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Article

Mercury Speciation in Urban Landfill Leachate by Cold Vapor Generation Atomic Absorption Spectrometry using Ion Exchange and Amalgamation

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Foi desenvolvido um sistema em linha para a especiação de Hg orgânico (Hg_{org}) e Hg inorgânico (Hg_{inorg}) em chorume. Clorocomplexos produzidos a partir do Hg_{inorg} são separados em uma coluna trocadora de ânions. O Hg retido na coluna é eluído com $NaBH_4$ na presença de HCl. O Hg^0 produzido é medido por espectrometria de absorção atômica com geração de vapor frio (CV AAS). O Hg_{org}, que não fica retido na coluna, é misturado com $NaBH_4$ produzindo espécies voláteis de Hg, as quais são amalgamadas numa rede de Au/Pt. O Hg é removido desta coluna por aquecimento a 600 °C e medido por CV AAS. Para a especiação de Hg_{inorg} e Hg_{org} em chorume, as amostras são centrifugadas, filtradas e tratadas com HCl. Os limites de detecção (3 s) são 9 e 12 ng L^{-1} de Hg para Hg_{inorg} e Hg_{org}, respectivamente. A freqüência de análise é 22 h^{-1}.

This work deals with on line speciation of organic Hg (Hg_{org}) and inorganic Hg (Hg_{inorg}) in urban landfill leachate. Chlorocomplexes of Hg_{inorg} are produced in HCl medium and retained on an anion exchange column. The retained Hg is eluted with $NaBH_4$ in presence of HCl. Hg^0 is produced and then measured by cold vapor atomic absorption spectrometry (CV AAS). Hg_{org} does not interact with the resin and is mixed with $NaBH_4$ at the exit of the column producing volatile species of Hg that are then amalgamated by a gauze of Au/Pt. Mercury is removed from the gauze by heating to 600 °C and subsequently measured by CV AAS. For Hg_{inorg} and Hg_{org} speciation in urban landfill leachate, the samples are centrifuged, filtered and treated with HCl. The detection limits (3 s) of Hg_{inorg} and Hg_{org} are 9 and 12 ng L^{-1} of Hg, respectively. The analysis frequency is 22 h^{-1}.

Keywords: mercury speciation, landfill leachate; flow analysis, ion exchange, amalgamation, CVG AAS

Introduction

In several countries, the urban waste is usually discarded in landfills, producing toxic leachate and toxic gases. The rainwater percolation through the residues and its inherent aqueous fraction comprise the leachate, which is characterized by high concentration of organic matter, salts, suspended particles and toxic elements.[1,2] Mercury is one of the elements often present in landfill leachate and become an environmental problem.[3]

Inorganic Hg (Hg_{inorg}), mainly as Hg^0 and Hg^{2+}, is generally disposed in urban landfills,[4] where it can associate to colloidal particles, complex with organic matter and/or bind to sulfides.[5] Under anaerobic conditions a significant fraction of Hg is transformed into more toxic species. Inorganic mercury may be transformed to other toxic species in landfill, such as methyl mercury, ethyl mercury and phenyl mercury.[6] However, the concentrations of ethyl mercury and phenyl mercury are very low and usually not detected by conventional techniques. Despite the possibility of formation of many organic and inorganic compounds of Hg in the environment, methyl mercury is usually the most abundant Hg_{org} species found in environmental samples,[7-9] whereas Hg^{2+} is the main Hg_{inorg} species.

The levels of total Hg (Hg_{tot}) in the leachate are generally lower than 1 µg L^{-1}.[4] Works related to speciation of Hg in gases emitted from landfills have already been published[7,8] but few dealt with Hg speciation in landfill leachate.[10] Mercury speciation in this kind of sample is a challenging task owing to low Hg species concentration.

Speciation analysis usually involves a step of separation, in which the element species are generally separated by liquid-liquid extraction[11-13] or solid phase extraction (SPE).[14-18] SPE has been frequently used in conjunction

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with flow injection systems (FI), allowing on-line analyte pre-concentration and matrix separation, which also reduces contamination and loss of analyte. It is worth mentioning that these features are very important when low concentration of a given species is determined. Gas chromatography[19-21] or liquid chromatography,[22] combined with element-selective techniques, such as atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS) or inductively coupled plasma mass spectrometry (ICP MS) have been used to measure the concentration of Hg species.

