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Flow injection spectrophotometric method for chloride determination in natural waters using $Hg(SCN)_2$ immobilized in epoxy resin

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Abstract

A flow injection (FI) spectrophotometric method was proposed for the determination of chloride ion in natural waters. The determination of chloride was carried out by reaction with $Hg(SCN)_2$ immobilized in an epoxy resin bead in a solid-phase reactor (SPR) and the thiocyanate ions released were determined spectrophotometrically at 480 nm after complexing reaction with Fe(III). The analytical curve for chloride was linear in the concentration range from 5.6×10^{-5} to 2.2×10^{-4} mol l^{-1} with a detection limit of 1.4×10^{-5} mol l^{-1}. The relative standard deviation (R.S.D.) was 2.2% for a solution containing 2.2×10^{-4} mol l^{-1} ($n = 10$). The simple manifold allows a routine analytical frequency of 100 determinations per hour. The main advantage of the developed method is the 400% reduction of the Hg waste solution generated when compared to conventional methods for chloride determination based on the same spectrophotometric reaction.

Keywords: Chloride; Flow injection spectrophotometry; Solid-phase reactor; Green analytical chemistry

1. Introduction

Chloride is one of the most widespread analytes and its determination using simple and fast methods is necessary in different types of samples. Chloride determination based on flow injection systems (FI) has been based mainly on spectrophotometric procedures in which the reaction between mercury(II) thiocyanate and chloride leads to the displacement of thiocyanate and the formation of an intensely colored complex of Fe(III) [1–2]. This method is sensitive and selective, and several automatic and high sample throughput applications were reported [3,5]. Even though these methods have some favorable analytical characteristics, they require the use of a high concentration of mercury(II) in the reagent solution and this is not desirable from the viewpoint of clean chemistry. Therefore, efforts to replace it are recommended [6].

Flow injection methods implemented by using a solid-phase reactor (SPR) are mostly of the enzymatic type [7]. Most reported methods used expensive or unstable reagents that must be prepared fresh daily or assemblies including membranes that must be periodically cleaned and calibrated as their performance changes with time.

There is only one reference of a flow injection system for the determination of chloride using on-line solid mercury(II) thiocyanate minicolumns. Chloride was determined by quantifying the formed iron(III) thiocyanate using spectrophotometric detection. The linear response range was 2.8×10^{-5} to 8.5×10^{-4} mol l^{-1}. The sample throughput was 100 h^{-1} and the lifetime of the minicolumns was 50 injections [8].

Nowadays chemists are being trained to design products and processes with an increased awareness of their environmental impact. Outreach activities within the green chem-

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istry community highlight the potential for chemistry to solve many of the global environmental challenges we now face. The origins and basis of green chemistry chart a course for achieving environmental and economic prosperity inherent in a sustainable world [9].

Green chemistry involves the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances [10]. In addition to the reduced reagent consumption, the employment of solid-phase reagents also facilitates the storage of chemicals, reducing the risks of environmental accidents [11].

The work here described dealt with an alternative for the determination of chloride in natural waters. Chloride determination using flow injection methods has been mainly based on spectrophotometric procedures.

The immobilization approach used is based on the physical entrapment of the reagent via polymerization reactions of linear polystyrene chains. The immobilization procedure is fairly expeditious, simple and non-specific, and has found a new use for water insoluble solid reagents commercially available as fine powders as materials for making solid-phase reactors (SPRs) in a variety of configurations [7]. It should be mentioned that the direct packing of a column with an insoluble fine powder of a reagent is not usually feasible because it causes a pronounced increase of the hydrodynamic resistance.

2. Experimental

2.1. Apparatus

The FI assembly is depicted in Fig. 1. A peristaltic pump (Ismatec, model 7618-40) equipped with Tygon® tubes was employed to propel the carrier and solutions. The manifolds were built with polyethylene tubing (0.8 mm i.d.), except for the solid-phase reactor, which was constructed in PTFE tubing of 2.0 mm i.d. The sample introduction was carried out using a three-piece manual commutator.

The spectrophotometer was a UV–vis model 482 (Femto, São Paulo, Brazil), provided with a glass flow-cell (80 μl, 1.00 cm optical path).

A Varian Vista Axial (ICP-OES) was used to the determination of Hg in the waste solution.

