Determination of ultra-low volatile mercury concentrations in sulfur-rich gases and liquids

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A B S T R A C T

Determining mercury (Hg) concentrations in a wide range of naturally occurring liquids (i.e., groundwater, hydrothermal fluids, acid mine drainage, submarine groundwater discharge, etc.) and gases, (i.e., volcanic and hydrothermal emissions, flue gas, natural gas, land fill gas, etc.) has obstacles due to the presence of H_2S in many of such samples. The classical approach of trapping Hg on gold traps comes up against its limits due to "poisoning" of the traps by H_2S and problems for its determination by cold vapor atomic fluorescence spectrometry (CV-AFS). Due to low concentrations of Hg in these sample types it is often necessary to collect large amounts of liquid or gas in excess of 20 L, which makes transport to the laboratory difficult. With this in mind we developed a portable method for the collection of Hg from gases and liquids rich in H_2S.

The method uses an impinger set-up with an alkaline trap followed by two potassium permanganate - sulfuric acid traps. The potassium permanganate ($KMnO_4$) oxidizes elemental Hg vapor to Hg^{2+}, which remains in the $KMnO_4$ solution and thus can be analyzed by CV-AFS. Thus, rather than 25 L of sample, only a few mL have to be transported to the laboratory. A possible caveat of this approach is that naturally occurring gases are generally a mixture of several different gases, such as H_2, CH_4, SO_2 and H_2S, which can react with and thus consume $KMnO_4$. The influence of various gas compounds at different concentrations were tested for their effect on the trapping of Hg by $KMnO_4$. Hydrogen and CH_4 did not cause any interference, while SO_2 did react with the $KMnO_4$. When the oxidizing capacity in the first $KMnO_4$-trap was depleted due to SO_2, Hg was trapped in the second $KMnO_4$-trap, which acted as a safety trap. Good recoveries of 99.5 % were achieved for the Hg collected in both $KMnO_4$-traps. Nevertheless, when H_2S was introduced into the system, Hg recovery dropped by almost 50 %. This observation was attributed to the formation of mercury sulfide (HgS) in the trap when the oxidation capacity of the $KMnO_4$-trap was consumed. HgS cannot be reduced by stannous chloride ($SnCl_2$), which is necessary for detection by CV-AFS. The problem was overcome by adding an alkaline trap with the reductant sodium borohydride ($NaBH_4$) in front of the two $KMnO_4$-traps. In this trap H_2S was converted to S^{2-}, which does not reach the $KMnO_4$-trap while at the same time $NaBH_4$ prevented the oxidation of Hg to Hg^{2+} followed by precipitation as HgS. Good recoveries of 98.05 $\pm$ 3.6 % (n = 3) were obtained for Hg when a volume of 1000 mL H_2S was passed through the impinger train.

Field testing of the method verified the effect of H_2S on the trapping and ultimately the determination of Hg in the hydrothermal gas. With the alkaline trap we determined a Hg concentration of 358 ng m^{-3} Hg, while without the alkaline trap only 101 ng m^{-3} Hg. Thus, the set-up without the alkaline trap led to an underestimation of the real Hg concentration by 71.8 % and confirmed the necessity of an alkaline trap to overcome the interference of H_2S.

1. Introduction

The neurotoxin mercury (Hg) is ubiquitous in the environment, which is mainly due to the presence of volatile Hg species [1]. Volatile Hg impacts humans for two reasons: (1) gaseous Hg is taken up by our respiratory system and enters the bloodstream where it unfolds its toxic properties [2] and (2) gaseous Hg is part of in the global Hg cycle and will eventually be transformed and deposited as Hg^{2+} to soil and water [1]. Its toxicity can be fortified by methylation, biomagnification and bioaccumulation within the marine food chain [3,4] and will ultimately have an impact on humans [2]. Hence, the monitoring of volatile Hg is an important aspect of environmental monitoring. Natural

gas [5,6], landfill gas [7,8], coalbed methane and volcanic/hydrothermal emissions [9] can be a significant source of Hg, along with a large number of other harmful substances, such as CO_2, H_2S, etc.

Gaseous Hg consists of several Hg species with elemental Hg as the dominant species, sometimes referred to as GEM (gaseous elemental Hg). Another species is divalent Hg (Hg^{2+}), often referred to as reactive gaseous Hg (RGM) in atmospheric Hg analysis, which is often associated with particles in gas and has a limited volatility causing relatively rapid deposition [10]. Dimethylmercury is only detectable in traces in the atmosphere at specific locations like anaerobic hot spots with high bacterial activity [8].

The transport of a gas sample to the laboratory is generally impracticable because due to low Hg concentrations several liters of sample are required and the Hg species can change or adsorb to the sampling container (e.g., Tedlar® bags). There are several methods described in literature to either trap each Hg fraction individually or as total volatile Hg. Those methods are based on the adsorption of Hg to a solid material or use of a trapping solution [11–13]. Gold traps are the classical approach for the collection of total gaseous Hg [14]. An alternative to gold traps are activated carbon traps, which have a large surface area and can be additionally impregnated with bromine, iodine, chlorine or sulfur to enhance the adsorption behavior of Hg [15,16].

