Identification and analysis of copper oxychloride technical (TC) fungicide samples

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Abstract: This study showed the qualitative and quantitative analysis of main ingredients in copper oxychloride TC samples, providing basis for improving product quality and perfecting process. While described the analysis of active ingredient, soluble in water-alcohol, water, loss on dry, CL—and the content of trace impurities, Pb, Cd and As. Chemical titration was used to determine content of Copper oxychloride in (TC) samples, content of Pb, Cd, As were determined by Microwave Atomic Emission Spectrophotometer, and water content, loss on dry, soluble in water-ethanol were determined. The sample was conducted in compliance with the protocol which incorporated the recommendation made in CIPAC Guidelines.

Keywords: Copper oxychloride (TC), CIPAC, qualitative, quantitative analysis, Chemical titration and Microwave Atomic Emission Spectrophotometer

1. Introduction

Copper oxychloride 3Cu(OH)2.CuCl2 (common name is an inorganic copper fungicide. Iupac name dicopper chloride trihydroxide (approximate composition (Pesticide Manual 16 edition 2012).

The sample is normally green or bluish-green powder. The content of Cu2+ in theory is 59.5%, but usually is lower in industrial product for it containing crystal water. Insoluble in water, ethanol, ether, soluble in ammonia, decomposes when heated 8 hours under 250ºC, with the formation of water and copper chlorides.

2. Specifications and identity of active substances

Table (1): Specification of Copper oxychloride (TC)

Common name : Copper oxychloride
Uses : Fungicide
Chemical name : Dicopper chloride trihydroxide
CAS : 1332-40-7
Molecular formula : $Cu_2H_3ClO_3$
Molecular weight : 213.6

Composition	Specification
Copper oxychloride, w/w	^{3} 92.0%
Total copper,w/w	^{3} 54.7%
Soluble in water-alcohol, w/w	£ 1.5% Maximum: 10 x X mg/kg, where X is the copper content(g/kg
Loss on dry, w/w	£ 2.0% Maximum: 20 g/kg
Water, w/w	£ 3.0%
Pb	< 200 mg/kg Maximum: 0.5 x X mg/kg, where X is the copper content(g/kg)
Cd	< 10 mg/kg Maximum: 0.1 x X mg/kg, where X is the copper content(g/kg)
As	Maximum: 0.1 x X mg/kg, where X is the copper content(g/kg)

3. Materials and methods

3.1. Apparatus and agents for copper content

3.1.1 Apparatus

Weighing bottle
250ml volumetric flask
500ml three necked bottle
250ml beaker
50 ml burette
Electric heating-jacket, zeolite, funnel

3.1.2. Agents

Hydrochloric acid 1:1
Starch indicator
Ammonia (d=0.880 g/ml)
$Na_2S_2O_3$ solution 0.1N
Acetic acid (332 g/l)
NaF saturated solution
KSCN solution (400 g/l)
Litmus paper
Copper oxchloride TC sample
Country of origin – China
(Provided by CAPL)(250g)

3.1.3. Test procedure

The weight about 0.5g (TC) sample to 250ml three necked bottle, add in 25ml (1:1) hydrochloric acid and several zeolites, and keep boiling for several minutes. After cooled, transfer the solution into 250ml volumetric flask, filter if necessary. Then dilute to volume with wash water of three necked bottle and distilled water, absorb 50ml solution to another 250ml three necked bottle.

On the other hand, added in ammonia under oscillating until the color of the solution turned to deep blue. While added in acetic acid to litmus agent, after litmus agent shows acid, added in more 2ml acetic acid, cool it to 15 - 20ºC, add 10ml KI solution, put on plug, water seal, then oxcillate slightly to complete mixing.
Titrate with $Na_2S_2O_3$ standard solution to grass yellow, add in 2ml starch indicator and KSCN solution, titrate to blue disappear totally.

