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21 September 2024

UNIVERSITÀ DEGLI STUDI DI TORINO

Flow injection method for the determination of silver concentration in drinking water for spacecrafts

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Abstract

A flow injection method has been developed for determination of silver. The method is based on a reduction reaction with sodium borohydride which leads to the formation of a colloidal species which is monitored at a wavelength of 390 nm.

The reaction variables flow rate, sodium borohydride concentration and pH, which affect sensitivity, were investigated and their effects were established using a two-levels, three-factor experimental design. Further optimization of manifold variables (reaction coil and injection volume) allowed us to determine silver in the range 0.050–5.0 mgL^{-1} with a minimum detectable concentration of 0.050 mgL^{-1}. Silver is added, as biocide, to drinking water for spacecrafts. The chemical species of silver, present in this kind of sample, were characterized by a procedure based on the selective retention of Ag^{+} onto a 2.2.2. cryptand based substrate followed by determination of the non-bound and bound (after elution) Ag^{+} by the FIA method. The method optimized was applied to a drinking water sample provided for the launch with the Automated Transfer Vehicle (ATV) module Jule Verne to the International Space Station (March 9th 2008).

1. Introduction

Silver and silver containing compounds are used for several applications including industrial and medicine. In fact, it is well known that silver ions and silver containing compounds are highly toxic to microorganisms so that silver ions are added as antibacterial component in several formulations and for the coating of medical devices. Soluble silver compounds are used to disinfect drinking water, as well as electrolytically dissolved silver.

The World Health Organization includes silver in a colloidal state produced by electrolysis of silver electrodes in water, and colloidal silver in water filters as two of a number of water disinfection methods to provide safe drinking water in developing countries [1]. There is no simple test for measuring the silver content of the drinking water. The measurements taken with the existing tests show a considerable degree of error and the most effective method to produce water of adequate quality is to dose the water with controllable amounts of silver. In other words, the control is carried out basically through the dosing and not following it analytically.

Silver, and most of all, colloidal silver, is a concern of the safety of drinking water on manned spacecrafts. Silver was added to the drinking water supplies of Russian Mir orbital station [2] and the International Space Station (ISS) [3]. At present, at concentrations up to 0.5 mgL^{-1}, silver is used as bacterial growth inhibitor in drinking water for the crew of space missions [4] and it is considered a NASA's priority quality water parameter. The determination of silver in environmental samples, mainly water, can be accomplished by spectrometric techniques, such as atomic absorption spectroscopy [5], or by voltammetric techniques [6]. Nevertheless, simple, rapid, sensitive and selective, low-cost analytical techniques are more often desired and spectrophotometric methods usually meet these needs.

Just focusing on those methods involving complexation reactions of Ag$^+$ in aqueous medium only, they require reagents not often available on the market, that should be synthesized for the purpose, and require the presence of surfactants to enhance the absorbance of the complex formed [7]. Lately, a method combining the capabilities of solid-phase extraction for preconcentration and the diffuse reflectance spectroscopy for the colorimetric detection of the silver complex with the reagent 5-(p-dimethylaminobenzylidene) rhodanine and with a nonionic surfactant (Brij 30) as additive, impregnated onto a solid-phase extraction disk, was tested for the determination of silver ions in waters intended for human consumption during space missions [4]. The basics of this study were improved and the design and initial ground-based performance evaluation of multiplexed colorimetric solid-phase extraction were reported [8] and translated to a method that just started a six-months (September 2009-March 2010) of tests aboard the ISS [9].

Another topic concerning drinking water on manned spacecrafts is the assessment of the chemical form of silver (colloidal [3,9] or silver ions [10]) exerting the biocide action.