Several methods have been proposed for pre-concentration of Hg/matrix separation, such as amalgamation[23,24] or sorption of complexes of Hg by resins placed inside columns.[17,18,25-27] Stable complexes of Hg are produced by reaction of Hg_{inorg} with anions, such as SCN^-, CH_3COO^-, I^-, Br^- and Cl^-. The anionic complexes of Hg produced are strongly held by anion exchange resin, while Hg_{org} species typically produce neutral compounds in the presence of these anions and are not retained. Consequently, the separation of Hg_{inorg} and Hg_{org} is possible.[16,17,26,27] Anionic chlorocomplexes of Hg (mainly $[HgCl_3]^-$, $[HgCl_4]^{2-}$ and $[HHgCl_4]^-$) are produced in HCl medium and retained in columns packed with Dowex 1-X8 or IRA 400.[17,26,27] Thiourea, L-cysteine, $SnCl_2$ and $NaBH_4$ can be used for elution of Hg from the resin.[16,17,27]

In this work we propose a new approach to speciation of Hg_{inorg} and Hg_{org}, using a sequential and selective retention of chlorocomplexes of Hg_{inorg} by anion-exchange resin and amalgamation of Hg_{org}. $NaBH_4$ is used to remove the Hg from the anion-exchange resin (in a column), while the amalgamated Hg_{org} (in an Au/Pt gauze) is removed by heating. The speciation and pre-concentration of Hg_{inorg} and Hg_{org} are on-line performed, whereas both Hg_{org} and Hg_{inorg} are determined, allowing better accuracy and precision. The proposed method is applied to the speciation of Hg_{org} and Hg_{inorg} in urban landfill leachate. In this work, all Hg species that do not interact with the anion exchange column and react with sodium tetrahydroborate producing volatile Hg species, which are then amalgamated by the gold gauze, are considered as Hg_{org}.

Experimental

Reagents

All chemicals used throughout this work were of analytical reagent grade. Ultra pure water (18.2 MΩ cm) was obtained from a Milli-Q (Millipore, USA) system. The carrier gas used was 99.996% argon from White Martins, Brazil.

Sodium tetrahydroborate ($NaBH_4$ from Vetec, Brazil) solution was prepared fresh daily by dissolving the reagent in 0.05% (m/v) sodium hydroxide (NaOH from Merck, Germany). Hydrogen peroxide (H_2O_2), hydrochloric (HCl) and nitric (HNO_3) acids (all from Merck) were used. These acids were further purified by sub-boiling distillation in quartz still (Milestone, DuoPur, Italy) for the samples and analytical solutions preparation. A 1000 mg L^{-1} Hg^{2+} stock solution (from Merck) was used; solutions ranging from 50 to 1500 ng L^{-1} Hg^{2+} were prepared in 1.0 mol L^{-1} HCl by serial dilutions of the Hg^{2+} stock solution. A Hg_{org} stock solution containing 100 mg L^{-1} (as Hg) was prepared from CH_3HgCl (Aldrich, USA). The CH_3HgCl was firstly dissolved in 1 mL of methanol and then the desired volume was completed by addition of 1.0 mol L^{-1} HCl. Calibration solutions of Hg_{org} ranging from 50 to 2500 ng L^{-1} of Hg were prepared in 0.5 mol L^{-1} HCl mediun, by serial dilutions of the CH_3HgCl stock solution. Fresh Hg^{2+} and CH_3HgCl calibration solutions were prepared whenever used.

A strongly basic anion resin (Dowex 1-X8) in chloride form was used to separate and pre-concentrate the Hg_{inorg}. The resin particles diameter was in the range of 100 to 200 mesh. A small column was prepared by putting 30 mg of this resin inside a polyethylene tube (10 mm length and 3 mm i.d.), whose ends were sealed with polyurethane foam. This column allowed at least 200 cycles of pre-concentration/separation.

A small column (from PerkinElmer, Norwalk, USA) containing a gauze of Au/Pt inside was used to retain and pre-concentrate the Hg_{org}.

All the glass and plastic materials used were thoroughly washed with a HNO_3 10% (v/v) solution. After that, they were rinsed with distilled water and left to dry in clean environment.

Instrumental

A flow injection-vapor generation system coupled to an atomic absorption spectrometer was used for on-line separation, pre-concentration and determination of the Hg species. A Vario 6 FL atomic absorption spectrometer (AnalytikJena, Jena, Germany) equipped with a quartz cell (100 mm length and 10 mm i.d.) and deuterium background corrector was used. A Hg hollow cathode lamp operated at 4.0 mA was used as radiation source. The wavelength was set at 253.7 nm and the spectral band pass at 0.8 nm. All measurements were made by integrated absorbance (peak area).

