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Article

Flow System for Pre-Concentration and Spectrophotometric Determination of Reactive Mercury

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Um novo sistema em fluxo é apresentado com a finalidade de pré-concentrar e determinar o mercúrio reativo em efluentes. O sistema é baseado na redução do mercúrio reativo presente em 500 mL de amostra com uma solução de Sn(II). O mercúrio reduzido é arrastado por uma corrente de argônio que passa por um tubo de vidro (comprimento de 60 cm, e diâmetro interno de 3 mm) inclinado a 15º. A superfície interna desse tubo é recoberta previamente com um filme líquido de uma solução oxidante contendo H_2O_2 (12%, m/v) e HNO_3 (3,0 mol L^{-1}) produzida após a introdução e passagem de um monossegmento líquido contendo esses reagentes. O Hg^0 arrastado sofre um processo oxidativo e o Hg(II) formado é retido no filme. Após 10 minutos de arraste o fluxo de argônio é interrompido e um monossegmento (350 μL) contendo PAR [4-(2-piridilazo) resorcinol], 1,0 x 10^{-3} mol L^{-1} em tampão amônia / cloreto amônio (4,0 mol L^{-1}; pH 9,0) é introduzido e passa através do tubo de vidro. Um complexo fortemente colorido é formado entre o PAR e o Hg(II) o qual é levado ao sistema de detecção constituído por um diodo emissor de luz (LED, $\lambda_{máx}$ = 525 nm) e um detector fotodiodo. O tempo de processamento de uma amostra é de 12 min. O sistema é lavado e uma nova camada de líquido é formada, preparando o sistema para uma nova determinação. Esse método concentra a amostra 148 vezes e permite a obtenção de um limite de detecção de 0,16 μg L^{-1}.

A new flow system to pre-concentrate and determine reactive mercury in effluents by photometry is presented. The system is based on the reduction of the reactive mercury present in a 500 mL sample with a Sn(II) solution. The reduced mercury is swept out by an argon stream and carried to a straight glass tube (60 cm long, 3 mm i.d.) inclined in an angle of 15º. The inner surface of this tube has been previously covered by a renewable liquid layer of an oxidant solution containing H_2O_2 (12%, m/v) and HNO_3 (3.0 mol L^{-1}) produced after introduction and passage of a liquid monosegment containing those reagents. The swept Hg^0 undergoes an oxidative process and the Hg(II) formed is retained in the layer. After a 10 min sweep time interval the argon flow is stopped and a reagent monosegment (350 μL) containing PAR [4-(2-pyridylazo)resorcinol], 1.0 x 10^{-3} mol L^{-1}, in an ammonia/ ammonium chloride buffer (4.0 mol L^{-1}; pH 9.0) is introduced and passes through the glass tube. A strongly coloured complex between PAR and Hg(II) is formed and carried to the detection system composed of a light emitting diode (LED, λ_{max} = 525 nm) and a photodiode detector. Sample processing time is about 12 min. The system is washed and a fresh liquid layer is formed, preparing the system for a new determination. This method concentrates the sample by a factor of 148 and achieves a detection limit of 0.16 μg L^{-1}.

Keywords: reactive mercury, pre-concentration, spectrophotometry, flow analysis

Introduction

Reactive mercury corresponds to the fraction of mercury present in a sample that can be reduced by a Sn(II) solution under standard conditions of temperature and pH, producing metallic mercury. This fraction is usually composed of inorganic Hg(II) and labile organic mercurial compounds. The amount of reactive mercury present in this form has been used to indicate the toxic potential of effluents and the upper limit of concentration permitted has been established as 10 μg L^{-1} for effluents and 1 μg L^{-1} for drinking water.[1,2]

The majority of analytical methods employed for determination of reactive mercury are based on the generation of a cold vapour of mercury, produced by adding a reductant such as Sn(II) or sodium tetrahydroborate to the sample. The mercury is usually swept from the reaction flask and transported to a gas cell where its atomic absorbance is measured.[3-6] Cold

