

## Determination of Copper and Zinc Contents in Brass Plating Solutions by Titrimetric Analysis: A Review

By Z. Panossian\*, J.V. Ferrari & M.B. de Almeida

Several titrimetric methods of analysis found in the literature for the determination of copper and zinc content in brass plating baths show procedural errors or, in certain cases, their applications are limited to a specific kind of plating bath. This paper presents a brief review and critical analysis of these methods and establishes suitable methodologies for the determination of these metal contents in brass plating baths. Direct analyses for the determination of copper (iodometric titration) and zinc (EDTA complexometric titration with xylenol orange indicator) have been shown to be very effective because they provide accurate results for a wide range cyanide brass plating bath compositions.

The composition and color of electroplated brass depend, among other parameters, on the copper and zinc composition. Therefore, the contents of these two metals must be rigorously controlled by an analytical method that provides accurate results and can be applied to any brass solution, regardless of its composition (copper, zinc, cyanide, etc).

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### Nuts & Bolts: What This Paper Means to You

Plating bath analysis is difficult enough for single metals, and the procedures for commonly plated alloys, such as brass, present a greater challenge. The authors have undertaken a critical review of analytical methods of measuring copper and zinc in brass solutions. A number of the methods on which their findings are based were developed for applications other than plating, and have been adapted by the authors to metal finishing use.

The simplicity, quickness and relatively low cost make titrimetric analysis one of the most widely used methods by metal finishing companies for plating bath control.<sup>1</sup> The literature reports several titrimetric methods of analysis to determine plating bath composition<sup>1-3</sup> and also reports the difficulties found when dealing with metal contents in baths composed of more than one metal, as is the case with brass and other alloy plating baths.<sup>3-6</sup> This is why most of these methods are based on titration with ethylene diamine tetraacetic acid salt (EDTA). This reagent has low selectivity because it forms complex salts with many cations of double, triple or quadruple charge.<sup>7</sup> Further, the metal indicators used in these titrations, such as 4-(2-pyridylazo)-resorcinol (PAR)<sup>8</sup> and Eriochrome Black T (EBT) also present low selectivity. These factors require the use of specific procedures that differ from analyses of plating baths composed of a single metal that are in current use. However, in some cases, these procedures do not always avoid built-in errors.

This work originated from the technological services carried out by PRUMO\*\* in companies that do brass plating. It was found that titrimetric analysis was widely used, which, in the view of those companies, provided inaccurate results. A literature search showed that several methods for determining the concentration of zinc and copper in brass plating baths<sup>2-6</sup> were available. In these methods:

1. The determination of zinc content was carried out by means of EDTA complexometric titration with the EBT indicator.
2. The determination of copper was carried out by means of EDTA complexometric titration with PAR or 1-(2-pyridylazo)-2-naphthol (PAN) indicators, or by means of iodometric titration.

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\*\* PRUMO – Mobile Units Project for Technological Service for Micro and Small Businesses, created in Brazil in 2001 aiming to offer technological support for the metal finishing businesses. The project is conducted by a trained team with the support of a mobile laboratory which had facilities to carry out several types of tests and analyses such as plating bath analysis, thickness measurement, Hull cell test, etc., seeking to solve the detected problems.

- The determination of copper plus zinc content was carried out by means of EDTA complexometric titration. The copper (or zinc) contents was obtained by the difference of this result and the one obtained by an analysis for zinc (or copper) content.

This paper presents a brief review and critical analysis of these methods and establishes suitable methods for the determination of copper and zinc content in brass plating solutions.

## Review of analytical methods

### Theoretical aspects of complexometric titration

In regard to composition, it is important to remember that in a cyanide brass plating solution, the metal ions are present in the form of the following complexes:  $[\text{Cu}(\text{CN})_3]^{-2}$ ,  $[\text{Zn}(\text{CN})_4]^{-2}$  and  $[\text{Zn}(\text{OH})_4]^{-2}$ . Moreover, it is important to mention that, during EDTA titration, other complexes are formed. Table 1 presents the molecular formulae of all these complexes, including those formed during EDTA titration, with their respective stability constants. Among the complexes presented in Table 1, the Cu(I) cyano complex is the most stable and the zinc ammonium complex is the least stable.

