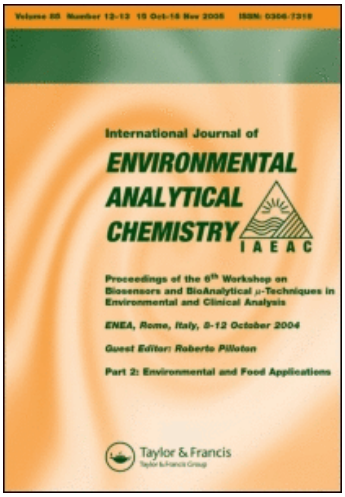

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A NEW SOLID SORBENT SYSTEM FOR RAPID MONITORING OF PARAQUAT AND DIQUAT

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A new solid sorbent system is developed for the monitoring of paraquat and diquat in the environment. The reagent system for the indicator tube consists of glucose and sodium hydroxide impregnated over silica gel and a humectant calcium chloride. This reagent system has also been used for the preparation of reagent paper. Glucose is used here as a very good reducing agent for the reduction of paraquat/diquat in an alkaline medium to give a stable blue coloured free radical ion. After exposing the indicator tubes and test paper to paraquat and diquat for a constant time, the blue colour developed could be compared with those obtained from standards. Alternatively the coloured compound was extracted in water and measured at 600 nm. The lower limit of detection is 0.1 μgm^{-3} and 0.5 μgm^{-3} of paraquat and diquat, respectively, for the reagent papers and indicator tubes. The lower limit of determination by spectrophotometric procedure is 0.5 μgm^{-3} and 1 μgm^{-3} of air for paraquat and diquat respectively. The preparation of indicator tubes, test papers and their applications for the detection and determination of paraquat and diquat in air, biological and food samples is described in this paper.

Keywords: Paraquat; diquat; solid sorbent system; spectrophotometry; biological samples

INTRODUCTION

Paraquat (1,1′ dimethyl-4,4′ bipyridylium ion) and diquat (1,1′-ethylene-2,2′ bipyridylium ion) are 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] Both paraquat and diquat are toxic to man, the former being implicated in many deaths.[3] Paraquat causes 'Paraquat lungs' in which honeycombing of the lungs and hardening of breathing

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tracts occurs due to development of pulmonary fibrosis caused by retention of the ions in lungs, while diquat produces "Parkinsonism" in man.[4]

Because of their toxicity and significance several methods based on different analytical techniques have been reported for the determination of paraquat and diquat, i.e. Automatic continuous flow spectrometry,[5,6] SPE,[7] RIA,[8] HPLC,[9,4] liquid chromatography,[10] spectrophotometry,[11–16] etc. Many of the earlier reported spectrophotometric methods are less sensitive and suffer from poor dye stability.[12–15]

A brief literature survey was carried out, very few solid sorbent systems are reported for their monitoring.[5]

In the present paper a new solid sorbent system is proposed for the rapid monitoring of paraquat and diquat in the environment. The reagent system for the indicator tube consists of glucose and sodium hydroxide impregnated over silica gel and a humectant. The reagent system was also used for the preparation of test papers. After exposing the indicator tubes and test paper to paraquat and diquat for a constant time, the blue colour developed was extracted in water and measured at 600 nm. The advantage of the method is mainly its sensitivity, easy availability of glucose as a simple, inexpensive and nontoxic reducing agent and the greater stability of the blue radical ion. The method has been applied for the detection and determination of paraquat and diquat in air, biological and food samples.

EXPERIMENTAL

Apparatus

A Carl Zeiss spekol with 10 mm matched silica cells was used for all spectrophotometric measurements. 35 ml midget impingers and PIMCO calibrated rotameters were used for air sampling.

Reagents

All chemicals used were of AnalaR grade. Double distilled deionized water was used throughout the study.

Paraquat: Supplied by ICI India Limited: Stock solution of 1 mg/ml in water.

Diquat: Supplied by Fluka Chemical Company, Switzerland: Stock solution of 1/mg/ml in water.

Silica gel: BDH (100–200 mesh).

Ethylenediaminetetraacetic acid disodium salt (EDTA): 1% aqueous solution. Saturated ammonium chloride solution.

Preparation of reagent: 1 g of each glucose and sodium hydroxide were taken in a 25 ml beaker and to it 10 ml of water were added. Then 1 ml of 10% calcium chloride (humectant) was added and stirred with glass rod. This reagent was used for the preparation of indicator tubes and test papers.

Preparation of impregnated silica gel: 3 g of silica gel was mixed with 5 ml of the reagent solution. This impregnated silica gel was ready to be filled in the indicator tubes.

