HYDROXYTRAZENES AS CHELATING AGENTS IN ANALYTICAL CHEMISTRY

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SUMMARY

Studies on hydroxytriazenes covering (A) Synthesis of hydroxytriazenes; (B) Tautomerism; (C) Structure of 3-hydroxy-1,3-diphenyl-triazene and its analogues; (D) Analytical applications; (E) Ionisation constants of hydroxytriazenes; (F) Stability constants of metal chelates of hydroxytriazenes; (G) Spot tests for hydroxytriazenes; (H) Spectrophotometric determination of hydroxytriazenes and (I) Miscellaneous studies of hydroxytriazenes have been reviewed.

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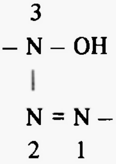
Cupferron (ammonium salt of nitrosophenyl hydroxylamine) is one of the most widely used reagents for the separation and estimation of various metal ions. However, the complexes prepared from it, as well as the reagent itself, are thermally unstable and so they are considered unsuitable for direct weighing. The reagent is also photosensitive and even on careful storage undergoes gradual deterioration. To remove these defects, the first successful attempt was made by Schome /1/, who replaced the nitroso group by benzoyl and examined the utility of benzoyl phenylhydroxylamine as an analytical reagent. Shome /2/ also indicated the possibility of replacing the benzoyl group by other substituents. Sogani and Bhattacharya /3/ made a detailed study of this aspect, and prepared a large number of substituted phenyl hydroxylamines *viz.* formyl, acetyl, urea and thiourea derivatives etc. and ultimately discovered an excellent series of compounds in the azo derivatives. Sogani *et al.* /4-9/ have prepared numerous compounds of this series. However, Bamberger /10/, Gebhard and Thompson /11/ are to be accredited for synthesising a number of hydroxytriazenes for the first time. The complexing ability of these compounds was first of all examined by Elkins and Hunter /12/.

These compounds have been given the names: diazohydroxyamine compounds and triazene oxides (the azoxy analogue in the triazene series) in "Chemistry of Carbon Compounds" edited by Rodd /13/. However, Sogani *et al.* preferred to name these compounds as the 3-hydroxytriazene family. The common functional grouping possessed by these compounds may be represented as



$$\begin{array}{l} \;3 \\ -\mathrm{N}-\mathrm{OH} \\ \;| \\ \;\mathrm{N}=\mathrm{N}- \\ \;2\quad 1 \end{array}$$

The analytical applications of this class of organic reagent were reviewed by Purohit /14/, and subsequently Chakraborti and Majumdar /15/ reviewed the work done during the decade 1967–76.

A. SYNTHESIS

A survey of the literature reveals that hydroxytriazenes have been prepared by the following three methods:

I: Reaction of phenyl hydrazine or a substituted phenyl hydrazine /10/ with aliphatic or aromatic nitro or nitroso compounds.

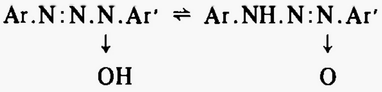
II: Coupling reaction of diazo compounds /3/ with alkyl or aryl substituted hydroxylamines.

III: By oxidation of diazoaminobenzene with peroxy benzoic acid /16/ in a suitable solvent.

In general, the second method has been more widely used.

B. TAUTOMERISM

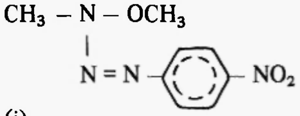
On page 307 of Rodd's "Chemistry of Carbon Compounds" Vol. III$^{\mathrm{A}}$ Chapter VI, it is stated that: "The so called diazohydroxyamino compounds can be regarded as the tautomeric forms of triazene oxides, the azoxy analogue in the triazene series.



$$\mathrm{Ar.N\!:\!N.\underset{\overset{\downarrow}{OH}}{N}.Ar'} \rightleftharpoons \mathrm{Ar.NH.N\!:\!\underset{\overset{\downarrow}{O}}{N}.Ar'}$$

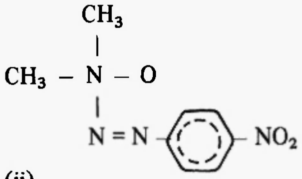
The tautomerism is also reflected in the existence of both the O- and N-ethers, the latter being exclusively formed by the action of alkyl iodides on the metal salts of diazohydroxyamino compounds (E. Bamberger, Ber., 1897, **30**, 2285: *cf.*, however, A.B. Boese *et al.*, J. Amer. Chem. Soc., 1931, 53, 3530). This recalls the behaviour of primary nitrosoamines, nitramines and nitrosophenyl hydroxylamines under similar conditions."

It is rather surprising to find this misleading statement in such a standard work. On consulting the two references above cited one does not find any mention of 1-N-alkyl derivatives, although mention is made of 3-N(or O)-alkyl derivatives which cannot be related to tautomerism. To cite a specific example, Bamberger (loc. cit.) describes the preparation of only one O-alkyl derivative i.e. 3-methoxy-3-methyl-1-p-nitrophenyl triazene.



(i)

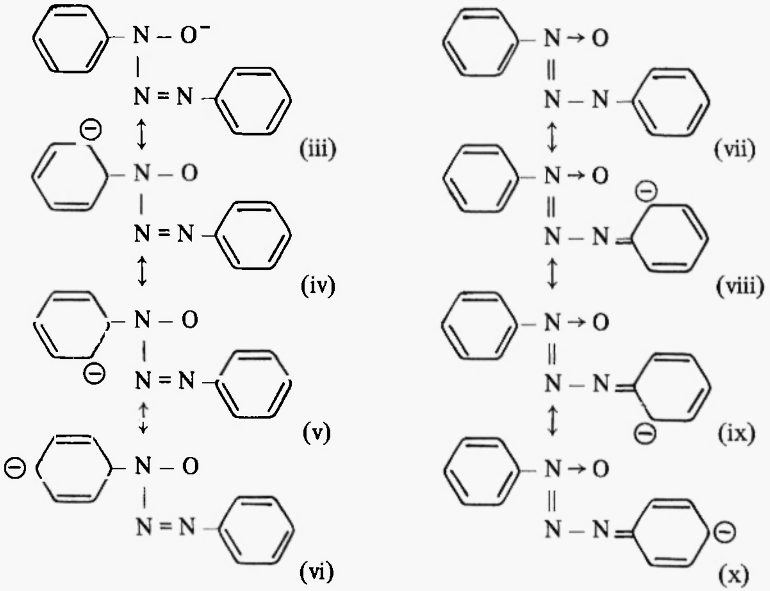
by mixing methyl iodide (2 moles) and 3-hydroxy-3-methyl-1-p-nitrophenyl triazene (1 mole) in alcohol followed by a slow addition of alcoholic caustic potash over 3-4 hours. However, Boese *et al.* (loc. cit.) prepared (i) by the action of p-nitrophenyl diazonium chloride on O,N-dimethyl hydroxylamine as a stable yellow crystalline compound, m.p. 66°. It was not identical with the compound prepared by Bamberger which had a m.p. 142°. Boese /17/ suggested that the compound prepared by Bamberger was not (i) but,



(ii)

This amine oxide structure for Bamberger's compound, however, seems to be quite probable, as N,N-disubstituted hydroxylamines when treated with methyl iodide give amine oxide with liberation of HI. However, this problem is still unresolved, and more work is needed to clarify it.

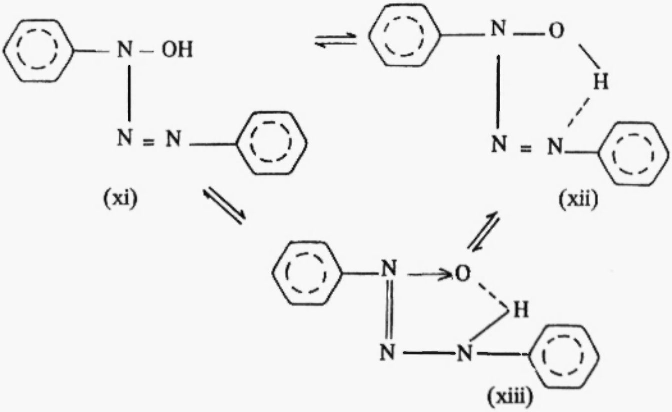
On the basis of UV absorption studies, Calzolari and Furlani /18/ suggested that 3-hydroxy-1,3-diphenyl triazene either exists in a single form or that the two tautomeric forms have identical spectra. Purohit *et al.* /8/ also suggested the existence of a hydrogen-bonded structure and its tautomeric forms on the basis of spectral studies, and they derived the same conclusion from the dissociation constant value of 3-hydroxy-1,3-diphenyl triazene /19/, pk = 11.41. The anion has been assigned the following resonating forms:



Structures (iii) to (x) indicate that the charge on the anion is distributed over two benzene rings, hence 3-hydroxy-1,3-diphenyl triazene was expected to be a stronger acid than phenol. However, the pk value provided just the opposite picture. This suppression of acid character led Purohit *et al.* /7/ to suggest the hydrogen bonded structure and its tautomeric forms (xii) and (xiii).

C. STRUCTURE OF 3-HYDROXY-1,3-DIPHENYL TRIAZENE AND ITS ANALOGUES

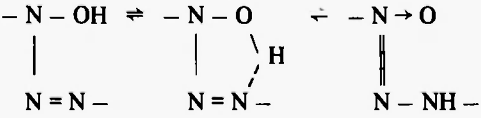
The structure of 3-hydroxy-1,3-diphenyl-triazene (HDPT) (xi) was suggested by Purohit *et al.* /7/ to exist in an intra-moleculary hydrogen-bonded form (xii) and its tautomeric form (xiii).



This view also supported by UV and IR spectral studies carried out by the same authors. IR spectra in KBr showed bands at 3480 cm^{-1} and 3190 cm^{-1} for νOH and νNH, respectively.

However, the 3480 cm^{-1} band was not in evidence in carbon tetrachloride, and Mitsuhasi *et al.* /20/ reported the position of a second band at 3250.6 cm^{-1} and it was established to be νNH by studies on ^{15}N (nitrogen remote from oxygen) in labelled HDPT. The band position in the labelled HDPT was 3243.7 cm^{-1} i.e. the position lowered by 6.9 cm^{-1} from that of the unlabelled compound. The same authors also described similar studies on ^{15}N labelled 3-hydroxy-1-p-methoxy-phenyl-3-phenyl triazene and the band was identified at 3237.6 cm^{-1}, which led them to conclude that form (xiii) is predominant. However, the complete spectra were not analysed by them.

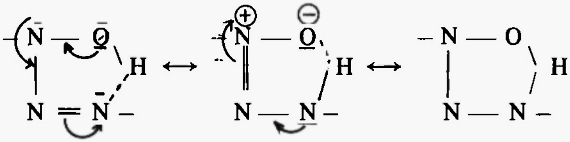
The existence of tautomeric forms is expected due to the possibility of migration of the H-atom through formation of an intermediate chelate (xiv)



$$\begin{array}{lcllcl} -\mathrm{N}-\mathrm{OH} & \rightleftharpoons & -\mathrm{N}-\mathrm{O} & & \rightleftharpoons & -\mathrm{N}\rightarrow\mathrm{O} \\ \;| & & \;| \quad \diagdown_{\mathrm{H}} & & & \;\| \\ \mathrm{N}=\mathrm{N}- & & \mathrm{N}=\mathrm{N}- & & & \mathrm{N}-\mathrm{NH}- \end{array}$$

(xiv)

The oxygen atom in this hydroxy triazene group being an electron donor leads to an increase in the negative charge on the nitrogen atom. This increases the affinity of the H-atom for nitrogen. However, a complete transfer of the H-atom does not occur because oxygen is more electronegative than nitrogen. Thus a hydroxytriazene structure has been proposed with a very stable chelate ring (xvii) by Purohit (unpublished results).



(xv) (xvi) (xvii)

Delocalisation of electron density in the ring leads to strengthening of the N – N, and N – O bonds and to their equalisation. There is an increase in the symmetry of the π-electron cloud of the molecule.