The EDTA titration is more efficient in an alkaline medium. However, insoluble metal hydroxides are formed under alkaline conditions. For this reason, titration is usually made in an ammonium medium so that the metal ions form ammonium complexes and remain in the dissolved form. Besides ammonia, the use of metal indicators is indispensable to the detection of the equivalence point. These indicators change color when complexed to metal ions. This causes a visible color change at the equivalence point, after addition of a small excess of the titrant.

**Table 1**  
Complexes Present in Brass Plating Baths and those formed during EDTA Titration and their Respective Stability Constants<sup>9</sup>

Ion	Complex	Origin	K*
Cu <sup>+</sup>	$[\text{Cu}(\text{CN})_3]^{-2}$	Present in the brass plating bath	$1.0 \times 10^{27}$
	$[\text{Cu}(\text{NH}_3)_2]^+$	Formed during the EDTA titration when adding ammonium compounds	$7.4 \times 10^{10}$
Cu <sup>+2</sup>	CuEDTA <sup>-2</sup>	Formed during the EDTA titration	$6.3 \times 10^{18}$
Zn <sup>+2</sup>	$[\text{Zn}(\text{OH})_4]^{-2}$	Present in the brass plating bath	$2.8 \times 10^{15}$
	$[\text{Zn}(\text{CN})_4]^{-2}$	Present in the brass plating bath	$1.0 \times 10^{17}$
	ZnEDTA <sup>-2</sup>	Formed during the EDTA titration	$0.5 \times 10^{17}$
	$[\text{Zn}(\text{NH}_3)_4]^{+2}$	Formed during the EDTA titration when adding ammonium compounds	$2.9 \times 10^9$

\* Stability constant or formation constant

According to what is known, there are at least three complexes in the EDTA titration of metal ions:

- metal-EDTA complex
- metal-ammonium complex
- metal-indicator complex.

In order for EDTA titration to work, it is necessary that the metal-EDTA complex be the most stable, followed by the metal-indicator and metal-ammonium complexes, in that order. In terms of stability constant, this can be represented in the following manner:

$$K_{\text{EDTA}} > K_{\text{indicator}} > K_{\text{ammonium}} \text{ and } K_{\text{hydroxide}}$$

At the beginning of the titration, the metal-ammonium and metal-indicator complexes are present and the color assumed by the solution comes from the metal-indicator complex. It is important to note that, in spite of the greater stability of the metal-indicator complex, the metal-ammonium complex is also formed because, in the analysis solution, there is more ammonium than indicator.

When the titration begins, the following sequence takes place:

- EDTA, forming the strongest complex, displaces the metal ions from the ammonium complex (less stable).
- When the EDTA binds to all metal ions dissociated from the ammonium complex, the metal ions from indicator complex begin to be chelated.
- When the EDTA binds to all of metal ions dissociated from the indicator complex, the solution changes color, marking the endpoint titration.

For an EDTA titration to be successful, certain requirements must be fulfilled, including:

- pH control must be rigorous because for each type of metal indicator, there is a specific pH range suitable for the titration.
- The indicator must be chosen in such a way that the displacement of the following equilibrium be quickly observed:  
  
Metal indicator complex  $\leftrightarrow$  metal-EDTA complex
- The indicator must be very sensitive to the metal ions analyzed so that the titration endpoint is as close as possible to the equivalence point.
- The indicator concentration must be at least 100 times lower than the metal concentration.

As already mentioned, when a single metal ion is analyzed, the EDTA titration is easily done. However, when several metal ions are present, analysis interferences may occur. In these cases, some alternatives can be adopted, such as:

- The use of a specific indicator for each metal ion.
- Separation by precipitation followed by filtration before the titration.
- The use of masking or demasking agents.

## Zinc content

Referring again to Table 1,  $[\text{Cu}(\text{CN})_3]^{-2}$  is more stable than  $[\text{Zn}(\text{CN})_4]^{-2}$ . Furthermore, the  $[\text{Zn}(\text{CN})_4]^{-2}$  and  $\text{ZnEDTA}^{-2}$  complexes have very similar stabilities. Therefore EDTA is not able to dissociate the cyanide complex to enable binding with zinc ions. Consequently, the  $[\text{Zn}(\text{CN})_4]^{-2}$  complex must be destroyed in order to demask the zinc ions.