A differentiation between short-lived, oxidized Hg (Hg^{2+}) and elemental Hg can be achieved by arranging liquid traps in a sampling train of several impingers. Although speciation of volatile Hg is not the focus of this publication, part of this method can be easily adapted for trapping total volatile Hg and is therefore described briefly. The Ontario Hydro method (ASTM D6784-02) is used for the quantification of elemental, oxidized, particulate and total Hg in the gas stream from coal-fired power stations. This method uses a sampling train consisting of a filter and seven impingers. The filter removes the particles and particle bound Hg and is followed by the first three impingers filled with a potassium chloride (KCl) solution for trapping Hg^{2+}. Potassium chloride is typically used for the complexation and trapping of Hg^{2+} and has been used for the speciation of RGM in the atmosphere in mist chambers or denuders [14]. The fourth impinger is filled with a mixture of hydrogen peroxide (H_2O_2) and nitric acid (HNO_3) and the last three impingers with potassium permanganate ($KMnO_4$) in sulfuric acid (H_2SO_4)and the oxidizing properties of these solutions are used for collecting elemental Hg [17].

Oxidant solutions used as liquid traps are corrosive and require careful handling when transported in comparison to solid sorbents but are generally less expensive. The main advantage of oxidant solutions is a better compatibility with interfering compounds in the gas and multiple subsamples can be analyzed from one $KMnO_4$-trap while a gold trap offers only a single analysis. Bagnato et al. [12] for example used gold traps to collect Hg from hydrothermal gas emanating in the Aeolian arc in the Tyrrhenian Sea, followed by detection by CV-AFS. Yet, Ferrara et al. [11] observed problems when Hg was collected from volcanic fumaroles on gold traps and attributed this to the poisoning of the gold trap by hydrogen sulfide (H_2S) and thus, used a 0.5 M $KMnO_4$-solution in H_2SO_4 to overcome that problem. The oxidizing solution reduces elemental Hg to Hg^{2+}, the acid decomposes dimethylmercury to $MeHg^+$ by which is then converted to Hg^{2+}, while the oxidant and volatile Hg^{2+} is complexed by sulfate (SO_4^{2-}) and kept in solution. However, the determination of Hg is not compromised for volcanic emissions. The other important sources of Hg, natural gases, landfill gases and coalbed methane can also contain elevated H_2S concentrations [18–23].

Volatile Hg is a fraction of total Hg in the water phase and can be up to 35 % of total dissolved Hg in sea water [24], but is generally lower in groundwater or estuarine water [24,25]. By purging a liquid sample with an inert gas stream volatile Hg is released and can be collected in a gold trap, a method almost identical to the collection of Hg from gas

Table 1
Minimum, maximum and median concentration of gases in hydrothermal gases from MSWHS; the data is from Champagne Hot Springs on the Lesser Antilles, [33] Bahía Concepción in Mexico, [34] Punta Mita in Mexico, [35] Milos Island (Greece), [36] Panarea (Italy) [12] and Lihir Island (Papua New Guinea) [30].

Gas	c(Min)/mmol/mol	c(Max)/mmol/mol	c(Median)/mmol/mol
CO_2	0.89	988	838
N_2	1.8	880	109
CH_4	< 0.01	122	3.70
H_2S	< 0.01	80.9	3.20
H_2	< 0.01	30	0.10
O_2	0.01	4.5	1.20
Ar	0.8	7.2	4.40
He	0.004	0.44	0.03

samples [26,27]. Mason et al. [26] for example, used gold traps for the analysis of volatile Hg species in seawater. Other aqueous samples, such as hydrothermal fluids or groundwater, however, may prove to be more difficult to sample, because they can contain an appreciable quantity of dissolved H_2S [20,28,29], which is detrimental to the determination of Hg with gold traps. Thus, the use of liquid traps might be a better option to analyze Hg in such samples.

With this in mind, the aim of this study was the development of a trapping method for total gaseous Hg from natural, or for that matter any, gas or liquid sample potentially high in H_2S. Initially the focus was on hydrothermal vent gas and gaseous volcanic emissions for the study of gas emanations from marine shallow-water hydrothermal systems and volatile Hg in hydrothermal fluids [e.g., [30–32]] In such gases H_2S may not be the only detriment, since the emanating gas consists of several different gases with some of them having reductive properties and some containing sulfur. The composition of the emanating gas is determined by the surrounding geology and a variety of subsurface reactions [30,31] and can therefore vary from location to location. Table 1 lists minimum, maximum and median concentrations of each gas in mmol/mol from vents at marine shallow water hydrothermal systems around the world.

In general, CO_2 is the main compound in most gases except in vent gas from Baja California, where the gas consists mainly of N_2 with up to 87.5 % [34,37]. Methane (CH_4) varies from 0 to 12.2 % with a median concentration of 3.7 % [12,33–36] and H_2S can contribute up to 8.09 % and hydrogen (H_2) up to 3.0 % to the vent gas composition while 8.09 % H_2S is only the top mark and not the rule for most gas samples [36]. On average, most hydrothermal vents emit up to 0.3 % H_2S [12,33–36]. Sulfur dioxide (SO_2) was not reported for any of the gases from marine vents (Table 1), although Aiuppa et al. [38] reported for the La Fossa Crater fumarolic field on Vulcano Island, Italy a ratio of SO_2 to H_2S from 0.4 to 7.5 %, which would make SO_2 a minor gas component. In hydrothermal systems, the gas emanates into sea water and the water-soluble SO_2 dissolves quickly into the surrounding water [12]. Of all components present in the hydrothermal gas, H_2S presents the greatest challenge when collecting Hg, because (1) it forms a strong bond with Hg^{2+} and (2) it reacts with and thus, consumes $KMnO_4$ in the trapping solution. The other constituents SO_2 and H_2 are also possess reductive properties and CH_4 can be oxidized by $KMnO_4$, hence all three gases can react with the trapping compound, $KMnO_4$ [39–41].