D. ANALYTICAL APPLICATIONS

1. 3-Hydroxy-1,3-diphenyl triazene (HDPT) /3, 4, 21/

This reagent prepared by coupling phenyl hydroxylamine with benzene diazonium chloride, is a light yellow compound with m.p. 119–120. This is a stable compound and can be preserved indefinitely. Most of its metal complexes are granular with definite compositions. They are thermally stable and suitable for direct weighing. The complexes are insoluble in water and excess of the reagent can be removed by washing with dilute alcohol or by heating a weakly acidic solution to hydrolyse it to water-soluble products. Moreover, the washings can be checked for the presence of reagent by adding a drop of sodium hydroxide solution which results in a intense yellow colour, if alcohol is used and a blue colour if the reagent is hydrolysed. Below pH 3.0 the reagent precipitates Cu(II), Pd(II), Fe(III), V(VI), Ti(IV) and molybdate. But, only the Cu(II) and Pd(II) complexes are stable if the acidic reaction mixture is heated. Using alcohol as solvent, the spectral characteristics of the reagent are reported as λmax. 238 nm with logϵ 4.186 and λmax. 348 nm with logϵ 4.328.

1(a) Determination of Pd(II) /4, 21, 22/

3-Hydroxy-1,3-diphenyl triazene precipitates Pd(II) quantitatively between pH 1.6 and 8. The yellowish green, granular complex is soluble in organic solvents such as chloroform, carbon tetrachloride, acetone and benzene. It is crystallised from acetone as silky yellowish brown coloured needles with m.p. 252°. The spectral characteristics of the complex in alcohol are λmax. 255 and 413 nm with logϵ 4.585 and 4.384 respectively.

For the determination of Pd(II), the pH is kept between 2 and 3 with the help of hydrochloric acid and sodium acetate or sodium potassium tartrate solution. A 20 to 25% excess of the reagent is added. Palladium(II) can be estimated in the presence of Ni(II), Co(II), Zn, Al, Cr(III), Cd, Mn(II), Sb(III), Bi, As(III), Be, UO_2, Fe(III), Zr, Ce(IV) and nitrate. Sodium acetate or sodium potassium tartrate should be avoided when Pd(II) is to be separated from Ce(IV) and Zr and the pH should be adjusted by dilution only. Prolonged heating in presence of buffer solutions causes turbidity and high results are obtained. Au(III), Ag and Os(IV) interfere, as they are reduced to their metallic state by the reagent. However, Pt(IV) can be tolerated up to 10 fold excess. The separation from Rh(IV), Ru(III), Ir(III), Th, Sn(IV), Pb, Ti(IV), molybdate, fluoride and phosphate has also been discussed. Alkali and alkaline earth metal ions do not form precipitates with the reagent and need not be separated.

This reagent has been claimed to be superior to dimethylglyoxime.

Kazumasa Ueda *et al.* /23/ also determined Pd(II) spectrophotometrically. Pd(II) forms a yellow green precipitate with HDPT extractable in benzene. The complex is stable for a long time. The optimum pH for extraction is between 3.5–4.5. The maximum absorption is at 414-417 nm. Beer's law is applicable upto 50 μg pf Pd(II) in 10.0 ml of benzene. The formula of the complex was established as PdR_2, the molar absorptivity 2.56×10^4 and sensitivity 0.0041 $\mu g\ cm^{-2}$ for absorbance 0.001. When Palladium(II) is determined spectrophotometrically, Fe(II), Fe(III), Cu(II), Os(IV), Sn(II), Sn(IV) and Hg(II) interfere.

Das and Shome /22/ have also determined Pd(II), spectrophotometrically. The metal complex was extracted into benzene. The colour of the complex is stable for 24 hours. Beer's law is obeyed between 0.2–5.5 μg/ml of Pd(II) in the pH range 3.6–5.6 at 415 nm with a molar absorptivity of 21900. The formula of the complex is reported to be PdR_2. In the determination of 57.5 μg of Pd(II), the following ions could be tolerated in mg., (given in parentheses) Ni^{2+} (1.42), Zn^{2+} (1.55), Cd^{2+} (1.50), Hg^{2+} (2.0), Mn^{2+} (1.25), Co^{2+} (1.49), Pb^{2+} (1.25), Bi^{3+} (1.70), Al^{3+} (1.60), Fe^{3+} (1.10), Th^{4+} (1.20), Ti^{4+} (0.70),

Sn^{4+} (0.90), V^{5+} (0.30), Mo^{6+} (0.30), W^{6+} (0.90) and U^{6+} (0.80). The anionic tolerance limits determined are tartrate (10 mg), fluoride (100 mg) and oxalate (10 mg).

1(b) Determination of Cu(II) /21, 22/

Cu(II) is precipitated by 3-hydroxy-1,3-diphenyl triazene between pH 1.7 and 7.0 with a slight excess of the reagent. The complex is chocolate brown in colour and is soluble in ether and acetone but only slightly in alcohol. The complex was crystallised from acetone as brown silky needles with m.p. 193°. The spectral characteristics in alcohol are reported as: λmax. at 248, 283 and 362 nm; and logϵ as 4.563, 4.132 and 4.572 respectively.

To facilitate hydrolysis of the excess reagent and to increase the specificity, Cu(II) is best determined between pH 2.3 and 3.0. It was found in the determination of 13-17 mg of Cu(II) that 50 mg each of Ni(II), Zn, Mn(II), Cd, Bi, Al, Cr(III), Hg(II), As(III), Pb(II), Sb(III), Zr, W(VI), Ce(IV), Th, Be, Co(II), Fe(II), Fe(III), Ti(IV), Sn(IV), nitrate, phosphate, fluoride, tungstate and molybdate could be tolerated. Ag, Au(III) and Os(IV) interfere due to their reduction to the metallic state, which can be prevented by the addition of cyanide. However, Cu(II) cannot be determined in the presence of Pd(II). Also Cu(II) cannot be quantitatively precipitated in the presence of V(V) and V(IV) as these are partially co-precipitated.

The reagent has been claimed to be superior to all other reagents for the determination of Cu(II) including salicylaldoxime and α-benzoinoxime.

1(c) Determination of Ni /21, 22/

Between pH 4.4 and 7.0, the deep yellow complex of Ni(II) is precipitated quantitatively. The complex is highly soluble in benzene, chloroform, and carbon tetrachloride, fairly soluble in ether and acetone and slightly soluble in alcohol. From acetone, it has been crystallised as bright yellow needles, m.p. 209°. In alcohol, the spectral characteristics are λmax. at 248, 320 and 410 nm and logϵ 4.455, 4.391 and 4.199 respectively. Ni(II) can be determined between pH 5.0 and 5.5 in the presence of Zn, Mn(II), Cd, Mg, As(III), Be, fluoride and phosphate.

Das and Shome /22/ have also used HDPT in the spectrophotometric determination of Ni. The complex formed in the pH range 6.4–8.0 is yellow in colour, stable for 72 hours and can be extracted into benzene. Beer's law is obeyed in the concentration range 0.4–3.5 μg/ml Ni at 422 nm. The molar absorptivity is 15200. Zn^{2+} (0.26 mg), Cd (0.12 mg), Hg^{2+} (2.0 mg), Mn^{2+} (0.18 mg), Cu^{2+} (0.50 mg), Pd^{2+} (0.75 mg), Pb^{2+} (1.0 mg), Bi^{3+} (1.7 mg), Al^{3+} (0.80 mg), Fe^{3+} (0.60 mg), Th^{4+} (1.25 mg), Ti^{4+} (1.0 mg), Sn^{4+} (0.30 mg), V^{5+} (0.25 mg), Mo^{6+} (1.20 mg), U^{6+} (1.00 mg), F^- (100 mg), oxalate (10 mg) and tartrate (10 mg) can be tolerated in the spectrophotometric determination of 50 μg Ni^{2+}.

1(d) Determination of Ti(IV)

Ti(IV) is precipitated quantitatively /21/ by HDPT, at pH 4.4-7.0. The complex dissolves appreciably when the concentration of alcohol in the reaction medium exceeds 5%. It decomposes above 55°, and hence the complex is not suitable for direct weighing.

1(e) Vanadium complexes

Dutta and Lahiry /24, 25/ concluded on the basis of X-ray, IR, magnetic moment and molecular weight data that V(V) and V(IV) form the same complex with 3-hydroxy-1,3-diphenyl triazene. V(V) is first reduced to V(IV) by the reagent and then the complex is formed by V(IV). Pyridine was reported to react with the vanadium complex. A number of vanadium(IV) and vanadium(V) complexes with hydroxy triazenes have been prepared and reported by others /26/. The reactions of the complexes with pyridine and picoline were also examined. The resulting mixed complexes were isolated, analysed and studied. However, vanadium has not been estimated quantitatively in either of the oxidation states with this reagent.

1(f) Cu(II) and Cd Separation

HDPT was used by Poonia and Gupta /27/ for the identification and separation of Cu(II) and Cd.

1(g) Determination of Thallium(III) /28/

Tl(III) has been determined spectrophotometrically with 3-hydroxy-1,3-diphenyl triazene with which it forms a 1:3 complex. The orange-red coloured complex is soluble in 70% alcohol and in aqueous solution is fully developed at pH 5.0–8.0, showing maximum absorption at 422 nm. Beer's law is obeyed in the concentration range 20 to 160 μg/ml of Tl(III). The Sandell's sensitivity index was found to be 0.45 μg/cm². A large number of foreign ions could be tolerated in the spectrophotometric determination of 200 μg of Tl(III), the limit in μg in each case is given in parentheses: In^{3+} (2000), Th^{4+} (2000), Zn^{2+} (2000), Ti^{4+} (1800), Al^{3+} (1800), Ga^{3+} (560), W^{6+} (360), Ce^{4+} (280), Zr^{4+} (200), Mo^{6+} (200), Cu^{2+} (160), Ni^{2+} (100), UO_2^{2+} (50) and Fe^{3+} (3). In the presence of fluoride ions large amounts of Fe(III), Th(IV), Al, Ti(IV) and Zr could be tolerated in the spectrophotometric determination of Tl(III). The precision and accuracy of the method were estimated and the relative error was 1.5% at 144 μg per ml and 0.9% at 444 μg per ml of Tl(III).

1(h) Spectrophotometric Determination of Fe(III) /22/

Fe(III) forms a blue-violet complex with this reagent at pH 4.0–5.7. The colour of the complex is stable and constant for 24 hours and can be extracted into benzene. The molar absorptivity is 9800. Beer's law is obeyed in the concentration range 0.5–3.9 μg/ml Fe(III). In the spectrophotometric determination of 65.25 μg of Fe(III), the ions tolerated were Ni^{2+} (1.4 mg), Zn^{2+} (1.25 mg), Cd^{2+} (1.2 mg), Hg^{2+} (2.0 mg), Mn^{2+} (1.2 mg), Co^{2+} (1.0 mg), Pb^{2+} (0.75 mg), Bi^{3+} (0.50 mg), Al^{3+} (1.4 mg), Ga^{3+} (0.23 mg), In^{3+} (0.60 mg), Th^{4+} (1.0 mg), Ti^{4+} (0.025 mg), V^{5+} (0.15 mg), Mo^{6+} (0.65 mg), W^{6+} (0.65 mg), U^{6+} (0.90 mg), oxalate (0.10 mg) and tartrate (10.0 mg).

1(i) Spectrophotometric Determination of Co(II) /22/

Co(II) forms brownish yellow complex with 3-hydroxy-1,3-diphenyl triazene which can be extracted into benzene. The colour is stable for 36 hours. Beer's law is obeyed in the concentration range 0.45–3.25 μg/ml Co(II) in the pH range 6.8–8.3 at 420 nm; the molar absorptivity is 14800. In the spectrophotometric determination of 45.3 μg Co(II), the amounts of ions tolerated in mg are Zn^{2+} (0.18),

Cd^{2+} (0.10), Hg^{2+} (2.0), Mn^{2+} (0.075), Cu^{2+} (0.50), Pd^{2+} (0.75), Pb^{2+} (1.0), Bi^{3+} (1.45), Al^{3+} (0.60), Fe^{3+} (0.32), Th^{4+} (0.80), Ti^{4+} (0.025), V^{5+} (0.15), Mo^{6+} (0.65), W^{6+} (0.65), U^{6+} (0.90), oxalate (0.10) and tartrate (10.0).

