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An efficient approach to designing and optimizing the analysis of Ni(II) by AdCSV in seawater

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ABSTRACT

A highly sensitive voltammetric method was developed for the determination of nickel in seawater at nanomolar concentrations. The measurement is based on the differential pulse cathodic adsorptive stripping of Ni(II) complexed with pyridoxal salicyloylhydrazone at a hanging mercury drop electrode. Optimal conditions were found following a two-step study strategy based on a Plackett Burman design and subsequently a modified simplex method. They were: deposition potential −0.8 V; deposition time 120 s; differential pulse scan mode; pulse amplitude −0.07 V; pulse time 0.04 s; voltage step 0.017 V; time interval for voltage step 0.05 s; supporting electrolyte ammonium chloride/ammonia (0.08 M, pH = 8.9) and concentration of PSH 5.32×10^{-6} M. The response of the system was found to be linear in a range of Ni concentrations from 0 to 306.7×10^{-9} M. The detection limit was found to be 0.04×10^{-9} M of Ni(II). The precision of the method was 1.4% for 3.4×10^{-8} M of Ni(II) and 1.48% for the blank at a significance level of 95% ($n = 9$). The method was free from interferences of inorganic salts and trace metals at usual concentrations in seawater. The application to seawater was demonstrated by analysis of CRM 505 and LGC 6016 certified reference estuarine water and real seawater samples from Tangier Bay (Morocco).

1. Introduction

Analysis of heavy metals at trace levels in natural water is very important in the field of environmental analysis due to their important roles in life. For that, atomic absorption techniques have been usually used. However, they offer many difficulties due to insufficient detection limits and/or matrix interferences of real samples and a preconcentration step is often required.

The use of electroanalytical techniques is another alternative widely employed, specially the stripping voltammetry. These methods are well-established for trace metal analysis and adsorptive processes (AdSV) can further lower detection limits of stripping voltammetry to the picomolar concentration levels. In addition, these techniques are inexpensive, simple, quick and very useful for saline matrices like seawater and estuarine water samples and for speciation studies.

In AdSV, the analyte is adsorbed on the working electrode (usually, mercury electrode) by means of a non-electrolytic process prior to the voltammetric scan [1]. This procedure avoids the main difficulties found in anodic stripping analysis (ASV) with metals with strong tendency to form intermetallic compounds, with low solubility on mercury electrode (e.g., solubility of Ni in Hg is 0.0021% [2], reacting irreversibly, and/or with very negative reduction potentials [3]). For trace metals, the method is based on the formation and interfacial accumulation of a metal complex on the working mercury electrode and subsequent measurement of the reduction peak of the accumulated complex. The formation of a monomolecular complex layer on electrode increases the sensitivity of voltammetric measurement because the metal is not dissolved in the mercury [2].

Nickel is a transition metal of both biological and geochemical importance. It is one of the essential trace elements among other metals such as cobalt, copper, zinc, and manganese in the diet, being a component of the enzyme urease and of five other important enzymes [4]. It is a moderate toxic element but it can cause allergic reactions and certain nickel compounds are carcinogenic [5]. It is used in a large number of alloys, including stainless steel, in batteries, chemicals, pigments and catalysts, and in the electrolytic coating of items such as chromium-plated taps and fittings used for tap water. This metal is released into the aquatic environment from both natural and human-made sources and is distributed by means of chemical, physical and biological processes [6]. In Europe, Ni is considered a priority substance in the Water Framework Directive (European Commission, 2000) [7], implying that environmental quality standards for this metal are required in the whole European Union. Natural water contains low concentration levels (8.52–25.56 nM), finding background levels of 5.11 nM in river water [8], 11.93 nM in surface water [9] or 2.73–4.26 nM

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Table 1
AdCSV methods for nickel analysis in water samples.