The total concentration of Hg in the solid and liquid phases of the landfill leachate samples was determined by cold vapor generation-atomic absorption spectrometry in batch mode; the hydride generating system HS 5 from AnalytikJena was used. In this case, conditions recommended by the manufacturer of the instrument were used. A microwave oven (Multiwave 3000, Anton Paar, Austria) and a centrifuge (Sigma 3K30, Germany) were used to prepare the samples.

Flow injection-cold vapor generation system

The flow injection-cold vapor generation (FI-CV) system used (Figure 1) consists of a peristaltic pump (Gilson, Minipuls 3, France), four three-way solenoid valves (Cole-Parmer, USA), a gas flow-meter (Key Instruments, USA) and two columns; one contains the ion exchange resin (IEC) and the other contains the gauze of Au/Pt. Tygon tubes with different internal diameters were used to pump the solutions through the FI system. Tubes of polytetrafluorethylene (PTFE), with 0.8 mm i.d., were used to carry the solutions through the FI system. Two home-made gas/liquid separators [GLS_1 (a glass tube, 100 mm length and 10 mm i.d.) and GLS_2 (a glass tube, 40 mm length and 7 mm i.d.)] were used. The GLS_2 was used only for the purpose of retaining drops of water that could reach the column of amalgamation and/or the quartz cell. With the introduction of the second gas-liquid separator, it was not necessary to use any desiccant agent that could retain the analyte and lead to incorrect results. Sequential separation, pre-concentration and determination of Hg_{org} and Hg_{inorg} in the same aliquot of the sample were possible by using the FI system shown in Figure 1.

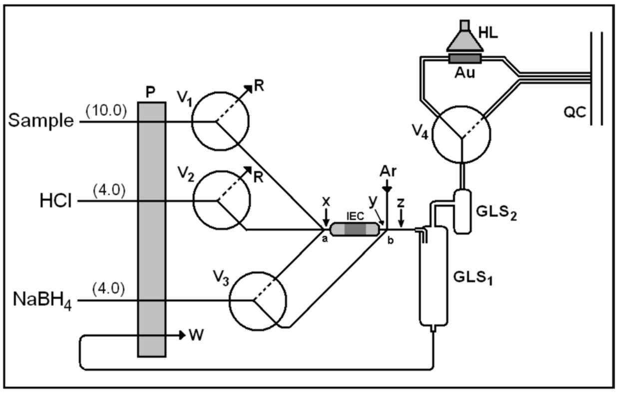

Figure 1. FI-CV system used for Hg_{org} and Hg_{inorg} speciation. P: peristaltic pump; V_1, V_2, V_3, and V_4: three-way solenoid valves; IEC: ion-exchange column; Au: Au/Pt amalgamation column; Ar: argon; GLS_1 and GLS_2: gas/liquid separators; HL: halogen lamp; QC: quartz cell; R: sample or reagent solution recycling; W: waste; x: 10 mm; y: 10 mm; z: 100 mm; **a** and **b**: confluences. Numbers in parenthesis indicate the solutions flow rate, in mL min^{-1}. Dotted line means the valve is closed in that direction.

Hg separation and pre-concentration procedure

Standard solutions containing 500 ng L^{-1} Hg (as Hg_{inorg} or Hg_{org}) were firstly used in order to evaluate the performance of the FI-CV system. The Hg solutions were acidified with HCl (the final concentration of HCl was 1.0 mol L^{-1}) and then passed through the IEC column (Figure 1). Only Hg-chlorocomplexes are retained by the resin inside the IEC, while the CH_3HgCl does not interact and passes directly through the column. When exiting this column, the effluent is mixed with a solution of $NaBH_4$ (at **b** in Figure 1), producing volatile species of Hg. The volatile Hg species produced are carried by argon to the amalgamation column where they are retained. Thus, Hg^{2+} (Hg_{inorg}) and CH_3HgCl (Hg_{org}) are separated and also pre-concentrated.

After a given period (60 s in this work) of pre-concentration and separation, the Hg^{2+} is removed from the IEC column by a $NaBH_4$ solution in presence of HCl (the $NaBH_4$ and HCl solutions are on-line mixed at confluence **a** in Figure 1). Hg^0 is produced and then transported by argon to the quartz cell (QC in Figure 1) of the atomic absorption spectrometer where the absorbance is measured. Next, the volatile Hg species that were retained in the amalgamation column are removed in the form of Hg^0 by heating to 600 °C. A halogen lamp (HL in Figure 1) placed 1 cm above the column is used for that purpose. The Hg^0 produced is carried to the quartz cell (QC in Figure 1) by Ar where the absorbance is measured. The FI system operation program is summarized in Table 1.

