*Asian Journal of Chemistry* Vol. 11, No. 3 (1999), 862–866

# Primary—Secondary Wavelengths Spectrophotometry to Improve the Determination of Trace Amounts of Nickel in Waste Water

HONG-WEN GAO
*School of Chemistry and Chemical Engineering, Anhui University, Hefei-230039, P.R. China*

In ammoniacal solution of nickel, in presence of iodine the conventional reaction of nickel ($Ni^{2+}$) with diacetyldioxime to form red complex has been applied for the improvement of the determination of trace amounts of nickel in water and waste water by the updated method named primary—secondary wavelengths spectrophotometry (PSWS). The results show that the analytical precision and accuracy were increased and gave the higher determination sensitivity than the ordinary spectrophotometry. The relative standard deviations were less than 1.3% and the recovery rate of Ni between 96 and 102%.

## INTRODUCTION

Nickel is one of the poisonous elements. Its compound may cause the allergic skin disease of body. It often exists in waters polluted by, for example the mining, metallurgical, electroplating and other industries. Its conventional spectrophotometric determination involve with diacetyldioxime[1], HINAP[2] and TAN[3] etc. But the former can give the high sensitivity and selectivity, and accurate result in ammoniacal solution and in the presence of iodine, so it remains to be applied widely for the analysis of trace amounts of Ni in environment samples. In this paper the above reaction was first to be used for improvement of determination of trace amounts of Ni by the updated method named primary—secondary wavelength spectrophotometry (PSWS). Because PSWS can give the higher precision and sensitivity than the conventional spectrophotometry and give the stable calibration model the results were all satisfactory. The nickel recovery rate was between 96 and 102%, the relative standard deviations (RSDs) less than 1.3% and the detection limit is only 0.01 mg/L.

For a suspension liquid or a colloid solution the absorbance (A) at wavelength $\lambda$ is relative with the particle's property factors, particle diameter parameter $\varphi$ and amounts parameter $\varepsilon$, their relation curve a is shown in Fig. 1 and their expression is followed by[4]:

$$A = \varphi\varepsilon^{-2}\lambda^{-\varepsilon} \qquad \ldots (1)$$

The absorption spectrum sketch curve b of a colored solution is shown in Fig. 1, too. We can see if curve b moves up $k_1$ distance to b′ position, both M and N

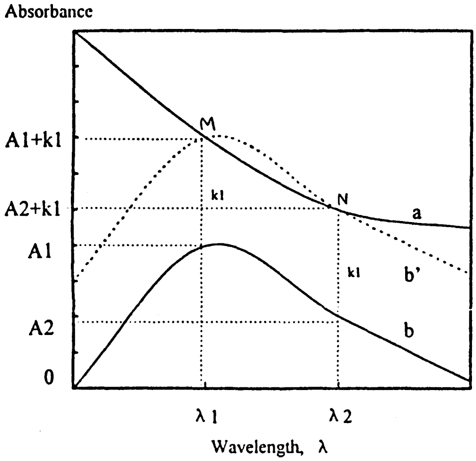

Fig. 1

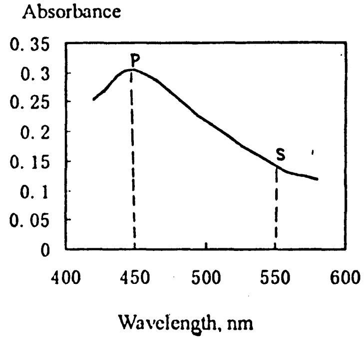

Fig. 2

are two intersect points that pass through curves b′ and a. The absorbances at M and N points should satisfy the equation 1. Therefore,

$$\begin{cases} A_1 + k_1 = k_2\lambda_1^{-y} & \ldots(2) \\ A_2 + k_1 = k_2\lambda_2^{-y} & \ldots(3) \end{cases}$$

Both $k_1$ and $k_2$ are optical parametres. Our experiments show that factor y is an exponent function with ligand amounts, that is with the determined component concentration (x mg/L) when $k_1 = 1$.

