# Physico-chemical evaluation of broad spectrum herbicide (glyphosate isopropyl ammonium 48%) liquid formulations of highly desirable samples in local market

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**Abstract:** The present study was carried out to investigate the physico-chemical parameters and stability of eleven formulations for glyphosate isopropyl ammonium (48% glyphosate IPA) collected from local market. The formulation samples (48% active ingredient) from one to eleven were stored under different storage conditions at zero ° C ± 1 for 7 days and at 54 ºC for 3& 14 days. The effect of storage at cold and hot conditions on chemical stability of Glyphosate IPA from samples number one to eleven were determined by HPLC. The active ingredient (%) decreased at cold conditions and it was clear at hot storage one, compared with the data obtained at initial time. Samples number 1,3,8,and 9 were less stable in both hot storage conditions at 54 ºC for 3 & 14 days, while storage at 54 ºC for 14 days accelerated the chemical composition of glyphosate IPA with samples number 2, 5, 7 and 11. On contrast the active ingredient % of glyphosate IPA in samples number 4,6,and 10 which were stored at 54 ºC for 14 days, and all samples were stored at zero ºC for 7 days were more stable. Moreover, another target of this study is to evaluate of some physical parameters after cold conditions (at 0 ºC ± 1 for 7 days) and hot conditions (at 54 ºC for 3 &14 days). No significant changes in density (gm/cm$^3$), specific gravity and refractive index were recorded, the surface tension and the acidity (% as $H_2SO_4$) were decreased in all tested glyphosate isopropyl ammonium formulations samples under cold & hot storage conditions compared with the same formulations at initial time, while the viscosity were increased with all tested formulations samples which stored at 0 ºC ± 1 for 7 days. On contrast the viscosity were decreased with all tested glyphosate isopropyl ammonium formulations which stored at 54 ºC for 3 &14 days. The physical properties of spray solutions of glyphosate isopropyl ammonium formulations samples, foaming test, emulsion stability, viscosity (cp), surface tension (dyne/cm), pH values, conductivity (mM), salinity (‰) and total dissolved salts (mg/l) were tested.

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**Key words:** Glyphosate isopropyl ammonium, physical or chemical properties, IR spectra.

## 1. Introduction:

The non-selective, post-emergence herbicide glyphosate (N-(phosphonomethyl)glycine) is one of the most widely used pesticides. It is utilized for weed control, i.e. in agriculture, forestry, urban areas and even aquaculture. It is usually formulated as soluble liquid the isopropyl amine and in case of the most common formulation Roundup Ultra active ingredient combined with the surfactant polyoxyethylene amine (POEA) **(Giesy *et al.*, 2000).** Due to cultivation of genetically modified glyphosate-resistant crops, the use of glyphosate clearly increased during the last years, raising again concerns regarding the potential environmental impact of this herbicide **(Kolpin *et al.*, 2006).** Due to its high adsorption tendency in soil (Kd values up to 900 L kg$^{-1}$) and its fast degradation by micro-organisms, glyphosate is generally regarded as having low potential to contaminate surface waters or groundwater **(Borggaard and Gimsing 2007; de Jonge *et al.*, 2001; Vereecken 2005)**.

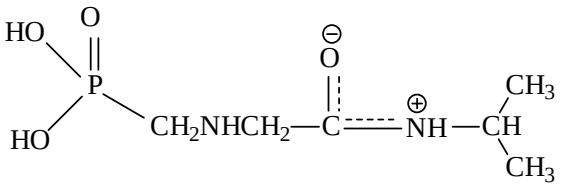
Glyphosate [N-(phosphonomethyl) glycine] is an active ingredient of the most extensively used foliar-applied, broad-spectrum herbicide, Roundup **(Malik *et al.*, 1989)**. This herbicide kills plants by inhibiting the shikimic acid pathway important for plant protein synthesis **(Schonbrunn *et al.*, 2001 and Amrhein *et al.*, 1980)**. Studies also showed that glyphosate inhibited the enzymatic activity of plant cytochrome P450 expressed in yeast, suggesting a similar action in plants **(Lamb *et al.*, 1998; Xiang *et al.*, 2005)**. The popularity of glyphosate stems from its low cost and effectiveness in controlling the majority of annual and perennial grasses and broad-leaved weeds **(Bradshaw *et al.*, 1997)**. Although glyphosate is believed to be less ecologically damaging than some other herbicide, its widespread usage in agriculture, forestry **(Powles *et al.*, 1998; Baerson *et al.*, 2002; Baucom and Mauricio 2004)**.

Pesticides may fail to comply with the **FAO/WHO meeting specification 2002** requires if is improperly stored. Chemical and physical instable usually lead to the deterioration of the active

ingredient content stability under variable climatic conditions as well as several cases **(Oscar Gordo *et al.*, 2010; Piertuigi *et al.*, 2002)**. The glyphosate IPA formulations were identified active ingredient percentage by using HPLC and, FT-IR to indicate for any disappearance of function groups.

## 2. Material and Methods

**Herbicide:**



**(Suggested Structure)**

**Chemical name:** Glyphosate isopropyl amine (Glyphosate IPA)
**Mol. wt.** : 212
**M. Formula** : $C_6H_{15}N_2O_4P$

The trade glyphosate isopropyl ammonium 48% were WSC formulation for Round Up , Herbazed®, Galialka® and Sun Up® (samples 1, 2, 3 and 5); AC for Clinic® (sample 6) and SL for Rophosate®, Herphosate®, Baron®, Ground Up®, Pilarsato® and Klash® ( samples 4, 7, 8, 9, 10 and 11), respectively. The samples were collected from recent local market with different registration numbers. The physical and chemical parameters of the collected glyphosate samples were examined initially, cold stored at 0 º C ± 1 for 7 days in the refrigerator and stored in glass bottles in the oven at 54 ºC for 3& 14 days according to **(Anonymous, 2002)**.

