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Research Article

SPECTROPHOTOMETRIC DETERMINATION OF CARTAP HYDROCHLORIDE IN COMMERCIAL SAMPLES OF PESTICIDES BY IRON (III) COMPLEXATION

N. RAZA[1], M. ASLAM[2]*, Z. NOREEN[3], A. H. CHAUHDRY[4], K. SULTANA[5], S. S. U. RAHMAN[5]

[1]Department of Chemistry, Bahauddin Zakariya University, Multan-60800, [2]Pakistan Council of Scientific and Industrial Research, Karachi-75280, [3]Division of Science and Technology, University of Education, Township Campus, College Road, Lahore, Pakistan. [4]GARL, GSP, Islamabad. [5]Department of Physics, Hazara University, Mansehra, Pakistan. Email: maslamchemist@hotmail.com

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ABSTRACT

A new spectrophotometric method was developed for the determination of cartap hydrochloride. It was converted into hydroxamic acid with alkaline hydroxylamine after heating at 70°C for 25 min, and then complexed with Iron (III) to form iron-cartap hydrochloride complex. The wavelength for maximum absorption of this complex was 542 nm. Various factors affecting the formation of iron-cartap complex were investigated. A linear calibration curve over the range from 6.3 µg ml^{-1} to 50µg ml^{-1} along with the molar absorptivity 3.39 x 10^3 l $mol^{-1}cm^{-1}$ was determined. Correlation coefficient, slope and intercept were calculated as 0.997, 29.386 and 0.033 respectively. The validity of the experimental results was tested analytically and statistically. The proposed method was applied for the determination of cartap in bulk and pesticide formulations. The sensitivity and reproducibility of the present study compared with established spectrophotometric method indicated that the performance of the proposed method was excellent.

Keywords: Cartap hydrochloride; Spectrophotometer; Ferric chloride; Complexation; Hydroxamic acid

INTRODUCTION

Pesticides are heterogeneous group of chemicals, such as chlorinated hydrocarbons, organophosphorous compounds, carbamates, etc. Among the carbamates the cartap hydrochloride (colorless crystalline, slightly hygroscopic solid with slight odor and hydrolyzed in neutral or alkaline media) is commercially used for control of chewing and sucking insects at potatoes, cabbage and other vegetables, as well as rice, maize, wheat, barley, cotton, sugarcane etc.

A variety of instrumental techniques have been reported for the residual analysis of cartap by GLC, Polarography and the product analysis by colorimetry [1]. Thin layer chromatography of cartap and modern TLC of various pesticides using multiple developments has also been described [2,3]. Flow injection system for the determination of organophosphate and carbamate pesticides has been carried out [4]. A simple, specific and rapid procedure for the determination of six largely used carbamate insecticides in milk has been evaluated [5]. Online enrichment and determination of some carbamates as well as after the formation of fluorophores from nitrogenous pesticides using photolysis interaction with OPA-2 mercaptoethanol for fluorescence detection in liquid chromatograph has been reported [6,7]. Comparative analysis of cartap in food using liquid chromatography–atmospheric pressure chemical ionization/mass spectrometry and liquid chromatography–post column fluorometry is also reported [8].

Gas chromatographic determinations and the anodic voltametric behavior of carbamate pesticides after their alkaline hydrolysis by producing electroactive phenol derivatives and applying the differential pulse voltamertric (DPV) method in the presence of perchloric acid has been investigated [9-11]. Spectrophotmetry (being relatively cheaper, easier, accurate and precise) is widely used in all aspects of life especially regarding pharmaceutical product analysis [12-14]. Majority of the other reported methods require expensive equipments and highly qualified personnel, which limit their extensive use for the analysis of cartap formulations.

In present work, UV/VIS spectrophotmetric method is used to analyze cartap hydrochloride in commercial pesticide samples. It was found that time required for the analysis of cartap by this method is relatively small. Also, the suggested method is considered to be economical due to the use of relatively cheap reagents.

MATERIALS AND METHODS

Apparatus

All absorbance measurements were made on a Perkin Elmer Lambda 3B spectrophotometer. Matched pairs of 10 mm glass cells were used throughout the experimental work.

Reagents and solutions

Solutions were prepared in doubly distilled water. A stock solution of cartap hydrochloride (1.25 mg mL-1) (Solex chemicals Pvt Ltd Pakistan, MW. 273.8 and purity 98%) was prepared by dissolving 0.1276 g in 100 mL of methanol. Further dilutions were made from it. Sodium hydroxide (8M by Merck) was prepared by dissolving 32 g in 100 mL. 6M hydrochloric acid was prepared by diluting 49.75 mL of concentrated hydrochloric acid in 100 mL. Hydroxylamine hydrochloride (5 M by Merck) was prepared by dissolving 34.25 g in 100 mL. Ferric chloride (5M by Merck) was prepared by dissolving 13.5 g in 0.1 M hydrochloric acid in 100 mL. Equal volumes of sodium hydroxide (8M) and hydroxylamine (5M) were mixed just before the complex formation, because alkaline hydroxylamine is stable only for few hours.

