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Clean up Determination of Paraquat Residue in Oil Matrix Method

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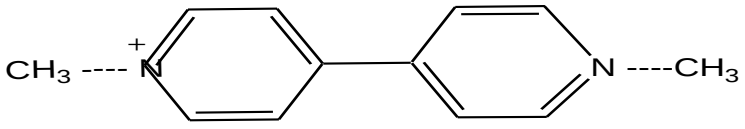
ABSTRACT

The experiment was to evaluate the feasibility of the method in determination of paraquat residue in palm oil and palm oil product. The method involved three steps: extraction of residue from the oil, clean up procedure using one type of resin, amberlite and spectrophotometric determination of the purified material. Using amberlite with glucose, the percentage recoveries were greater than 90% for 0.01 µg ml^{-1} level of concentration. The method with the use of Amberlite resin in the clean up step can give better recoveries of the analyze. Beer's law is obeyed over the concentration range of 0.5 – 15 µg of paraquat per 25 mL of the final solution (0.02 – 0.6 ppm) at 600 nm. The molar absorptivity and Sandell's sensitivity were found to be $2.2X10^4 \pm 100$ l mol^{-1} cm^{-1} and 0.004 µg cm^{-2} respectively. The method is highly reproducible and has been applied to determination of paraquat in environmental samples.

Keywords: Paraquat, Amberlite, Spectrophotometry, Palm oil, Glucose and environmental samples etc.

INTRODUCTION

Paraquat (1, 1' – ethylene – 2, 2' bipyridylium ion) is extensively used herbicides. These herbicides have achieved great prominence because of their wide spectrum of activity against grasses as well as most broad – leaved weed species[1, 2] Paraquat causes ' Paraquat lungs' in which honeycombing of the lungs and hardening of breathing tracts occurs due to development of pulmonary fibrosis caused by retention of the ions in lungs in men[3].



Bipyridium ion

The Commercial form of this ion is dichloride and di – (methyl paraquat dichloride sulphate) sold under the teade name of Grammoxone. It is a colourless crystalline solid, which is very soluble in water. The wide usage, occurrence in the plant kingdom and high toxicity of paraquat together with its advantages over other herbicides have necessitated the development of a sensitive and selective method for the determination of paraquat herbicide[4].

Because of the wide applicability and high toxicity of paraquat harbicide, numerous instrumental methods have been described for their detection/determination, such as, high-performance liquid chromatography[5], thin layer chromatography[6], AFSD[7], UV spectroscopy[8], polarography[9] and solid sorbent system[10] etc. The available spectrophotometric methods [11-14] are based on measurement of the reduced ion obtained by the reduction of paraquat with alkaline glucose solution.

In this paper, the method used for paraquat analysis is an adaptation of the Imperial Chemical Industry (ICI) United Kingdom method for oil containing crops such as rapeseed, sunflower seed, olives and grain, vegetables, fruits and others. The method involves a cation exchange clean up and reduction of paraquat by glucose and a free radical with an intense blue colour which absorbs strongly at 600 nm. Beer's law is obeyed over the concentration range of 0.5 – 15 µg of paraquat per 25 ml of the final solution (0.02 – 0.6 ppm) at 600 nm. The molar absorptivity and Sandell's sensitivity were found to be $2.2X10^4 \pm 100$ l mol $^{-1}$ cm $^{-1}$ and 0.004 µg cm $^{-2}$ respectively. The objective of this investigation was to study the suitability of this method for the determination of paraquat residues in oil using cationic exchange resins.

MATERIALS AND METHODS

Materials : The column for cation exchange resin chromatography consisted of a 25 mL glass burette packed with suitable resin, i.e., Amberlite IR – 120, each with mesh size of 14 – 52, partical diameter 0.3 – 1.18 mm. The reagents used were 98% concentrated sulphuric acid (Merck, Germany) sodium chloride AR grade (Merck, Germany), ammonium chloride AR grade (Merck, Germany), standard paraquat dichloride(Indian Explosive, India) 98% purity, glucose 0.2% (w/v) in 0.3 M sodium hydroxide and octan-2-ol AR grade (Merck, Germany) as anti-foaming agent Fig 1.

