Measurement of pesticides using ultraviolet visible spectrophotometer

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ABSTRACT

The amount of pesticides in agricultural products has been measured with different methods. In this remaining tests Picloram herbicides in real samples. Spectroscopy method UV-Vis, was measured by Dey Zvtasyvn discontinuous method. To this case that NH2 groups in the meta position (relative to the functional group COOH) in herbicide Picloram by sodium nitrite with hydrochloric acid, turned to salt Dey AZvnyvm and then with the help reagent Beta Nftvl were obtained combination color with Dey Azo, (bottom figure). Absorb in the wavelength was measured 405 nm and curve linear calibration was obtained in the concentration range 15 ppm - 1ppm. Detection limit 0.148 ppm is obtained small extent of 0.495 ppm and percent recovery for example, corn and barley, 100% and for pesticide formulation 102%. Results obtained indicative this is that with simple method cheap but meanwhile practical spectroscopy UV-Vis can be measured amount of insignificant the herbicide in the real samples.

Keywords: Pesticides, herbicides, Picloram, Range of colors Dey azo related to Picloram
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INTRODUCTION

Pesticides are synthetic or natural compounds that are used to control or eliminate pests. Some sources, pesticides to have defined in this case, the pesticides are compound or a mixture of several chemical compounds that be taken to prevent eliminate distance or reduce insect population, rodents, fungi, weeds or every kind of aquatic plants, animals and viruses, bacteria and microorganisms that are considered pests. Of course are exempt from this rule virus, bacteria and microorganisms that live in the human body or animals. Bio pesticides are included organisms that used to control pests of this definition can be concluded that always pesticides not make death to pest directly but it may be a means for kill pests (pheromones). Or disperse pests and cause reduction population its intended in place (repellents) or even not kill pests treated, but pesticides, affect on the its results (effective compounds in development). Attention to the fact it is essential there is a difference between Poison and Toxicant. Poison refers to any material have harmful effects on the living organisms. Conception more People of the word poison this is poison is cause kill, of pesticides on the living maybe is included immediate death or poisoning and or may not have any effect. Egyptians in 1200 BC, knew hemlock and aconite namely poison Tajol Muluk's roots. Homer in 1000 BC has spoken of burning sulfur to disinfect houses. Before1800 AD most of the materials used were at excretion pests, impure inorganic compounds were had effects on chitin insect body. Including compounds were substances such as Ash, Soot and even soft soil. Later other material was used like Soap, oil, Essence of turpentine, Camphor, Pepper and Sulfur leaves. The first composition of intestinal which has been used against insects is arsenic compounds likely that in the mid-sixteenth century with honey is consumed as poison baiting against ants. In the 1860s Paris green that copper salts was arsenic was used against Colorado beetle, worm apple and other leaf-eaters.

608

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The first organic pesticides that were used, likely Nicotine was that in 1763 was used as powdered leaves of tobacco plants against aphid. Rotenone another natural compounds that it was customary in the mid-1800s in Europe. Rotenone which is obtained from the roots of several plants at first in South America was used as fish killer. Still the combination offered and an appropriate pesticide is to control fruit and vegetable pests in the home. Synthetic pesticides with organic Structure with construction Para Dey Klorvbenzn was started in 1912 which was used against willow clothing. Thiocyanate in 1929 was produced as contact insecticides and in 1932 will take in France. The major change in the chemical industry, in 1939 was started with discovery D. D. T several other chlorinated combination. In 1946 phosphorus compounds in America were introduced and in 1951, entered the market the first Carbamate combination. Following the investigation to find low-risk compounds, was introduced the first compound synthetic Thyroid Payro that was stable against light in 1973. Chitin Synthesis as the first inhibitor was registered in 1977 and finally the first insecticide from the group Emydha was introduced in 1990.General in the late 40th and 50th twentieth century was introduced a wide range of pesticides. In the decade of 60, expanded technology application of pesticides and in the 80s was introduced finally 90's, was stable the broader adoption decade development.

