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DETERMINATIONS OF RELEVANT IMPURITIES IN COPPER AND SULPHUR COMPOUNDS USED AS PESTICIDES

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ABSTRACT

During the course of study of the Relevant Impurities in Copper and Sulphur compounds used as Pesticides, by a bunch of Copper samples (Copper Oxochloride [Three replicates]; Copper Hydroxide; Cuprous oxide; Copper Sulphate anhydrous; Copper Sulphate Tribasic and Copper Sulphate pentahydrate, respectively) and Sulphur samples (5 compounds) were tested to determine their Relevant Impurities of Arsenic, Cadmium and Lead. New analytical methods were devised to estimate; identify and confirm their Active Ingredients and its Relevant Impurities. The results obtained could be summarized as follows: All the concentrations of the Active Ingredients for the previous pesticides were in allowed limits and agreement with its Reference Active Ingredients. Results also revealed that the Arsenic concentrations in Copper samples ranged from 0.4938×10^{-3} to 12.4907×10^{-3} mg/kg before storage and 1.1759×10^{-3} to 4.6608×10^{-3} mg/kg after storage, while they were ranged from 0.4286 to 3.1328 µg/g before storage and 2.6118×10^{-3} mg/kg to 12.6566×10^{-3} µg/g after storage in Sulphur samples. The maximum allowed limits for Arsenic concentrations in Copper samples ranged from 5.92 to 49.20 mg/kg before storage and 5.80 to 48.57 mg/kg after storage while in Sulphur samples ranged from 352.665 to 407.49 µg/g before storage and 351.288 to 405.45 µg/g after storage. Results also showed that the Cadmium concentrations in Copper samples ranged from 0.0286 to 0.0822 mg/kg before storage and 0.0187 to 0.0772 mg/kg after storage, while they were ranged from 0.0217 to 0.0472 µg/g before storage and 0.0219 to 0.0495 µg/g after storage in Sulphur samples. The maximum allowed limits for Cadmium concentrations in Copper samples ranged from 5.92 to 49.20 mg/kg before storage and 5.80 to 48.57 mg/kg after storage, while in Sulphur samples ranged from 6.915 to 7.99 µg/g before storage and 6.888 to 7.95 µg/g after storage. The results also demonstrated that the Lead concentrations in Copper samples ranged from 0.4080 to 1.0948 mg/kg before storage and 2.7398×10^{-3} to 1.7956 mg/kg after storage; while they were ranged from 0.2106 to 0.3165 µg/g before storage and 0.2159 to 0.4264 µg/g after storage in Sulphur samples. The maximum allowed limits for Lead concentrations in Copper samples ranged from 29.6 to 246 mg/kg before storage and 29 to 242.85 mg/kg after storage, while in Sulphur samples ranged from 34.575 to 39.95 µg/g before storage and 34.575 to 39.75 µg/g after storage. Eventually, the aforementioned results clearly showed that all the previously evaluated Relevant Impurities in their tested pesticides demonstrated that; it has been below the international critical levels and have been justified within the tolerance and guidelines of FAO/WHO.

Key words: Pesticides; Sulphur; Copper; Storage; Heavy Metals; Relevant Impurities (Arsenic, Cadmium, and Lead)

1. INTRODUCTION

PESTICIDES contain the active principles and products conceived to act upon fundamental processes of living organisms and as a consequence have the potential to kill or fight pests (*Abdollahif Gholizadeh, et al., 2009*).

Sulphur and Copper compounds are extensively used as fungicides and bactericides (*Ambrus. A; et al. 2003*). Sulphur accounts for 15% of the inner core of the earth and 0.052% of its crust (*Anca E. Gurzau, et al., 2008*). The total Sulphur content of the earth is estimated to be about 18.2×10^{15} tons. Sulphur is an indirect food additive for use only as a component of adhesives (*Ata. S., et al., 2009*). Prolonged use of Sulphur may result in a characteristic dermatitis (*Berman, E, 1980*). Sulphur is the oldest recorded fungicide and has been used for more than 2,000 years. Early in agricultural history, the Greeks recognized its efficacy against rust diseases on wheat. Dusting elemental sulfur in powdered form is a common fungicide being used for controlling pathogens in grapes, strawberry, many vegetables, and several other crops. Sulphur is applied to plants in three formulations as wettable powders; as colloidal Sulphur and as lime sulphur. It has a good efficacy against a wide range of powdery mildew diseases as well as black spot. In organic production, sulfur is the most important fungicide. It is the only fungicide used in organically farmed apple production against the main disease apple scab under colder conditions. Biosulphur (biologically produced elemental Sulphur with hydrophilic characteristics) can be used well for these applications. Standard-formulation dusting sulfur is applied to crops with a sulfur duster or from a dusting

plane. Wettable sulfur is the commercial name for dusting sulfur formulated with additional ingredients to make it water miscible. It has similar applications, and is used as a fungicide against mildew and other mold-related problems with plants and soil. Sulfur is also used as an "organic" (i.e. "green") insecticide (actually an acaricide) against ticks and mites. A common method of use is to dust clothing or limbs with sulfur powder. Some livestock owners set out a sulfur salt block as a salt lick.

Although copper compounds may be toxic by inhalation, ingestion, injection, and skin or eye exposure, copper itself probably has little or no toxicity, although there are conflicting reports in literature (*Browning, E. 1969*). It is generally agreed that copper itself is less toxic than its salts (*Bulinski, R. 1993*). Copper salt are particularly irritating. The fumes and dust cause irritation of the upper respiratory tract (*Burlo, F., et al., 1999*). Acute poisoning from inhalation of copper containing dust has been reported to cause symptoms of heavy metal poisoning (*Carbonell-Barrachina, A.A. 1999*).

Heavy metals contamination is a major problem of our environment and they are one of the major contaminating agents of our food supply (*CFR, 1997; CIPAC E, 1993*). This problem is receiving more and more attention all over the world, in general and in developing countries in particular. The biological half-lives of these heavy metals are long and have potential to accumulate indifferent body organs and thus produce unwanted side effects (*CIPAC F, 1995; CIPAC Handbook, 1992*).

As certain heavy metals such as Lead, Cadmium, and Arsenic have been recognized to be potentially toxic within specific limiting values, a considerable potential hazard exists for human nutrition (*CIPAC I, 1974*).

Lead can trigger both acute and chronic symptoms of poisoning. Acute intoxications only occur through the consumption of relatively large single doses of soluble Lead salts. Chronic intoxications can arise through the regular consumption of foodstuffs only slightly contaminated with Lead. Lead is a typical cumulative poison. The danger of chronic intoxications is the greater problem (*CIPAC I, 1974; Davis, J.M; et al. 1990*).

Cadmium is concentrated particularly in the kidneys, the liver, the blood-forming organs and the lungs. It most frequently results in kidney damage (necrotic protein precipitation) and metabolic anomalies caused by enzyme inhibitions (*CIPAC I, 1974; Davis, J.M; et al. 1990*).