**(A) Chemical parameter:**

Determination of the active ingredient percent: The active ingredient percentages of the eleven tested glyphosate samples were determined before and after both cold and hot storage by HPLC with UV detector according **to (AOAC, 1990).**

**Reagents:**

Water – LC grade; Phosphoric acid ($H_3PO_4$) – 90% reagent grade; methanol and acetonitrile - LC grade; and glyphosate isopropyl ammonium (IPA)

**Preparation of standard solution:**

Weight 10mg (related to a purity of 100%) from glyphosate IPA reference standard of herbicide into a 10 ml volumetric flask (you can take another weight in different volume but with the same equivalence). And dilute to the mark with methanol LC grade and mixing well. This is the standard solution.

**Calibration:**

Calibration for the HPLC is usually carried out at concentrations related to that of sample found in formulation sample. Inject the glyphosate IPA standard solution onto HPLC column. Ensure reproducibility of injections to obtain glyphosate IPA retention time .Ensure linearity of standard injections with serial dilution. Using practice samples ensure baseline separation of glyphosate IPA peak.

**HPLC Analysis:**

The type of chromatographic system (Model Agilent , series 1100 solvent delivery system and quaternary pump) with a C18 stainless steel column (2.4 X 250 mm) and UV detector at 197 nm. Separation was done with an isocratic solvent system of acetonitrile/ deionized water with 0.1 % phosphoric acid (90/10) at a flow rate of 1.3 ml/min. The amount of glyphosate isopropyl ammonium was determined by comparison to external standard solutions. All reagents were HPLC grade **(Sherri 1990)**.

**Absorbance of different glyphosate isopropyl ammonium formulations in infrared (IR spectra):**

The Fourier transform infrared (Avtar 330 Thermo Nicolet) was used to study the effect of storage on the absorbance of function groups and finger print of Glyphosate isopropyl ammonium in the eleven tested formulations according to the method of **(Barbara 1985)** with some modification. Samples were prepared by homogenized 0/01 g of sample with 0.1 g of dry (KBr) by agatemortar and pests to a clean stainless steel slide and placed in piston to make a clear and thin film of desk sample.

**(B) Physical Parameters:**

The physical properties of glyphosate samples and their spray solutions in soft and hard water were carried out according to **Dobrat and Martijn (1995),** to detect acidity/ or alkalinity (MT 31.2), pH (MT 75), conductivity (MT 32), density and specific gravity (MT 3.1), persistent foam (MT 47.2) and solution stability (MT 41). Also, surface tension, refractive index and viscosity were carried out according to **American Society of Testing and Materials [A.S.T.M. (2001; 2002 and 2005)].**

## 3. Results

**(A) Chemical parameters:**

**I. Active ingredient percentage of glyphosate isopropyl ammonium trade samples:**

Data summarized in table (1) show that the persistence of active ingredient (%) of the tested glyphosate formulation samples was affected by storage conditions and exposure periods. The data indicated that the active ingredient (%) of glyphosate isopropyl ammonium in eleven different formulations initial samples were stable and the rate of decrease within permissible limits. Above 250 up to 500 the tolerance was ± 5% or the percentage of glyphosate active ingredient content (± 2.4%). All formulations under this study, when stored at zero ºC for 7 days, the active ingredient (%) of glyphosate isopropyl ammonium were 1.5, 2.8, -0.8, 0.8, -0.4, 0.6, 2.2, -.01, 3.9, 0.6 and 4% for samples from one to eleven, respectively. The accelerated storage at 54 ºC for 3 days was stable and the rate of decrease within permissible limit in glyphosate formulations samples number 2, 4, 5, 6, 7, 10 and 11 and their percentage of active ingredient were 4.7, 0.3, 0.5, 3.2, 1.3, -2.3 and 1.3, respectively. The accelerated chemical decomposition of active ingredient was lower than the tolerance of samples number 1, 3, 8 and 9, the active ingredient (%) of glyphosate isopropyl ammonium were 43.63, 42.75, 45.26 and 45.41, respectively. Also, the accelerated hot storage at 54 ºC for 14 days, the active ingredient (%) of glyphosate isopropyl ammonium in all formulations were degraded less than the tolerance content except formulation samples number 5, 6, 7, and 10 which was more stable than all other samples and the active ingredient (%) were 10.1, 19, 12.4, 5.2, 4.1, 4.4, 1.9, 5.7, 26.6, 4.6 and 20 % for samples from one to eleven, respectively.

**II. The effect of storage temperature on the absorbance of Glyphosate isopropyl ammonium at different formulations in infrared.**

The data obtained from the IR spectra of glyphosate isopropyl ammonium48% samples at (initial, at zero ºC for 7days, at 54 ºC for 3 &14 days of application) showed no significant changes in IR spectra during different types of storage. Data in table (2) showed the IR Spectra of glyphosate isopropyl ammonium herbicide at different formulations form one to eleven. The form for samples number 1, 2, 3 and 5 were WSC, and for samples number 4, 7, 8, 9, 10 and 11 were SL and AC form was sample number 6 at initial, hot storage and cold storage.The samples showed the characteristic bands of glyphosate isopropyl ammonium product for reaction between N-(phosphonomethyl) glycine, with 2-propylamine (1:1),for production of glyphosate isopropyl amine which have absorbance for lactam or lactim If the reaction was complete the product are glyphosate IPA which were have the lactam or lactim band in IR spectra at 1600 – 1650 $cm^{-1}$, but when this reaction was not completed the lactam or lactim band was not appeared in IR spectra and replace it by C=O group of acid which appeared at the range 1700-1720 $Cm^{-1}$

The absorbance bands of glyphosate IPA functional groups were peaks of N-H appears at 3420 ± 20 $cm^{-1}$, peaks of CH aliphatic appears at 2970 ± 20 $cm^{-1}$, peaks of O=C-N amide appears in the range of 1600 – 1650 $cm^{-1}$, peaks C-N appears in the range of 1320 – 1395 $cm^{-1}$, peaks of P=O appears at 1150 ± 30 $cm^{-1}$ and the peaks P-OH appears in the range of 910 – 1080 $cm^{-1}$.

