Analytical Chemistry
ISSN: 0974-7419

Analytical Chemistry: An Indian Journal

Research | Vol 17 Iss 1

The Development of a Mathematical Model of Nickel Release Analysis from Alloy Products

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Received: April 18, 2017; **Accepted:** June 20, 2017; **Published:** June 27, 2017

Abstract

We present a mathematical model to predict the amount of released nickel from Ni-Zn-Cu alloy products as a function of the amount of nickel content, the immersion time and the temperature. This mathematical model is developed based on orthogonal test and regression analysis. The validity of this model has been verified with up to 120 samples. The relative standard deviation (RSD) and the mean relative error (MRE) are only 7.31% and 7.62%, respectively. The development of this mathematical model will provide a fast and quantitative prediction of the amount of released nickel, with a reasonable accuracy. This model may, therefore, serve as a general guideline in the estimation of nickel release from Ni-Zn-Cu alloy products.

***Keywords:** Nickel release; Mathematical model; Orthogonal test; Regression analysis; Alloy products*

Introduction

Nickel based alloys are wildly used as metal jewelries (e.g. yellow and white gold), because nickel is inexpensive and can promote the durability and lusters to other metals. However, prolonged and direct skin contact with nickel may result in nickel allergy rash. Liden [1] reported that 10%-15% women, and 2%-4% of men in Europe were allergic to nickel. Double-blind placebo-controlled studies show that nickel-allergic individuals, may develop hand dermatitis if they are repeatedly exposed to nickel in low concentrations (10 ppm) [2-4], or orally exposed to nickel [5]. Today, nickel-allergy is often caused by wearing nickel based alloy jewelries [6] because nickel may release from its alloys [7].

Citation: Xu F, Jiang S, Chai M, et al. The Development of a Mathematical Model of Nickel Release Analysis from Alloy Products. Anal Chem Ind J. 2017;17(1):120.

As a consequence, Northern European countries, America and China have introduced nickel regulations to reduce nickel exposure and prevent nickel-allergy. The "94/27/EC" [8] regulation prescribed nickel release rate of 0.5 (µg·cm-2·week-1) as an upper limit for items to be in prolonged contact with the skin, and a maximum release rate of 0.2 (µg·cm-2·week-1) for piercing jewelries during epithelialization.

A number of analysis methods have, correspondingly, be proposed to evaluate the amount of released Ni from Ni based alloys. Although the quantitative methods, e.g. EN1811-1998 [9], EN12472-2005 [10], GB/T 19719-2005 [11], GB/T 28485-2012 [12], may accurately determine the released nickel, the analysis procedures usually take up to 10 days. By contrast, the qualitative analysis method proposed by CR 12471:2002(E) [13] can provide a reasonable prediction of released nickel from Ni-Zn alloys within only 5 h. Such a qualitative method has, therefore, been widely used in area of Ni-Zn alloy jewelries for in the past decades. Nevertheless, one significant drawback of the existing qualitative analysis method is that the reliability decreases when the sample contains Cu and Zn, because the rate of Ni release may significantly have affected by other 3d transition metals [13]. As up to 70% of the alloy jewelries are made of Ni-Cu-Zn based alloys, a new reliable qualitative analysis method for nickel release is highly desired. Herein, we propose a new method to predict the amount of released nickel from Ni-Cu-Zn alloys. Such qualitative analysis procedure can be completed within only 5 h. The validity of this method is verified by up to 120 alloy jewelry samples, 95% of the prediction agrees well with the results of quantitative analysis.

Experimental

Reagents and chemicals

Chemicals: Lactic acid, urea, nitric acid, sodium dodecylbenzene sulfate, sodium chloride (analytical pure, commercial available), nickel standard solution, (1000 mg L^{-1}, analytical pure, NSI Company of USA).

Degreasing solution: dissolve 5 g sodium dodecylbenzene sulfate in 1000 mL deionized water.

Testing solution: Mixed 900 mL deionized water, 100 g urea, 500 g sodium chloride and 100 g lactic acid together in 1000 mL beaker with stirring until dissolved. The testing solution was used within 3 h of preparation. 1% sodium hydroxide solution was used to adjust the pH of the test solution to 6.2, 6.4, 6.5, 6.6 or 6.8 before it was used.

Test sample Cu powder, Zn powder and Ni powder in proportion were melted in the intermediate frequency induction equipment, and were poured into stick using graphite mould after smelting. The stick sample was cut into Φ20 × 1.3 mm by spark cutting and polished to 1.2 mm by No.400 diamond abrasive paper. After being washed with ethyl alcohol and dried under hot wind the test samples were prepared.