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vapour atomic absorption (CVAA) determination is sensitive and can give reproducible and accurate results. The method has been mechanised by using the flow analysis technique, with many contributions reported in the literature.[7-11] Perhaps the most sensitive method for mercury determination is that based on the atomic fluorescence of the cold vapour generated after metal reduction.[12-15] The technique is capable of determining reactive mercury down to few parts per trillion if pre-concentration on gold wires is employed.[16] However, both the absorption and fluorescence methods are prone to the effects of moisture carryover, which can cause water condensation followed by gradual loss of detectability and baseline drift.[17]

The literature reports various pre-concentration methods used to improve the detection limits of the CVAA method. Columns containing beads covered with metallic gold, capable of amalgamating Hg^0, have been employed to achieve detection limits below ng L^{-1}.[6,16-18] Higher pre-concentration factors, of about 1000, have been recently reported by collecting the mercury on active carbon powder which is filtered and determined using the slurry sampling electrothermal atomic absorption spectrometry.[19] The graphite furnace technique has been also applied after pre-concentration in a single drop of organic solvent. An outstanding pre-concentration gain of 15,000 was obtained.[20]

Spectrophotometric methods based on the formation of complexes with mercury ions usually lack in detectability and efforts toward pre-concentration of mercury have been described elsewhere.[21,22] Furthermore, spectrophotometric methods are prone to interferences which arise from concomitants (mainly other metal ions) that could affect the accuracy of the determination by promoting a side reaction with the chromogenic agent and/or by competing with mercury in the pre-concentration step. On the other hand, the spectrophotometric method is less expensive and can be developed to employ portable, low cost equipment. The overall cost per analysis can be reduced and in-field determinations can be implemented without the constraints imposed by the use of atomic absorption (CVAA or GFAAS) or atomic fluorescence, that require more sophisticated, expensive instrumentation with high power requirements.

This work describes a spectrophotometric method for determination of mercury which has been mechanised using the monosegmented flow analysis technique.[23,24] The sample, in the proposed system, is presented in a batchwise and initially processed by the system in a discrete form. The system described here includes a new approach to the pre-concentration and determination of reactive mercury by molecular photometry, which is free of interference and does not employ any organic solvent. The pre-concentration of the analyte is made by sweeping the reduced mercury and passing its vapour over a layer of reagent which re-oxidises and retains the mercury in a medium that is free of interfering concomitants, as far as the subsequent spectrophotometric detection reaction is concerned. A thin layer containing reagents has been previously employed with flow systems aiming to achieve larger pre-concentration factors for liquid-liquid extraction methods[25,26] and to promote a reaction between an analyte present in a gaseous sample and the liquid layer.[27] In these contributions an improvement in detectability has been reported as a result of the low liquid layer volume and the increase in the contact area between liquid phases.

The spectrophotometric method proposed requires a simple photometric instrument based on a light emitting diode (LED) and a photodiode detector. The method is suggested as an alternative for in-field determination of reactive mercury in effluents and tap water.

Experimental

Reagents

All reagents were of analytical grade. Bi-distilled, deionised water was used throughout. Solutions of oxidant (hydrogen peroxide in nitric acid) were prepared daily by dilution of a 30% (m/v) H_2O_2 stock solution. The addition of HNO_3 was made in line in the flow manifold.

The reductant solution was prepared by dissolving 23.8 g of $SnCl_2{\cdot}2H_2O$ in 100.0 mL of a 10% HCl solution. The solution is purged with pure nitrogen for 30 min before use.

The complexing reagent solutions were prepared with PAR (4-(2-pirydylazo)resorcinol) dissolved in the buffer solution.

NH_3 / NH_4Cl buffer solutions (pH 9.2) of various buffering strengths were prepared by mixing 8.0 mL of aqueous NH_3 with 2.0 mL of NH_4Cl solution, both at concentrations of 1.0, 2.0, 3.0, or 4.0 mol L^{-1} and then taking the final volume to 100 mL. This pH has been previously reported as the optimum value for the formation of the PAR-Hg(II) complex.[28]

A stock Hg(II) standard solution, containing 1,000 mg L^{-1} of the metal, was prepared by dissolving 1.3535 g of $HgCl_2$ in 1 L of 1% HNO_3 solution in a high density polyethylene flask. Successive dilutions were employed to prepare the working mercury solutions containing 0.5% HNO_3 (m/v), daily.