**(B) Physical parameters:**

**Physical properties for different trade glyphosate isopropyl ammonium 48% samples:**

**a. At the initial time:**

Data obtained in table (3) illustrated the physical parameters of different formulations AC, SL and WSC of trade glyphosate samples it showed that, the free acidity of WSC formulated samples was higher than that of SL and AC samples. These values for samples 1, 2 and 3 were 15.14, 14.75 and 13.23 while it was 12.99 for sample 11. SL formulation as the highest value and the lowest value was 11.07 for sample 10 as SL formulation expressed as % of $H_2SO_4$.

The density of different AC, SL and WSC formulations have not any significant change in their values where the highest density was 1.1774 $gm/cm^3$ of sample 5 SL formulation, while the lowest value was 1.1491 $gm/cm^3$ of sample 9 SL formulation.

In agree with the density values of AC, SL and WSC formulation samples, the specific gravity also have not a significant change. The highest value was 1.180 of sample 5 SL formulation where the lowest value was 1.140 of sample 9 SL formulation.

By studying the free viscosity of different formulations AC, SL and WSC of eleven glyphosate trade samples it was found that, the viscosity of WSC formulations of samples 2, 3, and 1 in descending order were 74.96, 60.93 and 58.25 cp, while the highest value of SL and AC was 39.47 cp of sample 5 SL formulations and the lowest value was 11.21 cp for sample 4 of SL formulations, respectively.

With belongs to surface tension results of different formulations AC, SL and WSC for eleven trade glyphosate samples, there were no significant variation according to different types of formulation. The highest surface tension value was 56.9 $dyne/cm^2$ of sample 3 WSC formulation followed by 54.2

dyne/cm$^2$ of sample 10 SL formulation where the lowest values were 33.7 and 33.2 dyne/cm$^2$ of samples 7 and 4 SL formulations, respectively.

With the reference to refractive index of different formulations AC, SL and WSC of eleven glyphosate trade samples, the refractive index of WSC formulation of 2, 3 and 1 samples were 1.4394, 1.4353 and 1.4349 followed by SL and AC formulation where the maximum refractive index was 1.4344 of sample 5 SL formulation followed by 1.4278 of sample 6 SL formulation, while the lowest refractive index were 1.4164 and 1.4143 of samples 11 and 4, respectively.

**b. Cold storage at 0 °C for 7 days:**

Data presented in table (4) illustrated the physical parameters of different formulations AC, SL and WSC of eleven trade glyphosate samples after storage at 0°C for 7 days. Generally, the viscosity increase as the temperature decrease, where the viscosity of AC, SL and WSC formulations is inversely proportional with the temperature. The viscosity of AC, SL and WSC formulation samples after cold storage were increased generally. The maximum viscosity was 9% of sample 2 WSC formulation, where the minimum viscosity was 1% of sample 7 SL formulation.

The surface tension is directly proportional with temperature, as temperature decrease the surface tension decrease. The maximum depression in surface tension appear in sample 3 and 10 WSC and SL formulation and their values were 24.2 and 23.6 dyne/cm$^2$ where the minimum depression appeared for samples 5, 9 SL formulation and their values were 6.5 and 9.6 dyne/cm$^2$, respectively.

The density, specific gravity and refractive index for different formulations AC, SL and WSC of eleven trade glyphosate samples hadn't any significant variation between samples before and after cold storage.

The free acidity of trade glyphosate samples had not directed effect on the eleven samples of AC, SL and WSC different formulations.

The free acidity increases in the following samples 3 WSC and (5, 6 and 7) SL formulation where the maximum increase at samples 6, 7 SL formulations. Their values were 2.195 and 2.169 % as $H_2SO_4$, where the minimum increase appeared for samples 5 SL formulation by value 0.544 % as $H_2SO_4$.

The free acidity decrease in the following samples 1, 2, 4, 8, 9 and 11, where the maximum depression in free acidity at sample 2 WSC by 18% and the minimum depression found in sample 10 SL formulation by 2%, respectively.

**c. Accelerated hot storage at 54 °C for 3 days:**

Data showed in table (5) represents the physical parameters of different formulations AC, SL and WSC of seven trade glyphosate samples (2, 4, 5, 6, 7, 10 and 11) after storage at 54 °C for 3 days:

The free acidity decrease for all the samples with different formulation types AC, SL and WSC, except the samples 7 and 6 SL formulation, that their free acidity increase by 0.44 % as $H_2SO_4$, where the minimum depression were 0.02 and 0.39 % as $H_2SO_4$ for samples 4 and 10, respectively.

For density, specific gravity and refractive index, there were not any significant change for the properties of different formulations AC, SL and WSC for the seven trade glyphosate samples (2, 4, 5, 6, 7, 10 and 11).

The viscosity of different formulations AC, SL and WSC of eleven glyphosate trade samples were decreased where the viscosity is inversely proportional to temperature. The maximum depression in the viscosity were 6.88 and 3.77 cp for sample 3 WSC and 5 SL formulation, where the minimum depression in the viscosity were 0.04 and 0.06 cp for samples 4 and 11 SL formulation.

The surface tension properties of different formulations AC, SL and WSC of eleven trade glyphosate samples had a direct effect in the way of depression of surface tension. The maximum depression was 26.9 dyne/cm$^2$ of sample 10 SL formulation, where the minimum depression were 0.5 and 6.8 dyne/cm$^2$ for samples 8 and 7 SL formulation.