Procedure

To different aliquots of cartap (6.3 µg mL-1 to 50 µg mL-1) in 20mL test tubes, 3mL of alkaline hydroxylamine solution was added and heated to 70°C for 25 min. After cooling to room temperature, the contents along with rinsing were transferred to a 25 mL measuring flask. Then 2 ml of 6 M hydrochloric acid and 2.5 ml of 0.5 M ferric chloride were added. Hydrochloric acid (0.1 M) was used to make up the volume of the measuring flask. Absorbance measurements of the colored complex (reddish brown) were determined at 542 nm against reagent blank.

Test samples (real samples)

To check the labeled composition of cartap hydrochloride, five commercial samples of 4% finished product were obtained from the market and analyzed by the established [1] method and the proposed one. An aliquot of cartap hydrochloride equivalent to 250 mg was stirred with 100 ml of methanol in measuring flask. It was filtered through Whatman filter paper no. 42. The residue was washed with distilled water and the filtrate along with the washings was diluted with distilled water to 250 mL.

One ml of sample solution was mixed with 3 mL of freshly prepared alkaline hydroxylamine and heated at 70°C for 25 min in water bath of paraffin oil. After cooling to room temperature, the contents along with rinsing were transferred to 25 mL measuring flask. Then, 2 mL of 6 M hydrochloric acid and 2.5 ml of 0.5 M ferric chloride were added. Hydrochloric acid (0.1 M) was used to make up the volume of the measuring flask. Six determinations of each commercial sample were carried out.

RESULTS AND DISCUSSION

Effect of alkaline hydroxylamine

Different volumes of alkaline hydroxylamine were used keeping cartap hydrochloride, ferric chloride, hydrochloric acid concentrations and all other parameters constant. Absorption measurements were compared at 542 nm against reagent blank. Results are plotted in **Figure 1**. It was observed that the absorbance of complex showed gradual increase with an increase in the volume of alkaline hydroxylamine and reached a maximum at 3 ml. Above this amount of alkaline hydroxylamine, complex (iron cartap complex) was precipitated, a situation which can be attributed to the lower solubility of the complex under the prevailing conditions. The possible mechanism of the reaction is given in **scheme 1**.

Effect of hydrochloric acid

The concentration of hydrochloric acid required for the formation of iron-cartap hydrochloride complex was varied from 0.12 mol/L to 0.84 mol/L keeping the concentration of cartap hydrochloride, hydroxylamine etc. constant. The absorbance was compared at 542 nm using a reagent blank. The absorbance of iron-cartap hydrochloride complex versus the concentration of hydrochloric acid is plotted as shown in **Figure 2**.

Effect of ferric chloride

The effect of concentration of ferric chloride on the formation of iron-cartap hydrochloride complex has been shown in **Figure 3**. A series of solutions were prepared by varying the concentration from 0.01 M to 0.05 M while keeping all other parameters constant. The absorbance of iron-cartap hydrochloride complex was measured at 542 nm against a blank reagent. The absorbance of complex was found maximum at 0.05 M of ferric chloride. It was observed that by increasing the concentration (above 0.05 mol/L) of ferric chloride, unwanted chemical changes might occur, such as precipitation of iron-cartap complex due to its less solubility at the experimental conditions.

Effect of temperature

Iron-cartap hydrochloride complex was prepared at different temperatures from 45°C to 80°C. Absorbance of complex versus temperature has been plotted in **Figure 4**. The results indicated that 70°C was the optimum temperature for the formation of iron-cartap hydrochloride complex during the reaction.

Effect of heating time

The effect of heating time on the absorbance of iron-cartap with the optimum value of reaction temperature as well as other parameters was carried out from 5 to 35 min. Absorbance of complex versus heating time has been plotted in **Figure 5**. The experimental results indicated that the optimum time for the formation of iron- cartap hydrochloride complex was from 25 to 30 min.

Stability of complex

Stability of iron-cartap complex was observed from the start of the formation of complex up to 24 hrs as shown in **Figure 6**. It was found that stability of complex color was decreased with the passage of time. The experimental results indicated that the most suitable working time for the analysis of cartap by iron-cartap complexation was up to 2.5 hrs after its formation, which could be considered to be sufficient time for an analytical chemist to carry out the absorbance measurements.

Calibration curve

Calibration curve under optimum conditions of reagents as well as other parameters obeys Beer–Lambert's law from 6.3 μg mL^{-1} to 50 μg mL^{-1} of cartap hydrochloride. The results suggest that appropriate dilutions must be carried out as the linearity of the curve gets disappeared at higher concentration of cartap.