To overcome the above stated problems, we decided to use liquid traps instead of solid traps for the following reasons: (1) to avoid the interference of sulfur compounds like H_2S and (2) to have an inexpensive alternative to gold traps.

Here we report on the development of a field method that was used for the trapping of gaseous elemental Hg and volatile Hg with $KMnO_4$-solutions, paying close attention to the effects of H_2S, SO_2, H_2 and CH_4.

2. Experimental section

2.1. Reagents and material

De-ionized water (18 mΩ, Advantage A10, Millipore, USA) was used for the preparation of all aqueous solutions. Hydrochloric acid (HCl) (Optima Grade, Fisher Scientific) and sub boiled HCl (sub boiled from AnalaR Normapur, VWR) were used. Optima grade HCl was generally used for the preparation of Hg^{2+} solutions while the sub boiled HCl was used for all other purposes.

200 g stannous chloride dihydrate ($SnCl_2 \times 2H_2O$, Reagent grade, Alfa Aesar) were dissolved in 100 mL HCl and approximately 100 mL water and boiled for 1 min. The solution was then topped up to final volume of 1000 mL with Milli-Q water and purged with argon (Ar) overnight. 75 g hydroxylamine hydrochloride (ReagentPlus®, 99 %, Sigma-Aldrich) were dissolved in water and 0.250 mL 20 % $SnCl_2$ solution were added. The solution was topped up to 250 mL and purged with Ar overnight. Hg standards were prepared from 1 mg/L Hg^{2+} (Brooks Rand, USA) by further dilution in 0.2 M HCl.

H_2S was generated from sodium sulfide hydrate (AnalaR Normapur, VWR) by the addition of HCl. H_2 was generated in the laboratory from a sodium borohydride solution ($NaBH_4$, p.a, Merck) and HCl. SO_2 was generated from sodium sulfite (analytical grade, SERVA Feinbiochemica) and HCl. CH_4 was used from a gas bottle (N45, Air Liquide).

The trapping solution was a 10 % (v/v) H_2SO_4 solution with $KMnO_4$ in the range of 0.1 M up to 0.3 M. 30 % (m/v) hydroxylamine hydrochloride solution was used for reducing excess $KMnO_4$ to Mn^{2+} after the trapping of the Hg from the gas sample. The purity of the chemicals has a huge impact on the limit of detection in Hg analysis. Sulfuric acid and hydroxylamine hydrochloride did not contain a significant amount of Hg but the $KMnO_4$ was more problematic. We did test several $KMnO_4$ powders classified as "low in mercury" and the best option did contain 0.6 μg/kg Hg. $KMnO_4$ (ACS reagent, low in mercury, ≥ 99.0 %, Honeywell) and H_2SO_4 (AnalaR Normapur, VWR) were chosen for the trapping solution.

2.2. KMnO₄-trap solution

In preparation for the solution, 1.70 g $KMnO_4$ were weighed into a 60 mL certified Hg-free, glass VOC (volatile organic compounds) vial (to give a 0.3 M $KMnO_4$-solution). In a separate glass bottle, a 10 % (v/v) solution of H_2SO_4 was prepared and allowed to cool down. The $KMnO_4$ was dissolved in 36 mL diluted H_2SO_4 to make the final trapping solution. The acid solution was added to the $KMnO_4$ on the day of use because with time the $KMnO_4$ would oxidize and form manganese (IV)oxide (MnO_2).

2.3. Generating elemental Hg

To generate elemental Hg, 40 mL of Milli-Q water were filled into a 60 mL glass vial and 800 μL of the 10 μg/L Hg^{2+} stock solution were added (8 ng elemental Hg as total amount of Hg). Then 200 μL HCl were added followed by 200 μL of a 20 % (m/v) stannous chloride ($SnCl_2$) solution in 10 % HCl as reductant (see Eq. (1)). The impinger was built in-house and consisted of a Hg-free 60 mL VOC glass vial with a modified cap that contained one Pasteur pipette, which reached into the solution and a small glass rod as a gas outlet (see Fig. S1 (supplementary material) for the cap). The impingers were connected with PTFE tubing (1/4″ OD, 4 mm ID), which was fitted exactly into the top-part of the Pasteur pipette and glass rod. The elemental Hg was then immediately purged into the impinger train with Ar at a flow-rate between 0.5 and 0.7 L/min (Fig. 1).
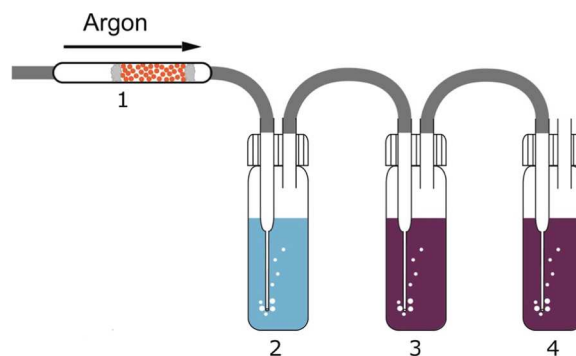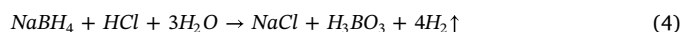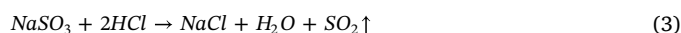
$$Hg^{2+} + Sn^{2+} \rightarrow Sn^{4+} + Hg(0)\uparrow \tag{1}$$

Fig. 1. Set-up of the sampling train. (1) gold trap for cleaning the inert gas, (2) Flask for generating Hg°, (3) and (4) are the KMnO₄-traps. The connections are based on Pasteur pipettes fitted into PTFE lined caps connected with ¼″ PTFE tubing.