**Accelerated hot storage at 54 °C for 14 days:**

Data showed in table (5) represents the physical parameters of different trade glyphosate samples (5, 6, 7 and 10) after storage at 54 °C for 14 days:

Generally, the free acidity of the treated glyphosate samples were decreased and the minimum decrease appeared for sample 10 SL by 0.49 % as $H_2SO_4$ while the reverse effect of the sample 7 SL formulation had the only increase of the free acidity by 0.43 % as $H_2SO_4$.

As we represented before for different storage condition (cold and hot) density, specific gravity and refractive index had not any significant oriented change for different glyphosate trade samples (5, 6, 7 and 10).

Also, as mentioned before, the viscosity is inversely proportional with temperature, as the temperature increases the viscosity decreases.

The trade glyphosate samples (5, 6, 7 and 10) showed generally decreasing in viscosity and their values were 13.74, 16.19, 33.02 and 36.50 cp, respectively.

Also the surface tension properties of glyphosate trade samples were decreased with the reference to their values before storage. The maximum depression in surface tension was 25.6 dyne/cm of sample 10 SL formulation. Sample 7 showed minimum depression in surface tension 4.9 dyne/cm.

**Table (1): Active ingredient percent of different trade samples Glyphosate isopropyl ammonium 48% at different storage times.**

| Pesticide used | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Initial | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 7 days at 0 °C ( ± 2.4% ) | 1.5 | 2.8 | -0.8 | 0.8 | -0.4 | 0.6 | 2.2 | -0.1 | 3.9 | 0.6 | 4.0 |
| 3 days at 54 °C | 9.0 | 4.7 | 10.2 | 0.3 | 0.5 | 3.2 | 1.3 | 5.2 | 7.1 | -2.3 | 1.3 |
| 14 days at 54 °C | 10.1 | 19.0 | 12.4 | 5.2 | 4.1 | 4.4 | 1.9 | 5.7 | 26.8 | 4.6 | 20.0 |

**Table (2): The effect of storage temperatures on finger print of different glyphosate IPA formulations by using IR spectrum.**

| Treat. | Type of bond at $cm^{-1}$ | Sample | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| **Initial** | **N-H** at 3420 ± 20 | 3527 | 3422 | 3422 | 3467 | 3422 | 3422 | 3423 | 3422 | 3423 | 3423 | 3422 |
| | **C-H** at 2970 ± 20 | 2987 | 2986 | 2991 | 2990 | 2992 | 2991 | 2995 | 2991 | 2990 | 2987 | 2985 |
| | **O=C-N** at 1600 -1650 | 1634 | 1634 | 1637 | 1635 | 1631 | 1634 | 1634 | 1634 | 1633 | 1631 | 1635 |
| | **C-N** at 1320 – 1395 | 1389 | 1398 | 1398 | 1398 | 1399 | 1321 | 1321 | 1321 | 1321 | 1322 | 1321 |
| | **P=O** at 1150 ± 30 | 1167 | 1166 | 1166 | 1168 | 1168 | 1167 | 1167 | 1166 | 1167 | 1167 | 1166 |
| | **P-OH** at 910 – 1080 | 915 | 916 | 916 | 914 | 915 | 917 | 916 | 915 | 916 | 915 | 917 |
| **Cold storage at O C for 7 days** | **N-H** at 3420 ± 20 | 3418 | 3445 | 3422 | 3400 | 3422 | 3461 | 3459 | 3451 | 3507 | 3553 | 3422 |
| | **C-H** at 2970 ± 20 | 2979 | 2975 | 2971 | 2977 | 2975 | 2979 | 2983 | 2991 | 2990 | 2993 | 2991 |
| | **O=C-N** at 1600 -1650 | 1634 | 1634 | 1633 | 1634 | 1632 | 1634 | 1635 | 1634 | 1635 | 1634 | 1631 |
| | **C-N** at 1320 – 1395 | 1323 | 1398 | 1389 | 1398 | 1398 | 1398 | 1322 | 1322 | 1322 | 1322 | 1321 |
| | **P=O** at 1150 ± 30 | 1167 | 1167 | 1166 | 1168 | 1168 | 1167 | 1168 | 1166 | 1168 | 1167 | 1167 |
| | **P-OH** at 910 – 1080 | 918 | 915 | 917 | 914 | 916 | 916 | 916 | 915 | 916 | 916 | 917 |
| **Accelerated storage at 54 C for 3 days** | **N-H** at 3420 ± 20 | 3421 | 3482 | 3417 | 3507 | 3422 | 3433 | 3477 | 3508 | 3453 | 3511 | 3422 |
| | **C-H** at 2970 ± 20 | 2980 | 2990 | 2973 | 2983 | 2979 | 2981 | 2977 | 2980 | 2991 | 2983 | 2989 |
| | **O=C-N** at 1600 -1650 | 1629 | 1635 | 1634 | 1636 | 1634 | 1646 | 1634 | 1631 | 1632 | 1635 | 1636 |
| | **C-N** at 1320 – 1395 | 1389 | 1397 | 1398 | 1399 | 1394 | 1388 | 1389 | 1322 | 1322 | 1322 | 1398 |
| | **P=O** at 1150 ± 30 | 1166 | 1165 | 1167 | 1168 | 1169 | 1167 | 1168 | 1167 | 1167 | 1167 | 1167 |
| | **P-OH** at 910 – 1080 | 917 | 917 | 918 | 914 | 916 | 913 | 917 | 914 | 916 | 916 | 917 |
| **Accelerated storage at 54 C for 14 days** | **N-H** at 3520 ± 20 | 3520 | 3530 | 3531 | 3515 | 3565 | 3566 | 3565 | 3547 | 3540 | 3422 | 3443 |
| | **C-H** at 2970 ± 20 | 2990 | 2980 | 2975 | 2977 | 2979 | 2971 | 2983 | 2985 | 2988 | 2980 | 2980 |
| | **O=C-N** at 1600 -1650 | 1635 | 1631 | 1646 | 1635 | 1635 | 1635 | 1635 | 1635 | 1634 | 1633 | 1635 |
| | **C-N** at 1320 – 1395 | 1322 | 1389 | 1322 | 1323 | 1399 | 1322 | 1322 | 1322 | 1322 | 1398 | 1322 |
| | **P=O** at 1150 ± 30 | 1163 | - | 1080 | 1168 | 1172 | 1167 | 1167 | 1167 | 1168 | 1167 | 1167 |
| | **P-OH** at 910 – 1080 | 917 | 917 | 918 | 915 | 914 | 916 | 916 | 914 | 916 | 916 | 917 |