Ligand[a]	Metal	Chemical conditions	Electrochemical conditions[b]	Analytical features for Ni[c]	Application	Ref.
p-MPAO	Ni	pH: 6.8 [L]: 5×10^{-6} M	HMDE, LS t_d: 3 min; E_d: −0.7 V	DL = 0.03 nM	River water	[13]
HNB	Ni	pH: 6 [L]: 3.3×10^{-5} M	Static MDE, LS t_d: 120 s; E_d: −0.5 V	DL = 1.7 nM Range: 1.7–426 nM	Doped mineral water	[14]
AACD	Cd, Ni, Co	pH: 6 [L]: 3.2×10^{-6} M	HMDE, DPS t_d: 60 s; E_d: −0.8 V	DL = 8.5 nM Range: 8.51–850 nM	Tap, ground and river water	[15]
DMG	Ni	(a) pH: 9 (b) Acid medium [L]: 10^{-4} M	HMDE, DPS (3 steps) (a) t_d: 120 s; E_d: −1.35 V (b) t_d: 30 s; E_d: −1.1 V	(a) DL = 0.2 nM Range: 1–100 nM (b) DL = 2 nM Range: 5–100 nM	Tap and river water	[16]
DMG	Ni, Co	pH: 9.3 [L]: 2×10^{-4} M	Hg film E, DPS t_d: 240 s; E_d: −0.8 V	DL = 6 nM Range: 21–759 nM	Tap water	[17]
DMG	Ni, Co	pH: 9.2 [L]: 10^{-4} M	Bi film E, SWS t_d: 300 s; E_d: −0.7 V	DL = 1.7 nM Ranges: 8.5–85; 17–170; 34–340; 85–850 nM	Certified river water	[18]
DMG	Ni, Co	pH: 7.4 [L]: 5×10^{-3} M	Pb film E, SWS t_d: 120s; E_d: −0.75 V	DL = 1.6 nM Range: 5–100 nM	Rainwater	[12]
DMG	Ni	pH: 9 [L]: 10^{-3} M	Bi film E, SWS t_d: 600s; E_d: −0.7 V	DL = 10 nM Range: 10–1000 nM	Ground and mineral water	[19]
DMG	Ni	pH: 9.5	HMDE, DPS t_d: 90s; E_d: −0.7 V	DL = 0.46 nM Range: 0.46–119 nM	Lake water	[20]
DMG	Ni	pH: 9.2 [L]: 2×10^{-4} M	Bi Film E, SWS t_d: 90 s; E_d: −0.7 V	DL = 1.7 nM Range: 1.7–340 nM	Certified river and spiked tap water	[21]
DMG	Ni	pH: 9.2 [L]: 10^{-4} M	HMDE, DPS t_d: 180 s; E_d: −0.7 V	DL = 0.1 nM	Seawater	[22]
Nioxime	Ni, Co	pH: 7.6 [L]: 10^{-4} M	HMDE, DPS t_d: 15 min; E_d: −0.6 V	DL = 0.45 nM Range: 0.45–20 nM	Seawater reference materials	[23]
DMG	Ni, Co	pH: 7.9 [L]: 2×10^{-4} M	HMDE, SWS t_d: 60–180 s; E_d: −0.7 V	DL = 0.05 nM	Seawater	[24]
DMG	Ni	pH: 8.3 [L]: 4×10^{-4} M	HMDE, SWS t_d: 60 s; E_d: −0.7 V	Blank value: 0.8 nM Range: 0.8–7.7 nM	Seawater	[25]
DMG, oxine, SA and nioxime	(a) Cu, Ni, Cd, Pb, Co, Zn (b) Cu, Ni, Co (c) (Cu, Pb, Cd) + (Ni, Co)	(a) pH: 7.6–8.5 [D]: 2×10^{-4} M [O]: 0.2×10^{-4} M (b) pH: 9.2 [SA]: 2×10^{-5} M [N]: 5×10^{-6} M (c) pH: 7.7 + 9.2 [O]: 10^{-5} M [N]: $9 \cdot 10^{-6}$ M	(a) HMDE, SWS t_d: 60 s; $E_{d:}$: −0.8 V (b) HMDE, DPS t_d: 60 s; E_d: −0.75 V (c) HMDE, SWS + DPS t_d: 60 s; E_d: −1.0 V + t_d: 30 s; E_d: −0.8 V	(a) DL = 0.22 nM Range: 0–350 nM (b) DL = 0.30 nM Range: 0–60 nM (c) DL = 0.36 nM Range: 0–35 nM	Seawater	[26]
DMG and catechol	Ni, Cu, V	pH: 7.4 [D]: 0.5 mM [C]: 0.7 mM	HMDE, DPS t_d: 200 s; E_d: −0.35 V	DL = 0.4 nM Range: >150 nM	Coastal seawater	[27]

[a] p-MPAO: 5-[(p-methyl-phenyl)azo]-8-aminoquinoline; HNB: hydroxynaftol blue; AACD: ammonium 2-amino-cyclopente dithiocarboxylate; DMG: dimethylglyoxime; nioxime: cyclohexane-l,2 dione dioxime; SA: salicylaldoxime.

[b] HMDE: hanging mercury dropping electrode; E: electrode; LS: linear scan; DPS: differential pulse scan; SWS: square wave scan.

[c] QL: quantification limit; DL: detection limit.

in Atlantic ocean water [10], but those are increased owing to pollution of water (i.e.: nickel concentration in Mersey Estuary (UK) ranged from about 10–230 nM depending on the proximity to the coast [11]). Considering the low content of nickel in water, sensitive analytical techniques are required.

Nickel determination cannot be performed by ASV because it does not form amalgams, being better the use of adsorption process for preconcentration step [12]. Therefore, a number of studies on the use of AdCSV for the determination of nickel have been reported and compared. These methods present advantages and disadvantages in relation to the sensitivity, selectivity and applicability to different types of samples. The most commonly used complexing agent for determining nickel is dimethylglyoxime (DMG), although some others and mixtures of ligands have also been used (Table 1) [12–27]. Most of the methods have been applied to water with no saline matrix (tap, mineral, lake, river, ground and rain water). The methods for nickel analysis in seawater are either not sufficiently sensitive or they require long deposition times making them time consuming. Thus, some improvements are still desirable.

In this paper, a new differential pulse adsorptive cathodic stripping voltammetric method (DP-AdCSV) for the determination of nickel in aqueous samples based on metal complexation with pyridoxal salicyloylhydrazone (PSH) is presented. This reagent has been used in the spectrophotometric and spectrofluorimetric determination of several metals such as zirconium, aluminium, titanium or copper [28–31]. However, the complexation capacity of PSH in the presence of metal ions for the potential use in metal determination by AdCSV has not been previously reported until now.

For this study, statistical strategies were used. Experimental designs are good statistical tools to determine in an efficient way the set of conditions required to obtain a proper process. Recently, these strategies have been recommended for the electroanalytical determinations, including the adsorptive stripping voltammetry. The analytical response depends on many experimental factors (pH, buffer composition and concentration, supporting electrolyte, complexing agent), instrumental ones (deposition potential and time, pulse amplitude, frequency, step potential...) and operational ones (stirring rate, purge time...). Besides their effect on the current enhancement, they may influence on other properties of the voltammetric measurement as peak shape, overlapping peaks or reproducibility. Because of that, classical optimization methods are lengthy, inadequate and they do not allow the measure of the influence of each variable has on the other; and consequently, screening and optimization designs of these parameters are highly recommended [32].

A two-step study strategy based on a Plackett Burman design and subsequently a modified simplex method has been followed, involving several chemical and instrumental parameters. Initial screening of selected variables was used to know the significance of their effects on the voltammetric responses of the PSH reagent and metal complex. A Plackett Burman screening design allows finding the empirical linear relationship between the response and the studied parameters (called factors). In addition, the experimental matrix can include experiments at the central level of each factor, not used for the model construction but used to test the model linearity. This type of design has great value in screening experiments when a large number of factors can have influence on the response [33].

