

## REMOVAL OF ZINC CATION FROM WASTEWATER COMING BY SPENT ACID SOLUTION OF ELECTROPLATING WORK

Georgeta GAVRIȘ<sup>1</sup>, Oana STĂNĂȘEL<sup>1</sup>, Alina CĂRĂBAN<sup>1</sup>, Gabriela BADEA<sup>1</sup>

University of Oradea, Faculty of Science, Department of Chemistry,  
 University str. no.1. Oradea, Romania  
 E-mail : georgeta\_gavris@yahoo.com\*

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*Abstract.* Crystalline form of zinc oxalate was extracted from waste waters, in specifically conditions as regarding pH, acid oxalic dose, concentration of cation  $Zn^{2+}$  and temperature due to low value of solubility product. By these method it was possible cleaning waste waters, recovery transitional metal Zn. The work parameters were pH 5,5. Dose of oxalic acid 100% excess, cation concentration  $C > 0,05M$ , temperature  $20^{\circ}C$ . White crystalline precipitate of zinc oxalate was washed, dried, and analysed through chemical methods, and thermal analysis in order to be established chemical composition, and technological conditions for obtaining zinc oxide as a secondary product using information through thermal analysis.

## INTRODUCTION

It is known much and different possibilities for treatment residual waters with heavy metals like nickel, cobalt, copper, lead, iron and others cations which can be provided especially from electrotechnical industries, electronic industries, electroplating process in alkaline or acids baths for protection surface. Waste waters and residual effluents are containing besides  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Cr^{6+}$ ,  $Zn^{2+}$  a various salt specifically for electroplating chlorides, sulfates, nitrates, chelating agents, surfactants, sulfuric acid, boric acid, fluorides. If the process goes in alkaline pH, then, residual solution have carbonates, phosphates, sodium hydroxide. The residual concentration of cations in waste solutions can be taken into account apart from 50- 100 mg/L up to 5-6 g/L according to [1, 2, 3]. The methods used in practice are ionic exchange, zeolithical absorbance, precipitation and flocculation, electrolysis, chemical reduction [4]. The cations precipitation with sodium hydroxide, carbonates, phosphates or lime stone gives amorphous compounds of Ni, Co, Cu, Cr, Pb or Zn [5] which are difficult to separate, wash, filtered, guard and store in a stable composition because their instability to air, humidity, CO<sub>2</sub>. Study about cleaning waste waters with zinc are presented in [3].

## MATERIALS AND METHODS

In order to obtain the result about chemical composition, it was employing next apparatus and reagents.

Analytical balance type Toledo

Flame atomic absorption spectrophotometer AAS 30 Germany for zinc determination

Magnetic stirrer for volumetric determination

Electrically system for drying precipitate of zinc oxalate

Derivatograph Paulik Paulik and Erdely-Hungaria for thermal analysis

Analytical reagents type Merck, Amex, Fluka

Twice distilled water on Simax apparatus Cehia

Standard Merck solution stock for spectrophotometry 1g Zn/L

Oxalic acid 0,5M, (F=1), complexon III 0,05M, (F=1), eriochrome black T, buffer ammonium tampon pH 10, hydrochloric acid 18% ultra pure., filter paper blue band.

Precipitated zinc oxalate was washed, dried and dissolved in hydrochloric acid 18% and solution was poured in volumetric flask of 100 mL. A suitable volume was analysed by volumetric method [6,7] using complexon III and indicator eriochrome Black T, buffer tampon pH 10. At the equivalence point, color changes from red to blue net.

1ml complexon III 0,05M corresponding to 3,2685 mg Zn.

Oxalate anion was analysed by volumetric method with potassium permanganate 0,1N (F= 1) at  $80^{\circ}C$ , in the presence of sulfuric acid 4N on magnetic stirrer. At the equivalence point, solution became colorless. 1mL  $KMnO_4$  0,1N corresponds to 4,4 mg  $C_2O_4$  [6]

Zinc content was analysed also by flame atomic absorption spectroscopy (FAAS) [8] using calibration graph of standard work solution 1000 mg/L named stock (1) and diluted stock(2) solution 100 mg/L.. The stock

(2) solution was prepared into 100 mL volumetric flask, using 10mL stock solution (1), 10 mL nitric acid 1N and distilled water

Into 5 volumetric flask 100 mL where introduced 0, 0,25, 0,5, 1, 2, mL stock solution(2).

Each balloon contains respectively 0, 0,25, 0,5, 1, 2, mg Zn or 0, 0,25, 0,5, 1, 2 mg Zn/L

The optimal and specifically technical conditions for these apparatus AAS-30 are presented in table 1.

