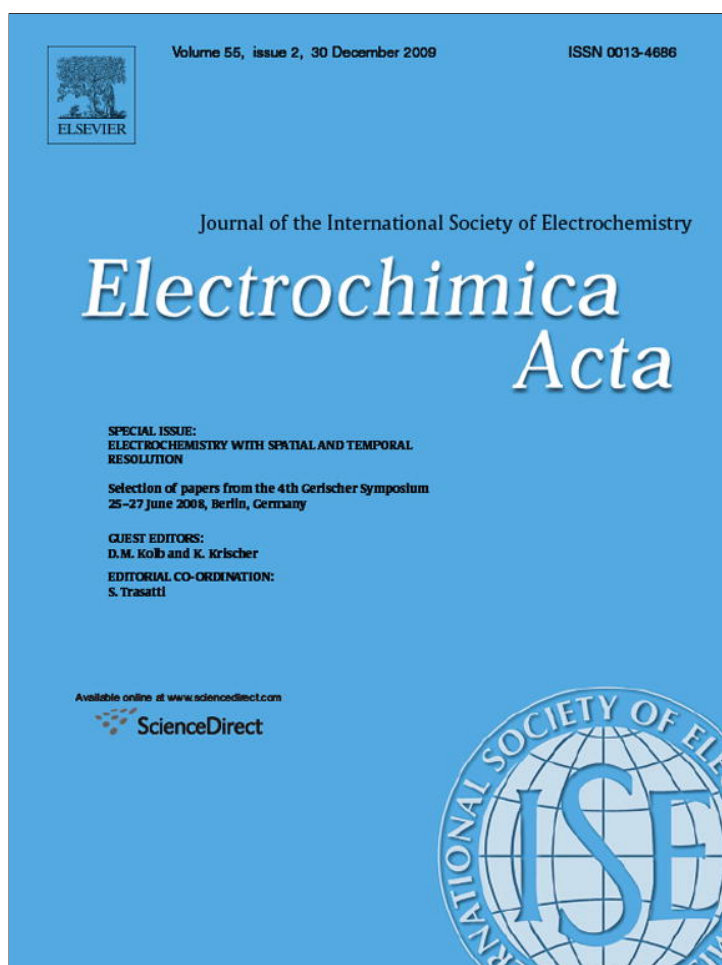


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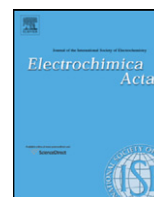
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Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Amperometric flow injection analysis as a new approach for studying disperse systems

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ARTICLE INFO

Article history:

Received 9 June 2009

Received in revised form 26 August 2009

Accepted 27 August 2009

Available online 3 September 2009

Keywords:

Dispersed systems

Flow injection

Amperometry

Copper quantification

Layered double hydroxides

ABSTRACT

Fast and simple quantitative determination in dispersed systems (layered double hydroxides – LDHs – suspensions in aqueous solutions) was performed by a procedure that couples flow injection and amperometric detection (FI-AM). LDH dispersions are injected in a continuous flow (1 mL min⁻¹) of 0.05 mol L⁻¹ KNO₃ solution and [Cu(H₂O)₆]²⁺, used as a probe, is detected at a glassy carbon electrode housed in a flat electrochemical cell. The current intensity, recorded at the selected working potential (–0.25 V vs Ag/AgCl/NaCl (3 mol L⁻¹)), presents a linear relationship with [Cu(H₂O)₆]²⁺ concentration and the procedure offers high sensitivity (slope = 0.036 μA/(μmol L⁻¹)), a low detection limit (=0.7 μmol L⁻¹) and a wide quantification range (4–200 μmol L⁻¹).

The method was applied to [Cu(H₂O)₆]²⁺ determination in two particular LDH-aqueous solution dispersed systems: (1) [Cu(H₂O)₆]²⁺ scavenging by etilendiamintetraacetic acid (EDTA) modified Zn-Al-LDHs, and (2) [Cu(H₂O)₆]²⁺ release from a copper doped Mg-Al-LDHs. The results obtained are comparable to those reported in previous works using different quantification techniques. FI-AM determination is applied without sample pretreatment (solid–supernatant separation) providing a high sampling rate (above 120 samples h⁻¹) that allows a better comprehension of the processes, particularly at the initial stages.