After that, the modified simplex was used as a multivariate nonlinear optimization tool of the significant variables. A simplex is a geometric figure defined by a number of points (vertices) equal to one more than the number of variables to optimize. Each point corresponds to an experiment under the conditions to be studied. The method forces the figure to move towards a region where the response is optimum. The modified simplex uses the reflection, the expansion and contraction of the figure during the procedure; and for every certain number of experiments, a previous trial is repeated [34]. The most important advantage of this method is the possibility of performing the simultaneous optimization of several response signals, considering the interaction among the variables [35]. This tool was an effective way of locating the optimum conditions for nickel analysis.

The analytical parameters as repeatability, linearity and accuracy were also investigated. The method was validated and applied successfully to the analysis of nickel in different natural waters: estuarine water and seawater.

2. Experimental

2.1. Reagents and solutions

Stock aqueous solutions of Ni(II) were prepared weekly by dilution of Ni(II) standard solution of 1000 mg l^{-1} (Merck, Germany) in 0.06 M HNO_3. PSH reagent was synthesized by reaction between pyridoxal and 2-hydroxybenzohydrazide (SH) purchased to Sigma–Aldrich (Germany) [28]. Aqueous solution of pyridoxal (1.1 g in 20 ml) and ethanolic solution of SH (1 g in 20 ml) were mixed under reflux heating 10 min, and cool at room temperature. Crystals were filtered off and washed with a large volume of ethanol. Subsequently, they were crystallized from 1:1 ethanol/water and dried at 110 °C. The reagent obtained was yellow ($C_{15}H_{15}N_3O_4$, formula weight, 301; m.p., 247 °C; CAS No.: 82970-90-9). A 1.33×10^{-3} M stock solution of PSH in extrapure absolute ethanol was prepared weekly and stored at 4 °C in darkness. Stability of stock solution of reagent was studied spectrophotometrically at 420 nm, being stable for one week.

Britton–Robinson buffer solutions were used to adjust the pH (range 2.6–11) during the previous experiments and the optimization of the method. These solutions were prepared according to previously reported [36], using o-boric acid, o-phosphoric acid, acetic acid and sodium hydroxide (Merck); constant ionic strength of 1.5 M was obtained by adding KCl. Ammonium chloride buffer was prepared using 4 M NH_3 and 2 M HCl Suprapur grade purchased from Merck, and used to adjust the pH at optimal conditions.

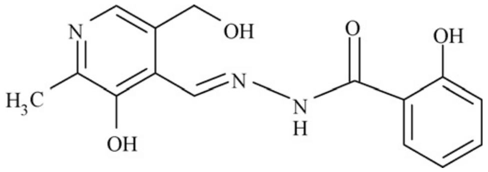

Fig. 1. Pyridoxal salicyloylhydrazone ligand (PSH).

All laboratory materials were acid cleaned (2 M HNO_3), rinsed with Milli-Q water and stored in a laminar flow cabinet. All reagents were of analytical-reagent or Suprapur grade and all solutions were prepared using Milli-Q deionised water (Millipore, USA) and distilled or extrapure ethanol (Scharlab, Spain). During voltammetric analysis, solutions were deoxygenated with high purity nitrogen (Air Liquide, Spain) prior to each experiment.

The certified reference materials (CRM), analyzed to determine the accuracy of the proposed method, were Community Bureau of Reference (BCR) CRM 505 and Laboratory of the Government Chemist (LGC) LGC 6016 C estuarine waters supplied by LGC Promochem SL (Spain).

The proposed method was applied to coastal water samples from Tangier Bay (Morocco). Samples were filtered through 0.45 μm pore size filters, acidified with HNO_3 of Suprapur grade (Merck) and stored until application of the method. Before analysis, organic matter of samples was destroyed by adding of 0.02 M hydrogen peroxide Suprapur (Merck) and UV digestion for three hours employing a 500 W high pressure mercury vapour lamp.

2.2. Instrumentation

Stripping measurements were performed with a Metrohm 757 VA Computrace Stand (Metrohm, Switzerland) with automated hanging mercury drop electrode as working electrode. The cell also included an Ag/AgCl reference electrode (saturated with 3 M KCl) and a platinum wire as auxiliary electrode. The stand was controlled by PC software VA Computrace 2.0 installed in a personal computer using a 5326 VA Computrace Interface (Metrohm, Switzerland). All measurements were made at room temperature. A Unicam Helios Gamma&Delta (Unicam Limited, UK) spectrophotometer was used for UV–vis spectroscopic measurements with 1 cm quartz glass cells (1 cm × 1 cm × 4.5 cm). A model 2001 pH-meter equipped with 52-02 combined glass-Ag/AgCl electrode (Crison, Spain) was used for pH measurements and pH 4 and 7 standards on the NBS pH scale were used for its calibration. Organic matter was removed for real water samples by UV irradiation with a Metrohm model 705 UV Digester (Metrohm, Switzerland) in quartz tubes. Sample handling and preparation of solutions were performed using polyethylene gloves and under a class 100 laminar flow hood cabinet Crusair model 9005-FL (Cruma, Spain) in order to avoid contamination of solutions and samples. Water used for experiments was purified by reverse osmosis with an Elix 3 system followed by deion-

Table 2

Chosen factors and selected levels for the Plackett–Burman design.

Parameter	Symbol	−1	0	+1
pH	pH	5	7	9
Deposition potential (V)	E_d	−0.2	−0.4	−0.6
Deposition time (s)	t_d	60	90	120
Pulse amplitude (V)	P	−0.04	−0.07	−0.1
Voltage step (V)	U_s	0.004	0.008	0.012
Time interval for voltage step (s)	t_s	0.1	0.6	0.9