3.1.4. Calculation

$$0.0635 \times 250 \times V \times N$$

$$\text{Total Cu (\%)} = \times \frac{\qquad\qquad}{50 \times W} 100$$

Where,
V = Volume of $Na_2S_2O_3$ standard solution used for titrating (ml);
N = Equivalent concentration of $Na_2S_2O_3$ standard solution (N);
W = Weight of sample (g)

$$\text{Copper oxychloride (\%)} = \times \frac{\text{Total copper}}{59.5} 100$$

Identity tests (**CIPAC H**) and Total copper [**CIPAC 1, p.226).**

3.2. Apparatus and agent for Pb, Cd, As content. (CIPAC 1A)

3.2.1. Apparatus

Microwave Atomic Emission Spectrophotometer
(4200 MP AES – Agilent technologies)
Volumetric flask (50ml, 100ml)

3.2.2. Agents

Nitric acid: AR
Distilled water
Purified Pb, Cd, As: AR

3.2.3.Test procedure

3.2.3.1. Draw Pb standard Curve

Preparation of Pb standard solution. Weight 0.1g Pb A.R, dissolve with 20ml 1:1 nitric acid, then transfer to 1000ml volumetric flask, dilute with (1:499) nitric acid to volume. Shake up and stand by (100 ppm Pb standard solution). Absorb certain amount of Pb standard solution to 100ml volumetric flask to get a series standard solution of 1.0, 2.0, 4.0, 10.0, 15.0 and 20.0 ppm. Under the conditions described above, spray into flame, detect the corresponding absorbance, and correct zero point with distilled water. Take the Pb concentration (ppm) as X-coordinate, absorbance (A) as Y-coordinate, draw A-C standard curve.

Draw Cd standard Curve

The weight 0.01g Cd A.R dissolved with 20ml (1:1) nitric acid, then transfer to 1000 ml volumetric flask, dilute with (1:499) nitric acid to volume, shake up and stand by (10ppm Cd standard solution). Absorb certain amount of Cd standard solution to 100ml volumetric flask to get a series standard solution of 0.05, 0.1, 0.5, 1.0, 1.5, and 2.0 ppm, detect and draw A-C standard curve.

Draw As standard Curve

Use the same way as Cd to get the standard curve of As.

3.2.3.2. Sample determination

Preparation of sample solution. Weight 1g TC sample to 100ml conical flask; dissolve with 1:1 nitric acid, if necessary, heat to complete dissolution. The filtrate was diluted with 1:499 nitric acid to volume, shake up and stand by.

Preparation of blank solution, without adding in (TC) sample, take the same procedure to prepare blank solution. Determine the sample under the same conditions used to determine the standard solution to get Absorbance of Pb, Cd, As and blank solution.

3.2.4. Calculation

Content of determined element (mg/kg) = $A_{sample} - A_{blank}$) × 50

3.3 Apparatus and agents for soluble in water-alcohol determination(CIPAC 1B)

3.3.1.Apparatus:

Weighing bottle
Centrifuge
Baking oven

3.3.2. Agent: Ethanol-water mixtures (95% ethanol : distilled water = 40:100)

3.3.3. Test procedure

The Weight2.5g TC sample (w, g) to a centrifuge tube, added in ethanol-water mixture, stir and oscillate for several minutes, then centrifugate, precipitation separated. 30 min later. Transfer upper to a weight-constant triangular bottle (x, g). Added distilled water to the centrifugal tube, stir, oscillate and centrifuge again, upper was transferred to weight-constant triangular bottle.

Evaporate water in triangular bottle to almost dry, bake the residues under 105ºC to constant weight (y, g).

3.3.4. Calculation

$$\text{Soluble in water-ethanol (\%)} = \frac{(y - x)}{w} \text{x } 100$$

3.4.Determination of water

3.4.1.Apparatus and agent

Apparatus: Moisture analyzer
Round bottom flask
300mm condenser tube
Agent: Toluene A.R

3.4.2.Test procedure

The weight (1.0 g) TC sample to round bottom flask, added in 100ml toluene (or benzene) and several capillary with length of 10-12mm. Heat and reflux at speed of 2-3d/s, till the water in acceptor didn't increase any more, hold on for 10 min, then stop heating. However capillary absorb toluene to wash condenser tube, till no water drop falling down. Cool it to room temperature, read water volume in acceptor.