Arsenic in inorganic and organic forms used previously as pesticides, plant defoliants, and herbicides may accumulate in agricultural soils and in plants. The phytoavailability of arsenic is primarily determined by arsenic species and concentration in the medium (*FAO, 1973; FAO 1998*). Arsenite, as (III) is more phytotoxic than arsenate, As (V) and both are much more phytotoxic than mon-sodium methane arsenic acid (MSMA) (*FAO 1998; FAO, 1999*). Inorganic arsenic inhibits enzyme activity and trivalent inorganic arsenic reacts with the sulphhydryl groups of proteins affecting many enzymes containing such groups (*FAO 1998; FAO 2002; FAO 2006_A*). The marked inhibitory effects of As (III) on mitochondrial respiration mediated by NAD-linked substrates appear to play a critical role in toxicity.

The overall goal of this investigation is to determine the Impurities [Arsenic, Cadmium, and Lead] that can be found in the samples of Sulphur and Copper pesticides under environmental conditions and determine its compliance to the FAO/WHO guidelines allowed (*FAO, 1998; FAO, 2006_A*).

2. MATERIAL AND METHODS

2.1. Sampling

Five sulphur samples were obtained randomly from the following sources: France, Helb, India, and Saudia.

Copper samples (8 samples) were taken randomly for the present study from the next sources:

- a. Copper Oxychloride [three replicates]: Germany, Peru, China.
- b. Copper Hydroxide : Germany.
- c. Cuprous oxide : Norway.
- d. Copper Sulphate pentahydrate : Egypt.
- e. Copper Sulphate anhydrous : Egypt.
- f. Copper sulphate Tribasic : Italy.

2.2. Storage Stability at Elevated Temperatures

2.2.1. Aim

To ensure that the properties of formulations are not adversely affected by storage at high temperature, and to assess their long-term storage stability at more moderate temperature, with respect to content of active ingredient (and a possible consequent increase in relevant impurities) and certain physical properties (*Labib, H.Y.; et al. 2008; Manomita Patra, 2004*).

2.2.2. Applicability

Specifications for all tested pesticides formulations.

2.2.3. Method

MT 46: Accelerated storage procedure (*Osol, A. ed,1980*).

2.2.4. Requirements

- a. After storage at 54 ± 2 °C for 21 days, the formulation must continue to comply with the requirements of appropriate clauses for content of active ingredient, relevant impurities, and particulate dispersion clauses. The average active ingredient content should not decline to less than 95% of the average content measured prior to the test, and relevant physical properties should not change to an extent that might adversely affect the application and/or safety.
- b. Where the formulation is neither suitable nor intended for use in hot climates and is adversely affected very high temperature the test conditions may need modifying.

2.2.5. Comments

Samples of the formulation taken before and after the MT 46 tests should be analyzed concurrently, after the test, in order to reduce the analytical error. Further information must be provided if the degradation of the active ingredient exceeds 5 % or a physical property is adversely affected. For example, the degradation products must be identified and quantified.

2.2.6. Copper and Sulphur Pesticides

2.2.7. Scope

- The objective is to accelerate the ageing of a product by heating.
- The test thus provides a useful guide on performance after storage in hot or temperate climates.

2.2.8. Apparatus

- Beaker 250 ml, 6 to 6.5 cm internal diameter.
- Metal disc plastic coated a loose fit in the beaker, and of such dimensions that an even pressure of 25 g/cm³ can be produced on the surface of the sample in the beaker.
- Oven thermostatically controlled to the specified temperature (± 2 °C).
- Dissector without desiccant.

2.2.9. Procedure

- Put the sample (20g) into the beaker and spread it, without using pressure, in a smooth even layer of constant thickness.
- Place the disc on the surface of the powder in the beaker and put it in the oven.
- After the specified time remove the beaker, take out the disc, and allow the beaker to cool in a desiccator.
- Carry out the appropriate tests specified in the general method of analysis for Pesticides e.g. susceptibility with 24 hour of cooling.
- Ensure that each sample taken is truly representative of that left in the beaker.
- Sampling of hard cake may be carrying out conveniently by removing several cores with a small diameter (6 mm) cork borer.

2.3. Identity Tests of Copper

2.3.1. Copper ^[24-28]

2.3.2. Reagents

- a) *Hydrochloric acid (HCL) = 5 mol/l.*
- b) *Nitric acid (HNO₃) = 5 mol/l.*
- c) *Ammonia solution 25%*
- d) *Potassium cyanide 10% aqueous solution.*
- e) *Ethyne solution in acetone.. Saturate acetone 10 ml with ethyne.*

2.3.3. Procedure

- i. **Cupric compounds:** Dissolve a small portion of the sample in hydrochloric acid (5 mol/l). when all the material has dissolved add ammonia solution, a bluish green basic salt is precipitated; add further ammonia solution until the precipitate just dissolves to give a deep blue solution. Add potassium cyanide solution drop wise and the blue colour disappears leaving a colourless solution.
- ii. **Cuprous compounds:** Dissolve a small portion of the sample in ammonia solution 5 mol/l; a colourless to pale blue solution is formed. Add ethylene in acetone, a red precipitate of copper acetylde is produced. Dissolve a small portion in Nitric acid (5 mol/l), add ammonia solution, a bluish green basic salt is precipitated. Continue as for (i).

2.3.4. Volumetric Thiosulphate method

Outline of method: cupric ions, formed by digestion with sulphuric acid-nitric acid mixture or hydrochloric acid, afford, with potassium iodide, cuprous iodide, and iodide. The latter is titrated with sodium thiosulphate.

2.3.4. 1. Reagents

- a. *Hydrochloric acid density 1.18. Dilute with water 1+1.*
- b. *Sulphuric acid density 1.84.*

- c. Nitric acid density 1.42.
- d. Urea.
- e. Ammonia solution density 0.880.
- f. Acetic acid glacial.
- g. Potassium iodide solution 332 g/l, iodide free.
- h. Potassium thiocyanate solution 400 g/l.
- i. Starch indicator solution RE27.1.
- j. Sodium thiosulphate standardized solution ($1/2 \text{Na}_2\text{S}_2\text{O}_3$)=0.1 mol/l; RE26.3.
- k. Standardized against pure metallic copper.
- l. Sodium fluoride solution saturated approximately 48 g/l. Store in polyethylene bottle.
- m. Litmus paper.

2.3.4. 2. Appartus

- a) Weighing bottle.
- b) Conical flasks 250 ml with ground-glass stoppers.
- c) Burette 250 ml.
- d) Hot plate.
- e) Volumetric flask 250 ml.
- f) Pipette 50 ml.
- g) Beaker 250 ml.
- h) Filter paper Whatman No: 2024 or equivalent.

