CHEMICAL ENGINEERING TRANSACTIONS
VOL. 55, 2016
A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Tichun Wang, Hongyang Zhang, Lei Tian

**ISBN** 978-88-95608-46-4; **ISSN** 2283-9216
DOI: 10.3303/CET1655053

# Monitoring Technology of Trace Heavy Metals in Seawater Based on Spectrophotometry

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This paper briefly describes the severity of the heavy metal pollution in seawater in recent years, and proposes a method for the detection of trace heavy metals in seawater based on spectrophotometric method. Establish water soluble trace $Zn^{2+}$, $Cu^{2+}$, $Ni^{2+}$, and $Cd^{2+}$ test system, first of all study the optimal measurement ranges of each ion, and carry out the additive research. The experimental results show that $Zn^{2+}$, $Cu^{2+}$, $Ni^{2+}$, and $Cd^{2+}$ four kinds of metal ions total concentration is in the range of less than 1200 mu g/L and it is in a good degree; and then study the algorithm feasibility and accuracy of measurement, and compares with the ICP-OES measurement results. It also tests the performance of experiment measurement system, and the measurement results have good consistency.

## 1. Introduction

In recent years, heavy metal pollution has become a serious environmental problem, and the continuous emergence of collective heavy metal poisoning incidents is a direct threat to the survival of mankind. The content of heavy metals in water does not have the obvious harm, but with the city expansion and the process of industrialization accelerating, a large number of industrial wastewater and domestic sewage are discharged into the water. The heavy metalse specially the dissolved heavy metals enter the water body, and produce a series of deleterious effects on the water organisms through drinking water, bioaccumulation, food chain and other ways, and ultimately do harm to human health. The scope of human activities continues to expand into the ocean, the resources absorbed from the ocean is increasing, and at the same time pollution problems it brings to the ocean are also increasing, resulting in heavy metal content in coastal waters increased significantly.

Marine heavy metal pollution is one of the pollutions that the marine environment pays much attention to. According to the related research, the pollution in Bohai coastal area is mainly caused by land-based pollutants that account for about 87% of the total amount of pollutants into the sea, and in land-based pollutants, what are discharged into estuaries from estuary accounts for about 95% (Abril et al., 2014). Bohai Bay is located in the hinterland of Bohai, and the land boundary is the Beijing, Tianjin, and Tangshan economic developed areas. Marine environment is seriously disturbed by human factors, and the water exchange is not smooth, especially in recent years, since that the Bohai Bay region has become China's third large-scale area manufacturing centre after the Pearl River Delta and Yangtze River Delta, the pressure that the rapid development of industry brings to the marine environment is increasing, and heavy metal pollution is more and more serious.

## 2. Calculation method

### 2.1 Multiple linear regression equation (MLR)

Multiple linear regression method is the regression analysis method established on the basis of simple linear regression. Compared with linear regression, multiple linear regression variables contain two or more factors, and it is the regression analysis to explain independent variables variation by variables. When using multiple linear regression to establish the analysis model in the actual situation, the model dependent variable is affected by many factors, so it can have many independent variables, but only one dependent variable.

Please cite this article as: Chen J.G., Bi W.H., 2016, Monitoring technology of trace heavy metals in seawater based on spectrophotometry, Chemical Engineering Transactions, 55, 313-318 DOI:10.3303/CET1655053

In the establishment of quantitative analysis model by multiple linear regression method, the selection of the independent variable and the dependent variable directly affects the prediction accuracy and stability of regression model. The selected statistical data is required to be complete, and for the independent variables and dependent variables with a significant linear relationship, the relationship among various independent variables should be guaranteed to be mutually exclusive. The analysis model of the multiple linear regression function is used to predict the concentration of a substance, thus to make the prediction value closer to the actual value.
Its mathematical expression is (Barton et al., 2016):

$$y=\beta_0+\beta_1x_1+\beta_2x_2+\cdots+\beta_mx_m+\varepsilon \tag{1}$$

In (1), $\beta_0,\beta_1,\beta_2,\cdots,\beta_m$ - Absorbance regression coefficient;

$x_i$ - Absorbance of the number i absorption spectrum;

$\varepsilon$ - Random error.