According to importance of pest control the provide food and health human society always have been searching more economical and less harmful ways to solve this problem. In fact, in the period after World War II, pesticides were a new and powerful tool for pest control. But as the only means of controlling the use of pesticides, has led to the emergence phenomena like resistance to certain pests and disease agents against pesticides along with adverse effects environment. Pesticides are named based on relatively pure chemical substance that is made in the factory and is called technical material. Technical material has been purified rather and containing 95% to 100% effective material. In most cases active ingredient cannot be directly applied against pests and should operations performed on it in order to practical use. The process of preparing is said formulation. Formulation is called to operation of the do on effective material until properties of the pesticide improve from storing, transport; application to be effective, influence stability and also health. Another reason for formulation of pesticides this is the in practice, a small amount effective material should be spread in many levels. Word Formulation in terms of commercial refers to the last step preparation of pesticides in factory and does not include taking steps like dilute pesticides by water. Investigated pesticides the Picloram (4 - Amino - 3, 5, 6 - Tryklrv - 2 - Pyridine carboxylic acid) a herbicide is that as extensive and widespread used for weed control in products sugar beets, rice, wheat and barley. Picloram is a herbicide containing pyridine that acts as a regulator's plant growth and as oksyn plant naturally are found in nature or like Indolaktyk acid hormone works that to prevent of protein synthesis. Generally Picloram for deciduous plants is more toxic than other grass and seeds. Picloram can remain active for a long time in soil the issue depends on the soil type and also to moisture and soil temperatures. Picloram as chemical is absorbed on clay particles and natural organic matter that naturally there are in soils, if the soil is poor the organic matter or clay Picloram may easily leak to surface and underground waters. According to the Institute for environmental Protection (EPA), maximum infection rate for Picloram in drinking water is 0.5 milligrams per liter.

MATERIALS AND METHODS

As we know absorption color combinations in the ultraviolet region and visible is measurable with the help device UV-Vis. Herbicide Picloram have NH2 groups in the para position (relative to the functional group COOH) According to the method Dey Azotasyvn by solution of sodium nitrite at Hydrochloric acid, turned to salt Dey Azvnyvm and then by using reagent solution at sodium hydroxide becomes to combination color with Dey Azo. For perform the test and ensuring formation colored product, test was performed this way that have taken approximately 5 ml of poison formula and it 1 ml from solution 15/0% Sodium Nitrite we add in the Hydrochloric acid in 0.36 M, after mixing, 1 ml of solution 0.5 percent Btanftvl at Sodium hydroxide was added 0.2 percent. Combinations colored obtained indicate that measurement it is possible to device spectrophotometer UV-Vis. Then with soluble 5 ppm standard Picloram, different experiments were performed with apply various reagents among Rezvrsynvl, Hydroquinone, 1,3,5 Tri-hydroxy benzene and Beta Nftvl holding constant the other solutions until first be determined type reagent. The measured absorption represents the absorption reagents paint maker at Sodium hydroxide 0.2 percent and water distilled twice, sample is included reagent solution at Sodium hydroxide 0.2 percent and witness solution containing 0.2 percent Sodium hydroxide in water distilled twice. Some of the samples were taken after putting in cell and cleaning the walls and then was read transfer cell to device absorption spectrophotometer and measurement absorption formed colors Dey azo, the sample was solution toxin 5 ppm Picloram along with solution sodium nitrite 0.02 percent in Hydrochloric acid, 1.6 percent and solution 0.02 percent reagent in Sodium hydroxide 0.2 percent. Witness in this experiment, is included solution water - Ethanol 50:50. It

609

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should be noted that total expenditure for absorption measurements must be such that involve two-thirds of the volume of the cell. In order to comparison and choose introducing and select the appropriate wavelength. Direction quantitative measurements of the absorption range of color reagent instrument and spectrum Dey azo colors from reaction were prepared with poison Picloram.
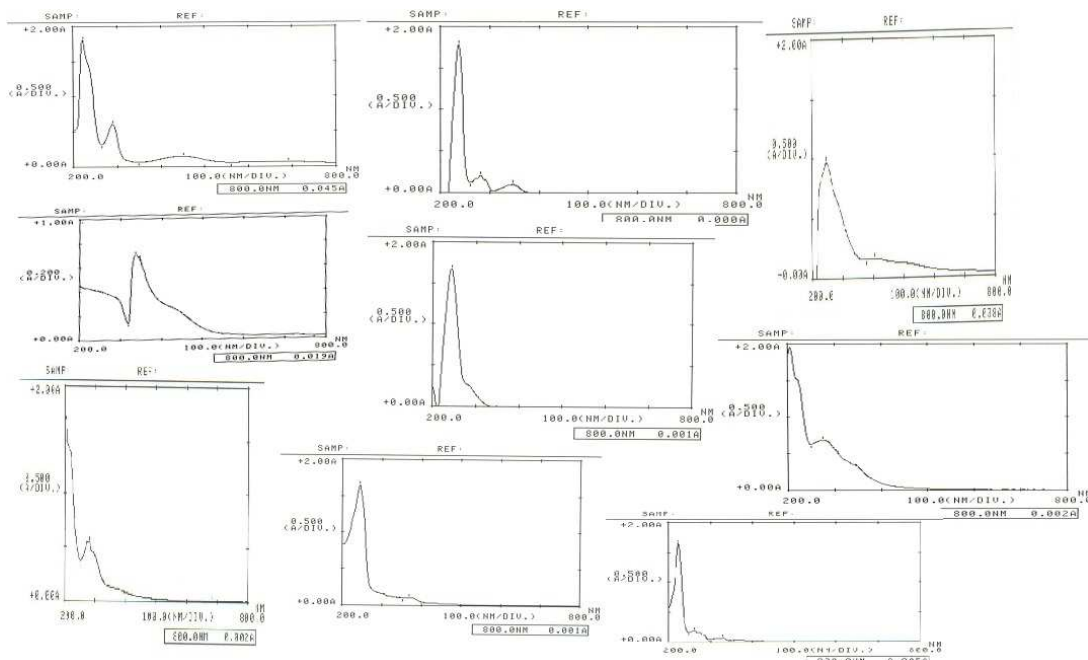

