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REPORT No. 22/R/55

The Ultra-Violet Spectroscopic Examination of Tetrazene

Waltham Abbey, Essex.

Reg 11600

December 1955

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The Ultra-Violet Spectroscopic Examination of Tetrazene

by

C. P. Conduit

This report does not contain classified information of overseas origin

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CONTENTS

Reference: XR.791/15

1. SUMMARY

Ultra-violet spectrophotometry has been used to investigate some of the properties of tetrazene in solution. On the basis of the results obtained, an ultra-violet absorption technique involving spectral measurements in acid and alkaline solution, is suggested as a rapid method for assessing the purity of tetrazene used in cap compositions, and the method is extended to the determination of tetrazene in V.H.2 composition.

The spectral studies support the tetrazene structure involving a tetrazole ring.

2. OBJECTS OF THE INVESTIGATION

To investigate the ultra-violet spectral characteristics of tetrazene in solution for the purpose of developing an assay method more specific than the existing chemical procedures.

3. INTRODUCTION

The acceptance of V.H.2 composition into Service use has necessitated the preparation of specifications for its ingredients including tetrazene. In particular, this requires a satisfactory method for determining the purity of tetrazene samples, and a number of chemical procedures for this purity assay have been put forward. The following is a brief survey of the field, together with comments on the applicability of each method.

3.1 The Semi-Micro Dumas Nitrogen Determination

This has been used for control work and has the merit that it can be readily checked against pure nitrogen-containing substances. Clearly, its chief drawback is that nitrogenous impurities are estimated as tetrazene, and it is probable that the chief contaminants would be of this nature.

3.2 The Acetic Anhydride Gasometric Method

This involves the decomposition of tetrazene in hot acetic anhydride. The stoicheiometry of the reaction is difficult to reconcile with the molecular formula, since about 5.5 mol. of nitrogen are evolved per mol. of tetrazene, and the figure is variable to the extent of some $\pm$ 5 per cent. Compounds related to tetrazene also decompose in this way, thus reducing the specificity of the method.

3.3 Argentometric Method

Tetrazene (1) gives an insoluble precipitate with silver nitrate in dilute nitric acid solution, and this has been developed by A.R.D.E., Swynnerton (2) into an analytical technique. However, doubt has been cast on the stoicheiometry of the reaction since it appears that more than one silver complex can occur, depending on the conditions of the precipitation. More important, it is not specific for tetrazene, since related tetrazole derivatives also give insoluble silver complexes.

/3.4 .....

3.4 Mercurometric Method

E.R.D.E. (3) have developed a method based on the precipitation of tetrazene by mercurous nitrate. This is analogous to the silver method but it has the advantage that only one complex is formed. Like the silver method, it is not specific since the reaction is given by a range of compounds containing a tetrazole ring in their structures.

3.5 Non-Aqueous Titration

This has been investigated by Kaye at Picatinny Arsenal (4), and involves the titration of tetrazene as a base with perchloric acid in glacial acetic acid as solvent. Again, this is not specific for tetrazene since other basic nitrogenous impurities are similarly titratable.

It is clear that the above methods may each be used to obtain some idea of the quality of a given sample of tetrazene, but in each case non-specificity is a serious limitation to their applicability.

These considerations led to the investigation of physico-chemical techniques for the assay of tetrazene, and ultra-violet absorption spectroscopy was felt to be particularly promising. Infra-red spectroscopy was also considered, but, since tetrazene is quite insoluble in the solvents usually employed in this field, no quantitative work was performed. (The paraffin mull and potassium chloride disc techniques are not sufficiently precise for the present requirements). A preliminary investigation in the ultra-violet region showed that in solution in dilute nitric acid, tetrazene shows an absorption band near 280 mμ. The band is very intense ($\epsilon_{max} = 1.6 \times 10^4$), so that milligram quantities may be handled. In view of this, a systematic investigation has been carried out.

4. GENERAL SPECTRAL CHARACTERISTICS

4.1 Method Employed and Results

In most of the work to be described, the tetrazene used was supplied by Messrs. I.C.I., Ltd. It was purified by dissolving several grams in 200 ml. of 4 M. nitric acid followed by reprecipitation with ammonia and drying over phosphoric oxide.

5.05 mg. of pure tetrazene were dissolved in 100 ml. of 1.00 N. hydrochloric acid. After diluting 20 ml. to 100 ml. with water, the absorption spectrum was examined over the wavelength range 205 - 345 mμ in 10 mm. silica cells using a Unicam SP. 500 spectrophotometer. 0.2 N. hydrochloric acid was placed in the solvent compensating cell, and cell matching corrections were determined with the solvent in both cells. The results are plotted as $E^{1\%}_{1cm.}$ - values against wavelength (mμ) in Fig. 1, curve A.

$E^{1\%}_{1cm.}$ = Optical density of a 1% solution measured in a 1cm. cell.

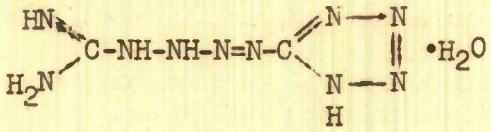
In future this will be simply referred to as E.

The absorption rises to a single intense maximum at 279 mμ, with an E-value of 805. (This corresponds with a molar extinction coefficient of 1.53×10^4, assuming a molecular weight of 188 for tetrazene).

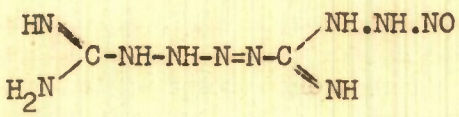
/4.2 .....

4.2 Correlation with Structure

The spectrum found for tetrazene in acid solution is consistant with the newly proposed (9) tetrazole ring structure (I), rather than with the older nitroso-hydrazine formulation (II).

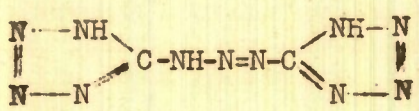


I.



II.

The tetrazole ring, per se, does not absorb in the spectral region above 200 mμ (5, 6), but the observed band at 279 mμ could arise by conjugation of the ring with the double-bond of the tetraz-1-ene chain attached to the carbon atom of the ring. This bathochromic shift of the tetrazole absorption is thus analogous to that produced on the Group II band of benzene at 200 mμ by substituents which can enter into conjugation with the ring. It is supported by the spectrum of ditetrazolyl-triazine (III) which possesses similar structural features and absorbs at 290 mμ. (See Section 7.4).