Over the last twenty-five years, flow injection analysis (FIA) has became one of the most popular techniques due to the ease with which manual methods, especially spectrophotometric techniques, adapt to it [11,12]. The versatility, simplicity, low-cost and small sample consumption of FIA make it suitable for on-line monitoring of analytes of interest in different processes. Despite this, at the best of our knowledge, only few studies are reported for the FIA determination of silver by spectrophotometry and none of those is a direct method. In our opinion this is due to the lack of specific reactions that can also fulfil the requirements (mainly kinetics) of FIA. A flow-injection method for the UV determination of silver(I) at concentrations higher than 0.3 mgL^{-1}, based on its reaction with nickelcyanide ion, $Ni(CN)_4^{2-}$, in ammoniacal buffer medium (pH 10) and subsequent measurement of the decrease in the absorption of the $Ni(CN)_4^{2-}$ complex was described [13].

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The catalytic effect of Ag(I) on the oxidation of gallocyanine by peroxodisulfate (T=40 °C) in the presence of 1,10 phenantroline dissolved in ethanol was proposed by Ensafi and Zarei [14] and applied for the determination of µgL^{-1} levels Ag(I) in river water samples after a preconcentration as high as 200-fold. Another approach based on the metal-exchange reaction between ethylenediaminetetraacetatomercury(II) in the aqueous phase and bis(diethyldithiocarbamate) copper(II) in the organic phase was used for the determination of silver(I) that in this system acts as the catalyst. Its concentration, at tenth of µgL^{-1} levels, can be determined measuring the decrease in the absorbance of the Cu(II)-DDTC complex after its extraction [15]; nevertheless this reaction system is not specific for Ag(I) only, since other metal ions, *e.g.* Cu(II), catalyse the same reaction.

This survey of recent publications clearly shows the complexity of the reactions involved, the need to use several reagents and the lack of a direct and simple method for Ag(I) determination.

The aim of this work is twofold: (i) the development of a new simple, rapid and direct method for silver determination and (ii) the assessment of the chemical form of silver in drinking water for spacecraft crew consumption.

The approach followed for the analytical determination of silver exploits the formation of silver colloid after reduction of Ag$^+$ ions with NaBH$_4$ (reaction time ~1 sec) and the monitoring of its absorbance at 390 nm inside a FIA system. The chemical variables of the system were optimized by a 2^3 factorial experimental design which enabled us to calculate the main and the interactive effects of the parameters affecting the absorbance response and to enhance the sensitivity in eight experiments only. Manifold variables of the FIA system were optimized in respect to these data. The optimized conditions (0.3 mM NaBH$_4$, pH 12.5, flow rate 1.2 mLmin^{-1}, 200 µL injection loop, 50 cm-length reaction coil) allowed us to directly detect 0.05 mgL^{-1} Ag$^+$. It must be underlined that no colorimetric reagent is needed.

To get information about the chemical form of silver for drinking water used for space missions, a new dedicated procedure was developed, using an IonPac Cryptand G1 column, containing 2.2.2. cryptand molecules, a bi-cyclic compound (macrocycle) capable of complexing metal cations. This column, recently marketed for anion-exchange chromatographic applications [16-18], was here exploited for the ability of the macrocycle to bind cations whose diameter is compatible with that of the macrocycle itself. The sample analyzed was the one launched with the Automated Transfer Vehicle (ATV) module Jule Verne to the International Space Station on March 9th 2008. To the best of our knowledge this is the first instance of using such a cryptand-based substrate for Ag$^+$ retention and the evaluation of its chemical species for water intended for manned spacecrafts.

2. Experimental

2.1 Reagents and solutions

Solutions of NaBH$_4$ (Merck, Darmstadt, Germany) were prepared daily in high purity water (18.2 MΩ·cm resistivity at 25 °C) obtained with a Milli-Q Academic equipment (Millipore, Billerica, MA). NaOH for pH adjustment was from Fluka (Milan, Italy), while AgNO$_3$ was from Sigma Aldrich (Milan, Italy).

