

Storage Stability and Quantitative Determination of Metalaxyl and Its Metabolite 2,6-Dimethylaniline in Wettable Powder (WP) Formulation

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Abstract: A sample of Metalaxyl 35% WP was supplied by Central Agricultural Pesticides laboratory from a local company and the country of origin of the sample is Jordan. The physical and chemical properties of the Metalaxyl 35% WP samples were examined initially, cold stored at $0\text{ }^{\circ}\text{C} \pm 1$ for 7 days in the refrigerator and stored in glass bottles in the oven at $54\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ for 3, 7, 14 and 28 days. The physical properties were carried out as follows Alkalinity, Density, Tapped density, pH and Wettability and the physical properties of their spray solutions under recommended dose in soft and hard were carried out as follows Persistent foam, Suspensibility, Conductivity, Surface tension and Viscosity. Generally, increasing time of hot storage for long time as 14 and 28 days at $54\text{ }^{\circ}\text{C}$ may causes damage of the samples nature which may have diverse effects on their fungicidal activity against their targets. The storage variation causes basisty variation referred to pH, conductivity and salinity may causes phytotoxicity for plants during using their spray solutions. Finally, the Metalaxyl content decreased with the time of storage and still within the limit till 21 days of storage at $54 \pm 2\text{ }^{\circ}\text{C}$. While after 28 days of storage the Metalaxyl content decreased till become out of the comply limit. On the other hand, the amount of metabolite 2,6-dimethylaniline increases with with the time of storage increase which may be reflected on the toxicity and biological activity of the sample.

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Key words: Metalaxyl 35% WP, storage conditions, physical and chemical properties.

1. Introduction

Metalaxyl (methyl N-(2-methoxyacetyl)-N-(2,6-xylyl)-DL-alaninate) is a systemic fungicide used to control plant diseases caused by Oomycete fungi of the order Peronosporales Schwinn *et al.*, (1977) and Houseworth, (1987). Its formulations include granules, wettable powders, dusts, and emulsifiable concentrates. Application may be by foliar or soil incorporation, surface spraying (broadcast or band), drenching, and seed treatment. Metalaxyl registered products either contain metalaxyl as the sole active ingredient or are combined with other active ingredients (e.g., captan, mancozeb, copper compounds, carboxin). It has low mammalian toxicity and is regarded as safe for general use. However combination of trace impurities present in technical material arising either during synthesis or storage, may lead to markedly deferent toxicities than would be expected from the toxicities of the individual components.

Adequate analytical methods of TLC, GLC, HPLC, MS, and other techniques are available for identification and determination of metalaxyl. In this work an analytical method was standardized for the

estimation and determination of metalaxyl and its impurities (2,6-dimethylaniline) in a formulation of metalaxyl 35% WP in different storage periods at $54 \pm 2\text{ }^{\circ}\text{C}$. This work is concerned with the identification of the impurities, which are commonly present or may be developed upon storage and identified by FAO in formulation metalaxylwattable powder (WP).

Determination was by gas chromatography using flame ionization detector (FID). The identification of compound was based on areas and retention times by using external standard. The method showed decrease in metalaxyl content with the time of storage while its metabolite 2,6-dimethylaniline content increased.

2. Materials and Methods

1. Fungicide:

2. Physical Parameters:

The physical properties of the Metalaxyl 35% WP samples under different storage condition were carried out according to CIPAC handbook methods as follows Alkalinity (MT 191), Density (MT 186), pH (MT 75.3) and Wettability (MT 53.3.3) Dobrat and Martijn, 1995 where Tapped density (ASTM B-527) was carried out according to American Society for

Testing and Materials, 2006. Also the physical properties of their spray solutions under recommended dose in soft and hard were carried out as follows; Persistent foam (MT 47.2) , Suspensibility (MT-54) and Conductivity(MT

32) (**Dobrat and Martijn, 1995**). Surface tension and Viscosity were carried out according to **American Society of Testing and Materials (ASTM D-1331, 2014 and D-2196, 2015)**.