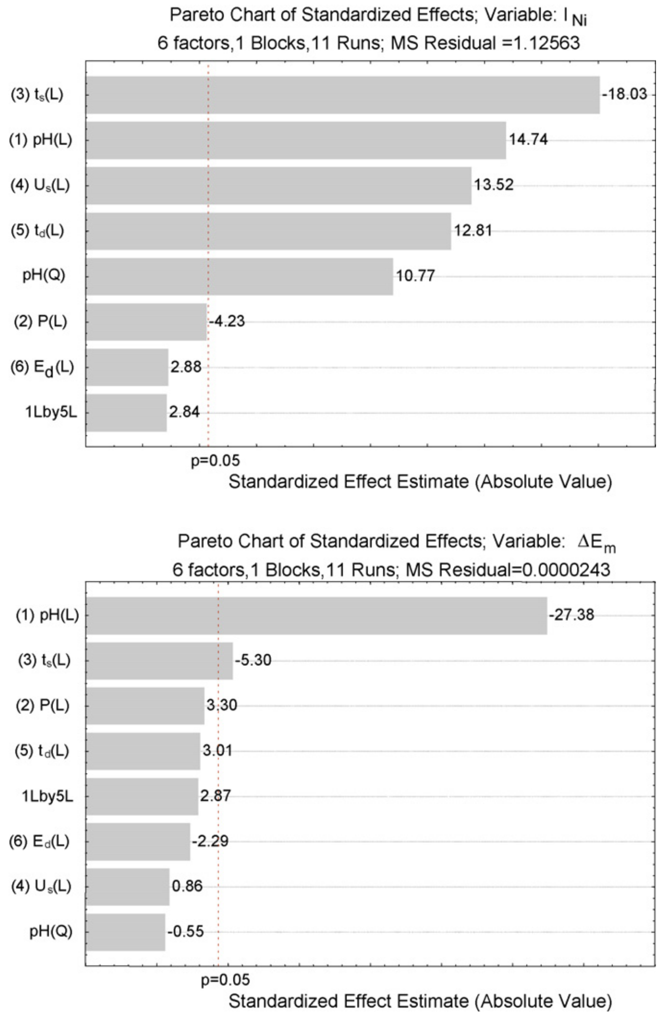

Fig. 2. Pareto's chart of the Plackett–Burman design for the intensity of the measurement of nickel–PSH complex peak (I_{Ni}) and for the difference of potential measurement between the neighbouring nickel–PSH and free PSH peaks (ΔE_m).

ization with an 18 MΩ cm^{-1} deionised Milli-Q system (Millipore, USA).

2.3. Procedure

Stripping analysis of nickel was carried out in 0.15 M Britton–Robinson buffer (pH = 2.6–11) for previous experiments or 0.08 M ammonium chloride buffer (pH = 8–10) for final conditions, containing 5.32×10^{-6} M PSH as the complexing agent. A 10–25 ml sample solution was deoxygenated for 5 min with high purity nitrogen and the adsorption of nickel complex was done using a preconcentration potential of −0.8 V under stirring conditions of 2000 rpm. After an equilibration time of 10 s, the adsorbed metal complex was stripped and voltammogram was recorded in the quiescent solution by applying a negative-going differential pulse scan. Scans of each experiment were repeated twice with a new hanging drop. The metal analysis was performed by standard addition method with a purge time of 10 s after each addition.

Statistical analysis was performed using the statistical software package STATISTICA (data analysis software system) version 7 [37] for reduced factorial design (Plackett–Burman design) and MultiSimplex 2.0.4 [38] for the Modified Simplex method.

Table 3
Fixed chemical and instrumental variables for the modified simplex.

Parameter	Symbol	Value
PSH concentration	[PSH]	5.32×10^{-6} M
Nickel concentration	[Ni(II)]	3.4×10^{-8} M
Buffer concentration	Britton–Robinson	0.15 M
Cell volume	V	25 ml
Pulse time	t_p	0.04 s
Drop size	ds	9 a.u
Stirring speed	r_s	2000 rpm
Equilibration time	t_e	10 s
Potential scan	E	−0.1 V to −1.25 V
Pulse amplitude	P	−0.07 V
Deposition potential	E_d	−0.8 V
Deposition time	t_d	120 s

3. Results and discussion

3.1. Choice of the ligand

PSH is a multidentate ligand with the chromogenic group (OH)C=C–CO–NH–N=C=C(OH) (Fig. 1). The IR spectra of solid PSH exhibits ν(N–H) and ν(N–H$^+$) of the pyridine ring absorption bands at c. 3350s and 3130w, and 2800mb cm^{-1}, respectively, whose protonation has appeared due to the migration of the phenolic OH group to the pyridine nitrogen, indicating that the ligand exists in the keto form as solid state. However, in solution and in the presence of some metal ions the ligand may co-exist in equilibrium with the tautomeric enol form. The tautomer by the loss of enolic proton can act as a charged tridentate ligand coordinating through the phenolic oxygen, the azomethine nitrogen and the carbonyl oxygen atoms. Other important IR bands correspond to the phenolic ν(C–O) stretching and bending vibrations at c. 1518s and 1280s cm^{-1}, and the band at 1630vs assigned to the ν(C=N) stretching vibrations [31]. Therefore, the ligand may function as a bidentate or tridentate ligand for complexing metals. The UV spectra of PSH shows two main absorption maxima at 230 and 300 nm in ethanol; they are found at 300 and 350 nm in acid aqueous solution with a bathochromic shift in moderately alkaline media [28]. PSH also shows good fluorescent which may be due to the occurrence of two hydroxyl groups in ortho-positions in the former reagent [29]. The ligand has an acid–base behaviour with two ionisation constants of pK_1 4 and pK_2 7.0, caused by protonation of the pyridine nitrogen atom and deprotonation of the hydroxyl group, respectively [28].

Some pyridoxal derivatives have been employed in inorganic analysis as spectrofluorimetric and spectrophotometric reagents (analysis of Zr(IV) [28] or Al(III) [29]) or for analytical biochemical purposes, but it is not known about their value in adsorptive stripping voltammetry. Therefore, different experiments were carried out to identify the behaviour of PSH on HMDE electrode in the presence of different metal ions. A cathodic peak for Ni–PSH complex was found and the suitability of this ligand for the proposal of a new AdCSV method for nickel analysis was examined.