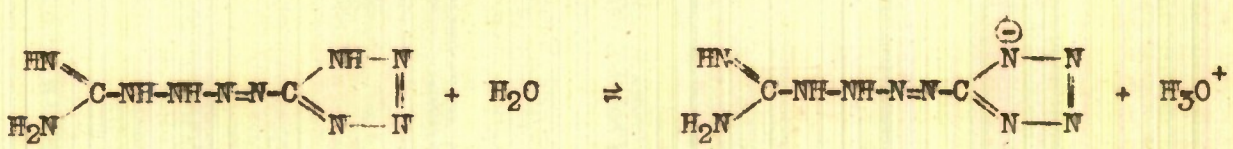


III.

5. THE DISSOCIATION OF TETRAZENE

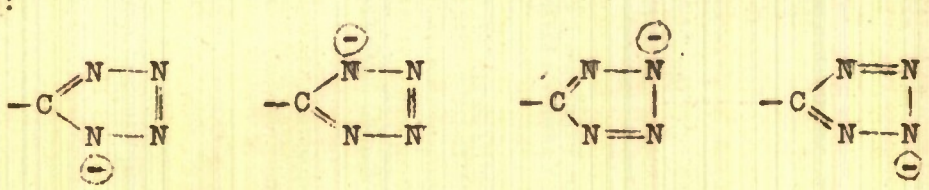
5.1 General

The hydrogen attached to the 1-nitrogen of the tetrazole ring has acidic properties, and the pK_a-values for a number of C-substituted derivatives have been measured (7). They vary over a wide range depending on the nature of the substituent: e.g., pK_a for tetrazole itself is 1.3×10^{-5}, whereas 5-azido-tetrazole is a strong acid. This suggests the possibility that tetrazene is also acidic, and the point is of importance in analytical work, since ionisation of the molecular is likely to affect its absorption spectrum. The dissociation in water may be written as follows:



IV

Due to the possibility of resonance, the negative charge on the tetrazole ring in the ion IV is likely to be distributed over the remaining three nitrogen atoms:



/In .....

In order to obtain evidence for this scheme of ionisation, the position of the tetrazene absorption maximum was measured over a range of pH-values from 0 to 8.

5.2 Method

40 mg. of tetrazene, accurately weighed, were dissolved in 250 ml. of 1.00 N. hydrochloric acid. 15 ml. of the solution was added to a mixture containing 50 ml. of M. sodium acetate, and a varying volume of 1.00 N. hydrochloric acid, and the whole diluted to 250 ml. with water (8), the solution being made molar with respect to sodium chloride. In this way, the range from pH = 0.5 to pH = 6.0 was covered. Clarke and Lubs buffer was used for pH = 6 - 8, while for pH.s of less than 0.5, solutions of hydrochloric acid were used. Except for the latter unbuffered solutions, all pH values were checked on a Cambridge-type pH-meter using a glass electrode and a saturated calomel reference electrode. The time was noted as the tetrazene dissolved in the initial acid solvent, and readings of the optical density were taken over the range 275 to 285 $m\mu$, and at 300 $m\mu$ at known intervals thereafter. This was necessary in order to allow for the slow decomposition of tetrazene in solution (Section 6), the readings being extrapolated to zero time; cell matching corrections were determined and applied to all the results.

5.3 Results and Discussion

With increasing pH the wavelength of maximum absorption is displaced from 279 $m\mu$, so that the absorption at this point falls, whilst that at 300 $m\mu$ rises. A plot of E at 300 $m\mu$ against pH is illustrated in Fig. 2. It shows that the absorption is constant below pH 0.8 and above pH 3.6. The shape of the curve is characteristic of an acid undergoing dissociation with rising pH of the solution. The E-value below pH = 0.8 corresponds to that of the undissociated molecule, whilst the constant value above pH = 3.6 is to be assigned to the acid anion. At intermediate points on the curve, the E-values correspond to mixtures of the two species, and may be used to determine their ratio (10).

Thus: $\dfrac{\text{Concentration of undissociated acid}}{\text{Concentration of acid anion}} = \dfrac{E - E_o}{E' - E} = \dfrac{[HX]}{[X^-]}$ 1

where E = E-value for the partially ionised mixture,
E_o = E-value for the undissociated acid HX,
E' = E-value for the acid anion X^-.

If the acid dissociation constant = K_a,

$$K_a = \frac{[H_3O^+][X^-]}{[HX]}$$

or, $-\log K_a = pK_a = -\log [H_3O^+] + \log [HX] - \log [X^-]$

$$\therefore pK_a = pH + \log \frac{[HX]}{[X^-]} \quad \text{.....2}$$

Combining equations 1 and 2 gives:

$$pK_a = pH + \log \frac{[E - E_o]}{[E' - E]}$$

/At .....

At the mid-point of the inflexion $E - E_o = E' - E$, so that:

$$pK_a = pH_m$$

From Fig. 2, $pH_m = 2.2 = pK_a$

$$\therefore K_a = 6.3 \times 10^{-2} \text{ moles/litre.}$$

These results show that tetrazene is indeed acidic and that the spectrum of the anion is somewhat different from that of the parent molecule. The K_a-value is fairly high, and this may be related to the favouring of the ionic form by the increased resonance energy which results by the loss of the proton from the tetrazole ring (Section 5.1). On the basis of the older nitrosohydrazine structure for tetrazene, it is difficult to formulate such an acidic function.

For analytical applications it is thus desirable to avoid the pH-range 0.8 to 3.6, and to work in the regions above or below, where the E-values are independent of pH. For the reasons discussed later, the region below pH = 0.8 is to be preferred.

6. THE STABILITY OF TETRAZENE IN SOLUTION

6.1 General Considerations

The solution of tetrazene in N. hydrochloric acid used in the determination of the absorption spectrum (Section 4.1) was re-measured after standing at room temperature for various intervals of time. The spectrum obtained after 145 hours is shown as curve B in Fig. 1, from which it is clear that extensive decomposition of the solute has occurred. After prolonged standing the solution showed almost no absorption. Table 1 gives the E-values at 280 mμ for intermediate ages of the solution.

TABLE 1

Time, hours	E at 280 mμ	$K = \frac{1}{t} \log \frac{E_t}{E_o}$
(a)	(b)	(c)
0	805	-
26	442	0.070
50	357	0.045
73	263	0.042
145	83	0.068

The figures in column (c) are the rate constants calculated for a first order decomposition. In the absence of temperature control, the constancy of K is sufficiently good to suggest that the kinetics are of this form.