**Table (3): Physical properties of different formulations AC, SL and WSC for different trade samples of Glyphosate isopropyl ammonium 48% at initial time**

| Pesticide used | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Free Acidity (% as $H_2SO_4$) | 15.14 | 14.75 | 13.23 | 12.50 | 12.95 | 12.94 | 12.15 | 11.61 | 12.64 | 11.07 | 12.99 |
| Density ($gm/cm^3$) | 1.1696 | 1.1768 | 1.1679 | 1.1647 | 1.1774 | 1.1616 | 1.1586 | 1.1593 | 1.1491 | 1.1540 | 1.1634 |
| Specific Gravity | 1.160 | 1.170 | 1.170 | 1.160 | 1.180 | 1.160 | 1.160 | 1.160 | 1.14 | 1.150 | 1.160 |
| Viscosity (cp.) | 58.25 | 74.96 | 60.93 | 11.21 | 39.47 | 33.12 | 16.37 | 21.66 | 20.08 | 13.79 | 18.80 |
| Surface Tension (dyne/cm) | 41.4 | 41.6 | 56.9 | 33.2 | 44.0 | 43.2 | 33.7 | 35.1 | 37.8 | 54.2 | 41.4 |
| Refractive Index | 1.4349 | 1.4394 | 1.4353 | 1.4143 | 1.4344 | 1.4278 | 1.4199 | 1.4218 | 1.4213 | 1.4164 | 1.4203 |

**Table (4): Physical properties of different formulations AC, SL and WSC for different trade samples of Glyphosate isopropyl ammonium 48% after 7 days of storage at 0 ºC**

| Pesticide used | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Free Acidity (% as $H_2SO_4$) | 13.867 | 12.495 | 14.357 | 11.858 | 13.484 | 14.305 | 13.769 | 10.486 | 13.181 | 10.829 | 12.299 |
| Density (gm/cm$^3$) | 1.1665 | 1.1742 | 1.1662 | 1.1615 | 1.1774 | 1.1625 | 1.1562 | 1.1595 | 1.1484 | 1.1508 | 1.1604 |
| Specific Gravity | 1.160 | 1.170 | 1.167 | 1.156 | 1.170 | 1.158 | 1.155 | 1.158 | 1.145 | 1.150 | 1.160 |
| Viscosity (cp.) | 62.05 | 81.66 | 62.87 | 11.42 | 39.89 | 34.68 | 16.49 | 21.83 | 21.02 | 14.49 | 19.37 |
| Surface Tension (dyne/cm) | 31.3 | 32 | 32.7 | 24.8 | 33.5 | 34.3 | 26.2 | 25.7 | 28.2 | 30.6 | 27.2 |
| Refractive Index | 1.4355 | 1.4401 | 1.4357 | 1.4143 | 1.4342 | 1.4284 | 1.4198 | 1.4218 | 1.4212 | 1.4165 | 1.4199 |

**Table (5): Physical properties of different formulations AC, SL and WSC for different trade samples of Glyphosate isopropyl ammonium 48% after 3 days of storage at 54 ºC**

| Pesticide used | 3 Days of storage at 54 ºC. | | | | | | | 14 Days of storage at 54 ºC. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | 4 | 5 | 6 | 7 | 10 | 11 | 5 | 6 | 7 | 10 |
| **Free Acidity** (% as $H_2SO_4$) | 12.69 | 12.84 | 11.43 | 13.38 | 12.59 | 10.78 | 12.59 | 11.27 | 12.25 | 11.94 | 10.58 |
| **Density** (gm/cm$^3$) | 1.175 | 1.164 | 1.179 | 1.164 | 1.158 | 1.151 | 1.162 | 1.1797 | 1.1639 | 1.1579 | 1.1527 |
| **Specific Gravity** | 1.18 | 1.17 | 1.19 | 1.17 | 1.16 | 1.16 | 1.17 | 1.185 | 1.170 | 1.160 | 1.160 |
| **Viscosity** (cp.) | 71.25 | 11.17 | 35.70 | 31.83 | 15.97 | 13.89 | 18.74 | 36.50 | 33.02 | 16.19 | 13.74 |
| **Surface Tension** (dyne/cm) | 28.0 | 24.6 | 32.8 | 32.6 | 26.9 | 27.3 | 27.9 | 33.2 | 32.5 | 28.8 | 28.2 |
| **Refractive Index** | 1.4398 | 1.4143 | 1.4341 | 1.4276 | 1.4193 | 1.4162 | 1.4196 | 1.4338 | 1.4274 | 1.4193 | 1.4157 |

**2. Physico-chemical properties of spray solutions for different trade formulations (AC, SL and WSC) of glyphosate isopropyl ammonium samples:**

a) At the initial time:

The obtained data in table (6) illustrated the physico-chemical properties of hard and soft water spray solution for the eleven trade glyphosate samples of different formulations (WSC, AC and SL) before storage.

The samples 1, 2, 3, 6 and 7 of different formulation WSC, AC and SL had not any foam for different types of water soft and hard, where hard water of samples 5, 8 and 10 SL formulations had foam about 3.7 and 3.5 ml, respectively.

The viscosity of all the eleven sample spray solution of hard and soft water spray solution for different formulation WSC, AC and SL had not a significant different in their values. The viscosity of the 24 spray solutions were found to be in the range of 2.18 to 2.26 cp.