2.4. Gas generation

H_2S and SO_2 were generated by the addition of 20 mL HCl to approximately 5 g of the solids, here sodium sulfide and sodium sulfite (see Eqs. (2) and (3)). H_2 was generated by the addition of 15 mL HCl to 75 mL of 0.7 % (m/v) $NaBH_4$ solution (see Eq. (3)).

$$Na_2S + 2HCl \rightarrow 2NaCl + H_2S\uparrow \tag{2}$$

$$NaSO_3 + 2HCl \rightarrow NaCl + H_2O + SO_2\uparrow \tag{3}$$

$$NaBH_4 + HCl + 3H_2O \rightarrow NaCl + H_3BO_3 + 4H_2\uparrow \tag{4}$$

CH_4 was purchased as a gas (methane N45, Air Liquide). The gases were collected in a self-assembled construction that resembled a Kipp's apparatus and then could be pumped through the trapping solutions (see Fig. S1 and S2). The gases flowed through the trapping solutions at a flow-rate of around 0.2 L/min. The volume used for each gas was calculated from the percentage of each gas in a typical hydrothermal vent gas assuming that a total of 25 L gas volume would be analyzed. 0.3 L of one gas component corresponded to 12 mmol/mol of the gas in 25 L and 1000 mL of one gas component corresponded to 40 mmol/mol (see Table 1 for the concentration of the different gases in the vent gas).

2.5. Alkaline tin(II)chloride and alkaline sodium borohydride solution

20 g NaOH (AnalaR Normapur, VWR) were carefully dissolved in approximately 90 mL Milli-Q water. In a small amount of Milli-Q water, 4 g $SnCl_2 \times 2H_2O$ were dissolved and added to the sodium hydroxide (NaOH) solution under stirring. The solution was filled up to 100 mL and purged for 1 h with Hg-free Ar. This solution was prepared on a daily basis to avoid the formation of a silver-grey precipitate of tin. Instead of $SnCl_2$, $NaBH_4$ was also tested as a reductant. In a 20 % (m/v) NaOH solution 0.5 g $NaBH_4$ (p. A., Merck) were dissolved and purged for 10 min with Hg-free Ar.

2.6. Preparing of traps for the Hg analysis with CV-AFS

The method for trapping volatile Hg was developed in such a way that the same 60 mL VOC vial used for the trapping and for the analysis. After the trapping, the $KMnO_4$ solution in the trap vial was decolorized by the addition of 5 mL pre-reductant (30 % hydroxylamine hydrochloride (m/v)). The pre-reductant was added carefully through the Pasteur pipette to avoid a strong reaction. Small black particles remained typically at the bottom of each trap but would dissolve when the vial was ultrasonicated or shaken for several minutes. The reaction of $KMnO_4$ or MnO_2 with hydroxylamine hydrochloride is exothermic and thus the solution was allowed to cool down following reaction and 200 μL of a 20 % (m/v) $SnCl_2$ solution were added and the vial capped with a septum cap prior to analysis by gold amalgamation cold vapor
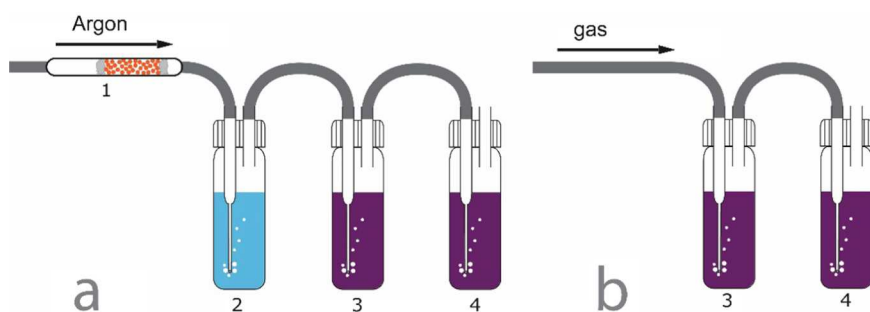
Fig. 2. Testing the influence of gases on the Hg trapping. Elemental Hg vapor and the gas were passed separately into the trapping solution. Fig. 2a shows the generation of elemental Hg vapor (2) and the subsequent trapping in the impingers (3) and (4). Fig. 2b shows the introduction of the test gas into the two $KMnO_4$-traps (3) and (4).

atomic fluorescence spectrometry (CV-AFS; MERX-T from Brooks Rand). Instrument setup and analytical procedure followed the US EPA method 1631 (without the oxidation step by BrCl).

2.7. Calculation of Hg concentration in gas samples

The total amount of Hg was determined as the absolute mass of Hg in the KMnO4-trap by CV-AFS. For the concentration of Hg in the gas, the absolute mass of Hg was divided by the gas volume used.

$$c(T - Hg\ in\ gas) = \frac{analyzed\ m\ (Hg)\ from\ KMnO_4 - trap}{gas\ volume} \quad (5)$$

3. Results and discussion

The use of gold traps is a common approach for collecting and analyzing volatile Hg in gases despite reports of significant poisoning of the gold traps by H_2S (see above). To better assess the potential of trap poisoning we did some preliminary tests by purging volatile Hg from fluid samples unto gold traps, following the approach that is commonly used for identifying the volatile Hg species in seawater [27]. The analysis was done with dual trap CV-AFS, where the sample gold trap was heated out in an Ar stream onto an analytical gold trap, which was heated afterwards and the vapor was analyzed in the AFS detector. Peak broadening and tailing was observed to such an extent that the quantification of Hg was impossible (see Figs. S3 and S4). When the same gold trap was loaded with a known amount of elemental Hg afterwards, the poisoning of the trap became more obvious because the detected concentration was about 4 times higher than expected. Heating the gold traps in an air stream was the only possibility to recover the gold trap again. During heating the gold trap in air, H_2S was transformed into SO_2 and burned off. We would therefore refrain from using gold traps and use liquid traps instead when H_2S is one component of the gas.