Table1.

The optimal and specifically technical conditions for these apparatus AAS-30.

Intensity I [mA]	Length [nm]	Slit [nm]	Sens [ppm]	Flame
5,0	213,9	0,2	0,012	Air/acetylene

## RESULTS AND DISCUSSIONS

It was weight 0.1158 g and 0,1088g zinc oxalate, ( as Materials and Methods), and were dissolved in two 100 mL volumetric balloons. The results of volumetric determination are shown in table 2 and by FAAS method in table3

Table2.

Contents of zinc and oxalate through volumetric titration.

No.	M [g]	V <sub>s</sub> [mL]	V <sub>complexon</sub> [mL]	Zinc [mg]	V <sub>KMnO4</sub> [mL]	Oxalate [mg]	%Zn	%C <sub>2</sub> O <sub>4</sub>	%H <sub>2</sub> O
1	0,1158	50	6,12	20,00	0,61	26,9	34,5197	46,47	19,011
2	0,1088	50	5,74	18,77	0,57	25,796	43,5197	46,47	19,011

Calibration graph zinc is shown in table 3 and figure 1

Table 3.

Concentration and absorbance of zinc standard etalons.

Nr.	Zn [mg\L]	Corr. Absorbance	Absorbance	Std. Dev. [mg\L]
1	0,00	-0,0001	0,00	0,0005
2	0,250	0,0626	0,0626	0,0004
3	0,5	0,1230	0,1230	0,0005
4	1	0,2419	0,2419	0,0003
5	2	0,4626	0,4626	0,0061

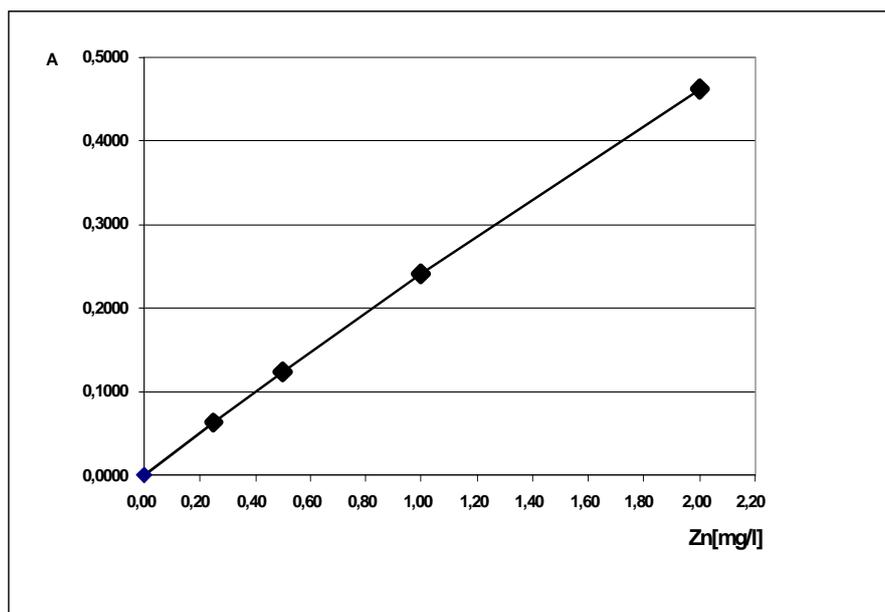


Figure 1. Calibration curve of zinc.

The chemical analysis through FAAS were made as follows . Solutions no.1 and 2 were ten twice diluted and it was taken 4 mL from each into two 100 mL volumetric flasks. Absorbance and percentage composition of zinc are shown in table 3

Table 3.  
Concentrations, absorbance and percentage content of zinc.

No	V <sub>s</sub> [mL]	Absorbance	Zinc content[mg]	%Zn
1	4	0,3842	0,160	34,52
2	4	0,3611	0,148	34,53

experiments, zinc form

Apart from chemical oxalate is in a dehydrate ZnC<sub>2</sub>O<sub>4</sub>\*2H<sub>2</sub>O.

#### THERMOGRAVIMETRIC AND THERMODIFFERENTIAL ANALYSIS (TTA)

The white and crystalline precipitate of zinc oxalate was studied by TTA on a derivatograph MOM Hungary using next technical parameters.[9].

TG-100 mg content

TG/sensibility 100 mg

DTG 1/5

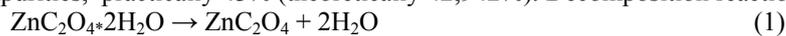
DTA 1/3

T (rate) 5<sup>0</sup>C/min, 500<sup>0</sup>C

Platinum cylindrical crucible, static air condition for DTA, reference sample alfa Al<sub>2</sub>O<sub>3</sub>.