Fungicide:

Common Name:	Metalaxyl (fungicide)
Chemical Structure	
IUPAC name	methyl <i>N</i> -(methoxyacetyl)- <i>N</i> -(2,6-dimethylphenyl)-DL-alaninate; methyl 2-[[2,6-dimethylphenyl)methoxyacetyl]amino}propionate
Chemical Name:	methyl <i>N</i> -(2,6-dimethylphenyl)- <i>N</i> -(methoxyacetyl)-DL-alaninate
CAS Number:	[57837-19-1]
Molecular Weight:	279.3
Molecular Structure:	C ₁₅ H ₂₁ NO ₄

3. Chemical Parameters:

A sample of Metalaxyl 35% WP was supplied by Central Agricultural Pesticides laboratory (Pesticide Analysis Research Department). It was provided by a local company and the country of origin of the sample is Jordan. The physical and chemical properties of the Metalaxyl 35% WP samples were examined initially, cold stored at 0 °C ± 1 for 7 days in the refrigerator and stored in glass bottles in the oven at 54°C ± 2 °C for 3, 7, 14 and 28 days according to **WHO and FAO specifications (1988)**. According to these specifications the determined average active ingredient after 14 days content must not be lower than 97% relative to the determined average content found before storage noting that the samples of the product taken before and after the storage stability test should be analyzed together after the test to reduce the analytical error.

4. Analytical procedures:

The method used for the determination of metalaxyl and its metabolite (2,6-dimethylaniline) in a formulation sample of metalaxyl 35% WP by GC (FID) on a capillary column using external standard.

4.1 Apparatus:

Gas chromatography- GC-system Agilent technologies 7890A instrument equipped Flame ionization detector (FID). A fused silica capillary column (30 m length, 0.53 mm-i.d., coated with methyl silicon gum HP-1, with 2.65 μm film thickness) was used. Nitrogen was used as a carrier gas with a flow rate of 20 ml. The injector (split less capillary

inlet system, injection volume 1 μl) and detector temperatures were 250°C and 300°C, respectively.

Oven temperature was programmed from 70°C to 240°C (3 mins) at a rate of 25°C / min for the determination of impurities of metalaxyl (2,6-dimethylaniline). While Oven temperature was programmed from 150°C to 270°C (3 mins) at a rate of 25°C / min for the determination of impurities of metalaxyl. Gas and corresponding flowrates:

Nitrogen (carrier) 25 ml per min.

Hydrogen 40 ml permin.

Air 400 ml permin.

4.2 Reagents

- Acetone HPLC grade
- Metalaxyl analytical standard (purity of 99%) was obtained from the Central laboratory of Agricultural pesticides.
- 2,6-dimethylaniline (purity of 99% were obtained from Sigma-Aldrich).

4.3 Preparation of standard solution

Weigh accurately 0.01 gm of 100 % metalaxyl reference standard (0.0101 gm of 99% metalaxyl reference standard) into 25 ml volumetric flask and add 25 ml of acetone. Shake well to homogenize.

Repeat this step using 2,6-dimethylaniline reference standard.

4.4 Preparation sample solution:

For metalaxyl determination, weigh accurately a quantity of the sample (0.0286 gm metalaxyl 35% WP) equivalent to 0.01 gm of 100 % metalaxyl reference standard into a 25 ml volumetric flask and add 25 ml of acetone. Shake well to homogenize. For

2,6-dimethylaniline determination, weigh accurately 1 gm of the sample (metalaxyl 35% WP) into a suitable 1 volumetric flask, and complete to 25 ml by acetone. Shake well to homogenize.

5.5 Estimation:

Inject 1 μ l from the reference standard solution into the GC followed by the sample note the peak area and the retention time of Metalaxyl standard and sample.

3. Results and Discussion

1. Physical Parameters:

1.1. The Metalaxyl 35% WP Samples

The data in table (1) illustrated the physico-chemical properties; alkalinity, bulk density, tapped density, pH at 1% solution and Wettability of metalaxyl 35% WP under different storage conditions; zero time (initial), cold storage at 0 °C for 7 days and hot storage at 54 \pm 2 °C for 3, 7, 14 and 28 days; respectively.

Table (1): Physical Properties of Metalaxyl 35% WP under Different Storage (Hot and Cold) Conditions.

Types of storages	Initial time 0	Cold storage at 0 °C for 7	Hot storages at 54 °C for			
			3 days	7 days	14 days	28 days
Free alkalinity(% of NaOH) CIPAC MT 191	0.20	0.17	0.23	0.27	0.3	0.35
PH of 1% solution CIPAC MT 75.3	9.5	8.79	9.5	9.9	10.3	10.7
Density (gm/cm ³) CIPAC MT 186	0.588	0.631	0.583	0.575	0.559	0.531
Tapped Density (gm/cm ³) ASTM B-527	0.769	0.851	0.746	0.714	0.694	0.641
Hausner Index (H.I)	1.37	1.34	1.28	1.24	1.24	1.21
Compressibility factor (C.F)	28.5	25.8	21.3	19.5	19.4	17.1
Wettability per second CIPAC MT 53.3.1	Less than 2	Less than 2	Less than 2		more than 2 minutes	

1.1.1 Alkalinity(%):

The alkalinity of metalaxyl 35% WP samples under different storage conditions; initial, cold and hot storage for 3, 7, 14 and 28 days were 0.2, 0.17, 0.23, 0.27, 0.3 and 0.35 % as NaOH. The samples of initial, cold and hot storage for 3 and 7 are acceptable where the other samples of hot storage for 14 and 28 days extremely increased by about 50% and 75% of the initial samples which may reflect the break of their formulations.