The flow system

Figure 1 shows the flow system proposed for pre-concentration and spectrophotometric determination of reactive mercury. All the three way solenoid valves (Neptune Research) are shown in the off state. The photometric detection system is made of a light emitting diode (LED) emitting at 525 nm and with a photodiode (RS-308067). A flow cell with 1.5 cm optical path was made of a glass tube of 2 mm inner diameter, bent in a "Z" form. The system is controlled by a micro-computer running a software written in VisualBasic 5.0 and employing a multifunction interface card (Advantech, PCL 711-S).

The fluids were pumped by an eight channel Ismatec peristaltic pump (model IPC – 78001-12) controlled by an RS-232 serial interface through the microcomputer.

The operation of the system consists of the following sequential steps (see Figure 1): (*i*) cleaning step: the three way valve V_1 is turned on and a stream of 0.1 mol L^{-1} of HNO_3 segmented by air is allowed to flow through the system for 30 s. V_1 is shut off and the remaining acid segments are swept out by the air carrier stream; (*ii*) preparation of the pre-concentration tube: valves V_3 and V_4 are turned on and 200 μL of the oxidant reagent, R_1, is injected into the system, passing through the inclined glass tube and forming a layer over the inner surface of the tube; (*iii*) mercury pre-concentration: the flask containing the sample is placed in the system and 2.0 mL of the Sn(II) solution is injected into it, using syringe S. Valves V_2, V_3, and V_5 are turned on. The Hg^0 formed is swept through the glass tube where it is re-oxidised and absorbed and pre-concentrated as Hg(II) in the oxidant liquid layer. After 10 min V_2 and V_3 and V_5 are turned off; (*iv*) mercury elution, reaction and detection: the injection port is moved to introduce 350 μL of the buffered PAR colour-forming reagent, R2, which passes through the glass tube, removing the Hg(II) by promoting the formation of the coloured complex, which is transported to the detector. The optical switch (OP) locates the front of this monosegment and informs the computer to start the data collection for a fixed time interval. A steady signal is obtained during segment passage through the flow cell.

The procedure re-starts at step (*i*) if more samples are being processed. The steps described above require analyst intervention only to place the sample and to add the Sn(II) reducing solution (in step *iii*). All the other operations are carried out under computer control.

CVAA determinations

Comparative determination of mercury in spiked industrial effluents and drinking water samples were performed as previously described by using a flow injection system coupled to a dedicated instrument for CVAA measurements. [9]