3.4.3.Calculation

Water content in TC samples was calculated as:

$$X(\%) = \frac{V}{W} \text{x } 100$$

Where,
V = Water volume in acceptor, ml
W --- Sample Weight, g

3.5. Determination of Loss on dry (CIPAC 1,MT 17.3,)

3.5.1.Apparatus

Baker Weighing bottle Desiccator

3.5.2.Test procedure

The weight10g (TC) sample to a weight weighing bottle, then put into baker, heat for 2 hours under 110ºC After, transfer weighing bottle to desiccator, cool to room temperature, weigh it again.

3.5.3. Calculation

$$\textbf{Loss on dry (\%)} = \times \frac{M_1 - M_3}{M_1 - M_2} \mathbf{100}$$

Where,
M_1--- Total weight of sample and bottle before baking, g
M_2 --- Weight of bottle, g
M_3 --- Weight of sample and bottle after baking, g

3.6. Determination of Cl^{-} in TC samples

3.6.1. Apparatus and agent

3.6.1.1. Apparatus

50ml titrates
Triangular bottle (100ml, 250 ml)
Funnel, electric heating-jacket

3.6.1.2. Agent

Nitric Acid, A.R
NH_4SCN standard solution (0.05053mol/L)
Distilled water 8%
Ferri-ammonium sulfate indicator
$AgNO_3$ standard solution (0.1025mol/L)

3.6.2.Test procedure

3.6.2.1. Determination of total Cl^{-}

The weight 0.25g (TC) sample to 250ml iodine graduated flask, added in 40ml distilled water to wet the powder, then add 10ml 20% HNO_3, heat to complete dissolution. Cool to room temperature; add in 1:1 HNO_3 solution, oscillation. Added accurately 20ml 0.1mol/L $AgNO_3$ standard solutions, shake up, added in 3ml 8% Ferriammonium sulfate indicator, then titrate with 0.05mol/L NH_4SCN standard solution, till the blue of Cu ion disappeared and light yellow came up and didn't fade away.

$$\textbf{Total Cl(\%)} = \frac{(C_1V_1 - C_2V_2) \times 0.03545}{M} \times 100$$

3.6.2.2. Determination of water soluble Cl

The weigh 2.0g (TC) sample to clean and dry 250ml triangular bottle, added in 100ml distilled water, oscillate and rapidly filter with funnel and filter paper. Filter cake was washed with 20ml water for three times, collect filtrate and water washing liquid to a 250ml triangular bottle, added in 5ml 1:1 HNO_3 solution, oscillate. Then added in accurately 15ml 0.1mol/L $AgNO_3$ standard solution, shake up, added in 3ml 8% Ferri-ammonium sulfate indicator, then titrate with 0.05mol/L NH_4SCN standard solution.

$$\textbf{Water soluble Cl(\%)} = \frac{C_1V_1 - C_2V_2) \times 0.03545}{m'} \times 100$$

Where,
C_1= Concentration of $AgNO_3$ standard solution, mol/L
V_1 = Volume of $AgNO_3$ standard solution added, ml
C_2 = Concentration of NH_4SCN standard solution, mol/L
V_2 = Volume of NH_4SCN standard solution used for titrating, ml
m, m' = Sample weight, g
0.03545 = Milligrammemol of CL ion

4. Results and Discussion

The sample of copper oxychloride TC was suspected to quantitative analysis for determination of active ingredient (metallic copper), soluble in water-alcohol, water, loss on dry, $CL^{-}$and the content of trace impurities, Pb, Cd and As.

Determination content of total copper and copper oxychloride in the TC sample based mainly on the principle of Oxidation-reduction titration method.

Table (2): total copper and copper oxychloride content results.

Determination of Pb, Cd, As in Copper oxychloride TC sample .based on the atomic absorption spectrometry method. As absorb digested sample into flame directly, atom formulated in the flame will absorb characteristics electromagnetic radiation. On the other hand,comparing absorbance of sample with that of standard solution, we can content of the detected atom.