2.2 Flow injection system

Fig. 1 shows a schematic diagram of the flow system used. A 4000i model pump (Dionex, Sunnyvale, CA, USA) was used to deliver high purity water as a carrier stream and the reduction reagent (NaBH$_4$) through PEEK tubing (0.25 mm i.d.). Standard solutions of Ag$^+$ were injected into the carrier stream with a sample injector (Rheodyne, 7125 Model). The loops and the reaction coils studied during optimization had an internal diameter of 0.5 and 1.07 mm, respectively. Mixing coil lengths (50-100 cm) and sample loop volume (60-200 µL) were varied individually to study the effects of dispersion while the other experimental parameters were kept constant.

A variable-wavelength UV-VIS spectrophotometer (VDM-II, Dionex) was used for monitoring the absorbance at 390 nm. The distance between the injection and the mixing point with NaBH$_4$ was kept constant at 23 cm throughout the work.

The analytical readout was based on the measurement of peak height (H). For the dispersion (D) calculation ($D=C°/C^{max}=H°/H^{max}$; C^{max}=concentration corresponding to the maximum of the recorded curve, C^0= original concentration of the injected sample solution), $H°$ was measured by infusion of a 1 mg/L Ag$^+$ solution into the spectrophotometric cell, directly, and had the value of 0.0285 AU, while H^{max} was the readout after the dispersion of the same Ag$^+$ concentration in the FIA system.

2.3 Retention procedure

To evaluate the retention yield, 10 mL of 1 mgL^{-1} Ag$^+$ were loaded at 0.5 mLmin^{-1} onto an IonPac Cryptand G1 column (30x3 mm i.d., Dionex). The eluate of the column was collected and a 200 µL aliquot injected on the optimized FIA system to evaluate the Ag$^+$ amount unretained. The column was washed (1 mL H$_2$O, 1 mLmin^{-1} flow rate) and to recover the retained Ag$^+$, several eluents (10 mL) were passed at a flow rate of 0.5 mLmin^{-1}, and analyzed with the developed method. When ammonia

was used as the recovery eluent, the solution was acidified, before the analysis, with 10 µL of concentrated HNO_3. Whenever the elution of Ag^+ from the column was not accomplished, the column was washed with 0.1 M KNO_3 (pH 2) for 2 hours. Before a new retention/elution procedure, the column was conditioned with 10 mL deionized water (0.5 mLmin^{-1}). At the optimized retention/elution conditions, a blank was analyzed in parallel.

2.4. Sample of drinking water for human spaceflight

The sample analyzed was kindly furnished by the laboratories of the Research Centre of SMAT (Società Metropolitana Acque Torino) which produced it, according to the Russian qualitative standards, for the launch with the Automated Transfer Vehicle (ATV) module Jule Verne to the International Space Station on March 9th 2008. This water is characterized by the following parameters: hardness 25 °F, 6 mgL^{-1} Na^+, 60 mgL^{-1} Ca^{2+}, 13 mgL^{-1} Mg^{2+}, 33 mgL^{-1} SO_4^{2-}, 1.4 mgL^{-1} K^+, 1.1 mgL^{-1} Cl^-, 0.005 mgL^{-1} Cr^{3+}, 0.005 mgL^{-1} Zn^{2+}, 0.004 mgL^{-1} Ni^{2+}, 400 µScm^{-1} conductivity, 250 mgL^{-1} dry residue, pH 8.5 and silver (maximum concentration 0.3 mgL^{-1}). Silver has been added electrolytically.

3. Results and discussion

3.1 Formation of colloidal silver

Ionic silver is instantaneously reduced by borohydride producing colloidal silver particles, according to reaction (1).

$$2AgNO_3 + 2NaBH_4 \rightarrow 2Ag + H_2 + B_2H_6 + 2NaNO_3 \qquad (1)$$

These particles, 5-10 nm size [19], exhibit an absorbance with a maximum located at short-wavelength (~390 nm). In Fig. 2 the absorbance spectrum for a solution containing 10 mgL^{-1} Ag^+ (9.2·10^{-5} M) and 6·10^{-4} M $NaBH_4$ is shown.