1(j) Spectrophotometric Determination of Mo(VI) /22/

Mo(VI) forms a deep yellow complex with HDPT in the pH range 2.0-4.0. The colour of the complex is stable for 6 hours only. The complex is soluble in ethanol (60.0%) and Beer's law is applicable for 1.0-15.0 μg/ml Mo(VI) at 420 nm. The molar absorptivity is 5100. In the spectrophotometric determination of 193.5 μg Mo(VI), the ions tolerated (in mg) are Ni^{2+} (1.25), Zn^{2+} (1.5), Cd^{2+} (1.6), Hg^{2+} (1.2), Mn^{2+} (0.75), Co^{2+} (1.4), Pd^{2+} (0.25), Cu^{2+} (0.20), Pb^{2+} (0.15), Al^{3+} (1.6), Ga^{3+} (0.35), In^{3+} (0.60), Fe^{3+} (0.01), Th^{4+} (1.2), Ti^{4+} (0.80), Sn^{4+} (0.40), V^{4+} (0.050), W^{6+} (1.4), U^{6+} (0.45), F^- (0.10), tartrate (0.18) and EDTA (0.40).

1(k) Polarographic Studies with 3-Hydroxy-1,3-diphenyl triazene

Calzolari and Furlani /18/ made polarographic studies of the detection and determination of HDPT. They reported that the reduction of the reagent is irreversible and the half-wave potential is dependent on concentration ranging from -0.723 to -0.685 V, in the range 0.3 to 0.1×10^{-3} M. The study was carried out at pH 2.18. The ultimate products after reduction are aniline and phenyl hydrazine, though different mechanisms have been suggested at different pH values.

2. 3-Hydroxy-3-phenyl-1-p-tolyl triazene

The reagent has been reported /5/ to be suitable for the gravimetric determination of Pd(II) and Cu(II). Carlos Marone *et al.* /29/ used the reagent for the separation and spectrophotometric determination of Ni, Co(III) and Cu(II) by extraction into benzene from aqueous solutions. Nickel and Cu(II) form intense yellow brown 1:2 complexes with the reagent, whereas Co(III) forms a 1:3 complex. Cu(II) is determined by extraction at pH 4.6 and the absorbance is measured at 400 nm. Ni is determined by extraction in the presence of ammonia at pH 8.6 at λmax. 420 nm and Co(III) by extraction at pH 8-10 after elimination of ammonia and oxidation of Co(II) to Co(III) by H_2O_2. The absorbance measurements are carried out at 410 nm. The microgravimetric determination of Pd(II) and Cu(II) was made with 3-hydroxy-3-phenyl-1-p-tolyl-triazene by Bhandari and Sogani /30/. The complexes of Pd(II) and Cu(II) were suitable for direct weighing. The composition of the complex was found to be $(C_{23}H_{12}N_3O_2)_2M$, where M = Cu(II) or Pd(II). 5 ml of standard Pd(II) or Cu(II) solution (containing 0.6 to 2.0 mg of the metal) were pipetted into a beaker and 0.2 ml of 1 M HCl and 0.2 ml of sodium acetate (10%) solution were added to it. The mixture was warmed and 1 ml of the reagent (1%) solution was added with stirring. 10.0 ml of hot water were added to this and the complex was digested on a water bath for 1 hour. After digestion, a filter stick was introduced and the liquid was sucked off. The contents of the beaker and the filter stick were washed with hot water. The beaker along with the stick was dried to constant weight in an oven at 120-130°. Gravimetric determinations were carried out in presence of diverse ions and the tolerance limits determined. Palladium (0.897 mg) and copper (0.640 mg) could be determined in the presence of 50 mg of each of the following ions: Co(II), Ni, Zn, Mn(II), Cd, Bi, Sb(III), Fe(II), Fe(III), Ti(IV), Pt(IV), Sn(IV), Zr, MoO_4^{2-} and PO_4^{3-} (100 mg) and F^- (100 mg). The interference due to Fe(II), Fe(III), Ti(IV) and molybdate was eliminated by using sodium fluoride (0.1 g) as the masking agent. The reagent is claimed to be superior to other reagents for the microgravimetric determination of Pd(II) and Cu(II).

3. 3-Hydroxy-1,3-p-ditolyl triazene

Purohit *et al.* /31/ prepared this compound and reported the preparation and analytical uses of five other methyl substituted and two chloro substituted hydroxy triazenes, along with this reagent. Out of these, 3-hydroxy-1,3-p-ditolyl triazene was found to be a selective reagent for the gravimetric estimation of copper and palladium. The compound forms stable complexes and has more favourable conversion factors than the parent compound i.e. 3-hydroxy-1,3-diphenyl triazene /32/.

Pd(II) forms a yellowish-brown complex with this reagent, which is soluble in chloroform and benzene. It is fairly soluble in ether and acetone, but only slightly soluble in alcohol. It can be crystallised from acetone m.p. 224°. The Cu(II) complex is chocolate-brown in colour and is soluble in organic solvents. It can be crystallised from acetone m.p. 195°. The Pd(II) (6.0 to 40.0 mg) and Cu(II) (10.0 to 30.0 mg) complexes were precipitated quantitatively between pH 1.8 and 7.0 and 2.3 and 7.0 respectively, with 15% excess of the reagent gravimetrically. Pd(II) was determined in the presence of Co(II), Ni, Zn, Cd, Mn(II), Fe(II), Fe(III), V(IV), Zr, Sb(III), Bi, Ce(IV), Cr(III), Be, molybdate, tungstate, Hg(II), As(III) and UO_2^{2+}, while Cu(II) was determined in the presence of Co(II), Ni, Zn, Cd, Mn(II), Hg(II), Fe(II), Fe(III), Cr(III), Al, Bi, Sb(III) and molybdate. However, Fe(II), Fe(III), Ti(IV) and molybdate interfered, but the interference was eliminated by adding sodium fluoride (0.5 g) as a masking agent.

4. 3-Hydroxy-3-phenyl-1-p-chlorophenyl triazene /20/

The compound obtained, by coupling para-chloroaniline with phenyl hydroxylamine, is a crystalline light greenish yellow compound, m.p. 140°. It is soluble in organic solvents, but insoluble in water. The compound in alcoholic solution shows λmax. at 235, 281 and 350 nm and logϵ 3.991, 3.874 and 4.183 respectively.

Determination of titanium /20/

Titanium was precipitated quantitatively as a bright orange complex by this reagent. The complex is stable up to 100°C in an aqueous acidic reaction medium, at optimum pH between 2.2 and 2.5. The complex on crystallization from alcohol forms bright yellow crystals m.p. 146°. Ti (10 mg) was determined in the presence of 50 mg each of Zn, Mn(II), Cd, Co(II), Ni, Hg(II), As(III), UO_2^{2+}, Th(IV), Mg, Cr(III) and Al. However, the complex is not of definite composition and has to be ignited to titanium dioxide before weighing. Zr, Ce(IV), Cu(II), Pd(II), Fe(II), Fe(III), Mo(VI) and V(V) interfere, because of coprecipitation. Phosphate and tungstate precipitate the corresponding titanium salts and hence interfere in the determination.

5. 3-Hydroxy-3-phenyl-1-o-nitrophenyl triazene

This compound was prepared by Khazova /33/ as an orange red crystalline compound with m.p. 150°, soluble in organic solvents such as alcohol, chloroform and carbon tetrachloride. The compound is reported as a qualitative reagent for the detection of Ni and Zn in the presence of Fe(II), Fe(III), Al and Mn(II). With Zinc it forms a red coloured precipitate at pH 5-6 (dilution limit 1 in 3×10^4) and with nickel it forms a violet coloured precipitate (dilution limit 1 in 5.2×10^4). The reagent has also been used in the colorimetric determination of zinc in ores /34/.

Determination of Zn /37/

The reagent 3-hydroxy-1-(2-nitrophenyl)-3-phenyl triazene forms a 1:2 (M:R) complex with Zn in a medium of optimum pH 10 (using borate buffer). The complex exhibits maximum absorption at 490 nm (ϵ = 16,000) and the colour is stable for three hours. Beer's law is obeyed over the range 0.1-5.0 $\mu g\ ml^{-1}$ Zn. Upto 17,000 fold amounts of Cd relative to Zn do not interfere. Precipitation of cadmium hydroxide at pH 10 is avoided by treating the solution with KI. A method based on these findings has been employed for determining 70 to 120 ppm of zinc in cadmium metal (0.5 g). The coefficient of variation is reported to be $< 4.2\%$.

6. 3-Hydroxy-3-phenyl-1-p-nitrophenyl triazene

This compound, prepared by coupling of p-nitrophenyl diazonium chloride with phenyl hydroxylamine, is greenish yellow with m.p. 182-184°, soluble in organic solvents such as alcohol, acetone and toluene and gives a yellow solution. It gives a red colour with strong alkali. Pochinok *et al.* /35, 36/ have reported the reagent for the detection and colorimetric determination of magnesium. In alkaline solution the colour changes from yellow to red between pH 11-12. A 0.05% solution of the reagent is prepared in alcohol and 2-3 ml of this solution are added to 100 ml of 1% sodium hydroxide which is used for all purposes. With magnesium in neutral or weakly acidic medium it develops a rose-violet or blue-violet colour depending upon the concentration of magnesium. The dilution limit is 1:1,000,000. However, if the concentration of magnesium is greater than 0.05 mg/ml, precipitation takes place. Alkali metals, alkaline earth metals and Pb(II) do not interfere. Al, Fe(III), Cr(III), Ni, Co(II), Mn(II) and Zn which are precipitated by sodium hydroxide do interfere and should be removed. The colour with magnesium is very intense and stable for one hour and is obtained when Mg is treated with the reagent containing 2 g borax, 0.6 g sodium hydroxide, 100 ml water and 3 ml of a 0.05% alcoholic solution of this reagent.

7. 3-Hydroxy-3-phenyl-1-o-carboxyphenyl triazene /38-43/

The reagent has been prepared by the reaction of diazotised anthranilic acid with phenyl hydroxylamine at 0 ± 2°. It is a light yellow compound which melts with decomposition at 165°. The reagent is soluble in organic solvents, insoluble in cold water and slightly soluble in boiling water. An aqueous solution of the reagent is prepared by suspension in water. Ammonia is added to it dropwise till the suspension dissolves resulting into a yellow coloured solution. Cu(II), Pd(II), Ti(IV), V(V) and V(IV) can be precipitated from acid solution. Co(II) and Ni can be precipitated from the solution of $\mathrm{pH} > 3.5$.

7(a) Determination of Titanium(IV)

Titanium(IV) forms a stable 1:2 complex with the reagent /38/. The complex is moderately soluble in chloroform and nitrobenzene, less soluble in pyridine and only slightly soluble in benzene, acetone, dioxan, ethanol, methanol and carbon tetrachloride. It can be crystallised from nitrobenzene or chloroform. The complex melts with decomposition at 283-284°. It is stable in acid solution but hydrolyses above pH 6.0.

Ti(IV) has been determined gravimetrically with the help of this reagent being separated from almost all common ions in the presence of EDTA, but its separation from Niobium(V) and Tantalum(V) was not possible. Fluoride interfers but can be masked by the addition of excess of Be solution. Hydrogen peroxide in the presence of EDTA prevents the reaction of Ti(IV) with the reagent. However, by boiling the solution with sodium hydroxide, this effect of H_2O_2 can be avoided. The pH should be adjusted to optimum value (2.5-5.0) before the precipitation of Ti(IV). The reddish orange titanium complex can be weighed directly after drying at 115-120°. The molecular formula of the titanium complex is reported to be $TiO(C_{13}H_{10}N_3O_3)_2$. Precipitation at lower pH is also quantitative but the complex has to be ignited to TiO_2 before weighing. An IR study of the complex reveals that the carboxyl group is unreactive, the stretching frequency of carboxyl group remaining unaffected. The reagent behaves as a bidentate ligand.

7(b) *Determination of Cu(II) and Pd(II)*

Cu(II) and Pd(II) have been determined gravimetrically with this reagent /38/. The precipitation is done at pH 3.0-6.0 for Cu(II) and at pH 3.0-5.5 for Pd(II). The precipitate is dried at 115-120° and is weighed as $M(C_{13}H_9N_3O_3)$. H_2O, where M = Cu(II) or Pd(II). The Cu(II) complex decomposes at 250°, while Pd(II) complex decomposes at 305°. Both the complexes are fairly soluble in pyridine, but only slightly soluble in acetone, benzene, chloroform and ethanol.

Cu(II) has been determined in white metal, brass, tin, bronze, german silver, monel metal, and chalcopyrites by this method.

