

Spectrophotometric determination of Isoproturon and Metoxuron in technical and formulation grade samples using citric acid—acetic anhydride reagent

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A spectrophotometric method for the determination of Isoproturon and Metoxuron in technical and formulation grade samples based on the reaction with citric acid-acetic anhydride reagent has been developed. The absorption maxima of the coloured compounds so formed are 408 and 409 nm and the molar absorptivities are 1.69×10^2 and $1.13 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$ respectively. The reaction variables have been optimized and the reaction mechanism is discussed. The method is simple, convenient and successfully applied for the determination of Isoproturon and Metoxuron in technical and formulation grade samples. The percent relative standard deviation is found to be in the range 0.6-1.55 for Isoproturon and 1.24-1.90 for Metoxuron.

Isoproturon [IPN] and Metoxuron [MTN] belong to phenylurea class of compounds widely used as pre or post emergent herbicides for the control of different weed species in cereals and carrots. Simple methods for their assay in technical and formulation grade samples are necessary for routine analysis and quality evaluation. Chemical¹, GC² and UV spectrophotometric³ methods are available for their analysis in literature, which are unsuitable for routine analysis for the reasons mentioned earlier⁴⁻⁶. In search of more convenient methods, spectrophotometric investigations of the chromogenic reaction between these herbicides and citric acid-acetic anhydride reagent⁷⁻¹⁰ have been carried out and their applications to technical and formulation grade samples have been examined.

Experimental Procedure

Apparatus—Shimadzu Model UV-240 and Perkin-Elmer Model Lambda-2 UV-Visible spectrophotometers with 1 cm matched quartz cells were used.

Reagents and materials—All the chemicals used were of Analar grade.

Citric acid-acetic anhydride reagent prepared freshly by dissolving 3, 5.5, 7.0 g of citric acid (Ranbaxy Laboratories Limited, India) in 4.2, 8.0, 10.0 mL methanol and diluted to 100 mL with

acetic anhydride (Ranbaxy Laboratories Limited, India).

Standard Isoproturon was supplied by M/s Bharat Pulverising Mills, Bombay, India and used as such. MTN was supplied by the Pesticides Division, IICT, Hyderabad, India and was used after recrystallisation in hot water.

Standard herbicide solutions were prepared by dissolving 0.2 g of IPN and MTN in methanol and diluted to 25 mL in a standard flask with methanol to provide working solutions.

Procedure—A portion (1.0 mL) of working sample solutions were transferred into 10 mL standard flasks. To which 1.0 mL citric acid-acetic anhydride reagent (7.0% for IPN and 5.5% for MTN) were added and the flasks were heated in boiling water bath for 60 min for IPN and at 90°C for 90 min for MTN, cooled to room temperature and volume was made up to 10 mL with methanol. The absorbance of the solution was measured at 408 nm for IPN and 409 nm for MTN against reagent blank.

Technical grade samples—About 0.2 g of technical grade samples were weighed accurately into a 25 mL standard flask, dissolved in methanol and the volume was made up to 25 mL with the same solvent and subjected to analysis using general procedure.

Formulation samples: About 0.4 and 0.25 g of formulations of IPN and MTN respectively were weighed accurately to which 50 mL methylene chloride was added and centrifuged filtered and

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the methylene chloride was evaporated. The residue was dissolved in methanol and transferred into a 25 mL standard flask and the volume was made up to 25 mL with methanol and subjected to analysis using general procedure.

Synthetic formulations (80%) for MTN were prepared and analysed due to non-availability of commercial formulations.

Results and Discussion

Optimisation of reaction variables—The absorption spectra of IPN and MTN with citric acid-acetic anhydride are shown in Fig. 1. The reaction variables have been optimised by varying each variable while keeping others constant for obtaining maximum colour development as shown in Figs 2 and 3. The optimum concentrations of various reagents for IPN and MTN respectively are found to be 55 min in boiling water bath and 90 min reaction time at 90°C, 1.0 mL 7.0% and 1.0 mL 5.5% citric acid-acetic anhydride reagent.

Beer's law, precision and Accuracy—The absorption maxima (λ_{\max}), the molar absorptivities, Beer's law range, slopes, correlation coefficients, precision and accuracy of the method are given in Table 1. The colour is stable for more than 25 min for IPN and 20 min for MTN.

