

Simplified Methods of Determining Co(II) and Ni(II) in Aqueous Samples

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An approach to simplifying the adsorptive stripping voltammetric determination of Co(II) and Ni(II) is presented. This method uses sodium sulfite as the supporting electrolyte which facilitates the removal of oxygen interference without the traditional necessity of purging with inert gas. The experimental time is reduced at least the amount of time required for de-oxygenation, a minimum of five minutes for 10 mL samples. Two complexing agents were tested for these two elements. The detection limits achieved are comparable to, or better than, those reported in previous literature.

Adsorptive stripping voltammetry (AdSV) has been known to give excellent sensitivity for a variety of trace metals at a mercury electrode (1). This method involves complexation of trace metals with metal specific ligands and adsorbing the resulting complex onto the mercury surface (drop or film). The adsorbed metal complex is electrochemically removed by scanning the electrode potential, usually in a reductive direction. Since this is a surface technique, it is suitable for determining ultra-trace levels (10^{-10} M) of metals in solutions.

Determination of Co(II) and Ni(II) is popularly performed in this manner using dimethylglyoxime (DMG) as the complexing agent. The underlying mechanism of the technique was explained by Jagner and co-workers (2). The procedure is carried out in a basic solution (pH 9) of NH_3/HCl buffer and other electrolytes. The solution is degassed prior to the analysis for at least 5 minutes. Then about 30s elapse while stirring to pre-concentrate the complexed metal on the mercury

surface. It is necessary to maintain an inert gas blanket over the solution throughout the analysis.

A recent publication focuses on Co(II) determination with Nioxime (cyclohexane-1,2-dione dioxime) as the complexing agent (3). This particular compound is said to provide enhanced sensitivity in the presence of NH_3 and nitrite ions. The method was used to determine Co(II) in seawater.

The work presented here focuses on the use of sodium sulfite solution as the background electrolyte to improve the analysis time for both Ni(II) and Co(II) determination. Sodium sulfite quenches O_2 in solution efficiently. This removes the need for deoxygenation of the solution, thus the analysis time is cut by at least five minutes. Hence, the inert gas supply is not required. The sulfite solution at 0.1 M concentration gives a pH of 9.3, thus additional chemicals such as NH_3 , HCl or NaOH , necessary for adjusting pH, are also eliminated. The sensitivity observed for both Ni(II) and Co(II) is excellent.

Experimental

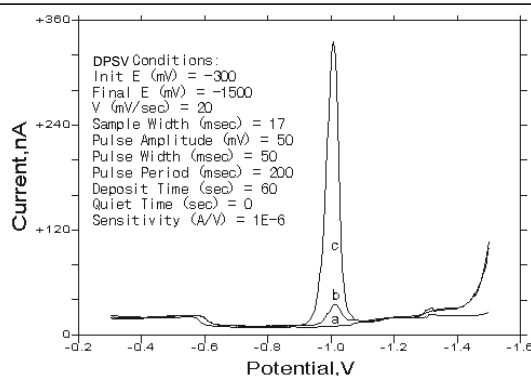
Chemicals and Instrumentation

The chemicals received from manufacturers were used without further purification. The complexing agents, DMG (99+% purity) and Nioxime (97% purity), and the supporting electrolyte, sodium sulfite (98+% purity), were purchased from Aldrich. Standard solutions of complexing agents were prepared in ethanol. Diluted Ni(II) and Co(II) spectroscopic standards (1000 ppm) were used to spike the samples. Water utilized for sample preparation was deionized using a NanoPure water purification system.

The instrument used for potential control in all the experiments was a BAS100 B/W Electrochemical Workstation (BAS, West Lafayette, IN). A CGME (BAS) was employed as the mercury drop working electrode. Reference (Ag/AgCl) and auxiliary (platinum wire) electrodes used throughout this work were from the same manufacturer.

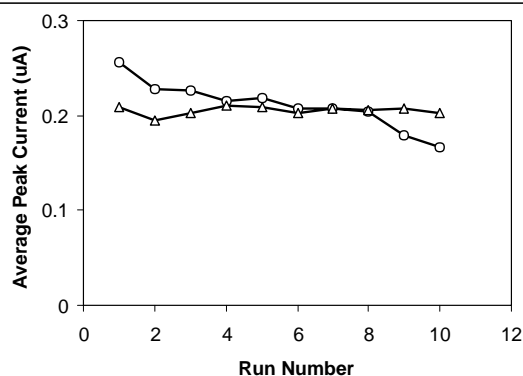
F1

DPSV response for 10 ppb Ni(II) compared with blank. (a) Blank without DMG, (b) blank with DMG, (c) 10 ppb Ni(II) added to (b). The runs were performed with a 60s deposit time in a non-stirred solution.