$$y = \alpha x^{\beta} \qquad \ldots(4)$$

where $\alpha$ and $\beta$ are constants with two wavelengths $\lambda_1$ and $\lambda_2$ respectively. In order to get maximum sensitivity the wavelength $\lambda_1$ is necessary to be selected at the point of the maximum absorption and it is named as primary wavelength ($\lambda p$): $\lambda p = \lambda_{max}$, also $Ap = A_1 = A_{max}$. The other wavelength $\lambda_2$ may be selected in experiment, wantonly but different $\lambda_2$ will give the different $\alpha$ and $\beta$ values. The $\lambda_2$ may be selected at the corresponding wavelength of $0.5A_{max}$ and it be named as secondary wavelength ($\lambda s$). So we can obtain the following expression from the above equation group.

$$\left(\frac{Ap + 1}{As + 1}\right) = \left(\frac{\lambda p}{\lambda s}\right)^{-y} \qquad \ldots(5)$$

From equation (5) we may calculate *y* value, which give x value from expression 4. We see both Ap and As will happen change at the same step when the experimental conditions, for example room temperature was varied. It is found (Ap + 1)/(As + 1) value varied little.

So equation (5) has the corrected function to operation conditions so that both $\alpha$ and $\beta$ are kept basically stable in y(x) model above.

From above principle we can say that PSWS is realy a dual-wavelength spectrophotometry but it has the different source and basis to compare with the other dual—wavelength methods[5, 6].

## EXPERIMENTAL

Visible spectra were recorded with a Model 722 spectrophotometer (Shanghai, China), in a 10 mm glass cell.

*Standard Ni(II) solution,* 100 *mg/L*: Dissolving 0.1 g of metal nickel (in 99.9%, Shanghai Reagent) in 10 mL of 50% nitric acid by heating then diluting to 1000 mL with ion exchange water.

*Standard Ni(II) solution,* 10 *mg/L*: Preparing with the above standard Ni solution.

*Diacetyldioxime solution*: Dissolving 0.5 g of diacetyldioxime (Shanghai Reagent) in 50 mL of concentrated ammonia water then diluting to 100 mL with ion exchange water. Ammonium citrate (50%). (A.R., Shangai Reagent) solution iodine solution, 0.05 mol/L: dissolving 12.7 g of iodine (A.R., Shanghai Reagent) in 200 mL of 10% potassium iodide (A.R., Shanghai Chemical) then diluting to 1000 mL with ion exchange water. EDTA solution, 5%.

*Recommended Procedures*: A known volume of a water sample containing less than 40 μg of Ni was taken in a 25 mL volumetric flask and added 2 mL of ammonium citrate solution, 1 mL of iodine solution and diluted to 20 mL with exchange water. Mixed well and added 2 mL of diacetyldioxime and 2 mL of 5% EDTA. Diluted to required volume. After 5 min, measure the transmittancy (T%) at 450 and 580 nm, respectively, against a reagent blank.

If a lot of suspending solid or organic complex was contained in a wastewater sample, the nitration procedure should be carried out with nitric acid to eliminate the interferring ions. After adjusting to neutral solution with sodium hydroxide solution the procedures above was carried out.

## RESULT AND DISCUSSION

*Absorption Spectra*: Figure 2 gave the absorption spectra of Ni complex solution. This solution's absorption reached maximum at 450 nm. According to the relative content in principle the primary wavelength should be selected at 450 nm. The secondary wavelength was arranged at 550 nm here. That is $\lambda p = 450$ nm and $\lambda s = 550$ nm.

*Effect of Diacetyldioxime Solution*: Figure 3 showed the effect of the addition of diacetyldioxime solution on factor y calculated from equation 5. We found if the addition of diacetyldioxime solution was more than 1.5 mL y remained almost constant and reached maximum. In this work, 2 mL of diacetyldioxime solution was selected.

*Calibration Gragh*: A series of standard Ni solutions were prepared and the absorbance of each was measured and plotted. According to the measurement results the curve of the logarithm, log Y of the exponent *y's* calculation value were all against the logarithm value of Ni amounts (X μg), log X was shown in Fig. 4.