The reagent behaves /38/ as tridentate ligand in the Cu(II) and Pd(II) complexes. IR spectra of these complexes show that Pd(II) and Cu(II) replace H-atoms of both the OH and COOH salt forming groups. The asymmetric stretching frequency of the carbonyl group is shifted to 1613 cm^{-1} in the Cu(II) complex and to 1650 cm^{-1} in the Pd(II) complex, whereas the OH band of the reagent is completely absent in both cases. The determination of Cu(II) and Pd(II) has been carried out in the presence of a large number of other ions /39/.

7(c) *Spectrophotometric determination of Fe(III), Ti(IV) and their separation from each other* /40/

With 3-hydroxy-3-phenyl-1-o-carboxyphenyl triazene, Fe(III) forms a 1:2 complex at pH 6.0-10.5, Ti(IV) forms a golden yellow 1:2 complex at pH 1.0-3.5 and V(V) forms a green 1:1 complex at pH 2.0-3.0, all of which may be extracted into chloroform. The absorption maxima are at 500 nm in the case of the Fe(III) complex; at 430 nm in the case of the Ti(IV) complex; and at 410 nm in the case of the V(V) complex.

The validity of Beer's law is observed in the range 1.0-12.0 ppm, 0.25-4.0 ppm and 1.0-6.0 ppm of Fe(III), Ti(IV) and V(V) complexes respectively. The molar absorptivities and the Sandell's sensitivity indexes have been determined. For the Fe(III) complex the sensitivity is 0.0112 $\mu g\ cm^{-2}$ and molar absorptivity is 4970. For the Ti(IV) complex the sensitivity is 0.0038 $\mu g\ cm^{-2}$ and molar absorptivity is 12454. The sensitivity of the colour reaction is 0.0062 $\mu g\ cm^{-2}$ while the molar absorptivity is 8255 in the case of the V(V) complex. Fe(III), Ti(IV) and V(V) have been determined in the presence of various ions.

For carrying out the separation of Fe(III), Ti(IV) and V(V) from each other, the Fe(III) complex is first extracted into chloroform at pH 9.5. The pH of the aqueous phase is adjusted to 1.0 and the Ti(IV) complex is extracted into chloroform and finally the V(V) complex is extracted into chloroform at pH 2.0. The Fe(III) complex is found to be paramagnetic and the V(V) complex, diamagnetic. The formula of the Fe(III) complex is $FeH(C_{13}H_9N_3O_3)_2$ and that of V(V) complex is $V_2O_3(C_{13}H_9N_3O_3)_2$. The IR spectra of the V(V) complex has also been studied.

7(d) Spectrophotometric determination of Ni, Cu(II) and Pd(II) in presence of each other /41/

Ni, Cu(II) and Pd(II) have been determined spectrophotometrically in the presence of each other. All three ions form a 1:1 complex with the reagent. The Ni complex is greenish yellow and it is obtained at pH 6.8-8.3 while the Cu(II) complex is yellowish-orange and is obtained at pH 2.4-3.5 and the Pd(II) complex is light green and is obtained at pH 2.2-3.8. Beer's law is obeyed in the concentration range 0.25-2.0 ppm at 420 nm for Ni and 0.5-4.0 ppm at 410 nm for both copper(II) and palladium(II). The sensitivities and molar absorptivities are, respectively 0.0029 $\mu g\ cm^{-2}$ and 20284 for Ni; 0.0067 $\mu g\ cm^{-2}$ and 16388 for Pd(II); and 0.0044 $\mu g\ cm^{-2}$ and 14516 for copper.

EDTA, citrate, oxalate, Co^{2+}, Pb^{2+}, Zn^{2+}, Fe^{3+}, La^{3+}, Ce^{3+}, Ti^{4+}, Th^{4+}, Zr^{4+} and UO_2^{2+} interfere in the determination of Ni. Whereas, EDTA, oxalate, $S_2O_3^{2-}$, Fe^{3+}, Ti^{4+} and V^{5+} interfere in the determination of Cu(II). However, EDTA, $S_2O_3^{2-}$, SCN^-, Ti^{4+} and Th^{4+} and V^{5+} interfere in the Pd(II) determination. Two methods have been followed for the determination of Cu(II), Ni and Pd(II) in presence of each other. In the first, sufficient oxalic acid is added to an aliquot, to suppress Cu(II) and Ni. Then sufficient sodium-thiosulphate is added to another aliquot to suppress Cu(II) and Pd(II), and Ni was determined as usual. Cu(II) is determined from the total absorbance, by subtraction. In the second method, ammonium thiocyanate is added to suppress Pd(II) and sodium thiosulphate for the suppression of both Cu(II) and Pd(II). The first method is more accurate, though takes more time.

Complexes such as CuRX, NiRX, CoRX and NH_4FeR_2, where R is reagent and X water, ammonia or pyridine have been isolated. The structures of these complexes /42/ have been discussed on the basis of their conductivities, X-ray powder diffraction patterns, magnetic susceptibilities, and electronic and IR spectra.

Chakraborti and Ladislav /43/ determined Cu(II), Pd(II), Ni, Ti(IV), V(V) and Fe(III) using 3-hydroxy-3-phenyl-1-o-carboxyphenyl triazene spectrophotometrically in ternary mixtures.

7(e) Determination of V(V)

Abbasi, Shahid Abbas /44/ reported that, vanadium(V) may be extracted from 3 to 6 M- HCl with N-(2-methoxyphenyl)-2-thenohydroxamino acid 0.05 M in chloroform. After five minutes, the organic layer is separated and dried and added to water at pH ≟ 1.5 and then 0.01 M 3-(2-carboxy phenyl)-1-phenyl triazene oxide 0.01 M in acetone is added, and the resulting colour in the chloroform phase is measured at 445 nm, the wave-length of maximum absorption. The Sandell sensitivity index of the complex is 5 $\mu g\ cm^{-2}$ and Beer's law is obeyed up to 20 ppm of vanadium. The effects of 48 ions on the extraction were studied but many did not interfere in concentrations up to 250 ppm. Results were reported for the determination of vanadium in ferrovanadium alloys and phosphate rocks.

8. 3-Hydroxy-3-phenyl-1-p-sulphonato (sodium salt) phenyl triazene /45-57/

Sogani *et al.* /45/ synthesised this light greenish yellow, needle-shaped crystalline compound. It is soluble in water, and also forms water-soluble complexes. The m.p. is 157° with decomposition and the pK value is 9.99. It shows λmax. at 235 and 345 nm with logϵ values of 4.178 and 4.441, respectively. Various metal ions have been determined colorimetrically using this compound.

8(a) Determination of Pd(II)

Sogani *et al.* /45/ used this reagent for the colorimetric determination of Pd(II) as did Durgapal and Sogani /46/. The composition of the complex was found to be PdR_2 (where R is the reagent anion). Maximum absorbance is observed at 413 nm but to avoid interference due to the reagent, wavelengths 420 and 430 were used. The sensitivity of the colour reaction is reported to be 0.05 ppm and the identification limit 0.05 μg of palladium in 0.15 ml of solution. Colour development is instantaneous and is ensured with a 3-fold-excess of reagent. Beer's law is obeyed over the concentration range 0.2-5 ppm and up to 85°, the absorbance remains unaffected. The determination of Pd(II) was carried out in the presence of Cu(II), Ni, Fe(III), Co(II), Pt(IV), Rh(IV), Ir(III) and Ru(III). The reagent was claimed to be superior to other spectrophotometric reagents for Pd(II).

8(b) Estimation of Fe(III)

With Fe(III), the reagent forms a bluish black water-soluble complex with maximum absorption at 520 and 650 nm at pH 2-4.3. The composition of the complex has been established as FeR_3 (where R is the reagent anion) by spectrophotometric and conductometric methods /47/. The formation of FeR and FeR_2 was indicated by both the methods. The colour sensitivity was found to be 0.2 ppm and the detection limit, 0.1 μg of iron in 0.15 ml of solution. Colour development is instantaneous and maximum with a four fold excess of reagent. Beer's law is obeyed in the iron concentration range 1-20 ppm. Fe(III) was determined /48/ in the presence of Co(II), Ni, Zn, Mn(II) and Fe(II). The possibility of its determination in presence of other metal ions was also discussed.

8(c) Determination of Molybdenum(VI)

With this reagent /49, 50/, Mo(VI) forms an orange yellow water-soluble complex at pH 2.8-3.7 with maximum absorbance at 416 nm. The composition of the complex was reported to be $(MoO)R_3$. Full colour development takes place in 20 minutes with a 6-fold excess of reagent. The sensitivity is reported to be 0.2 ppm and Beer's law is obeyed in the range 1.5 to 25 ppm. The kinetics of the reaction shows it to be first order with a specific rate constant of 0.1606. The determination of Mo(VI) was carried out in the presence of commonly associated ions such as Cu(II), Ni, Zn, Mn(II), Co(II), UO_2, Ca and W(VI).

The reagent is superior to thioacetic acid in having greater tolerance for W(VI).

8(d) Determination of Titanium /51/

A bright yellow complex is formed with Ti(IV) in the pH range 1.9-3.3 by the reagent. The absorption peak is observed at 405 nm, but to avoid reagent interference, the absorbance measurements are made at 425 nm. Colour development is instantaneous, but a 16-fold excess of the reagent is required for maximum absorbance. Spectrophotometric studies show that the composition of the complex is M:R::1:3. Beer's law is obeyed in the concentration range 0.3 to 2.5 ppm. Titanium was determined in the presence of Zn, Mn(II), Ni, Co(II), Cd, Hg(II), Mg, Be, Al and Cr(III). However, Cu(II), Fe(II), Fe(III), Pd(II), vanadate, phosphate, tartrate, fluoride and tungstate interfered.

8(e) Determination of Copper(II), Nickel and Cobalt(III)

Spectrophotometric and conductometric studies of the complexes of copper /52/, nickel /53/ and cobalt /54/ have been reported. Cu(II) forms an instantaneous pale yellow complex with maximum absorbance at 405 nm, in the pH range 4.4-6.2. The composition of the complex was reported as CuR_2. Ni forms a yellow complex in the pH range 3.8-5.9 with maximum absorbance at 420 nm and the composition of the complex is reported to be NiR_2. However, in this pH range the selectivity of the reagent is fairly low, so it is not considered very useful for the colorimetric determination of nickel. Cobalt(III) forms instantaneously a brown coloured complex in the pH range 4.3-5.9 with maximum absorbance at 390 nm and a plateau from 450-485 nm. The composition of the complex is reported to be CoR_3. Beer's law is obeyed over the concentration range 0.8-10 ppm. Colour development is maximum for a 1:6 ratio of cobalt to reagent. Conductometric measurements suggest the formation of CoR and CoR_2 along with CoR_3.

8(f) Determination of fluoride, phosphate, oxalate, citrate and tartrate

Sogani and Mehra /55/ developed an indirect method for the determination of fluoride. The colour of the Fe(III) complex with this reagent faded when fluoride ions were added to the complex. This observation was made the basis of an indirect determination of fluoride in the range 0.5 to 40 ppm.

Mehra and Sogani /56/, further made use of this principle for the determination of oxalate, phosphate, citrate and tartrate in acidic media. Linear calibration curves were obtained over a limited concentration range.

8(g) Complexometric determination of Fe(III)

The reagent has been found to act as a good metallochromic indicator for the complexometric determination of Fe(III) /57/. At the end-point, there is a sharp change in colour from bluish-black to colourless or light lemon yellow. Many ions do not interfere. The reagent has been used as an indicator /58/ in the complexometric determination of Fe(III) in soils, ores, cement and dolomite.

9. HDPT and its Other Sulphonic Derivatives in the Spectrophotometric Determination of Vanadium(V)

Chakraborti /59/ synthesised six reagents i.e. HDPT and sodium salts of its sulphonic acid derivatives. All six reagents were used in the spectrophotometric determination of V(V) and the results obtained are summarised in Table I-1.

In the case of Vanadium(V) and 1-(4-sulphonato, sodium salt-5-methylphenyl)-3-hydroxy-3-phenyl triazene, it has been reported that oxalate, F^-, Fe^{3+}, Pd^{2+}, MoO_4^{2-} Cr^{3+} and Ti^{4+} interfere seriously. However, the following ions could be tolerated up to the tolerance limits in ppm (given in parentheses): Ni^{2+} (50); Co^{2+} (10); Mn^{2+} (10); WO_4^{2-} (20); UO_2^{2+} (10); La^{3+} (30); Ce^{3+} (20); Zn^{2+} (100); Cd^{2+} (200); Hg^{2+} (100); As^{3+} (100) and Th^{4+} (40). Cu^{2+} could be tolerated up to 50 ppm only in the presence of sodium thiosulphate solution (1%). Further, Li^+, Na^+, K^+, Br^-, I^-, Cl^-, PO_4^{3-}, boric acid, citrate and tartrate did not interfere.