Preparation of indicator tubes: Well cleaned and dried graduated glass tubes size 6 × 0.5 c.m. I.D. were taken and one end was plugged with glass wool ~2 c.m. Then the dried reagent impregnated silica gel was filled to another 2 c.m. length and the remaining part of the tube was filled with glass wool. The both ends of tubes were sealed. These tubes were then kept in a desiccator.

Preparation of test papers: Whatman filter paper No. 1 was cut into strips of size 5 × 2 c.m and dipped in the reagent solution. Then the strips were taken out and dried for 1 hr in a snap action thermostat maintained at ~40°C.

Procedures

Procedure with Indicator Tubes

Prior to estimation of paraquat and diquat the sealed ends of the indicator tube were cut and one end of it was connected to a source of suction. The flow rate was controlled with a calibrated rotameter and maintained at 11 min^{-1} for 10 min. Now the indicator tubes were kept in oven, temperature maintained at ~60–90°C for 5 min. The blue colour stain developed over the silica gel indicated the presence of paraquat and diquat in air. The intensity and length of stain were proportional to the concentration of paraquat or diquat which was estimated by comparing the colour with that of standard treated similarly. Alternatively the coloured substance was extracted in 5 ml of water and the absorbance was measured at 600 nm.

Procedure with Reagent Papers

The reagent papers were exposed to paraquat or diquat (1–12 μg), sprayed in a closed chamber (40 × 60 × 40 c.m.) for 10 min. Now the reagent papers were kept in oven, temperature maintained at ~60–90°C for 5 min. The paper turned

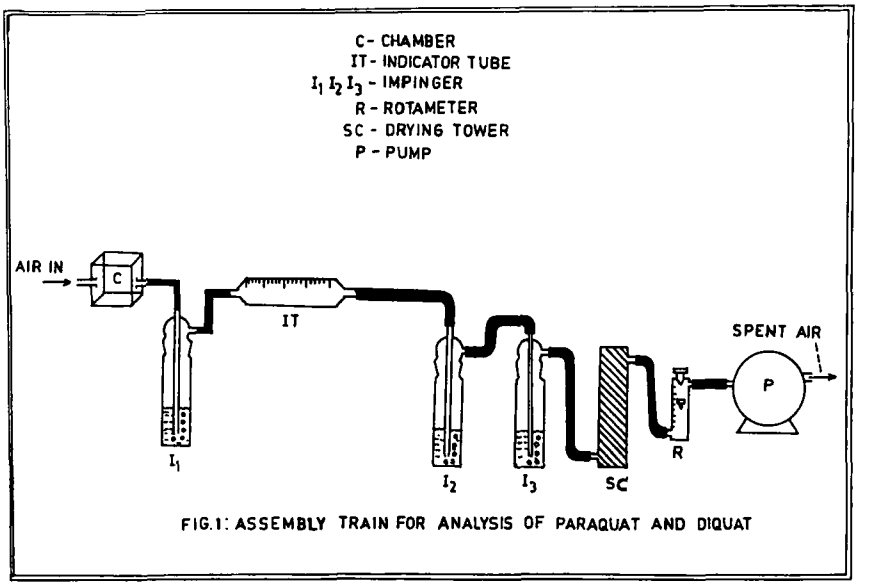

FIGURE 1 Assembly train for analysis of paraquat and diquat

blue in the presence of paraquat or diquat in air. The intensity of the colour was proportional to the concentration of paraquat or diquat. Quantitative evaluation was made by extracting the dye with 5 ml of water and measuring the absorbance at 600 nm.

Modified Sampling Train for the Simultaneous Estimation of Paraquat and Diquat in Air

A new technique was developed for the simultaneous detection/determination of paraquat and diquat in air (Figure 1). Air containing paraquat and diquat was drawn through a midget impinger, I_1 containing 10 ml of 0.2 N sodium hydroxide, which was further connected to a indicator tube and to more impingers I_2, I_3 each containing 10 ml of water, connected in series to a source of suction at a flow rate of 11 min^{-1} for 30 min. After sampling aliquots of impinger I_1, were taken and analysed for diquat[6,12] as described above. The blue stain developed in the indicator tube indicated the presence of paraquat. The I_2 and I_3 impingers did not show any measurable amounts of radical cation. Which indicated that the diquat precipitates completely only in the first impinger I_1 and does not pass through the sampling train, connected in series to the indicator tube IT and midget impingers I_2, and I_3 respectively. Paraquat did not absorb in

TABLE I Results of herbicide analysis ($\mu g\ m^{-3}$)

