The total time is recorded, i.e., the total volume of gas, and thus, the total mass of mercury ($W1$) that flows

Table 1 Performance of sorbents for removing mercury from a gas mixture

Sorbent	AC	s	Duncan
A1 + A2	3.38	0.465	A
A2	3.34	0.444	A
C1	2.93	0.508	AB
A1	2.52	0.360	B
C2	1.91	0.435	C

Gas flow = 200 mL min⁻¹; mercury concentration in the gas mixture = 6.35 µg L⁻¹; experiment time = 3 min. A1 and A2 columns contain Au and Pt, respectively. C1 and C2 columns contain activated carbon for general use and specifically for Hg, respectively. Absorptive capacity (AC) is expressed in µg Hg. Standard deviation (s) is for five replicates. Duncan test results to a level of 5%.

through the system during the experiment time can be calculated, as well as the mass of Hg that EHg does not retain during the experiment. In the following, AC is calculated.

A 2³ factorial design is used to evaluate the influence of the composition of the absorbent solution on the absorption capacity. All possible combinations between three factors ($N = 3$) and two levels of concentration ($k = 2$) are evaluated, i.e., a full factorial design is run. Three replicates for each combination ($n = 3$) are run. The following factors and levels are evaluated: (a) chloride concentration (0.48 and 0.96 mol L⁻¹), (b) hypochlorite concentration (0.63 and 1.26 mmol L⁻¹), and (c) EDTA concentration (0.30 and 0.60 mmol L⁻¹). The analysis of variance is used to identify the significance and the interaction between the factors for a significance level of 5%.

The mass of mercury is calculated comparing the height of the peak of the samples with the height of the peak from the standard. The peak of the standard is recorded after an injection of an aliquot of a gas mixture containing a mercury concentration is well established, as described elsewhere (Gardfeldt et al. 2002). A 50-µL syringe gas tight

with removable needle (model 1705, Hamilton, Reno, NV, USA) is used to transfer an aliquot of 10 µL of gas mixture kept at 6.5°C in a thermostatic bath (model MQBTC99-20, Microquimica, Florianópolis, Brazil), corresponding to a mass of 40.4 µg Hg. The aliquot is injected into the system through the septum in the SI (Figure 1). The analyte is pre-concentrated on a gold-coated sand trap, desorbed by heating, and the analytical signal corresponding to 40.4 µg Hg is then recorded.

Results and discussion

Solid sorbents

The mean absorption capacity ($n = 5$) for each solid and Duncan test for 5% significance level are shown in Table 1. The Duncan test shows that there is no significant difference in AC when using a pair of columns (A1 + A2) or only a platinum column (A2). Moreover, a similar performance is obtained using the column C1, although it shows an AC slightly below the previous ranges. The column containing gold particles (A1) provides an AC which is lower than A2, but its performance is comparable with C1. Although the coal used in column C2 is marketed specifically for removing gaseous mercury, this material had the lowest AC, i.e., it has the worst performance for the conditions tested. In summary, the results show that when using a platinum column, one can expect to remove 88.7% of the mercury, while using column C2 results in the removal of 50.1% of the mercury present.

Absorbent solutions

The ability of a hypochlorite solution to remove gaseous mercury is evaluated by measuring the AC for different sodium hypochlorite solutions (0.42, 0.84, 1.26, 1.68, and 2.10 mmol L⁻¹). The results are shown in Figure 2, and a direct relationship between AC and hypochlorite concentration, up to 1.68 mmol L⁻¹, is observed; after that, a

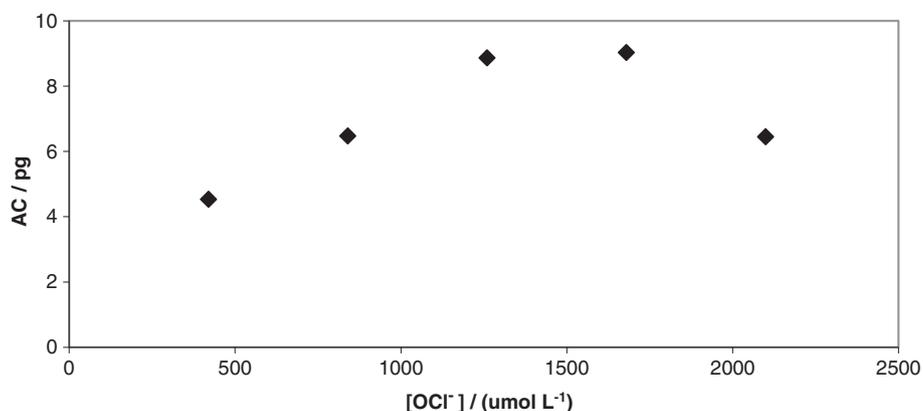


Figure 2 Influence of hypochlorite on absorption capacity. Variation of the AC of gaseous Hg due to the increase of the concentration of the aqueous solution of sodium hypochlorite [OCI⁻].