Thus, a method of analysis is needed which involves the use of a demasking agent for zinc ions which will not demask the Cu(I) ions. In order to do this, current methods recommend the addition of a formaldehyde solution (or a methanol/acetic acid solution or chloral hydrate). The formaldehyde reacts with the zinc cyano complex, according to the following reaction:<sup>7</sup>



Once the demasking of zinc ions is accomplished, formation of the  $[\text{Zn}(\text{NH}_3)_4]^{+2}$  complex is possible when ammonium compounds are added to the analysis sample. After addition of the EBT indicator, the titration with EDTA is carried out until the solution color changes from lilac to blue. This method does have some shortcomings related to the following factors:

1. *The amount of EBT indicator used:* The indicator concentration must be at least 100 times lower than the metal concentration in order for the titration endpoint to be easily detectable. It has been found that several analytical methods used an insufficient or excessive amount of indicator.

2. *The nature and amount of formaldehyde used:* Formaldehyde, besides being a potential carcinogenic agent, is poisonous and allergenic. Moreover, depending on the bath composition, the amount of formaldehyde used can be insufficient to promote zinc demasking. This is because the formaldehyde, besides reacting with the cyanide from the zinc cyano complex, also reacts with the free cyanide and the cyanide from the Cu(I) cyano complex, in an order kinetically determined as follows:  $\text{NaCN}_{\text{free}}, \text{CN}_{[\text{Zn}(\text{CN})_4]^{-2}}, \text{CN}_{[\text{Cu}(\text{CN})_3]^{-2}}$ , where:

- $\text{NaCN}_{\text{free}}$  is the free cyanide,
- $\text{CN}_{[\text{Zn}(\text{CN})_4]^{-2}}$  is the cyanide from zinc cyanide complex and
- $\text{CN}_{[\text{Cu}(\text{CN})_3]^{-2}}$  is the cyanide from Cu(I) cyanide complex.

Thus, if a brass plating bath contains a high amount of  $\text{NaCN}_{\text{free}}$ , the amount of formaldehyde added may not be enough to demask the zinc ions. On the other hand, if the formaldehyde is added in excess, in addition to the zinc ions, the Cu(I) ions may also be demasked. This leads to serious errors because the Cu(I) ions will interfere with the color change at the equivalence point.

It was experimentally verified that the formaldehyde excess in this analysis may also cause another error. When a large amount of formaldehyde is added (from 30 to 45 mL of 10% of formaldehyde solution) during the analysis, white precipitates formed (typical of zinc hydroxides) and the characteristic odor of ammonia was not noticed. In fact, the aldehydes react with ammonium compounds, resulting in the formation carbon-nitrogen double bond compounds.<sup>10</sup> This reaction accounts for the precipitation of zinc hydroxides, as a large formaldehyde excess reacts with all available ammonia, leading to the precipitation of hydroxides because the zinc ammonium complexes did not form.

## Copper content (only) and copper plus zinc content

The most serious sources of error found in literature for the copper analysis are related to the EDTA complexometric titrations using PAR or PAN indicators because both are not specific for either the copper or the zinc and so, these two metals are complexed by them. Usually the published methods refer to this method only for the determination of copper content, which is not true.

This method basically involves the decomposition of cyanides and the oxidation of Cu(I) to Cu(II) with an oxidant solution, followed by alkalization with ammonium buffer to bring the pH value to 10, and EDTA titration using PAN or PAR indicators. The Cu(II)-PAR complexes are formed at a pH above 5.0 and the zinc-PAR complexes at a pH above 8.0.<sup>11</sup>

Table 2 presents the stability constants of the indicator, ammonium and EDTA complexes with copper and zinc. The values of the stability constants of the EDTA and indicator complexes are higher for copper. However, this does not guarantee that only copper is determined. During titration, after EDTA binds with all copper in solution (both free copper and that complexed with ammonium and PAR indicator) the endpoint is still not seen. Immediately thereafter, the PAR binds with the zinc ions and thus, the endpoint is noticed only after all copper and zinc ions bind with the EDTA.