Fig. 1: Research findings

Standard solution Picloram 5 ppm with Sodium nitrite 0.02 percent in the Hydrochloric acid, percent and reagent N, N Dey Metil aniline 0.02 percent in the Sodium hydroxide 0.2 percent of between Referrers, reagent Beta Nftvl because less spectral interference and lack absorbed without herbicide Picloram was chosen in the desired district I.e. $\lambda = 405$.

Check the parameters and optimize conditions. For this purpose, the following parameters were evaluated: "Review effect of temperature on the reaction, Select the type of solvent, Determine the Optimize concentration reagent Beta Nftvl, The optimize concentration Sodium Nitrite, Set optimize concentration Sodium hydroxide, the optimize concentration hydrochloric acid".

Review effect of temperature on response Dey Azvtasyvn: All stages of preparation of soluble until mixture it is performed at constant temperature 30˚ C that as a result, fluctuations arising from temperature changes removed and calibration line obtained better and more accurate. Different temperatures examined of 27˚ C until about 40˚ C that results obtained has been similar in the temperature range 27˚ C until 30˚ C so in the ambient temperature namely 30˚ C is performed various stages of testing.

Select the type of solvent: Different solvents among Petroleum ether, acetone, ethanol, ethanol-water each one were examined with volume various and the best results was obtained when the was used of solvent Ethanol - water with concentration of 50: 50.Thus the fluctuations adsorption has been observed with other solvents, by using this solvent reduced to a minimum and was obtained desired results. So was used of Ethanol-water solvent 50: 50 and because of insoluble Picloram standard in water beginning desired concentration been solved Picloram standard in ethanol, then receipt to volume with water. For example to prepare100 Ml standard solution Picloram, beginning value and weighed of Picloram the standard resolved in 50 ml of ethanol and after with 50 ml double-distilled water. To volume was completed in balloon volume of 100 ml.

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Table 1: Check effect of Temperature on reaction Dey Azvtasyvn

Temperature	Density(ppm)	Absorption
°C 30- 27	1	0.01
	2	0.018
	3	0.025
	4	0.034
	5	0.041
35°C	1	0.01
	2	0.017
	3	0.014
	4	0.016
	5	0.013
40 °C	1	0.009
	2	0.011
	3	0.007
	4	-0.001
	5	0.012

Determination of optimal concentrations of reagents beta Nftvl: 10 ml of Picloram standard solution 9ppm produced in Ethanol-water solvent was mixed with 2 ml of sodium nitrite solution.0.02 percent at Hydrochloric acid, 1.6 percent after 2 minutes, stir in 2 ml of solution Beta Nftvl with different concentrations 0.01 to 0.03 percent Sodium hydroxide in 0.2 percent was added it absorption has been reported after 2 minutes stirring solution (Table 2, Figure 2).

Determine the optimum concentration of sodium nitrite: Solution 9 ppm of poison's Picloram provided in a suitable solvent namely ethanol -water was removed 10 ml of the above solution beginning 2 ml of sodium nitrite solution which was prepared by different concentrations of 0.01 to 0.03 percent in hydrochloric acid it was added to the 1.6 percent, stir after 2 minutes under 2 ml solution Btanftvl 0.02 percent Sodium hydroxide in 0.02 percent added to after 2 minutes that passed of stir the solution it has been reported absorption (Table 2, Figure 2).