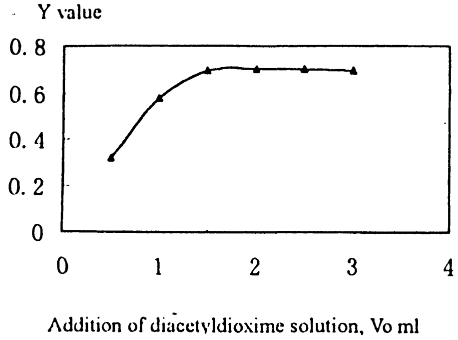

Fig. 3

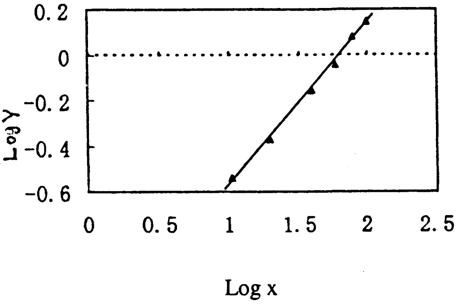

Fig. 4

We found that the curve linearity was better. The cut distance log α was calculated to be −1.31 and the oblique rate β to be 0.721 from the straight line in Fig. 4. The relation of $y$ with $x$ was therefore obtained by the following expression.

$$y = 0.049x^{0.721} \qquad \ldots (6)$$

*Effect of Foreign Ions*: According to the recommended procedure in the presence of ammonium citrate and EDTA, none of the following ions will affect the direct determination of 50 μg of Ni (< 10% error): 100 mg of $Cl^-$, $SO_4^{2-}$, $PO_4^{3-}$, $CO_3^{2-}$, $NO_3^-$; 10 mg of Ca(II), Mg(II), Ti(IV), $Br^-$; 3 mg of Pb(II), Fe(II), Zn(II), Co(II), Cr(III) and 0.5 mg of Cu(II), Mn(II).

*Precision and Detection Limit*: Six replicate determinations of standard Ni solutions containing 20.0 μg was carried out, the relative standard deviation (RSD) being 1.5%. However, the RSD with the single wavelength method was 3.9%. The precision for PSWS was therefore better than that for the ordinary spectrophotometric method.

We used $L_{min} = kSb/S$ to calculate the detection limit of Ni by PSWS, where $k = 3$, Sb named as standard deviation and S named as sensitivity. Replicate determination of twenty reagent blanks gave Sb of y value computed from $(Ap + 1)/(As + 1)$ was equal to 0.005. The analytical sensitivity S was equal to the above α value, 0.049. Therefore the detection limit of Ni was $L_{min} = 0.01$ mg/L.

TABLE-1
DETERMINATION OF NICKEL IN WATER SAMPLES

| Sample title | By conventional method | By PSWS | | |
|---|---|---|---|---|
| | | Added | Found | Recovery % |
| Waste water 1# | 15.1 | 0 | 15.1 14.8 14.8 | |
| | | 20.0 | 33.7 34.1 34.9 | 97 |
| Waste water 2# | 1.19 | 0 | 1.28 1.28 0.27 | |
| | | 1.00 | 2.33 2.27 2.31 | 102 |
| Waste water 3# | 0.145 | 0 | 0.150 0.147 0.146 | |
| | | 0.200 | 0.339 0.342 0.344 | 96 |

*Samples Analysed*: As a test of the method Ni was determined in waste water. The results were listed in Table-1. We found the results by the recommended method is comparable with the conventional method. The RSDs were less than 1.3% and the recovery rate of Ni between 96 and 102%.

## REFERENCES

1. F.X. Chen and X.Q. Lin, *Chin J. Environ. Monitor.*, **3**, 59 (1987).
2. U.B. Talnar, *Anal. Chim. Acta*, **51**, 53 (1970).
3. Havard R. Hovind, *Analyst*, **100**, 769 (1975).
4. H.W. Gao, Proceedings of 4th Asian Chemical Congress, Beijing, p. 372 (1991).
5. ______, *Recl. Trav. Chim. Pays-Bas*, **114**, 61 (1995).
6. H. Watanabe and H. Ohmori, *Talanta*, **26**, 959 (1979).

(*Received*: 9 January 1999; *Accepted*: 3 April 1999) AJC-1710