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1. Introduction

Quantitative determination in dispersed systems is a common task for researchers and analysts in diverse areas: environmental and colloidal science, biochemistry, pharmacy, etc. Usually, spectroscopic methods, such as atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and UV–vis spectroscopy have been used for these matrixes [1–3] as they are highly accurate and sensitive. However, these techniques become slow and time-consuming as a previous separation step of the solid from the supernatant is required. Therefore, analytical procedures offering fast, simple and accurate determinations in dispersed systems are still required.

On-line analytical techniques, which combine sampling and detection without sample pretreatment, are becoming usual for continuous measurements in different media [4,5]. Among them,

flow injection (FI) systems have received considerable attention due to their high reproducibility, analysis speed, simplicity and flexibility [6–8]. Several detection methods have been used in FI, such as spectroscopy [9], chemiluminescence [10], amperometry [11], stripping voltammetry [12], etc. However, amperometric sensors are relatively inexpensive and robust and present high sampling rate and sensitivity [13].

Layered double hydroxides (LDHs) are lamellar compounds that produce stable aqueous dispersions [14]. These solids present brucite-like layers with partial isomorphous substitution of divalent by trivalent cations, giving rise to a positive charge excess compensated by anions placed in the interlayer space [15]. The general formula of these solids is given by [M^{II}_{1-x}M^{III}_x(OH)₂]Aⁿ⁻_{x/n} · nH₂O, where M^{II}, M^{III}, Aⁿ⁻ represents the divalent cation, the trivalent cation and the interlayer anion, respectively. LDHs dispersed in aqueous solution present anion exchange properties and, at low pH values, dissolution reactions.

Different electroactive ions (such as copper) can be introduced in the LDH structure [15,16] so the dispersions can be afterwards analyzed by electrochemical techniques. Copper determination by electroanalytical techniques (mainly anodic stripping voltammetry) has been widely studied [17,18]. However, there are only a

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few works dealing with electro analytical determination in disperse systems [19]. Among these techniques, amperometry [20,21] is simpler, provides a high sampling rate and can be easily adapted to on-line analytical techniques [22]. Copper containing dispersions (either in solution or in the solid) of soils, clays, layered hydroxides, etc. are frequent samples in materials, colloidal or environmental science areas [23–25]. Spectrometric techniques are regularly used for copper determination in these matrixes [23,26], which are limited by the need of sample pretreatment (solid–supernatant separation by filtration, centrifugation, etc.) hampering the study of the initial stages (below 2 min or 3 min) of interfacial processes. Copper determination in LDH–aqueous solution systems is relevant to study various LDHs applications: sorbents for pollution remediation, antacids, drug vehiculization, etc.

In this work a sensitive, simple and reproducible procedure for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ quantification in LDH–aqueous solution dispersions, based on a flow injection system with amperometric detection (FI-AM), is described. The analytical parameters are determined and compared with those of spectroscopic techniques (AAS and UV–vis). This procedure is applied to the study of processes taking place in LDH–aqueous solution systems as an example of its application in aqueous dispersions. Particularly, the method was applied to quantify $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ in two particular experiments: (1) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ scavenging by etilendiamintetraacetic acid (EDTA) modified Zn–Al–LDHs, and (2) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ release from a Cu^{2+} doped Mg–Al–LDHs. This procedure is intended to be an alternative, simple and fast tool to study disperse systems. Therefore, the discussion is centered in the analytical procedure and the advantages of using the proposed approach in such systems.

2. Experimental

2.1. Apparatus

The flow injection system has been previously described [6,22]. It consists on a peristaltic pump (Gilson Miniplus 3), adjusted to 1.0 mL min^{-1} flow rate and a Rheodyne Type 7125 injection valve with a $20 \mu\text{L}$ sample injection loop. Quantifications were performed in an electrochemical flow cell with a stainless steel block as auxiliary electrode, a $51 \mu\text{m}$ TG-2M Teflon cell gasket (MF-1046 Bioanalytical Systems, BAS), and an LC-4C amperometric detector (BAS). The working potential was applied to a carbon disk electrode (3 mm diameter MF-2012 BAS) vs a $\text{Ag}/\text{AgCl}/\text{NaCl}$ 3 mol L^{-1} reference electrode (RE-4 BAS), allowing the current to decay to its stationary value after each measurement.