Determine the optimal concentration of sodium hydroxide: Solution 9 ppm of poison's Picloram in a suitable solvent namely Ethanol-water provided,10 ml of the above solution beginning with 2 ml of sodium nitrite solution at Hydrochloric acid, 1.6 percent with optimal concentration of sodium nitrite in the previous step namely 0.02 percent mixed, after 2 minutes, after 2 min, stir in 2 ml solution 0.020 percent Btanftvl in sodium hydroxide with concentration of 0.1 to 0.3 percent was added to it and after 2 minutes, stir again, reported absorption (Table 2, Figure 2).

Determine the optimal concentration of hydrochloric acid Klryk: Soluble 9 ppm of poison's Picloram at suitable solvents namely Ethanol-water provided 10 ml of the above solution. Beginning with 2 ml of sodium nitrite solution with optimal concentration of 0.02 percent in hydrochloric acid was mixed with different concentrations of 1.31 to 1.97 percent, after 2 Minutes discovering Stir 2 ml Btanftvl soluble the optimum concentration of 0.02 percent in sodium hydroxide with optimum concentration namely 0.2 percent was added to it and stirring after 2 minutes re-uptake has been reported (Table 2, Figure 2).

Table 2: Absorption color Dey azo in wavelength 405 nm prepared

| Reagent Beta Nftvl in Sodyom 0.2 percent		Hydrochloric acid 1.6 percent		Sodium hydroxide in reagent 0.02 percent		Hydrochloric acid in sodium nitrite 0.02 percent	
Density Btanftvl (percent)	Absorption	Sodium nitrite concentration (percent)	Absorption	Sodium hydroxide concentration (percent)	Absorption	Hydrochloric acid concentration (percent)	Absorption
0.01	0.074	0.01	0.076	0.1	0.075	1.31	0.079
0.015	0.08	0.015	0.08	0.15	0.081	1.46	0.085
0.02	0.087	0.02	0.086	0.2	0.085	1.6	0.09
0.025	0.086	0.025	0.086	0.25	0.085	1.75	0.088
0.03	0.085	0.03	0.085	0.3	0.084	1.97	0.087

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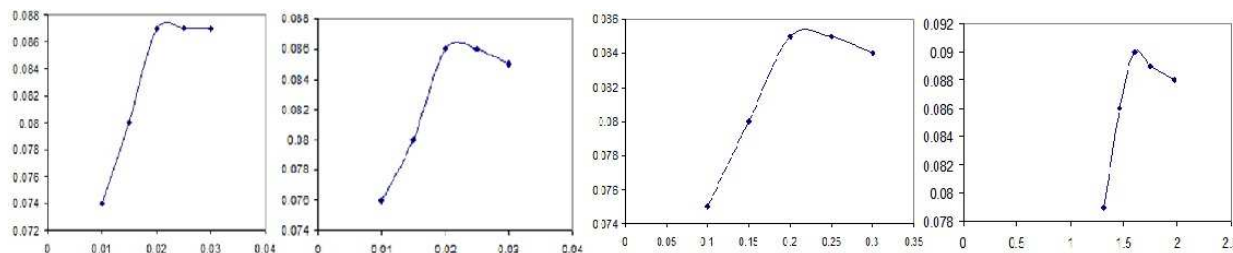
Figure 2: Absorbance changes color Dey azo according to concentrations

Draw the calibration curve: Solutions with various concentrations was prepared of standard Picloram.10 ml of each one of them beginning with 2 ml of 0.02 percent solution Sodium Nitrite at Hydrochloric acid 1.6 percent mixed and was stirred 2 minutes. Then 2 Ml of soluble 0.02 percent Beta Nftvl at Sodium hydroxide 0.2 percent was added to it the mixture was stirred for 2 minutes. About all concentrations used mentioned process was repeated and were obtained the following results (Table and Figure 3).

Table 3: Absorption color Dey azo in wavelength 440 nm prepared by various concentrations of the standard herbicide Picloram

Concentration of picloram standard (ppm)	Absorption	Concentration of picloram standard (ppm)	Absorption
1	0.01	9	0.091
2	0.018	10	0.093
3	0.025	11	0.1
4	0.034	12	0.124
5	0.041	13	0.128
6	0.045	14	0.13
7	0.066	15	0.131
8	0.073	-	-

