STUDIES AND RESEARCH REGARDING CONCENTRATION INFLUENCE ON THE LINEARITY CURVE OF SPECTROSCOPIC CALIBRATION IN NICKEL-PLATING BATHS

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Abstract:
The paper analyzes the concentration influence of nickel-plating baths components on photometric absorption in view of establishing the concentration limit at which the non-linearity of calibration curve takes place. The regression equations are also established for the work in non-linear area.
Keywords: concentration, calibration curves, regression equations, non-linear area

Abstract:
În lucrare este analizată influenţa concentraţiilor componentelor băilor de nichelare asupra absorbţiei fotometrice; cu scopul de a stabili limita de concentraţie de la care se instalează neliniaritatea curbei de etalonare. De asemenea se stabilesc ecuaţiile de regresie pentru lucrul în zona neliniară.
Cuvinte cheie: concentraţie, curbe de etalonare, ecuaţii de regresie, zonă neliniară.

Résumé:
Le travail analyse l'influence des concentrations des components dans les bains de nickelage sur l'absorption photométrique dans le but d'établir la limite de concentration de laquelle la non-linéarité de la courbe d'étalonnage s'installe. On établie aussi les equations de régression pour le travail dans la zone non-linéaire.
Mots clef: concentrations, courbes d'étalonnage, équations de régression, zone non-linéaire.

Introduction

In order to get the automatic control of electroplating baths, including those of nickel-plating, online measurement of components concentration in baths is needed. Such measurement is possible through the chemical instrumental analysis way only with real time data teletransmission and processing. The most complete information in this case may be provided by spectroscopic analysis, especially spectrophotometry of molecular absorption. It is obvious that the classic method"sample put to be analyzed" requires longer periods of time, excluding the bath real time control and adjust. Under these conditions there is only one working method, the "device near electroplating bath" with recirculation and continuous analysis of a small part of electrolyte or "spectrophotometric floating well in bath" [GUT,06] with data distance-transmission.

The paper belongs to the promotion experiments of this technique and has as its main goal to evaluate the possibility of nickel ion concentration spectrophotometric measurement and to establish influence factors.

As it is known spectroscopic concentration determinations in visible spectral ultraviolet field are based on monochromatic light interaction with the analyzed component, in this case nickel. At a certain wavelength, the relation between incident light intensity I_0 and radiation intensity passing through the analyzed sample is given by the following formulae, which are different expressions of Lambert-Beer's law.

$$I = I_0 \cdot 10^{-\alpha \cdot l} \quad (1)$$

$$T = I/I_0 = 10^{-\alpha \cdot l} = 10^{-A} \quad (2)$$

$$A = E = \varepsilon \cdot c \cdot l = \lg {}^{1}/_{T} = \lg {}^{I_0}/_{I} \quad (3)$$

Where: I – transmitted light intensity;

I_0 – incident light intensity;

ε - absorption molar coefficient (constant specific to every substance at a certain wavelength);

c – substance concentration to be analyzed in solution [%, weight/volume];

l – absorption layer thickness [cm];

T – transmittance (transmission) is the ratio between the transmitted light intensity (I) and incident light intensity (I_0).

A – absorption (absorbance) of a solution (optical density, extinction), is the decimal logarithm of transmittance inverse (T), that is the decimal logarithm of the ratio between incident light intensity (I_0) and transmitted light intensity (I) and is proportional to solution concentration (c), absorption layer thickness (l). [GUT,00], [PIE,89].

The standard or calibration curve is obtained by graphic representation of absorption values depending on concentration values (using different concentrations of standard solution), at a certain wavelength (at which the substance to be analyzed has maximum absorption). In the field of low concentrations absorption (extinction) is directly proportional to concentration.

Generally, component concentrations in electroplating baths are encountered in the field of high concentrations and so they should deflect from the standard spectroscopic curve linearity in visible- ultraviolet spectral field.