Table 1. Program of FI system operation and respective functions

Time (s)	Valve (on)	Function
0 -10	V_2	IEC[a] conditioning
11 - 71	V_1, V_4	Separation and pre-concentration of Hg species. The Hg_{inorg} is retained in the IEC and the Hg_{org} in the amalgamation column
72 - 82	V_2	IEC cleaning
83 - 123	V_2, V_3	Reductive elution of Hg_{inorg} from IEC and Hg measurement
124 - 164	V_4	Thermal removal of Hg_{org} from Au/Pt gauze and Hg measurement

[a] IEC: ion exchange column

Samples

Landfill leachate samples were collected in 1 L amber glass flasks. After collection, the samples were kept in refrigerator (temperature around 4 °C) until the determination of Hg, which was carried out up to 6 h after collection. The samples were collected in two stabilization ponds that contain the leachate produced by the municipal landfill. Household waste had been disposed in this landfill for 30 years. The stabilization ponds are about 0.5 m depth, while the area comprises 1000 m^2. The mean values of pH, suspended solids and DQO of the collected samples were 7.90 ± 0.20, 340 ± 62 mg L^{-1} and 2480 ± 420 mg L^{-1} O_2, respectively.

Total Hg determination in landfill leachate

Owing to the presence of suspended solid particles, the leachate was centrifuged for 10 min at 15,000 rpm. The supernatant was removed and filtered through a 0.45 µm pore size-filter. The particles retained by the filter were removed with 6.0 mol L^{-1} HNO_3 and then added to the solid fraction that had previously been separated by centrifuging. The liquid and solid fractions thus obtained were digested separately in pressurized quartz vessels in microwave oven.

Aliquots of 20 mL of the liquid fraction or the solid fraction were transferred to separate quartz vessels, to which 6 mL of concentrated HNO_3 and 1 mL of H_2O_2 (30%) were added. For recovery tests, aliquots of the samples were spiked with 50 ng of Hg (in the form of Hg^{2+} or CH_3Hg^+) and then subjected to the same treatment. The quartz vessels were closed and then heated for 10 min at 1000 W and 5 min at 1200 W. Blanks were prepared in the same way. After cooling, the solutions volume was completed to 50 mL with water and then the total concentration of Hg (Hg_{tot}) was determined by CV-AAS.

Mercury speciation in urban landfill leachate

The speciation of Hg_{inorg} and Hg_{org} was done separately in the liquid and solid fractions of the landfill leachate, following the procedure schematized in Figure 2. In summary, 25 mL of the liquid phase were transferred to a 50 mL polyethylene flask and the volume completed by addition of 2.0 mol L^{-1} HCl. The final solution was then processed in the FI-CV system coupled to the atomic absorption spectrometer. The solid fraction (about 30 mg) was tansferred to a 50 mL polyethylene flask to which 10 mL of 6.0 mol L^{-1} HCl were added. The mixture was gently shaken and then heated in microwave oven for 3 min at 60 W.[28,29] After reaching the room temperature, the volume of the mixture was completed to 50 mL with water and then centrifuged at 15,000 rpm for 15 min. Hg_{org} and Hg_{inorg} were measured in the supernatant. Blanks were prepared in the same way as samples. The accuracy was checked by addition of 20 ng of Hg (as CH_3Hg^+ or Hg^{2+}) to 30 mL of leachate, which was then subjected to the same treatment above described. It is important to emphasize that there is no appropriate certified reference material available for landfill leachate. Therefore, recovery tests for CH_3Hg^+ and Hg^{2+} and total Hg determination were used to check the accuracy.

Results and Discussion

Hg_{inorg} preconcentration

The retention of Hg_{inorg} in the IEC column is influenced by the concentration of HCl in the sample solution, because the HCl is required to form the main anionic chlorocomplexes of Hg that are retained in the column. These complexes have high affinity with anionic resins such as Dowex 1-X8, feature that allows the separation of Hg_{inorg} and Hg_{org}. According to Figure 3, the Hg^{2+} absorbance increases with the HCl concentration increasing up to 0.1 mol L^{-1} and then remains constant. However, it was observed that the accuracy was improved when the concentration of HCl was in the range of 0.5 to 1.0 mol L^{-1}. Moreover, formation of precipitate was observed in HCl medium if the acid concentration was 2.0 mol L^{-1} or higher than this, probably due to the presence of organic compounds. Therefore, the concentration of HCl in the sample and solutions of Hg^{2+} was fixed in 1.0 mol L^{-1}.