$\beta_0+\beta_1x_1+\beta_2x_2+\cdots+\beta_mx_m$ is used to estimate the mean E(y) of y, namely:

$$E(y)=\beta_0+\beta_1x_1+\beta_2x_2+\cdots+\beta_mx_m \tag{2}$$

It is assumed that $\varepsilon \sim N(0,\delta^2)$ , $y \sim N(\beta_0+\beta_1x_1+\beta_2x_2+\cdots+\beta_mx_m,\delta^2)$ , and $\beta_0,\beta_1,\beta_2,\cdots,\beta_m,\delta^2$ are the undetermined constants that have no relationship with $x_1,x_2,\cdots,x_m$ .

**2.2 Principal component regression equation (PCA)**
Principal component regression is the process of using orthogonal transform to convert the complex spectral data matrix into mutually independent matrix. The principal components selection determines the scale of principal component regression equation prediction error. The number of principal component is too large or too small will reduce the accuracy of the prediction results (Calisi et al., 2013). Too large principal component will lead to over-fitting that, and too small principal component will occur lack of fitting.
The mathematical expression for the principal component regression is:

$$A_{m\times n}=C_{m\times R}\cdot X_{R\times n} \tag{3}$$

$$A_{m\times n}=T_{m\times h}\cdot W_{m\times n}+E_{m\times n} \tag{4}$$

In (3) and (4), $A_{m\times n}$ - Absorbance matrix of a substance;

$C_{m\times R}$ - Concentration matrix of solution;

$X_{R\times n}$ - Absorbance coefficient matrix;

$T_{m\times h}$ - Abstract concentration matrix;

$W_{m\times n}$ - Abstract absorption coefficient matrix;

$E_{m\times n}$ - Residuals matrix.

(3) Partial least squares regression equation (PLS)
The partial least squares method combines the advantages of multiple linear regression, principal component regression and canonical correlation analysis. It can carry out regression modeling when there is serious multi-linearity in variables. It is the most widely used regression analysis method, which can be applied to nonlinear fitting. It determines the number of variables through the repeat extraction of effective data in the spectrum and at last verifies whether the model is significant (de la Gala Morales et al., 2014).
The mathematical expression of partial least square method is:

$$Y=X\cdot Q+E \tag{5}$$

In (5), Y - Response matrix;
X - Prediction value matrix with p variables and n sample points;
Q - Regression coefficient matrix of matrix X;
E - Error matrix.

## 3. Comparison of calculation methods and results prediction experiment

### 3.1 Comparative analysis of experimental results

The Gauss elimination algorithm is used to measure the concentration point data of the test set. Since that the result of MLR calculation is not ideal, 3 kinds of principal components PCA obtained and the four components PLS obtained are compared (Fu et al., 2013).

*Table 1: PCA and PLS algorithm regression calculation results comparison (μg/L)*