A UV–vis spectrophotometer (Shimadzu UV1601) with a 1.0 cm quartz cell and an atomic absorption spectrometer (PerkinElmer AA-3100) were used for spectroscopic experiments [2,27].

2.2. Solutions and reagents

All solutions were prepared with purified water ($18 \text{ M}\Omega$ Milli Q, Millipore System). Analytical grade copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Anedra) was used as standard without further purification, while a 0.05 mol L^{-1} KNO_3 solution was used as supporting electrolyte. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ stock solutions were prepared weekly by dissolving an accurately weighed quantity of the chemical in the electrolyte solution. Further standard solutions were prepared by adequate dilutions. All remaining chemical were reagent grade.

All the experiments were performed at room temperature and the solutions and dispersions were prepared in supporting electrolyte solution.

2.2.1. Solid LDH synthesis

Layered double hydroxides were used to prepare the dispersions that will be used as samples. The solids were synthesized follow-

ing standard methods for this kind of compounds and, according to the structural characterization of the samples (elemental chemical analyses, PXRD – Siemens D-5000 and FT-IR – Spectrum One PerkinElmer); single, well crystallized phases were obtained [2,15,27].

Based on the performed FI-AM experiments, the synthesized solids are divided in two groups:

- $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ scavenging experiments. An EDTA modified Zn–Al–LDH solid was prepared by anionic exchange: a nitrate intercalated Zn–Al–LDH, previously synthesized by the coprecipitation method, was dispersed in an EDTAH_2^{2-} solution. This solid will be named *sorbent-LDH* and its chemical formula is: $[\text{ZnAl}(\text{OH})_4][\text{Zn}(\text{EDTA})]_{0.34}(\text{NO}_3)_{0.32} \cdot 1.58\text{H}_2\text{O}$, where Zn^{2+} and Al^{3+} are the layer constituting cations and $[\text{Zn}(\text{EDTA})]^{2-}$ is the interlayer anion.
- $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ release experiments. Two carbonate intercalated Cu^{2+} doped Mg–Al–LDH solids were prepared using the direct coprecipitation method at pH 9 from a solution containing the layer metal cations at two $\text{Cu}/(\text{Mg} + \text{Cu})$ molar ratios. The obtained solids will be named *10%* and *1%Cu-doped-LDH*. Their chemical formulae (are $[\text{Mg}_{1.88}\text{Cu}_{0.12}\text{Al}(\text{OH})_6](\text{CO}_3)_{0.5} \cdot 2\text{H}_2\text{O}$ and $\text{Mg}_{1.98}\text{Cu}_{0.02}\text{Al}(\text{OH})_6(\text{CO}_3)_{0.5} \cdot 2.1\text{H}_2\text{O}$, respectively, where Cu^{2+} , Mg^{2+} and Al^{3+} are the layer constituting cations and CO_3^{2-} is the interlayer anion.

2.3. Study of disperse systems

2.3.1. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ scavenging by sorbent-LDH

The uptake experiments were performed by mixing a *sorbent-LDH* suspension (containing 0.01 g of solid) and a $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ solution, obtaining a dispersion with initial $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} = 260 \mu\text{mol L}^{-1}$. The suspensions were continuously stirred during the experiment and $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ concentration was determined by directly injecting the dispersion in the FI-AM system and recording the copper current signal as a function of time, reaching a sample rate of ca. $120 \text{ samples h}^{-1}$.

2.3.2. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ release by Cu-doped-LDH

These experiments were carried out by dispersing 0.25 g of *Cu-doped-LDH* (either 1% or 10%) in 250 mL supporting electrolyte at pH 4.7 to induce layer dissolution. The suspensions were continuously stirred during the experiment. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ concentration was determined by directly injecting this dispersion in the FI-AM system and recording the copper current signal as a function of time, reaching a sampling rate of ca. $120 \text{ samples h}^{-1}$.