**F2**

Dependence of the peak current for Co(II) on the amount of complexing agent.

- - 4 μ M Nioxime
- ▲ - 20 μ M Nioxime.

**Procedure**

A 10 mL portion of the 0.1 M sodium sulfite solution was contained in a CGME cell vial. After testing several other voltammetric techniques, Osteryoung Square Wave Stripping Voltammetry (OSWSV) was employed as the tool to evaluate the performance of this method. It provided the best behavior in terms of the sensitivity and the speed. Duplicate runs in the blank solution were performed first to see the electrochemical features in the absence of the complexing agent. Then the appropriate amount of the complexing agent was introduced. After stirring, the same voltammetry experiment was performed in this solution. Then, using 10 ppm Ni(II) and Co(II) standards, the concentration of each ion was increased in 10 ppb steps and the assay was performed.

Results and Discussion**Complexing Agent's Specificity and Concentration**

DMG was initially tested for the determination of Ni(II) alone. As in published work, the concentration of

DMG in the sample was adjusted to 0.02 mM by spiking with 20 μ L of the 0.1 M standard solution. The sulfite blank showed a well-defined peak for background Ni(II). From successive spikes of Ni(II), this blank level was found to be approximately 0.7 ppb. Purification of the blank was not attempted for this work. Simultaneous additions of Ni(II) and Co(II) gave rise to peaks with irreproducible peak currents for Co(II). The Ni(II) peaks were well behaved. These experiments were performed with a pre-concentration potential of -300 mV. Under these conditions DMG appeared to be more specific towards Ni(II). The voltammograms for the blank with and without DMG and added 10 ppb Ni(II) are compared in **F1**. Note: these runs are from Differential Pulse Stripping Voltammetry (DPSV). These runs were performed with a 60s pre-concentration time with no stirring. Since there is a very large signal for this time length, much shorter (or zero) accumulation times could still provide sufficient signal. As seen from the plot, there is no oxygen signal either in the early

or later regions of the potential window used.

In testing linearity for both metals, the Ni(II) additions resulted in good linearity ($R^2=0.995$) over a 0 to 60 ppb range with a sensitivity of 6 nA/ppb (with 0 sec deposit time), whereas Co(II) sensitivity was poor (0.4 nA/ppb) with an R^2 value of 0.969 over the 0 to 50 ppb range. The data points for these plots were the average of three runs at each concentration. For Ni(II), the highest relative standard deviation, 6%, was seen at 10 ppb level and the rest showed a variation of around 1%. For Co(II), the deviation was close to 12% at the lower end and performance was not satisfactory throughout the concentration range chosen. Increased concentration of DMG to 2 mM did not improve the behavior.

Repeated determination of Ni(II) with 10s (non-stirred) pre-concentration and increased square wave frequency (200 Hz) improved the reproducibility to 2% ($n=10$) at the 10 ppb level and the sensitivity to 20 nA/ppb with similar linearity ($R^2=0.996$) over the same range of concentration. This shorter accumulation could increase the dynamic range as can be seen later in the discussion.

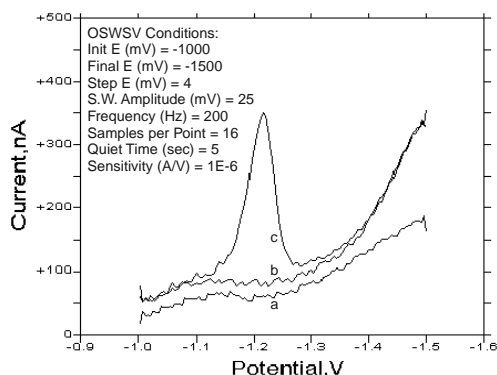
Nioxime was tested next for Co(II) determination. As described in published works (3), 20 μ L of a 2 mM standard solution was used to adjust the concentration of Nioxime (4 μ M) in solution initially. During preliminary experiments with this concentration, the Co(II) signal decayed with time (12% deviation over 10 runs at 10 ppb level). It was suspected that the lower concentration of Nioxime could be responsible for the poor reproducibility. The experiment was repeated with 20 μ M Nioxime. This time the signal was stabilized to within 2% over 10 runs as seen from **F2**. These runs were achieved with 10s (non-stirred) pre-concentration and a square wave frequency of 200 Hz.