TABLE I–1

Spectrophotometric determination of Vanadium (V) with HDPT and its sulphonic derivatives

	Compound	Solvent	Colour	λ max. nm	Beer's law range ppm	Sensitivity $\mu g\ cm^{-2}$	ϵ	pH	Composition
1.	3–Hydroxy–1,3–diphenyl triazene	Water + Ethanol	Yellow	410	0.25–10	0.0085	5875	3.1–4.2	1:1
2.	3–Hydroxy–3–phenyl–1–p–sulphonato phenyl triazene (Na–salt)	Water	Yellow–green	400 410*	0.25–10	0.0085	5875	3.3–4.3	1:1
3.	3–Hydroxy–3–phenyl–1–o–sulphonato phenyl triazene. Na–salt	Water	Yellow–green	400 410*	–	0.026	–	–	–
4.	3–Hydroxy–3–phenyl–1–m–sulphonato–phenyl triazene. Na–salt	Water	Yellow–green	400 410*	0.25–12	0.0095	5250	3.6–4.6	1:1
5.	3–Hydroxy–3–phenyl–1–(4–sulphonato–5–methyl–phenyl) triazene. Na–salt	Water	Yellow–green	410	–	0.05	–	–	–
6.	3–Hydroxy–3–phenyl–1–(4–sulphonato–5–methyl phenyl) triazene. Na–salt	Water	Yellow–green	400 410*	0.1–8.0	0.0075	6625	3.0–4.4	1:1

* Working wavelengths

10. 3-Hydroxy-3-phenyl-1-(2-carboxy-4-sulphonatophenyl) triazene /60, 61, 62/

This is a yellowish green coloured compound prepared by the coupling of a diazotised 5-sulphoanthranilic acid with phenyl hydroxylamine. It is water-soluble and decomposes at 163°. It is a good colorimetric reagent for various metal ions. However, no colour reaction is observed with Ti(IV).

10(a) Determination of Fe(III) /60/

Fe(III) forms a bluish-violet complex with the reagent at pH 3.3-4.5. The maximum absorbance is observed at 410 nm, Beer's law is obeyed up to 12.0 ppm of Fe(III). The composition of the complex is reported as FeR_2 with an instability constant 3.48×10^{-8}. The molar absorptivity is 5275 and the sensitivity of the reaction is 0.0108 $\mu g/cm^2$. Pd(II), Cu(II), Mo(VI) and V(V) should be absent as they form coloured complexes, and phosphate, fluoride oxalate, tartrate, citrate, EDTA and thiosulphate must be absent.

10(b) Determination of Mo(VI) /60/

Molybdenum(VI) forms a yellowish green 1:2 complex with the reagent at pH 3.0-4.2. The maximum absorbance is observed at 405 nm. Beer's law is obeyed up to 12 ppm. The sensitivity and molar absorptivity are 0.0207 $\mu g\ cm^{-2}$ and 4812, respectively. The instability constant is 2.526×10^{-7}. Pd(II), V(V), Cu(II), phosphate, citrate, tartrate, oxalate and EDTA interfere.

10(c) Determination of V(V) /61/

A golden yellow complex is formed by vanadium(V) with this reagent at pH 3.0-6.5. Maximum absorption is observed at 405 nm and Beer's law is obeyed up to 6.0 ppm of V(V). The molar absorptivity and Sandell sensitivity index are 6623 and 0.0078 $\mu g\ cm^{-2}$ respectively. The composition of the complex is reported as 1:1 (M:R). EDTA, Pd(II), Cu(II) and Fe(III) interfere and should be absent. A method has been developed for the determination of Fe(III), Mo(VI) and V(V) in presence of each other with the use of masking agents e.g. thiosulphate for Fe(III) and sodium fluoride for both Mo(VI) and Fe(III).

10(d) Determination of Cu(II) and Pd(II) /60/

Cu(II) and Pd(II) have been determined spectrophotometrically. Cu(II) forms a light yellow 1:2 complex with the reagent in the pH range 4.8-8.4. Beer's law is obeyed between 0.3-3.0 ppm at 400 nm. Pd(II) forms golden yellow 1:2 complex at pH 4.2-8.0. Beer's law is obeyed between 0.4-5.0 ppm at 410 nm. The values of sensitivities and molar absorptivities are, respectively 0.043 μg cm^{-2} and 15333 for copper(II) and 0.0055 μg cm^{-2} and 20222 for palladium(II).

Ni^{2+}, Co^{2+}, Pd^{2+}, Fe^{3+}, V^{5+}, MoO_4^{2-}, EDTA,, oxalate and thiosulphate interfere in the determination of Cu(II). Whereas, Cu^{2+}, Fe^{3+}, V^{5+}, MoO_4^{2-}, EDTA and thiosulphate interfere in the determination. However, in presence of oxalate ions (20 mg), Pd(II) tolerates the presence of Cu^{2+} (80 ppm), Fe^{3+} (100 ppm), V^{5+} (50ppm) and MoO_4^{2-} (200 ppm). The reagent is highly selective for palladium(II).

Cu(II) and Pd(II), in presence of each other, have been spectrophotometrically determined with the help of masking agents. Determinations were further made /61/ in the following four sets of combinations: (a) Cu(II), Pd(II) and V(V); (b) Cu(II), Pd(II) and Mo(VI); (c) Pd(II), Fe(III) and V(V) and (d) Pd(II), Mo(VI) and V(V).

10(e) Determination of Ni /59/

Ni forms a greenish yellow complex with the reagent at pH 7.8-9.2. The complex is stable for four hours. Beer's law is obeyed in the concentration range 0.25-1.5 ppm at 400 nm. The molar absorptivity of the complex is 34524 and the sensitivity of the reaction is 0.00172 μg cm^{-2}.

10(f) Metallochromic indicator for Fe(III)

The reagent finds use as a metallochromic indicator for the titration /62/ of Fe(III) in the presence of a number of cations. The colour change during the titration with EDTA is from deep blue to green and finally to yellow. The colour change at the end-point is sharp and becomes sharper still in the presence of Co(II) sulphate. However, at the end-point the colour change is from deep blue to pink in the presence of Co(II). Ba^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Mn^{2+}, Al^{3+}, Fe^{2+}, and Cr^{3+} do not interfere and Ni^{2+} is tolerated up to 15 mg in 50 ml of solution.

10(g) Determination of oxalate and fluoride

The bluish-violet colour of the Fe(III) complex at pH 3.3-4.5 fades on the addition of either oxalate or fluoride. The amount of Fe(III) is directly proportional to the fading due to the formation of a more stable complex. A spectrophotometric method /61/ is reported on this basis for the determination of oxalate and fluoride.

11. 3-Hydroxy-3-phenyl-1-(2-carboxy-5-sulphonato-phenyl) triazene /63/

This reagent is a light yellow crystalline compound, highly soluble in water, m.p. 186°C with decomposition. It is claimed by Chakraborti /63/ to be the most efficient reagent among the triazenes for the spectrophotometric determination of Fe(III) and V(V).

11(a) Determination of Fe(III)

Fe(III) forms a bluish black complex having λmax. at 400 nm at pH 3.3-10.2. Beer's law is obeyed in the concentration range 1.0-8.0 ppm. The Sandell sensitivity index and the molar absorptivity values are 0.0071 $\mu g\ cm^{-2}$ and 7890, respectively. The formula of the complex is reported to be FeR_2. The instability constant is 6.3×10^{-8}.

Fe(III) has been determined in the presence of Cu(II), Co(II), Ni, Mn(II), Pd(II), Ir(III), Ru(III), Pt(IV), Rh(IV), Mo(VI) and W(VI).

11(b) Determination of Vanadium(V)

V(V) forms a greenish yellow 1:1 complex with the reagent at pH 2.1-5.9. The wavelength of maximum absorption is 400 nm. The sensitivity of the reaction is 0.00548 $\mu g\ cm^{-2}$ and the molar absorptivity is 9180. Beer's law is obeyed between 0.5-5.0 ppm of vanadium(V). The instability constant is 2.2×10^{-5}. Only Fe(III) and Ti(IV) interfere.

11(c) Determination of Pd(II), Mo(VI), Ni, Cu(II) and Ti(IV)

The reagent 3-hydroxy-3-phenyl-1-(2-carboxy-5-sulphonato-phenyl) triazene has been used for the determination of Pd(II), Mo(VI), Ni, Cu(II) and Ti(IV). The results reported /63/ are given in Table 1-2.

The reagent has also been used in the determination of metal ions present in binary mixtures with the help of complexing agents. The binary mixtures studied are (a) V(V) and Cu(II); (b) V(V) and Pd(II); (c) Fe(III) and Cu(II) and (d) Fe(III) and Pd(II).

12. 3-Hydroxy-1-(4-nitrophenyl)-3-(4-sulphonato-phenyl sodium salt) triazene /64/

This reagent forms a 2:1 complex with Hg(II) at pH 6.5-9. Beer's law is obeyed for 0.4-8.0 μg ml^{-1} of Hg(II). The molar absorptivity was found to be 28700. The tolerance limits of various ions have been studied. Fe^{3+} and Ca^{2+} could be tolerated up to 30 fold excess of the reagent; Cu^{2+} was tolerated up to 100 fold and 150 fold excess of Co^{2+}, Ni^{2+}, Pt^{4+} and Pb^{2+} were tolerated. However, Ag^{+}, Ba^{2+}, Mn^{2+}, Sn^{2+}, CN^{-}, SCN^{-}, S^{2-}, Cl^{-}, Br^{-}, Fe^{2+} and I^{-} interfere.

13. p-(3-Hydroxy-3-phenyl triazeno)-phenyl trimethyl ammonium chloride /65, 66/

Gaur *et al.* /65, 66/ used diazotised p-amino dimethyl aniline coupled with phenyl hydroxylamine to obtain this compound. It was converted to the corresponding quaternary ammonium iodide by treatment with methyl iodide. Finally, the chloride salt was obtained by treating the quaternary ammonium iodide with freshly precipitated silver chloride. The product melts at 184° with decomposition and gives a colour reaction with Ni, Cu(II), Co(II), Mn(II), Cd, Zn, Pb, Fe(II), Fe(III), V(IV), Ti(V), Pd(II), Hg(II) and Ag. The optimum pH and sensitivities of reactions of hydroxytriazenes with the above mentioned metal ions have been reported. The solubilising effect of the quaternary ammonium group has also been reported. It has been observed that this group is valuable for the con-

TABLE I-2

3-Hydroxy-3-phenyl-1-(2-carboxy-5-sulphonato phenyl) triazene

Ion	Colour	Maximum Absorbance nm	pH range	Beer's law applicable ppm	Optimum range, ppm	Composition	Sensitivity $\mu g\ cm^{-2}$	Molar absorptivity	Stability of complex (hrs)	Dissociation constant
Pd(II)	Yellow	410, 420*	1.0–6.7	0.5–7.0	1.0–7.0	1:2	0.0072	15178	36	4.0×10^{-11}
Mo(VI)	Light yellow	410–430	–	–	–	–	0.168	–	–	–
N	Yellow-green	410	9.8–10.5	0.125–1.5	0.25–1.5	–	0.0018	34375	18	–
Cu(II)	Yellow-green	400, 410*	1.8–9.7	0.26–4.0	0.5–4.0	1:2	0.0042	15161	48	5.0×10^{-11}
T (IV)	Golden yellow	420	1.8–3.5	0.25–5.0	0.5–5.0	–	0.0057	7108	10	–

* Working wavelength.

version of organic precipitants to colorimetric reagents. The composition of the complex with bivalent metal ions is reported as 1:2 and with trivalent metal ions, it is reported to form 1:3 complexes. However, no quantitative studies have been reported as yet.

14. 3-Hydroxy-3-(p-dimethylamino phenyl)-1-phenyl triazene

Purohit *et al.* /67/ used this reagent to determine Ru(III) spectrophotometrically. The composition of the complex is reported as 1:1. The following conditions were found to be optimum. Absorption maximum 490 nm; pH 7.7–7.8; Ru: reagent = 1:40; colour stable for at least one week; Beer's law obeyed in the concentration range of 2-400 μm. The molar absorptivity is 2.5×10^{-4} mol^{-1} cm^{-1}. The Sandell sensitivity index is 0.004 $\mu g/cm^2$.