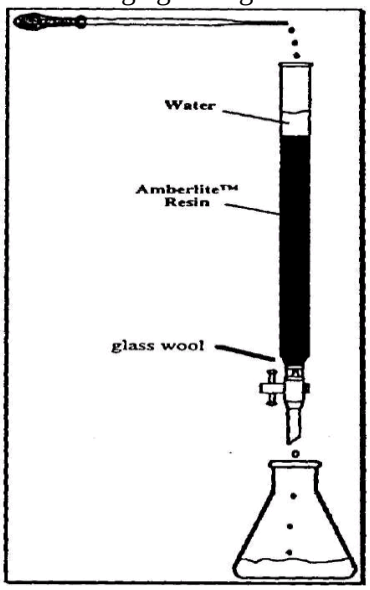


Fig. 1 Amberlite IR – 120

Apparatus: Heating was carried out using an electro thermal heating mantle of two liters capacity to hold a one liter round-bottom boiling flask fitted with a water – cooled reflux condenser. A Systronic

spectrophotometer model-104 and pH meter model 335 was used for pH measurements. A Remi C-854/4 clinical centrifuge force of 1850 g with fixed swingout rotors was used for centrifugation.

Paraquat standard and working standard solutions: A stock solution of 1mg mL^{-1} was prepared in saturated ammonium chloride solution. Working standard solution was prepared by appropriate dilution of the stock standard solution with saturated ammonium chloride solution.

Preparation of sample: 50 g of oil were placed in a one liter boiling flask, than 250 mL water and 25 mL of concentrated sulphuric acid was added. Some anti – bumping granules and 1 mL of octan - 2 - ol were also added. Contents of the flask (with a reflux condenser attached) were heated on a heating mantle. Occasionally, the flask was swirled to minimize localized overheating until the solution started to boil. After the solution was boiled for five hours and it was allowed to cool. The condenser was rinsed with 50 mL water and the solution transferred into a one liter separating funnel. The oil layer was then separated from the aqueous solution.

Preparation of ion-exchange column for clean up procedure: The ion-exchange column was prepared by filling with a slurry containing 3.5 gm of resin in water into a 25 mL burette. The resin was washed successively by eluting it with 20 mL saturated sodium chloride solution and then with 50 mL water at the rate of 5 mL min^{-1}. The aqueous sample solution was then allowed to percolate through the resin column was then washed successively with the following solution at a rate of 3-4 mL min^{-1}. (1.) 25 mL water, (2.) 100 mL 2.5% (w/v) ammonium chloride solution), and (3.) 25 mL water.
The paraquat was then eluted from the column with saturated ammonium chloride solution at a flow rate of about 1 ml min^{-1}. The first 50 ml were collected in a 50 mL volumetric flask. One sets of experiment using one type of resin for the clean up procedure were carried out.

Spectrophotometric measurement: 10 mL of eluent were pipetted into a test tube. 2 mL of 0.2 % glucose were added and the solution was mixed by gently inverting the tube once or twice. A portion was placed in a 1.0 cm cell and the absorbance at 600 nm was recorded. A blank (10 mL saturated ammonium chloride) was treated in the same way as the sample and its absorbance was recorded. The actual absorbance of the analyze was the difference between absorbance of the sample and that of the blank **fig 01**.

Calibration Curve: The 5 µg ml^{-1} of working standard was diluted accordingly with the appropriate volumes of saturated ammonium chloride solution to obtain solutions containing paraquat in the range of 0.1 to 2 µg mL^{-1}. These solutions were then treated with glucose and their absorbance values at 600 nm were recorded. A calibration curve of the absorbance at 600 nm of the solutions against the concentrations of paraquat (µg mL^{-1}) was drawn **fig 2and 3.**

Recovery studies: Palm olein, previously analysed and found to be free of paraquat residue was fortified with 0.05-2.00 µg ml^{-1} of paraquat solution was made, 10 µg ml^{-1} working standard solution. Experiments carried out using the spiked palm olein. All the samples were subjected to extraction, clean up procedure and spectrophotometric determination. The clean up procedure for experiment was performed using Amberlite was used.
The concentration of paraquat in the oil sample (µg gm^{-1}) was calculated as follows:

$$\frac{\text{Volume of elute from column (mL)}}{\text{Weight of sample (g)}} \text{X Concentration in elute (µg } mL^{-1})$$