Determination of commercial samples (real samples)

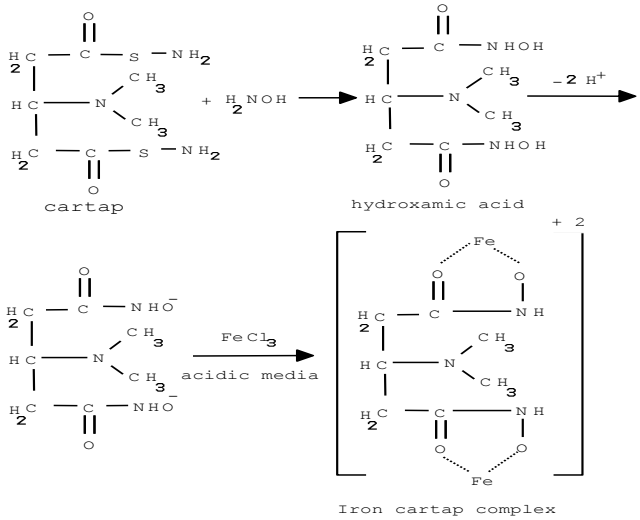
Absorbance measurements of the colored complex (reddish brown) were determined at 542 nm against reagent blank. Standard deviation of both of the methods was found to be 0.048, which showed a good agreement between the established method and the proposed one as shown in **Table 1**.

Effect of interferences on the analysis of cartap

During the interference studies, 20μg/ml of cartap was used for each determination. More than 98% recovery of cartap was obtained in the presence of possible interferences in cartap hydrochloride formulations, a situation which could be attributed to the fact that the effect of excepients on analysis of cartap was not significant as shown in **Table 2**.

Recovery of cartap from spiked samples

Samples of 100 g silica sand obtained from Northern areas of Pakistan were contaminated with 20, 30, 40, 50, and 60 μg of cartap hydrochloride. Six determinations of each concentration were performed. The percentage ratio between real and obtained concentrations was calculated as shown in **Table 3**. The recovery rate of the method varies within 96 to 99% for concentrations between 20 and 60 μg. The small losses of cartap during the recovery may be due to its extraction with methanol.



Scheme 1: Possible mechanism of the reaction.

Table 1: Results of cartap hydrochloride analyzed by the proposed and the standard methods.

No.	Company name	Trade name	Standard method	Developed method ±SD
1	Solex chemicals	Cartap	4.06 ± 0.32	4.02 ± 0.38
2	Warble chemicals	Cartap	3.99 ± 0.66	3.94 ± 0.45
3	Arista (FMC)	Padan	4.0 ± 0.45	4.08 ± 0.62
4	Pan Pacific	Kadan	4.03 ± 0.42	4.01 ± 0.32
5	Pak agro	Rezex	3.97 ± 0.58	3.93 ± 0.64

Table 2: Determination of cartap in the presence of excepients by the proposed method

Excepient	Amount taken µg/mL	% recovery ± RSD (n = 6)
Silica	500	98.5 ± 0.41
Talc	200	98.8 ± 0.38
Polyethylene glycol	150	98.0 ± 0.47
Phosphoric acid	50	99.5 ± 0.23

Table 3: Recovery rate in control 100 g silica sand samples, contaminated with cartap.

Amount of added cartap in µg/100 g	Measured concentration µg/ 100 g (mean ± Std)	Recovery rate, %
20	19.8 ± 0.08	99.00
30	29.5 ± 0.18	98.3
40	39.0 ± 0.24	97.5
50	48.4 ± 0.45	96.8
60	57.6 ± 0.67	96

Reproducibility and sensitivity of proposed method

Six consecutive determinations for each of the following cartap concentrations: 20, 30, 40, 50, and 60 µg per 100 g of silica sand were performed. The mean values, the standard deviation and coefficient of variation were calculated. Sensativity was determined as the percentage difference between mean measured concentrations and the real (added) concentration as shown in **Table 4**.

Reproducibility of the proposed method shows coefficient of variation between 0.40 % (for 20 µg/100 g sample) and 1.01 % (60 µg/100 g sample), which suggests that the precision of the method is satisfactory as it is within –15 % to + 15%. Statistical parameters for the present method, applied for the determination of cartap hydrochloride by iron complex formation, are given in **Table 5**.