| No. | $Zn^{2+}$ | $Cu^{2+}$ | $Ni^{2+}$ | $Cd^{2+}$ | $Zn^{2+}$ | | $Cu^{2+}$ | | $Ni^{2+}$ | | $Cd^{2+}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | PCA | PLS | PCA | PLS | PCA | PLS | PCA | PLS |
| 1 | 40 | 20 | 20 | 20 | 51.7 | 54.3 | 28.6 | 32.1 | 27.5 | 29.4 | -- | * |
| 2 | 40 | 40 | 30 | 30 | 49.2 | 47.6 | 49.1 | 46.4 | 31.9 | 28.0 | -- | * |
| 3 | 40 | 60 | 40 | 40 | 48.5 | 47.9 | 71.2 | 69.3 | 52.3 | 50.7 | -- | * |
| 4 | 40 | 80 | 50 | 50 | 49.1 | 46.5 | 83.5 | 83.7 | 56.2 | 57.4 | -- | 79.8 |
| 5 | 80 | 20 | 40 | 30 | 92.6 | 89.1 | 33.6 | 28.9 | 49.2 | 48.6 | -- | * |
| 6 | 80 | 40 | 20 | 20 | 89.7 | 88.4 | 57.5 | 56.4 | 31.7 | 30.8 | -- | * |
| 7 | 80 | 60 | 30 | 50 | 87.3 | 86.0 | 72.1 | 78.6 | 38.9 | 37.3 | -- | 59.4 |
| 8 | 80 | 80 | 50 | 40 | 84.5 | 88.7 | 91.3 | 86.8 | 57.6 | 58.1 | -- | 42.6 |
| 9 | 120 | 20 | 50 | 40 | 135.8 | 130.4 | 26.2 | 30.5 | 56.0 | 55.7 | -- | * |
| 10 | 120 | 40 | 40 | 50 | 129.7 | 126.3 | 50.6 | 48.3 | 43.4 | 44.8 | -- | 79.8 |
| 11 | 120 | 60 | 30 | 20 | 133.5 | 127.9 | 66.4 | 65.7 | 40.5 | 37.6 | -- | * |
| 12 | 120 | 80 | 20 | 30 | 132.4 | 126.0 | 90.8 | 92.3 | 28.4 | 27.7 | -- | * |
| 13 | 160 | 20 | 30 | 50 | 177.3 | 176.2 | 30.2 | 28.9 | 38.6 | 36.4 | -- | 30.7 |
| 14 | 160 | 40 | 20 | 40 | 170.8 | 176.7 | 51.7 | 52.6 | 31.3 | 27.5 | -- | * |
| 15 | 160 | 60 | 50 | 30 | 168.3 | 169.4 | 70.5 | 62.0 | 58.2 | 54.1 | -- | * |
| 16 | 160 | 80 | 40 | 20 | 172.5 | 164.8 | 87.2 | 83.9 | 45.6 | 43.9 | -- | * |

In Table 1, -- represents PCA algorithm to analyze and calculate the $Cd^{2+}$ concentration, * refers to when the PLS algorithm to calculate the $Cd^{2+}$ concentration is negative or Gauss equations without solution, give up the $Cd^{2+}$ concentration calculation.

From Table 1, it is known that the sensitivity of the system to the concentration of $Cd^{2+}$ is low, and in the sample preparation, $Cd^{2+}$ concentration, relative to other four kinds of ions, the concentration is low. In PCA algorithm, $Cd^{2+}$ as a non-principal component is no longer involved in the formation and calculation of linear equations, and the effective components are high in value. It is possibly caused by small deviation of the system actual performance when the system corrects and measures the curve (Huang et al., 2016); only when PLS algorithm has certain requirements on $Cd^{2+}$ concentration and total metal ion concentration can it achieve the ideal effect. By contrast, the PLS algorithm has better superiority.

### 3.2 Repetitiveness Test Experiment

For the using solution whose concentration points randomly prepared by PLS algorithm are $Zn^{2+}$, $Cu^{2+}$, $Ni^{2+}$ and $Cd^{2+}$, repetitiveness of absorbance is measured under different times and temperatures. The stability and repeatability of the system are also tested, and the repetitiveness test results are shown in Table 2.