The relationship between LDH layer dissolution and $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ concentration was determined in separate 30 mL dispersions containing 0.03 g of *1%Cu-doped-LDH* solid at increasing HNO_3 concentrations (from 1 to 33 mmol L^{-1}) which are intended to produce LDH erosion [15]. After equilibration, the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ concentration was determined by FI-AM. The dissolution process was also followed by turbidimetry, measuring the UV–vis absorbance at 400 nm .

3. Results and discussion

3.1. Operational parameters and techniques comparison

The $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ quantification was performed amperometrically, at a negative potential, using the reduction reaction of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ to metallic Cu^0 . The hydrodynamic voltammogram of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Cu}(\text{EDTA})]^{2-}$ solutions was performed in the 0 to -0.8 V potential range (Fig. 1). A current plateau is reached between -0.25 and -0.6 V for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ solution. Consequently,

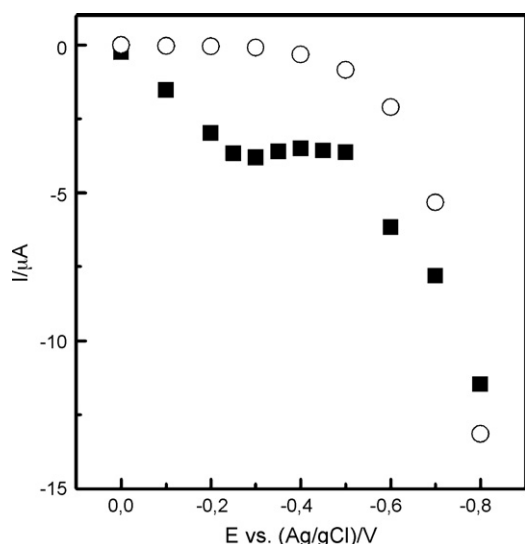


Fig. 1. Hydrodynamic voltammograms of $100 \mu\text{mol L}^{-1}$ $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (■) and $[\text{Cu}(\text{EDTA})]^{2-}$ (○) solutions. Flow rate = 1 mL min^{-1} ; sample injection volume = $20 \mu\text{L}$.

a -0.25 V working potential was selected to avoid interferences. At this potential value, the other LDH components (Zn^{2+} , Mg^{2+} , Al^{3+} , NO_3^- , CO_3^{2-}) do not present reduction signals, indicating that these ions do not interfere in $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ quantification. The $[\text{Cu}(\text{EDTA})]^{2-}$ hydrodynamic voltammogram shows that the current remains practically constant and very low below -0.5 V . This result is particularly important when studying $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ scavenging by sorbent-LDH (Section 3.2.1) because the interlayer anion may be released by anionic exchange or by LDHs layers dissolution at acid pHs [27]. Consequently, the selected working potential allows determining the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ concentration in solution without interferences of the EDTA complex.

The reduction current dependence with $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ concentration was studied in the $2\text{--}1000 \mu\text{mol L}^{-1}$ range (see Supplementary material). A linear relationship was obtained for concentrations up to $200 \mu\text{mol L}^{-1}$. The regression curve, obtained by the least square method was:

$$i(\mu\text{A}) = 0.09 - 0.036[\text{Cu}(\text{H}_2\text{O})_6]^{2+} (\mu\text{mol L}^{-1}).$$

The limit of detection (LOD) was calculated as $3.3S_0/a$ (where S_0 is the standard deviation of the blank and a the slope of the calibration curve [28]). The obtained value is $0.7 \mu\text{mol L}^{-1}$ (Table 1).

The inter-day reproducibility of the method was calculated after obtaining three independent calibration curves ($4\text{--}200 \mu\text{mol L}^{-1}$ range) on different days and at different conditions (electrolyte solution, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ standard solutions, electrode polishing, etc.). A t -test was used to compare their slopes. The calculated t parameter was 0.42, which is lower than 4.303, the critic t value corresponding to 95% of confidence interval for a degree of freedom of 2. Therefore, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ determination by FI-AM is very

Table 1

Analytical parameters of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ quantification with FI-AM system, UV-vis and AAS.

Technique	Calibration range (μM)	Slope ^a	R^{2b}	LOD ^c ($\mu\text{mol L}^{-1}$)
FI-AM	4–200	-3.1×10^{-2}	0.998	0.7
UV-vis	$(0.2\text{--}60) \times 10^3$	17.7×10^{-3}	0.999	56.0
AAS	3–80	4.3×10^{-4}	0.998	1.0

^a In $\text{nA } \mu\text{M}^{-1}$ for FI-AM, μM^{-1} for UV-vis and AAS.