Source	*Herbicide Found (Standard Deviation)**			
	A		*B*	
	Paraquat	*Diquat*	*Paraquat*	*Diquat*
Working	1.6 (±0.02)	1.5 (±0.05)	1.2 (±0.08)	1.5 (±0.05)
environment[a]	4.3 (±0.08)	2.6 (±0.06)	1.9 (±0.04)	2.8 (±0.06)
	4.5 (±0.05)	3.9 (±0.04)	4.6 (±0.03)	2.1 (±0.03)
Laboratory air[b]	1.6 (±0.08)	1.9 (±0.06)	4.3 (±0.02)	1.6 (±0.06)

*Results of three replicate analysis.
[a]In agriculture fields.
[b]In the laboratory where herbicide were allowed to escape in the air.

the first impinger I_1 and is carried away to the indicator tube IT, where it is completely absorbed to give a blue stain. Thus the interference of diquat in the determination of paraquat can be eliminated by removing diquat by precipitation with sodium hydroxide. I_2 and I_3 impingers did not show the presence of paraquat and diquat. The separation efficiency of diquat and paraquat was ~100% (Table I).

Procedure for the Detection/Determination of Paraquat and Diquat in Human and Food Samples

Preparation of column for the extraction of paraquat from samples

Paraquat and diquat being ionic cannot be extracted with organic solvents. A silica gel column was used to separate paraquat or diquat from various samples. A 10 ml glass column (2–6 mm ID) with a plug of glass wool placed just above the stopcock was used. Silica gel (2 g) was weighed out, packed into the column and then washed with water. A fresh column was used for each experiment.

Detection/Determination of Paraquat and Diquat in Blood, Urine and Mother's Milk

The presence of paraquat and diquat has been reported in human sample.[17] Hence the method was applied for their detection/determination in blood, urine and mother's milk. Samples were taken from persons, exposed to paraquat or diquat during field application. Prior to the determination of paraquat or diquat in human samples 1 ml of 1% EDTA and 1 ml of 1% trichloroacetic acid were added to remove the interference of various metal ions and for deproteinization respectively.[18] The samples were filtered and allowed to pass through silica gel column at a flow rate of 1 ml per min. The paraquat was absorbed by silica gel which was later eluted by passing 10 ml of saturated ammonium chloride at a

TABLE II Determination of paraquat and diquat in human samples.

Herbicide	*Sample**	*Herbicide found*	
		Proposed method μg**	*Reported*[16] *method* μg**
	Blood/serum		
Paraquat	A	2.86 (±0.03)	2.75 (±0.05)
	B	3.25 (±0.05)	3.16 (±0.06)
Diquat	A	5.23 (±0.02)	5.18 (±0.05)
	B	6.03 (±0.01)	5.92 (±0.02)
	Urine		
Paraquat	A	3.57 (±0.01)	3.45 (±0.04)
	B	2.76 (±0.02)	2.68 (±0.03)
Diquat	A	6.18 (±0.02)	6.09 (±0.05)
	B	5.15 (±0.04)	5.08 (±0.06)
	Mother's milk		
Paraquat	A	3.06 (±0.03)	2.98 (±0.06)
	B	2.68 (±0.01)	2.53 (±0.02)
Diquat	A	5.35 (±0.02)	5.27 (±0.05)
	B	6.07 (±0.01)	5.95 (±0.02)

* Size of sample—2 ml.
** Mean of three replicate analyses.
Values in parentheses are standard deviations.

flow rate of 2 ml per min. and collected in a 10 ml calibrated flask. The volume was made up to the mark with water, 5 ml aliquot of this solution was taken and sprayed in a closed chamber (40 × 60 × 40 cm). The indicator tubes were connected to a source of suction and the air was drawn through the tube at a flow rate of 11 min^{-1} for 10 min.[19] The test papers were exposed to the chamber for 10 min. Now the indicator tubes and test papers were kept in oven, temperature maintained at ~60–90°C for 5 min. A blue stain in the indicator tubes and test papers indicated the presence of paraquat or diquat in human sample. Alternatively the coloured substance was extracted in 5 ml of water and the absorbance was measured at 600 nm. (Table II).

Detection/Determination of Paraquat and Diquat in Food Samples

Different samples of plant materials like, apples, sugarcane foliages and potatoes (10 g. of each) were collected from the field where paraquat or diquat had been sprayed. The samples were weighed, macerated and blended in a mixer. To the blended sample 1 ml of 1% EDTA was added and it was extracted with 10 ml of 18 N sulphuric acid. After extraction the volume was made up to 25 ml with water and allowed to pass through silica gel column at a flow rate of 2 ml per min. The column was washed with 2 × 25 ml of water 2–3 times to remove excess of acidity remained in the column. The absorbed paraquat or diquat was eluted by passing 25 ml of saturated ammonium chloride and collected in a calibrated flask, made up to the mark. 5 ml aliquots of this solution was taken,

TABLE III Determination of paraquat and diquat in food samples.