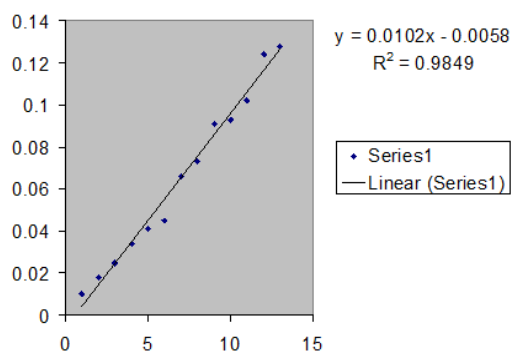$y = 0.0102x - 0.0058$
$R^2 = 0.9849$

Figure 3: Changes absorption color Dey azo according to concentration of standard Herbicides picloram in wavelength 405 nm

Table 4: Calculate the standard deviation of the slope and width of the source

C(X)	A(Y)	Yˆ	$(Y-Y\hat{})^2$	$(X_i-\overline{X})^2$	X_i^2
1	0.01	0.0044	$10^{-5} \times 3.1360$	49	1
2	0.018	0.0146	$10^{-5} \times 1.156$	36	4
3	0.025	0.0248	$10^{-8} \times 4$	25	9
4	0.034	0.035	$10^{-6} \times 1$	16	16
5	0.041	0.0452	$10^{-5} \times 1.764$	9	25
6	0.045	0.0554	$10^{-4} \times 1.081$	4	36
7	0.066	0.0656	$10^{-7} \times 1.6$	1	49
8	0.073	0.0758	$10^{-6} \times 7.84$	0	64
9	0.091	0.086	$10^{-5} \times 2.5$	1	81
10	0.093	0.0962	$10^{-5} \times 1.024$	4	100
11	0.102	0.1064	$10^{-5} \times 1.936$	9	121
12	0.124	0.1166	$10^{-5} \times 5.476$	16	144
13	0.128	0.1268	$10^{-6} \times 1.44$	25	169
14	0.13	0.137	$10^{-5} \times 4.9$	36	196
15	0.131	0.1472	$10^{-4} \times 2.624$	49	225

612

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$Y = 0.0102X - 0.0058$

$$S_{\frac{y}{x}} = \sqrt{\frac{\sum(Y - \hat{Y})^2}{n-2}} \rightarrow S_{\frac{y}{x}} = 0/00679$$

$$S_b = \frac{S_{\frac{y}{x}}}{\sqrt{\sum(x_i - \bar{x})^2}} \rightarrow S_b = 0/0004 \qquad \%RSD_{Slop} = \frac{4\times10^{-4}}{1/02\times10^{-2}}\times100 = 3/9\%$$

$$S_a = S_{\frac{y}{x}}(\frac{\sum x_i^2}{n\sum(x_i - \bar{x})^2})^{\frac{1}{2}} \rightarrow S_a = 5/69\times10^{-4} \qquad \%RSD_{Intercept} = \frac{5/69\times10^{-4}}{0/0058}\times100 = 9/8\%$$

The limit of detection and limit of Quantification: The detection limit indeed minimum concentration that an analytical method. Is capable to know it and is equal to three times the standard deviation control signal division on slope of the calibration curve. Small extent of also is equal to tenfold standard deviation control signal division on slope of the calibration curve.

Standard deviation of the control: Solution containing10 ml of ethanol-water solvent was prepared with 2 ml of solution of 0.02 percent Sodium Nitrite at Hydrochloric acid, 1.6 percent and 2 ml of 0.02 percent reagent Beta Nftvl at Sodium hydroxide 0.2 percent, and required volume of the above solution after transfer to both cell blank and sample, was placed in the UV-Vis spectrophotometer and its uptake was reported in other words, in both cell blank and sample, control solution located and this action was repeated 13 times the results are reported In the Table 5.

Table 5: Absorption observed the determination standard deviation witness

Visit Times was conducted	Absorption observed	Visit Times was conducted	Absorption observed
1	0.001	8	0.091
2	0.001	9	0.093
3	0.001	10	0.1
4	0.001	11	0.124
5	0.001	12	0.128
6	0.001	13	0.13
7	0.001	-	-

$\bar{A} = 0.00138 \quad \rightarrow S_b = 5.05\times10^{-4}$

$Y = 0/0102 X - 0/0058 \xrightarrow{} m = 0/0102$

Detection limit $= \dfrac{3Sb}{m} \xrightarrow{Sb=5.05\times10^{-4}}$ Detection limit $= 0.148$ ppm

Limit of quantifying $= \dfrac{10Sb}{m} \xrightarrow{Sb=5.05\times10^{-4}}$ Limit of quantifying $= 0.495$ppm

Determining the percentage Recovery in the real examples: To determine percent recovery examined samples of corn, barley and formulated Pesticides, in two separate containers of wheat weighs 15 grams and the sample container, 10 ml of solution 9 ppm standard picloram and within the control water, add 10 ml of ethanol after evaporation of both solvents contained within the washed with 10 mL of solvent after shave solution to 2 ml of 0.02 percent Sodium Nitrite at Hydrochloric acid, 1.6 percent added stir after 2 minutes. 2 ml of 0.02 percent Btanftvl at Sodium hydroxide 0.2 percent of added after stirring again the absorbance was measured by Spectrophotometer. Also about Barley was repeated the above steps.