3.2 Effect of chemical variables

It is well known that sodium borohydride is stable at basic pHs. Preliminary experiments pointed out that $NaBH_4$ concentration, pH and flow rate were factors that can affect the absorbance response. When a list of variables to be investigated has been completed, an experimental design is usually chosen in order to estimate the influence of the different variables on the result. In screening studies, linear or second order interaction models are common, such as in full factorial or fractional factorial designs. The former design is limited to the determination of linear influence of the variables,

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while the latter allows for interaction terms between variables to be evaluated as well. Eventually, the variables with the largest influence on the procedure can be identified [20]. To investigate the effect of each of the above mentioned factors and to subsequently optimize the response, a two-level, three-factor factorial design (2^3) has been planned. The levels chosen for each factor during the experiments are listed in Table 1, and the design matrix with the coded variables, together with the absorbance response (peak height) obtained after injection of 1 and 5 mgL^{-1} Ag$^+$ are shown in Table 2.

3.2.1 Estimation and interpretation of the effects

Main and interactive (two-factor and/or three-factor interactions) effects of the parameters investigated were calculated by the Yates' algorithm [21], whereas the effects were interpreted by means of a normal probability plot (Table 3). Data analysis (Fig. 3) evidences the main effects of (i) flow rate; (ii) pH and (iii) NaBH$_4$ and the interaction effect of (iv) pH-flow rate as significant on the response of the reduction reaction of Ag$^+$ to colloidal silver. In particular, an increase of the concentration of NaBH$_4$ enhances the absorbance of the colloidal silver, as well as the simultaneous increase of pH and flow rate.

As an example of the usefulness of the experimental design performed, the responses of experiments 1 and 8 are compared in Fig. 4. Experimental conditions 8 are to be considered as optimal to obtain the highest response. Nevertheless, it should be remarked that relative standard deviation (RSD %) for the lowest Ag$^+$ concentration level is as high as 26%. Therefore, further optimization of the method was performed, following the indications provided by the experimental design, at slightly decreased flow rate (0.3 mM NaBH$_4$, pH 12.5, 1.2 mLmin^{-1}), where RSD % for 1 ppm Ag$^+$ was 9.3%. It must be underlined that the decrease of flow rate is efficacious in the decrease of the dispersion of the sample zone [22,23].

3.3 Effect of manifold variables

The influence of variables such as injected volume and reaction coil length on the sensitivity was studied since these variables greatly affect dispersion in a FIA system [22].

The effect of the injected volume on the absorbance of colloidal silver was tested under optimum chemical conditions in the range 60-200 µL. The results (Table 4) show that, accordingly to the theory of FIA, the peak height rose, and hence dispersion decreased, by increasing the sample loop volume and decreasing the reaction coil length. Thus, a sample volume of 200 µL and a coil length of 50 cm were selected.

On the other hand, a coil length of 50 cm corresponds to a residence time of 22 sec which is fully compatible with the kinetics of the formation of colloidal silver (the reaction takes place in 1 sec [19]) and with its stability. It is worth of mention that at all the conditions evaluated, the FIA system can be referred to as at limited dispersion (1<D<3).

3.4 Analytical characteristics of the method

Under obtained optimized conditions, silver concentration can be determined in the ranges of 0.05–5.0 mgL^{-1} (r^2 = 0.9989). The lowest Ag^+ level injected represents the minimum detectable concentration (see Fig. 5) which was estimated by consecutive injections of diluted samples. The relative standard deviation, for three repeated injections of 0.050 mgL^{-1} in three different sets of experiments, was 10.2%. The accuracy of the method was assessed by the analysis of six solutions containing Ag^+ within 0.30 and 0.65 mgL^{-1} by ICP-MS and the method developed. A paired t-test (p=0.05) applied to the data obtained by the two methods indicated that the methods are not different. A F-test (p=0.05) was also performed which indicated a non significant difference between the precisions of the two methods.