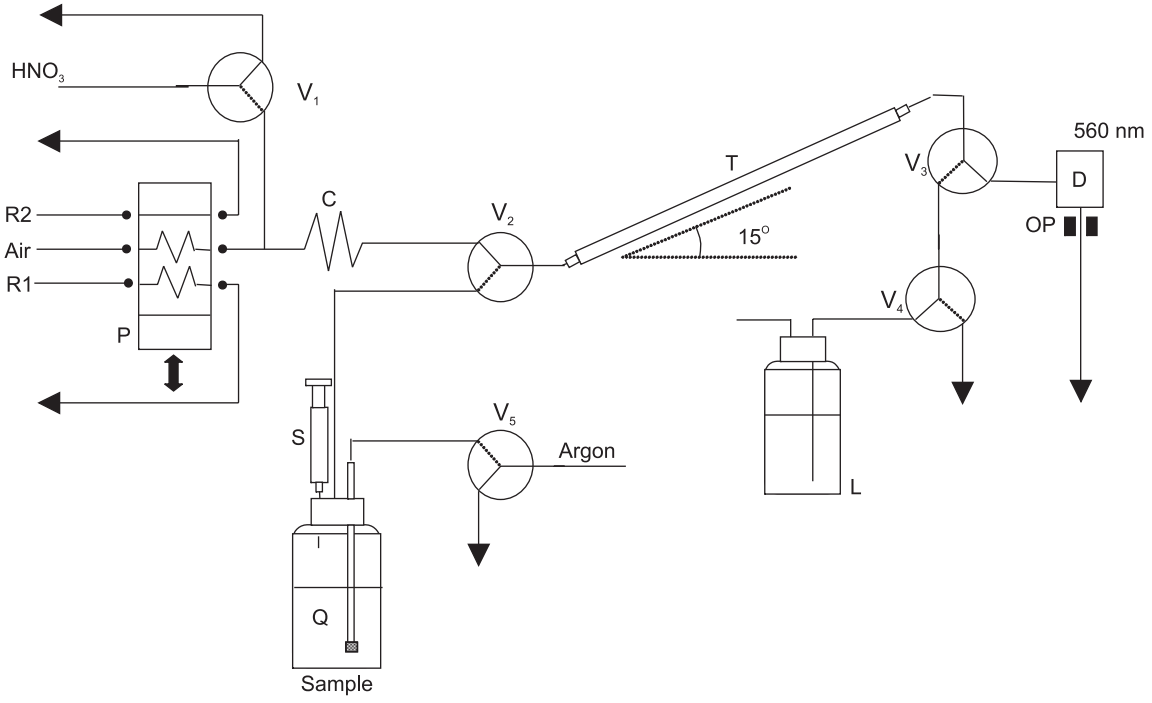

Figure 1. Schematic diagram of the proposed system for pre-concentration and spectrophotometric determination of reactive mercury. V_1-V_5, electromechanical three way valves; P, injection port; R1, PAR/Buffer reagent; R2, H_2O_2/HNO_3 reagent; S, 10 mL syringe; Q, synterised glass scrubber; T, glass tube; L, Hg^0 trapping solution (0.5 mol L^{-1} K_2CrO_4 in 1.0 mol L^{-1} H_2SO_4); D, spectrophotometric detector; OP, optical switch.

Results and Discussion

Initial experiments were carried out in order to verify the formation of the liquid layer on the wall of the glass tube. It was observed that reproducible deposition of the layer was attained after liquid monosegment passage by inclining the tube (with 3 or 5 mm inner diameter) at a angle of about 15° in relation to the plane of the bench. This angle shows the best performance to avoid draining the liquid layer from the internal tube wall.

Stability of the PAR-Hg(II) complex

The literature reports a high stability for the PAR-Hg(II) complex.[21] However, there is no information about its stability in a strong acid oxidising medium, where it will be produced in the proposed flow system. Therefore, the stability of the complex was investigated as a function of both the PAR and the buffer concentrations in the colour forming reagent, and the HNO_3 and H_2O_2 concentrations in the oxidising reagent layer. Table 1 shows the ranges of concentrations investigated.

Table 1. Concentration range of the reagents evaluated during the study of the stability of the PAR-Hg(II) complex

Reagent	Concentration range
PAR	1.0×10^{-4} – 1.0×10^{-3} mol L^{-1}
NH_3 / NH_4Cl buffer	1.0 – 4.0 mol L^{-1}
HNO_3	1.0 - 5.0 mol L^{-1}
H_2O_2	3 – 24% (m/v)

The complex PAR-Hg(II) was formed in a medium buffered at pH 9.2 employing standard solutions containing Hg(II) over the range of 1 to 10 mg L^{-1}. The formation of the complex is favoured by higher concentrations of PAR up to 1.0×10^{-3} mol L^{-1}. However, the blank, due reagent absorption, is also increased and, at that concentration, PAR is close to its solubility limit. Thus, the PAR concentration was fixed at 1.0×10^{-3} mol L^{-1}.

The effect of the strength of the NH_3 / NH_4Cl buffer at pH 9.2 was evaluated. 200 μL of the oxidizing reagent with the concentrations shown in Table 1 were injected in the glass tube. An oxidant/acidic liquid layer was formed on the glass tube wall. A monosegment of 350 μL containing the previously formed complex PAR-Hg(II) was injected and passed through the glass tube. It was observed that the concentration of the buffer must be higher than 3.0 mol L^{-1} in order to maintain the pH in the optimum range after passage of the segment through the glass tube. Thus, the concentration of the buffer was selected to be 4.0 mol L^{-1}. This concentration of the buffer maintains the pH of the PAR solution even if an oxidising solution containing up to 5.0 mol L^{-1} of HNO_3 is employed to produce the layer.