Zinc oxalate derivatogram is presented in figure 2.

The product loses crystallisation water (theoretically m=19,011%), practically=19%, between 100-140<sup>0</sup>C. Thermal decomposition of zinc oxalate begins at 340<sup>0</sup>C and stops at 370<sup>0</sup>C, when ZnO is obtained, free from impurities, practically 43% (theoretically 42,942%). Decomposition reactions were:



All dates obtained by thermal analysis confirm chemical composition of zinc oxalate like dehydrate, ZnC<sub>2</sub>O<sub>4</sub>\*2H<sub>2</sub>O, white, crystalline precipitate, insoluble in water.

In these case, zinc oxalate obtained in cleaning process of waste waters and recovery as subproduct may be used to obtain zinc oxide at low temperature for different utilisations . The process is economical end easy to realise. Zinc oxide is in pure form because Co and CO<sub>2</sub> leaves the system.

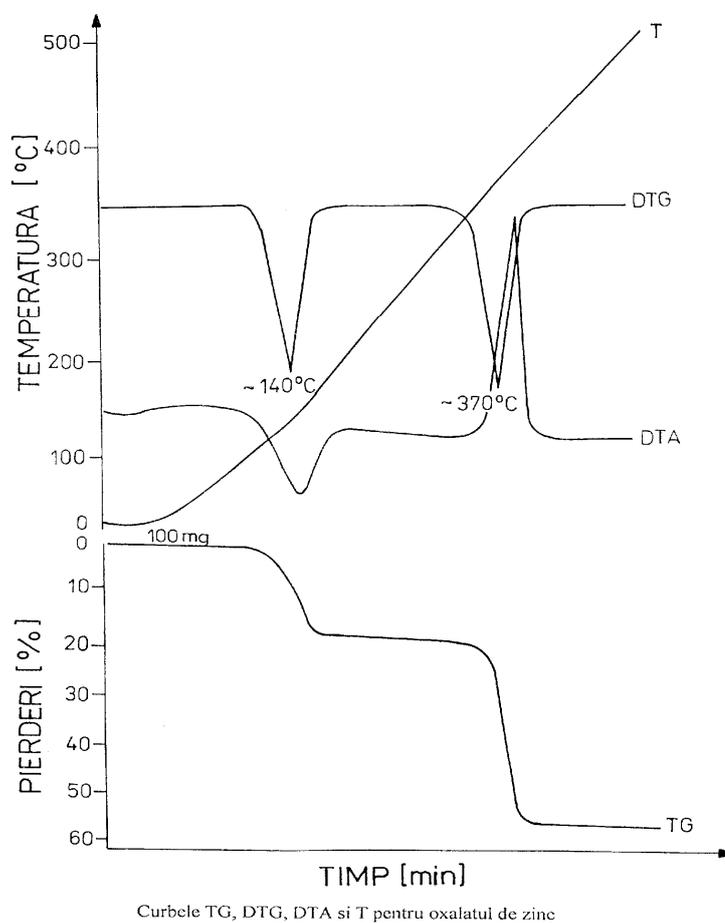


Figure 2. T, TG, DTG, DTA curves of zinc oxalate.

Dictionary of figure 2:

Pierderi =waste

Temperatură = temperature

Curbele =curves

Timp = time

Oxalatul de cobalt = cobalt oxalate

## CONCLUSIONS

Zinc recovery ions process from waste waters goes with 99,5% efficiency in the following optimal conditions:  $[Zn] > 0,05M$ ,  $pH = 5,5$ , oxalic acid excess 100%,  $T = 20^{\circ}C$ . The chemical composition of zinc oxalate proved by volumetric and instrumental methods is a form of dehydrate  $ZnC_2O_4 \cdot 2H_2O$ , white crystalline precipitation. The low value of product of solubility for zinc oxalate is an advantage for cleaning waste waters with zinc ions contents.

The crystalline precipitate can be washed, dried, and has a good stability on air and water face to amorphous compounds of carbonates, hydroxides or phosphates. [10].

Zinc oxalate could be turn into zinc oxide on low temperature, between  $340-370^{\circ}C$  based on derivatogram. After zinc oxalate recovery, excess of oxalic acid and the rest of zinc could be eliminated using

limes stone 10%. In these case, oxalic acid precipitates like calcium oxalate, and rest of zinc, precipitates like zinc hydroxide. The effluents could be eliminated according to SR ISO 8288. The obtained small quantities of mud is saved in adequate conditions.

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