2.2. Reagents and solution

All the chemicals used were of analytical-grade reagent and were prepared using Millipore (Bedford, MA, USA) Milli-Q water. Single analyte 1.00 g l^{-1} stock solutions were prepared from $Hg(SCN)_2$, NaCl, $Fe(NO_3)_3 \cdot 9H_2O$, KH_2PO_4, $NaNO_3$, $(NH_4)_2SO_4$, $NaNO_2$, Na_2CO_3 and $NaHCO_3$. Reference solutions within the ranges 1.0–10.0 mg l^{-1} $NO_3{}^-$, $NO_2{}^-$, $PO_4{}^{3-}$, $SO_4{}^{2-}$, $CO_3{}^{2-}$, $HCO_3{}^-$ and Cl^- were prepared by appropriated dilutions.

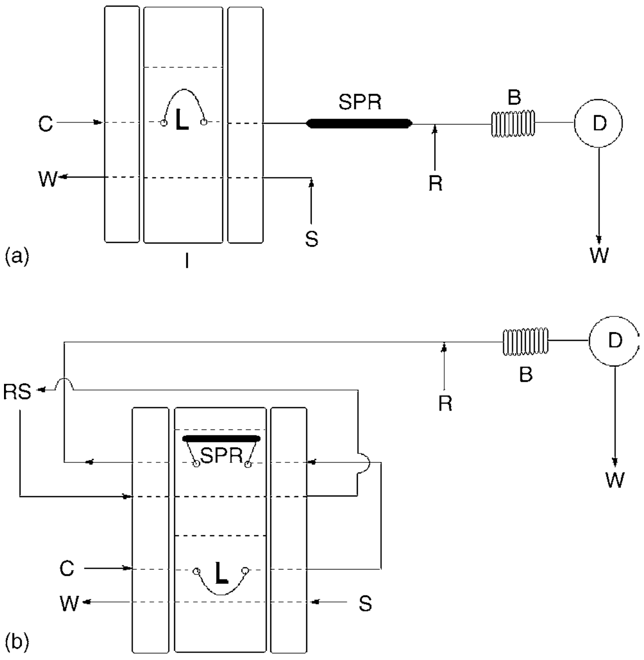

Fig. 1. Schematic diagram of the flow injection system used for preliminary experiments (a) and used for chloride determination (b). C: carrier (water); W: waste; S: sample or reference solution; RS: $Hg(SCN)_2$ regenerating solution; SPR: solid-phase reactor; RS: nitrate ferric solution; B: tubular coiled reactor; D: spectrophotometer (λ= 480 nm).

The solution employed for the regeneration of the solid-phase reactor (S) was prepared by dissolving under gentle heating 0.12 g $Hg(SCN)_2$ in 100 ml water.

A solution containing 0.15 mol l^{-1} $Fe(NO_3)_3 \cdot 9H_2O$ in 0.15 mol l^{-1} HNO_3 was freshly prepared and the carrier solution used (C) was distilled/deionized water.

The immobilization of $Hg(SCN)_2$ was made using a commercial epoxy resin (mixture of resin P342 and catalyst from Reforplás Brazil in a 1:1 mass ratio).

2.3. Preparation and immobilization of $Hg(SCN)_2$

The preparation of the solid-phase reactor was carried out as follows: a mass of 0.7 g $Hg(SCN)_2$ was mixed with 1.5 g of epoxy resin and homogenized by manual stirring; 1.5 g of catalyst was added and the stirring was continued until an increase of viscosity was observed. The material was kept at room temperature for 2–3 h. Then it was broken up by a hammer and ground in a Tecnal mill (Model TE 631/1, Piracicaba, SP, Brazil). The particle size was selected by passing the pulverized material through sieves with different mesh sizes.

The solid-phase reactors were constructed by packing in a PTFE tubing (8.0 cm × 2.0 mm i.d) with particles of 0.50–0.35 μm that were insert with aid of a syringe. One of the end was plugged with a small piece of polyurethane foam to retain the epoxy particles containing $Hg(SCN)_2$ immobilized. The solid-phase reactor was inserted in the injector-commutator in the usual position of a sample loop (Fig. 1b).