$Y = 0/0102 x - 0/0058$, Related to corn $Y= 0.006$, $X = 9$

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Percent recovery $\dfrac{\text{Concentrations obtained}}{\text{The actual concentration}}$

Percent recovery poison's Picloram of corn= $\dfrac{9}{9} \times 100 = 100$

Percent recovery poison's Picloram of corn= $\dfrac{9}{9} \times 100 = 100$

$\dfrac{9}{9} \times 100 = 100 =$ Percent recovery poison's Picloram of barley and $= 9 \quad \rightarrow x = 0.006$, Y Related to barley

$\dfrac{15.3}{15} \times 100 = 102\% =$ Percent recovery formulated poison and $15.3 \rightarrow$ x= 0.013 =Y Related to formulated poison

RESULTS AND DISCUSION

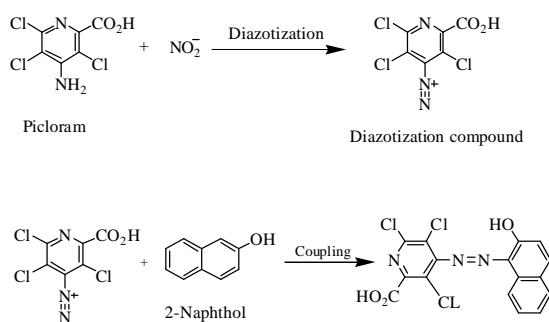After selecting reagents, reaction Dey Zvtasyvn done as follows:

Figure 4: Diazotization compound

To do reaction Dey azo Tasyvn, reagent consumption should be with conjugate .Because of was used Nftvl beta reagent, 1, 3, 5 Tri-hydroxy benzene, Hydroquinone, Rzvrsynvl and N, N-dey imethyl aniline that due to link conjugated benzene ring, accumulation of electron cloud has been high in there and well can by Picloram that due to department of killer electrons COOH on the benzene ring, accumulation of electron cloud is low it do reactions to Dey AZvtasyvn. Figure 12, shows the structure of the reagent.
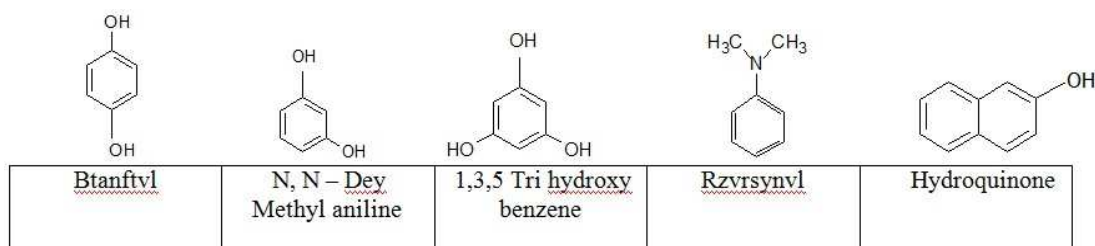

Figure 5: Structure reagent consumption

As can be seen in Figure 5, based on the way exposure OH on the benzene ring in mentioned reagents expected be created of reaction between salt Dey AZvnyvm and reagent Rzvrsynvl two products a hydroquinone product Btanftvl a product, 1,3,5 Tri-hydroxy benzene a product.

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Due to the high absorption observed related to the composition of the reaction reagents 1,3,5 tri hydroxy benzene the herbicide Picloram in the 405 nm region, Also monoculture being the represents in response Dey Azvtasyvn, expected reagent 1,3,5 tri hydroxy benzene is appropriate reagent for the reaction but seeing the range of dye maker, 1,3,5 Tri-hydroxy benzene (Figure 4) showed this represents a high absorption in the 405 nm region and comparison the Figure 8 was determined uptake observed in the 405 area. Not related to colors Dey azo formed in the presence of Picloram.