2.3.4.3. Procedure

i. Sample not containing Copper (I) Oxide or more than 20% of Copper

- a) **Preparation of sample:** Weigh (to the nearest mg) sufficient sample (wg) to contain about 0.75 g of Copper, transfer to a 250 ml conical flask, add hydrochloric acid (25 ml) and a few pumice granules, boil for a few minutes, and cool. Transfer, quantitatively to a Volumetric flask 250 ml, filtering if necessary, make up to the mark with washings from the conical flask and filter. Pipette 50 ml of the well-mixed solution into a 250 ml conical flask.
- b) **Determination:** Add ammonia solution, keeping the solution constantly swirled, until the precipitate, which first forms, redissolves to give a deep blue colour. Add acetic acid until just acid to litmus paper, then 2 ml in excess, and cool to 15 to 20 °C. add sodium fluoride solution (5 ml) and Potassium iodide solution (10 ml), close the flask with a stopper previously moistened with water, and swirl to mix. Titrate with the thiosulphate to a pale straw colour, add starch solution (2 ml) and potassium thiocyanate solution (5 ml). Continue the titration until the blue colour is just discharged (t ml). If the blue colour returns within 3 to 5 min insufficient sodium fluoride has been added to mark the excess of iron.
- c) **Calculation:**

$$\text{Copper content} = \frac{317 \times t \times N}{w} \text{ g/kg.}$$

Where:

N = normality of the sodium thiosulphate solution.

t = volume required for the titration (ml).

w = mass of sample taken (g).

ii. Sample containing Copper (I) oxide and not more than 20% of Copper

- a) **Preparation of sample.** Weigh (to the nearest 0.1 mg) sufficient sample to contain about 0.15 g of Copper (wg) into 500 ml conical flask, add nitric acid (15 ml), Sulphuric acid(5 ml),and a few pumice granules. Boil on a hot plate until dense white fumes appear and a blue green solution with a white sediment remains. If brown colour persists in the sediment, or brown fumes are evolved on adding a few drops of nitric acid, add further nitric acid (5 ml) and boil again. Repeat, if necessary. Cool, then add cautiously water (50 ml); heat on a hot plate to boiling, and boil until free from brown fumes. Add urea (0.5 gm) and continue boiling for a farther 5 min. Cool to room temperature.
- b) **Calculation:**

$$\text{Copper content} = \frac{63.5 \times t \times N}{w} \text{ g/kg.}$$

iii. Sample containing more than 20% of Copper and/or Copper (I) Oxide

- a. **reparation of sample.** Weigh (to the nearest mg) sufficient sample to contain about 0.75 g of Copper (wg) into a 250 ml conical flask, add nitric acid (15 ml), Sulphuric acid (10 ml), and a few pumice granules. Boil on a hot plate until dense white fumes appear and a blue green solution with a white sediment remains. If brown colour persists in the sediment, or brown fumes are evolved on adding a few drops of nitric acid, add further nitric acid (5 ml) and boil again. Repeat, if necessary. Cool, then add cautiously water (50 ml); heat on a hot plate to boiling, and boil till free from brown fumes. Add urea (0.5 gm) and continue boiling for a further 5 min. Cool to room temperature, transfer to the volumetric flask, and make up to the mark with distilled water. Mix well and pipette a 50 ml aliquot into a 250 ml conical flask.

2.4. Identity tests of sulphur (Ioccc, 1996; Khair, M.H. 2009)

Outline of method: The Sulphur is converted by refluxing with sodium sulphite to sodium thiosulphate. The thiosulphate is then titrated with standard iodine solution.

2.4.1. Reagents

- Sodium sulphite crystals; $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$.
- Formaldehyde 35% solution.
- Ethanol 95%.
- Acetic acid 20% aqueous solution.
- Iodine standardized solution. ($1/2 \text{ I}_2$) = 0.1 mol/l, RE 16.1.
- Starch indicator solution RE 27.1.

2.4.2. Apparatus

- Weighing bottle.
- Conical flasks 300 ml with ground-glass necks.
- Reflux condenser to fit the end of the condenser should be square cut, not oblique, so that the walls of the
- Flask is washed down by the refluxing mixture.
- Measuring cylinder, 50 ml.
- Measuring cylinder, 25 ml.
- Volumetric flask 250 ml.
- Pipette 100 ml.
- Burette 50 ml.

2.4.3. Procedure

- a) Determination.** Weigh (to the nearest 0.1 mg) sufficient sample (wg) to contain about 0.250 g of sulphur, and transfer to conical flask. Wet the sample thoroughly with Ethanol (25 ml). Add water (30 to 40ml) and Sodium sulphite crystals (5g). Attach the Reflux condenser, warm the mixture slowly to dissolve the sulphur, and then boil for 1 h shaking the flask from time to time. At the end of this time all the particles of sulphur ought to be dissolved. If not, continue heating the mixture. If elemental sulphur is present, shake the flask frequently on order to wash the particles of undissolved sulphur back into flask. Cool the solution, remove the condenser, and transfer quantitatively, to the volumetric flask. Make up to the mark with water, mix thoroughly, filter if necessary and pipette 100 ml into a conical flask, Add formaldehyde (12.5 ml) and allow the mixture to stand for 5 min. add acetic acid (10 ml) and titrate immediately with iodine (t ml) using starch as indicator. 1 ml iodine, ($1/2 \text{ I}_2$) = 0.1 mol/l = 0.032 g Sulphur.

b) Calculation:

$$\text{Sulphur content} = \frac{8.02 \times t}{w} \text{ g/kg}$$

Where: t = ml required for the sample determination.

w = mass of sample taken (g).

- c) Correction for thiosulphate.** Weigh (to the nearest 0.1 mg) sufficient sample (mg) to contain about 0.250 g of sulphur, and transfer to a 250 ml conical flask. Add water to suspend the product and shake the mixture to dissolve the thiosulphate. Make up to the mark mix thoroughly, and filter or centrifuge the suspension at 3000 r.p.m. for 15 to 30 min. Pipette 100 ml into a 300 ml titration flask, add formaldehyde (12.5 ml) and allow to stand for 5 min. add acetic acid (10 ml) and titrate immediately with iodine (b ml) using starch as indicator.

d) Correction :

$$\text{Sulphur content from thiosulphate present} = \frac{8.02 \times b}{m} \text{ g/kg}$$

Where: b = ml required for the thiosulphate determination.

m = mass of sample taken (g).

Subtract the content found from that obtained under (b)

2.5. Determination of Relevant Impurities in Copper and Sulphur Pesticides samples**2.5.1. Chemicals**

All the Chemicals used were Analytical Grade Reagents at least. The element standard solutions used for creating the calibration curves were prepared from 1000 mg/l Merck stock solution of relevant element.

2.5.2. Sample Preparations**2.5.2.1. Dissolution of Coppers Compounds (FAO 2006_B; Jarup, L. 2003)**

To the nearest mg, about 1 g of Copper compound was accurately weighed and transferred to 150 ml flat bottom flask. Sulphuric (10ml) + nitric acid (15 ml) mixture was added and gently evaporated on sand bath until

white fumes of sulphuric acid just ceased. Few drop of sulphuric acid and evaporated again. The residue was dissolved in distilled water, filtered if needed and transferred into 300 ml beaker. Ammonia solution constantly was added and swirled until the precipitate, which was first formed, redissolved to give a deep blue colour. The solution was boiled on hot plat until ammonia fumes disappeared. The sample was cooled to room temperature, washed with distilled water and finally transferred quantitatively into 50 ml volumetric flask.