Table (3): Pb, Cd, As in Copper oxychloride TC sample (Average of two replicate)

4.1. Determination content of soluble in water -alcohol in TC sample.

Centrifugally separate soluble and insoluble in water-alcohol todetermine the content of soluble.

Number	Sample weight (g)	Total CU (%)	Copper oxychloride (%)
R1	0.5028	55.86	93.88
R2	0.4991	56.38	94.75
R3	0.5011	55.91	93.96

	Pb (mg/kg)	Cd (mg/kg)	As (mg/kg)
R1 and R2	16.4	4.6	2.4
	15.8	5.0	2.6
Average	**16.1**	**4.8**	**2.5**

Table (4): soluble in water alcohol (ethanol) percentage

Number	w (g)	x (g)	y (g)	Soluble in water-ethanol (%)
R1	2.0123	42.4015	42.5303	1.28
R2	2.0532	41.6312	41.8116	1.80
R3	2.1918	42.1011	42.1180	1.69

4.2. Water content percentage

Determination content of water in TC sample based on constant boiling distillation.

Table (5): water content percentage

Number	w (g)	x (g)	Water content (%)
R1	19.34	0.46	2.4
R2	20.06	0.44	2.2
R3	20.88	0.54	2.6

4.3 Loss of dry percentage

Determine content of evaporable material when baking TC sample. Bake TC sample for several hours under certain temperature, weight difference before and after baking is the weight lost on dry.

Table (6): Loss of dry percentage:

Number	M_1 (g)	M_2 (g)	M_3 (g)	Loss on dry (%)
R1	36.2426	30.3275	36.1266	1.96
R2	36.5297	30.4475	36.4148	1.89
R3	36.3981	30.2234	36.282	1.88

Determination content of Cl^- in Copper oxychloride TC sample.

Cl^-in digested TC sample will react with $AgNO_3$ standard solution, then the excess $AgNO_3$ is titrated with NH_4SCN standard solution, using Ferriammonium sulfate as indicator. The results showed percentage of total chlorine compatible with the chemical structure and molecular weight of CL and copper oxychloride.

Table (7): content of total and water soluble Cl^- in Copper oxychloride TC sample

	Number	Sample weight (g)	C_1 (mol/L)	C_2 (mol/L)	Content (%)	Average value (%)
Total Cl	R1	0.2778	0.1025	0.05053	16.58	16.56
		0.2659	0.1025	0.05053	16.53	
	R2	0.2755	0.1025	0.05053	16.48	16.55
		0.2571	0.1025	0.05053	16.62	
	R3	0.2534	0.1025	0.05053	16.65	16.53
		0.2700	0.1025	0.05053	16.51	
Water soluble Cl	R1	2.4342	0.1025	0.05053	1.38	1.34
		2.6644	0.1025	0.05053	1.29	
	R2	2.4675	0.1025	0.05053	1.35	1.33
		2.5346	0.1025	0.05053	1.32	
	R3	2.4109	0.1025	0.05053	1.41	1.39
		2.4604	0.1025	0.05053	1.37	

References:

CIPAC Handbooks, 1 (1970), 1A (1980), 1B t1983), 1C (1985) and ID (1988)

[CIPAC 1, 44.0/1/M1/1.2, p.226 (Referee method) or 44.0/1/M2/1.2(c), p.230 and CIPAC 1A, p. 1168].

Total copper

CIPAC 1, MT 17.3, p.874)**Loss on drying)**

CIPAC 1A, 44.0/2/M2/2.6, p.1168.**Arsenic determination**

CIPAC 1A,MT 92, p.1603).**Lead determination.**

CIPAC 1B,MT 98, p.1915).**Copper soluble in water**

CIPAC H, p. 96. **Identity tests**

FAO SPECIFICATIONS FOR PLANT PROTECTION PRODUCTS, COPPER OXYCHLORIDE, Rome, 1991

Manual on development and use of FAO and WHO specifications for pesticides, November 2010 - second revision of the First Edition

Pesticide Manual, 16th Edition, 2012