The trapping efficiency of a $KMnO_4$ solution for gaseous Hg was first tested with Ar as an inert gas for validating the method without the influence of a reactive gas component. The experiment was performed as shown in Fig. 1 with one impinger for generating elemental Hg vapor, a sampling trap and one safety trap. From a total amount of 8 ng elemental Hg, 99.5 ± 4.1 % and 102.5 ± 3.1 % (n = 3) were recovered from the first $KMnO_4$-trap filled with 0.05 M and 0.1 M $KMnO_4$ solution in 10% H_2SO_4, respectively. No Hg was found in the second trap. The concentration of $KMnO_4$ in the trapping solution was raised to 0.3 M $KMnO_4$ because: (1) 0.3 M $KMnO_4$ is a concentration close to the solubility maximum of $KMnO_4$ in water (with 0.40 M $KMnO_4$ being soluble in water at 20 °C), (2) that concentration will give the highest possible oxidative capacity for real gas samples with a challenging gas composition, where for example H_2, CH_4 and SO_2 and H_2S will also consume $KMnO_4$ and thus, leave less to react with the Hg and (3) a concentration of 0.3 M $KMnO_4$ corresponds almost to a 5% $KMnO_4$ solution, which is used in the Ontario Hydro method (ASTM D6784-02) for the determination of Hg.

Using this experimental setup with Ar as the carrier gas, Hg was not found in the safety trap (trap 2), while in trap 1 97.2 ± 2.9 % (n = 4)

of the elemental Hg were found. When Hg-free air was used as a carrier gas, 96.5 ± 1.2 % (n = 3) were detected in $KMnO_4$-trap 1 and none in the safety trap.

3.1. Hydrogen (H_2) and its effect on mercury (Hg) collection

H_2 is a gas with reductive properties and especially nascent H_2 is able to reduce a $KMnO_4$ solution [42], hence H_2 may interfere in the trapping of Hg due to the decomposition of $KMnO_4$ or a potential chemical/spectral interference. To assess H_2 interference, two different experiments were performed, where H_2 and elemental Hg were introduced separately into the trapping solutions. First, Hg was trapped in the $KMnO_4$-solution (see Fig. 2a) and H_2 was afterwards passed through the $KMnO_4$-solution (Fig. 2b). If H_2 remobilized the trapped Hg, the concentration of Hg would decrease in the first trap and be carried into the second trap. In the second experiment, H_2 was passed first through the trapping solution (see Fig. 2b) followed by the Hg vapor (Fig. 2a).
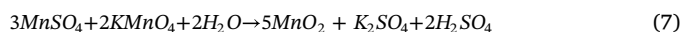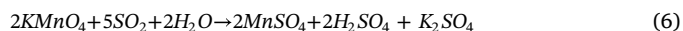
Approximately 300 mL H_2 gas were passed through the two traps, which were filled with 0.3 M $KMnO_4$ solution and then 8 ng elemental Hg were carried in an Ar stream into the traps. When analyzed, 97.0 ± 2.7 % (n = 3) of Hg was recovered from trap 1. The experiment was repeated the opposite way, with Hg first and then H_2 being passed through the trap solutions, and 94.9 ± 2.0 % (n = 3) of the Hg was recovered. Even when 1000 mL of H_2 were passed through the traps prior to the Hg trapping or afterwards, no interference was observed (95.5 % and 92.41 % (n = 1)). Hence, no significant interference was observed from H_2 gas.

3.2. Methane (CH_4) and its effect on mercury collection

Belavin et al. [39] did report the oxidation of CH_4 with $KMnO_4$ in a temperature range from 40 to 100 °C at measurable rates, thus CH_4 could react with the $KMnO_4$ and decrease the amount of $KMnO_4$ for the trapping of Hg. As a first test 300 mL CH_4 were passed through the $KMnO_4$-traps and no formation of manganese(IV) oxide (MnO_2) was observed. Hence, all following tests were conducted with 1000 mL CH_4 gas. When Hg was first trapped and then the CH_4 was passed through the two traps, the recovery of Hg was 95.0 ± 3.6 % (n = 3) from trap 1 and no Hg was found in trap 2. When the CH_4 was first passed through the traps and then followed by Hg, 96.1 ± 4.4 % (n = 3) were found in trap 1 and nothing in trap 2. Seemingly, CH_4 did not interfere with the trapping of Hg in a $KMnO_4$-solution at ambient temperature.