2.5.2.2. Calculation of Relevant Impurities (FAO 2006_B)

- Arsenic : Maximum: $0.1 \times X$ mg/kg, where X is the copper content (g/kg).
- Lead : Maximum: $0.5 \times X$ mg/kg, where X is the copper content (g/kg).
- Cadmium1/Maximum: $0.1 \times X$ mg/kg, where X is the copper content (g/kg).

2.5.2.3. Digestion of Sulphur (Ioccc 1996; Khair, M.H. 2009)

About 1 g, to the nearest 0.01 g, of dried sulphur sample was weighed into a loosely stoppered Kjeldahl flask in a fume cupboard and 40 ml of bromine-carbon tetrachloride reagent was added. The flask was allowed to stand for 30 min with occasional shaking. Fifty-mil liter of concentrated nitric acid in small portions was added, avoiding shaking to prevent the formation of avoilent reaction. Swirling the flask was followed to initiate the reaction, which may have begun immediately. The acid was continued to be added and occasionally cooling in an ice bath was allowed to prevent overheating and excessive fumes. Any unoxidized sulphur remained more (about 5 ml) bromine- and 10 ml of concentrated nitric acid were added. When all sulphur was oxidized to sulphuric acid, heating over moderate bunsen flame was done to remove bromine, nitric acid and carbon tetrachloride, and then strong heating was applied until fumes of sulphur trioxide were evolved. Cooling with the addition of 10 mL concentrated nitric acid was done and repeated evaporation till the sulphur trioxide fumes were again evolved. When the solution was colourless the process was completed, 50 mL of water was added, and repeating the evaporation of sulphur trioxide was done. The process was repeated three times to remove the last traces of nitric acid, allowed to cool and diluted to mark of 50 ml volumetric flask and cooled to 10⁰C. In the case sulphur perchloric and sulphuric concentrated acid mixture was added instead of nitric acid.

2.5.2.4. Calculation of Relevant Impurities

- Arsenic; (Khair, M.H. 2009):maximum: $5.1\bar{x}$ µg/g, where \bar{x} is the percentage of sulfphur content.
- Lead : maximum: $0.5\bar{x}$ µg/g, where \bar{x} is the percentage of sulfphur content.
- Cadmium1/Maximum: $0.1\bar{x}$ µg/g, where \bar{x} is the percentage of sulfphur content.

2.4.3. Instrumentation

Thermo Elemental Atomic Absorption spectrophotometer [model: solar M] was used for all the measurements. The instrument software adjusted the current, wavelength and slit bandwidth of each element automatically. Arsenic was determined using the hydride generation kit [modil: VP100].

3. RESULTS AND DISCUSSION

Table 1. Concentration of the active ingredients in Copper samples

Trade name	common name	% active Ingredient Concentration		
		Reference Active Ingredients ⁽¹⁾	Before storage ⁽²⁾	After storage ⁽²⁾
Copromac	Copper Oxychloride	50% ⁽³⁾	49.20% ⁽³⁾	47.79% ⁽³⁾
	3Cu(OH) ₂ .CuCl ₂	Cu	Cu	Cu
Cobox	Copper Oxychloride	50% ⁽³⁾	49.98% ⁽³⁾	48.57% ⁽³⁾
	3Cu(OH) ₂ .CuCl ₂	Cu	Cu	Cu
Sokong	Copper Oxychloride	30% ⁽³⁾	29.51% ⁽³⁾	29.21% ⁽³⁾
	3Cu(OH) ₂ .CuCl ₂	Cu	Cu	Cu
Patrol	Copper Oxychloride	30% ⁽³⁾	28.68% ⁽³⁾	28.53% ⁽³⁾
	Cu(OH) ₂	Cu	Cu	Cu
Cuprous KZ	Cuprous oxide	50% ⁽³⁾	49.11% ⁽³⁾	48.55% ⁽³⁾
	Cu ₂ O	Cu	Cu	Cu
Delcup	Copper sulphate pentahydrate	6% ⁽³⁾	5.92% ⁽³⁾	5.80% ⁽³⁾
	Cu SO ₄ .5H ₂ O	Cu	Cu	Cu
Crunch	Copper sulphate anhydrous	10% ⁽³⁾	9.28% ⁽³⁾	9.12% ⁽³⁾
	Cu SO ₄	Cu	Cu	Cu
King	Copper sulphate Tribasic	36% ⁽³⁾	34.42% ⁽³⁾	34.22% ⁽³⁾
	3Cu(OH) ₂ . Cu SO ₄	Cu	Cu	Cu

NB⁽¹⁾: Reference Active Ingredients: concentrations of Active Ingredients to tested Copper pesticides, which previously registered internationally^(24&25)
 NB⁽²⁾: storage at 54± 2 °C for 21 days^(24&25)
 NB⁽³⁾: The total Copper content shall be declared (g/kg) and when determined, the content obtained shall not differ from that declared by more than +/- 5% declared content^(24&25)

Table 1 lists the above results of concentration of the Active Ingredients that found before and after storage⁽²⁾ in Copper samples; its calculations were based on its Reference Active Ingredients. It has been demonstration that above results clearly showed that all calculated concentrations for these Active Ingredients has been founding before and after storage⁽²⁾ compatibly with its Reference Active Ingredients⁽¹⁾. As recorded in Table (1).

Data in table 2 summarize the FAO Maximums for concentrations of Arsenic, Cadmium, and Lead (mg/kg)in Copper samples (Copper Oxychloride [Three replicates] ; Copper hydroxide ; Cuprous Oxide ; Copper

Sulphate anhydrous ; Copper Sulphate tribasic and Copper Sulphate Pentahydrate respectively). It was found that the maximum allowed limits for Arsenic concentrations were 49.20 ; 49.98 ; 29.51 ; 28.68 ; 49.11 ; 5.92 ; 9.28 and 34.42 mg/kg respectively before.