We have carried out a study on the nickel-plating process of the nickel sulphate electrolyte, known as the Watts bath, in order to establish the way the absorption parameter of components in electroplating baths from the field of high concentrations varies and to obtain a mathematical model describing as exactly as possible its phenomenology. (table 1).

Table 1. Nickel-plating Watts Bath Composition

Electrolyte composition	Electrolyte concentration (g/l)	Ni^{2+} content in electrolytes (mg Ni^{2+}/ml)
Nickel chloride, $NiCl_2 \cdot 6H_2O$	50 -60	12.3949 – 14.8794
Nickel sulphate, $NiSO_4 \cdot 7H_2O$	250 - 320	52.4911 – 65.0889
Boric acid, H_3BO_3	40 - 45	-
Total	340 - 415	64.886 – 79.9683

Studies regarding Watts's electrolytes behaviour during the electrolytic nickel-plating process depending on the plated base material and applied nickel-plating type have opened the way to development of modern nickel plating, higher yield and fast high temperature deposition baths.

The nickel sulphate-based nickel plating bath advantages are:

1. Simple maintenance of electrolytes due to simple qualitative composition in the sense of avoiding the uncontrolled secondary processes accruing after mixing and homogenizing the three solutions.
2. Economic efficiency resulted from greatly lower prince of pure nickel sulphate as compared to nickel chloride.
3. Longer life time of the devices used at metallic electroplating due to the more reduced corrosive character of nickel sulphate-based electrolyte as compared to the one exclusively made of nickel chloride and long lasting functioning as well.
4. The obtained electroplated deposits have generally lower internal tensions, and the probability of forming rough deposits is low. [MAR,84], [GRÜ,05]

Experimental

Experiments have been made using UV-VIS spectrophotometer, Spekol 11, in solutions consisting of chemical substances of (99.99 %) analytical purity. Solutions of electrolyte obtained according to table 2 were subjected to spectrophotometric analysis.

Table 2. Electrolyte solutions put under analysis

Solution	Volume of electrolyte solution at indicated concentration (ml)	Completed volume of distilled water
1	10	90
2	20	80
3	30	70
4	40	60
5	50	50
6	60	40
7	70	30
8	80	20
9	90	10
10	100	-

Table 3 shows the nickel ions concentrations of the solutions put under spectrophotometric determinations.

Table 3. Ni^{2+} Concentrations in the analyzed solutions

Electrolytes / Solution	Nickel chloride, (mg Ni^{2+}/ml)	Nickel sulphate, (mg Ni^{2+}/ml)	Mixture: Nickel chloride, Nickel sulphate, (mg Ni^{2+}/ml)	Watts Bath: Nickel chloride, Nickel sulphate, Boric Acid, (mg Ni^{2+}/ml)
1	1.23949	5.24911	6.4886	6.4886
2	2.47898	10.49822	12.9772	12.9772
3	3.71847	15.74733	19.4658	19.4658
4	4.95796	20.99644	25.9544	25.9544
5	6.19745	26.24555	32.443	32.443
6	7.43694	31.49466	38.9316	38.9316
7	8.67643	36.74377	45.4202	45.4202
8	9.91592	41.99288	51.9088	51.9088
9	11.1554	47.24199	58.3974	58.3974
10	12.3949	52.4911	64.886	64.886

Results and discussion

1. Preliminary determinations:

Preliminary determinations regarding absorption values at different wavelengths have been made for the following solutions: ***$NiCl_2 \cdot 6H_2O$ (50g/l)***; ***$NiSO_4 \cdot 7H_2O$ (250g/l)***; ***mixture ($NiCl_2 \cdot 6H_2O$ (50g/l) + $NiSO_4 \cdot 7H_2O$ (250g/l))***; ***Watts Bath ($NiCl_2 \cdot 6H_2O$ (50g/l) + $NiSO_4 \cdot 7H_2O$ (250g/l) + H_3BO_3 (40g/l))***. The absorption spectra of these solutions have been obtained by graphic representation of absorption values depending on wavelength.