3.5 Influence of foreign ions

In this stage the influence of cations (i.e. Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Fe^{3+}) on the determination of 0.1 mgL^{-1} Ag^+, was investigated. The tolerance limit was defined as the ratio of the concentration of foreign ion to silver in correspondence of which the added ions cause a relative error less than 10% (Table 5). It should be noted that alkali metals as well as Ca^{2+} and Ba^{2+} are not interferents, whereas Mg^{2+} exhibits little interference that decreases the tolerance limit to 100. Transition metals such as Cd^{2+}, Cu^{2+} and Pb^{2+} exhibit interference that can be nevertheless masked with the addition of EDTA. In the presence of a M:EDTA=1:2, the tolerance limit for these cations is 100.

It should be mentioned that ions at the concentrations present in the formulated drinking water do not interfere with Ag^+ determination (see further, § 3.7).

3.6 Optimization of retention and elution procedure for Ag^+

To get information about the chemical form of silver present in drinking water used for space missions, a procedure was optimized using the IonPac Cryptand G1, containing 2,2,2 cryptand molecules.

A cryptand is a bi-cyclic compound capable of complexing metal cations. The binding constant of 2,2,2 cryptand with Ag^+ is $10^{9.6}$ [24] and hence the formation of a complex with Ag^+ is highly favoured and the selective retention of the ionic form of Ag^+ (over colloidal or hydroxospecies of silver) on the IonPac Cryptand G1 is expected. This is the first instance of the use of a cryptand-base column for the retention of Ag^+ ions.

Retention experiments were performed as detailed in the experimental session.

To recover the Ag^+ adsorbed, several eluents were tested. As a first attempt, the affinity of the cryptand with K^+ (binding constant $10^{5.4}$ [24]) and Ba^{2+} (binding constant $10^{9.5}$ [25]) was exploited and solutions containing 10 mL of: (*i*) 20-100 m*M* KNO_3 and (*ii*) 20 m*M* $BaNO_3$ were tested. Although 20 mM represents a molar excess as high as 2000-folds in respect to the Ag^+ loaded, none of the procedures was efficacious for the recovery of Ag^+. Taking advantage on the enhancement of the stability constant values in methanol [25], an eluent containing (iii) 20 mM KNO_3 in 95:5 (v/v) $CH_3OH:H_2O$ medium was tested. At these conditions, a recovery of about 10% for Ag^+ was achieved. A recovery of 93±7% (n=3) was finally obtained with (iv) ammonia, pH 12, very likely for the formation of the $Ag(NH_3)_2^+$ complex. It is important to underline that the retention of Ag^+ ions onto the Cryptand G1 column and its satisfactory recovery allow also for the preconcentration of Ag^+ and for the improvement of the minimum detectable concentration.

3.7 Applications

As recalled in the introduction, the determination of Ag^+ in potable water is a concern of water quality for International Space Station (ISS) crew consumption.

To evaluate the suitability of the proposed method for this topic, a simulated water sample intended for ISS crew consumption was prepared according to the characteristics listed in §2.4 containing 0.3 mgL^{-1} Ag^+. The Ag^+ concentration was determined by the standard addition method. The Ag^+ concentration estimated was 0.316±0.022 mgL^{-1} (r^2=0.9578).

Subsequently, the sample produced for the launch with the Automated Transfer Vehicle (ATV) module Jule Verne to the International Space Station (March 9th 2008) was passed, in triplicate experiments, through the Cryptand G1 column according to the protocol optimized in § 3.6 for the selective retention of Ag^+ ions. After recovery with ammonia, the eluate was analyzed by the FIA

method. The results obtained indicated that $72.2 \pm 2.9\%$ (0.149 ± 0.006 mgL^{-1}) of total Ag (0.207 mgL^{-1}, determined by ICP-MS) was in the Ag$^+$ ionic form. To evaluate the presence of colloidal species, absorbing at 390 nm, the sample was analyzed by FIA without the addition of the NaBH$_4$ reagent and no signal was detected.