*Table 2: System repetitiveness test results*

| No. | Test time | Temperature | The measured value | | | | The error (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $Zn^{2+}$ | $Cu^{2+}$ | $Ni^{2+}$ | $Cd^{2+}$ | $Zn^{2+}$ | $Cu^{2+}$ | $Ni^{2+}$ | $Cd^{2+}$ |
| 0 | 4:00pm, 2012-11-17 | 14°C | 165.8 | 35.3 | 19.1 | 18.1 | 3.63 | 11.75 | 36.3 | 39.7 |
| 1 | 9:00am, 2012-11-18 | 13°C | 168.3 | 31.7 | 23.4 | 16.4 | 5.18 | 20.75 | 21.3 | 45.3 |
| 2 | 12:00, 2012-11-18 | 22°C | 169.7 | 37.8 | 24.6 | 23.8 | 6.06 | 5.5 | 18.0 | 20.7 |
| 3 | 4:00pm, 2012-11-18 | 17°C | 162.4 | 43.6 | 26.3 | 28.6 | 1.5 | 9.01 | 12.3 | 4.6 |
| 4 | 9:00am, 2012-11-19 | 14°C | 156.2 | 47.1 | 29.4 | 35.7 | 2.38 | 17.75 | 2.0 | 19.0 |
| 5 | 12:00, 2012-11-19 | 20°C | 151.5 | 48.5 | 31.7 | 39.8 | 5.31 | 21.25 | 5.6 | 32.7 |
| 6 | 4:00pm, 2012-11-19 | 16°C | 147.6 | 45.4 | 35.8 | 40.2 | 7.75 | 13.5 | 19.3 | 34.0 |
| 7 | 9:00am, 2012-11-20 | 13°C | 158.7 | 39.3 | 39.5 | 37.4 | 0.82 | 1.75 | 31.7 | 24.7 |
| 8 | 12:00, 2012-11-20 | 20°C | 166.9 | 34.9 | 40.2 | 23.9 | 4.31 | 12.75 | 34.0 | 13.0 |
| 9 | 4:00pm, 2012-11-20 | 16°C | 174.1 | 32.2 | 42.7 | 20.6 | 8.81 | 19.5 | 42.3 | 31.3 |

## 4. Seawater sample analysis

### 4.1 Seawater pretreatment and sample preparation

(1) Sample pretreatment

The sample to be tested is taken from the Qinhuangdao Tang River estuary deep the sea for 10 meters. The preserved samples to be tested are filtered through the qualitative filter and then injected into the digestion tank after 0.45 mμm membrane filtration.

(2) Metal ion color

Add 5mL buffer and 2mL color liquid to 10mL seawater samples to be measured. After stirred and evenly mixed, keep static for 1min, eliminate the bubbles in the solution, and then in accordance with the standard measurement method, respectively carry out the standard measurement experiment of 5 g/L, 10 g/L, 25 g/L, 50 g/L for each ion (Lin et al., 2013), and the standard solution is injected into measurement pool with the mode of circulating flow to measure.

(3) Compare the sample preparation

5mL buffer and 2mL color liquid are followed by added to 10mL seawater samples. After stirred and evenly mixed, keep static for 1min, eliminate the bubbles in the solution, and then the mixed solution is injected into the compared pool with the mode of circulating flow. The determination of the same substrate samples does not need replacing the contrast solution.

### 4.2 Comparison of system measurement and ICP-OES measurement results

The measurement results of$Zn^{2+}$, $Cu^{2+}$, $Ni^{2+}$ and $Cd^{2+}$ are compared with the results of ICP-OES measurements, and the results are compared with the algorithms introduced in the previous sections.

Instrument: Perkin Elmer Optima 8000 inductively coupled plasma optical emission spectrometry (ICP-OES) and its related instruments (Shi et al., 2014).

The absorbance values of the samples measured at different times are shown in Table 3, and the concentration measurement values and ICP-OES values are shown in Table 4.