Reaction mechanism—Although the reaction is known since 1935 specific for tertiary nitrogen atom, very little is known about the chemistry of colour formation. A systematic study of the colour formation was carried out by Connors and Ifan¹¹ and postulated the formation of carbon

suboxide ($O=C=C=C=O$) is responsible for effective reactive species. However, the final species due to which the colour has been observed was not identified. Two other possible mechanisms^{12,13} reported involve the formation of aconitic anhydride and its association with the sample component. The latter two mechanisms probably support the former in producing carbon suboxide which ultimately reacts with the sample.

Thus the authors would like to propose a probable mechanism for the reaction as we are also of the opinion that citric acid loses two moles of water in hot acetic anhydride medium to give *cis*-aconitic anhydride leading to carbon suboxide type of species (Scheme-1) with four carbon atom chain which reacts with IPN or MTN to give a coloured product having absorption in visible region. The λ_{\max} of the chromogenic species indicates the presence of the *cis*-aconitic acid in accordance with the literature report¹⁴. The larger intensity could be due to the presence of extended conjugation. The molar absorptivity data (Table 1) are also in confirmity that MTN is more polar than IPN. However, attempts to isolate the absorbing species for characterization were not successful, may be due to their polar nature.

Application—The method has been applied for the determination of a number of technical grade and formulation samples of IPN and MTN and the results are shown in Table 2. The per cent relative standard deviations are in the range of 0.60-1.55 for IPN and 1.24-1.90 for MTN. The

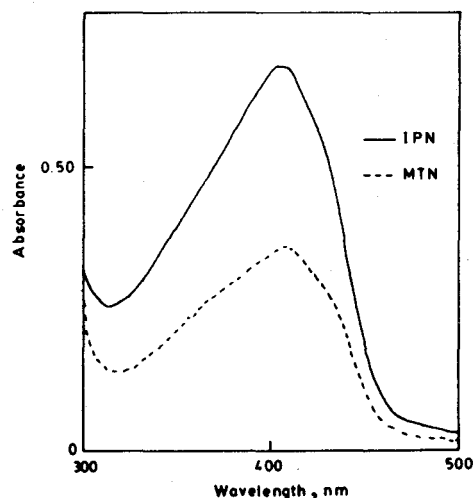


Fig. 1—Absorption spectra of IPN (—) and MTN(---) [2.5 mL 2.0% IPN + 5.0 mL 3.0% citric acid-acetic anhydride and 40 min heating in boiling water bath. Against reagent blank 2.0 mL 1.0% MTN + 1.0 mL 5.5% citric acid-acetic anhydride and heating at 90°C for 65 min. Against reagent blank

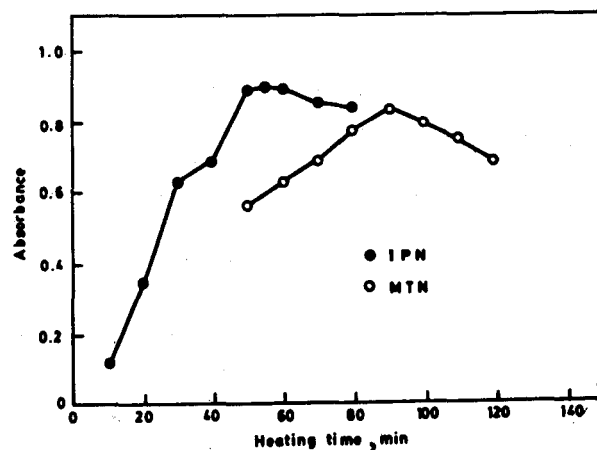


Fig. 2—Effect of heating time on colour formation

(●) 2.5 mL 2.0% IPN + 5.0 mL 3.0% citric acid-acetic anhydride + variation in heating time (in boiling water bath). Against reagent blank

(○) 2.0 mL 1.0% MTN + 1.0 mL 5.5% citric acid-acetic anhydride + variation in heating time at 90. Against reagent blank