Table 2. FAO Maximums for Concentration of Arsenic, Cadmium, and Lead (mg/kg) in Copper samples

Trade name	common name	Before storage ⁽¹⁾			After storage ⁽¹⁾		
		Arsenic mg/kg	Cadmium mg/kg	Lead mg/kg	Arsenic mg/kg	Cadmium mg/kg	Lead mg/kg
Copromac	Copper Oxochloride 3Cu(OH) ₂ .CuCl ₂	49.20	49.20	246	47.79	47.79	238.95
Cobox	Copper Oxochloride 3Cu(OH) ₂ .CuCl ₂	49.98	49.98	249.9	48.57	48.57	242.85
Sokong	Copper Oxochloride 3Cu(OH) ₂ .CuCl ₂	29.51	29.51	147.55	29.21	29.21	146.05
Patrol	Copper Oxochloride Cu(OH) ₂	28.68	28.68	143.4	28.53	28.53	142.65
Cuprous KZ	Cuprous oxide Cu ₂ O	49.11	49.11	245.55	48.55	48.55	242.75
Delcup	Copper sulphate pentahydrate Cu SO ₄ .5H ₂ O	5.92	5.92	29.6	5.80	5.80	29
Crunch	Copper sulphate anhydrous Cu SO ₄	9.28	9.28	46.4	9.12	9.12	45.6
King	Copper sulphate Tribasic 3Cu(OH) ₂ . Cu SO ₄	34.42	34.42	172.1	34.22	34.22	171.1
Reference		24					

NB⁽¹⁾: storage at 54± 2 °C for 21 days ^(24&25)

Storage ⁽²⁾; while its concentrations after storage as follow: 47.79 ; 48.57 ; 29.21 ; 28.53 ; 48.55 ; 5.80 ; 9.12 and 34.22mg/kg respectively after storage ⁽²⁾. Results also showed that the maximum allowed limits for Cadmium concentrations were 49.20 ; 49.98 ; 29.51 ; 28.68 ; 49.11 ; 5.92 ; 9.28 and 34.42 mg/kg respectively before storage ⁽²⁾; while its concentrations after storage ⁽²⁾ as follow: 47.79 ; 48.57 ; 29.21 ; 28.53 ; 48.55 ; 5.80 ; 9.12 and 34.22mg/kg respectively. On the other hand that the maximum allowed limits for Lead concentrations were 246 ; 249.9 ; 147.55 ; 143.4 ; 245.55 ; 29.6 ; 46.4 and 172.1 mg/kg respectively before storage ⁽²⁾; while its concentrations after storage ⁽²⁾ as follow: 238.95 ; 242.85 ; 146.05 ; 142.65 ; 242.75 ; 29 ; 45.6 and 171.1 mg/kg respectively. As recorded in Table (2).

Data in table 3 clearly showed that the concentrations of Arsenic, Cadmium and Lead (mg/kg) in Copper samples (Copper Oxochloride [Three replicates] ; Copper Hydroxide ; Cuprous oxide ; Copper Sulphate anhydrous ; Copper Sulphate Tribasic and Copper Sulphate pentahydrate respectively). It was found that the concentrations of Arsenic were 0.6108×10^{-3} ; 0.4938×10^{-3} ; 0.8548×10^{-3} ; N.D⁽²⁾ ; 12.4907×10^{-3} ; 0.9264 ; 2.8967×10^{-3} and N.D⁽²⁾ mg/kg respectively before storage ⁽²⁾; while its concentrations after storage ⁽²⁾ as follow: 3.0592×10^{-3} ; 1.1759×10^{-3} ; 2.4240×10^{-3} ; 4.6608×10^{-3} ; 2.7253×10^{-3} ; 2.7398×10^{-3} ; 2.3144×10^{-3} and 3.3619×10^{-3} mg/kg respectively. Results also revealed that the concentrations.

Table 3. Concentration of Arsenic, Cadmium, and Lead (mg/kg) in Copper samples

Trade name	common name	Before storage ⁽¹⁾			After storage ⁽¹⁾		
		Arsenic mg/kg	Cadmium mg/kg	Lead mg/kg	Arsenic mg/kg	Cadmium mg/kg	Lead mg/kg
Copromac	Copper Oxochloride 3Cu(OH) ₂ .CuCl ₂	0.6108×10^{-3}	0.0822	1.0238	3.0592×10^{-3}	0.0673	1.0764
Cobox	Copper Oxochloride 3Cu(OH) ₂ .CuCl ₂	0.4938×10^{-3}	0.0427	0.8446	1.1759×10^{-3}	0.0245	0.9347
Sokong	Copper Oxochloride 3Cu(OH) ₂ .CuCl ₂	0.8548×10^{-3}	0.0446	1.0948	2.4240×10^{-3}	0.0187	1.2081
Patrol	Copper Oxochloride Cu(OH) ₂	N.D ⁽²⁾	0.0690	0.4407	4.6608×10^{-3}	0.0555	0.5919
Cuprous KZ	Cuprous oxide Cu ₂ O	12.4907×10^{-3}	0.0286	1.06395	2.7253×10^{-3}	0.0743	1.7956
Delcup	Copper sulphate pentahydrate Cu SO ₄ .5H ₂ O	0.9264	0.0343	0.4080	2.7398×10^{-3}	0.0306	2.7398×10^{-3}
Crunch	Copper sulphate anhydrous Cu SO ₄	2.8967×10^{-3}	0.0795	0.5395	2.3144×10^{-3}	0.0772	0.5456
King	Copper sulphate Tribasic 3Cu(OH) ₂ . Cu SO ₄	N.D ⁽²⁾	0.0486	0.4391	3.3619×10^{-3}	0.0240	1.3445
Reference		24					

NB⁽¹⁾: storage at 54± 2 °C for 21 days ^(24&25).
NB⁽¹⁾: N.D = not Detected.

Of Cadmium 0.0822 ; 0.0427 ; 0.0446 ; 0.0690 ; 0.0286 ; 0.0343 ; 0.0795 and 0.0486 mg/kg respectively before storage ⁽²⁾; while its concentrations after storage ⁽²⁾ as follow: 0.0673 ; 0.0245 ; 0.0187 ; 0.0555 ; 0.0743 ; 0.0306 ; 0.0772 and 0.0240 mg/kg respectively. On the other hand, the concentrations of Lead were 1.0238 ;

0.8446 ; 1.0948 ; 0.4407 ; 1.06395 ; 0.4080 ; 0.5395 and 0.4391 mg/kg respectively before storage⁽²⁾. Results indicated that the concentrations of Lead after storage⁽²⁾ as follow 1.0764 ; 0.9347 ; 1.2081 ; 0.5919 ; 1.7956 ; 2.7398×10^{-3} ; 0.5456 and 1.3445 mg/kg respectively. As shown in Table (3).

Table 4 lists the above results of Concentrations of the Active Ingredients that found before and after storage⁽²⁾ in Sulphur samples, its calculations are based on its Reference Active Ingredients. It has been demonstrating that above results clearly showed that all calculated concentrations for these Active Ingredients has been founding before and after storage⁽²⁾ compatibly with its Reference Active Ingredients As recorded in Table (4).