Apparatus

s20 pH meter. Mettler toledo, Inductively coupled plasma spectrometer (In short ICP), Optima7300DV, PerkinElmer Company of USA,Wb/ob, thermostat water bath, Memmert company of Germany.

Procedure

Gently swirl the samples for 2 min in degreasing solution at room temperature. Rinse thoroughly with deionized water and dry using an absorbing cloth. Suspend the sample by its holder in the test vessel and add an amount of testing solution corresponding to approximately 1 mL cm^{-2} of sample surface area, in which the suspended sample area was totally immersed. Close the vessel with a tight lid to prevent the evaporation of the test solution. Leave the vessel undisturbed in a thermostatically controlled water-bath without agitation for 168 hrs. After immersion, remove the sample carefully from the solution and quantitatively transfer the release solution to an appropriately sized volumetric flask. The sample was washed with dilute nitric acid.

The testing solutions were directly injected into the ICP. ICP parameters are referred to EN1811 and its operation parameters are presented in TABLE 1.

TABLE 1. **ICP parameters.**

Item	**ICP parameter**
Power/kW	1.10
Plasma flow/L min^{-1}	15.0
Atomizing gas pressure/kPa	200
Observing height/mm	10
Reading duration/s	5
Reading times	3
Auxiliary gas flow/L min^{-1}	1.50

Results and Discussion

Effects of pH on the rate of nickel release

The rate of nickel release may affected by the pH values. Considering the weak acidity of human sweat, a number of measurements of nickel release were carried out at the pH of 6.2, 6.4, 6.5, 6.6 and 6.8. Samples with a composition of Cu: Zn: Ni=73.1:14.7:12.2 in w.t. were treated separately with testing solutions under 30°C. The release of nickel after 168 h of immersion is shown in FIG. 1.

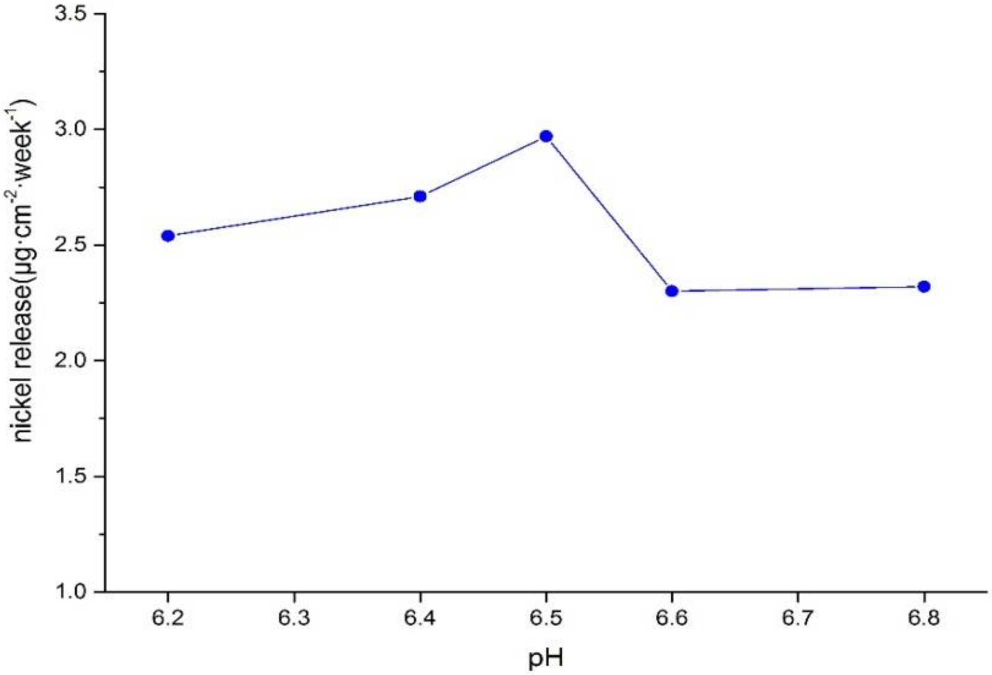

FIG.1. **Effect of pH on nickel release.**

It can be seen from FIG. 1 that the maximum rate of nickel release occurs when pH value is 6.5. The pH 6.5 is, therefore, selected for the following orthogonal tests.

