

Methylmercury Determination In Sub-Ppb Level By Cold Vapor Analysis: Facts, Mechanisms And Optimization

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Abstract: Recent reports, according to international organizations, on the highly toxic presence of methyl-mercury (MeHg) in the environment, classify it among the major/priority environmental pollutants. Understanding the need to find new, but also safe, sources of usable water and to monitor the current ones, regarding water quality, the aim of this study is to investigate the determination of MeHg by the application of cold vapor analysis, providing useful facts, considering the method's optimization, in order to be adopted also from other researchers. During the cold vapor analysis organic or/and inorganic mercury atomization takes place chemically by the addition of an appropriate reducing agent. The most known relevant agent is SnCl_2 , which however is able to reduce only the inorganic Hg. Instead, NaBH_4 is capable to reduce both Hg forms, but a pre-treatment of the sample is required, namely the addition of KMnO_4 . Therefore, in this work, the reagents' concentration was studied, and their role was clarified in every step of the proposed method analysis. According to the results, the addition of at least 0.0005% w/v KMnO_4 and 0.005% w/v NaBH_4 is needed in the aquatic sample for a reliable MeHg measurement. In fact, the formed MnO_2 , that produced by the reduction of residual KMnO_4 from NaBH_4 , was found to catalyze the MeHg atomization reaction.

Keywords: methyl-mercury; cold vapor analysis; water quality; water monitoring;

1. Introduction

According to European Commission, mercury is included in the high priority pollutants list, regarding water policy [1]. Mercury is released in environment mainly as its inorganic (IHg), or elemental form, through anthropogenic emissions. Organic mercury (OHg), mainly as the methyl-mercury (MeHg) form, is created through biotic mechanisms (bacterial actions) under anoxic conditions, when the inorganic and elemental Hg species are entering water resources and sea water. MeHg is the most toxic substance among the other mercury compounds, due to its higher ability for bioaccumulation. In other words, it can accumulate in the living tissues and therefore, increases gradually its concentration in the food chain, e.g starting from the micro-organisms, such as plankton, going to small fishes and finally, ending to the contamination of humans [2].

As a result of water pollution, through the appearance of toxic pollutants, such as MeHg, the need to monitor the quality of water, used to meet the various human needs, becomes mandatory [3]. Especially, when taking into account the water scarcity in many regions worldwide, the aforementioned need becomes even greater, in an effort to explore new/alternative water resources for potential re/use. Regarding mercury, its hazardousness is also reflected in the lowest drinking water regulation limit, as set by international organizations, among the other toxic metals, which is at $1 \mu\text{g/L}$ of total Hg. However, as in the aqueous phase the dominant form of mercury is the methylated one, precise analytical methods should be developed respectively, being able to determine the specific pollutant species at the sub-ppb levels. Cold vapor analysis is a well known technology that can fulfill this criterium, but according to the relevant literature, there is no a commonly acceptable unified experimental procedure and therefore, further investigation is still required [4, 5].

The aim of this study is to evaluate the two major reagents, used in cold vapor analysis for mercury atomization, namely SnCl_2 and NaBH_4 and furthermore, to investigate the possibility of an appropriate pre-treatment step in order to optimize the MeHg determination, namely the addition of KMnO_4 . Moreover, the initial experimental pollutant's concentration was in the range of 0-10 $\mu\text{g/L}$, i.e. close to the realistic environmental pollution cases, while as matrix a natural-like water was applied, prepared according to National Sanitation Foundation, in an effort to replicate the actual field conditions during the evaluation of the analytical method.

2. Materials and Methods

2.1. Reagents

Mercury working standard solutions were prepared for both species, i.e. inorganic and organic. Regarding IHg, a 1000 mg IHg/L standard solution (prepared mainly for atomic adsorption spectroscopy) was used. Instead, a 50 mg OHg/L working solution was prepared by dissolving 31.29 mg of reagent grade MeHgCl in 50 mL HCl 6 N and diluted to 0.5 L with distilled water. Similarly, freshly made working standard solutions were prepared by dissolving reagent grades of KMnO_4 (0.2% w/v), NaBH_4 (1% w/v) and SnCl_2 (1% w/v) in 0.5 N HNO_3 , 0.1 N NaOH and concentrated HCl prior to distilled water dilution, respectively.