Table 4. Concentration of the active ingredients in Sulphur samples

Trade name	common name	% active Ingredient Concentration		
		Reference Active Ingredients ⁽¹⁾	Before storage ⁽²⁾	After storage ⁽²⁾
Thiofan	Sulphur S	80% ⁽³⁾	79.20% ⁽³⁾	79.11% ⁽³⁾
Heliosoufre	Sulphur S	70% ⁽³⁾	69.15% ⁽³⁾	69.11% ⁽³⁾
H Sulphur	Sulphur S	80% ⁽³⁾	79.90% ⁽³⁾	79.50% ⁽³⁾
Solfan	Sulphur S	70% ⁽³⁾	69.30% ⁽³⁾	68.88% ⁽³⁾
Microvit	Sulphur S	80% ⁽³⁾	79.05% ⁽³⁾	78.33% ⁽³⁾

NB⁽¹⁾: Reference Active Ingredients: concentrations of Active Ingredients to tested Sulphur pesticides, which previously registered internationally⁽²⁹⁾
 NB⁽²⁾: storage at 54± 2 °C for 21 days⁽²⁹⁾
 NB⁽³⁾: The total Sulphur content shall be declared (g/kg) and when determined, the content obtained shall not differ from that declared by more than +/-2. 5% declared content⁽²⁹⁾

Table 5. FAO Maximum for Concentration of Arsenic, Cadmium, and Lead (µg/g) in Sulphur samples

Trade name	common name	Before storage ⁽¹⁾			After storage ⁽¹⁾		
		Arsenic mg/kg ²⁸	Cadmium mg/kg	Lead mg/kg	Arsenic mg/kg ²⁸	Cadmium mg/kg	Lead mg/kg
Thiofan	Sulphur S	403.92	7.92	39.6	403.461	7.911	39.555
Heliosoufre	Sulphur S	352.665	6.915	34.575	352.665	6.915	34.575
H Sulphur	Sulphur S	407.49	7.99	39.95	405.45	7.95	39.75
Solfan	Sulphur S	353.43	6.93	34.65	351.288	6.888	34.44
Microvit	Sulphur S	403.155	7.905	39.525	399.483	7.833	39.165
Reference		29			29		

NB⁽¹⁾: storage at 54± 2 °C for 21 days⁽²⁹⁾.

Data in Table 5 summarize the FAO Maximums for concentrations of Arsenic Cadmium and Lead (µg/g) in Sulphur samples. It was found that the maximum allowed limits for Arsenic concentrations were 403.92 ; 352.665 ; 407.49 ; 353.43 and 403.155 µg/g respectively before storage⁽²⁾ ; while its concentrations after storage⁽²⁾ as follow 403.461 ; 352.665 ; 405.45 ; 351.288 and 399.483 µg/g respectively. Results also showed that the maximum allowed limits for Cadmium concentrations were 7.92 ; 6.915 ; 7.99 ; 6.93 and 7.905 µg/g respectively before storage⁽²⁾ ; while its concentrations after storage⁽²⁾ as follow 7.911 ; 6.915 ; 7.95 ; 6.888 and 7.833 µg/g respectively. On the other hand, the maximum allowed limits for Lead concentrations are 39.6 ; 34.575 ; 39.95 ; 34.65 and 39.525 µg/g respectively before storage⁽²⁾ ; while its concentrations after storage⁽²⁾ as follow 39.555 ; 34.575 ; 39.75 ; 34.44 and 39.165 µg/g respectively. As shown in Table (5).

Table 6. Concentration of Arsenic, Cadmium, and Lead (µg/g) in Sulphur samples

Trade name	common name	Before storage ⁽¹⁾			After storage ⁽¹⁾		
		Arsenic mg/kg ²⁸	Cadmium mg/kg	Lead mg/kg	Arsenic mg/kg ²⁸	Cadmium mg/kg	Lead mg/kg
Thiofan	Sulphur S	3.1328	0.0217	0.2222	2.6118×10^{-3}	0.0394	0.3082
Heliosoufre	Sulphur S	0.4286	0.0472	0.3165	12.6566×10^{-3}	0.0456	0.3896
H Sulphur	Sulphur S	0.5065	0.0370	0.2354	10.0078×10^{-3}	0.0329	0.3484
Solfan	Sulphur S	2.1510	0.0405	0.2860	8.1219×10^{-3}	0.0219	0.2159
Microvit	Sulphur S	1.5354	0.0323	0.2106	5.7133×10^{-3}	0.0495	0.4264
Reference		29			29		

NB⁽¹⁾: storage at 54± 2 °C for 21 days⁽²⁹⁾.

Data in Table 6 clearly showed that the concentrations of Arsenic, Cadmium and Lead ($\mu\text{g/g}$) in sulphur samples. It was found that the concentrations of Arsenic were 3.1328 ; 0.4286 ; 0.5065 ; 2.1510 and 1.5354 $\mu\text{g/g}$ respectively before storage⁽²⁾ ; while its concentrations after storage⁽²⁾ as follow: 2.6118 $\times 10^{-3}$; 12.6566 $\times 10^{-3}$; 10.0078 $\times 10^{-3}$; 8.1219 $\times 10^{-3}$ and 5.7133 $\times 10^{-3}$ $\mu\text{g/g}$ respectively. Results also revealed that the concentrations of Cadmium were 0.0217 ; 0.0472 ; 0.0370 ; 0.0405 and 0.0323 $\mu\text{g/g}$ respectively before storage⁽²⁾ ; while its concentrations after storage⁽²⁾ as follow 0.0394 ; 0.0456 ; 0.0329; 0.0219 and 0.0495 $\mu\text{g/g}$ respectively. On the other hand, the concentrations of Lead were 0.2222; 0.3165; 0.2354; 0.2860 and 0.2106 $\mu\text{g/g}$ respectively before storage⁽²⁾. Results indicated that the concentrations of Lead after storage⁽²⁾ as follow 0.3082; 0.3896; 0.3484; 0.2159 and 0.4264 $\mu\text{g/g}$ respectively. As recoded In Table (6).

Estimation of Relevant Impurities

- There may be substantial difference in the chemical composition of technical- grade products of the same active ingredient manufactured under different conditions, from different raw materials, or by different routes of synthesis, resulting difference in impurity content may significantly affect the toxicological properties of pesticide product.
- Relevant impurities are those that may exhibit pronounced toxic effects compared to the active ingredient that affect phytotoxicity or physical properties of formulations and result in undesirable residues in food, or cause environmental contamination.
- The first safety assessment of an active ingredient by a regulatory body considers toxicological data developed on a representative batch of technical products, with the assumption that the material produced commercially by the original or generic manufacturer's has an equal or higher content of active ingredient and contains the same fewer impurities at equal or lower concentrations as the fully characterized technical product used in toxicological tests.
- Three steps are essential for ensuring the safety of commercial technical grade pesticide products, whether produced by the original manufacturer or by generic manufacturers.
- First: the identification and chemical structural detection of the impurities must be elucidated. This should include positive identification of major ($\geq 1\%$) and all toxicologically or environmentally relevant impurities ($\geq 0.1\%$).
- Second, in addition to recognition of minimum active ingredient content, official specification should also list relevant impurities and their maximum permissible concentrations.
- Implementation of these specifications should be aided by a decision making scheme for establishing similarity of subsequently evaluated technical products.
- Third, appropriate analytical methods for the detection and quantification of impurity levels should be developed and employed in a quality-monitoring program associated with the manufacturing and formulation process (Sachs, R.M. et al. 1971).