3.3. Sulfur dioxide (SO_2) and its effect on mercury collection

The influence of SO_2 on the trapping of Hg was tested because of its highly reductive properties. In the presence of H_2SO_4, SO_2 reacts with $KMnO_4$ to form SO_4^{2-}, MnO_2 and Mn^{2+} (see Eqs. (5) and (6)), thus consuming $KMnO_4$.

$$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow 2MnSO_4 + 2H_2SO_4 + K_2SO_4 \quad (6)$$

$$3MnSO_4 + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4 \quad (7)$$

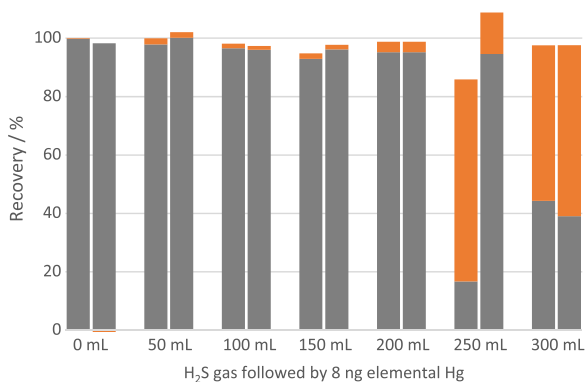To aid overall trapping of Hg the newly formed MnO_2 is known to

Fig. 3. Volumes of hydrogen sulfide (H₂S) ranging from 0 to 300 mL were passed through two KMnO₄-traps and 8 ng elemental Hg was transported afterwards into the traps with Ar. The experiment was done twice for each volume of H₂S. The recoveries of Hg in trap 1 (grey) and trap 2 (orange) are shown in % (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

absorb Hg^{2+} on its active surface sides [43].

SO₂ is a minor gas component in most hydrothermal vent gases. With 300 mL SO₂ passing through the two traps, the first trap formed a suspension of brown MnO_2 precipitating in the purple solution, while the second trap was not affected and kept the purple color. When 8 ng elemental Hg vapor were passed through the trapping solution afterwards, 97.7 ± 1.2 % (n = 3) were found in trap 1 and no Hg in trap 2. When the experiment was reversed, with elemental Hg passing first through the trapping solutions followed by 300 mL SO₂, 99.6 ± 2.5 % (n = 3) were recovered from trap 1 and no Hg was found in trap 2.

The volume of SO₂ was increased to 1000 mL. The purple solution in trap 1 changed the color to brown and later to black the more SO₂ was passed through the solution. After approximately 800 mL SO₂ were passed, the solution lost its purple color and a clear solution with small black particles of MnO_2 remained. Trap 2 kept the purple color but a small amount of brown MnO_2 had already formed. Then, elemental Hg was passed through the solution and upon analysis, 9.2 ± 6.7 % (n = 3) of the Hg were found trap 1 and 90.2 ± 8.6 % (n = 3) were found in trap 2. The standard deviations for the recovery rates in trap 1 and trap 2 were higher because the concentration of Hg in trap 1 varied. The concentration of Hg trapped in both traps as a sum was 99.5 ± 2.7 %, thus a good recovery with a good standard deviation was accomplished for the trapping in the presence of SO₂, where the oxidative capacity was completely consumed in trap 1.
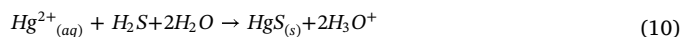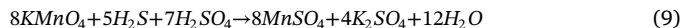
When Hg was first collected in the KMnO₄-traps, it was expected that all the Hg would be found in trap 1 even though 1000 mL SO₂ would be passed afterwards through the trapping solutions. In fact, 92.7 ± 0.4 % were found in trap 1 and a small amount of 7.5 ± 0.8 % were found in trap 2. A small portion of the Hg trapped in trap 1 got apparently remobilized in the SO₂ gas stream, but was trapped again in trap 2. The combined recovery for Hg in both traps was 100.3 ± 1.4 %.

3.4. Hydrogen sulfide (H₂S) and its effect on mercury collection

H₂S can disturb the trapping of Hg twofold: (1) it is a highly reductive gas like SO₂ which will react with the oxidant KMnO₄ and therefore decreases the amount of the reactant responsible for the trapping; (2) it is a sulfur-containing compound and especially H₂S is a known interferent (chemical and spectral interference) for Hg detection by cold vapor atomic fluorescence spectrometry (CV-AFS) [44,45].

KMnO₄ was reduced by the H₂S to Mn^{2+}, which became evident by the disappearance of the purple color after enough H₂S was passed through the KMnO₄-trap. H₂S was oxidized to elemental sulfur which floated on top of the solution in the form of small, yellow particles but the amount of the sulfur was too small in comparison to the amount of

H₂S used. Therefore, SO_4^{2-} had to be main product of this redox reaction (see Eqs. (7) and (8)).

$$2KMnO_4 + 5H_2S + 3H_2SO_4 \rightarrow 5S + 2MnSO_4 + K_2SO_4 + 8H_2O \tag{8}$$

$$8KMnO_4 + 5H_2S + 7H_2SO_4 \rightarrow 8MnSO_4 + 4K_2SO_4 + 12H_2O \tag{9}$$

$$Hg^{2+}_{(aq)} + H_2S + 2H_2O \rightarrow HgS_{(s)} + 2H_3O^+ \tag{10}$$

First, 8 ng elemental Hg were passed through the KMnO₄-traps followed by 250 mL H₂S. When the two traps were analyzed for their Hg content, only 1.1 ng Hg (14.6 ± 0.5 %, n = 2) were found in trap 1 and none in trap 2. Trap 1 had lost most of its oxidizing power and some H₂S was kept in solution instead of being oxidized to sulfur or SO_4^{2-}. The free amount of H₂S did bind to Hg^{2+} and formed a compound not reducible by $SnCl_2$, which is a necessary step in the Hg-detection by CV-AFS (see Eq. (10)). Hence, the experiment was repeated and changed in such a way that the two traps were purged for 5 min with Ar afterwards to lose excess H₂S. Then 6 mL 0.3 M KMnO₄ in 10 % H_2SO_4 were added to regain oxidizing capacity. The traps were left standing for 30 min before the pre-reductant was added. When analyzed, the recovery of Hg in trap 1 was 96.1 ± 4.0 % (n = 3) and 2.1 ± 1.7 % in trap 2. The additional preparative steps after the actual trapping were therefore incorporated into the standard protocol every time when the KMnO₄-trap had a slight color change to brown.