The View spectrum related to reagents paint Maker Hydroquinone and Rzvrsynvl without the presence Picloram in district 405 nm was determined mentioned reagents also have high absorption rather in this area. So Btanftvl because less spectral interference and lack absorption reagent paint maker Btanftvl in district 405 nm, was chosen as reagent consumption. In the study area, maximum absorption were obtained in district 388 nm but to eliminate the interference spectrum, district 405 nm because less spectral interference and also having high absorption in level comparison the absorption views in district 388 nm, was chosen as the area studied to selecting suitable solvent was tested different solvents:

Petroleum Solvent Ether, acetone: In the use of this solvent two phases were observed that after adding a solution of sodium nitrite at Hydrochloric acid and reagent solution at Sodium hydroxide, disconnect the upper phase and reported its absorption. But a fluctuation is seen in absorption that to remove these oscillations do as follows: After adding Sodium Nitrite to Picloram solution in petroleum ether, acetone, isolated the upper phase and was added to it reagent solution at Sodium hydroxide but was not obtained combination colored because after adding Sodium Nitrite to Picloram solution is obtained combine pregnant Salt Dey Azvnyvm that goes into the water phase and since in the organic phase was separated was not. Salt Dey Azvnyvm that in the presence reagent be achieved combination colored Dey labeled azo, has not been observed colour of product. The other method to remove the fluctuations observed in the absorbance, this was instead solution reagent in the sodium hydroxide was used of reagent solution in the water in other words, Sodium hydroxide was removed because was probability Sodium hydroxide hydrogen the COOH in the Picloram has attracted and will cause disruptions in response but with this change, was not obtained colour of product. Based on was determined reagent consumption should be prepared in the solution Sodium hydroxide.

Ethanol solution, after use of single-phase solvent ethanol mentioned fluctuations was less than in absorption but was seen always.

Water-ethanol solution: the ratio of 50:50, because being insoluble Picloram herbicides in water beginning Picloram the in certain volume of ethanol resolved and then with volume against ethanol consumption we raise the volume by using double-distilled water. In use of this solvent reached to minimum swing adsorption. Therefore, the solvent was chosen as solvent consumption.

The limit of detection and limit of quantifying: The limit of detection, indeed minimum concentration that an analytical method. Is able to recognize it? For determination the detection limit and limit quantifying the, as the in Section calibration chart drawing was expressed of the optimal concentration Sodium Nitrite in hydrochloric and reagent at Sodium hydroxide was used with different concentrations Picloram in both cell blank and sample, control solution was placed and absorbance called this process was repeated 13 times the results obtained this has been done:

$\overline{A} = 0.00138 \quad \longrightarrow \quad Sb = 5.05 \times 10^{-4}$

$Y = 0/0102\ X - 0/0058 \quad \longrightarrow \quad m = 0/0102$

The detection limit $= \dfrac{3Sb}{m} \xrightarrow{\ Sb = 5.05 \times 10^{-4}\ }$ the detection limit = 0.148 ppm

Limit of quantifying $= \dfrac{10Sb}{m} \xrightarrow{\ Sb = 5.05 \times 10^{-4}\ }$ limit of quantifying = 0.495 ppm

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To determine the percentage of recycled was of the actual examples Barley, maize, and herbicide formulation in determining the percentage of recycled is discussed in real samples. The results are as follows:

Percent recycled corn = 100%
Percent recycled Barley = 100%
Percent recycled venom Formulated = 102%

With performance experiments have been in this project, it was determined that to measure residual herbicides Picloram you can use of method UV-Vis spectroscopy that unlike methods that were previously used such as: Square wave volt meter, HPLC, GC, SPME-GC-MC and etc. It is a way cheap, simple and yet applied this method to measure other residual herbicides among Kobeks also in real samples, be used with changes represent and solution concentrations of consumed and expected for other herbicides from this category, Also might have necessary performance.