These kinetic parameters confirm that in reality, the EDTA volume consumed represents the total of the copper and zinc ions. The ammonium complexes do not interfere in the analysis because of their low stability.

In order to determine copper plus zinc content, the literature also mentions this same analytical method. However, in this method, it is difficult to visualize the endpoint (In this analysis, the endpoint is noticed by the color change from blue to green, when the PAR indicator is used.) and it is highly dependent on the operator's visual skill, because there is actually an intermediate color between blue and green.

In short, the literature cites a great number of methods for the direct determination of copper based on iodometry. It was experimentally verified that they present no problems despite the fact that in brass plating, copper is the only metal that can present two oxidation states. Thus, the possible interferences from the presence of the zinc ions in the bath are eliminated.

**Table 2**  
**Stability Constants of the Complexes Formed in EDTA Titration with a PAR Indicator for the Determination of Copper and Zinc Content**

Ion	Complex	$K^{8,8}$
Cu <sup>+</sup>	CuEDTA <sup>-</sup>	$6.3 \times 10^{18}$
	Cu(II) - PAR	$1.0 \times 10^{14.8}$
	$[\text{Cu}(\text{NH}_3)_4]^{+2}$	$2.2 \times 10^{13}$
Zn <sup>++</sup>	ZnEDTA <sup>-</sup>	$5.0 \times 10^{16}$
	Zn(II) - PAR	$1.0 \times 10^{10.5}$
	$[\text{Zn}(\text{NH}_3)_4]^{+2}$	$2.9 \times 10^9$

**Table 3**  
**Brass Plating Bath Compositions used for Testing the Analytical Methods**

Bath	CuCN (Cu <sup>+</sup> ) (g/L)	Zn(CN) <sub>2</sub> (Zn <sup>+2</sup> ) (g/L)	ZnO (Zn <sup>+2</sup> ) (g/L)	NaCN (g/L)	NaOH (g/L)	Na <sub>2</sub> CO <sub>3</sub> (g/L)
1	28.5 (20.0)	-	25.0 (20.0)	100	20.0	40.0
2 (Red brass)	30.0 (21.3)	2.0 (1.1)	-	49	-	-
3 (White brass)	16.8 (11.9)	60.0 (33.4)	-	60	60	-
4 (High speed process)	87.5 (62.0)	6.0 (3.3)	-	112.5	60	40

### The best method for determining the copper and zinc content in brass plating solutions

Three analytical methods found in the literature<sup>2,12,13</sup> were studied to seek out the best analytical method to determine the metal contents in brass plating solutions. Two of them are related to the direct determination of copper and zinc content and the third relates to the determination of the sum of the two metal contents.

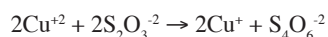
To guarantee that the composition of the bath would not interfere in the applicability of the methods, different cyanide bath compositions were used. All of the baths were prepared at our laboratory with analytical grade reagents. Table 3 presents the composition of these baths.

#### Direct analysis of zinc content by EDTA complexometry<sup>12,13</sup>

This method was originally developed for analysis of mineral samples and was adapted for application to plating bath analyses.

Similar to many others found in literature, the method involves cyanide decomposition with an oxidant, to release copper and zinc ions. In this titration, xylenol orange is used as an indicator at a pH ranging from 5.0 to 5.5 (stabilized by an acetate buffer solution). This metal indicator is not specific for zinc, as it also binds to copper. Thus, during the titration it is necessary to use a masking solution. One of the great advantages of this method is the elimination of formaldehyde in the analysis, which as already mentioned is a potential carcinogenic agent and creates problems if too little or too much is used.

Formaldehyde is replaced by a masking solution based on sodium thiosulfate which acts to reduce Cu(II) to Cu(I). In the univalent state, copper does not bind with EDTA. The following reaction shows the reduction of Cu(II) by thiosulfate.



The titration endpoint is noted by the color change from purple to yellow. The proposed methodology is as follows:

- (a) Pipette an aliquot of plating solution into a 250 mL Erlenmeyer flask. The aliquot volume will depend on the actual concentration of zinc ions in the brass plating bath. The following volumes are recommended:
- 2 mL for zinc contents above 20 g/L
  - 5 mL for zinc contents from 10 g/L to 20 g/L

- 10 mL for zinc contents from 5 g/L to 10 g/L
- 20 mL for zinc contents below 5 g/L.