2.4. Flow system and procedure

A schematic diagram of the flow manifold is shown in Fig. 1. The flow system with a relocatable solid-phase reactor used to determine chloride in water samples is shown in Fig. 1(b). Optimization of the reaction conditions was carried out with the FI system depicted in Fig. 1(a).

The chloride reference solution or sample was introduced into the carrier stream with aid of an injector-commutator with a sample loop of 500 μl. Deionized water flowing at 5.5 ml $\min^{-1}$ was used as carrier. A 0.15 mol l^{-1} nitrate ferric solution in 0.15 mol l^{-1} HNO_3 flowing at 1.0 ml $\min^{-1}$ was introduced at the confluence point X, the tubular coiled reactor length was 100 cm. When the chloride solution was injected and transported by the carrier stream towards the solid-phase column, the SCN^- ions released react with the nitrate ferric reagent solution to yield a colored cromophore measured at 480 nm. The absorbance is proportional to the chloride concentration.

Water samples A, B and C were collected at the Tietê river in Barra Bonita (São Paulo, Brazil), and samples D and E at the lake in the University Federal of the São Carlos (São Paulo, Brazil). All samples were kept in polyethylene bottles. The samples A, B and C were collected at the surface, about 1 and 3 m profundity, respectively. The samples D and E were collected at the surface in different points of the lake. The analysis were carried out in the same day by the proposed procedure and by the method described in the literature (Standard Methods, [12]). Before analysis, the samples were filtered and 10-fold diluted.

3. Results and discussion

The reaction between mercury(II) thiocyanate and chloride leads to the displacement of thiocyanate and the formation of an intensely colored complex with Fe(III) [1,2]. When an aqueous chloride solution flown-through the column packed with $Hg(SCN)_2$ entrapped in the epoxy resin, SCN^- ions were released from the column. The optimization of chemical and hydrodynamic parameters was carried out using the flow injection system depicted in Fig. 1(a).

3.1. Solid-phase reactor

The response of the flow injection system was studied by varying the reactor inner diameter and length, the $Hg(SCN)_2$:epoxy resin mass ratio, and the particle sizes.

The reactor internal diameter evaluated was 1.0, 1.5, 2.0, and 3.0 mm. The reactors with 1.0 and 1.5 mm i.d. were very difficult to pack. The reactor with 3.0 mm i.d. caused a pronounced dispersion of the sample zone. The reactor with 2.0 mm i.d. led to good sensitivity and suitable stability of the baseline. Consequently, all further experiments were carried out using this latter reactor.

Table 1
Studied parameters of the solid-phase reactor

Variable	Tested range	Selected value
Reactor internal diameter (mm)	1.0, 1.5, 2.0, 3.0	2.0
Mean particle size (μm)	0.50–0.35, 0.35–0.25	0.50–0.35
Reagent/resin ratio (m/m)	13, 20, 26, 33, 46	20
Reactor length (cm)	4.0, 6.0, 8.0, 12.0	8.0

The influence of the length of the solid-phase inside the reactor was evaluated from 4.0 to 12 cm. The absorbance signals increased with increment of the reactor lenght, but an undesirable augment of the hydrodynamic pressure was observed for reactors longer than 8.0 cm. A 8.0 cm SPR length was selected to further experiments.

The following $Hg(SCN)_2$:epoxy resin mass ratios were evaluated: 13, 20, 26, 33 and 46% (m/m). The sensitivity increased when the concentration of $Hg(SCN)_2$ incorporated in the epoxy resin was increased. The use of higher concentrations of $Hg(SCN)_2$ was not possible due to difficulties for homogenization of the polymeric material.

Particle sizes in the range 0.50–0.35 and 0.25–0.35 μm were evaluated. The range 0.50–0.35 μm showed better sensitivity. Lower particles sizes increased the hydrodynamic pressure in the flow injection system. So, the range of 0.50–0.35 μm was selected to further experiments.

Table 1 shows the experimental parameters investigated and the values selected.