4. Conclusions

A new simple, rapid and selective flow injection procedure was developed for the determination of silver with spectrophotometric detection after optimizing the chemical and manifold variables involved in the system. Quantitation limits of 0.050 mgL^{-1} Ag$^+$ can be achieved. The performance of the method in terms of sensitivity, precision and accuracy and its simplicity in terms of reagent, reaction time, wastes, and equipment pose the basis for the miniaturization and portability of the system to the real-time monitoring of Ag$^+$ biocide in water for human space missions.

In parallel, a retention method based on sorption of a 2,2,2-cryptand based substrate, highly selective for the silver(I) form, allowed us to optimize a retention/recovery procedure and to assess the amount of Ag$^+$ ions present in drinking water for human space missions. The optimized retention procedure can also be exploited for preconcentration of Ag$^+$ ions.

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Table 1. Factors and levels tested for the 2^3 experimental design.

Factors	Lowest (-)	Highest (+)
NaBH$_4$ (mM)	0.03	0.3
pH	10.5	12.5
Flow rate (mLmin^{-1})	0.6	1.8

Table 2. Design matrix for the 2^3 experimental design with the coded variables. Experiments were performed in a randomized order.

Run number	NaBH$_4$	pH	Flow rate	Response (height)	RSD (%)
1	-	-	-	1430[a] 5570[b]	5.2 7.6
2	+	-	-	1390[a] 10760[b]	3.4 6.4
3	-	+	-	1360[a] 7040[b]	2.7 3.3
4	+	+	-	2030[a] 11080[b]	7.3 3.5
5	-	-	+	1250[a] 2670[b]	7.8 6.7
6	+	-	+	1380[a] 6450[b]	5.6 3.5
7	-	+	+	1480[a] 6820[b]	3.8 4.5
8	+	+	+	1880[a] 13710[b]	26.0 1.5

Loop: 100 µL; reaction coil: 50 cm.
[a] 1 mgL^{-1} Ag$^+$
[b] 5 mgL^{-1}Ag$^+$

Table 3. Estimation of the effects obtained with the Yates' algorithm and calculation of the cumulative probability P for normal probability plot.

Rank of the effect (i)	Assignation of the effect	Estimate of the effect	P(%)[a]
1	Flow	-1,202	7.1
2	NaBH$_4$,Flow	0,358	21.4
3	NaBH$_4$,pH	0,489	35.7
4	NaBH$_4$,pH,Flow	1,067	50.0
5	pH,Flow	2,405	64.3
6	pH	3,3	78.6
7	NaBH$_4$	4,975	92.9

[a] P is calculated according to the formula $P_i=100 \cdot (i\text{-}0.5)/T$, where T is the total number of the effects

Table 4. Effect of the variation of the injected volume and of the coil length on dispersion. Other conditions as for Fig. 6.

Injected volume (μL)	Coil Length (cm)	D
60	50	3,01
100	50	1,78
200	50	1,62
200	90	1,93
200	100	2,03

Table 5. Evaluation of interferents (Na^+, K^+, Ca^{2+}, Ba^{2+}, Mg^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Fe^{3+}) on the determination of 0.1 mgL^{-1} Ag^+.