The continuous variation (Job's method) and the mole ratio methods were applied in order to establish the stoichiometry of the complex used in this study. 8:2 aqueous–ethanolic solutions of nickel chelate buffered at pH 8.9 were prepared and their absorbances were measured at 420 nm with visible spectrophotometer. The nickel/ligand ratio obtained was 1:2 and the stability constant β_{ML2} of the formed complex was 1.16×10^{11}. In addition, the stability of the metal complex in aqueous–ethanolic medium was studied using a solution prepared by adding 1 ml of 1.33×10^{-3} M PSH and 0.5 ml of 1.33×10^{-3} M Ni(II). The stability of this solution was measured spectrophotometrically

Table 4
Simplex design with significant variables and values for two responses: Ni–PSH peak intensity (I_{Ni}) and peaks overlapping between Ni–PSH and free PSH (ΔE_m) (solutions containing 3.4×10^{-8} M Ni(II) ion and 5.3×10^{-6} M PSH) (F: first simplex; R: reflexion; E: expansion; C^+: positive contraction; C^-: negative contraction; *: not possible).

Vertex[a]	pH	U_s (V)	t_s (s)	I_{Ni} (−nA)	ΔE_m (V)	Type
1	8.5	0.016	0.05	44.35	0.133	F
2	8.5	0.008	0.15	3.66	0.127	F
3	9.5	0.008	0.05	25.47	0.093	F
4	9.5	0.016	0.15	9.55	0.096	F
5	9.8	0.019	0.02	***	***	R
6	8.8	0.011	0.12	9.35	0.121	C^-
7	8.4	0.007	0.00	***	***	R
8	9.2	0.014	0.11	12.25	0.112	C^-
9	9.3	0.014	0.02	***	***	R
10	8.9	0.012	0.10	14.42	0.121	C^-
11	8.7	0.010	0.02	***	***	R
12	9.1	0.013	0.09	18.55	0.132	C^-
13	9.2	0.013	0.03	***	***	R
14	9.0	0.012	0.08	21.38	0.117	C^-
15	8.2	0.019	0.10	8.75	0.130	R
16	9.2	0.011	0.06	30.47	0.108	C^-
17	8.7	0.013	0.04	***	***	R
1(R−1)	8.5	0.016	0.05	43.27	0.130	F
18	9.0	0.013	0.08	19.75	0.130	C^-
19	8.8	0.015	0.05	60.25	0.133	R
20	8.7	0.016	0.03	***	***	E
21	8.7	0.015	0.03	***	***	R
22	8.9	0.013	0.07	31.80	0.130	C^-
23	8.3	0.018	0.05	32.12	0.130	R
24	8.2	0.020	0.03	***	***	R
25	8.7	0.015	0.06	50.38	0.133	C^-
26	9.0	0.013	0.06	42.10	0.119	R
27	8.8	0.014	0.06	45.03	0.130	C^+
28	9.0	0.013	0.06	42.28	0.132	R
29	8.6	0.015	0.05	42.63	0.133	C^-
30	8.6	0.016	0.05	47.40	0.128	R
19(R−1)	8.8	0.015	0.05	60.75	0.133	R
31	8.8	0.016	0.06	59.85	0.130	R
32	8.9	0.015	0.06	52.32	0.133	R
33	9.0	0.016	0.05	64.00	0.125	R
34	8.8	0.016	0.05	65.66	0.130	R
35	8.8	0.017	0.04	***	***	E
36	8.9	0.015	0.04	***	***	R
37	8.8	0.016	0.06	58.58	0.130	C^-
38	8.6	0.015	0.06	45.3	0.133	R
19(R−2)	8.8	0.015	0.05	60.04	0.133	R
39	8.9	0.016	0.05	66.91	0.125	C^-
40	8.9	0.015	0.04	***	***	R
41	8.8	0.016	0.06	58.79	0.130	C^-
42	8.9	0.017	0.06	72.14	0.131	R
43	8.9	0.018	0.06	71.67	0.120	E
44	8.9	0.017	0.05	70.57	0.131	R
45	8.8	0.017	0.06	71.34	0.131	R
34(R−1)	8.8	0.016	0.05	68.54	0.130	R

[a] n(R−m): m replicate of the n experiment.

at 420 nm. The complex solution was stable at least for two weeks.

3.2. *Preliminary experiments*

Previous electrochemical studies of PSH were carried out and a reduction peak was found depending on the pH of the supporting electrolyte and indicating the involvement of protons in the reduction processes. The peak decreased and showed shifts (about −0.518 V at pH 2.6 to −0.932 V at pH 9.6) to high negative values as the pH increased. With the addition of Ni(II) to PSH solution, another stripping peak was found showing the adsorptive characteristics of the metallic complex. The cathodic peak for Ni–PSH complex was found at slightly higher values of potentials than PSH peak depending on the pH (about −0.800 V at pH 2.6 to −1.150 V at pH 9.6). Therefore, not only the complex capacity of PSH with nickel at different pH values was taken account, but also the possibility of peaks overlapping between the free PSH peak and the metal complex peak.

3.3. *Optimization strategies*

In this paper, a Plackett–Burman method has been used as screening design. This method allows determining the effects of process parameters (called factors) on chosen responses [32,39]. Six factors were considered as potentially relevant for this study. The appropriate selection of experimental domain for each factor was made from prior experiences and knowledge of the assay system (Table 2). Two responses were chosen for the optimization: the intensity of the measurement of nickel–PSH complex peak (I_{Ni}) and the difference of potential measurement between the neighbouring nickel–PSH and free PSH peaks (ΔE_m) measured at maximum I. Although the main purpose was to achieve the best sensitivity for the determination of nickel, the possible interference by peaks overlapping with peaks of PSH was also taken into account. An eight-run matrix was used and three experiments at the central level of each factor were also included; two replicates for each experiment were performed. The experiments were carried out in a randomised order. No significant parameters were kept fixed: pulse time (t_p), 0.04 s; drop size (ds), 9 a.u.; stirring speed (r_s) 2000 rpm; buffer concentration (Britton–Robinson), 0.15 M; equilibration time (t_e), 10 s; volume of sample solution, 25 ml; potential scan, −0.1 V to −1.25 V; reagent concentration, 1.25×10^{-5} M PSH; and Ni(II) concentration, 7.7×10^{-8} M.