The reversed experimental set-up with H₂S gas being passed first through the KMnO₄-traps followed by the elemental Hg was performed with different volumes of H₂S from 50 to 300 mL (Fig. 3).

More than 95 % of Hg were recovered from trap 1 when up to 150 mL H₂S were previously passed through the two traps. At around 200 mL H₂S, the oxidative capacity of the KMnO₄ in trap 1 diminished slowly and a break-through of Hg into trap 2 was observed. When 300 mL H₂S were used, 41.7 ± 5.3 % Hg were found in trap 1 and 55.9 ± 5.3 % in trap 2. Thus, the sum of Hg collected in both traps still reached more than 95 %.

Concentrations of H₂S of up to 80.9 mmol/mol in gas samples were reported previously (see above), which corresponds to 2000 mL H₂S in a 25 L gas sample. The trapping method was therefore tested with higher volumes of H₂S. When 1000 mL H₂S were passed through a set of KMnO₄-traps previously treated with elemental Hg, the first trap did clear up at approximately 650 mL H₂S and the second trap at approximately 900 mL H₂S. 1000 mL H₂S were therefore sufficient to consume the full oxidation capacity of both traps. Additionally, only 50.4 % Hg were recovered from trap 1 and none was found in trap 2. A chemical interference did obviously occur again and none of the steps before (i.e., purging with an inert gas and adding 6 mL oxidant solution) did help to overcome the problem. Higher volumes of H₂S did therefore cause more problems: (1) deactivation of the trapping capacity and (2) an irreconcilable chemical interference (i.e., precipitation of HgS).

H₂S is a weak acid that dissociates in an alkaline solution to H^+ and HS^-, which then further dissociates to H^+ and S^{2-}, which both are nonevolatile sulfur anions. An alkaline solution as a trap before the two KMnO₄-traps could therefore solve the problem by trapping H₂S. However, the question was if Hg could also be trapped in a solution that had previously trapped H₂S because of the strong affinity of Hg with HS^- and S^{2-}. Elemental Hg is mobile enough to not react with sulfide but it needs to be guaranteed that the Hg remains in its volatile, elemental form. The addition of the reductant $SnCl_2$ should prevent oxidation and thus ensure that Hg remained in its volatile form. Thus, 100 mL of a 20 % NaOH (m/v) solution was prepared containing 1 % $SnCl_2 \times 2H_2O$ (m/v). The high concentration of NaOH was chosen because other vent gas components would react as well with NaOH, mainly CO_2 (more than 90 % in most vent gases). 100 mL of the alkaline $SnCl_2$ solution was used in an impinger which preceded the set of KMnO₄-traps. Fig. 4 shows an illustration of the new set-up.

When 8 ng elemental Hg were first passed through the modified impinger train followed by 1000 mL H₂S, the alkaline $SnCl_2$ solution
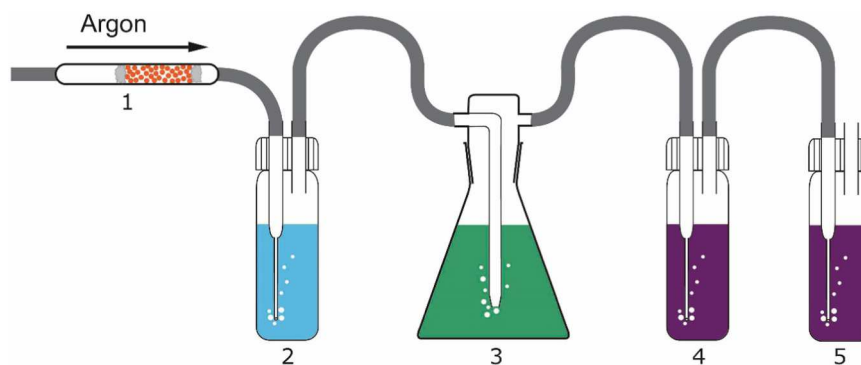
Fig. 4. Set-up of the new sampling train. (1) gold trap for cleaning the inert gas, (2) Flask for generating Hg°, (3) contains the alkaline $SnCl_2$ (or $NaBH_4$) solution and (4) and (5) are the $KMnO_4$-traps.

turned black and the two $KMnO_4$-solutions kept their purple color. H_2S was successfully trapped in the alkaline trap and $105.1 \pm 0.7\%$ Hg were detected in the first $KMnO_4$-trap and no Hg in trap 2. When the experiment was reversed and 1000 mL H_2S were passed first through the impingers and then Hg, $76.3 \pm 1.6\%$ Hg were detected in trap 1 and no Hg in trap 2. Precipitation of a black precipitate of tin(II) sulfide (SnS) [e.g., [46]] in the alkaline trap is the likely explanation for the decreasing recovery of Hg with an increasing volume of H_2S. With the formation of the SnS, the amount of the reductant $SnCl_2$ decreases dramatically and Hg adsorbs most probably to the newly precipitated SnS. An alternative to $SnCl_2$ could be $NaBH_4$ [47,48], although rarely used in CVAFS. $NaBH_4$ was tested in combination with the alkaline solution. 500 mg $NaBH_4$ were dissolved in 100 mL 20 % (m/v) NaOH. The solution was purged for 10 min with Hg-free Ar to remove any impurities of Hg.