The surface tension of the hard water spray solution of the eleven trade glyphosate samples of different formulation were higher than that of the soft water spray solution of the same sample. The hard water spray solution of sample 4 SL had the highest value, 68 dyne/cm$^2$, followed by sample 2 WSC, 67 dyne/cm$^2$, while soft water spray of sample 9 SL had the lowest surface tension, 40 dyne/cm$^2$, followed by sample 1 WSC formulation, 41 dyne/cm$^2$.

Soft and hard water spray solutions of sample 5 SL formulation have highest acidic nature, 4.24 and 4.2, followed by sample 9 SL, 4.42 and 4.38, where sample 2 WSC formulation has the lowest acidic nature, 5.02 and 4.97, followed by sample 1 WSC, 4.95 and 4.87 with the same sequence of spray solutions.

Generally, conductivity is directly proportional to salinity and T.D.S. as the conductivity increase the salinity and the T.D.S. of the spray solution increase. Also, the hard water spray solution of the eleven trade glyphosate samples had higher values of the later properties than that of soft water for the same sample. The hard water spray solution of samples 5 and 2 SL and WSC formulations had the highest value for the corresponding properties as follows (7.33 and 6.9 ms), (4.0 and 3.8 ‰) and (3950 and 3700 mg/L), respectively. While, the soft water spray solution of samples 6 and 9 SL formulation had the lowest values for the later physical properties as follow (5.6 ms), (3.0 ‰), and (2940 and 2950 mg/L), respectively.

**(b) After storage at 0 °C for 7 days:**

The data obtained in table (7) mentioned the physico-chemical properties of hard and soft water spray solutions for the eleven trade glyphosate samples after cold storage at 0 °C for seven days in the refrigerator.

The samples 1, 2, 3, 6 and 7 of different formulations WSC, AC and SL had not any foams for different types of water soft and hard, while the foam of other samples 4, 5, 9, 10 and 11 were increased. Generally, soft water of samples 4 and 10 SL formulation had the highest foam value (about 24 ml) and for sample 8 SL was 32 ml, where the hard water of sample 5 SL had the lowest value of foam; about 5 ml.

Also, as mentioned above, the viscosity of samples before storage, showed no significant change in the viscosity property for all the spray solutions of the eleven samples.

Generally, the cold storage at 0 °C for 7 days, had not direct significant change on the acidic nature (pH value) of the soft and hard water spray solution of the eleven glyphosate samples, where the variation was about ± 0.16 than that before storage at the initial time.

The cold storage decreases the surface tension of all hard and soft water spray solution than that before storage at the initial time. Also, the surface tension of hard water was higher than that of soft water for the same sample. The highest surface tension appear in samples 6, 7 and 3 SL and WSC formulation hard water spray solution, where their values were 49.7 and 48 dyne/cm, while the lowest surface tension appear in samples 4 and 5 SL formulation soft water spray solution and their values were 32.7 and 33.5 dyne/cm.

Finally, conductivity, salinity and T.D.S of the eleven samples soft and hard water spray solution were decreased after cold storage at0 °C for 7 days than that before storage at the initial time. The hard water spray solution of the eleven trade glyphosate samples had higher values of the later properties than that of soft water for the same samples. The hard water spray solution of samples 5, 2 and 4 SL and WSC formulation had the highest value for the corresponding properties as follows (6.66, 6.37 and 6.22 ms), (3.6, 3.5 and 3.4 ‰) and (3550, 3340 and 3310 mg/L), respectively. While, the soft water spray solution of samples 9, 1 and 10 SL and WSC formulations had the lowest values for the later physical properties as follow (5.14, 5.21 and 5.22 ms), (2.8 ‰ for all) and (2680, 2710 and 2720 mg/L), respectively.

**(c) After storage at 54 °C for 3 days:**

The data obtained in table (9) illustrated the physico-chemical properties of hard and soft water spray solutions for the successful trade glyphosate samples 2, 4, 5, 6, 7, 10 and 11 after hot storage for 3 days at 54°C.

Generally, the hot storage has not a pronounced effect on foam and viscosity measurement of the spray solutions for the successful samples.

The accelerated hot storage decrease the surface tension of the spray solution than before storage, the highest decrease appear for samples 4, 6 at average 40% of their values for hard and soft water spray solution.

The acidic nature of the spray solution hadn't any oriented effect after storage for the soft water samples, where the change in acidic nature was ± 0.17 than samples before storage with the relation between acidity and conductivity, salinity and T.D.S. it was found that the latter properties decrease where acidity decrease and vis versa.

**(d) After storage at 54 °C for 14 days:**

The data obtained in table (8) illustrated the physico-chemical properties of hard and soft water spray solution for the successful trade glyphosate samples 5, 6, 7 and 10 after hot storage for 14 days at 54 °C. The percentage of foam for the successful samples was in the allowed range except sample 5 SL soft water where its value was 15 ml. Also, the viscosity of the spray solution of the successful samples 5, 6, 7 and 10 had not a significant change than the samples before storage. The long hot storage of the samples for 14 days, increase their acidic nature with the reference to the spray solutions of the samples before storage. Also, as we mentioned before for the correlation between acidity and conductivity, salinity and T.D.S. their values were increased as the acidity increased for the spray solution of the successful samples.