The Orthogonal Test

Ni content, immersion time and temperature are main factors that determine the nickel release[14]. Taking nickel content (A), immersion temperature(B) and immersion time(C) as input parameters, a 3-factor-and-4-level orthogonal test ($L_{16}(4^3)$) was developed to estimate the rate of nickel release. The levels of the factors used in orthogonal test are listed in TABLE 2.

TABLE 2. **Levels and factors of orthogonal test for nickel release ($L_{16}(4^3)$).**

Factors	**Levels**			
	1	2	3	4
(A)nickel content/%	1.75	4.73	11.12	15.84
(B)Temperature/°C	25	30	36.5	40
(C)immersion time/h	24	72	120	168

To obtain reliable results, three specimens were prepared and tested for each experimental condition. The average value of three measurements was taken as the final result. The results of the orthogonal test of 16 performances are listed in TABLE 3.

TABLE 3. **Results of orthogonal experiment for nickel release.**

No.	**A** **Nickel content/%**	**B** **Temperature/°C**	**C** **Immersion time/h**	**Nickel release** **/μg·cm^{-2}·week^{-1}**
1	1.75	25	24	0.137
2	1.75	30	120	0.287
3	1.75	36.5	168	0.367
4	1.75	40	72	0.321
5	4.73	25	120	0.725
6	4.73	30	72	0.637
7	4.73	36.5	168	0.949
8	4.73	40	24	0.673
9	11.124	25	168	1.677
10	11.124	30	24	1.22
11	11.124	36.5	120	1.747
12	11.124	40	72	1.592
13	15.84	25	72	1.979
14	15.84	30	168	2.515
15	15.84	36.5	24	1.86
16	15.84	40	120	2.435
Ⅰ$_j$	1.112	4.518	3.89	
Ⅱ$_J$	2.984	4.659	4.529	
Ⅲ$_J$	6.236	4.923	5.194	
R$_J$	7.677	0.503	1.618	

Ⅰ$_j$, Ⅱ$_J$, Ⅲ$_J$ – sum of nickel release of level 1, level 2 and level 3, respectively.

R$_J$- range: the difference between the largest sum value and the smallest sum value of each factor.

The orthogonal tests show that the nickel release increases with the increasing nickel content, immersion temperature and immersion time.

Extreme value difference analysis of the orthogonal test showed $R_A>R_C>R_B$, indicating the nickel release is mostly influenced by the nickel content, then the immersion time, lastly the immersion temperature.

Mathematical model to predict the amount of released nickel

Applying regression analysis method to the orthogonal test resulted in the equation as following:

$Y=0.134A+0.0105C+0.003B-0.558$ $R2^{=}0.986$ (1)

Here, Y is nickel release ($\mu g\cdot cm^{-2}\cdot week^{-1}$), A is the nickel content (%), B is the immersion temperature (°C) and C is the immersion time (h).

The F test was employed to evaluate the regression equation. The analysis of variance is shown in TABLE 4.

TABLE 4. **Results of variance analysis.**

	Sum of square	**Degree of freedom**	**Mean square**	**F**	**F-crit $F_{0.05}(3,12)$**
Regression	916.143	3	305.381	283.486	3.49
Residue	12.927	12	1.077	/	
Total	929.070	15	/	/	

Since $F=283.486>F_{0.05}$ (3,12), Equation (1) is significant.

The coefficient of Equation (1) indicates the weights of variables to the rate of nickel release. As the values of coefficients obtained from regression analysis are in good agreement with those obtained from extreme value difference analysis, we believe Equation (1) can work as a predictive mathematical model for nickel release. In order to prove this, 120 samples were analyzed with quantitative analysis method and our mathematical model. When the Ni content is less than 0.5%, the nickel releases are found to be negligible with both methods. For Ni content in the range of 1.75%-15.90%, the predicted values are in good agreement with those obtained from quantitative analysis (see FIG. 2).