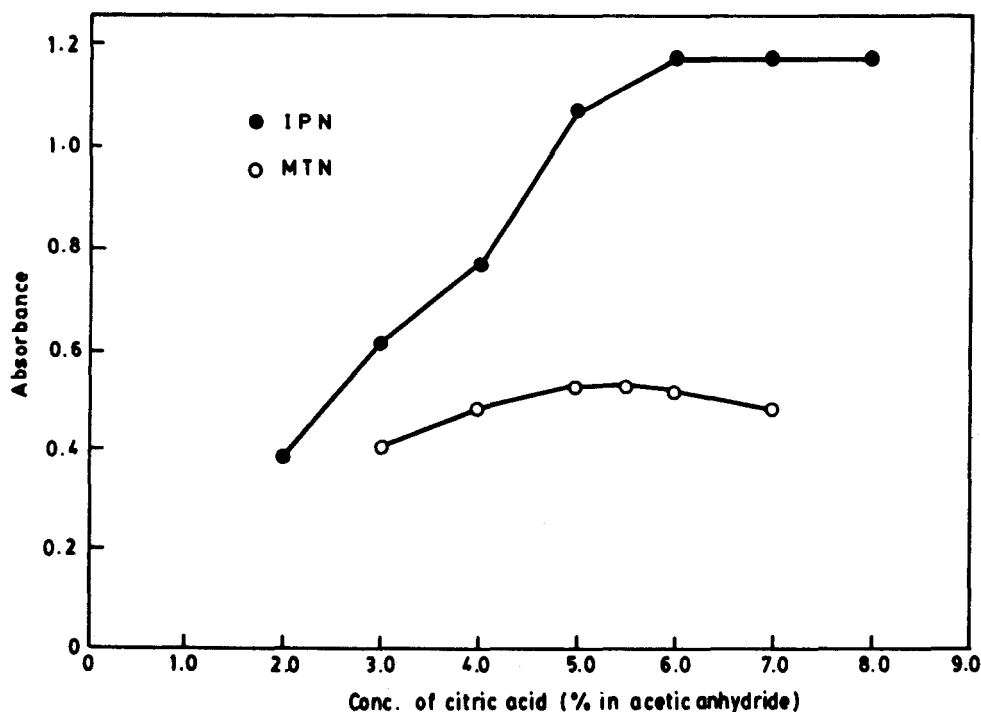


Fig. 3—Effect of reagent concentration.

(●) 1.0 mL 2.0% IPN + varying amounts of citric acid-acetic anhydride reagent + heating in boiling water bath for 55 min. Against reagent blank

(○) 2.0 mL 1.0% MTN + varying amounts of citric acid-acetic anhydride reagent. Heating time at 90 for 65 min. Against reagent blank

Table 1—Beer's law, precision and accuracy

	IPN	MTN
λ_{max} , nm	408	409
Beer's law range, mg/mL	0-1.2	0.04-1.6
Molar absorptivity $[\epsilon]$ L mol ⁻¹ cm ⁻¹	1.69×10^2	1.13×10^2
Slope, mg/mL	0.074047	0.54095
Intercept/A	0.029026	0.039607
Correlation coefficient	0.9989	0.9990
Relative error, %	<2	<2