The measurements to determine the acid dissociation constant, described above, provided further data on the stability of tetrazene in solution. Below pH 2, no change in the optical density of the solutions could be detected over periods up to 30 - 45 minutes. Between pH 2 and 7, the optical density decreased by up to 5 per cent during this time, and above pH 7 the rate of decomposition increased rapidly. For completeness, the kinetics of the reaction in alkaline solution were investigated in more detail.

/6.2 .....

6.2 Method

40 mg. of tetrazene were dissolved in 250 ml. of 1.00 N. hydrochloric acid. 15 ml. of this solution were added to buffer mixtures of glycine plus sodium hydroxide, and the whole diluted to 250 ml. with water. The time was noted as the acid tetrazene was added to the buffer mixture. The optical density was measured at intervals of time against a similar buffer mixture in the reference cell. The readings were continued until the optical density fell to zero. Cell matching corrections were determined and applied to the results. The pH of each solution was measured on a pH-meter using a normal hydrogen electrode against a saturated calomel reference electrode.

6.3 Results and Discussion

If D_t = corrected optical density at time t, and D_∞ = the final optical density at the end of the reaction, the amount of tetrazene remaining at time t is proportional to $D_t - D_\infty$. The results for three pH-values, 9.95, 10.64 and 11.44, are presented in Tables 2a, 2b and 2c.

TABLE 2a

pH = 9.95

Time, minutes	$(D_t-D_\infty)_{280}$	log (D_t-D_∞)
4	0.670	-0.174
6	0.666	-0.176
12	0.656	-0.183
20	0.639	-0.195
30	0.617	-0.210
50	0.583	-0.234
70	0.548	-0.261
140	0.435	-0.362
180	0.387	-0.412
200	0.365	-0.438
240	0.324	-0.490
290	0.278	-0.556
320	0.250	-0.603
340	0.236	-0.627

TABLE 2b

pH = 10.64

Time, minutes	$(D_t-D_\infty)_{280}$	log (D_t-D_∞)
3	0.682	-0.166
7	0.637	-0.196
9	0.612	-0.213
11	0.589	-0.230
15	0.547	-0.262
21	0.498	-0.303
25	0.468	-0.330
30	0.431	-0.366
40	0.364	-0.439
65	0.243	-0.614
90	0.165	-0.783
120	0.110	-0.959
200	0.048	-1.319
240	0.035	-1.456
260	0.030	-1.523
300	0.024	-1.620
350	0.018	-1.745

TABLE 2c

pH = 11.44

Time, minutes	$(D_t-D_\infty)_{280}$	log (D_t-D_∞)
4	0.263	-0.580
6	0.199	-0.701
8	0.140	-0.854
10	0.097	-1.014
12	0.069	-1.161
14	0.050	-1.301
17	0.031	-1.509
21	0.016	-1.796
27	0.007	-2.155
37	0.002	-2.699

/For .....

For each pH-value, a plot of t against log $(D_t - D_\infty)$ gives a good straight line showing that the decomposition is of the first order with respect to tetrazene. The slope of each line is given by:

$$\text{Slope } S = -k/2.303,$$

where k is the first order velocity constant defined by $-dc/dt = kc$.

$$\text{Hence } k = -2.303S.$$

The value of S for each plot was determined by the method of least squares giving the values of k for each pH as shown in Table 3.

TABLE 3

pH	k sec^{-1}	log k.
9.95	5.18×10^{-5}	-4.283
10.64	2.16×10^{-4}	-3.663
11.44	2.68×10^{-3}	-2.572

In general, the rate of decomposition of tetrazene in solution is given by:

$$-d[T]/dt = k_1 [T]^n [HO]^m$$

where [T] = concentration of tetrazene and [HO] = concentration of hydroxyl ions.

For constant pH the term $k_1 [HO]^m$ becomes the constant k of Table 3, and it has been shown above that n = 1, since the decomposition is of the first order with respect to tetrazene.

$$\text{i.e. } -d[T]/dt = k[T]$$

$$\text{Now, } k = k_1 [HO]^m$$

$$\therefore \log k = \log k_1 + m \log [HO]$$

The value of m may now be determined from the dependence of k on pH. Putting in the usual way $[HO] = K_w/[H_3O]$ we have:

$$\log k = \log k_1 + m \log K_w + m.pH.$$

Hence, the plot of log k against pH should be a straight line of slope m. When so treated, the results in Table 3 gave a good linear plot with a slope of S = m = 1.22, showing that the decomposition is of the first order with respect to the hydroxyl ion. For interest, the overall rate constant k_1 was determined from the intercept of the plot of log k versus log [HO] at log [HO] = 0, whence:

$$\log k = 0.60 + 1.22 \log [HO]$$

$$\text{i.e. } \log k_1 = 0.60 \text{ and so } k_1 = 4.0 \text{ litre.mol.}^{-1}\text{sec.}^{-1}.$$

/The .....

The overall rate equation thus becomes:

$$-d\,[T]/dt = 4.0\,[T][HO] \text{ mol. litre.}^{-1}\text{sec.}^{-1}$$

This result is of value for predicting rough values for the loss of tetrazene by decomposition in solution under the various conditions of acidity which may be encountered in projected analytical schemes.

7. THE SPECTROPHOTOMETRIC DETERMINATION OF TETRAZENE

7.1 Calibration

Tetrazene may be determined quantitatively by the usual spectrophotometric technique of measuring the optical density of the unknown solution and finding the concentration by reference to an established calibration curve prepared from measurements on a number of standard solutions. On the basis of the results described above, it is necessary to work in an aqueous acid medium in order (a) to ensure a constancy in the molecular species present and (b) to keep the rate of spontaneous decomposition negligible. A specimen calibration curve is shown in Fig.3; it was obtained as follows:

Quantities of tetrazene in the range 40 - 200 mg. were dissolved in 100 ml. of 4 M. nitric acid, and a 5 ml. aliquot of each solution was diluted to about 500 ml. with water. 10 ml. of concentrated hydrochloric acid were then added and the mixture made up to 1000 ml. with water. The hydrochloric acid was added in order to lower the pH below the value 0.8 required to suppress the acidic dissociation of the tetrazene as discussed in Section 5. 5 ml. of the nitric acid used as solvent was similarly treated for use in the reference cell.

The optical density of this series of standards was measured at 280 mμ in 10 mm. silica cells and corrected for cell window absorption.