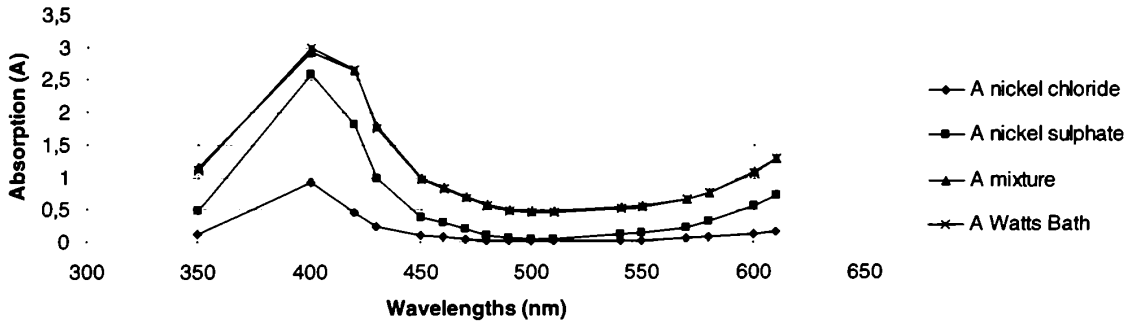

Figure 1. Solution Preliminary Spectrogram: $NiCl_2 \cdot 6H_2O$ (50g/l); $NiSO_4 \cdot 7H_2O$ (250g/l)

It is recommended that one should not work at absorption maximum since this is placed at higher values than 2.5, fact that leads to a weaker reading resolution, taking into consideration that the measuring area is greatly compressed due to the logarithmic scale. In this case we recommend that measurement should be made at a 400 – 450 nm wavelength.

Therefore determinations having in view the influence of other parameters on the measured value should be also carried out.

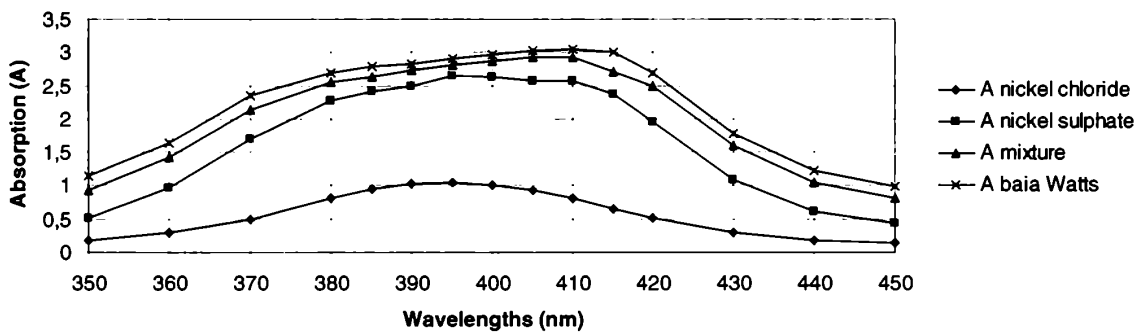

Figure 2. Solution Spectrogram: $NiCl_2 \cdot 6H_2O$ (50g/l); $NiSO_4 \cdot 7H_2O$ (250g/l)

One can see from the spectrogram in figure 2 showing absorption of the same solutions from the first determination set depending only on wavelength at 350 – 450 nm intervals that the absorption maximum of the four analyzed solutions occurs at the wavelength of 410 nm. Whence we way deduce that nickel cation maximum absorption is at this wavelength of 410 nm.

2. Ni^{2+} determinations in nickel chloride solutions

According to Lambert – Beer Law, when absorption values are graphically represented depending on increasing values of solution concentrations, at a wavelength near to maximum absorption, a linear function is obtained. The straight line slope is molar absorptivity ε, on the condition that the layer thickness went through by radiation is of 1 cm. [PIE,89]

The graphic representation of absorption values, obtained in practice, depending on increasing values of nickel ion concentration from nickel chloride solution (see table 2) at 410 nm wavelength, is a linear function (figure 3) with the following equation: $y = 0{,}0604x - 0{,}0167$. We may deduce from

the straight line equation that nickel ion molar absorptivity in the aqueous nickel chloride solution is ε = 0.0604.

