

Trace Nickel Determination with Phenylthiocarbamate in Sea Water by Adsorptive Stripping Voltammetry

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Um método voltamétrico, baseado nas propriedades voltamétricas adsorptivas do complexo níquel- fenilditiocarbamato foi avaliado e testado para determinar traços de níquel em água do mar. Os resultados foram melhores em água do mar que em solução padrão. Cobalto e zinco não apresentaram nenhuma interferência nas condições de análises. Os parâmetros experimentais ótimos foram os seguintes: $C_{DDTC} = 3 \times 10^{-3}$ M; $E_{pre} = -0,85$ V; pH=9,2; $t_{pre} = 3-5$ min. O limite de detecção, depois de 15 minutos de pré-concentração, com agitação da solução, foi de $0,026 \mu\text{g/l}$. Os seguintes resultados de precisão ($s\%=4,39$) e exatidão (% de recuperação = 101 ± 10) foram obtidos.

A voltammetric method, based on the adsorptive properties of the nickel-phenylthiocarbamate complex, was used to determine traces of this metal in sea water. The study showed that only cobalt and zinc interfere, but not under the present conditions. After optimization of the instrumental and experimental parameters, the possibility of determining nickel (II) in sea water was evaluated. Optimal experimental conditions were found to be: $C_{DDTC} = 3 \times 10^{-3}$ M; $E_{pre} = -0.85$ V; pH=9.2; $t = 3-5$ min. The limit of detection is $0.026 \mu\text{g/l}$ after 15 min preconcentration with stirred solution. The results of precision and recovery were 4.39% and $101\% \pm 10\%$, respectively.

Key words: *nickel traces; adsorptive stripping voltammetry.*

Introduction

Adsorptive Stripping Voltammetry (AdSV) is one of the most important techniques for the determination of trace concentrations of metals in natural waters (rivers, lakes, oceans, etc.). This technique has been used for the determination of nickel with dimethylglyoxime, based on the potentiostatic adsorption of the complex¹.

This paper describes the determination of trace concentrations of nickel (II) in sea water by AdSV with a new adsorption agent, phenylthiocarbamate, selected previously².

Experimental

Reagents and Solutions

All solutions were prepared with Millipore Milli-Q water. The metal standard solutions were prepared by diluting A.A.S standard (1000 mg/l.).

Nitric and perchloric acids were of suprapur grade (Merck). Super dry nitrogen was used to remove dissolved oxygen.

The buffer solutions were purified by liquid-liquid extraction with sodium diethylthiocarbamate in carbon tetrachloride media. The sea water samples were collected, filtered ($0.45 \mu\text{m}$ pore size) and stored naturally at 1°C .

The purification of buffer solutions, collection and treatment of the sea water samples and other conditions were described elsewhere³.

Apparatus

Voltamperograms were obtained with a PAR 174A polarograph in conjunction with a PAR 303 electrode and a PAR 0089 recorder. The pH was measured with a Corning pH-meter and a combined pH/calomel. reference electrode.

The glassware, plastic containers, utensils, etc., were soaked for several days in 7M nitric acid and then rinsed with Millipore Milli-Q water before use. The addition of reagents and dilutions were done with automatic micropipettes.

Procedures

A 5ml aliquot of standard or sample solution is pipetted into the electrochemical cell and ammonia buffer (pH 9.2) is added to the stirred solution. The solution is purged with nitrogen to remove oxygen before addition of Φ DTC to avoid oxidation of the reagent.

The solution is then purged with nitrogen for 20 min, the preconcentration potential is applied to the stirred solution and, after a 20 s rest period, a negative-going scan is initiated and the resulting curve recorded. Aliquots of the nickel (II) standard solution are then added and the preconcentration/reduction cycle is repeated with a new mercury drop.

Optimization of Experimental Conditions

The optimal experimental conditions were obtained keeping one parameter constant and changing the others: $C_{\Phi DTC} = 3 \times 10^{-3} M$, $E_{pre} = -0.85 V$, $pH = 9.2$, $t = 3-15 min$, $apt = 100 mV$, $v = 10 mV/s$, $s = 0.5 mA$, drop size = medium.

Results and Discussion

Principal evidences of reliability of the method were observed in the linear scan mode (Figure 1).

Neither the supporting electrolyte nor phenyldithiocarbamate present peaks at $-1.4 V$; this peak is, however, observed when the experiment is carried out with the

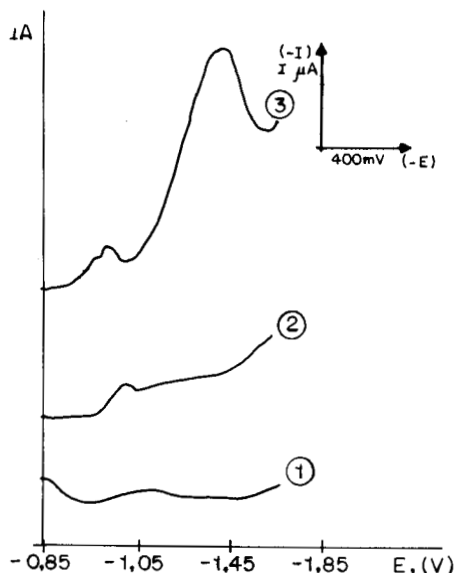


Figure 1. DC.AdSV Behavior of the Ni(II)- Φ DTC system at the hanging mercury drop electrode. (1) $NH_4^+ / BO_3^- = 0.02 M$; (2): (1) + Φ DTC = $2 \times 10^{-4} M$; (3): (2) + Ni(II) = $10 \mu g/l$; $E_{pre} = -0.65 V$; $v = 100 mV/s$; $t_{pre} = 5 min$.