*Table 3: Bohai Bay coastal water sample test absorbance data concentration*

| Times | 575 nm | 605 nm | 620 nm | 650 nm |
|---|---|---|---|---|
| 1 | 0.059 851 8 | 0.070 329 0 | 0.080 598 9 | 0.050 850 1 |
| 2 | 0.059 792 4 | 0.070 317 7 | 0.080 595 4 | 0.050 847 6 |
| 3 | 0.059 815 6 | 0.070 342 2 | 0.080 586 3 | 0.050 855 2 |
| 4 | 0.059 864 8 | 0.070 325 0 | 0.080 600 1 | 0.050 862 2 |
| Average | 0.059 831 2 | 0.070 328 4 | 0.080 595 2 | 0.050 853 8 |

*Table 4: Test concentration data of water samples in Bohai Bay (μg/L)*

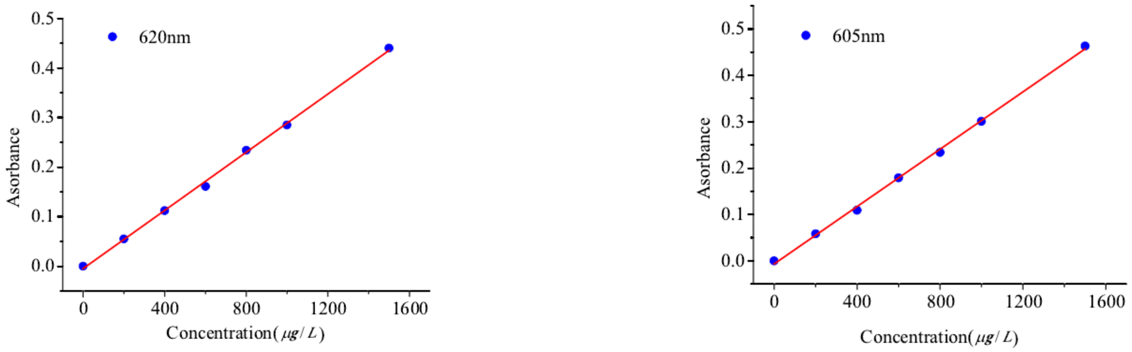
| Times | $Zn^{2+}$ | | $Cu^{2+}$ | | $Ni^{2+}$ | | $Cd^{2+}$ | |
|---|---|---|---|---|---|---|---|---|
| | PLS | ICP | PLS | ICP | PLS | ICP | PLS | ICP |
| 1 | 142.7 | 164.8 | 31.5 | 42.7 | 20.8 | 27.4 | 18.1 | 33.6 |
| 2 | 167.3 | 159.2 | 42.7 | 46.8 | 43.5 | 35.7 | 42.5 | 31.3 |
| 3 | 151.6 | 168.1 | 29.4 | 39.6 | 51.4 | 28.2 | 53.7 | 36.6 |
| 4 | 181.4 | 154.8 | 33.5 | 37.4 | 48.7 | 39.8 | 43.8 | 37.4 |
| Average | 160.8 | 161.7 | 53.6 | 41.6 | 40.9 | 32.8 | 39.5 | 34.7 |

From Table 3, it is known that, after 4 times measurement, the concentration of Zn2+, Cu2+, Ni2+ and Cd2+ is similar, and the mean are respectively 164.225 μg/L, 41.625μg/L, 34.725μg/L, and 32.775μg/L. It is close to ICP-OES measured concentration, and the measured result has a good consistency.