^b Pearson's coefficient.

^c Limit of detection.

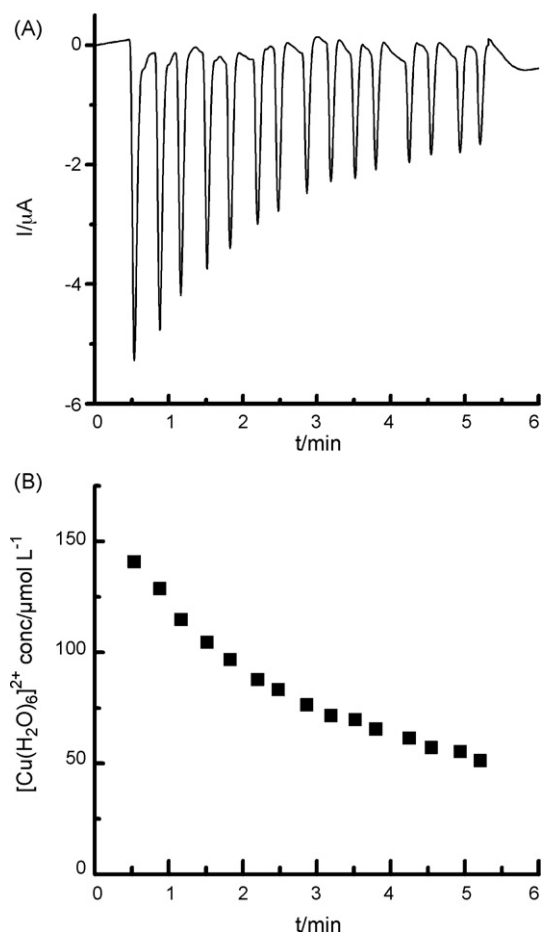


Fig. 2. Amperometric signal (A) and $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ concentration (B) vs time curves for a $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ uptake experiment with sorbent-LDH sample (initial $\text{Cu}(\text{NO}_3)_2$ concentration = $260 \mu\text{mol L}^{-1}$; initial solid concentration = 0.33 g L^{-1}). Flow rate = 1 mL min^{-1} ; sample injection volume = $20 \mu\text{L}$.

reproducible as it gives comparable calibration curves in different experiments.

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ calibration curves were also performed by UV-vis spectroscopy (at 800 nm) and AAS (Table 1). Comparing the data given in Table 1, it follows that FI-AM technique presents higher sensitivity and narrower but lower linear range than UV-vis and shows comparable sensitivity and wider linear range than AAS. However, the main advantage of FI-AM technique is that dispersions are straightforwardly determined whereas, with the other two techniques, supernatant separation from the solid is necessary. Therefore, the measurement rate in disperse systems is greatly improved by FI-AM.

3.2. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ determination in LDH-aqueous solution systems

3.2.1. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ scavenging by sorbent-LDH

EDTA modified LDHs uptake metal cations from aqueous solutions and thus, the solid is used as a heavy metal cation scavenger [2,25]. Then, when sorbent-LDH sample is dispersed in a $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ solution, the metal cation concentration decreases.

Fig. 2A shows the current signal with consecutive injections of dispersed sorbent-LDH in $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ solution. A continuous current diminution is observed, corresponding to concentration values in the $140\text{--}50 \mu\text{mol L}^{-1}$ range (Fig. 2B). As shown in Fig. 2B, the first data is recorded 40 s after beginning the experiment. The