The linearity was tested between 10 and 50 ppb in increments of 10 ppb, and showed an R^2 value of

F3

Blank and sample response for Co(II) in the presence of Nioxime.

(a) Blank sulfite solution without Nioxime, (b) the same solution with added Nioxime (4 μ M), and (c) 10 ppb Co(II) spiked into (b).

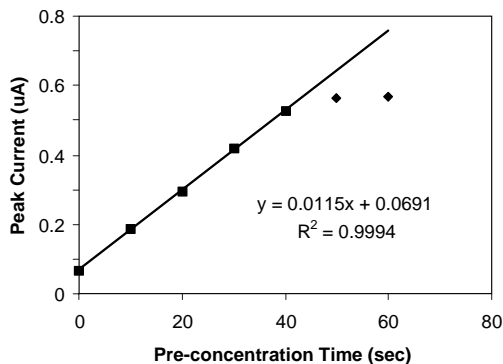


F4

The effect of

pre-concentration time on the peak current. The plot was constructed with 10 ppb Ni(II)/DMG system.

The linear regression was performed only for the first 5 points.



0.998. A plot was constructed showing the average peak current from 10 runs at each concentration. The reproducibility within each concentration was within about 2%. A typical voltammograms for blank, with and without Nioxime, and 10 ppb Co(II) are shown in **F3**. The pre-concentration potential for Co(II) was changed to -1000 mV in order to avoid any Ni(II) interference. However, it appeared that the peak potentials for Ni(II) and Co(II) are about 200 mV apart, hence at low concentrations, simultaneous analysis would be possible. When determining Ni(II) with Nioxime, although there was good response, the reproducibility of the signal was poor. Based on these observations, it appears that there is some specificity of Nioxime toward Co(II). Nevertheless, the depth of this work is not sufficient to claim there does not exist a protocol that can be carefully tuned to perform simultaneous determinations of both metals. Further work is necessary in this direction.

Surface Saturation Effects

Adsorptive stripping analysis is always faced with the difficulty of

surface saturation. The general assumption in AdSV work assumes monolayer or less coverage (4,5). The technique works best when the pre-concentration is carefully controlled to achieve this situation. Non-linear behavior is a result of overloading the electrode surface. The pre-concentration time is an easy parameter to control in order to avoid this phenomenon.

The behavior of the Ni(II)/DMG system at 10 ppb metal concentration with different pre-concentration times was tested. The observed behavior is depicted in **F4**. During these experiments the pre-concentration was performed while stirring. Each data point is the average of three runs that showed less than 3% relative standard deviation. Experimental parameters used were similar to those in **F3**. It is clear that from 0 to 40s, the accumulation with stirring gives rise to linear behavior. Beyond this point, surface saturation takes place for this concentration of Ni(II). It is also clear that the sensitivity of the technique is so high that even 0s accumulation is sufficient to perform the analysis, and thus extend the dynamic range. Avoidingatura-

tion effects is not a difficult task. Method development for a particular assay should be based on knowledge from similar experiments.

Conclusion

The use of sodium sulfite as the supporting electrolyte has eliminated the need for de-oxygenation in adsorptive stripping voltammetry for Co(II) and Ni(II). This approach improved the technique by shortening the experimental time at least by the amount of time required to de-oxygenate the sample, usually a minimum of 5 minutes for a 10-mL volume. It also removed the need for extra chemicals, including the inert gas used for deoxygenating. Sodium sulfite could be suitable for any assay performed at pH 9 using the AdSV technique. Further studies on the properties of the complexes formed in sulfite medium would be of interest for this application.

Two complexing agents, DMG and Nioxime, examined here show some specificity towards Ni(II) and Co(II), respectively. Based on the data presented here, the author believes that the determination of these ions in aqueous samples would be best performed individually. This approach provides better reproducibility and avoids possible peak resolution problems. Thorough experimentation would be necessary in this aspect as well. Finally, the elimination of a de-oxygenation step in the protocol makes it an ideal candidate for automation. Further work in this direction is underway.

References

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