*Sample**		*Paraquat found*** μg		*Diquat found*** μg	
		Proposed method	*Reported[16] method*	*Proposed method*	*Reported[16] method*
Wheat	A	2.68 (±0.01)	2.59 (±0.03)	—	—
	B	3.56 (±0.02)	3.45 (±0.06)	—	—
Apple	A	3.42 (±0.04)	3.38 (±0.08)	—	—
	B	2.93 (±0.02)	2.87 (±0.03)	—	—
Sugarcane	A	—	—	5.26 (±0.02)	5.15 (±0.05)
	B	—	—	6.32 (±0.06)	6.22 (±0.07)
Potato	A	—	—	5.18 (±0.03)	5.02 (±0.05)
	B	—	—	6.05 (±0.01)	5.95 (±0.02)

* Size of sample - 10 g.
** Mean of three replicate analyses.
Values in parentheses are standard deviations.

sprayed in a closed chamber (40 × 60 × 40 cm). The indicator tubes were connected to a source of suction and the flow rate was controlled with a calibrated rotameter and maintained at 1 l min^{-1} for 10 min.[19] The test papers were exposed to the chamber for 10 min. The indicator tubes and test papers were then stained and the dye was extracted in water as described above, which indicated the presence of paraquat or diquat in food samples (Table III).

RESULTS AND DISCUSSION

The blue compound formed in the indicator tubes as well as in the test papers was extractable in water and exhibited maximum absorbance at 600 nm. As low as 0.1 μg of paraquat and 0.5 μg of diquat could be detected by the method. The molar absorptivity of the colour system is 2.9×10^4 l mol^{-1} cm^{-1} and 2.7×10^4 l mol^{-1} cm^{-1} for paraquat and diquat, respectively. Linear absorbance values were obtained up to 5 μg ml^{-1} of paraquat (Beer's law 0.5–5 μg m^{-3}) and 10 μg ml^{-1} of diquat (Beer's law 1–10 μg m^{-3}) respectively, which are sufficient for all practical purposes. Colour intensities obtained at constant flow rate could satisfactorily be compared.

Effect of humidity on the colour development was studied, it was found that colour development did not occur under extremely dry conditions. In fact it was found that certain amount of humidity was always necessary and was maintained by adding a few drops of calcium chloride to the reagent solution.

The effect of temperature on the colour reaction was studied and it was found that maximum colour was obtained when the indicator tubes and test papers were kept in oven at temperature range of ~60–90°C, after exposure to paraquat or diquat. At higher temperature the absorbance value decreased, while below ~60°C no colour was obtained (Table IV).

Table 4. Effect of temperature on colour reaction.

Concentration of paraquat / diquat = 4 μg m^{-3}.

Temperature ° C		Absorbance*, 600 nm	
		Paraquat	Diquat
30 ↑		—	—
40	No colour obtained	—	—
50		—	—
60		0.640	0.320
70		0.640	0.325
80		0.645	0.320
90		0.640	0.325
100		0.520	0.230
110	colour faded	0.430	0.140
120		0.310	0.085
130 ↓		0.200	0.045

* Mean of three replicate values.

Effect of other gaseous pollutants normally present in environment was studied by exposing the reagent papers and indicator tubes to chlorine, bromine, hydrogen cyanide, ammonia, carbon dioxide, phenol, sulphur dioxide, nitrogen dioxide prior to its exposure to paraquat or diquat. It was found that these gaseous pollutants did not interfere up to more than 100 μg ml^{-1} in colour development. The effect of the interference of various pesticides such as, parathion, DDT, BHC, 2, 4, -D, 2, 4, 5, -T, carbofuran, kelthane etc were also studied and it was found that they do not interfere up to ~ 200–300 μg ml^{-1}.

The indicator tubes and reagent papers prepared as described were stable up to ~6 months when kept in closed bottles in a desiccator. The colour formed with paraquat or diquat was also stable for several days. The test papers and indicator tubes gave reproducible results under optimum conditions.

Applications

The proposed sorbent system was applied satisfactory for the quantitative and semiquantitative evaluation of paraquat and diquat in air, human and food samples. Tables I, II and III. The results were found to be in good agreement with the reported method.[16]

The method can be directly applied for the detection/determination of paraquat and diquat in agricultural fields where these pesticides have been sprayed.

CONCLUSION

The proposed sorbent system is simple, sensitive and stable. The colour development in very rapid in comparison with the other reported reagents. The lower limit of detection is 0.1 μgm^{-3} and 0.5 μgm^{-3} for paraquat and diquat, respectively, and results obtained are reproducible. More over, the sorbent system is very easy to prepare and handle. The proposed train is efficient for separation as well as simultaneous detection/determination of paraquat and diquat in air.

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