The plot of optical density against concentration is seen to be a good straight line showing that within the concentration range employed, the solutions accurately obey Beers' Law.

7.2 The Effect of Impurities

The preparation of a calibration curve involves the use of a suitably pure specimen of the material. In this work, commercial tetrazene was dissolved in 4 M. nitric acid and reprecipitated by the addition of the calculated quantity of 4 M. ammonia. The addition of ammonia was controlled so that the temperature did not rise above 15° - 20°C. After filtration, the tetrazene was washed with cold water and then dried to constant weight over phosphoric oxide. This procedure is justified since it was found that repetition of the process on a given sample did not affect the E-value at 280 mμ. Thus, the constancy of E is here analogous to the principle of the constancy of the melting-point as a criterion of the purity of typical organic compounds.

This method for the assay of tetrazene is more specific than the chemical procedure discussed in Section 3 since non-absorbing impurities do not interfere. Certain uncharacterised impurities may absorb at 280 mμ and would therefore be estimated as tetrazene, but their presence may be detected by the further measurements described below.

7.3 The Products of Alkaline Hydrolysis

Tetrazene is decomposed very rapidly by 0.1 N. aqueous potassium hydroxide,

/but at a .....

but at a nominal tetrazene concentration of around 1 mg./100 ml., the resulting solution shows almost no absorption spectrum. This position is changed at higher concentrations, and Fig. 4, curve A shows the result of dissolving 120 mg. of tetrazene in 250 ml. of 0.1 N. potassium hydroxide. The absorption rises to a maximum at 303 mμ, with an E-value of 7.60, and passes through a minimum at 278 mμ (E = 5.80). The spectrum obtained by first decomposing tetrazene in alkali as above and then making the solution acid is illustrated as curve A′ in Fig. 4. In acid solution, the absorption maximum of the hydrolysis products at 303 mμ is replaced by a weak inflexion at 275 - 280 mμ, showing that these products consist of substances capable of undergoing acid-base dissociation of the type:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

This is consistent with the work of Lieber et al. (9) which has established 5-azido-tetrazole as the chief alkaline hydrolysis product, and this substance is known to be acidic (7). Since no 5-azido-tetrazole was available it was not possible to make a spectral comparison.

7.4 The Examination of Tetrazene for Purity

The spectrum obtained after alkaline hydrolysis may be used in conjunction with the absorption of a freshly prepared sclution in acid to determine the quality of any tetrazene sample.

Table 4 contains the E-values at 280 mμ for several samples of tetrazene, which are distinguished as follows:

A. Commercial tetrazene purified as described in Section 7.2.

B. Tetrazene from I.C.I. lot 479B. This was some years old and had a marked yellow colour.

C and D. Two synthetic samples prepared by Dr. T. M. Walters in this Establishment (see Section 9).

The E-values were determined as described for the standard calibration curve, the solutions containing about 1 mg. of tetrazene per 100 ml.

TABLE 4

Expt.No.	Sample:			
	A	B	C	D
1	774	780	765	784
2	770	783	762	782
3	780	775	769	777
4	769	781	770	779
5	772	780	766	780
Mean	773	779	766	780
S	4.36	3.08	3.24	2.74

S = Standard Deviation with 4 degrees of freedom.

/It is .....

It is clear that these results do not differ greatly from one sample to another. However, curves A, B, C and D in Fig. 4 show the corresponding results obtained by dissolving about 120 mg. of each sample in 250 ml. of 0.1 N. potassium hydroxide. The spectra of samples B, C and D are now seen to differ markedly from that for the pure sample A and also from one another. The maxima for B and D lie in the region 320 - 325 mμ, whilst that for C shows little more than an inflexion at about 320 mμ. Thus, although the measurements on dilute tetrazene solutions in acid (Table 4) reveal little difference between the samples, the presence of impurities is effectively demonstrated by the results obtained after alkaline decomposition.

It has not so far been possible to establish the identity of the impurities present in samples B, C and D. By the nature of reaction employed for the manufacture of tetrazene, it might have been thought that 1:3-ditetrazolyl-triazine (Section 4.2) would be a likely contaminant. The spectrum of this material is presented in Fig. 5 for acid, neutral and alkaline solution (curves A, B and C respectively). Due to the two tetrazole rings, it should behave as a dibasic acid, and in consequence its spectrum changes with pH as the curves in Fig. 5 show. However, in alkaline solution λ_{max} lies at 333 mμ which is significantly different from the values given by samples B, C and D, above, so that the presence of this compound as an impurity is unlikely. Explicit details for carrying out these tests are included as an Appendix to this report (p. 13).

7.5 Conclusions

In the absence of precise information concerning the nature of the impurities present in the samples B, C and D, the tests for purity outlined above are somewhat arbitrary. However, the procedure is very rapid and is well suited for manufacturing control purposes. Since the purification of tetrazene is not difficult, the method would also be of value for final inspection, even if subsequent work shows that the impurities of the type found in samples B, C and D do not affect the performance of the material. In any case, until characterisation of these impurities is achieved it is not possible to say whether the spectral results are due to significant quantities of low absorbing material or to mere traces of substances possessing very high extinction coefficients.

8. THE DETERMINATION OF TETRAZENE IN V.H.2 CAP COMPOSITION

The determination of the tetrazene content of V.H.2 cap composition may be carried out spectrophotometrically. The composition is made up as follows:

	%, w/w
Lead Styphnate	38
Barium Nitrate	39
Calcium Silicide	11
Lead Peroxide	5
Antimony Sulphide	5
Tetrazene	2

Saundersson (2) has described the complete analysis of this composition. The barium nitrate and lead styphnate are removed successively by extraction with water and ammonium acetate, respectively. The lead peroxide is then removed by a mixture of potassium iodide and ammonium acetate in 50 per cent acetic acid. The tetrazene in the residue is then dissolved out by 4 M. nitric acid and determined by precipitation as the silver nitrate complex. In the present work, since only the tetrazene was to be determined, the first three components were extracted simultaneously using the reagent for lead peroxide.

/8.1 .....