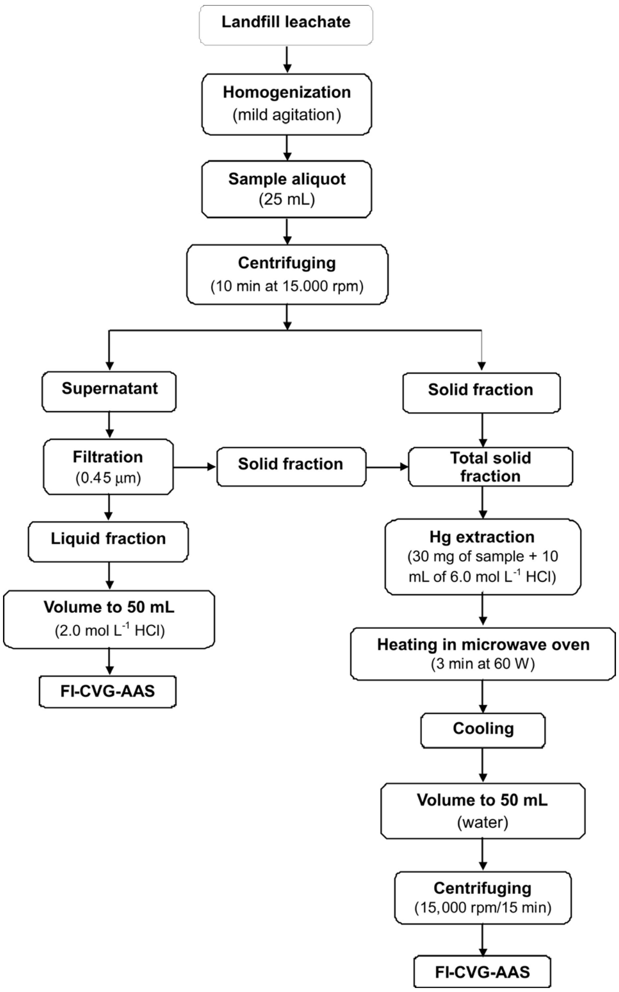

Figure 2. Sample preparation procedure for Hg_{org} and Hg_{inorg} speciation in urban landfill leachate.

Regarding to the sample flow rate, it was observed that the Hg^{2+} signal was nearly the same in the range of 2.5 to 15.0 mL min^{-1} (Figure 3). However, if the sample flow rate was higher than 10 mL min^{-1} the precision was worse (RSD higher than 10%).

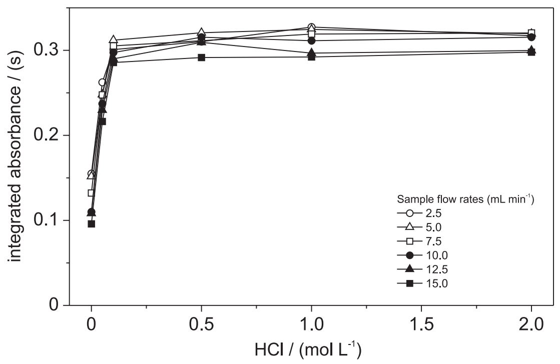

Figure 3. Influence of HCl concentration on Hg^{2+} pre-concentration. Hg^{2+} solution concentration 500 ng L^{-1}; $NaBH_4$ (0.1% m/v) and HCl (3.0 mol L^{-1}, used for Hg elution) solutions flow rate: 3 mL min^{-1}; carrier gas flow rate: 100 mL min^{-1}.

Hg_{inorg} elution

Mercury elution from the Dowex 1-X8 resin is difficult because of the strong interaction between the Hg chlorocomplexes and the resin. Few reagents are suitable for the elution; only those who have high affinity with the Hg_{inorg} or are able to convert the Hg_{inorg} chlorocomplexes into other species of Hg are feasible. L-cystein or mixture of $SnCl_2$ and HCl have been proposed[16,17,26] for removing Hg from the Dowex 1-X8 resin.