1. Arsenic:

Based on sufficient evidence from human data Arsenic has been reported to be a human carcinogen (Sachs, R.M. et al. 1971; Sathawara, N.G., et al. 2004). Increased lung cancer mortality was observed in multiple human populations exposed primarily through inhalation. In addition, increased mortality from multiple internal organ cancers (liver, kidney, lung, and bladder) and an increased incidence of skin cancer were observed in populations consuming drinking water high in inorganic arsenic. Trivalent Arsenic (Arsenite) is more toxic than pentavalent Arsenic (Arsenate). Acute ingestion of more than 100 mg of inorganic Arsenic is likely to cause significant toxicity. Acute ingestion of 200 mg or more of Arsenic trioxide may be fatal in an adult (Sathawara, N.G., et al. 2004; Seiler, H.G. et al. 1988).

Table (3) reveals the concentrations of Arsenic in Copper Oxychloride; copper Hydroxide; Cuprous oxide; Copper Sulphate anhydrous; Copper Sulphate Tribasic and Copper Sulphate pentahydrate samples. From the previous table it was found that Arsenic concentrations in Copper samples ranged from 0.4938 $\times 10^{-3}$ to 12.4907 $\times 10^{-3}$ mg/kg before storage⁽²⁾ and 1.1759 $\times 10^{-3}$ to 4.6608 $\times 10^{-3}$ mg/kg after storage⁽²⁾. In additions: the maximum allowed limit Arsenic concentrations in Copper samples ranged from 5.92 to 50.20 mg/kg before storage⁽²⁾ and 5.80 to 48.57 mg/kg after storage⁽²⁾. On the other hand; the previously results from Table (6) showed that the Arsenic concentrations in Sulphur samples ranged from 0.4286 to 3.1328 $\mu\text{g/g}$ before storage⁽²⁾ and 2.6118 $\times 10^{-3}$ to 12.6566 $\times 10^{-3}$ $\mu\text{g/g}$ after storage⁽²⁾. The maximum allowed limit Arsenic concentrations in Sulphur samples ranged from 357.561 to 417.69 $\mu\text{g/g}$ before storage⁽²⁾ and 351.288 to 415.65 $\mu\text{g/g}$ after storage⁽²⁾; this means that the concentrations of Arsenic determined in selected samples were well below the critical limit.

2. Cadmium:

Cadmium is known as a highly toxic metal (Sachs, R.M. et al. 1971; Sathawara, N.G., et al. 2004). Cadmium inhibits the sulfhydryl group (SH) within the enzymes and affects the hydroxy1, carboxy1, phosphaty1, cysteiny1, and histidy1 side chains of proteins, purines, and porphyrin. It can also disrupt the pathways of oxidative phosphorylation. Cadmium competes with the absorption of some essential elements such as Iron, Zinc, and Copper. The element may also interfere with the release of iron by transferring. Cadmium ingestion produces symptoms such as nausea, salivation, vomiting followed by diarrhea with abdominal discomfort and pains. Cadmium is accumulated in the human body. Accumulation is continuous, because Cadmium has a long biological half-life. The accumulation rate of the element is 40 $\mu\text{g/day}$. The symptomatology of chronic Cadmium poisoning, due to accumulation, involves emphysema of the lung, mild liver damage, anemia, proteinuria, renal

tubular damage, some dental changes, and impairment of the sense of smell (anosmia). A characteristic disease of chronic Cadmium poisoning is called Itai-itai manifested by renal dysfunction in combination with osteomalacia or severe osteoporosis. This disease is quite prevalent in Japan due to consumption of rice grown in fields close to Cadmium smelters. All terrestrial, seafood's, and even cigarette smoke contain Cadmium. The average overall concentration of Cadmium in the human body is approximately 429 µg/kg of body weight. The concentration of Cadmium in tears is below 3.0 ng/mL Cadmium in blood may reflect current exposure, whereas in urine may indicate chronic exposure at low levels and exposure ; in urine may indicate chronic exposure at low levels and causing nausea 'salivation' vomiting followed by diarrhea with abdominal discomfort and pains.

Table (3) reveals the concentrations of Cadmium in Copper Oxychloride; Copper Hydroxide; Cuprous oxide; Copper Sulphate anhydrous; Copper Sulphate Tribasic and Copper Sulphate pentahydrate samples. From the previous table it was found that Cadmium concentrations in Copper samples ranged from 0.0286 to 0.0822 mg/kg before storage ⁽²⁾ and 0.0187 to 0.0772 mg/kg after storage ⁽²⁾. In additions: the maximum allowed limit for Cadmium concentrations in Copper samples ranged from 5.92 to 50.20 mg/kg before storage ⁽²⁾ and 5.80 to 48.57 mg/kg after storage ⁽²⁾. On the other hand, data presented from table (6) clearly show that the Cadmium concentrations in Sulphur samples that ranged from 0.0217 to 0.0472 µg/g before storage ⁽²⁾ and 0.0219 to 0.0495 µg/g after storage ⁽²⁾. Also its mximum allowed limit for Cadmium concentrations in Sulphur samples ranged from 7.011 to 8.19 µg/g before storage ⁽²⁾ and 6.888 to 8.15 µg/g after storage ⁽²⁾; this means that the concentrations of Cadmium, determined in selected samples were well below the critical limit.

3. Lead:

It is considered as a general protoplasmic poison having cumulative, slow acting, and subtle properties (Sathawara, N.G., et al. 2004; Thompson, R.H.S., 1948). It exerts much of its biochemical activity through sulfhydryl inhibition due to its high affinity for sulfur. Lead also interacts with carboxyl and phosphoryl groups and interferes with heme synthesis. Lead toxicity may occur by ingestion, inhalation, and through skin cuts. Organic lead compounds are absorbed into body tissues and penetrate the intact skin more rapidly than inorganic compounds. Organic lead compounds may affect nervous tissues more readily than inorganic lead compounds. About 5 to 10% of the lead ingested is absorbed into the body. The rest discharged with the faces.

Table (3) reveals the concentrations of Lead in Copper Oxychloride; Copper Hydroxide; Cuprous oxide; Copper Sulphate anhydrous; Copper Sulphate Tribasic and Copper Sulphate pentahydrate samples. From the previous table it was found that concentrations of Lead in Copper samples ranged from 0.4080 to 1.0948 mg/kg before storage ⁽²⁾ and 2.7398×10^{-3} to 1.7956 mg/kg after storage ⁽²⁾. In additions, its maximum allowed limits of Lead concentrations in Copper samples ranged from 2 9.6 to 251 mg/kg before storage ⁽²⁾ and 29 to 242.82 mg/kg after storage ⁽²⁾. The antecedent results obtained from 0.2106 to 0.3165 µg/g before storage ⁽²⁾ and 0.2159 to 0.4264 µg/g after storage ⁽²⁾. On the other hand, the maximum allowed limits of Lead concentrations in Sulphur samples ranged from 35.055 to 40.90 µg/g before storage ⁽²⁾ and 34.575 to 40.75 µg/g after storage ⁽²⁾; this means that the concentrations of Lead, determined in selected samples were well below the critical limit (Sathawara, N.G., et al. 2004; Thompson, R.H.S., 1948).