The NSF water was prepared by diluting 252 mg NaHCO_3 , 12.14 mg NaNO_3 , 0.178 mg $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 2.21 mg NaF, 70.6 mg $\text{NaSiO}_3 \cdot 5\text{H}_2\text{O}$, 147 mg $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and 128.3mg $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in 1 L of distilled water [6].

2.2. Mercury determination

Mercury concentration was determined by using a Bacharach cold vapor mercury analyzer system (Coleman-Model 50B). In particular, 100 mL of the sample, pre-treated or not, is placed in a ground-necked flask and the reducing agent was added (NaBH_4 or SnCl_2). A nozzle, also grounded, was fitted directly to the flask, which allows the formed metal hydride to be trapped in the now closed flask-instrument system. Within 2 min the concentration has stabilized inside the instrument and the percentage of transmittance was recorded through an ultraviolet lamp (wavelength 253.7 nm). The limit of detection (LOD), according to the manufacturer, is 0.2 $\mu\text{g Hg/L}$.

3. Results and Discussion

3.1. Comparison of reagents

The first step to confirm the functionality/applicability of proposed method is to highlight the existing problem and to evaluate the appropriate sample's pretreatment. Indeed, by applying the two common reducing agents for Hg atomization (i.e. NaBH_4 or SnCl_2) during the cold vapor analysis, it was proved that only NaBH_4 is capable for the efficient MeHg atomization [7]. According to Fig. 1, presenting the corresponding calibration curves, the addition of SnCl_2 (0.05% w/v) can oxidize sufficiently the IHg form ($R^2= 0.997$). On the other hand, no change in the transmittance value was observed, when SnCl_2 used for the MeHg oxidation, and so the corresponding data are not presented. Instead, when the NaBH_4 reagent (0.05% w/v) was used, then the MeHg oxidized to its elemental mode, but not sufficiently enough. The corresponding calibration curve indicates that for OHg concentration above 5 $\mu\text{g/L}$, this method yielded rather inaccurate transmittance values ($R^2= 0.954$). In addition, by applying acidic conditions (using 0.1 N HCl) to this procedure, only slight variations in transmittance were obtained ($R^2= 0.935$) [8].

In order to be developed a reliable methodology, it was considered as necessary the application of an appropriate pre-treatment step, i.e. before the addition of NaBH_4 in the sample. For this purpose the reagent KMnO_4 (0.0005% w/v) was selected, due to its high oxidizing ability, which favors the conversion of MeHg to Hg^{2+} and hence, the metal's atomization rate is expected to be increased [9]. According to the respective results, the combination of NaBH_4 with the pre-treatment step can minimize the value of transmittance for the highest examined MeHg concentration (10

$\mu\text{g/L}$) and yields a reliable calibration curve ($R^2=0.998$). To investigate the effect of KMnO_4 on MeHg, the calibration curve with the addition of SnCl_2 was also conducted. The corresponding data verified the MeHg conversion to its Hg^{2+} form, but the respective efficiency of this transformation is rather limited and linear ($R^2=0.997$), meaning that only a part of the initial concentration was modified to the non-methylated mode during the pre-treatment step. The proved reliability of the previous method was mainly attributed to a 2nd mechanism, which co-exists during the determination; i.e. the excess of KMnO_4 reacted with NaBH_4 , resulting in the secondary production of MnO_2 , which was also confirmed by the discoloration of sample. As a result, the produced MnO_2 behaved as catalyst in the atomization reaction of MeHg [10].