The H_2O_2 in the liquid layer does not impart any degradation of the PAR-Hg(II) complex when present up to a concentration of 28% (m/v), even if the oxidising solution presents an acid level as high as 3.0 mol L^{-1}.

The initial concentrations for further study and optimisation of the system were then established as: PAR 1.0×10^{-3} mol L^{-1}; buffer 4.0 mol L^{-1}; HNO_3 3.0 mol L^{-1}; and H_2O_2 6% (m/v).

Optimisation of the pre-concentration step

Once the initial concentrations of reagents and the stability of the PAR-Hg(II) complex were determined, the optimisation of the pre-concentration step was carried out.

Samples of 500 mL of a standard solution containing 25 μg L^{-1} of Hg(II) were employed for evaluation of the effect of the concentration of H_2O_2, HNO_3 and physical parameters such as flow rate, length and inner diameter of the glass tube and Hg^0 purge time interval. Steps 1 to 4 of the operating procedure described above were followed for evaluation of the effect of the parameters on the analytical signal. The reagent solution employed always contains PAR with a concentration of 1.0×10^{-3} mol L^{-1} in a 4.0 mol L^{-1} NH_3/NH_4Cl buffer. A volume of 350 μL of this solution was injected as a monosegment in order to extract and react with the mercury collected by the oxidant film during the pre-concentration operation.

Effect of the H_2O_2 and HNO_3 concentrations

Figure 2 shows the effect of changing these reagent concentrations on the analytical signal. Based on these results a concentration of 12% (m/v) and 3.0 mol L^{-1} of both H_2O_2 and HNO_3, respectively, were suitable for collecting the metallic mercury, converting it and retaining it as Hg(II). Thus, these concentrations were adopted for the further studies described below.

Effect of the diameter and length of the glass tube

Figure 3 shows the effect of changing the diameter and length of the glass tube on the analytical signal for mercury pre-concentration and determination. A tube 60 cm long, with a inner diameter of 3 mm, was selected.

Effect of the gas purge flow rate and purge time interval

It was observed that the argon flow rate did not significantly affect the analytical signal if it was kept in

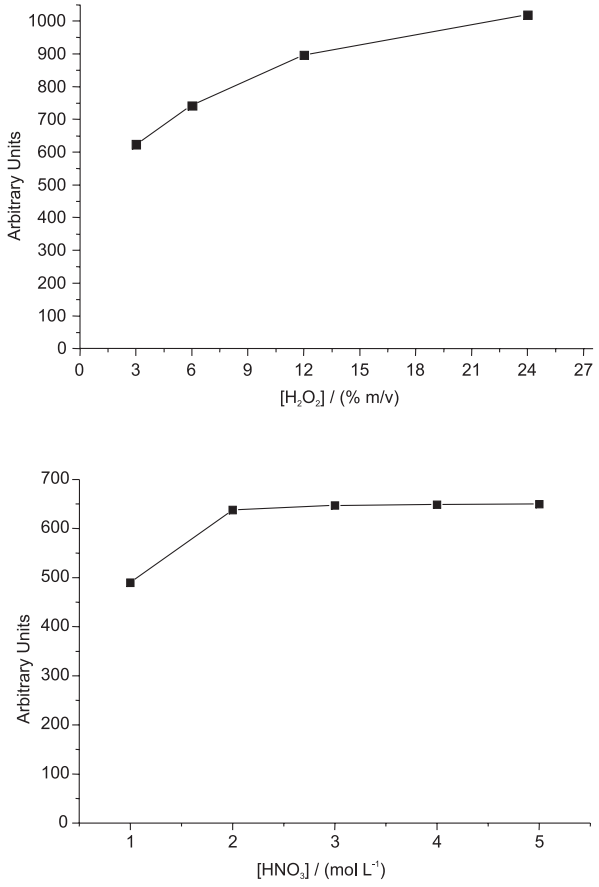

Figure 2. Effect of the H_2O_2 and HNO_3 concentrations on the analytical signal.

the range from 0.2 to 1.0 L min^{-1}. The purge time intervals must be higher than 10 min to ensure sufficient and reproducible removal of the Hg^0 from the sample after addition of the Sn(II) solution. The efficiency of Hg^0 removal also increases by employing a 5.0 mm diameter glass tube fitted with a porous sinterised glass plug immersed in the sample for the mercury purge.