1.1.2 PH of 1% solution:

The pH values of 1% solution of metalaxyl 35% WP samples were alkaline, their alkalinity increased from initial time to hot storage at different time intervals 3, 7, 14 and 28 days as follows; 9.5, 9.5, 9.9, 10.3 and 10.7, respectively where the later 2 samples may cause phytotoxicity on plants. The cold storage sample was less alkaline than the other samples where its value was 8.8 approximately.

1.1.3 Bulk Density:

The bulk density of Metalaxyl samples were decreased descendingly from initial to the hot storage at different time intervals 3, 7, 14 and 28 days and their values were 0.588, 0.583, 0.575, 0.559 and 0.531 gm/cm³ were the metalaxyl samples of cold storage was the highest value 0.631 gm/cm³.

1.1.4 Tapped density(cp):

Also the tapped density of metalaxyl samples take the same way for the density values where the tapped density decrease descendingly from initial (zero time) to the hot storage at different time intervals 3, 7, 14 and 28 days and their values were 0.769, 0.746, 0.714, 0.694 and 0.641 gm/cm³ which appeared that by increasing the time of hot storage the impacting of the samples increased that may be destroying the nature of wettability powder characters of its formulation.

On the other hand, Carr's compressibility factor (C.F %) and Hausner index (HR), are measuring of the powder flow tendency. These two factors measured according to the equations

$$C.F = [(\rho_{\text{tap}} - \rho_{\text{bulk}}) / \rho_{\text{tap}}] \times 100$$

$$H.I. = \rho_{\text{tap}} / \rho_{\text{bulk}}$$

The data presented in table (1) showed the flow properties of the tested fungicide through different storage conditions. The samples of hot storages for 14 and 28 days, their Hausner indexes were lower than 1.25 and also their Compressibility factor were lower than 20.0% which indicates that the powder is poor flowability according to **Abdullah and Geldart (1999)** while, the other storage conditions were free flowing where their H.I higher than 1.25 and also their C.F > 20.0% means which agree with **Schüssele and Bauer-Brandl (2003)**.

1.1.5 Wettability:

The Wettability nature of wettable powder formulation must take place not more than 2 minutes without swirling according to the FAO and WHO specification. According to this fact, the initial, cold and hot storage for 3 and 7 days metalaxyl 35% WP were acceptable as a wettable powder formulation where their wetting time were less than 2 minutes while the other samples of 14 and 28 days took more than 2 minutes which reflect the break of its formulation as a wettable powder.

Generally, the later study on Metalaxyl 35% WP samples appeared that, increasing time of hot storage for long time as 14 and 28 days at 54 °C

which give indication for the stability of the sample during two years of manufacturing Cowlyn (1993). Also it may cause damage of the samples nature which may have diverse effects on their fungicidal activity against their targets.

1.2 Spray solution of Metalaxyl 35% WP Samples:

The data presented in table (2) illustrated the physico-chemical properties; persistence foam, pH, conductivity, salinity, suspensibility, viscosity and surface tension of metalaxyl 35% WP samples spray solutions (soft and hard) water under different types of storage (initial time, cold storage at 0 °C for 7 days and hot storage at 54 °C for 3, 7, 14 and 28 days

Table (2): Physical Properties for Spray Solutions of Metalaxyl 35% WP under Different Storage (Hot and Cold) Conditions.

Test	Initial time		Cold storage at 0°C for 7 days		Hot storages at 54°C for							
	S	H	S	H	3 days		7 Days		14 Days		28 Days	
					S	H	S	H	S	H	S	H
Foam per ml	2	3	2	3	3	4	3	5	7	9	11	15
PH	9.81	9.93	8.80	8.98	9.90	9.99	10.01	10.10	10.30	10.45	10.40	10.73
Conductivity \square mhos	210	710	200	860	240	750	250	790	310	850	350	910
Salinity ‰	0.2	0.7	0.2	0.8	0.2	0.7	0.2	0.7	0.3	0.8	0.3	0.9
Suspensibility %	78	75	75	75	73	71	67	61	63	57	55	50
Viscosity (cpois)	2.13	2.15	2.14	2.16	2.10	2.15	2.2	2.2	1.81	1.72	1.65	1.53
Surface Tension Dyn/cm	27		25		26		26		30		32	

S= softwater

H=hardwater

1.2.1 Foaming Test:

The percentage of foam for spray solutions soft and hard water of metalaxyl samples at initial time, cold storage and hot storage for 3, 7 and 14 days were acceptable while it was not acceptable for sample hot stored for 28 days because its value exceed the 10%.