The results of the analysis of the variance on the data were represented by the Pareto chart in Fig. 2. It can be deduced that there were five significant effects at 95% confidence level for the maximum intensity of the Ni–PSH peak, namely: t_s (−), pH (+), U_s (+), t_d (+) and the square pH value; P and E_d were not significant effects in the range studied. The ΔE_m response was only affected by the pH (−) and t_s (−) factors. Therefore, the most significant parameters were the pH value with opposite influence over the two responses and the time interval for voltage step (t_s) with a negative influence over both responses.

From the results of the Plackett–Burman design, several variables were kept fixed (Table 3), whilst a modified simplex with the significant variables (the pH value, t_s and U_s) was carried out in order to obtain the optimal conditions by using the software Multisimplex 2.0.4 [38]. The deposition time (t_d) was fixed at maximum value studied in the Plackett–Burman design. Higher values of this variable were not studied in the simplex method in order to avoid long analysis times. Two response variables (the sensibility of the method, I_{Ni} and the selectivity of the measurement, ΔE_m) were considered for the evaluation of the efficiency of the voltammetric determination as above for the previous design. They were evaluated simultaneously applying the same weights during the advance of the simplex by the software. The initial simplex with 4 vertices (3 variables) was performed by assignment of a reference value and a step size for each variable. The conditions of the initial vertices were the experiments 1–4 in Table 4. The process was continued until the optimum conditions were reached. The values for the two responses of each run can be seen in the Table 4.

The criterion selected for stopping the simplex was based on the comparison of the variance of the proposed method for I_{Ni} (variance of experiment number 33 = 2.584, for n = 4) with the variance of each simplex [40]. This comparison was carried out using the corresponding F-values for probability value of p = 0.50. The process was stopped for simplex 43 (after 45 different experiments), including experiments 42, 44, 45 and 34(R−1) with similar conditions. They showed a variance value of 2.391 for I_{Ni} values ranging from 68.54 to 72.14 nA (n = 4). The differences of potential measurement between the neighbouring nickel–PSH and free PSH peaks for these experiments were similar (ΔE_m range: 0.130–0.131 V). The following values of variables: pH 8.9, voltage step 0.017 V and time interval for voltage step 0.05 s, were used for further studies.

3.4. Improvement of the voltammetric peak

A universal buffer solution was used during optimization process because the changes in pH values were easier. Once the optimum value was known (pH = 8.9), the use of a simple buffer solution with better blank values seemed more recommended. 0.08 M NH_4Cl/NH_3 buffer solution was used and the background signals were lower. Furthermore, the values of nickel–PSH and PSH voltammetric peaks were increased 4.5 times and 1.9 times, respectively, with the same electrochemical conditions.

Although the separation between the nickel (II) and free PSH neighbouring peaks was adequate at optimal conditions, the influence of different concentrations of ligand was studied. The effect of PSH concentration on the intensity of the measurement of nickel–PSH complex peak (I_{Ni}) using 0.08 M NH_4Cl/NH_3 buffer solution at pH 8.9 is shown in Fig. 3. The values of PSH ranged from 0.33×10^{-6} M to 5.32×10^{-6} M and three concentrations of Ni(II) were used (3.4×10^{-8} M, 6.8×10^{-8} M and 10.2×10^{-8} M). Reproducible voltammetric signals for Ni(II) were obtained using higher PSH concentrations of 1.33×10^{-6} M and the overlapping between the reagent and metal complex signals did not happen. Fig. 4 displays an example of voltammograms showing the effect of PSH concentration on the nickel–PSH complex and PSH peaks for 10.2×10^{-8} M Ni(II) concentration.

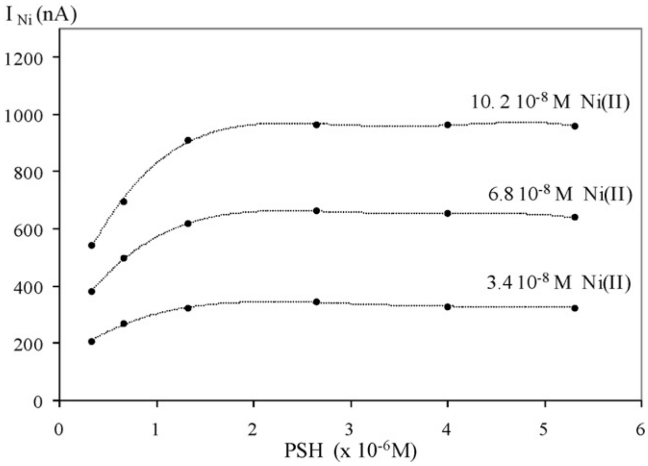

Fig. 3. Effect of PSH concentration on the intensity of the measurement of nickel–PSH complex peak (I_{Ni}) using 0.08 M NH_4Cl/NH_3 buffer solution at pH 8.9.

3.5. Analytical performance of the method

The linear range for Ni(II) determination was evaluated under the optimum experimental conditions. The calibration graph was linear over the range of 0–306.7×10^{-9} M of Ni(II), adding 5.32×10^{-6} M of PSH and employing 120 s as deposition time. The correlation equation obtained was: I_{Ni} (nA) = 7.92×10^9 C_{Ni} + 40.69, with R^2 = 0.998 (n = 14) and where C_{Ni} is the molar concentration of Ni(II). According to the IUPAC method of calculation, the detection limit was DL = $3\,s_b/m$, where s_b is the blank standard deviation and m is the slope of the calibration graph [41], and it was found to be 0.04×10^{-9} M of Ni(II). The precision of the method was 1.4% for 3.4×10^{-8} M of Ni(II) and 1.48% for the blank samples, at a significance level of 95% (n = 9).