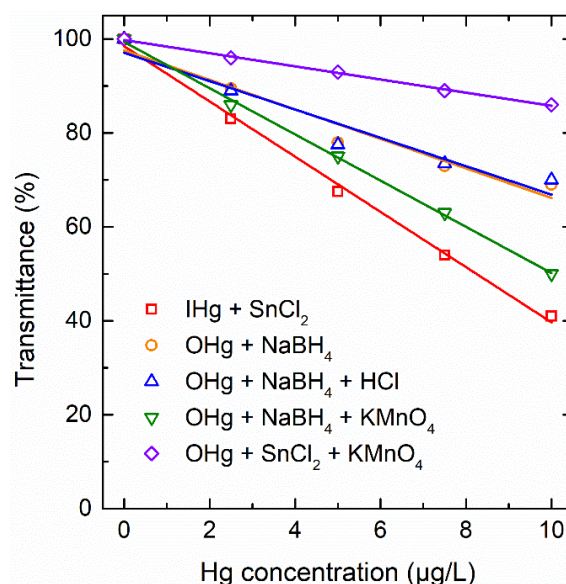


Figure 1. Calibration curves of OHg and IHg by applying various reagents and pre-treatment steps.

3.2. Reliability of analytical procedure

Since the use of reagents KMnO_4 and NaBH_4 was shown to be capable of providing a reliable calibration curve, then the method was also tested in terms of providing quantitative data, when possible interferences are occurring [7]. For this purpose, the standar addition method was applied, where at each sample a constant concentration of MeHg equal to $2.5 \mu\text{g/L}$ is added, which is considered as a theoretical value, intended to be co-determined/co-verified, as well as a variable concentration of IHg in the range between 0 to $7.5 \mu\text{g/L}$. By extending the resulting curve, it is possible to determine the theoretical MeHg concentration, which will be equal to the point of intersection at the 100% permeability value. According to Fig. 2, the respective data provided a high linearity curve ($R^2=0.998$), whereas the estimated concentration of MeHg, through its intersection (red line), differs only slightly from the theoretical one (i.e. 2.58 instead of $2.50 \mu\text{g/L}$); thus, proving the high reliability of the proposed method with 103% recovery, i.e. within the acceptable analytical limits.

Another interesting fact, resulting from the determination of OHg, IHg and mixed OHg/IHg by NaBH_4 , was the different trasmittance values yielded for a constant concentration of total Hg (Fig. 1 and 2). These vairations were attributed to the formation of CH_3HgH , a methyl-mercury hydride volatilized among with Hg^0 [5].

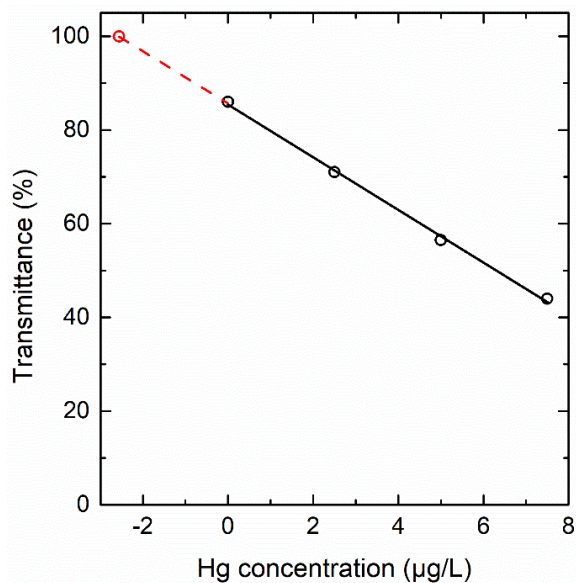


Figure 2. Determination of 2.5 µg OHg/L by applying the standar addition method.

3.3. Optimazation of analytical procedure

The next step, regarding the optimization of applied method, was to investigate the effect of KMnO_4 and NaBH_4 concentrations, i.e. the two reagents used in the proposed MeHg determination by the cold vapor analysis, especially after proving that they can react with each other [9]. The initial MeHg concentration in each sample was 10 µg OHg/L, as the highest concentration of investigated range, while the matrix was the NSF water, as before. By keeping the NaBH_4 content constant (0.05% w/v) in the samples, it was concluded that the measured transmittance showed its lower value at 0.0005% w/v KMnO_4 , while a further increase in its concentration caused no further changes (Fig. 3). Then, and keeping the KMnO_4 content constant as previously determined, it was found that the optimum content of NaBH_4 was 0.005% w/v, i.e. an order of magnitude lower, than in the initial experiments.