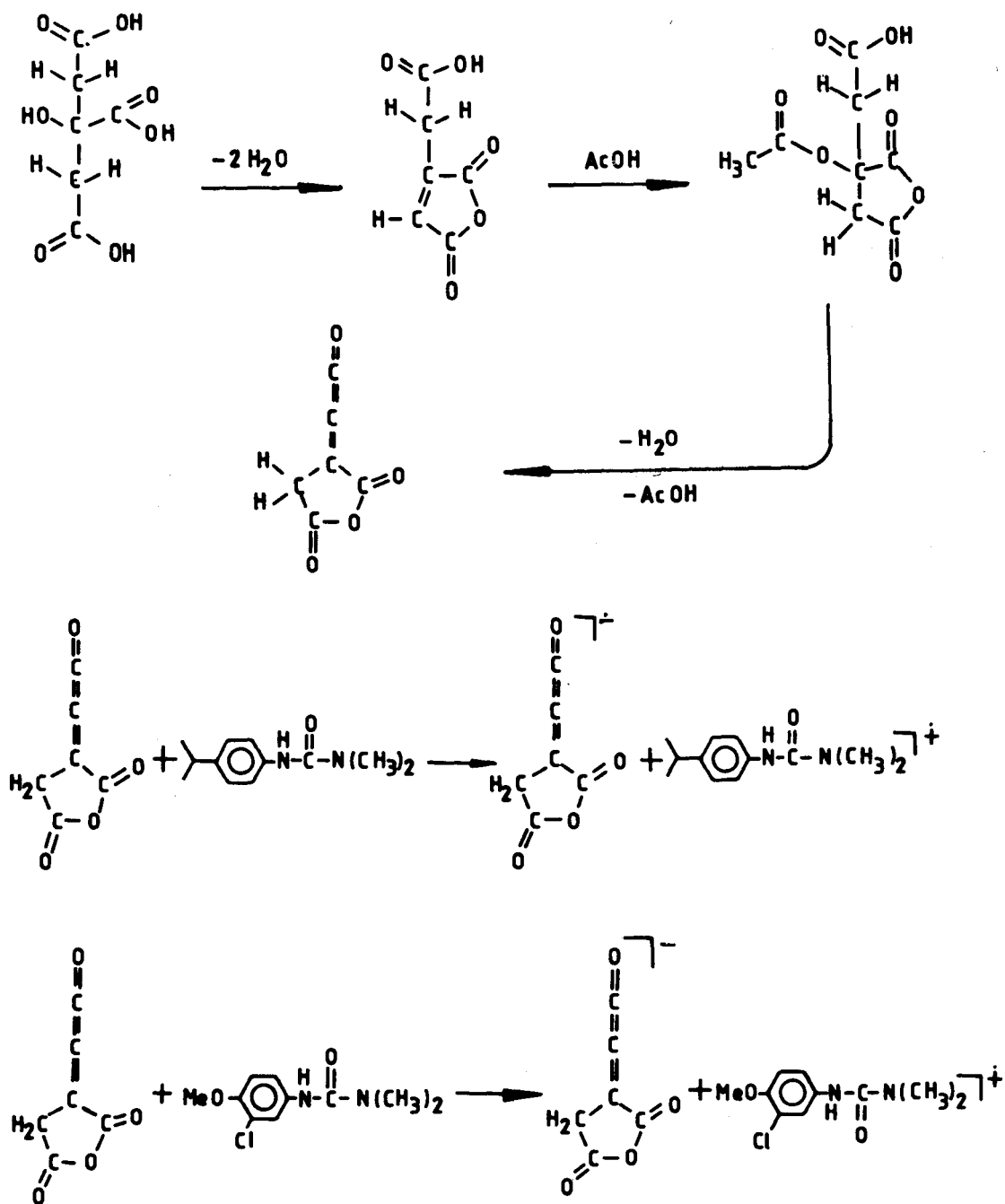
Table 2—Assay of IPN and MTN

Sample	Comparison method (n=5)	Present method (n=8)	Recovery %	Relative standard deviation %
IPN				
Technical grade	99.35	99.10	99.75	0.58
	98.38	98.97	100.60	1.27
	98.62	98.92	100.30	1.38
	99.56	98.21	98.64	1.53
Formulation (labelled 50%)	50.52	51.07	101.10	1.39
	49.95	48.71	97.52	1.14
	50.25	50.32	100.14	1.56
MTN				
Technical grade	98.92	99.67	100.76	1.68
	99.23	98.90	99.67	1.71
	93.22	93.94	100.78	1.47
Formulation (80%)	80.21	78.94	98.42	1.75
	78.12	80.11	102.55	1.90
	80.75	79.74	98.75	1.24

results are also compared with the reported method and presented in Table 2 which are found to be in agreement.

Interferences—The method does not have any interferences as the reagent is specific for tertiary nitrogen atom and no other compounds containing tertiary nitrogen atom other than the analytes are expected to be present. Water inhibits the reaction and therefore proper care should be taken for nonaqueous medium.

Advantages—The method does not involve time, consuming distillation, thermal and photo decomposition as reported earlier¹⁻³. Further, the



Scheme - 1

present method is superior to our earlier methods⁴⁻⁶ as far as the simplicity of the reagent is concerned but it is inferior with regard to sensitivity. Therefore, the present method can be employed for routine analysis of technical grade and formulation samples of IPN and MTN, where the sample quantity is not a limitation.

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