A mixture of $SnCl_2$ (10% m/v) and HCl (2.0 mol L^{-1}) was investigated in the present work. Unfortunately, it took more than 180 s to finish the Hg elution from the IEC column. $NaBH_4$ and HCl were then investigated, whose solutions were on-line mixed in the FI system (confluence **a** in Figure 1). In this case, the elution of Hg_{inorg} was completed within 60 s, but it was necessary to adjust the concentration of $NaBH_4$ because of hydrogen production, which deteriorated the sensitivity and stability of the FI-CV system. In order to overcome this drawback, the $NaBH_4$ and HCl solutions concentrations were investigated individually. Sensitivity, time for analyte elution and stability of the FI-CV system were taken into account. According to Figure 4, the highest sensitivity is observed for HCl when its concentration is about 3.0 mol L^{-1}. The $NaBH_4$ concentration influence on Hg_{inorg} is also depicted in Figure 4, where we can note that the highest signal is obtained when the concentration of $NaBH_4$ is 0.1% (m/v). The analyte signal decreasing as a function of reductand increasing may be due to the greater quantity of hydrogen produced, which dilutes the Hg vapor cloud in the quartz cell.

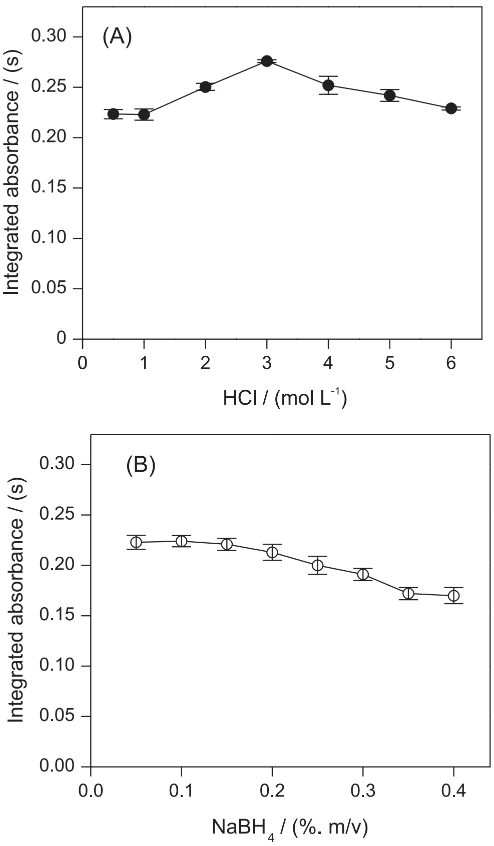

Figure 4. Influence of HCl and $NaBH_4$ concentration on Hg^{2+} elution. Hg^{2+} solution concentration: 500 ng L^{-1} in 1.0 mol L^{-1} HCl; $NaBH_4$ and HCl solutions flow rate: 3 mL min^{-1}; sample flow rate: 10 mL min^{-1}; carrier gas flow rate: 100 mL min^{-1}. In (A) $NaBH_4$ 0.1% (m/v) and (B) HCl 3.0 mol L^{-1}.

The influences of HCl and $NaBH_4$ solutions flow rate (mixed in confluence **a** in Figure 1) to elute Hg from the IEC column were investigated. It was observed that the absorbance was almost the same when the flow rates ranged from 1 to 6 mL min^{-1}. The argon flow rate was also investigated and the best performance was observed for a flow rate of 100 mL min^{-1}. Small drops of water were transported to the quartz cell at higher argon flow rate, hampering the correct determination of Hg. Moreover, tailed peaks were observed if the gas flow rate was less than 50 mL min^{-1}. All established conditions are summarized in the Table 2.

Hg_{org} preconcentration

As previously discussed, organic Hg species produce neutral compounds in presence of HCl and do not interact with anion exchanger resins. In the present work, after passing through the IEC column, the Hg_{org} was transformed into volatile species and then amalgamated by the Au/Pt gauze (Figure 1). Parameters that influence on the generation of volatile Hg_{org} species, their amalgamation, releasing from the Au/Pt gauze and transportation to the quartz cell were investigated. The best conditions were then established (Table 2). At the conditions shown in Table 2, the effluent of the IEC column containing Hg_{org} and HCl (1.0 mol L^{-1}) was merged with a 0.1% (m/v) $NaBH_4$ solution at a flow rate