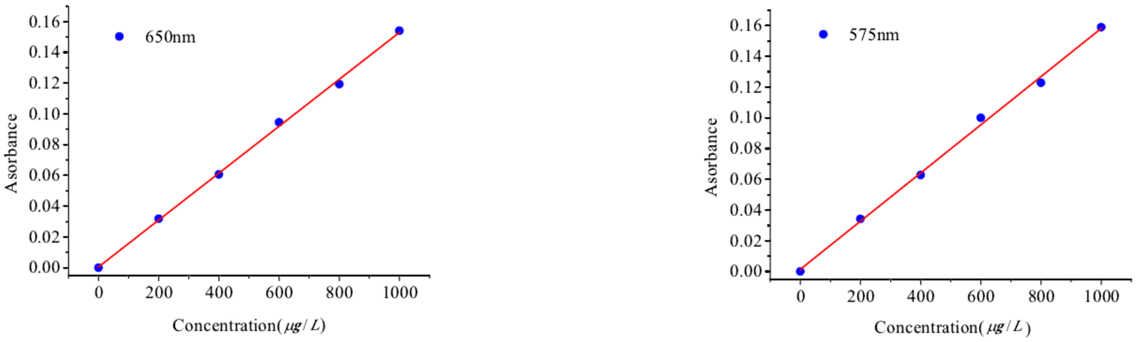
## 5. Results analysis

From the experimental data in Table 1, Table 2, and Table 3, it is known that, the principal component reconstruction conversion matrix, obtained by the chemical measurement matrix and the concentration matrix of PCA algorithm based on the multi-group, can make the spectral data with mutual interference converted into independent data by using orthogonal transform; the nonlinear iteration regression analysis method of PLS data decomposition and regression analysis provides a method to analyze nonlinear and not independent spectral data (Sueoka et al., 2016); although both the PCA algorithm and PLS algorithm have good adaptability in chemo-metrics multi-component measurement, in the case of many kinds of trace heavy metal in seawater with different contents, the selection andf calculation cut-off condition of principal component is greatly restricted. With the shortcoming of stability, accuracy and sensitivity of the electric power measurement system, it brings greater interference to the measurement. The problem should be solved from the top level of the system, such as wavelength narrow line width, background noise, flexible optical path, data filtering, sensitivity balance design and so on.

Add 5mL buffer and 2mL color liquid to a 25mL volumetric flask, and then respectively add 10mL metal ion solution with concentration of 0μg/L, 200μg/L, 400μg/L, 600μg/L, 800μg/L and 1000μg/L. Respectively choose the center wavelength of 575nm, 605nm, 620nm, and 650nm filters correspond to the maximum absorption wavelength of 580.81nm, 604.31nm, 626.00nm and 658.24nm (Sungur et al., 2015), to make absorbance measurements. The $Cd^{2+}$ path is 2cm, and the other ion path is 1cm. The corresponding values of $Zn^{2+}$, $Cu^{2+}$, $Ni^{2+}$, and $Cd^{2+}$ concentration - absorbance and the fitting curves are shown in Figure 1.



*a) Zn2+ absorbance linear fitting in linear measurement range  b) Cu2+ absorbance linear fitting in linear measurement range*



*c) Ni2+ absorbance linear fitting in linear measurement range    d) Cd2+ absorbance linear fitting in linear measurement range*

*Figure 1.Absorbance linear fitting of metal ions in linear measurement range*

The experimental results show that the $Zn^{2+}$ in the 0-1500μg/L range is in accordance with Lambert - Bill's law, and the linear correlation coefficient of the regression equation is 0.99538; $Cu^{2+}$ in the 0-1500μg/L range is in accordance with Lambert - Bill's law, and the linear correlation coefficient of the regression equation is 0.9974; $Ni^{2+}$ in the 0-1000μg/L range is in accordance with the Lambert - Bill's law, and the linear correlation coefficient of the regression equation is 0.99528; $Cd^{2+}$ in the 0-1000μg/L range is in accordance with Lambert - Bill's law, and the linear correlation coefficient of the regression equation is 0.99661 (Yemets et al., 2015).

Multi-wavelength calibration spectrophotometric method is established based on Lambert - Bill's law and the additivity of absorbance data. As a result, for making the determination results have a good accuracy and precision, in the choice of measuring wavelength, the absorbance data of each metal ion must have good additivity. The experimental results show that the total addition concentration of the four kinds of metal ions, in the range of no more than 1200μg/L, the linear addition degree is good, and the total absorbance error is no more than 5%.

## 6. Conclusion

In this paper, the measurement range of heavy metal ions is separately measured, and the addition experiments of four kinds of ion are carried out. The experiment results show that the four metal ions, in four measured bands, have good linear additivity, which meets the basic conditions of multi-group linear regression measurement. The results show that the PLS partial least squares algorithm has a good regression accuracy and anti-interference ability, but the regression calculation of low concentration data is easy to introduce the interference of other measurement data.

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