Effect of re-extraction of the mercury pre-concentrated in the liquid layer

The four step procedure described above contemplates only one passage of the extracting/complexing (PAR at pH 9.2) reagent after the mercury has been re-oxidised and pre-concentrated in the reagent layer. An experiment was made to evaluate the effect of increasing the number passages of the same segment through the tube. This was accomplished by moving the extracting/complexing reagent monosegment forward and backward many times before it was finally directed to the detector for final measurement. Figure 4 shows that the spectrophotometric signal increases by incrementing the number of times the segment passes through the glass tube. In Figure 4, three

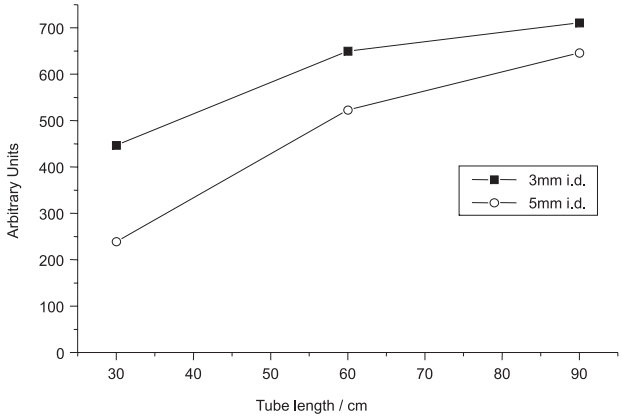

Figure 3. Effect of the glass tube dimensions on the analytical signal.

extractions mean that the monosegment was admitted to the glass tube, transported up to its end, moved back to the beginning of the tube and then moved forward again, passing the whole tube length three times, where the mercury has been collected by the oxidant liquid layer is present.

Effect of sample volume

Figure 5 shows the effect of changing the sample volume, containing 25 μg L^{-1} of Hg(II) on the analytical signal. A volume of 500 mL was selected as the best compromise between sample consumption and detectability.

Final analytical conditions

Based on the results reported above the experimental conditions shown in Table 2 have been selected. Using these experimental conditions, the detection limit (three times the blank (n=10) divided by the slope of the

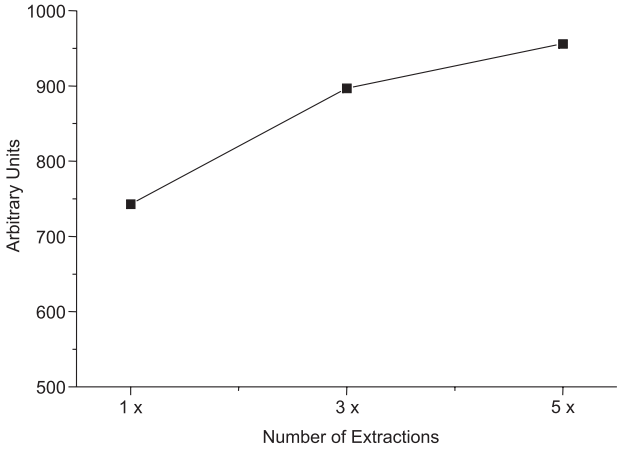

Figure 4. Effect of the number of extraction using the same reagent segment on the analytical signal.