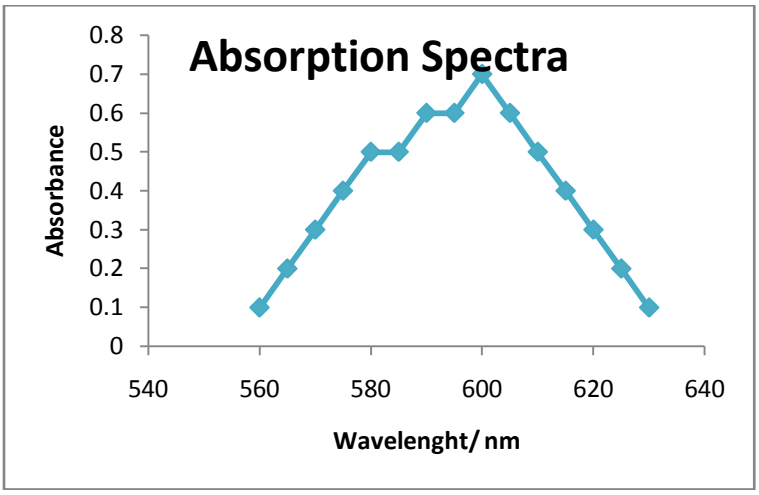


Fig 2 : Absorption Spectra of paraquat

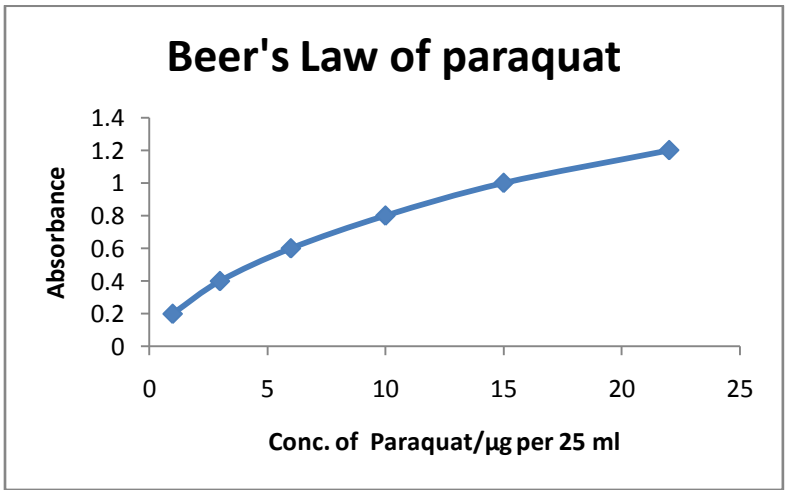


Fig 3. Beer's Law of paraquat

Time and Temperature: A period of 2 min was sufficient for reduction and full colour development. The most suitable temperature range for the reaction was between 20 and 30^{0}C as this was the range in which maximum colour development occurred. Outside of this temperature range the absorbance value was found to decrease.

Effect of Foreign Species: The effect of various interfering co-pollutants and pesticides was studies in other to assess the validity of the method. Known amount of metal ions and pesticides were added to the sample solution. Those metal ions that formed hydroxides such as Fe^{3+} and Al^{3+} interfered with the method owing to precipitation in the basic solution; this can be prevented by the addition of 1 ml of 5% EDTA solution prior to the addition of the NaOH solution. The tolerance limits (in ppm) for various foreign species in a solution containing 10 µg of parquat per 25 mL are given in table 1.

Table -1. Effect of foreign species. Concentration of paraquat, 10 µg per 25 mL of solution.

Foreign species	**Tolerance limit**** (ppm)
2, 4-D, 2, 4, 5, -T, DDT	2000
Parathion, BHC	1400
Pb^{2+} , Monocrotophos	1000
Ca^{2+}, Al^{3+}, Fe^{2+}, *Fe^{3+}, Kelthane	850
Zn^{2+}, Cd^{2+}, Mg^{2+}, PO_4^{3-}	500
Benzene, Methyl alcohol	350
*Cu^{2+}, SO_4^{--}, NO_2^- , NO_3^-	200
Benzene, Toluene	80

* Amount tolerated with 1 ml of EDTA solution added. **Amount tolerated can vary by ± 2%.

Determination of paraquat in water: River water samples, which received run off water from agricultural field, were collected. These samples were filtered through a Whatman No. 40 filter paper. Aliquots of water sample containing paraquat was passed through the column at a flow rate of 7 - 8 mL min^{-1}. The paraquat was absorbed on the silica gel and was subsequently eluted by the passing 50 ml of saturated ammonium chloride through the column at a flow rate of about 3 mL min^{-1}. The eluted paraquat was collected in a 50 mL calibrated flask. The volume was made up to the mark de- ionized water and paraquat was determined by proposed method (Table 2).