The experiment was conducted as described above, where 8 ng elemental Hg vapor were passed first through the impinger train consisting of an alkaline solution with $NaBH_4$ and two $KMnO_4$-traps. Afterwards, 1000 mL H_2S gas were passed through the impinger train. The alkaline solution turned yellow with the addition of the H_2S and the two $KMnO_4$-traps kept their purple color. When analyzed by CV-AFS, $96.7 \pm 3.6\%$ (n = 3) of the Hg were recovered from the first $KMnO_4$-trap and none in the safety trap 2. The experiment was then performed with H_2S passing first trough the impinger train followed by 8 ng elemental Hg. Even though the elemental Hg had to pass here through an alkaline solution loaded with sulfide ions, $99.4 \pm 3.1\%$ (n = 3) of Hg were recovered from the first $KMnO_4$-trap and none from the second. Good Hg recoveries were found when an alkaline solution with $NaBH_4$ was used as a pre-trap for H_2S. The experiments showed no carry-over of Hg from $KMnO_4$-trap 1 into $KMnO_4$-trap 2. For estimating the general carry-over, a high concentration of Hg (4000 ng Hg) was passed through the impinger train and 4133 ± 106 (n = 3) ng Hg were analyzed in trap 1 and 0.54 ± 0.41 ng in trap 2. The Hg signal from trap 2 was clearly distinguishable from the general background noise nevertheless the break-through from trap 1 into trap 2 was only 0.01 %.

To evaluate the suitability of our method to work outside a controlled laboratory environment, we tested the method during a visit to the island of Panarea in the Aeolian Arc. The Mediterranean Sea around Panarea is host to several hydrothermal areas, some of which are known to vent a gas phase with measurable concentrations of Hg [12]. The gas sample was collected directly into a Tedlar® bag from an area, which was previously sampled by Bagnato et al. [12]. Tedlar® bags are usually the container of choice when collecting larger gas samples [e.g., [49]] and since we collected 25 L of gas the use of a gas bag was unavoidable. After collection the sample was immediately brought to our field laboratory where the impinger train was set up (Fig. 5). When the gas was passed through the impinger train with the help of a vacuum

pump, the alkaline trap turned yellow-brown with time and became hot. The alkaline trap was therefore cooled in an ice bath during the trapping process. The high concentration of CO_2 in the gas is the best explanation for the warming of the alkaline trap. To evaluate and verify the effect of H_2S on the trapping and ultimately the determination of Hg in the hydrothermal gas, the sample was passed through the impinger train once with and once without the alkaline trap for two gas samples from the same location. With the alkaline trap we determined a Hg concentration of $358\ ng\ m^{-3}$ Hg, while without the alkaline trap only $101\ ng\ m^{-3}$ Hg. Thus, the set-up without the alkaline trap led to an underestimation of the real Hg concentration by 71.8 % and confirmed the necessity of an alkaline trap to overcome the interference of H_2S.

4. Conclusions and future work

An efficient and practical method for the trapping and analysis of Hg from hydrothermal gases, volcanic emissions and gases high in H_2S was developed as an impinger train, which consisted of liquid alkaline and $KMnO_4$-traps to overcome interference problems arising from H_2S in the sample. The method can also be used for collection and analysis of volatile mercury in liquids rich in H_2S.

Of the gases tested for their interference on the determination of Hg in gaseous samples only H_2S was identified as problematic. To remove H_2S from the sample matrix, a trap filled with an alkaline solution and $NaBH_4$ was inserted into the impinger train prior to the $KMnO_4$-traps. In summary, the collection of Hg from gaseous samples is based on an impinger train consisting of 3 traps, where trap 1 contained 100 mL alkaline solution with 500 mg $NaBH_4$ and traps 2 and 3 contained 36 mL 0.3 M $KMnO_4$ in 10 % (v/v) H_2SO_4. The NaOH in trap 1 is removing H_2S from the sample matrix, while the $NaBH_4$ is maintaining reducing conditions, which are necessary to keep Hg in its elemental state to prevent removal due to oxidation. Trap 3, which is identical to trap 2 was added for safety, i.e., not to lose any Hg once the $KMnO_4$ in trap 2 would be consumed. After the trapping, excess $KMnO_4$ was destroyed by adding hydroxylamine hydrochloride and then the impinger head was removed and replaced by the original cap of the VOC vial, which was transported to the laboratory for Hg analysis by CV-AFS. The use of the VOC vials as traps and sample containers more or less eliminated the danger of carry-over (cross contamination) from sample to sample, because every impinger train consisted of new VOC vials. In the laboratory Hg was measured directly from the VOC vials (traps) by CV-AFS after adding 200 μL 20 % (m/v) $SnCl_2 \times 2H_2O$ to each vial.

Additional tests and development are planned to evaluate the possibility to use the alkaline trap in front of a gold trap and thus collect Hg from H_2S-rich gases without the use of $KMnO_4$. The use of gold traps instead of $KMnO_4$ traps would further facilitate collection and transport from the field to the laboratory.

Fig. 5. Impinger train setup with Tedlar® bag to the right, followed by the alkaline and two KMnO₄-traps and a vacuum pump at the end (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2019.02.070.

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