Table 2. Conditions for Hg_{inorg} and Hg_{org} speciation using FI-CVG AAS

Parameter	Investigated	Established	
		Hg_{inorg}	Hg_{org}
HCl concentration in the sample, mol $L^{-1\,a}$	0 - 2.0	1.0	1.0
$NaBH_4$ concentration, % (m/v)	0.05 - 0.4	0.1	0.1
HCl concentration, mol $L^{-1\,b}$	0.5 - 6.0	3.0	3.0
Sample flow rate, mL min^{-1}	2.5 - 15	10	10
$NaBH_4$ and HCl solutions flow rate, mL min^{-1}	1.0 - 6.0	4.0	4.0
Argon flow rate, mL min^{-1}	50 - 300	100	100
Temperature for Hg_{org} desorption, °C	300 - 800	-	600
Pre-concentration time, s		60	60
Sample throughput, h^{-1}		22	22
Characteristic mass, ng		80	85
Calibration curve, ng L^{-1}		50 - 1500	50 - 1500
Limit of detection, ng L^{-1}		9	12
Calibration curve^c		y = 0,00051.x – 0,0013	y = 0,00042.x + 0,0071
Correlation coefficient of calibration curve (r)		0.998	0.995
Relative standard deviation, %		< 7	< 5

^{a}For Hg_{org} volatile generation and Hg_{inorg} retention; ^{b}IEC conditioning and Hg_{inorg} elution; ^{c}y: integrated absorbance (s); x: s (ng $L^{-1})^{-1}$

of 4.0 mL min^{-1}. The volatile Hg_{org} species produced were then transported to the Au/Pt column by argon at a flow rate of 100 mL min^{-1}. Next, the retained Hg was removed from the gauze by heating at 600 °C. Under catalytic influence of the noble metals (Au and Pt) the organic gaseous mercury species are decomposed and then amalgamated.[29] Thus, prior decomposition of the volatile Hg species for Hg^0 production and subsequent amalgamation is not required.

The influence of $NaBH_4$ concentration was also investigated for CH_3Hg^+ (not shown in Figure 4) and it was observed that the analyte signal increased in presence of up to 0.1% (m/v) $NaBH_4$, remaining constant at higher concentrations. In previous studies[28,30] it was observed the CH_3Hg^+ signal was negligible at low $NaBH_4$ concentration but reached a maximum in presence of 0.75% (m/v) $NaBH_4$. However, in those works the $NaBH_4$ had to be sufficient to transform the entire CH_3Hg^+ to Hg^0 in order to be detected by AAS. In the present work, the volatile Hg species (mainly CH_3HgH) are previously reduced to Hg^0 by the noble metals (Au/Pt in the amalgamation column)[29] prior to the determination by AAS. As a consequence, a lower amount of $NaBH_4$ is needed. In addition, the same solution of $NaBH_4$ (fixed in 0.1% m/v) can be used for both Hg_{inorg} and Hg_{org} determination.

Influence of Hg species concentration

Organic and inorganic Hg species are present in different concentrations in the sample and each one can influence the separation of the other. The influence of the concentration of each species on the separation was investigated by setting up the concentration of Hg^{2+} in 100 ng L^{-1} and increasing the concentration of CH_3Hg^+ and *vice versa*. According to Figure 5, one Hg species do not affect the separation of the other for concentrations of 1500 ng L^{-1} Hg_{inorg} or Hg_{org}. It was also observed that the capacity of the IEC and amalgamation columns used were limited to 40 ng of Hg^{2+} and 65 ng of Hg (in the form of CH_3HgCl), respectively.

Determination of Hg in landfill leachate

For Hg_{inorg} and Hg_{org} speciation, the liquid fraction of the samples was acidified with HCl, while the solid fraction was acidified with HCl and heated in microwave oven[30] in order to extract the Hg species, as summarized in Figure 2. The concentrations of Hg_{inorg} and Hg_{org} determined in both fractions are shown in Table 3. We can see that the sum of Hg_{inorg} and Hg_{org} determined by using the proposed speciation method is in agreement with the concentration of Hg_{tot} determined by CV AAS. Moreover, the recoveries of the spiked Hg^{2+} and CH_3HgCl are in the range of 98 to 105%. These results demonstrate the reliability of the proposed method for Hg speciation. It is also important to note in Table 3 that the ratio of H_{org} to Hg_{tot} in both fractions of the sample is expressive, showing that the Hg_{inorg} may be converted to more toxic species of Hg in municipal landfills. The concentrations of methyl mercury found in the liquid fraction of the leachate samples analyzed in the