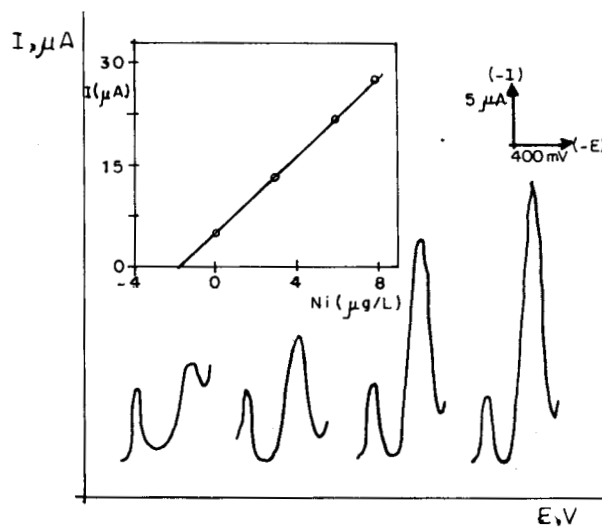


Figure 2. Voltamperograms and DPAdSV curve for the determination of Ni(II) with Φ DTC in acid digested sea water. Nickel (II) standard additions: 3, 6 and $8 \mu g/l$. $t_{pre} = 10 min$.

preconcentration step. This fact confirms the adsorption of the complex.

In Figure 2 a typical example of the determination of nickel in a sea water sample is presented, with three standard additions and the analytical curve in the inset. It is observed that the sensitivity and resolution of the peaks are very satisfactory justifying that saline waters constitute an ideal electrolyte for voltammetry.

Influence of Acid Digestion on the Nickel determination

Nitric and perchloric acids were chosen considering that sulphuric acid is a dehydrating agent which can cause strong reducing conditions. The nitric and hydrochloric acids generally do not extract all the organic matter. The results, presented in Table 1, show a difference of $0.91 \mu g/l$. This means that the results were not significantly affected by realizing the acid digestion. The low observed difference can be explained in three manners: existence of a low concentration of organic matter, high stability of the $Ni(\Phi DTC)_2$ complex or inefficient digestion.

Table 1. Effect of the organic matter in sea water samples.

Nº	Ni(II) in sample not digested ($\mu g/l$)	Ni(II) in sample digested ($\mu g/l$)	difference ($\mu g/l$)
1	0.77	1.67	0.90
2	0.80	1.72	0.92
$\bar{\mu}$	0.78	1.69	0.91

Statistical Evaluation of the Method

The accuracy of the proposed procedure was tested on the basis of recovery of different nickel quantities (Equation 1)⁵. The found values, given in Table 2, are in good agreement with the added values.

$$\% \text{ recovery} = \frac{\text{found concentration}}{\text{added concentration}} \times 100 \quad (1)$$

The reproducibility of six analyses of a sea water sample, for concentrations of 2 µg/l nickel (II) is 4.9% for a preconcentration time of ten minutes. This result was considered very satisfactory.

In order to calculate the detection limit (DL), a solution containing solely the support electrolyte was digested. The average values of current and the standard deviation were 1.37 µA and 0.06 µA, respectively. The DL was calculated on the basis of the Equation 2.

$$DL = \frac{K \times sB}{m} \quad (2)$$

According to the IUPAC method of calculation, the detection limit (3σ) is 0.026 µg/l for nickel.

Conclusion

In our laboratory efforts have been devoted to develop the coordination chemistry and the analytical potentialities of dithiocarbamates⁶⁻⁸. As part of this work we described here an analytical method to determine Ni(II) in sea water by AdSV. The proposed method exhibit similar characteristics as those described in the literature, for the traditional dymethylglyoxime¹, dioxime⁹ and 2,5-dimercapto-1,3,4-thiadiazole¹⁰, chelating agents: reproducibility, s%= 4.39%; accuracy of recovery = 101% ± 10% and detection limit was of 0.026 µg/l.

Table 2. Statistical evaluation of the recuperation of Ni(II) in sea water sample.

Ni(II) added (µg/l)	Ni(II) found (µg/l)	% of recovery	Sensitivity of the meth. (µA/ppb.min)	r ^{2*}
0.2	0.210	104.50	0.459	0.999
1.0	0.999	99.97	0.272	0.994
2.0	1.990	99.67	0.296	0.999
2.0	2.000	100.00	0.288	0.996
2.0	2.380	118.50	0.224	0.999
3.0	2.440	81.33	0.288	0.999
4.0	4.268	106.00	0.280	0.995
$\bar{\mu}$		101.42±10	0.275**±10 ⁻²	0.998±10 ⁻³
s		11.05	0.026	0.002
s(%)		10.89	9.439	0.247

* correlation coefficient.

** n°-1 excluded.

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