- (b) In a fume hood, add ammonium persulfate crystals [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] until the solution turns to a dark green color. This process is exothermic. The purpose of this step is cyanide decomposition. During this step the solution can turn to a brown color before turning green. If the brown color persists, interrupt the analysis and begin the procedure again. As an alternative to persulfate, concentrated nitric acid (HNO<sub>3</sub>) can be used, followed by the addition of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and heating until white or brown fumes disappear.
- (c) Add 10 mL of distilled water and let it cool.
- (d) Add acetate buffer solution (pH 5.5) to bring the pH value to around 5.5. After that, the solution turns blue, characteristic of Cu(II) ions in aqueous solution. The composition of this buffer solution is: 150 g of anhydrous sodium acetate (NaCH<sub>3</sub>COO) and 15 mL of glacial acetic acid for each liter of distilled water.
- (e) Add the masking solution until the solution turns to a transparent pale yellow (almost colorless). The amount of masking solution added will depend on the copper content in the brass bath. Usually, 20 to 50 mL is necessary. The composition of this masking solution is: 100 g of sodium thiosulfate pentahydrate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O) for each liter of distilled water.
- (f) Add about 0.1 g of 0.1% xylenol orange indicator (m/m). In this step, the solution turns purple. The indicator is prepared as follows: 1 part of indicator ground with 100 parts of NaCl (sodium chloride). The mixture is stored in an amber flask.
- (g) Titrate with 0.0575 mol/L standard EDTA solution. The endpoint is easily noticed when the solution turns yellow.
- (h) The zinc content in the bath is determined by the following formulas:

$$\text{g/L Zn} = (\text{mL}_{\text{EDTA}} \times M_{\text{EDTA}} \times 65.39) / V_{\text{aliquot}}, \text{ or}$$

$$\text{g/L Zn} = (\text{mL}_{\text{EDTA}} \times \text{cf} \times 3.76) / V_{\text{aliquot}}$$

where:

- $mL_{EDTA}$  = volume of EDTA solution in the titration (mL),
- $M_{EDTA}$  = molarity of EDTA solution (mol/L),
- cf = correction factor for the 0.0575 mol/L EDTA solution.
- $V_{aliquot}$  = aliquot solution volume (mL).

**Direct analysis of copper content by iodometric titration**

This method, already established in the literature,<sup>7</sup> is quite practical and suitable for the direct determination of copper content in brass solutions because there is no zinc interference, as already mentioned. The proposed methodology is as follows:

- (a) Pipette 2 mL of the plating solution into a 250 mL Erlenmeyer flask.
- (b) In a fume hood, add 15 mL of concentrated nitric acid and 5 mL of concentrated sulfuric acid. The purpose of this step is cyanide decomposition as well as oxidation of Cu(I) to Cu(II). In this procedure, ammonium persulfate cannot be used because the excess of this salt cannot be eliminated efficiently. This causes significant analytical errors.
- (c) Heat the flask solution (at the fume hood) until the solution turns blue-green and the white or brown fumes disappear. After that, add 20 mL of distilled water and let it cool. The purpose of this step is to eliminate the excess nitric acid.
- (d) Add 5 g of potassium iodide (KI). The flask solution will turn brown.
- (e) Titrate with a solution of fresh pre-standardized 0.1 N sodium thiosulfate pentahydrate ( $Na_2S_2O_3 \cdot 5H_2O$ ) until the solution color turns pale yellow.
- (f) Add 0.5 mL of a fresh 1% starch indicator solution (The solution turns dark blue.) and continue the titration until the dark color disappears.

(g) The copper content in the bath is determined by the following formulas:

$$g/L \text{ Cu} = mL_{thiosulfate} \times N_{thiosulfate} \times 31.785, \text{ or}$$

$$g/L \text{ Cu} = mL_{thiosulfate} \times cf \times 3.1785$$

where:

- $mL_{thiosulfate}$  = volume of sodium thiosulfate consumed in the titration (mL),
- $N_{thiosulfate}$  = normality of sodium thiosulfate solution (N),
- cf = correction factor for the 0.1 N sodium thiosulfate solution.