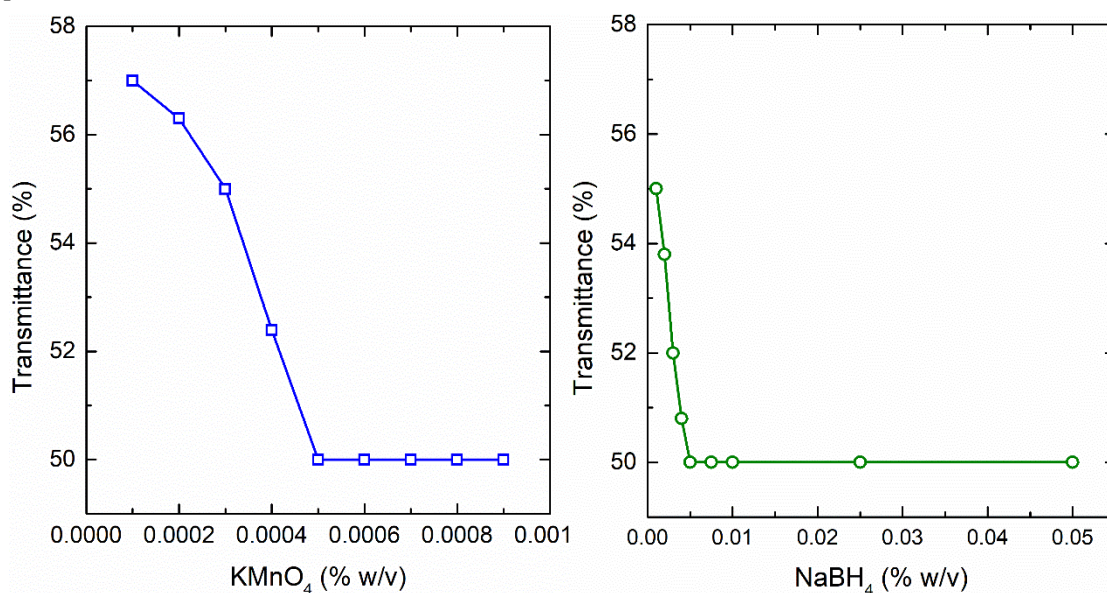


Figure 3. Effect of KMnO_4 and NaBH_4 concentration, considering the transmittance percentage of 10 µg OHg/L.

3.4. Interferences of the analytical procedure

Since the addition of $\text{KMnO}_4/\text{NaBH}_4$ content was proved to be crucial and due to the oxidizing behavior of KMnO_4 , some interferences may occur. Initially, it should be clarified that none of the ions contained in NSF water, i.e. common ions usually existing in natural waters, had any effect in the results obtained by this method. This aspect was proved also by using distilled water as matrix/background for the analytical determination, without observing any variations in transmittance values [4]. Moreover, and in order to avoid any contamination of the samples, e.g. by the presence of possible impurities of mercury in the used reagents, it is preferable to apply the minimum optimized concentrations of reagents, while keeping constant their rate. Instead, interferences are expected, when the sample contains metals that may be oxidized by KMnO_4 , such as Fe [11]. In that case, the inhibitory agent must be firstly neutralized by the KMnO_4 addition in order to obtain reliable results, and therefore, a different $\text{KMnO}_4/\text{NaBH}_4$ content should be defined.

4. Conclusions

In this study the determination of methyl-mercury by the application of cold vapor analysis was investigated and optimized in order to provide useful information, regarding the method's mechanism, and being able to be adopted by other researchers as well. A key factor is considered to be the addition of KMnO_4 in a pre-treatment step, during which the OHg can be partially converted to Hg^{2+} , acting also as a MnO_2 source, through its (secondary) reaction with NaBH_4 , which is behaving as catalyst during the measurement. This method proved to be reliable and without interferences, thus making it suitable for determining sub-ppb levels of MeHg in natural waters.

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Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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