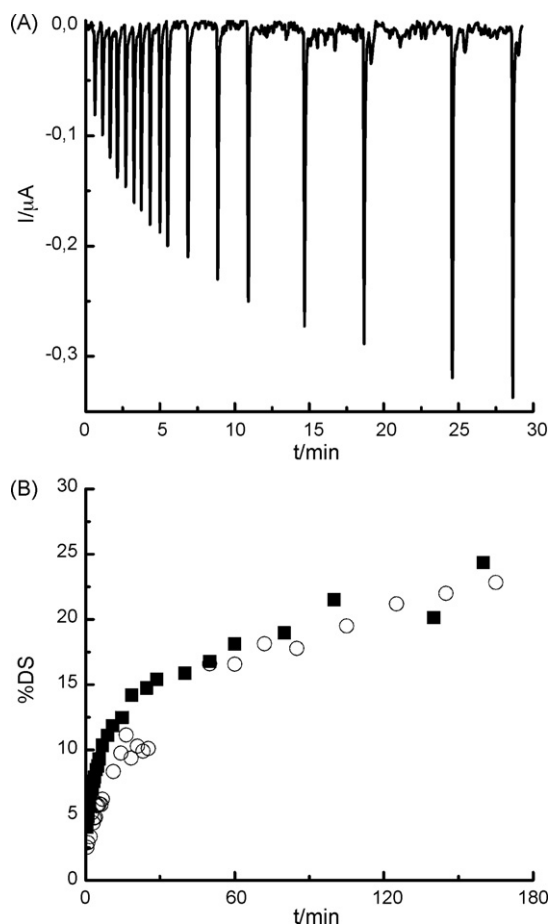


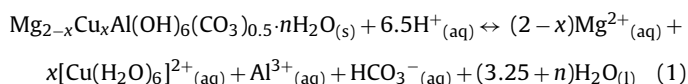
Fig. 3. (A) Amperometric signal vs time for a 1% Cu-doped-LDH dispersion; (B) sample dissolution percentage (%DS) vs time for 1% Cu-doped-LDH (■) and 10% Cu-doped-LDH (○) sample dispersions (0.25 g in 250 mL, pH 4.7). Flow rate = 1 mL min⁻¹; sample injection volume = 20 μL.

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ decrease was followed up to reaching the equilibrium after 180 min (results not shown).

Both the equilibrium concentrations and the kinetics of the process determined by FI-AM are consistent with those formerly attained by AAS technique [2]. However, as already stated, FI-AM technique is faster and more selective than AAS, making available experimental data which were not reported before [27].

3.2.2. $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ release by Cu-doped-LDH

Copper cations can be incorporated to the layers of LDHs [29]. Consequently, when 1% or 10% Cu-doped-LDHs are dispersed in acidic solutions, a $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ release into the solution is expected due to the solid erosion, according to the reaction:



The dissolution process can then be followed by determining the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ concentration.

Fig. 3A shows current signal for successive injections of 1% Cu-doped-LDH dispersed in a buffered (pH 4.7) solution. As it was the case in $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ scavenging by sorbent-LDH experiments, a high measurement rate is obtained, allowing an exhaustive study of the dissolution kinetics, especially at the early stages. A $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ concentration increase is observed, corresponding to $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ concentration values between 3 and 10 μmol L⁻¹. These low concentration values are related to the low copper content of the solid (0.6%, w/w). The $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cation concentration

at a given time ($[\text{Cu}(\text{H}_2\text{O})_6]^{2+}_t$) is directly used to quantify the magnitude of LDH erosion by calculating, for instance, the sample dissolution percentage (%DS):

$$\%DS = \frac{[\text{Cu}(\text{H}_2\text{O})_6]^{2+}_t \times 100}{[\text{Cu}(\text{H}_2\text{O})_6]^{2+}_{\text{max}}}$$

where $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}_{\text{max}}$ is the maximum copper concentration in the Cu-doped-LDH dispersions, as calculated from the chemical formula. Fig. 3B shows the %DS as a function of time of 1% and 10% Cu-doped-LDH solids dispersed at pH 4.7. Both samples present the same dissolution extent and kinetic profile, indicating that copper doping (at least up to 10%) does not affect the dissolution behavior.

Following the Cu-doped-LDHs dissolution by FI-AM allows quantifying the absolute amount of the dissolved solid. Fig. 4A shows %DS vs initial nitric acid concentration curves of 1% Cu-doped-LDH solid dispersed in aqueous solution at equilibrium. A linear relationship is obtained up to 100% DS and remains constant afterwards, which confirms that the amperometric signal gives a quantitative measurement of the solid dissolution. Furthermore, the experimental (23 mmol L⁻¹) and calculated (28 mmol L⁻¹) proton concentrations required to reach 100% DS are in good agreement.