8.1 Method

Small quantities of V.H.2 composition of the order of 50 mg. were weighed into a G.4 sintered-glass crucible and extracted with 3 x 2.5 ml. quantities of a solution containing 100 g. ammonium acetate, 12.5 g. potassium iodide in 200 ml. of 50 per cent acetic acid. After washing with 2 x 2.5 ml. volumes of water, the remaining lead styphnate was removed using 3 x 2.5 ml. portions of 20 per cent ammonium acetate solution, and the residue washed with 4 x 2.5 ml. volumes of cold water. The tetrazene in the residue was then extracted by adding a measured 1.00 ml. volume of 4 M. nitric acid, finally washing with further 4 x 2.5 ml. volumes of water. The filtrate from this last extraction was diluted to 200 ml. with 0.1 N. hydrochloric acid, and its optical density measured at 280 mμ. The reference cell was filled with a solution made up from 1 ml. of the 4 M. acid diluted in a similar way. Cell corrections were determined and applied to the readings, and the tetrazene concentration could then be read off from the calibration curve (Fig. 3).

8.2 Results and Discussion

Six replicate determinations of the tetrazene content of the composition are shown in Table 5.

TABLE 5

Expt.No.	% Tetrazene Found
1	1.55
2	1.50
3	1.52
4	1.50
5	1.46
6	1.55
Mean	1.51
Standard deviation	0.035
Coefficient of variation	2.29%

The precision of these results is excellent, bearing in mind that only 1 mg. of tetrazene is used in the determination. The departure of the mean value, 1.51 per cent, from the nominal 2 per cent specified for V.H.2 may be due either to a deterioration of the tetrazene during storage, or to loss of tetrazene by its solubility in the reagents used for the extraction of the other soluble ingredients. The latter explanation is unlikely, since the use of double the stated volumes of the reagents did not affect the results.

It was found necessary to ensure that the lead styphnate was completely removed prior to the extraction of the tetrazene, since the styphnate ion possesses intense absorption around 280 mμ.

/9. .....

9. CONCLUSIONS

It is considered that the work described in this report represents a satisfactory basis for a rapid and specific method for determining the purity of tetrazene, and for its determination in cap composition. The lack of knowledge concerning the identity of the impurities present is not a serious drawback, and it is hoped to obtain more information on this point from further work, now in progress, into the detailed chemistry of the compound.

With regard to the two synthetic samples of tetrazene C and D in Section 7.4, recent X-ray powder photographs taken by Mr. J. R. C. Duke of E.R.D.E. have been shown to differ from those for standard commercial material. It is not certain as yet whether the samples concerned are chemical species different from tetrazene, or whether they are merely polymorphs: their sensitivity is said to differ also.

10. ACKNOWLEDGMENTS

Thanks are due to Mr. E. Brown and to Dr. T. M. Walters for many valuable discussions, and to the latter for supplying a number of samples used in the work.

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/12. .....

12. APPENDIX:

THE DETERMINATION OF THE PURITY OF TETRAZENE

NOTE It is to be remembered at all times that tetrazene is a sensitive material, so that all precautions should be taken when handling it.

12.1 Reagents Required

1. 0.1 N. Potassium hydroxide solution.

2. 4 M. Nitric acid solution.

3. Pure tetrazene: Dissolve 2 g. of commercial tetrazene in 100 ml. of 4 M. nitric acid. Cool the solution to 5°C and make neutral to methyl orange by adding 4 M. ammonia. Make the addition slowly and with stirring, keeping the temperature below 15° - 20°C. Filter off the precipitated tetrazene, wash with three or four 5 - 10 ml. volumes of cold water and dry to a constant weight over phosphoric oxide.

12.2 Method

12.2.1 Test A

Weigh accurately two 0.10 g. portions of the sample to be tested and dissolve in exactly 100 ml. of 4 M. nitric acid. Dilute 5 ml. of this solution to 1000 ml. with water, adding 10 ml. of concentrated hydrochloric acid, and make a similar dilution on the acid used as the solvent. Measure the optical density of the tetrazene solutions over the wavelength range 270 - 290 mμ at 2.5 mμ intervals in 10 mm. fused silica cells against the acid blank in the compensating cell, using a Unicam SP.500 spectrophotometer or an equivalent instrument. Repeat the measurements on two solutions prepared in a similar manner from pure tetrazene (see Note, p. 14). Determine cell matching corrections at each wavelength with the acid blank in both cells.

Calculate the purity of the sample as follows:

$$\text{Percentage of tetrazene in the sample} = \frac{100w_2(D_1 - \Delta D_1)}{W(D_2 - \Delta D_2)}$$

w_2 = mean weight of pure tetrazene taken.

W = mean weight of sample taken.

D_1 and ΔD_1 = mean optical density and cell correction for sample solution at 280 mμ.

D_2 and ΔD_2 = mean optical density and cell correction for standard solution at 280 mμ.

12.2.2 Test B

Weigh accurately 0.12 - 0.13 g. of the sample to be tested and dissolve in exactly 250 ml. of 0.1 N. potassium hydroxide: allow to stand for 10 minutes. Measure the optical density over the wavelength range 260 - 360 mμ at 5 mμ intervals as described in Test A above, but with 0.1 N. potassium hydroxide in the compensating cell. Repeat the procedure with pure tetrazene, and calculate the E-values at each wavelength as follows:

/E = 0.4 .....

$$E = 0.4(D - \Delta D)/W$$

W = weight of sample taken (grams) and

D, ΔD are the densities and cell corrections at each wavelength.