Determination of paraquat in grain samples: Various samples of wheat and rice each of 20 gm were taken, collected from agricultural field, where paraquat had been sprayed as an insecticide. The samples were weighted, crushed and homogenized, then filtered by adding 250 ml of water. The filtrate was placed in a 500 mL separating funnel and then allowed to pass through the silica gel column at flow rate of 7 – 8 mL min^{-1}. The column was washed with 25 mL of water and the paraquat absorbed on the silica gel was eluted with 50 mL of saturated ammonium chloride at a flow – rate of about 3 mL min^{-1}. The eluted paraquat was collected in a 50 mL calibrated flask. The volume was made up to the mark with de – ionized water and paraquat was determined by proposed method (Table 2).

Table 2. Recovery of paraquat from water, grain and plant materials.

Samples	Paraquat originally found*(µg) Proposed method (a)	Paraquat added / µg (b)	Total paraquat found * (c)	Difference (c-a)	Recovery % (c-a)/b x 100
Agricultural waste water [a]	8.0 11.5 21.0	12 24 48	19.50 34.50 66.50	11.50 23.50 45.50	95.83 95.83 94.79
Wheat [b]	11.0 15.0 16.0	12 24 48	22.40 38.33 63.80	11.40 23.33 47.80	95.00 97.20 99.50
Rice[b]	10.0 13.0 15.0	12 24 48	21.30 36.00 59.90	11.30 23.00 44.90	94.16 95.83 93.54
Potato[b]	7.0 13.0 16.0	12 24 48	18.40 36.60 61.30	11.40 23.60 45.30	95.00 98.33 94.37
Grass[b]	8.0 14.0 15.0	12 24 48	19.70 37.00 60.30	11.70 23.00 45.30	97.50 95.80 94.30

* Mean of three replicate analyses
a Sample collected from agricultural field
b Sample collected from different field.

Determination of paraquat in plant materials: Samples of potato and grass were collected from agricultural fields that had been treated with paraquat. The samples were macerated and homogenized in a mixer. Water (150 mL) was added in order to macerated the vegetables and the mixture was filtered through a buchner funnel. The resulting solution was filtrated using a vaccum pump and the filtrated was collected. The residue was washed with two 100 mL portions of water. The combined filtrated was placed in a 500 ml separating funnel and then allowed to pass through the silica gel column at a flow - rate of 7 - 8 mL min^{-1}. The column was washed with 25 mL of water and the paraquat absorbed on the silica gel was eluted with 50 mL of saturated ammonium chloride at a flow - rate of 3 - 4 mL min^{-1}. The eluted paraquat was collected in a 50 mL calibrated flask. The volume was made up to 50 mL with de - ionized water and parquat was determined as described above. In order to establish the validity of the method, different samples of water, grain and vegetables were taken. To these samples known amounts of paraquat were added and the solution analysed by using the proposed method. The recoveries ranged from, which is in agreement with the reported method. (Table 2).

RESULTS AND DISCUSSION

The spectrophtomeric method for analysis for the determination of paraquat residue in environmental materials. In this method, sulphuric acid was used to free the paraquat from the absorbed or bound state, followed by clean up through a resin column. In this experiment, the method was used to determine paraquat residue in palm oil.

Recovery results using Amberlite: Two levels of concentration, 0.05 and 0.5 µg g^{-1} of parquat, were evaluated to test suitability of Amberlite IR –120 resin in the determination of paraquat residue in palm olein. The recovery of paraquat using Amberlite was nearly quantative, as can be seen in table 3. For a concentration of 0.05, the recovery was 98.5% and for 0.50, the recovery was 99.7%.

Table 3. Recovery of paraquat residue using Amberlite resin.

N = 4, R^2 = 0.9998, Slope = 0.4520 (± 0.0055)

Spiked samples (µg gm^{-1})	Absorbance at 600nm*	Amount found (µg gm^{-1})	Recovery (%)	Average (%)	S. D.	C. V. (%)
0.05	0.035	0.0490	98.0	98.5	6.03	6.53
0.05	0.033	0.0488	97.8	-	6.35	6.47
0.50	0.234	0.4910	98.2	99.7	0.84	0.86
0.50	0.248	0.4960	99.2	-	0.97	0.96

* Mean of two with three reading for each sample.
S. D = Standard Deviation
C. V = Calculated Value

APPLICATIONS

Paraquat is ionic and cannot be extracted with organic solvents. Owing to its polar nature, it is readily absorbed by plant materials and is difficult to remove. For the determination of paraquat in water, grain and plants materials, a silica gel column was used to separate paraquat from the samples.

CONCLUSIONS

The resin Amberlite IR –120 can be used to clean up procedure for paraquat and recovery was also more consistence for this resin. The herbicides paraquat can be determined down to a level of 0.02 ppm in water and grain samples by using the proposed method. The method was applied to the determination of paraquat in water, grain and plant samples by oil matrix method.

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