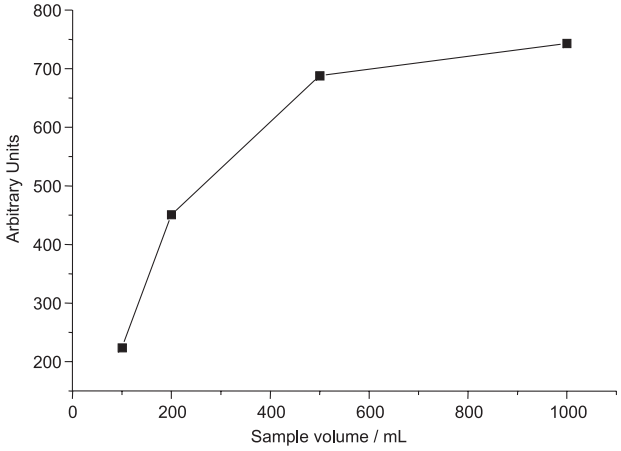

Figure 5. Effect of the sample volume on the analytical signal.

analytical curve) and the linear response range were 0.16 μg L^{-1} and 0.5 – 20 μg L^{-1}, respectively.

When the signals obtained for sample solutions containing 2.5 and 15 μg L^{-1} of mercury(II) were compared with the signal of a pre-formed PAR / Hg(II) complex using the same experimental conditions, it was possible to infer a pre-concentration factor of 148 times. It means, for instance, that a sample containing 10 μg L^{-1} of Hg(II) will produce a monosegment whose absorbance is equivalent to a PAR/Hg(II) complex obtained for a solution containing 1.48 mg L^{-1} of the metal ion. This represents a very good pre-concentration gain. However, a theoretical gain of 1,280 times in the original mercury concentration can be calculated by supposing a quantitative transference of the mercury present in sample to the liquid layer, whose volume was found to be equal to 41.6 μL, and its ideal distribution (homogeneous distribution of the metal in a total volume of the liquid layer plus that of the monosegment containing the PAR reagent, whose volume is 350 μL). It means that under the final experimental conditions recommended in this work the gain is only about 11% of the theoretical value.

The mass balance of the process was evaluated employing solutions containing 10 and 25 μg L^{-1} of Hg(II). The mercury remaining in the sample flask and that collected in the trap at the end of the pre-concentration glass tube were evaluated by CVAA.[9] The results for both concentrations investigated show that, after running the pre-concentration step, about 20% of the mercury stays in the sample flask while 45% was found in the trap. These results also permit estimating that about 35% of the mercury would be retained in the liquid oxidant layer. To investigate if this was true, the mercury present in the liquid layer was eluted with 350 μL of a 0.5 mol L^{-1} HNO_3 solution and the eluted volume was collected in a volumetric flask, diluted to 25 mL and measured by CVAA. The results shown that this fraction contains, in fact, about 30% of the mercury. Therefore, the extraction of the retained mercury with the alkaline PAR reagent solution is not as effective as an acid monosegment of the same volume. The amount extracted may be increased by performing multiple extractions of the retained mercury in the same monosegment, as shown in Figure 4. However, after 5 successive extraction there is a increase of only 30% in the analytical signal. This means that a large portion of the absorbed mercury is still retained on the glass wall and the alkaline reagent employed is not capable of recovering a significant portion of the metal, probably due the presence of silanol groups at the glass wall, due the high pH values employed, which can competitively retain the PAR-Hg(II) complex.

The use of acid eluate to remove the mercury from the glass tube can increase the metal recovery substantially. However, in the present work, this fact was not exploited because the detectability achieved with the alkaline reagent was sufficient for determination of the reactive mercury in the concentration ranges significant for effluent samples and because the use of an acidic eluent will add some unnecessary complexity to the flow manifold because the colour forming reaction will need to be processed after the segment leaves the glass tube. However, use of an acidic eluent solution could be the first step in the direction of an even more sensitive method for mercury determination.

Interference in the proposed method would come only from components in the sample matrix which could affect the reduction of Hg(II) because the re-oxidation, complex formation and spectrophotometric determination are performed in the absence of any concomitant originally present in the sample. The effect of concomitants on the reduction of Hg(II) by Sn(II) and recovery of the Hg^0 formed has been established elsewhere[29-31] and have not been repeated here. The effect of concomitants was previously

Table 2. Final experimental parameters for mercury determination

Sn(II) reductor solution volume / conc.	2.0 mL / 20% (m/v)
PAR / (NH_3/NH_4Cl buffer) / volume / flow rate	1.0 x 10^{-3} mol L^{-1} / 4.0 mol L^{-1}/ 350 μL / 2.0 mL min^{-1}
H_2O_2/HNO_3	12% (m/v) / 3.0 mol L^{-1}
Glass tube length / inner diameter / inclination	60 cm / 3 mm / 15°
Hg^0 purge time / argon flow rate	10 min / 0.5 L min^{-1}
Number of extractions	1
Sample volume	500 mL

observed for the presence of sulphide, chloride, copper and tellurium, for concentration levels that are not usually observed in effluent samples, the application for which this method has been developed.