3.2. Flow injection system configuration

Two FI systems were evaluated (Fig. 1(a) and (b)). The first one used a SPR positioned in the analytical path before the detector and it was used to optimize chemical and hydrodynamic parameters. In the second system, the SPR was positioned in the injector–commutator such as a sample loop and an intermittent stream was used to regenerate it. For improving the performance of the SPR and extend its lifetime, an intermittent stream of a $Hg(SCN)_2$ solution was flown-through it. This procedure avoided the continuous flow of a solution containing mercury(II) and decreased the amount of toxic wastes generated. The following $Hg(SCN)_2$ concentrations were investigated for the regenerating solution: 0.03, 0.06, 0.12, and 0.24% (m/v). As it can be seen in Fig. 2, the absorbance signals increased gradually with the augment of $Hg(SCN)_2$ concentration up to 0.24% (m/v), but this concentration is practically the solubility of this salt. Thus, to avoid the use of a water-bath, necessary to obtain this solution, a 0.12% (m/v) $Hg(SCN)_2$ solution was used in all further experiments.

3.3. Optimization of chemical variables

The effect of the concentration of the nitrate ferric solution on sensitivity was evaluated from 0.03 to 0.30 mol l^{-1} range in 0.15 mol l^{-1} of nitric acid. Best sensitivity was obtained using 0.20 mol l^{-1} nitrate ferric solution. However, this solu-

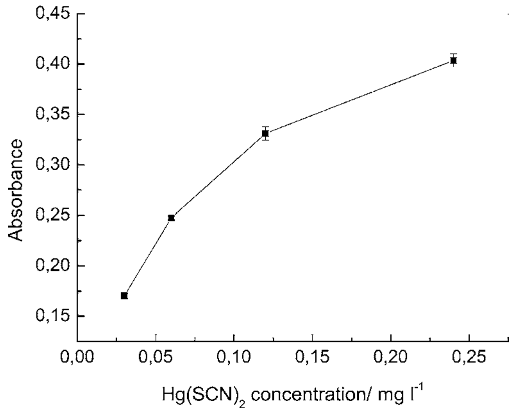

Fig. 2. Effect of the $Hg(SCN)_2$ concentration on the absorbance signal for chloride determination using an intermittent stream.

tion caused impregnation of the reagent in the optical flow-cell and affected the stability of the baseline. Thus, all further measurements were carried out using a $0.15\,mol\,l^{-1}$ solution.

The effect of the HNO_3 concentration from 0.05 to $0.20\,mol\,l^{-1}$ on the sensitivity was also evaluated. The absorbance signal increased with increasing concentration of nitric acid up to $0.15\,mol\,l^{-1}$ and then levels off between 0.15 and $0.20\,mol\,l^{-1}$. The baseline was unstable when this latter concentration was employed. The concentration of $0.15\,mol\,l^{-1}$ was then selected.

3.4. Flow injection parameters

The effect of FI variables, such as, carrier and reagent flow rates, tubular coiled reactor and sample volume, were investigated considering the best compromise conditions between absorbance intensity, repeatability, and analytical frequency. The optimization followed a univariated approach. The ranges studied and the optimum values are presented in Table 2.

The sample volume was varied from 300 to 750 μl by changing the length of the sample loop in the injector. The absorbance signals increased when the sample volume varied from 300 to 500 μl, but no further increment was observed for higher sample volumes. It seems that this latter volume represents the infinite volume condition for this flow injection system.

Table 2
Chemical and FI parameters studied and selected on the optimization of flow injection system

Variable	Studied	Selected
Reactor length (cm)	40–150	100
Sample volume (μl)	300–750	500
$Fe(NO_3)_3$ flow rate ($ml\,min^{-1}$)	0.4–1.5	1.0
Carrier flow rate ($ml\,min^{-1}$)	2.5–5.5	5.5
$Hg(SCN)_2$ ($mg\,l^{-1}$)	0.03–0.24	0.12
Fe^{3+} ($mol\,l^{-1}$)	0.03–0.30	0.15
HNO_3 ($mol\,l^{-1}$)	0.05–0.20	0.15

The influence of the length of the tubular coiled reactor was studied in the 40–150 cm range. The sensitivity increased with increase of length up to 100 cm and stayed constant for reactors bigger than that. A 100 cm was chosen as a compromise between sensitivity and analytical frequency.