1.2.2 pH:

All hard water spray solution samples of metalaxyl under different storage conditions their pH values were greater than their soft water samples. The pH range of spray solutions varied between 8.8 for soft water cold storage as minimum values where it was more alkaline for hard water of 28 days. Hot storage samples and its value were 10.73. The alkalinity of soft and hard water spray solutions for 14 and 28 days; where the highest value which reflects the effect of their hot storage.

1.2.3 Conductivity:

Also, the conductivity of all hard water spray solutions was higher than that of soft water spray solutions at the same conditions. The conductivity of spray solution soft and hard increased from initial then followed by cold storage, hot storage for 3, 7 and 14 days where the conductivity of soft,

hard water spray solutions for 28 days were the highest where the values were 350 and 910 μ mhos.

1.2.4 Salinity:

Also, the salinity as a percentage of thousands for hard water spray solution is greater than of soft water of metalaxyl samples of the same conditions. The salinity of soft water solutions were 0.2 ‰ as a lower values for initial, cold storage and hot storage samples for 3 and 7 days while the salinity of hard water spray solution were the highest for 28 days hot storage at $54 \pm 2^\circ\text{C}$.

1.2.5 Suspensibility:

Also the salinity, the suspensibility of hard water spray solution is greater than of soft water of metalaxyl sample of the same conditions. The salinity for soft water solution of metalaxyl were 0.2 ‰ as a lower values for initial time, cold storage and hot storage for 3, 7 at $54 \pm 2^\circ\text{C}$ were passed suspensibility test and their values were 78, 75, 75, 73, 71, 67 and 65% respectively. Soft and hard water spray solutions for hot storage for 14 and 28 days were failed in suspensibility because their values were 60, 57, 55 and 50%, respectively.

1.2.6 Viscosity:

The viscosities of soft and hard water spray

solutions for metalaxyl samples at initial, cold and hot storage for 3 and 7 days varied in the range of 2.10 to 2.2 cp and their average values was 2.15 cp but the other viscosities values were decreased than this average by almost 25:40% of their values.

1.2.8 Surface Tension:

The surface tension of the spray solution soft and hard water for the four types of storage was approximately constant in the range of $26 \text{ dyne/cm}^2 \pm 1$ but the surface tension of the two later hot stored samples for 14 and 28 days were increased by 15 and 23 %, respectively.

Finally, the initial, cold and hot storage for 3 and 7 days at $54 \pm 2 \text{ }^\circ\text{C}$ did not affect on the Metalaxyl 35% WP samples. Physical properties like alkalinity, bulk density, tapped density, pH and wettability were not affected where the others were affected by the long time of storage and distorted the WP formulation nature which reflects on the physico-chemical properties of their spray solutions in both soft and hard water. They were failed in persistence foam, suspensibility and make decrease in viscosity of their spray solutions which decreased their adhering on the surface of the leaf. Also, their surface tension increased which increasing the drift of spray solutions drops from the surface of plant leaves **Moustafa, et al. (1990)** and **Tawfik, Mona and El-Sisi (1987)**. The storage variation causes basisty variation referred to pH **El-Kady (2007)** and **Hussein, et al. (2009)**; conductivity and salinity may cause phytotoxicity for plants during using their spray solutions.

2. Chemical analysis:

The research around pesticides is a growing area in the field of analytical chemistry perhaps due to the fact that every year new pesticides are synthesized in order to achieve more effective products with a minor application rate (Sekhon, 2009). Metalaxyl [(R,S) methyl-N-(2-methoxyacetyl)-N-(2,6-xylyl)-dl-alaninate is an acylamine fungicides (included into the amide group), being the most widely known member of this group. This fungicide, synthesized in 1977, is widely used to control plant diseases caused by pathogens of the Oomycota division, in particular,

against *Phytophthora infestans* and *Phytophthora blight* **Fischer, et al. (1982)**. The active ingredient of the commercially metalaxyl 35 % WP formulation used in this experiment is the S-enantiomer. Many research workers have studied the effect of metalaxyl as a fungicide but the effects of temperature and storage stability on pesticide breakdown and their effect on the activity of the pesticide have not generally been described quantitatively more enough.