3. CONCLUSION

1. The chemical composition and purity of so-called inerting redient used in formulating a pesticide such as carriers, solvents, surfactants, and adjutants may affect the stability of the active ingredient.

Furthermore:

- a. During extended storage degradation products may be formed, which pose toxicological hazards to consumers of treated food.
 - b. For safety and efficacy assessment, in agreement with the principles outlined in the 5th edition of the FAO manual on specification of plant protection (Sachs, R.M. et al..1971; U.S. (IRIS) U.S. 2000).
2. Relevant impurities are those that may be exhibit pronounced toxic effects compared to the active ingredient, affect phytotoxicity, and physical properties of formulations, and result in undesirable residues in food, or cause environmental contamination.
 3. Routine surveillance of Copper and Sulphur pesticides allowed the good judgment of the effect of the contamination of those compounds on the environmental, particularly, contamination by toxic metals such as Arsenic, Cadmium, and Lead, which is considered to be of great importance due to the difficulty of their removal from environmental resources.
 - a) Higher levels of these toxic elements may cause harmful effects to humans and other living organisms. Therefore, conducting such experiments of examining the levels of toxic impurities in currently used compounds (pesticides) such as Copper and Sulphur compounds id of great indispensability.
 - b) Hassel (Webb, J.L.,1966) reported that in USA, preparations containing calcium arsenate were often preferred to lead arsenate because of fears associated with environmental contaminations with lead.

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تقدير الشوائب المصاحبة لمركبات النحاس والكبريت المستخدمة كمبيدات

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مركز البحوث الزراعية - المعمل المركزى للمبيدات - قسم بحوث تحليل المبيدات - الدقى - الجيزة².

تم تحديث دراستنا الحالية بدراسة قياس نسبة الشوائب المصاحبة (الزرنيخ والكادميوم والرصاص) لثمانية نماذج من مركبات النحاس وهى كالتالى :
أوكسى كلوريد النحاس (ثلاثة مقرارات) ؛ هيدروكسيد النحاس ؛ أكسيد نحاسوز ؛ كبريتات النحاس اللامائية ؛ كبريتات النحاس ثلاثية القاعدة ؛ كبريتات النحاس المائية وكذلك خمسة نماذج من مركبات الكبريت وجميعها مستخدمة كمبيدات.
وقد تم استخدام طرق تحليلية جديدة لتقدير وقياس وتأكيد مكوناتها من المواد القياسية وكذلك نسبة الشوائب المصاحبة.
وقد اشارت النتائج النهائية الى ان تركيز المواد الفعالة للمبيدات المختبره فى نطاق الحدود الدولية للمواد الفعالة المرجعية التى اقرتها التسجيلات الدولية للمبيدات سالفة الذكر. ومن جهة اخرى امكن تلخيص النتائج المتحصل عليها من قياس نسبة الشوائب المصاحبة على النحو التالى :
 1.01759×10^{-3} الى 12.4907×10^{-3} مجم/كجم قبل التخزين⁽²⁾ و 0.4938×10^{-3} الى 3.1328 ميكروجرام/ جرام قبل التخزين⁽²⁾ و 4.6608×10^{-3} مجم/كجم بعد التخزين⁽²⁾ بينما تراوحت تركيزات الزرنيخ فى الكبريت من 0.4286 الى 3.1328 ميكروجرام/ جرام قبل التخزين⁽²⁾ و 12.6566 ميكروجرام/ جرام بعد التخزين⁽²⁾. بينما من الثابت والمعروف بناء على التسجيل الدولى للمبيدات سالفة الذكر ان الحدود 2.6118×10^{-3} الى 3 القصوى لتركيزات الزرنيخ فى النحاس من 5.92 الى 50.20 مجم/كجم قبل التخزين⁽²⁾ و 5.80 الى 48.57 مجم/كجم بعد التخزين⁽²⁾ بينما تراوحت الحدود القصوى لتركيزات الزرنيخ فى الكبريت من 351.561 الى 417.69 ميكروجرام/جرام قبل التخزين⁽²⁾ و 351.288 الى 415.65 ميكروجرام/جرام بعد التخزين⁽²⁾
وقد تراوحت تركيزات الكادميوم فى النحاس من 0.0822 الى 0.0286 مجم/كجم قبل التخزين⁽²⁾ و 0.0187 الى 0.0772 مجم/كجم بعد التخزين⁽²⁾ بينما تراوحت تركيزات الكادميوم فى الكبريت من 0.0217 الى 0.0472 ميكروجرام/جرام قبل التخزين⁽²⁾ و 0.0219 الى 0.0495 ميكروجرام/جرام بعد التخزين⁽²⁾ ومن المعروف ان الحدود القصوى لتركيزات الكادميوم فى النحاس من 5.92 الى 50.20 مجم/كجم قبل التخزين⁽²⁾ و 5.80 الى 48.57 مجم/كجم بعد التخزين⁽²⁾ بينما تراوحت الحدود القصوى لتركيزات الكادميوم فى الكبريت من 7.011 الى 8.19 ميكروجرام/جرام قبل التخزين⁽²⁾ و 6.888 الى 8.15 ميكروجرام/جرام بعد التخزين⁽²⁾.
ايضا تراوحت تركيزات الرصاص فى النحاس من 0.4080 الى 1.0948 مجم/كجم قبل التخزين⁽²⁾ و 0.2106 الى 0.3165 $\times 10^{-3}$ ميكروجرام/جرام قبل التخزين⁽²⁾ و 0.2159 الى 0.4264 ميكروجرام/جرام بعد التخزين⁽²⁾ ومن المعروف ان الحدود القصوى لتركيزات الرصاص فى النحاس من 29.6 الى 251 مجم/كجم قبل التخزين⁽²⁾ و 29 الى 242.85 ميكروجرام/جرام بعد التخزين⁽²⁾ بينما تراوحت الحدود القصوى لتركيزات الرصاص فى الكبريت من 35.055 الى 40.90 ميكروجرام/ جرام قبل التخزين⁽²⁾ و 34575 الى 40.75 ميكروجرام/جرام بعد التخزين⁽²⁾.
وكانت النتائج النهائية تشير الى ان جميع نتائج الشوائب المصاحبة للمبيدات المختبره داخل حدود التجاوزات الدولية الامنه التى اقرتها منظمى الاغذية (FAO/WHO) والزراعة والصحة العالمية)

ملحوظة (1): المواد الفعالة المرجعية: وهى قيم التركيزات الاصلية للمواد الفعالة المدرجة ضمن بيانات التسجيلات الدولية لمبيدات النحاس والكبريت المسجلة دولياً

(FAO 2006B; GALAS-GORCHEV, H. 1991)

ملحوظة (2): تم تخزين المبيدات المختبره تحت الظروف القياسية الدولية التى اقرتها منظمى الاغذية والزراعة والصحة العالمية وهى التخزين لمدة

14-21 يوماً على 54 درجة مئوية ± 2

(FAO 2006B; GALAS-GORCHEV, H. 1991; Khair, M.H.2009; Merck Index,983)