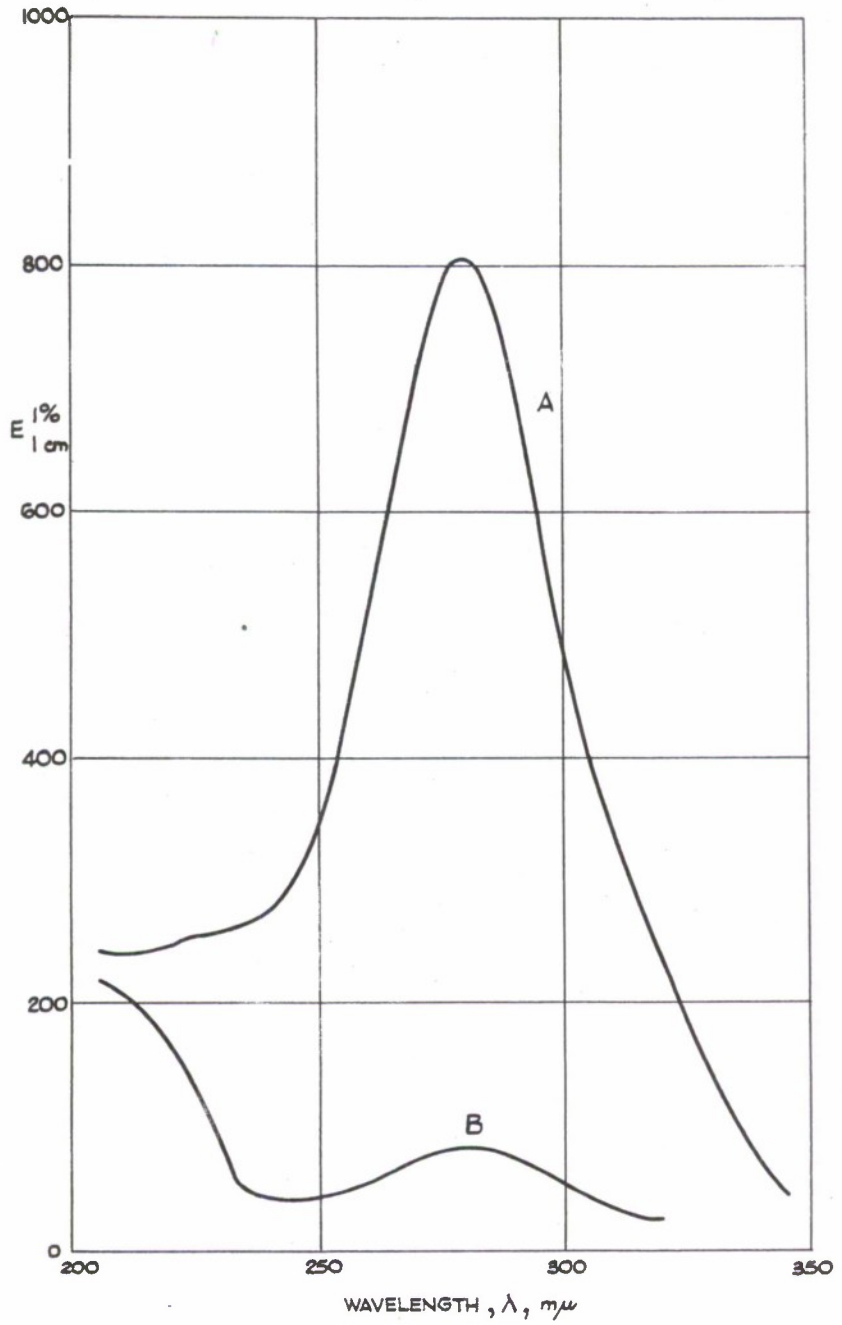
12.3 Interpretation of the Results

As explained in Section 7, the purity determination by Test A may be vitiated by the presence of absorbing impurities, and Test B is therefore used to detect the presence of such material. If Test B gives a spectrum agreeing closely with that for pure tetrazene, then Test A may be used for the determination of the percentage purity of the sample. The agreement between the test sample and the standard in Test B should be within $\pm$ 5 per cent, and the absorption maximum should lie within $\pm$ 2 - 3 $m\mu$ of that for the standard.

12.4 Note

In carrying out Test A, the tetrazene solution should be measured as soon as possible after making up, and in any case within 30 minutes.