**Indirect analysis of copper (or zinc) content by EDTA complexometry**

The basis of this method was described previously and as noted, it has an endpoint that is difficult to see. The proposed methodology is as follows:

- (a) Pipette 2 mL of the plating solution into a 250 mL Erlenmeyer flask.
- (b) Add 5 mL of distilled water.
- (c) In a fume hood, add ammonium persulfate crystals [ $(NH_4)_2S_2O_8$ ] until the solution turns to an intense green or blue color. This process is exothermic. During this step, the solution may turn to a brown color before turning green or blue. If the brown color persists, interrupt the analysis and begin the procedure again. As an alternative to the persulfate, concentrated nitric acid ( $HNO_3$ ) can be used, followed by the addition of concentrated sulfuric acid ( $H_2SO_4$ ) and heating until white or brown fumes disappear.
- (d) Add 50 mL of distilled water and let it cool.
- (e) Add ammonium hydroxide ( $NH_4OH$ ) until the solution turns deep blue, a characteristic of Cu(II) ions in aqueous solution.

**Table 4**  
**Results of the Direct Determination of Copper and Zinc Content in the Brass Plating Baths by Direct Titrimetric Analysis**

Bath	Cu nominal value g/L	Cu experimental g/L		Zn nominal value g/L	Zn experimental g/L	
		Mean*	Standard deviation		Mean*	Standard deviation
1	20.0	20.2	0.2	20.0	20.2	0.1
2 (Red brass)	21.3	21.2	0.2	1.1	1.2	0.03
3 (White brass)	11.9	12.2	0.2	33.4	33.1	0.4
4 (High speed process)	62.0	60.8	1.2	3.3	3.0	0.1

\*Mean of three determinations

- (f) Add 5 drops of 0.1% PAR solution. The solution will remain blue.
- (g) Titrate with 0.1 mol/L standard EDTA solution. The endpoint is noted by the color change from blue to green.
- (h) The copper (or zinc) content in the bath is determined by the following formulas:

For copper,

$$\text{g/L Cu} = \left\{ \frac{(V_{\text{EDTA}0.1\text{N}}) - [(0.0306 \times \text{Zn}) / (M_{\text{EDTA}0.1\text{N}})]}{M_{\text{EDTA}0.1\text{N}}} \right\} \times 31.773 \text{ or}$$

$$\text{g/L Cu} = [(V_{\text{EDTA}0.1\text{N}}) - (0.306 \times \text{Zn})] \times 3.1773 \times \text{cf}$$

For zinc,

$$\text{g/L Zn} = \left\{ \frac{(V_{\text{EDTA}0.1\text{N}}) - [(0.0315 \times \text{Cu}) / (M_{\text{EDTA}0.1\text{N}})]}{M_{\text{EDTA}0.1\text{N}}} \right\} \times 32.695 \text{ or}$$

$$\text{g/L Zn} = [(V_{\text{EDTA}0.1\text{N}}) - (0.315 \times \text{Cu})] \times 3.2695 \times \text{cf}$$

where:

$V_{\text{EDTA}0.1\text{N}}$  = Volume of EDTA consumed in the titration (mL),

$M_{\text{EDTA}0.1\text{N}}$  = molarity of the EDTA solution,

Zn = zinc concentration (g/L) obtained from the direct analysis method,

Cu = copper concentration (g/L) obtained from the direct analysis method,

cf = correction factor for the 0.1 mol/L EDTA solution.

### Results

The results presented in Table 4 were obtained by using the direct analysis methods for determining copper and zinc content in brass plating solution compositions as presented in Table 3. Three replicate determinations were done for each bath. As shown in Table 4, the experimental values obtained were very close to the nominal ones for all plating solution compositions studied.

### Conclusion

The direct analyses for the determination of copper (iodometric titration) and zinc (EDTA complexometric titration with xylenol orange indicator) were found to be very effective. They provided accurate results for several cyanide brass plating bath compositions.

### Acknowledgement

The authors thank the State of São Paulo Research Foundation (FAPESP) for the financial support for the PRUMO project, during 2001 and 2002.

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