Metalaxyl and its metabolites containing 2,6-dimethylaniline have been determined by GLC with a flame ionization nitrogen detector **Anon., (1995)**. Quantitative estimation of Metalaxyl and its metabolite 2,6- dimethylaniline impurity present in the sample was done by comparing the area of known concentration of purified and known concentration standard with those in the samples. The values of areas, migration times and resolution were obtained using the Chem. Station software. The Metalaxyl content differ from that declared (35 %) by more than the following amounts.

Declared content Permitted tolerance

Up to 250 g/kg $\pm 6\%$ and above 250 up to 500 g/kg $\pm 5\%$ of the declared content.

Maximum amount of the metabolite 2,6-dimethylaniline is 0.1% of the metalaxyl content (1g/kg) according to FAO specifications of metalaxyl wettable powders. As the amount of the metabolites is very minor as shown from the specification, their determination requires analytical methods sensitive enough to be able to detect and quantify. 2,6- dimethylaniline is amino aromatic compound used as a chemical intermediate in the manufacture of pesticides and other products **Ethyl corp, (1990)** and **Kuney, (1991)**. It is used for the synthesis of metalaxyl, and may be present in trace amount in the sample, which may further react with acid chloride the manufacturing process to give the methoxyacetylated impurity. According to FAO specification its amount should not exceed 0.1 % of the total metalaxyl content in the sample.

Table 3: Shows the retention time, peak area and concentration of metalaxyl in the formulation sample at different periods of storage:

Injected solution	Retention time (min.)	Storage period	Peak area	Metalaxyl content Percent by mass
Metalaxyl St solution	4.275	-----	5539.95020	-----
Metalaxyl sample solution	4.275	Before storage	5706.82666	36.05 %
Metalaxyl sample solution	4.275	3 days	5549.79443	34.84 %
	4.274		5478.30420	
Metalaxyl sample solution	4.278	7 days	5372.93994	34.14 %
	4.279		5436.11719	
Metalaxyl sample solution	4.279	14 days	5301.20898	33.56 %
	4.279		5323.53564	
Metalaxyl sample solution	4.283	21 days	5255.21045	33.37 %
Metalaxyl sample solution	4.283	28 days	5048.1858	32.06 %

Table 4: Shows the retention time, peak area and concentration of metalaxyl metabolite 2,6-dimethylaniline in the formulation sample at different periods of storage:

Injected solution	Retention time (RT) (min.)	Storage period	Peak area	2,6-dimethylaniline content (gm/kg) formulation
2,6-dimethylaniline St solution	3.692	-----	7882.08789	-----
2,6-dimethylaniline sample solution	3.690	Before storage	4.48336	0.0057
2,6-dimethylaniline sample solution	3.691	3 days	4.29857	0.0055
2,6-dimethylaniline sample solution	3.691	7 days	5.18836	0.0066
2,6-dimethylaniline sample solution	3.691	14 days	5.26285	0.0067
2,6-dimethylaniline sample solution	3.691	21 days	5.73877	0.0073
2,6-dimethylaniline sample solution	3.691	28 days	6.32968	0.008

Table 5: Shows the retention time, peak area and concentration of metalaxyl metabolite 2,6-dimethylaniline in the formulation sample at different periods of storage:

Injected solution	Retention time (RT) (min.)	Storage period	Peak area	2,6-dimethylaniline content (gm/kg) of Metalaxyl content
2,6-dimethylaniline St solution	3.692	-----	7882.08789	-----
2,6-dimethylaniline sample solution	3.690	Before storage	4.48336	0.0158
2,6-dimethylaniline sample solution	3.691	3 days	4.29857	0.0157
2,6-dimethylaniline sample solution	3.691	7 days	5.18836	0.0193
2,6-dimethylaniline sample solution	3.691	14 days	5.26285	0.0199
2,6-dimethylaniline sample solution	3.691	21 days	5.73877	0.0218
2,6-dimethylaniline sample solution	3.691	28 days	6.32968	0.0250

The results of tables (4) and (5) show that 2,6-dimethylaniline amount increases with the time of storage but within the limit of specification. During the first 14 days its concentration were scarcely increased, which agree with **Oscar Gorodo (2010)**. While table (3) shows that metalaxyl content decreases with the time of storage and still within the limit and comply with FAO specification till 21 days of storage at 54 ± 2 °C. While after 28 days of storage the metalaxyl content decreased till become out of the comply limit which may be reflected on the toxicity and biological activity of this sample.

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