The effect of carrier flow rate in the response was studied in the range of $2.5–5.5\,ml\,min^{-1}$. It was found that the sensitivity increased with the increase of the flow rate. Then, a carrier flow rate of $5.5\,ml\,min^{-1}$ was selected as optimum, because it showed the best repeatability, compromise between sensitivity and analytical frequency and stability for the baseline. As observed, the residence time was not a critical parameter due to the fast rate of the reaction. The nitrate ferric solution stream flow rate was studied in the range of $0.4–1.5\,ml\,min^{-1}$ with a carrier stream flow rate of $5.5\,ml\,min^{-1}$. It was found that the sensitivity increased to $1.0\,ml\,min^{-1}$, above which it showed a decrease. Then, a nitrate ferric solution flow rate of $1.0\,ml\,min^{-1}$ was selected as optimum.

3.5. Stability of solid-phase reactor containing $Hg(SCN)_2$

The stability (lifetime) of the solid-phase reactor under the established conditions was studied by running calibration graphs, using freshly made reagent solutions in different

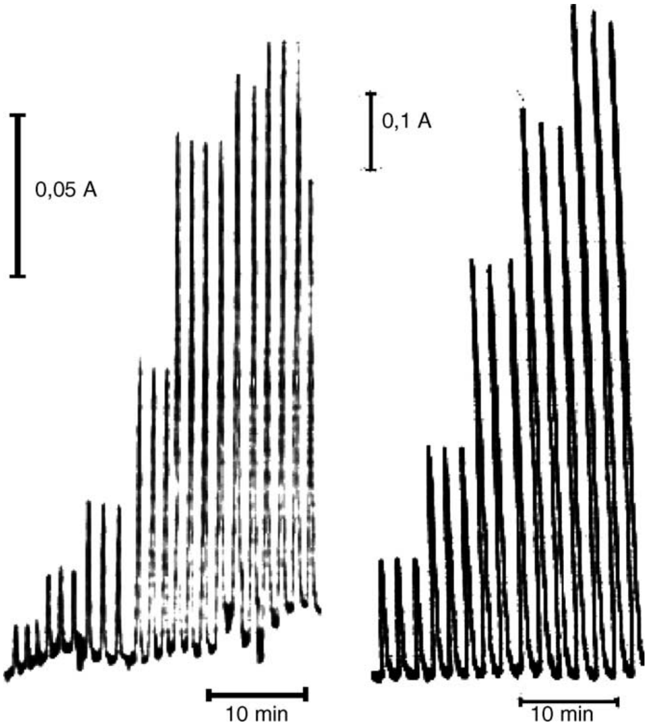

Fig. 3. Analytical curves for chloride determination. On the left is shown the recordings obtained with the first system (Fig. 1(a)), it is triplicate for the reference solutions of chloride and the concentrations were 5.0, 10.0, 20.0, 30.0, 40.0 and $50.0\,mg\,l^{-1}$. On the right is shown the recordings obtained with the second system with intermittent stream (Fig. 1(b)), it is triplicate for the reference solutions of chloride and the concentrations were 5.0, 10.0, 20.0, 30.0 and $40.0\,mg\,l^{-1}$.

Table 3
Determination of chloride in natural waters using the official method [12] and the flow injection spectrophotometric procedure[a]

Sample	Chloride($mg\,l^{-1}$)		Relative error[b] (%)
	Official method	Flow procedure	
A	34.0 ± 0.2	36.0 ± 0.1	5
B	34.0 ± 0.1	37.0 ± 0.1	9
C	35.0 ± 0.1	35.0 ± 0.2	0
D	3.0 ± 0.2	3.4 ± 0.1	14
E	3.8 ± 0.1	4.0 ± 0.1	5

[a] $n = 3$; confidence level 95%.

[b] Relative error between FI-spectrophotometric versus official method value.

working sessions. Five reactors were tested. The relative standard deviation of the slope was 2.5% and the lifetime of the reactors was about 1.000 determinations.

The regeneration of the SPR using the $Hg(SCN)_2$ solution as an intermittent stream extends the column lifetime of the column to around 1.000 consecutive measurements. The system without column regeneration (Fig. 1(a)) led to a lifetime 60% shorter and the repeatability was worse.

3.6. Interference studies

In order to investigate the selectivity of the FI proposed, the effect of the anions SO_4^{2-}, PO_4^{3-}, CO_3^{2-}, HCO_3^{-}, NO_2^{-}, and NO_3^{-} were investigated by the analysis of $10\,mg\,l^{-1}$ chloride reference solution in the presence of these anions at same concentration. Only carbonate caused a significative positive interference of 15% when present at the same concentration as the analyte.