**Table (6): Physico-chemical properties of Glyphosate isopropyl ammonium spray solutions of different recommended trade names at initial time.**

| Pesticide Used | 1 | | 2 | | 3 | | 4 | | 5 | | 6 | | 7 | | 8 | | 9 | | 10 | | 11 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Spray Solution / Measurement | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W |
| Foaming (mm) | - | - | - | - | - | - | 0.6 | 0.5 | 3.7 | 3.5 | - | - | - | - | 3.5 | 2.8 | 3.5 | 3.0 | 3.5 | 3.2 | 2.9 | 2.5 |
| Solution stability | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass |
| Viscosity (cp.) | 2.21 | 2.21 | 2.22 | 2.21 | 2.22 | 2.23 | 2.22 | 2.18 | 2.26 | 2.24 | 2.26 | 2.24 | 2.22 | 2.21 | 2.21 | 2.20 | 2.20 | 2.21 | 2.20 | 2.20 | 2.20 | 2.19 |
| Surface Tension (dyne/cm) | 46 | 41 | 67 | 50 | 52 | 49 | 72 | 62 | 63 | 57 | 66 | 72 | 52 | 54 | 55 | 45 | 65 | 40 | 48 | 44 | 53 | 49 |
| pH | 4.78 | 4.95 | 4.97 | 5.02 | 4.71 | 4.76 | 4.40 | 4.39 | 4.20 | 4.24 | 4.51 | 4.54 | 4.42 | 4.46 | 4.51 | 4.56 | 4.38 | 4.42 | 4.60 | 4.63 | 4.40 | 4.45 |
| Conductivity (ms) | 5.91 | 5.73 | 6.90 | 6.81 | 6.06 | 5.97 | 6.82 | 6.45 | 7.33 | 6.96 | 6.03 | 5.60 | 6.50 | 6.18 | 6.64 | 6.45 | 5.84 | 5.60 | 6.19 | 5.73 | 6.45 | 5.95 |
| Salinity (‰) | 3.2 | 3.1 | 3.8 | 3.7 | 3.3 | 3.2 | 3.7 | 3.5 | 4.0 | 3.8 | 3.3 | 3.0 | 3.5 | 3.3 | 3.6 | 3.5 | 3.2 | 3.0 | 3.3 | 3.1 | 3.5 | 3.2 |
| T.D.S (mg/l) | 3210 | 3020 | 3700 | 3620 | 3200 | 3140 | 3620 | 3430 | 3950 | 3710 | 3190 | 2940 | 3450 | 3260 | 3520 | 3440 | 3090 | 2950 | 3270 | 3000 | 3410 | 3160 |

**H.W = hard water S. W = soft water**

**Table (7): Physico-chemical properties of Glyphosate isopropyl ammonium spray solutions of different recommended trade names after (7) days of storage at 0 ºC.**

| Pesticide used | 1 | | 2 | | 3 | | 4 | | 5 | | 6 | | 7 | | 8 | | 9 | | 10 | | 11 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Spray Solution / Measurement | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W | H.W | S.W |
| Foaming (mm) | - | - | - | - | - | - | 5 | 24 | 22 | 17 | - | - | - | - | 19 | 23 | - | 9 | 20 | 24 | 19 | 12 |
| Solution stability | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass |
| Viscosity (cp.) | 2.28 | 2.27 | 2.28 | 2.25 | 2.27 | 2.26 | 2.24 | 2.23 | 2.25 | 2.21 | 2.25 | 2.24 | 2.26 | 2.22 | 2.26 | 2.25 | 2.24 | 2.24 | 2.25 | 2.23 | 2.23 | 2.23 |
| Surface Tension (dyne/cm) | 40 | 37.9 | 45 | 42.4 | 48 | 43.6 | 33.5 | 32.7 | 33.5 | 33.5 | 49.7 | 47.8 | 48 | 46.5 | 38.9 | 36.9 | 36 | 38.9 | 35.1 | 34.3 | 37.9 | 34.3 |
| pH | 4.73 | 4.76 | 5.00 | 5.03 | 4.74 | 4.77 | 4.44 | 4.46 | 4.28 | 4.32 | 4.62 | 4.65 | 4.56 | 4.59 | 4.67 | 4.69 | 4.54 | 4.58 | 4.76 | 4.79 | 4.53 | 4.58 |
| Conductivity (ms) | 5.57 | 5.21 | 6.37 | 6.34 | 5.72 | 5.54 | 6.26 | 5.93 | 6.66 | 6.30 | 5.35 | 5.33 | 5.91 | 5.84 | 6.04 | 5.90 | 5.30 | 5.14 | 5.53 | 5.22 | 5.93 | 5.60 |
| Salinity (‰) | 3.0 | 2.8 | 3.5 | 3.4 | 3.1 | 3.0 | 3.4 | 3.2 | 3.6 | 3.4 | 2.9 | 2.9 | 3.2 | 3.1 | 3.3 | 3.2 | 2.9 | 2.8 | 3.0 | 2.8 | 3.2 | 3.0 |
| T.D.S (mg/l) | 2920 | 2710 | 3380 | 3350 | 3010 | 2910 | 3310 | 3150 | 3550 | 3350 | 2810 | 2790 | 3210 | 3080 | 3190 | 3110 | 2790 | 2680 | 2900 | 2720 | 3130 | 2970 |

**H.W = hard water S. W = soft water**

**Table (8): Physico-chemical properties of Glyphosate isopropyl ammonium spray solutions of different recommended trade names after accelerated storage at 54 ºC for different times.**