Solid erosion was also followed by turbidimetry (absorbance at 400 nm), a technique usually employed for these studies [30]. As shown in Fig. 4B, a linear dependence between the sample absorbance and the %DS determined by FI-AM is obtained, confirming the relationship between the layer erosion and the amperometric signal. As expected, the absorbance value reaches zero when the solid is completely dissolved (%DS = 100). The FI-AM based procedure for erosion determination presents advantages

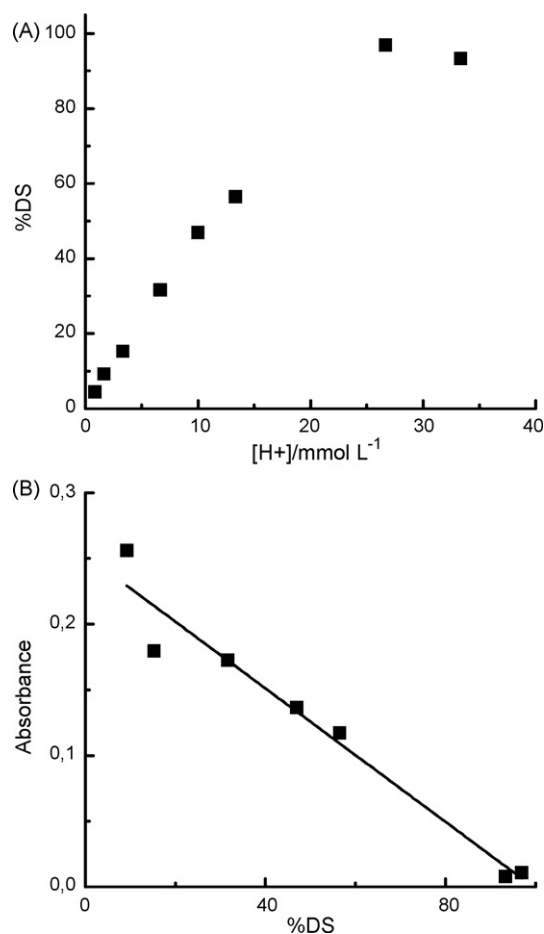


Fig. 4. (A) Sample dissolution percentage (%DS) at equilibrium vs initial HNO₃ concentration ($[\text{H}^+]$); (B) absorbance at $\lambda = 400$ nm vs %DS for dispersions containing 0.03 g of 1% Cu-doped-LDH sample in 30 mL 0.05 mol L⁻¹ KNO₃ solution.

when compared with turbidimetry. This last method does not present adequate sample rate and reproducibility [30] and quantification (if possible) is a rather complex task since reliable standards are difficult to prepare.

4. Conclusions

On-line analytical techniques coupled to amperometric detection present important advantages for quantitative determination of electroactive analytes in disperse systems as they avoid sample pretreatment. The FI-AM procedure provides simple and fast analysis (120 samples h^{-1}), wide measurement range (4–200 $\mu\text{mol L}^{-1}$) and high sensitivity (LOD = 0.7 $\mu\text{mol L}^{-1}$) for $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ determination. These analytical parameters are comparable to those obtained by UV–vis and AAS techniques.

This method has been successfully employed to the study of processes that take place in dispersed LDH-aqueous solution systems: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ uptake by an EDTA intercalated Zn-Al-LDH and dissolution of copper doped Mg-Al-LDH. In both cases the FI-AM procedure provides easy, fast and reliable quantitative determination of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ concentration, allowing a more detailed comprehension of the processes involved in $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ scavenging/release by the corresponding LDH solids in comparison with spectrometric methods.

The proposed analytical approach can be easily extended to other electroactive analytes such as pharmaceutically active compounds (ranitidine, azithromycin), and environmental pollutants (phenols and phenol derivatives) and also to other matrixes, as cationic clays, polymers, etc. The FI-AM system described in this work is extremely simple, and on-line pretreatment steps can be incorporated to improve the system performance.

Acknowledgements

Financial support from SECyT-UNC, CONICET, AECl, Junta de Andalucía and MCyT are gratefully acknowledged. RRD and EMR thank AECl and CONICET for the scholarships granted.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2009.08.053.

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