Alkali and alkaline earth metals, Zn, Cd, Hg(II), Mn(II), Cr(III) and Al do not interfere. However, Rh(III), Pd(II), Fe(III), Cu(II), Ni, Co(II), Ti(IV) and V(V) interfere seriously.

15. 3-Hydroxy-3-methyl-1-phenyl triazene /68/

This is a silky white, needle shaped, crystalline compound, m.p. 69°. The compound is soluble in alcohol, alcohol-water mixtures and hot water. Fe(III) forms a greenish blue water-soluble complex with the reagent /68/. Absorption maxima were observed at 400, 490 and 625 nm between pH 3.1–4.5. Fe(III) was determined at 625 nm. Beer's law is obeyed up to 10 ppm of Fe(III). The formula of the complex was established as FeR_3 and the sensitivity is 0.2 ppm. However, the reagent has not been claimed to be superior to other reagents.

16. 3-Hydroxy-3-methyl-1-p-tolyl triazene

Gupta and Sogani /6/ have synthesised this compound and reported that it is a highly selective reagent for the gravimetric determination of Pd(II) and Cu(II).

16(a) Gravimetric determination of Palladium

Pd(II) is quantitatively precipitated, using twice the theoretically required quantity of reagent, between pH 1.0 and 6.0. The selectivity is enhanced by maintaining the pH between 1.2 and 3.0. The Pd(II) complex is violet-brown and granular in nature. It is highly soluble in organic solvents such as ethanol, methanol and ether and fairly soluble in chloroform and benzene. The complex has been crystallised from benzene as fine crystals, m.p. 239°. A procedure for the separation of Pd(II) from platinum has also been given. As^{3+}, Sb^{3+}, Bi^{3+}, Al^{3+}, Cr^{3+}, Be^{2+}, Th^{4+}, U^{4+}, UO_2^{2+}, Zr^{4+}, tungstate, phosphate, borate, fluoride, alkali and alkaline earth metals did not interfere.

16(b) Gravimetric determination of Copper

Cu(II) forms a reddish brown complex with the reagent between pH 3.2 and 6.0. The quantity of reagent required is more than 2½ times that of copper. The reagent is most selective between pH 3.3-4.0. The solid Cu(II) complex was crystallised from ethanol as reddish brown, shining crystals with m.p. 186°. As^{3+}, Sb^{3+}, Bi^{3+}, Al^{3+}, Cr^{3+}, Bi^{2+}, Th^{4+}, U^{4+}, UO_2^{2+}, Zr^{4+}, tungstate, phosphate, borate, fluoride, alkali and alkaline earth metals do not react with the reagent.

17. 3-Hydroxy-3-methyl-1-(o-carboxyphenyl) triazene /69, 70/

Majumdar *et al.* /69, 70/ prepared this colourless crystalline compound with m.p. 186°. It is stable and can be stored indefinitely. The compound is soluble in acetone, ethanol, methanol, nitrobenzene and dioxan. The solubility in benzene, carbon tetrachloride, chloroform and hot water is less.

17(a) Determination of Titanium(IV) /69/

The reagent has been used in the gravimetric determination of titanium (1 to 40 mg) in the pH range 2.0-4.5. The orange yellow Ti(IV) complex $TiO(C_8H_8N_3O_3)_2$ is stable up to 320°. The complex may be weighed directly after drying at 120°. The complex explodes violently at its decomposition temperature. It is only slightly soluble in chloroform, dimethyl formamide, nitromethane and pyridine. It is insoluble in benzene, carbon tetrachloride, ethanol and methanol.

The following metal ions: Co(II), Ni, Mn(II), Zn, Cd, Hg(II), Mg, Cr(III) and Pd(II) are tolerated up to 100 mg each. Separation from Ce(IV), Th(IV), La(III), Co(II), UO_2 and Nb(V) has been made.

Ta(V) was tolerated up to 60 mg. F^-, PO_4^{3-}, MoO_4^{2-} and WO_4^{2-} are tolerated up to 100 mg each in the gravimetric determination of Ti(IV). Interference due to Fe(III) and V(V) (100 mg each) could be overcome by the addition of 1 g EDTA. Interference due to PO_4^{3-} (100 mg) was prevented by tartaric acid (1 g). Be could be used as a masking agent for F^- which interferred seriously. The asymmetric stretching frequency of the carboxyl group in the reagent (1670 cm^{-1}) remains unchanged in the complex, thus suggesting that the ortho-carboxy group does not participate in complex formation.

17(b) Spectrophotometric determination of Fe(III) /70/

Fe(III) forms a 1:1 complex at pH 1.5-2.0 with this reagent and a 1:2 complex is formed at pH 4.0-9.4. In both cases, Beer's law is obeyed in the concentration range 1.1 to 35.8 ppm and 1.1 to 17.9 ppm, respectively. The complex formed at pH 1.5-2.0 is green in colour with a molar absorptivity of 1.3×10^3 at 690 nm, while the complex formed at pH 4.0-9.4 is violet in colour with a molar absorptivity of 3.6×10^3 at 510 nm. Both complexes can be extracted into chloroform. The former complex melts at 220° with decomposition and has a magnetic moment μ_{eff} = 6.02 B.M., whereas the latter complex is stable even up to 320° and has a magnetic moment μ_{eff} = 5.91 B.M.

Citrate, oxalate and tartaric acid (each 500 mg) do not interfere. Addition of excess of Be eliminates the interference due to F^-.

Tolerance of the following ions up to 200 ppm each has been observed: WO_4^{2-}. MoO_4^{2-}, Ce^{3+}, La^{3+}, Lanthanides, Nb^{3+}, UO_2^{2+}, BO_3^{3-}, AsO_3^{3-}, Zr^{4+}, Th^{4+}, Zn^{2+}, Cd^{2+} and Hg^{2+}. However, when Co^{2+}, Ni^{2+}, Cr^{3+} or Mn^{2+} are present, the pH should be kept at 4-5. A procedure for the removal of these ions has also been described.

17(c) Spectrophotometric determination of Ti(IV) /70/

The reagent has been used for the spectrophotometric determination of titanium(IV). It forms a golden yellow complex at pH 1.0-3.5 that can be extracted into chloroform. Beer's law is obeyed up to 7.7 ppm and maximum absorbance is observed at 410 nm with a molar absorptivity of 7.3×10^3. The titanium complex can be back extracted from chloroform solution into concentrated sulphuric acid, where it forms a violet solution. The maximum absorbance of this violet solution is at 530 nm. Beer's law is obeyed in the concentration range 2.0 to 23.9 ppm and the molar absorptivity is 2.4×10^3. Fe(III), Cu(II), Cr(III), VO_3^- and EDTA interfere seriously in chloroform. However, when the chloroform layer is back-extracted into 98% concentrated sulphuric acid, the interference of Fe(III), Cu(II) and Cr(III), up to 200 ppm of each, can be eliminated.

In general, Ti(IV) forms /38, 63, 69, 70/ a stable complex with hydroxy triazenes when a carboxyl group is present in the ortho position of the phenyl ring attached to nitrogen atom-1. The importance of the carboxyl group at the ortho position has been discussed, e.g. in the stable Ti(IV) complex, the presence of a carboxyl group at the ortho position is necessary, even though the hydroxy triazene might act as a bidentate ligand. On the basis of infra-red spectral studies, a hydrogen bridged structure has been proposed for the Ti(IV) chelate. It has also been proposed that the hydroxyl hydrogen of the carboxyl group forms a hydrogen bond with the titanyl oxygen. This is indicated in the lowering of νTi=O below 600 cm^{-1} and the disappearance of νO-H of the carboxyl group.

17(d) Spectrophotometric studies of Vanadium(IV) and Vanadium(V) complexes /70/

Complexes of vanadium(IV) and vanadium(V) with the reagent may be extracted into chloroform at any pH, but not quantitatively. On back-extraction with 98% sulphuric acid from chloroform solution, the vanadium(V) complex shows an absorption maximum at 550-560 nm and the vanadium(IV) complex at 550 nm. The complexes are stable for a few hours only, but appear to be identical in acidic solution. However, two kinds of V(V) complexes which are pH dependent have been isolated. The yellow variety, obtained at pH 5.0 is anionic as it is absorbed by anion exchange resins whilst the other variety, obtained at pH = 1, is a black neutral complex. The formula of the yellow variety is $H[VO(OH)_2(C_8H_7O_3N_3)]$ and that of the black variety is $VO_2(C_8H_8O_3N_3)$. The former chelate is diamagnetic, with m.p. 193°, whereas, the latter is paramagnetic in nature with m.p. 214°. IR spectral studies of these complexes have also been reported.

When an ethanolic solution of a vanadyl salt is added to an ethanolic solution of the reagent, a green precipitate of composition $VO(C_8H_7O_3N_3)$ is obtained. The complex does not decompose or melt up to 340°. It is insoluble in methanol, benzene or chloroform, but dissolves in hot pyridine. Magnetic susceptibility measurements and IR spectral studies of the complex were reported.

18. Hydroxy Triazenes of Anthraquinones and Substituted Anthraquinones /71/

Pochinok *et al.* /72/ have synthesised six hydroxy triazenes of anthraquinone and substituted anthraquinones by coupling anthraquinone diazonium salt with phenyl hydroxylamine. These compounds are phenyl-(anthraquinonyl-2)-oxytriazene (m.p. 207-10°); phenyl-(anthraquinonyl-1)-oxytriazene (m.p. 185-90°); phenyl-(1-nitro-anthraquinonyl-2)-oxytriazene (m.p. 150-52°); phenyl-(3-sulpho-anthraquinonyl-2)-oxytriazene (m.p. above 336°); phenyl-(1-chloro-anthraquinonyl-2)-oxytriazene (m.p. 180-82°) and phenyl-(7-sulpho-anthraquinonyl-2)-oxytriazene (m.p. above 325°). They also prepared the sodium salts of sulphoquinonyl derivatives.

The sodium and potassium salts of these hydroxy-triazenes in pyridine give colour reactions with metal ions. The colour given by Mg, Ni, Co(II) and Mn(II) is intense red. Tl(III), Ca, Cd, Zn, Pb, Sr, Cr(III) and Hg(II) give a red colour. An aqueous solution of these hydroxy triazenes in water gives a blue-green colour with Ni, a violet colour with Mn(II) and a green colour with cobalt and calcium. The pyridine solution of phenyl-(anthraquinonyl-2)-oxytriazene and its K, Ni and Mg salts give absorption maxima at 435 nm, 510 nm, 510 nm and 505 nm respectively. However, no quantitative method of determination of any metal ions with these hydroxy triazenes has been described by them.

19. 3-(2-Naphthyl)-1-phenyl triazene 1-oxide /72/

Chatlangya, Bhandari and Sogani prepared this reagent by coupling 2-naphthalene diazonium chloride with phenyl-hydroxylamine in molar proportion in acetate buffer at 0°. It is crystallised from benzene, m.p. 180°.

The reagent is used as 1.0% solution in ethanolic 0.5% KOH.

Determination of Palladium(II)

Palladium(II) 10-25 mg is precipitated quantitatively as a greenish precipitate at pH 2.5-3.5 (from acetate-HCl medium). A 20-25% excess of the reagent is used for complete precipitation. The complex is digested on a water-bath, filtered and washed with 25% aqueous alcohol, subsequently with 95% alcohol and then dried at 120° to 125°. The conversion factor is 0.1687. In the gravimetric determination of 10-25 mg of Pd(II), there is no interference from 0.1 g of Co(II), Ni, Zn, Mn(II), Cd, Hg(II), Be, Mg, Pb, Al, As(III), Cr(III), Th(IV), Rh(IV), Ru(III), UO_2(IV), tungstate, phosphate, fluoride, alkali and alkaline earth metals. The interference of Zr(IV), Sn(IV), Ti(IV) and Mo(VI) is masked with sodium fluoride and that of Bi and Sb(III) with sodium potassium tartrate. However, Au(III), Sn(II), V(IV) and V interfere.

20. 3-(p-Acetophenyl)-1-methyl-triazene-1-oxide /73/

Biswas, Ray and Lahiri /73/ first prepared this reagent. The compound was obtained as light yellow crystals, m.p. 175°.