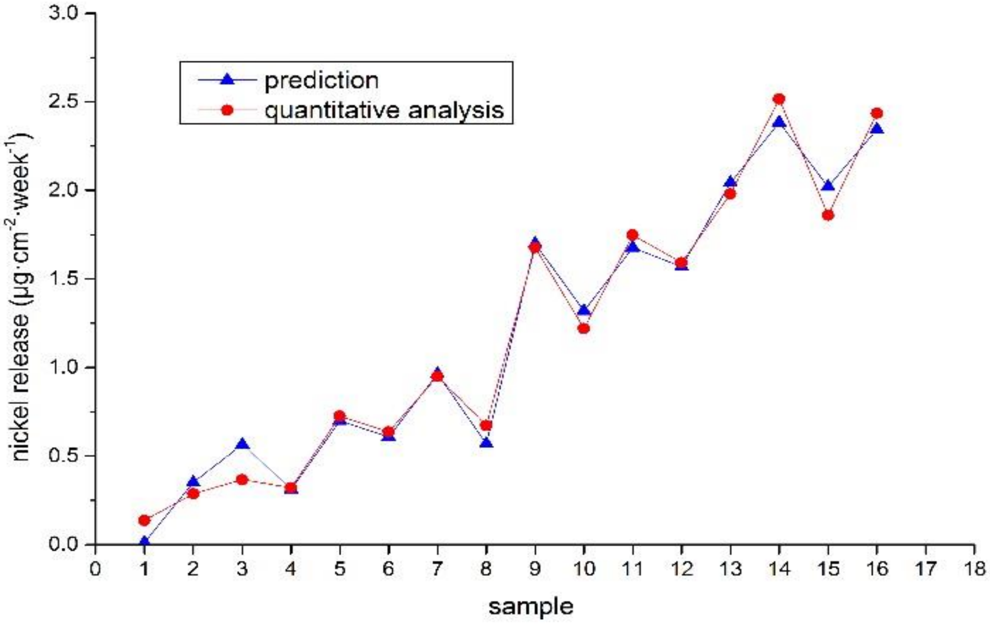

FIG. 2. **The amount of released nickel predicted with our mathematical model (represented with blue triangles), and measured with quantitative analysis method (represented with red dots).**

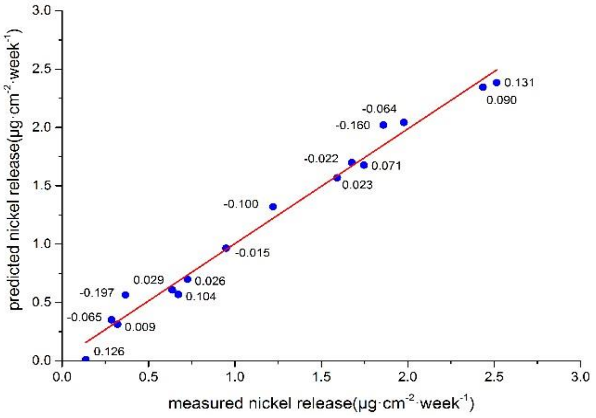

FIG. 3. **Comparison of the nickel releases of samples observed with those estimated by Equation (1). In mathematical statistics, the residual error refers to the difference between observed value and the predictive value.**

The results are shown in FIG. 3. The statistics parameters of the model are shown in TABLE 5.

TABLE 5. **The statistics parameters of the model.**

Parameters	**Value**
relative standard deviation (RSD)	7.31%
root mean square error (RMSE)	9.44%
average of absolute relative deviation (AARD)	14.48%
standard deviation error (SDE)	2.44%

It can be seen from FIG. 2 and TABLE 5 that, the predicted nickel release with our mathematical model is quite consistent with those of quantitative analysis. The reliability of this model can be further verified with additional experiments (shown in TABLE 6).

TABLE 6. **Predicted and measured nickel release.**

No.	**Nickel content/%**	**Immersion temperature/℃**	**Immersion time/h**	**Nickel release (prediction) /μg·cm^{-2}·week^{-1}**	**Nickel release (quantitative analysis) /μg·cm^{-2}·week^{-1}**	**Mean relative error（MRE）/%**
1	12.98	25	120	1.804	1.906	7.62
2	12.98	30	24	1.569	1.304	
3	12.98	36.5	72	1.781	1.852	
4	12.98	40	168	2.106	2.223	

It can be seen from TABLE 6. that the predicted nickel releases agree well with the measured values, indicating that the proposed mathematical model is reasonably accurate.

Conclusions

Based on the orthogonal test and regression analysis, a simple mathematical expression was developed to predict the nickel release. The model was capable of calculating the nickel release of artificial jewelry from nickel content, immersion time and temperature. The RSD of the model was 7.31% and MRE of the prediction of nickel release was 7.62%, showing that the mathematical model was a promising way for the determination of the nickel release of the Ni-Cu-Zn based alloy products.

Funding

Project (2015IK298) supported by General Administration of Quality Supervision Inspection and Quarantine of the People’s Republic of China

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