Because of electroanalytical techniques employed to analyze nickel usually allow simultaneous analysis of cobalt, the proposed method was applied to the determination of this metal in the same conditions as those optimized for nickel. The linear range for Co(II) determination was over the range from 0 to 169.7×10^{-9} M of Co(II)

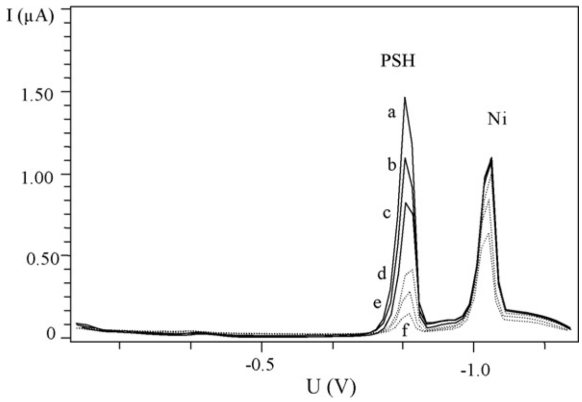

Fig. 4. An example of voltammograms showing the effect of PSH concentration on the nickel–PSH complex and PSH peaks. Electrolyte containing 0.08 M NH_4Cl/NH_3 at pH 8.9, 10.2×10^{-8} M Ni(II), and PSH concentrations of: (a) 5.32×10^{-6} M; (b) 4.00×10^{-6} M; (c) 2.66×10^{-6} M; (d) 1.33×10^{-6} M; (e) 0.67×10^{-6} M; (f) 0.33×10^{-6} M.

Table 5
Study of interferences by salts for Ni(II) determination in solutions containing 3.4×10^{-8} M Ni(II) ion.

Interference	Concentration ($\mathrm{g\,l^{-1}}$)	Recovery (%)
NaCl	23.94	97.4
$MgCl_2$	10.83	97.6
Na_2SO_4	3.99	99.0
$CaCl_2$	1.49	101.8
KCl	0.677	98.2
$NaHCO_3$	0.196	100.8
KBr	0.098	101.8
H_3BO_3	0.027	97.5
$SrCl_2$	0.024	101.0
NaF	0.003	97.9

with 120 s as deposition time. The correlation equation obtained was: I_{Co} (nA) = $1.69 \times 10^9\ C_{Co} + 11.60$, with $R^2 = 0.996$ ($n = 8$) and the detection limit was found to be 1.55×10^{-9} M of Co(II). Nevertheless, cobalt analysis could be better optimized.

3.6. Interference studies

Possible interference by different salts present in natural water with the cathodic adsorptive stripping voltammetry of nickel was investigated by the addition of the salt at the usual concentrations in seawater [42] to a solution containing 3.4×10^{-8} M of Ni. The results of the analysis of nickel by the standard addition method are summarized in Table 5. From the results, it can be concluded that the method is free from interferences of saline matrix. In addition, the influence of other trace metals present in seawater has also been evaluated at higher concentrations than those usually found in seawater samples. Table 6 shows the percentages of recovery of this study. Related to trace metals, no interfering effects were found even though their concentrations exceeded the usual concentrations in seawater. Furthermore, some metals produced voltammetric peaks at other measurement potentials as copper, lead, cadmium, zinc and cobalt. Therefore, based on the encouraging results obtained, this reagent could be applied to the simultaneous analysis of different metals in water.

3.7. Real samples analysis

The accuracy of the method for nickel was assessed by analyses of two types of reference certified estuarine water: CRM 505 and LGC 6016, with different contents of metal. The method was also applied to two samples of real seawater from the Tangier Bay (Morocco) with a peristaltic pump, at a depth of ca. 0.30–0.50 m below the sea-surface. Samples were filtered through 0.45 μm pore size filters, acidified with HNO_3 and stored until the application of the method. The samples showed the following values for chemical parameters: seawater 1, pH 7.87 and salinity 32.0; and seawater 2, pH 8.10 and salinity 32.2. Four replicates of each reference materials and real samples were analyzed after UV digestion with hydrogen peroxide for the organic matter removal. Nickel was measured using PSH–Ni AdCSV by the standard addition method. The results in Table 7 were in good agreement with the certified values and those obtained using DMG–Ni AdCSV method proposed by Metrohm UK Limited Company for seawater [43]. The relative errors were ranged from −5.21% to +3.24%, indicating the successful applicability of the PSH–Ni AdCSV method.

Table 6
Study of interferences by trace metals for the Ni(II) determination in solutions containing 3.4×10^{-8} M Ni(II) ion.

Interference	Concentration (nM)	Recovery (%)
V(V)	100	97.4
Fe(III)	100	97.6
Cu(II)	100	99
Zn(II)	100	101.8
Al(III)	100	98.2
Mn(II)	100	100.8
Pb(II)	100	100.1
Co(II)	3	101.8
Pd(II)	3	97.5
Bi(III)	3	101.0
Cd(II)	3	97.9
Tl(I)	3	97.7
Zr(IV)	3	97.8
Ti(IV)	3	99.5

Table 7
Determination of nickel by applying the new proposed method to certified reference estuarine waters (CRM 505 and LGC 6016) and real seawater samples from Morocco coast.

Sample	Ni Concentration (nM)		Relative error (%)
	Expected	Found[d]	
CRM 505	24 ± 2[a]	24.9 ± 0.9	+3.2
LGC 6016	3169 ± 51[a,b]	3101 ± 68	−2.2
Seawater 1[e]	22.5 ± 0.4[c]	23.2 ± 0.3	+2.8
Seawater 2[e]	14.6 ± 1.3[c]	13.8 ± 0.2	−5.2

[a] Certified value.
[b] Certified values as $\mu\mathrm{g\,l^{-1}}$: 186 ± 3.
[c] Determination by AdCSV (DMG-Ni) [43]; $n = 4$.
[d] $n = 4$.
[e] Seawater samples were collected from the Tangier Bay (Morocco).

4. Conclusions

Nickel can be effectively analyzed by differential pulse adsorptive stripping voltammetry using pyridoxal salicyloylhydrazone (PSH) as ligand. The application of statistical methods allowed the effective optimization of the chemical, electroanalytical and operational parameters. The new method provides a very good detection limit, being lower than those showed by the other AdCSV conventional methods when they are applied to seawater, with a large linear range of applicability. It shows a very suitable resolution, accuracy and reproducibility, and it is free from interferences of inorganic salts and trace metals at usual concentrations in seawater. Using the optimized conditions, others metals can be detected (copper, lead, cadmium, zinc and cobalt). Further studies to explore the use of PSH in AdCSV may lead to a new approach to the simultaneous metals analysis.