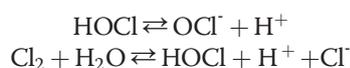
Table 2 Results of ANOVA

Causes of variation	df	SS	MS	F
OCl ⁻	1	38,286.4	38,286.4	1,380.0
EDTA	1	2,668.1	2,668.1	96.2
Cl ⁻	1	379.0	379.0	13.7
OCl ⁻ × EDTA	1	4,873.7	4,873.7	175.7
OCl ⁻ × Cl ⁻	1	1,401.7	1,401.7	50.5
EDTA × Cl ⁻	1	3,407.5	3,407.5	122.8
OCl ⁻ × EDTA × Cl ⁻	1	1,746.6	1,746.6	63.0
Treatment	7	52,763.0	7,537.6	271.7
Residual	16	44.9	27.7	
Total	23	53,206.9		

Value *F* for a significance level of 5% = 2.66. *df*, degrees of freedom; *SS*, sum of squares; *MS*, mean square; *F*, Fisher *F* test value.

reduction in AC is observed. The distribution of the concentrations of OCl⁻, HOCl, and Cl₂ essentially depends on the pH and the chloride concentration (see reactions below). Since in this experiment no buffer solution is used, then the increased concentration of hypochlorite causes the pH to increase and a decrease of the chlorine concentration. Thus, for hypochlorite concentrations higher than 2.10 mmol L⁻¹, an effective reduction of chlorine concentration must have taken place, leading to the consequent reduction of AC, as seen in Figure 2.

A study shows that the removal of gaseous mercury for the hypochlorite solution depends mainly on the presence of Cl₂ (Zhao and Rochelle 1999). However, the concentration of chlorine in the hypochlorite solution is defined by the following equilibria:



The mutual influence of the concentrations of hypochlorite and chloride on mercury removal is experimentally investigated by a 2³ factorial design with the following factors: concentration of hypochlorite, chloride, and EDTA, investigated at two levels of concentration.

The results in Figure 2 are used to define the hypochlorite concentrations to be tested, being chosen as 0.63 and 1.26 mmol L⁻¹. The highest hypochlorite concentration is chosen based on the maximum AC seen in Figure 2, and the lowest concentration is chosen as 50% of that value.

Zhao and Rochelle (1999) have demonstrated that, when using 1.0 mol L⁻¹ NaCl in the presence of sodium hypochlorite, the concentration of mercury in the gas phase is stabilized for their experiments. However, when using 0.1 mol L⁻¹ NaCl, those authors proved that the mercury concentration gradually increased in the gas phase (Zhao and Rochelle 1999). Thus, to perform the tests, 0.48 and 0.96 mol L⁻¹ chloride concentrations are chosen.

It is assumed that the use of EDTA can increase AC because EDTA ensures the stabilization of Hg²⁺ formed by redox reaction, since the logK_{est} HgEDTA ranges from 21.5 to 23.5. The selected concentrations are 0.30 and 0.60 mmol L⁻¹ to perform the tests, ensuring large excess of this reagent with respect to the concentration of Hg²⁺.

Table 2 shows the results of analysis of variance, and it can be seen that the *F* values for the main factors (OCl⁻, Cl⁻, and EDTA) are significant at the 5% level, but the interactions between these factors are also significant in the same level. So, it is not recommended to compare directly the means of the factors (Vieira and Hoffmann 1989). For this reason, the influence of OCl⁻ and Cl⁻ inside the EDTA level is evaluated, which is shown in Figure 3a,b. It is clear that increasing the hypochlorite concentration also increases AC regardless of the concentrations of chloride or EDTA. Increasing the chloride concentration will increase AC only for the lower concentration of EDTA (0.30 mmol L⁻¹).

Conclusions

The use of a column containing a platinum coil proves to be more suitable for removing gaseous mercury, among the solid sorbents tested. The use of a solution of 1.26 mmol L⁻¹ OCl⁻, 0.48 mol L⁻¹ Cl⁻, and 0.6 mmol L⁻¹ EDTA has an absorption capacity of 167 pg for gaseous Hg. This solution can purify gases that shall be used to analyze mercury in environmental samples, but the higher the mercury concentration in the gas, the more frequent

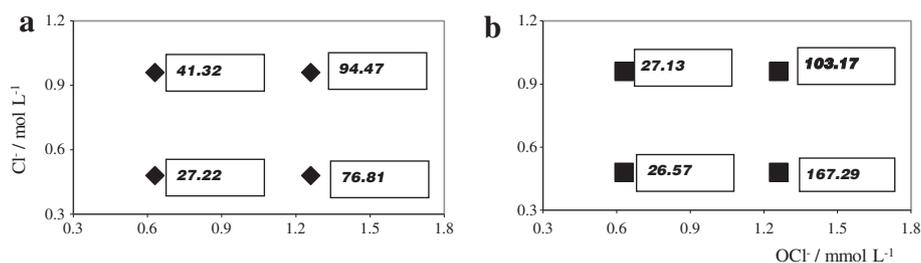


Figure 3 Representation of the interaction between hypochlorite, chloride and EDTA concentration. The interaction OCl⁻ × Cl⁻ for EDTA (a) 0.30 mmol L⁻¹ (diamonds) and (b) 0.60 mmol L⁻¹ (squares) is considered. The numerical values inside the graph represent the AC (pg Hg) for each condition tested.

the substitution of the solution. It also should be pointed out that it is a very easy way to remove the gaseous mercury and to get good blanks, even when a high-purity gas is not available.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

CMIT carried out the laboratorial experiments. LFHN drafted the manuscript. GF participated in the design of the study and performed the statistical analysis. MRM conceived and coordinated the study. All authors read and approved the final manuscript.

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