| | 3 Days of storage at 54 °C. | | | | | | | | | | | | | | 14 Days of storage at 54 °C. | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Pesticide Used** | 2 | | 4 | | 5 | | 6 | | 7 | | 10 | | 11 | | 5 | | 6 | | 7 | | 10 | |
| **Spray Solution / Measurement** | **H.W** | **S.W** | **H.W** | **S.W** | **H.W** | **S.W** | **H.W** | **S.W** | **H.W** | **S.W** | **H.W** | **S.W** | **H.W** | **S.W** | **H.W** | **S.W** | **H.W** | **S.W** | **H.W** | **S.W** | **H.W** | **S.W** |
| **Foaming** (mm) | - | - | 4 | 9 | 14 | 18 | - | - | - | - | 8 | 11 | 7 | 6 | 6.0 | 15.0 | - | - | - | - | 5.0 | 6.0 |
| **Solution Stability** | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass |
| **Viscosity** (cp.) | 2.22 | 2.24 | 2.17 | 2.19 | 2.19 | 2.17 | 2.20 | 2.20 | 2.24 | 2.18 | 2.23 | 2.20 | 2.23 | 2.24 | 2.17 | 2.18 | 2.23 | 2.21 | 2.23 | 2.20 | 2.18 | 2.20 |
| **Surface Tension** (dyne/cm) | 38.7 | 38.6 | 32.9 | 34.6 | 30.9 | 31.2 | 37.9 | 42.6 | 36.2 | 37.5 | 33.9 | 34.7 | 36.0 | 37.7 | 31.0 | 32.5 | 48.2 | 46.7 | 43.8 | 40.9 | 30.0 | 32.0 |
| **pH** | 5.04 | 4.98 | 4.36 | 4.33 | 4.17 | 4.20 | 4.57 | 4.48 | 4.45 | 4.41 | 4.52 | 4.50 | 4.35 | 4.28 | 4.07 | 4.16 | 4.39 | 4.42 | 4.28 | 4.35 | 4.49 | 4.51 |
| **Conductivity** (ms) | 6.40 | 6.45 | 6.16 | 6.28 | 6.71 | 6.62 | 5.33 | 5.58 | 6.66 | 4.92 | 5.44 | 5.65 | 5.79 | 5.94 | 6.70 | 6.38 | 5.52 | 5.17 | 5.95 | 5.71 | 5.54 | 5.47 |
| **Salinity** (‰) | 3.5 | 3.5 | 3.4 | 3.4 | 3.7 | 3.6 | 2.9 | 3.0 | 3.6 | 2.6 | 2.9 | 3.0 | 3.1 | 3.1 | 3.6 | 3.5 | 3.0 | 2.8 | 3.2 | 3.1 | 3.0 | 3.0 |
| **T.D.S** (mg/l) | 3400 | 3480 | 3290 | 3320 | 3600 | 3500 | 2790 | 2960 | 3530 | 2560 | 2840 | 2960 | 3040 | 3130 | 3560 | 3370 | 2870 | 2710 | 3140 | 3000 | 2950 | 2900 |

**H.W = hard water** **S. W = soft water**

## 4. Discussions

In this work, we are studying the chemical properties of different trade glyphosate samples under different storage conditions (cold storage at 0ºC for 7days and hot storage at 54 ºC for 3 and 14 days) respectively. The active ingredient % was affected for the samples 1,3,8 and 9 after hot storage for 3 days at 54ºC where their degradation were more than permission limit. Also, by continuous hot storage until 14 days at 54 ºC the degradation of active ingredient appeared for the samples 2, 4 and 11 more than the limit of permission where the samples 5, 6, 7 and 10 were stable and their active ingredient were not affected by cold and hot storage conditions which comply with **Pesticides Specifications (2006)** for the important of hot and cold storage test which give the indication of efficiency of the pesticide samples during two years of manufacture and **Cowlyn, (1993).**

Also, by studying the functional group and their intensity by IR tools, we found the band of lactam-lactim isomerization at 1600-1650cm$^{-1}$ where appeared the formation of glyphosate isopropyl ammonium **(Silverstein *et al.*, 1996).** The intensity of lactam-lactim bond were not affected by cold storage at 0 ºC for 7days for all samples but their was decreased during hot storage for 3 days at 54 ºC for the samples 1, 3, 8 and 9 by continuous hot storage for 14 days at the same temperature the intensity of lactam-lactim bands was decreased for samples 2, 4 and 11 where the intensity of samples 5, 6, 7 and 10 was constant which reflected the their stability and comply with % of active ingredient analysis by HPLC **(Eto, 1974).**

Also, we are studying the physical properties of different formulation of trade glyphosate samples before and after storage conditions (cold for 7 days at0ºCand hot storage at 54ºC for 3 and 14 days). By monitoring the succeeded samples 5, 6, 7 and 10 we found a changing in their physical properties, the acidity of the promising samples was slightly decreased at hot storage foe 3 days and by continuous

storage for 14 days the acidity also decreased while its values of other samples were changing randomly. The changing of acidity during storage of glyphosate samples agree with that obtained by **El-Kady, (2007)** and **Hussein *et al.*, (2009).**

The viscosity is inversely proportional with temperature so, the viscosity of the samples at cold storage were the highest one followed by the initial state where, there were a slightly decrease in viscosity after hot storage for 3 days at 54ºC by continuous hot storage for 14 days, the viscosity of samples 1, 2, 3, 4, 8, 9 and 11 samples were depressed while it was moderately decreased for samples 5, 6, 7 and 10. The changing in viscosity during hot storage agree with that obtained with **Seiz, (1953)** which indicated the inversely proportional relation sheep between viscosity and temperature of pesticide liquid formulation.

The surface tension was affected inversely by temperature where as the temperature increase the surface tension decrease. All the promising samples 5, 6, 7 and 10 their surface tension values were decreased slightly after 3 days of hot storage and by continuous storage for 14 days the surface tension was decrease moderately. The relation between surface tension and temperature comply with **Osipew, (1964)** studies who indicated the inversely relation sheep between them in pesticide liquid formulation.

Generally by comprising the physical properties of the promising sample (5 WSC formulation), sample (6 AC formulation) and samples (7, 10 SL formulation) we expected that, sample 5 WSC was the best one followed by sample 6 AC, 7 and 10 SL formulations, respectively due to the following reasons; the viscosity of sample 5 was the highest one which make strong adhering on the surface of the herbs leaf **(Richardson, 1974; Furmidge, 1962)**. Also, it's highly acidity prevent the degradation of active ingredient during dilution by spray field water which it was slightly alkaline. By decreasing the surface tension the drop of spray solution will be spread easily on the leaf surface of herbs and did not drift which increase the time of penetration of herbicide through its target **(Tawfik *et al.*, 1987; Moustafa *et al.*, 1990)**. In the further studies we will evaluate the herbicidal activity of trade glyphosate samples on its targets.

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