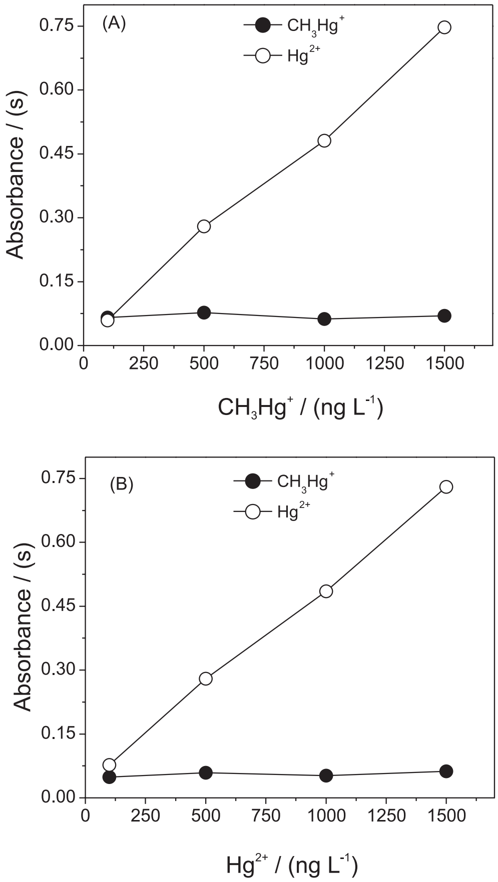

Figure 5. Influence of CH$_3$Hg$^+$ concentration on Hg^{2+} separation (A) and Hg^{2+} on CH$_3$Hg$^+$ separation (B). In (A) the Hg^{2+} concentration was fixed in 100 ng L^{-1} while that of CH$_3$Hg$^+$ was varied. In (B) the CH$_3$Hg$^+$ was fixed in 100 ng L^{-1} (as Hg) and that of Hg^{2+} was varied. All solutions were processed at the established conditions shown in Table 2.

present work are in the same order of magnitude of those found by Öman and Junestedt.[10] However, these authors did not detect methyl mercury in the solid fraction of the leachate samples.

The detection limits of Hg$_{inorg}$ and Hg$_{org}$ were 9 and 12 ng L^{-1} (as Hg), respectively. They were obtained from 3s criteria, being s the standard deviation of 10 replicates of the blank, treated in the same way as samples and sequentially measured. The main characteristics of the proposed Hg speciation method are shown in Table 2.

Conclusions

A novel method combining ion exchange and amalgamation was developed for speciation of Hg$_{inorg}$ and Hg$_{org}$ by CV AAS. The pre-concentration and speciation of Hg$_{inorg}$ and Hg$_{org}$ in urban landfill leachate, a complex matrix, is possible by using the proposed method. The sample preparation is relatively simple, provided that care is taken in order to avoid the Hg species modification. The speciation of Hg$_{inorg}$ and Hg$_{org}$ can be carried out in less than 3 min. The pre-concentration and especiation made on-line avoids losses of volatile species of Hg and contamination, while the consumption of reagents is low. The sample preparation, analyte pre-concentration and elution can be made by using only HCl and NaBH$_4$, which reduces the production of waste. Moreover, the determinations of Hg$_{org}$ and Hg$_{inorg}$ can be made sequentially in the same sample aliquot. Elution of Hg from the anion exchanger resin is fast and memory effects are reduced with the use of NaBH$_4$.

It was found that the ratio of Hg$_{org}$ to Hg$_{tot}$ in the urban landfill leachate is expressive, revealing a possible conversion of Hg$_{inorg}$ to more toxic Hg species.

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Table 3. Mercury concentration in liquid and solid fractions of landfill leachate. Values are the mean and standard deviation of 3 sample replicates

Samples		Hg$_{tot}$[b] (digested sample)	Hg$_{inorg}$[c]	Hg$_{org}$[c]	Hg$_{tot}$[c] (Hg$_{inorg}$ + Hg$_{org}$)	Agreement[d] (%)
1	Liquid fraction (ng L^{-1})	289 ± 7	213 ± 6	61 ± 2	274 ± 6	95
	Solid fraction[a] (ng g^{-1})	727 ± 12	472 ± 9	217 ± 4	689 ± 10	95
2	Liquid fraction (ng L^{-1})	273 ± 12	201 ± 8	65 ± 3	266 ± 9	97
	Solid fraction[a] (ng g^{-1})	740 ± 15	465 ± 11	206 ± 9	671 ± 10	91
3	Liquid fraction (ng L^{-1})	270 ± 14	194 ± 10	52 ± 5	246 ± 11	91
	Solid fraction[a] (ng g^{-1})	695 ± 17	486 ± 13	221 ± 12	671 ± 18	102

[a] Dry weight at 105 °C; [b] Determined by CV AAS; [c] Determined by the proposed FI-CV AAS method; [d] Calculated from the mean values of Hg$_{tot}$ and the sum of Hg$_{inorg}$ + Hg$_{org}$

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