Samples of industrial effluents and drinking water were analysed by the proposed system and the results show that the mercury concentration, if present, was below the detection limit of the proposed method. Therefore, the validation of the proposed method was carried out by spiking these samples and comparing the results with the standard CVAA method. The results are compared in Table 3 showing an acceptable agreement between the recoveries for both methods and allowing the conclusion that the proposed method can be used for routine determination of reactive mercury in industrial effluents.

Table 3. Comparative results for recovery of reactive mercury in spiked industrial effluent and tap water. Samples 3-5, 7 and 8 from effluent of a mercury recycling industry and samples 1, 2 and 6, tap water

	[Hg(II)] / (μg L^{-1})		
Sample	After spiking to	CVAAS*	Proposed system*
1	1.5	1.6 ± 0.1	1.5 ± 0.1
2	2.5	2.4 ± 0.2	2.3 ± 0.2
3	5.0	4.8 ± 0.1	4.7 ± 0.2
4	7.5	7.5 ± 0.1	7.5 ± 0.1
5	10.0	9.8 ± 0.2	9.6 ± 0.3
6	10.0	9.7 ± 0.2	9.3 ± 0.5
7	15.0	14.3 ± 0.4	15.2 ± 0.3
8	20.0	19.5 ± 0.7	18.7 ± 0.4

* Mean of three determinations ± estimate of the standard deviation.

Conclusions

A flow system employing a liquid monosegment of reagents is described, which is capable of pre-concentrating and determining reactive mercury in effluents using a simple photometric reaction with PAR. The determination reaction becomes substantially free of interference because mercury probably will be the only metal isolated from the matrix under the reducing conditions employed. A high gain was attained in detectability by pre-concentration in the reagent layer and an inexpensive photometer, based on a low cost LED/photodiode arrangement, is employed for the determinations. The system demands little power for its operation and can thus be useful for in field analyses while the operation is computer controlled.

About five samples can be processed per hour and the sample volume (500 mL) does not constitute a serious limiting factor, considering the abundance of efluent samples and recalling that larger samples may also be more representative.

The stability of the analytical curve was tested over a four months period. The acidic peroxide reagent needs to be prepared daily. However, the other reagent solutions are stable at least for one month. The slope and intercept values (in arbitrary units) of ten calibration curves change only from 121.04 to 125.68 and 1.79 to 6.48, respectively. This small change in the regression coefficients attests to the stability of the system and allows for simple maintenance of the calibration.

The detectability (detection limit of 0.16 μg L^{-1}), accuracy and precision achieved are sufficient for the purpose of the determining reactive mercury and are compatible with the accepted highest allowed concentrations of 10 μg L^{-1}. However, the pre-concentration gain could be improved in the future by searching for a better geometry of the glass tube, by finding more efficient reagents to form the oxidant layer on the glass tube wall and, as demonstrated here, by eluting the metal in a acidic medium. In addition, longer optical path flow cells could be used to improve even more the detection limit of the proposed method. [32, 33]

The system described and evaluated in this work does not intend to compete with other approaches, presenting higher detectability, such as atomic absorption and/or atomic fluorescence but offers a low cost alternative, which is field adaptable, and useful for most of the required mercury determinations.

The proposed system can also have application in many other determinations where a volatile analyte or a volatile compound can be swept out from the sample and carried to the pre-concentration tube, where a variety of reactions can be used to retain and to determine such substances. For instance, the use of this system for pre-concentration of species that can generate volatile hydrides for simple spectrophotometric and/or GFAA detection is presently being studied in the authors' laboratory as is being evaluated the miniaturisation of the system aiming to reduce sample consumption.

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