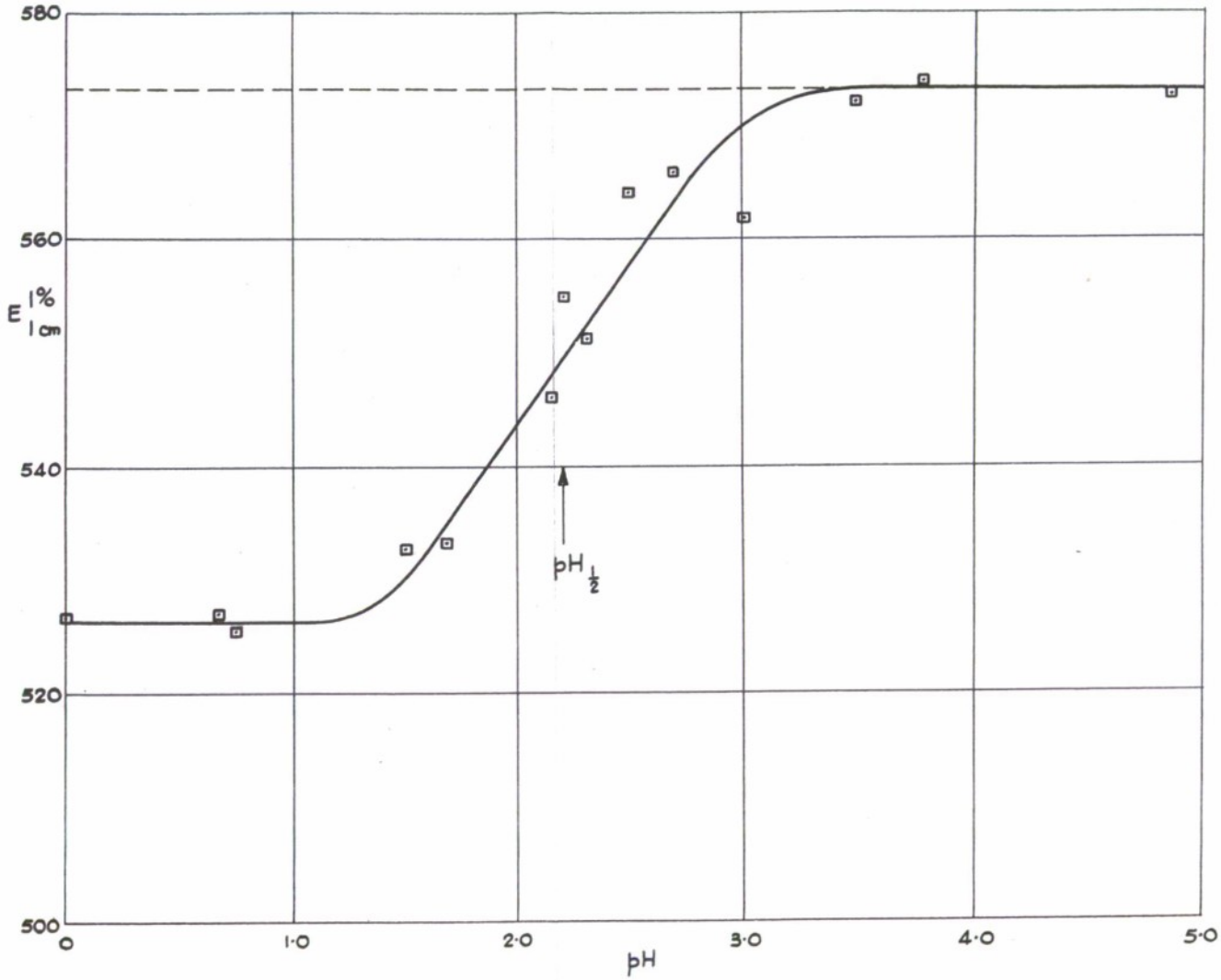
M.No.470/55
S.No.433/GMM



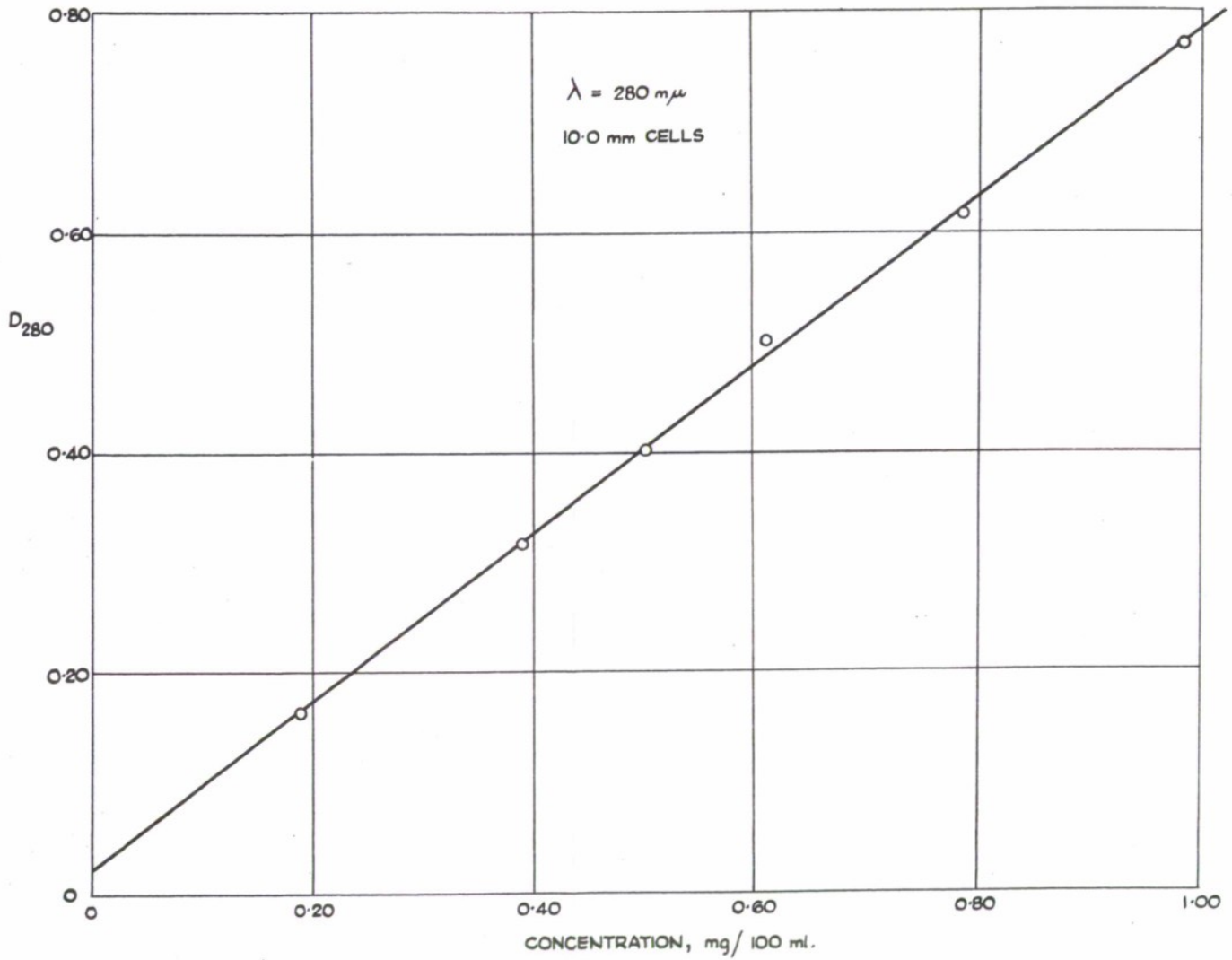
CURVE A : IN N HCl

CURVE B : AFTER STANDING FOR 145 HOURS

THE ABSORPTION SPECTRUM OF TETRAZENE. FIG. 1.