REFERENCES

[1] J. Shah, M. Rasul jan, N. Bashir, *Anal. Sci.*, 22, **2006**, 145.
[2] I. SuBova, A. K. Assandas, M. C. Icardo, J. M. Calatayud, *Anal. Sci.*, 22, **2006**, 21.
[3] Y. pico, R. Rodriguez, J. Manes*, Trends Anal. Chem.*, 22, **2003**, 133.
[4] K. Maastovska, S. J. Lehotary, *J. Chromatogr. A*, 926, **2001**, 291.
[5] H. Li, J. Li, G. Li, J. Jen, *Talanta*, 63, **2004**, 547.
[6] L. L. Atrache, S. Sabbh, J. P. Morizur, *Talanta*, 65, **2005**, 603.
[7] P. Mikus, I. Valaskova, E. Havrank, *Talanta*, 65, **2005**, 1031.
[8] J. Zhang, Z. Hu, X. Chen, *Talanta*, 65, **2005**, 986.
[9] X. Yang, X. Wang, X. Zhang, *J. Sep. Sci.* , 29, **2006**, 677.
[10] K. Swinney, J. Pennington, D. J. Bornhop, *J. Microchem.*, 62, **1999**, 154.
[11] H. J. Issaq, G. M. Janini, K. C. Chan, T. D. Veenstra, *J. Chromatogr. A*, 1053, **2004**, 37.
[12] S. Hu, M. Zhang, D. Pang, J. Cheng, *Anal. Sci.*, 16, **2000**, 807.
[13] X. Cheng, Q. Wang, S. Zhang, W. Zhang, P. He, Y. Fang, *Talanta*, 20, **2006**, 115.
[14] Z. Pawlicova, J. R. Garcia, I. Sahuquillo, M. C. Icardo, J. M. Calatayud, *Anal. Sci.*, 22, **2006**, 29.
[15] M. P. Macro, D. Barcelo*, Meas. Sci. Technol*., 7, **1996**, 1547**.**
[16] T. Sun, J. Jia, D. ZHong, Y. Wang, *Anal. Sci.*, 22, **2006**, 293.
[17] M. Losito, I. Zambonin, *Anal. Chem.*, 71, **1999**, 1366.
[18] C. liang, H. peng, L. Nie, S. Yao, *Anal. Chem.,* 367, **2000**, 551.
[19] J. F. Huertas, M. O. Iruela, A. M. Garcia, A. Gonzalez, A. Sanchez, *J. Chromatogr. A*, 1102, **2006**, 280.
[20] G. S. Nunes, D. Barcelo, *Analysis Magazine*, 26, **1998**, 156.
[21] M. Hakkarainen, *J. Chromatogr. A*, 1010, **2003**, 9.
[22] T.P. Ruiz, C. M. Lozano, V. Tomas, J. Martin, *Anal. Chim. Acta*, 514, **2003**, 259.
[23] M. chicharro, A. Zapardiel, E. Bermejo, A. Sanchez, R. Gonzalez, *Electroanalysis,*16, **2004**, 311.
[24] K. Mervartova, J. M. Calatayud, M. C. Icardo, *Anal. Lett.*, 38, **2005,** 179.
[25] X. Yang, X. Wang, X. Zhang, *J.sep. sci*., 29, **2006**, 677.
[26] T. Sun, J. Jia, N. Fang, Y. Wang, *Anal. Chim. Acta*, 530, **2005**, 33.
[27] L. L. Atrache, S. Sobbah, J. P. Morizur, *Talanta*, 65, **2005**, 603.
[28] S. Rossi, A. P. Dalpero, S. Ghini, R. Colombo, A. G. Sabatini, S. Griotti, *J. Chromatogr. A*, 905, **2001**, 223.
[29] K. C. Ting, P. J. Kho, J. Assoc, *Off. Anal. Chim.,* 74, **1991**, 991.
[30] C. H. Marvin, I. D. Brindle, C. D. Hall, M. Chiba, *Anal. Chem.*, 62, **1990**, 1495.
[31] M. L. Jeong, D. J. Chesney, *Anal. Chim. Acta*, 389, **1999**, 53.
[32] C. S. Brunete, A. Rodriguez, J. L. Tadeo, *J. Chromatogr. A*, 1007, **2003**, 85.
[33] M. Kochman, A. Gordin, P. Goldshlag, S.J. Lehotay, A. Amirav, *J. Chromatogr. A*, 974, **2002**, 185.
[34] J. Wu, C. Tragas, H. Lord, J. Pawliszyn, *J. Chromatogr. A*, 976, **2002**, 357.
[35] J. Slobodnik, S. J. Oussoren, M. E. Jager, M. Honing, B. L. Baar, U. A. Brinkman, *Analyst*, 127, **1996**, 1327.
[36] J. M. Nogueira, T. Sandra, P. Sandra, *J. Chromatogr. A*, 996, **2003**, 133.
[37] Y. Ni, P. Qiu, S. Kokot, *Anal. Chim. Acta*, 537, **2005**, 231.
[38] P. Mikus, I. Valaskova, E. Havranek, *Talanta*, 65, **2005**, 1031.
[39] L. B. Santos, J. C. Masini, *Talanta*, 72, **2007**, 1023.
[40] K. D. Pawar, S. P. Joshi, S. R. Bhide, S. R. Thengane, *J. Biotechnology*, 130, **2007**, 346.