20(a) Determination of Cu(II)

The reagent precipitates 2 to 30 mg of Cu(II) at pH $\cong$ 7 (tartrate medium) when heating to 80°C and adding an ethanolic solution of the reagent to give a chocolate brown precipitate of the copper complex. The precipitate is digested on a hot water bath for 30 min., collected, washed with ethanol (20%), dried at $\doteq$ 115° and then weighed. The conversion factor is 0.1419. Cu(II) has been determined in the presence of Fe(III), Zn, Al, UO_2^{2+}, Hg(II), Be, Mg, Cd, Bi(III), As(III), Sb(III), Pb, molybdate and tungstate using suitable masking agents. Anions such as fluoride (500 mg), phosphate (50 mg), arsenate (50 mg), borate (50 mg), thiocyanate (200 mg), tartrate (1500 mg), citrate (100 mg) and oxalate (100 mg) could be tolerated in the determination of 2-30 mg Cu(II). The determination of Cu(II) in alloys *viz.* brass, tin bronze, aluminium bronze and manganese bronze has also been reported. With this method, the average relative error is reported to be ±0.49% and the relative standard deviation, ±0.38%.

20(b) Determination of Ni and Palladium(II) and their separation in binary mixtures /74/

The reagent 3-(p-acetophenyl)-1-methyl-triazene oxide precipitates Ni as a greenish yellow complex, in the pH range 6.5-10.2 from an ammonical medium. The precipitate is washed with hot (80°C) water, dried at 120° and weighed as $Ni(C_9H_{10}O_2N_3)_2 \cdot 2H_2O$. The conversion factor is 0.1226, Similarly Pd(II) has been precipitated as a buff coloured precipitate at pH 1.0-8.0 (pH adjustment with ammonia solution), washed with hot water, dried at 120° and weighed as $Pd(C_9H_{10}O_2N_3)_2$. The conversion factor for Pd(II) is 0.2168. Ni and Pd(II) have been determined in the presence of different foreign ions using suitable masking agents.

With this method, an average error of ±0.14% and ±0.16/ respectively, has been reported in gravimetric determinations of 3-30 mg of Ni(II) and 2.5-40 mg of Pd(II).

As there is a clear margin in the pH ranges for the precipitation of Ni and Pd(II), they have been estimated in the presence of each other from binary mixtures simply by controlling the pH.

20(c) Mixed ligand nickel complexes /75/

Lahiri, Biswas and Ray /75/ prepared the nickel complex (NiL_2) of this reagent i.e. they prepared bis-3-(p-acetophenyl)-1-methyl triazene-N-oxide nickel. They also prepared mixed complexes of the type NiL_2X_2 where X = pyridine, β-picoline, γ-picoline, quinoline and isoquinoline. All the complexes prepared were characterised by elemental analysis, magnetic susceptibilities at room temperature, reflectance spectral data in the solid state, electronic spectral data in solution and infra-red spectral studies. Based on these studies, a six coordinated trans-pseudo-octahedral configuration has been suggested for all the mixed ligand nickel complex (NiL_2X_2).

21. Other Hydroxytriazenes

Bhargava and Sogani /76/ synthesised eight aryl-azo-bis-oximes, reported their spectral characteristics and screened these for their utility in determination of various metal ions. The phenyl-azo-bis-cyclohexanone oxime was used for gravimetric determination of copper and nickel. The functional group responsible for complex formation in aryl-azo-bis-oxime is the same as in hydroxytriazenes i.e. $-N(OH) \cdot N=N-$.

Krishnaswamy and Bhargava /77/ synthesised 3-hydroxy-3-benzyl-1-phenyl triazene and nine other substituted compounds of this series.

The qualitative reactions of 3-hydroxy-3-benzyl-1-p-chlorophenyl triazene with different metal ions have been reported. It was indicated that these reagents could be used in gravimetric analysis. However, no quantitative determinations were made.

Bhattacharya and Ray /78/ reported the preparation and physicochemical studies of Co(II), Ni, Cu(II), Pd(II) and V(IV) complexes of 3-(o-carbomethoxyphenyl)-1-methyl triazene oxide and 3-(o-acetophenyl)-1-methyl triazene oxide. These two hydroxytriazenes were reported to act as tridentate ligands. Visible, IR-spectral magnetic moment and conductance studies suggest octahedral stereochemistry for the Ni and Co(II) complexes. However, square planar geometry was proposed for the complexes of Cu(II).

Krishnaswamy *et al.* /79/ first prepared tetradentate hydroxytriazenes. *N*-1,1'-(4,4'-biphenyleno)-bis-(3-*N*-hydroxy-3-*N*-phenyltriazene) was obtained by coupling tetrazotised benzidine with phenyl hydroxylamine. The compound is yellow in colour, m.p. 147-148°. The composition of its Cu(II) and Ni complexes is reported to be 1:1. The high thermal stabilities and extreme insolubility of these complexes suggest that they are macro-molecular in nature.

Krishnaswamy and Bhargava /80/ for the first time prepared *N*-1,1'-(3,3'-disulphonato-4,4'-biphenyleno)-bis-(3-*N*-hydroxy-3-*N*-phenyltriazene). They used it as a colorimetric reagent for the determination of Pd(II) and Mo(VI). Beer's law is obeyed between 2.0-8.0 ppm at pH 1.5-4. For the Mo(VI) complex Beer's law is obeyed between 1.0-15.0 ppm at pH 2.5-3.5. The reagent forms coloured complexes with Ti(IV), V(V), Cu(II), Ni, Co(III) and Fe(III). However, the reagent is not suitable for the colorimetric determination of these metal ions, because excess interferes seriously.

Behera and Chakraborty /81/ prepared another tetradentate hydroxytriazene, by coupling tetrazotised 2,2'-diamino diphenyl with methyl hydroxylamine. It is a yellow, needle shaped, crystalline compound, m.p. 196-197°. The Ni complex gives green crystals, m.p. 251-252°, the Pd(II) complex, violet crystals m.p. 256-257°, the Co(II) complex – red crystals, m.p. 208-209° and the Cu(II) complex melts at 252-253°. The UV, Ir, and visible spectra, P.M.R. and magnetic susceptibilities of these complexes have also been reported. On the basis of which, the authors have suggested a cis-planar MN_2O_2 coordination sphere for these complexes.

E. IONISATION CONSTANTS OF HYDROXYTRIAZENES

Hydroxytriazenes are very weak acids. It has been reported that their ionisation constants cannot be determined satisfactorily by conductometric and potentiometric methods. However, most of them give either an intense or faint yellow colour with alkali. In the case of 3-hydroxy-1,3-diphenyltriazene, the absorption peak at 348 nm seen in neutral or acidic medium is shifted to 393 nm in alkaline medium. This provides a basis for the spectrophotometric determination of pK values of the hydroxytriazenes /29, 82, 83/. The ionisation constants of a large number of hydroxytriazenes have been reported on this basis and the effect of substitution on pK values has been discussed /83-85/.

F. STABILITY CONSTANTS OF METAL CHELATES OF HYDROXYTRIAZENES

The stability constants of the Pd(II), Cu(II), Ni, Zn and Mn(II) complexes of various hydroxytriazenes in a 70% v/v dioxan-water mixture have been determined by Dugar /85/ and Purohit *et al.* /86/. The stabilities were determined by using the Bjerrum-Calvin pH-titration technique. Substitution effects on the metal chelate stabilities have been described and discussed /87, 88/. A linear correlation between pK and $\log\beta_1$ and $\log\beta_2$ has also been established. The stability sequence reported is

$$Pd > Cu > Ni > Zn > Mn.$$

The effect of substitution in the benzene ring of various hydroxytriazenes on the stabilities of the Pd(II) /89/ and Cu(II) /90/ complexes has been studied. The pK values of the reagents with first and overall stability constants of Pd(II) and Cu(II) complexes have been correlated.

Purohit /91/ discussed the resonance and chelate stabilities of the Pd(II), Cu(II), Ni, Zn and Mn(II) complexes with HDPT and 3-hydroxy-3-methyl-1-phenyltriazene.

The conclusion has been drawn that the stabilities of metal chelates depend not only on the resonance in the chelate ring, but also on the resonance in the remaining part of the reagent molecule.

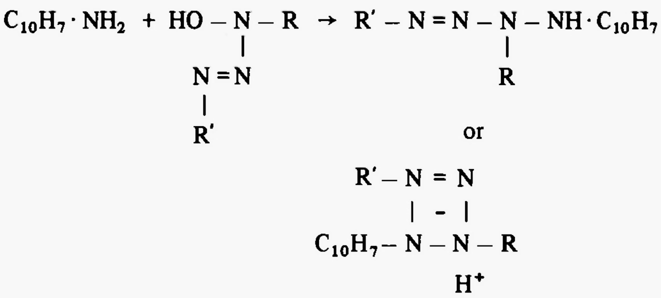
G. SPOT TESTS FOR HYDROXYTRIAZENES

Two different methods for spot tests of hydroxytriazenes have been developed by Purohit /92, 93/.

Identification of Hydroxytriazenes, First Method /92/

The first method consists in the formation of pink or reddish-brown colours when one drop of an acetic acid solution of hydroxytriazene (0.001% w/v) is treated with two drops of an acetic acid solution of α-naphthylamine. Gentle warming further intensifies the colour. The test was carried out with eighteen hydroxytriazenes.

It has been proposed that the development of the colour is possibly due to the formation of a tetrazene or a cyclic tetrazene.



$$C_{10}H_7\cdot NH_2 + HO-\underset{\substack{|\\ N=N\\ |\\ R'}}{N}-R \rightarrow R'-N=N-\underset{\substack{|\\ R}}{N}-NH\cdot C_{10}H_7$$

or

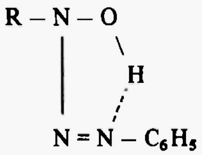
$$\begin{array}{c} R'-N=N \\ |\;\;-\;\;| \\ C_{10}H_7-N-N-R \\ H^+ \end{array}$$

A quantitative study of this reaction was made for the colorimetric determination of nine of these hydroxy-triazenes /94/. The above formulation is supported by the results obtained.

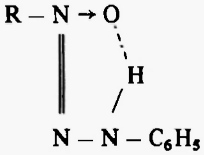
Identification of Hydroxytriazenes, Second Method /93/

The second method consists of adding 2-5 drops of a saturated solution of picric acid in ethanol to a pinch of solid or a drop of hydroxytriazene solution in ethanol. The reaction mixture is heated on a water bath at 55-60°. A red colour characteristic of hydroxytriazene picrate develops, indicating the presence of a hydroxytriazene group. This test was performed for 35 compounds and positive results were obtained in all cases.

On the basis of other studies, an intra molecular hydrogen bonded structure 'A' and a tautomeric form 'B' were proposed for hydroxytriazenes:



‘A’



‘B’

The reaction of hydroxytriazenes with α-naphthylamine can be interpreted as evidence for the form ‘A’. However, the test with picric acid lends support to the contribution of the tautomeric form ‘B’. Both amino oxide ($\equiv N \rightarrow O$) and secondary amino ($= N - H$) groups are known to form picrates of red colour. Thus the picrate formation suggests the presence of these groups which are present in form ‘B’.

H. SPECTROPHOTOMETRIC DETERMINATION OF HYDROXYTRIAZENES

Purohit and Kusum Goswami /94/ have carried out the spectrophotometric determination of 3-hydroxy-1,3-diphenyltriazene and its derivatives. α-Naphthylamine is found to form complexes with hydroxytriazenes. The absorption spectra of HDPT α-naphthylamine complex has been obtained and after an elapse of three hours the absorption becomes constant, and thereafter remains so for 24 hours. However, the reaction can be brought to completion more rapidly by heating the reaction mixture at 65-70° for 30 minutes. Beer's law is obeyed between 0.4-400 ppm of HDPT at pH 2.0-2.5. The wavelength used for the absorption studies was 535 nm. The molar absorptivity and Sandell sensitivity index were 7.5×10^3 and 0.0028 $\mu g\ cm^{-2}$, respectively. With eight other hydroxytriazenes, similar studies were made and the results were reported. The formation of a pink colour by HDPT and other hydroxytriazenes with α-naphthylamine may be due to the condensation product of two compounds formed upon the elimination of a water molecule. The pink coloured condensation product was either a tetrazene or a cyclic tetrazene.