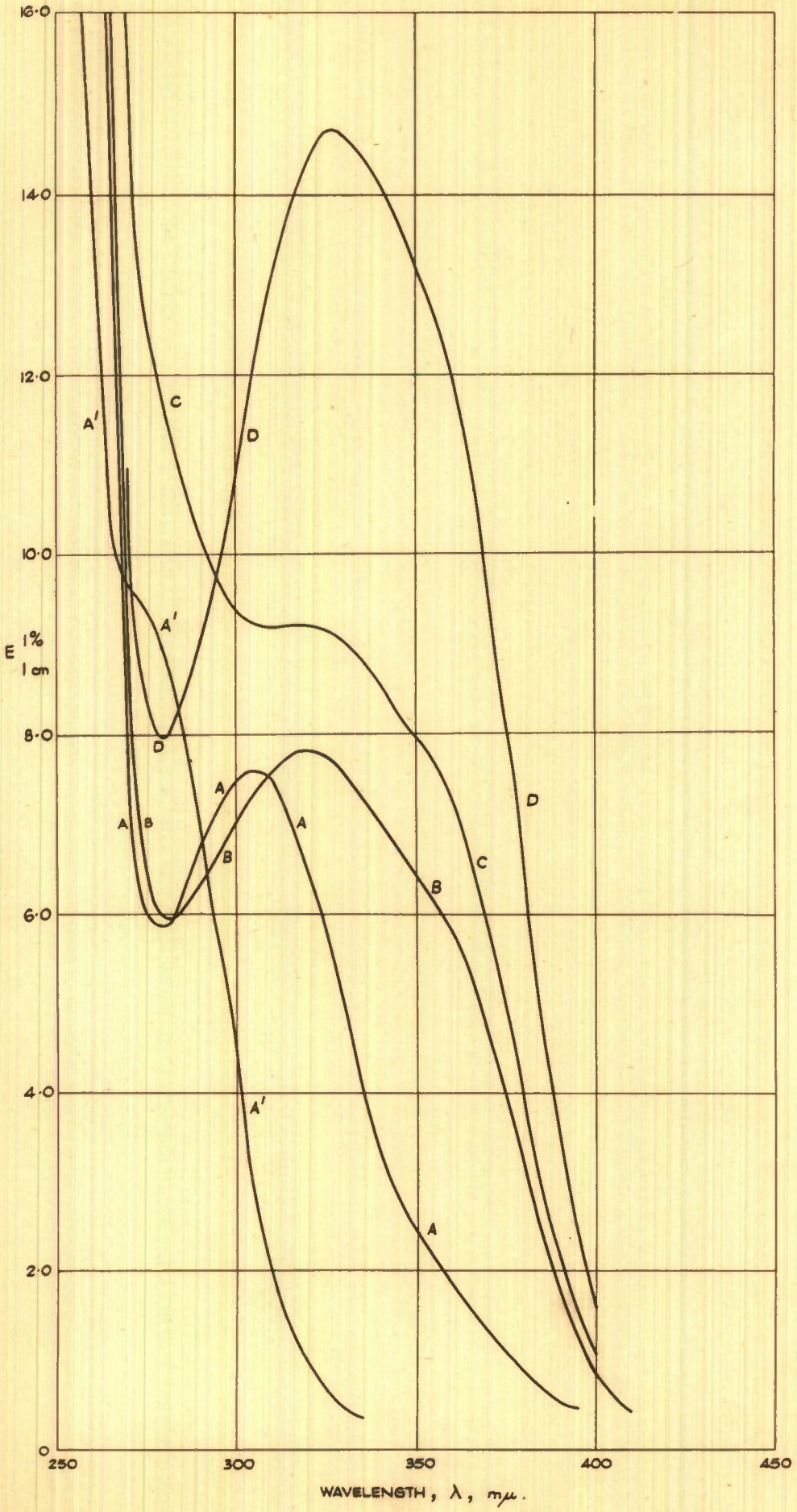


THE VARIATION IN TETRAZENE ABSORPTION WITH pH AT λ = 300 mμ. FIG. 2.



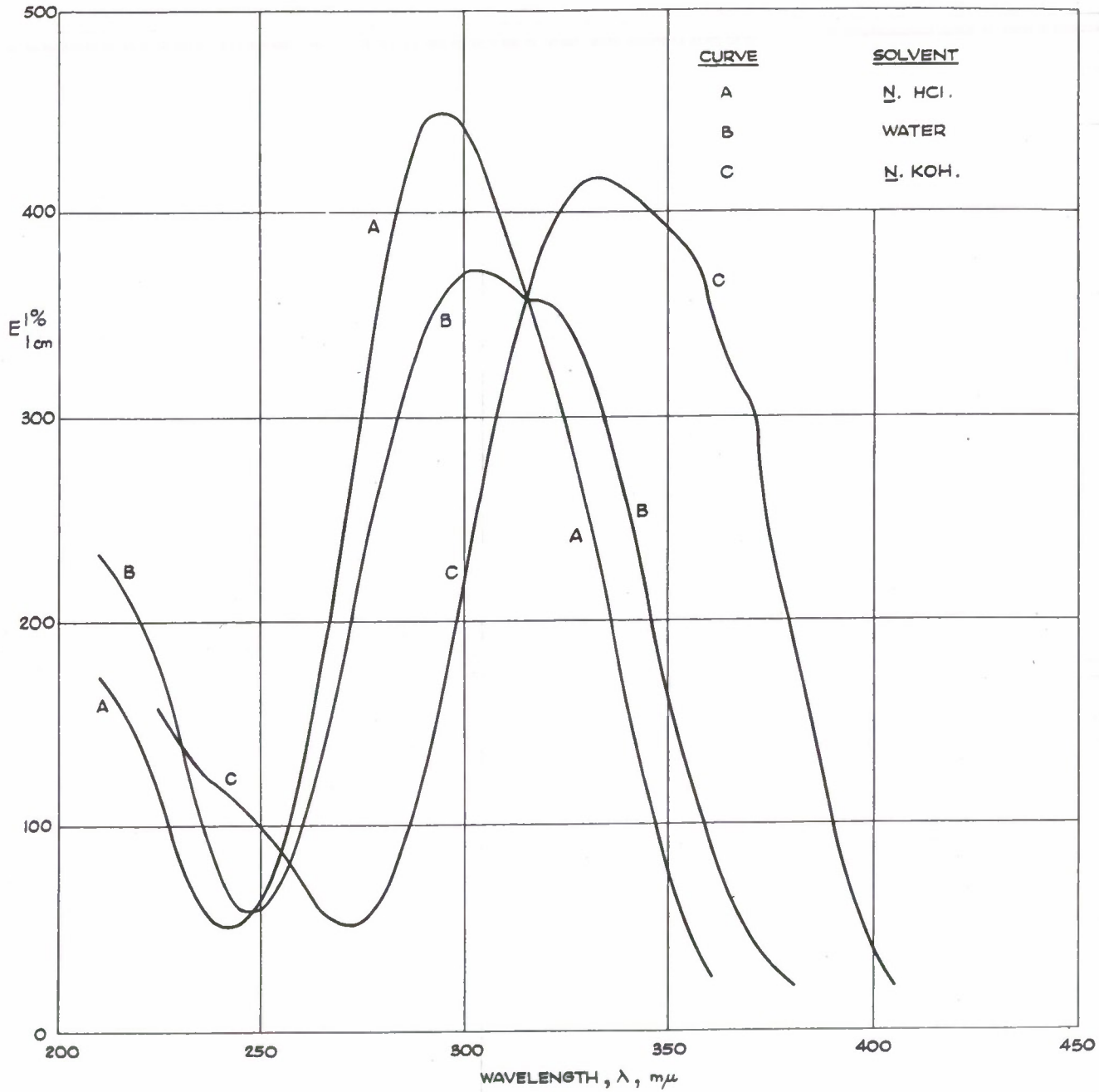
CALIBRATION CURVE FOR TETRAZENE

FIG. 3.



ABSORPTION SPECTRA OF THE ALKALINE HYDROLYSIS PRODUCTS OF VARIOUS SAMPLES OF TETRAZENE (IN N KOH)

FIG. 4.



THE ABSORPTION SPECTRUM OF SYM.- DITETRAZOLYLTRIAZINE.

FIG. 5.

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The spectral studies support the tetrazene structure involving a tetrazole ring.

14 pp., 5 fig., 5 tables.

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