3.7. Analytical curve and applications

Adopting the conditions recommended in Tables 1 and 2, the analytical curve was linear in the concentration range 5.6×10^{-5} to $2.2 \times 10^{-4}\,mol\,l^{-1}\,Cl^{-}$ ($A = 0.0815 + 0.02575 C_{Cl^{-}}$; $r = 0.9936$, where A is the absorbance and $C_{Cl^{-}}$ the concentration of chloride in $mol\,l^{-1}$). The detection limit was estimated as $1.4 \times 10^{-5}\,mol\,l^{-1}$ (three standard deviation of the blank/slope of the analytical curve) at the 95% confidence level and the coefficient of variation to chloride solution $2.2 \times 10^{-4}\,mol\,l^{-1}$ was 2.2% ($n = 10$). The analytical frequency was 100 determinations per hour (Figs. 3 and 4).

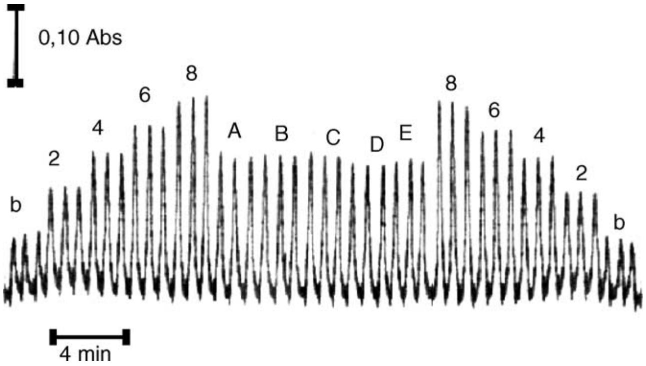

Fig. 4. Recordings obtained for chloride determination in natural water. Reference solutions: b-blank; 2,4,6, and 8 $mg\,l^{-1}$. A,B,C,D, and E are samples.

Applying *t*-test for paired data, it was found that all results are in agreement at the 95% confidence level and within acceptable range of errors. The results for chloride determined in 5 samples presented in Table 3 confirms the accuracy of the FI spectrophotometric procedure using an on-line solid-phase reactor containing $Hg(SCN)_2$.

4. Conclusions

The developed flow system did not show significant differences in analytical performance when compared to oth-

Table 4
Analytical performance of flow injection systems applied to chloride determination

	Ref. [2]	Ref. [3]	Ref. [4]	Ref. [5]	Ref. [8]	Proposed
Linear range ($mol\,l^{-1}$)	2.8×10^{-4} to 2.8×10^{-2}	2.8×10^{-6} to 1.7×10^{-4}	$(0–1.1) \times 10^{-3}$	8.4×10^{-6} to 7.0×10^{-4}	2.8×10^{-5} to 8.5×10^{-4}	5.6×10^{-5} to 2.2×10^{-4}
R.S.D. (%)	<2.38	<1	–	–	1.0	2.2
Samples	Natural and drink waters	Ethanol	River waters	River and pond waters	Tap waters	Natural water
Analytical frequency (h^{-1})	15	120	300	18	100	100
Detection limit ($mol\,l^{-1}$)	–	–	–	8.5×10^{-6}	5.5×10^{-6}	1.4×10^{-5}

–: not reported.

Table 5
Reagents consumption in spectrophotometric flow injection procedures for determination of chloride

Milligram per determination	Ref. [2]	Ref. [3]	Ref. [4]	Ref. [5]	Ref. [8]	Proposed
Fe(III)	18.4	138	7.21	11.1	5.62	50.0
Hg(II)	1.72	190	0.68	0.60	1.14	0.12
SCN^{-}	1.00	110	0.40	0.80	0.66	0.07

ers method for determining chloride as it can be seen in Table 4. The feasibility of the proposed flow injection system with immobilized $Hg(SCN)_2$ reagent for reducing reagent consumption was confirmed as shown in Table 5. The amount of the Hg toxic reagent consumed per determination was reduced from 190 mg in a single line flow injection system [3] to 120 μg with the proposed flow system. The Hg concentration in the residue is lower than that allowed by the Brazilian's law CONAMA [13].

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