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References

[1] A.Z. Abu Zuhri, W. Voelter, Fresenius' J. Anal. Chem. 360 (1998) 1.
[2] S.B. Adeloju, in: Y. Picó (Ed.), Food Toxicants Analysis, Elsevier, Amsterdam, 2007, p. 667 (Chapter 18).
[3] R.M. Takeuchi, A.L. Santos, P.M. Padilha, N.R. Stradiotto, Anal. Chim. Acta 584 (2007) 295.
[4] R.K. Thauer, Science 293 (5533) (2001) 1264.
[5] H.A. Mckenzie, L.E. Smythe, Quantitative Trace Analysis of Biological Materials, Elsevier, Amsterdam, 1988.
[6] B. Berkowitz, I. Dror, B. Yaron, Contamination Geochemistry: Interactions and Transport in the Subsurface Environment, Springer Verlag, Berlin Heidelberg, 2008.

[7] European Commission, Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy, Off. J. Eur. Union L327 (22 December 2000) 1–72.

[8] B. Salbu, E. Steinnes, Trace Elements in Natural Waters, CRC Press, Boca Raton, 1995.

[9] U. Forstner, G.T.W. Wittmann, Metal Pollution in the Aquatic Environment, 2nd revised ed., Springer-Verlag, Berlin, 1983.

[10] OSPAR, Agreement on background concentrations for contaminants in seawater, biota and sediment. Convention for the protection of the marine environment of the north-east Atlantic, 2006.

[11] M. Martino, A. Turner, M. Nimmo, Mater. Chem. 88 (2004) 161.

[12] M. Korolczuk, K. Tyszczuk, M. Grabarcczyk, Electrochem. Commun. 7 (2005) 1185.

[13] Z. Zhang, Z. Cheng, S. Cheng, G. Yang, Talanta 38 (1991) 1487.

[14] P.A.M. Farias, A.K. Ohara, I. Takase, S.L. Ferreira, J.S. Gold, Talanta 40 (1993) 1167.

[15] A. Ensafi, K. Zarei, Talanta 52 (2000) 435.

[16] M. Korolczuk, Talanta 53 (2000) 679.

[17] O.A. Farghaly, Microchem. J. 75 (2003) 119.

[18] M. Morfobos, A. Economou, A. Voulgaropoulos, Anal. Chim. Acta 519 (2004) 57.

[19] S. Legeai, S. Bois, O. Vittori, J. Electroanal. Chem. 591 (2006) 93.

[20] D. Monticelli, E. Ciceri, C. Dossi, Anal. Chim. Acta 594 (2007) 192.

[21] C. Kokkinos, A. Economou, R. Ioannis, T. Speliotis, Anal. Chim. Acta 62 (2008) 111.

[22] C.M.G. Van den Berg, Sci. Total Environ. 49 (1986) 89.

[23] J.R. Donat, K.W. Bruland, Anal. Chem. 60 (1988) (1988) 240.

[24] H. Zhang, R. Wollast, J.C. Vire, G.J. Patriarche, Analyst 114 (1989) 1597.

[25] O. Abollino, M. Aceto, G. Sacchero, C. Sarzanini, E. Mentasti, Anal. Chim. Acta 305 (1995) 200.

[26] C. Colombo, C.M.G. Van den Berg, Anal. Chim. Acta 337 (1997) 29.

[27] A. Cobelo-Garcia, J. Santos-Echeandía, R. Prego, O. Nieto, Electroanalysis 17 (2005) 906.

[28] M. Gallego, M. Valcárcel, García-Vargas, Anal. Chim. Acta 138 (1982) 311.

[29] M. Gallego, M. Valcárcel, M. García-Vargas, Analyst 108 (1983) 92.

[30] M. Gallego, M. Valcárcel, M. García-Vargas, Microchim. Acta 79 (3–4) (1983) 289.

[31] M. Mohan, N.K. Gupta, M. Kumar, N.K. Jha, W.E. Antholine, Inorg. Chim. Acta 197 (1992) 39.

[32] M. Esteban, C. Ariño, J.M. Díaz-Cruz, Crit. Rev. Anal. Chem. 36 (2006) 295.

[33] C.R. Teixeira Tarley, G. Silveira, W. Nei Lopes dos Santos, G. Domingues Matos, E. Galvão Paranhos da Silva, M. Almeida Bezerra, M. Miró, S.L. Costa Ferreira, Microchem. J. 92 (2009) 58.

[34] P.W. Araujo, R.G. Brereton, Trends Anal. Chem. 15 (2) (1996) 63.

[35] N. Ferreirós, G. Iriarte, R.M. Alonso, R.M. Jiménez, Talanta 69 (2006) 747.

[36] C. Mongay, V. Cerda, Ann. Chim. 64 (1974) 409.

[37] STATISTICA, Data Analysis Software System, Version 7, Statsoft Inc., USA, 2004.

[38] MultiSimplex, Version 2.0.4., MultiSimplex AB (publ), Karlskrona, Sweden, 1998.

[39] K. Chauhan, U. Trivedi, K.C. Patel, Bioresour. Technol. 98 (2007) 98.

[40] C.K. Bayne, I.B. Rubin, Practical Experimental Designs and Optimization Methods for Chemists, VCH Publishers, Deefiel Beach, FL, 1986, p. 205.

[41] G.L. Long, J.D. Winefordner, Anal. Chem. 5 (1983) 712A.

[42] K. Grasshoff, M. Ehrhardt, K. Kremling, Methods of Seawater Analysis, 2nd ed., Verlag-Chemie GmbH, Weinheim, 1983, p. 365.

[43] Methrom, Determination of nickel and cobalt in seawater, VA Application Note No. V-69, 2004, http://www.metrohm.com/infocenter/applications/notes/index.php4.