I. MISCELLANEOUS STUDIES OF HYDROXYTRIAZENES

Zacharias and Chakravorty /95/ reported the preparation of 3-hydroxy-3-methyl-1-phenyltriazene; 3-hydroxy-3-ethyl-1-phenyltriazene and 3-hydroxy-3-n-propyl-1-phenyltriazene. They also prepared ortho- F, Cl, Br, I, $-OCH_3$, $-OC_2H_5$ and $-SCH_3$ derivatives of these three hydroxytriazenes. Electronic spectra, IR spectra and magnetic moment measurements suggest that Co(II) complexes are pseudo-octahedral in both solid and benzene solution phases. However, the complex of Co(II) with ortho-iodo-hydroxytriazene is planar in the crystalline state. Nickel complexes are diamagnetic in the crystalline state, but become paramagnetic in the solution phase, and possess distorted octahedral geometry, both in solid and in solution phases.

Zacharias *et al.* /96/ proposed:

$$\text{planar}\,(S = 0) \rightleftharpoons \text{octahedral}\,(S = 1)$$

equilibrium in the complex with ortho-chlorosubstituted hydroxytriazenes.

Zacharias and Chakravorty /97/ have reported IR and PMR studies of the dinuclear Ti(IV) complexes of 3-hydroxy-3-methyl-1-p-tolyl triazene. The complexes were obtained as orange-red crystals by treating titanium(IV) tetrachloride with a methanolic solution of the reagent. Crystallisation of the complexes was carried out with petroleum ether (60-80°); An oxo-bridged structure $R_2Ti(Cl)$-o-$Ti(Cl)R_2$ was proposed.

Chakravorty *et al.* /98/ prepared derivatives of 3-hydroxy-3-methyl-1-phenyl triazene with methyl substituents in ortho, meta and para positions, along with 3-hydroxy-3-ethyl-1-phenyl triazene. They also prepared tris chelates of Co(II) with these compounds. The stereochemistry of Co(III) complexes was discussed on the basis of IR and PMR spectral studies. The authors claimed that the complexes exist exclusively in the trans form. The non-existence of the cis-isomer has been attributed to steric factors. The chelates are reported to show electronic transitions at, or about, 19000 cm^{-1} and 29400 cm^{-1}. Probable assignments were made.

Chacko and Manoharan /99/ discussed the electronic and EPR spectra of the bis- 1-methyl-3-(2-chloro-6-methyl) phenyl triazene-1-oxide cobaltate(II) complex. The molecule is characterised by orthorhombic g- and A-tensors (^{59}Co) with Hamiltonian parameters. The quadrupolar contribution to the spin Hamiltonian is significant resulting in the appearance of forbidden transitions in the single crystal and polycrystalline spectra. On the basis of the spin Hamiltonian parameters and optical spectra, the electronic structure was discussed in terms of a formal d_{yz} ground state indicating a fairly strong out-of-plane bonding in the YZ plane.

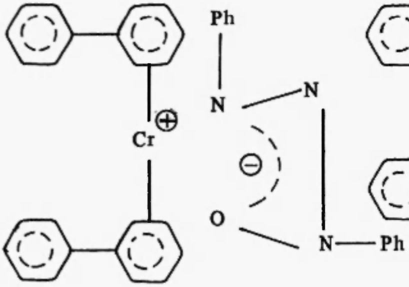
Dwivedi and Shrivastava /100/ reported studies on the structure of the bis- [1-methyl-3-o-chloro-phenyl triazene-1-oxide] Co(II) complex. Using the heavy atom method, it was established that the complex is in the orthorhombic space groupings $P2_12_12_1$ with four molecules of $C_{14}H_{14}N_6O_2Cl_2Co$ in a unit cell of dimensions a = 19.305 Å, b = 13.287 Å and c = 7.045 Å. In the complex, the two hydroxytriazene molecules are in the cis-position with respect of each other. The ligands function as tridentate ligands with O, N, and CI coordinating atoms. The chlorine atoms attached to the benzene are found to be weakly coordinated to Co(II), thus completing a distorted octahedral coordination. The distance between Co – CI is reported to be 2.98 Å while all the other bond distances and bond angles are found to be normal.

Behera and Chakravorty /101/ reported studies of Ni, Pd(II) and Cu(II) complexes with about ten alkyl hydroxytriazenes. The complexes show, crystal field bands at low energies. Ni complexes have been found to be diamagnetic in the solid state. Moreover the benzene and chloroform solutions of the Ni(II) complexes of all the ligands were reported to show slight paramagnetic character, with the exception of those ligands which had non-coordinating ortho substituents in the benzene ring of the molecule. Pd(II) complexes with ortho substitution in the benzene ring were reported to exist in isomeric forms. The separation of isomeric forms by column chromatography was accomplished, in one case only. The magnetic moments of all the Cu(II) complexes are reported to be normal.

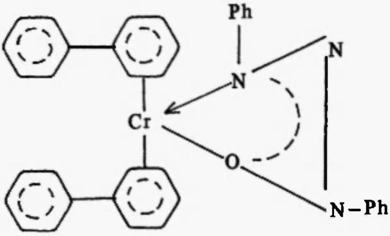
Borisov, Zykova and Yashunskii /102/ synthesised 3-hydroxy-3-methyl-1-p-ethoxy phenyl triazene; 3-hydroxy-3-benzyl-1-ethoxyphenyl triazene and other 3-alkyl or aryl hydroxytriazenes, having para methoxy and ethoxy substituents in the phenyl group at the 1-position. The vanadium(V) complexes of these hydroxytriazenes were also prepared. All these compounds have tuberculostatic activity, which falls considerably in presence of blood serum. However, the V(V) complexes of these hydroxy triazenes were found to be more active than the hydroxytriazenes themselves.

Abakumov, Cherkasov and Razuvaev /103/ oxidised HDPT by silver oxide, lead dioxide or potassium ferricyanide in an aqueous solution. The oxidation was studied with the help of E.S.R. The results indicated the formation of a triazene oxy radical which decomposes with the formation of nitrogen, nitrosobenzene and a phenyl radical. Thus it is possible that at room temperature, the aromatic hydroxytriazenes may be used as a source of phenyl radical.

Domrachev and Abakumova /104/ synthesised bis-diphenyl chromium-1,3-diphenyl-3-hydroxytriazenate as a green-yellow compound. The complex was prepared by adding a benzene solution of hydroxytriazene to a benzene solution of $(Ph)_2Cr(O)$, with the simultaneous passage of oxygen through the solution. On the basis of the appreciable solubility of the complex in nonpolar solvents (benzene, chloroform and toluene), IR and EPR studies, the complex bis-diphenyl chromium 1,3-diphenyl-3-hydroxytriazenate was proposed to have an ionic structure (A) with a very small contribution from the covalent structure (B).



(A)



(B)

Abakumov and Sanaeva /105/ estimated the reactivity of aryl radicals produced by the oxidation of hydroxy triazenes by a nitroxide method. The oxidation of 1-aryl-3-hydroxytriazenes by different oxidising agents leads to the formation of free aryl radicals, nitrogen and nitroso compounds. The relative reactivity of the radicals – $C_6H_5^{\cdot}$, p-$C_6H_4CH_3^{\cdot}$, p-$C_6H_4OCH_3^{\cdot}$, p-C_6H_4Br and p-$C_6H_4NO_2^{\cdot}$ was determined by the method of competing reactions in a toluene-ethyl benzene mixture. The selectivity of aryl radicals increases when these form π-complexes with naphthalene.

Razuvaev *et al.* /106/ synthesised 3-hydroxy-3-tert-butyl-1-aryl triazenes and their oxidative decomposition were studied by EPR spectra. The oxidation products of these are, phenyl radicals, nitrogen and 2-nitroso-2-methylpropane. Five p-substituted 3-hydroxy 3-tert-butyl-1-phenyl triazenes were prepared by them for this purpose.

Behera and Chakravorty /107/ reported for the first time the preparation of the tris complexes of Rh(III) and Cr(III) with hydroxytriazenes. The Cr(III) complex of 3-hydroxy-3-methyl-1-phenyltriazene was prepared by adding an alcoholic solution of this reagent (0.5 gm) to an aqueous solution of chromic chloride (0.18 g) containing urea (1.1 g). The resultant solution on heating on an oil bath at 55-60° for 24 hours gave a black coloured crystalline complex which was recrystallised from acetone m.p. 190-191°. Following the same method, the Cr(III) complex of 3-hydroxy-3-methyl-1-m-methylphenyl triazene and Rh(III) complexes of 3-hydroxy-3-methyl-1-phenyl triazene; 3-hydroxy-3-methyl-1-m-methylphenyl triazene and 3-hydroxy-3-methyl-1-p-methylphenyl triazene were prepared. Rh(III) chelates have trans stereochemistry, established on the basis of electronic spectra, IR spectra and PMR studies. No attempts were made to establish the stereochemistry of the Cr(III) chelates. However, the electronic spectra of Cr(III) complexes are characterised and discussed.

Dutta and Sharma /108/ reported electronic and IR spectral studies of oxo-vanadium(IV), Fe(III), Co(II), Ni and Cu(II) chelates with some hydroxytriazenes. In the case of the vanadium complexes, they showed that only one complex is formed, whether it is prepared from vanadyl sulphate or from ammonium vanadate. The authors also reported that ferrous ions react with hydroxytriazenes in air to form ferric derivative of the corresponding hydroxytriazene. They have further shown that the solid state spectrum of FeR_3 obtained from ferrous ammonium sulphate was exactly similar to the one obtained from ferric ammonium sulphate. The mixed chelates of Co(II) with dipyridyl and o-phenantroline was reported to have compositions $[CoR_2 \cdot dipy]$ and $[CoR_2 \cdot Ophenan.]$, respectively.

Dutta and Sharma /109/ used 3-hydroxy-3-methyl-1-o-carboxyphenyl triazene to prepare the complexes of Zn, Cd and Hg(II). The Zn and Cd complexes with the reagent on mixing with o-phenanthroline give corresponding mixed chelates. The analytical and IR data of mono(ligand) metal(II) chelates indicated the apparent coordination number three. A polymeric $(MR)_n$ structure has been suggested. Polymerisation may be either through N → O oxygen or C = O oxygen of the COO^- group. However, polymerisation through the C = O oxygen of the COO^- group has also been postulated on the basis of IR studies.

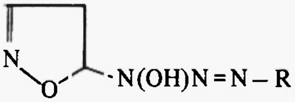
Dutta and Sharma /110/ studied the complexes of Zn, Cd, Hg(II) and Co(II) with 3-(o-chlorophenyl)-1-methyl-triazene-1-oxide; 3-(o-methoxyphenyl)-1-methyltriazene-1-oxide; 3-(o-chlorophenyl)-

1-phenyl triazene-1-oxide. It is established that the complexes formed have a metal:reagent ratio of 1:2. Electronic and IR spectra were also discussed. The authors reported the mixed chelates of Co(II), Zn and Cd with the above mentioned triazene-1-oxide and o-phenanthroline/ dipyridyl.

On the basis of IR studies carried out on HDPT and its substituted compounds, Behera and Zacharias /111/ reported that triazene-1-oxides exists both as intermolecular as well as intramolecular hydrogen bonded species in solution. However, ortho substituted-compounds are exceptions, because they exhibit only intramolecular hydrogen bonding.

Sturm and Armburst /112/ prepared a number of 3-hydroxy-(2-isoxazolin-5-yl)-1-aryltriazenes and used these as intermediates in the preparation of dyes and pesticides.

Sturm *et al.* /113/ prepared hydroxytriazenes of the type



where R = ph, m-$CH_3 \cdot C_6H_4$, p-$Cl \cdot C_6H_4$ and o-$CH_3O \cdot C_6H_4$, by the reaction of $CH_2(CH{=}NOH)_2$ with the corresponding diazotised anilines.

Atom polarisation of the trans-Cu(II)-3-hydroxy-1,3-diphenyl triazene complex in dioxan has been reported by Macqueen and Smith /114/.

HDPT and other aromatic triazenes have been used as promoters /115/ in processing rubber-carbon-black-mixes. They are effective in natural rubber, butadiene and isoprene polymers and copolymers derived from > 50% of these diolefins.

Gubler /116/ prepared about forty alkyl and aryl hydroxytriazenes with a view to evaluating their insecticidal and acaricidal properties. He screened these compounds in different forms such as powders, pastes, emulsions and sprays against different kinds of insects and mites.

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