Table 4: Precision (repeatability) and accuracy of the proposed method

Amount of added cartap in µg/100 g	Measured concentration µg/ 100 g (mean ± Std)	CV %	Accuracy, %
20	19.8 ± 0.08	0.40	-1.0
30	29.5 ± 0.18	0.6	-1.66
40	39.0 ± 0.24	0.6	-2.5
50	48.4 ± 0.45	0.9	-3.2
60	57.6 ± 0.67	1.01	-3.98

Table 5: Determination of cartap by iron complex formation

Parameters	Results
Concentration range	6.3 µg ml^{-1} – 50 µg ml^{-1}
λ max	542 nm
Molar absorptivity	3.39 x 10^3l $mol^{-1}cm^{-1}$
Coefficient of variation	0.40 – 1.01 % (20 µg, 60 µg /100 g)
Correlation coefficient	0.996
Standard deviation of established, and proposed	0.048086
% Recovery	96 % - 99 %
Accuracy and precision	-1.0, –3.98 % (20 µg, 60 µg /100 g)
Slope	29.385
Intercept	0.0301
Variance	0.0023
Covariance	0.0009

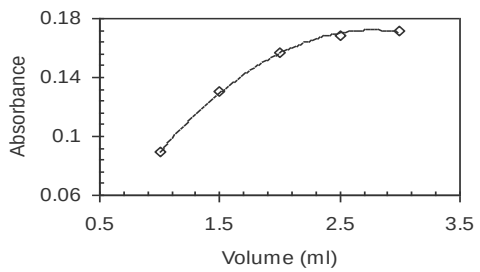


Fig. 1: Effect of alkaline hydroxylamine on iron-cartap complex using cartap (1ml, 1.25 mg/ml), hydrochloric acid (6 M), ferric chloride (0.5 M) and temperature (70°C) at 542 nm for 25 min

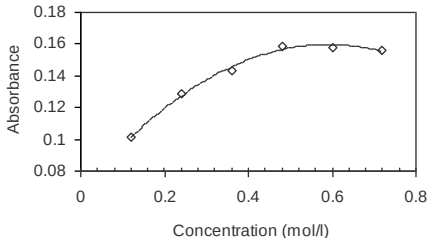


Fig. 2: Effect of hydrochloric acid on iron-cartap complex using cartap (1ml, 1.25 mg/ml), alkaline hydroxylamine (5 M), ferric chloride (0.5 M) and temperature (70°C) at 542 nm for 25 min.

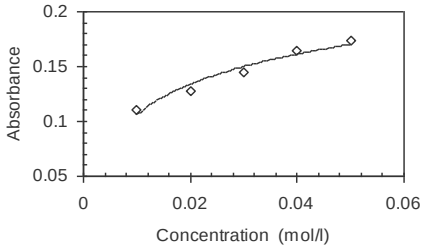


Fig. 3: Effect of ferric chloride on iron-cartap complex using cartap (1ml, 1.25 mg/ml), alkaline hydroxylamine (5 M), hydrochloric acid (6 M) and temperature (70°C) at 542 nm for 25 min.

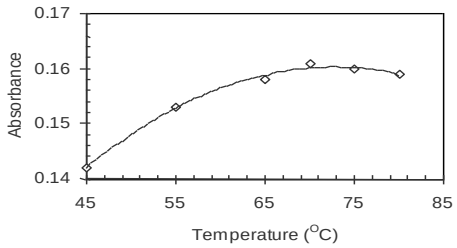


Fig. 4: Effect of Temperature on iron-cartap complex using cartap (1ml, 1.25 mg/ml), alkaline hydroxylamine (5 M), hydrochloric acid (6 M) and ferric chloride (0.5 M) at 542 nm for 25 min

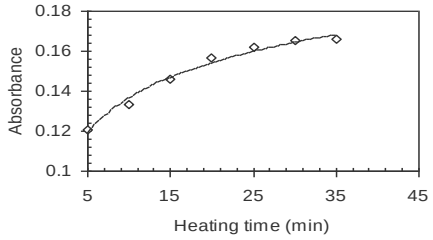


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Fig. 5: Effect of heating time on iron-cartap complex using cartap (1ml, 1.25 mg/ml), alkaline hydroxylamine (5 M), hydrochloric acid (6 M), ferric chloride (0.5 M) and temperature (70°C) at 542 nm.

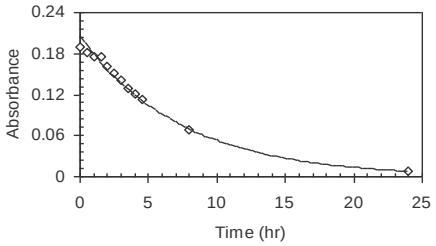

Fig. 6: Stability of the complex color using cartap (1ml, 1.25 mg/ml), alkaline hydroxylamine (5 M), hydrochloric acid (6 M), ferric chloride (0.5 M) and temperature (70°C) at 542 nm.

CONCLUSIONS

The experimental results indicate that the cost as well as the time required for analysis of cartap by the present method is relatively economical. It may be concluded that the suggested spectrophotometric method is highly sensitive, accurate, rapid, economical and easy for routine analysis of cartap hydrochloride in bulk and commercial formulations.

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