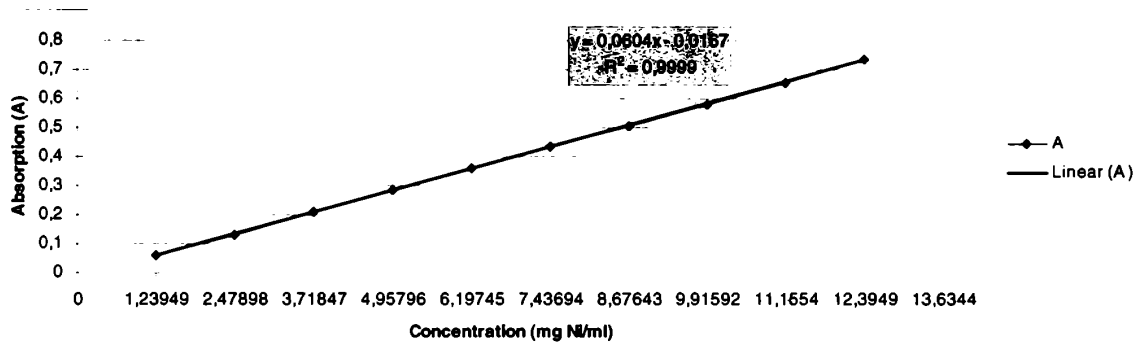

Figure 3. Absorption variation depending on Ni^{2+} concentration in nickel chloride, at λ = 410 nm

3. Ni^{2+} determinations in nickel sulphate solutions, in mixture solution (nickel chloride and sulphate) and in Watts bath solution

The graphic representations of absorption values depending on increasing concentrations of nickel ion in nickel sulphate solutions, in mixture solution (nickel chloride and sulphate) and in Watts bath solution (table 2) are non-linear and show negative derivations from Lambert-Beer's law (figure 4, figure 5, figure 6).

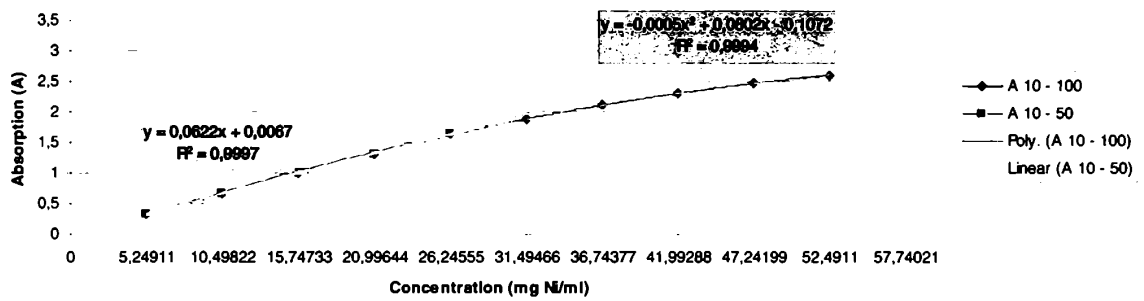

Figure 4. Absorption variation depending on Ni^{2+} concentration in nickel sulphate, at λ = 410 nm