Species	Tolerance limit (ppm_{ion}/ppm_{Ag+})
Na^+, K^+, Ca^{2+}, Ba^{2+}	1000
Mg^{2+}, $Cd^{2+\,a}$, $Cu^{2+\,a}$, $Pb^{2+\,a}$	100
Fe^{3+}	5

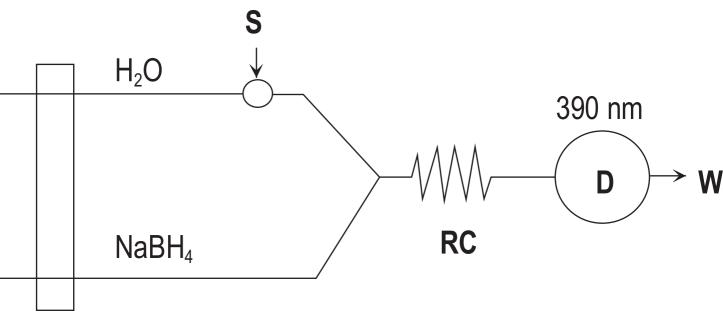[a] in the presence of EDTA (M:EDTA=1:2)

Figure Captions

Fig. 1. Schematic diagram of the flow system. S: injection valve; RC: reaction coil; D: spectrophotometric detector; P: pump.
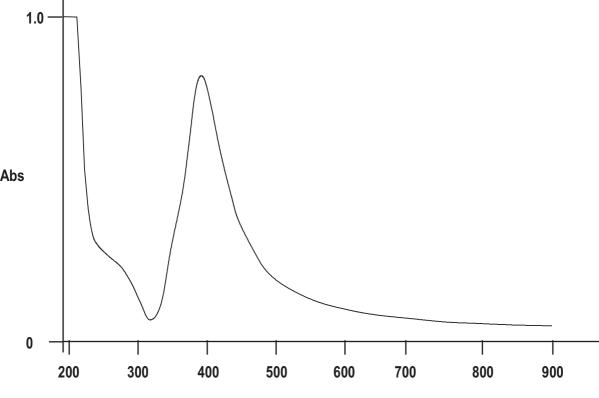
Fig. 2. Absorbance spectrum of the colloidal silver solution. Conditions: 10 mgL^{-1} Ag^+ ($9.2 \cdot 10^{-5}$ M) in $6 \cdot 10^{-4}$ M $NaBH_4$. Reference: H_2O.

Fig. 3. Normal probability plot of the main and interactions effects calculated by the Yates' algorithm.
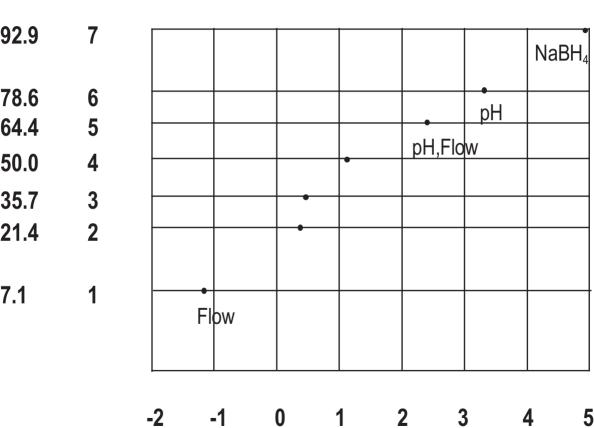
Fig. 4. Progress of the optimization of the response of 5 mgL^{-1} Ag^+ through the 2^3 factorial experimental design. The response is compared for run 1 (0.03 mM $NaBH_4$, pH 10.5, flow rate 0.6 $mLmin^{-1}$) and run 8 (0.3 mM $NaBH_4$, pH 12.5, flow rate 1.8 $mLmin^{-1}$). Injection loop: 100 μL; reaction coil: 50 cm.

Fig. 5. Determination of 50 μgL^{-1} Ag^+ under the optimized chemical and manifold FIA conditions: 0.3 mM $NaBH_4$, pH 12.5, flow rate 1.2 $mLmin^{-1}$, 200 μL injection loop, 50 cm-length reaction coil.

P(%)	i
92.9	7
78.6	6
64.4	5
50.0	4
35.7	3
21.4	2
7.1	1

NaBH$_4$

pH

pH,Flow

Flow

-2 -1 0 1 2 3 4 5

Estimates of the effects