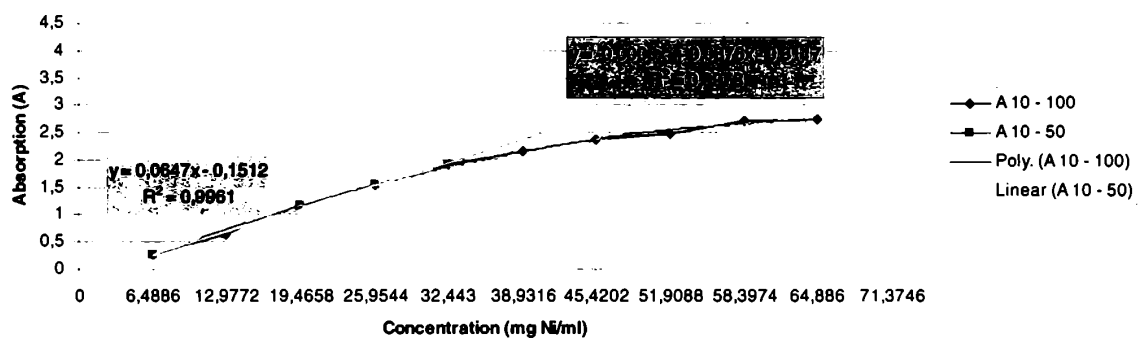

Figure 5. Absorption variation depending on Ni^{2+} concentration in mixture (nickel chloride and sulphate), at λ = 410 nm

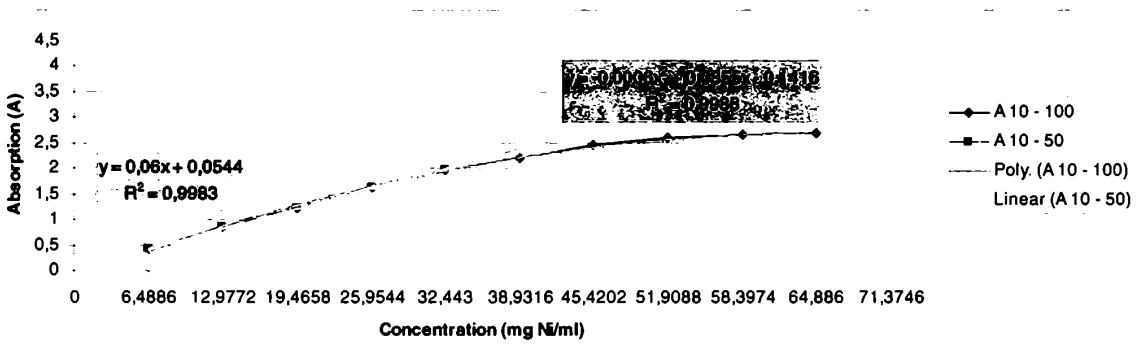

Figure 6. Absorption variation depending on Ni^{2+} concentration in Watts bath, at $\lambda = 410$ nm

Lambert – Beer's law is respected in the following nickel ion concentration intervals: 5.24911 – 26.24555 mg Ni^{2+}/ml in sulphate solution, 6.4886 – 32.443 mg Ni^{2+}/ml in mixture solution (nickel chloride and sulphate) and 6.4886 – 32.443 mg Ni^{2+}/ml in Watts bath solution. The straight line equation in figure 5 is identical with the straight line equation in figure 6, even though the nickel ion concentration interval in mixture solution (nickel chloride and sulphate) is the same as the one from Watts bath solution. The difference might be explained by slight increase of absorption value in the case of Watts bath solution by adding boric acid. In the high concentration field of over 26.24555 mg Ni^{2+}/ml in sulphate solution, over 32.443 mg Ni^{2+}/ml in mixture solution (nickel chloride and sulphate) and over 32.443 mg Ni^{2+}/ml in Watts bath solution, a polynomial quadric relation between absorption and concentration values may be established.

The polynomial relation between nickel ion absorption and concentration in Watts bath solution is: $y = -0{,}0006x^2 + 0{,}0855x - 0{,}1416$.

Conclusions

The chemical composition of nickel-plating baths can be efficiently and rapidly controlled by molecular absorption spectrophotometry.

It is possible to make measurement for the standard composition of electroplating solution without diluting it. But taking into consideration that the reading resolution is lower at this composition due to the logarithmic reduction of measurement scale, a higher precision and a performing data processing soft are needed.

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