A REVIEW OF HYDROXYTRIAZENES

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The application of hydroxytriazenes as analytical reagents has been reviewed after 1997, i.e. from 1998 to 2001 (Gorji *et al.* /1/). The literature on the recent work done on hydroxytriazenes has been reviewed and it is found that, apart from being useful analytical reagents for spectrophotometric and complexometric determination of transition metal ions, they have also found application as bioactive compounds. The details of λ_{max} or working wavelength with pH conditions etc. have been given in this review.

Ressalan *et al.* /2/ have reported the use of 3-hydroxy-3-m-tolyl-1-m-nitrophenyltriazene as a metallochromic indicator for the complexometric determination of trace amounts of chromium (III). Using this reagent as an indicator the selective complexometric determination of Cr (III) in binary and ternary metal ion mixtures has also been done. The end point of the titration is marked by change of colour from violet to yellow at a pH between 5.2 to 6.0 using hexamine. It is reported that the presence of 20 fold excess of eleven diverse cations and anions did not interfere with the determination of 5.2 mg of Cr (III). It has been further reported that the amount of metal ions found was in good agreement with the amount of metal ions actually present, indicating that the determinations are quite accurate. For the sake of comparison parallel titrations have been carried out using xylenol orange as indicator. Thus a useful method for the complexometric determination of chromium (III) has been developed.

Ressalan *et al.* /3/ have reported the use of 3-hydroxy-3-p-tolyl-1-o-nitrophenyltriazene at 60-65°C in hexamine buffer (pH 5.2 to 6.0). The colour reaction results in the formation of a stable dark grassy green chromium complex. The chromium (III): reagent ratio in this complex is 1:2

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with absorption maximum at 510 nm. The molar absorptivity and Sandell's sensitivity values of the complex are 635 L/mole cm and 81.84 ng/cm^2 respectively at the working wavelength 514 nm. Beer's law is valid in the concentration range of $1.0x10^{-4}$ to $6.0x10^{-4}$ M of Cr(III). The standard deviation of the method for the determination of the metal is found to be 12.99±0.0015 (0.94%) ppm of chromium. The presence of 100 ppm of 15 diverse cations and anions did not interfere with the determination of 12.99 ppm of chromium (III). Thus a useful and simple method for spectrophotometric determination of chromium has been established.

Ressalan *et al.* /4/ have reported the use of 3-hydroxy-3-phenyl-1-o-carboxyphenyltriazene at 60-70°C in hexamine buffer (pH 5.5 to 6.8). The colour reaction between reagent and Cr(III) results in the formation of a stable brownish yellow chromium complex. The chromium (III): reagent ratio in this complex is 1:2 with absorption maximum at 416 mm. The molar absorptivity and Sandell's sensitivity values of the complex are 17933 L/mole cm and 2.89 ng/cm^2 respectively at the working wavelength 424 nm. Beer's law is obeyed in the concentration range $5.0x10^{-6}$ to $3.0x10^{-5}$M of chromium. The standard deviation of the method for the determination of the metal is found to be 1.299±0.0028 (0.21%) ppm for chromium. The presence of 100 ppm of 15 diverse cations and anions did not interfere with the determination of 1.299 ppm of chromium (III).

Ombaca *et al.* /5/ have synthesized four hydroxytriazenes and screened their insecticidal activity against one-day-old Drosophila melanogaster Meig using a residue film method. The LC_{50} values ranged from 3.9 – 16.8 ppm.

Ombaca *et al.* /6/ have synthesized four hydroxytriazenes and screened their insecticidal activity against one-day-old Drosophila melanogaster Meig (vinegar or fruit fly) using a residue film method. The LC_{50} values obtained for these hydroxytriazenes have been compared with the LC_{50} values obtained for commercial insecticide Heptachlor. Values of LC_{50} vary from 12.567 ppm to 2.218 ppm. The results thus show that hydroxytriazenes can be further explored as potential insecticidal compounds.

Ressalan *et al.* /7/ have reported the use of 3-hydroxy-3-phenyl-1-o-hydroxyphenyltriazene at 60-70°C in the spectrophotometric determination of Cr (III). The complex is reddish brown, stable, and does not change thereafter. The composition of the complex is 1:2 (Cr:R) with absorption maxima at 456 nm and optimum pH 5.5 to 6.6. The molar absorptivity and Sandell's sensitivity values are 1500 L/mole cm and 34.6 ng/cm^2 respectively at the working wavelength 464 nm. Beer's law is obeyed in the concentration

range $5.0x10^{-5}$ to $3.0x10^{-4}$ M of chromium. The standard deviation (10 measurements) for 12.99 ppm of chromium was found as 0.037 ppm (0.28%). Interference studies with 27 diverse cations and anions have also been performed.

Ressalan *et al.* /8/ have reported the use of 3-hydroxy-3-m-sulphonato (sodium salt) phenyl-1-o-nitrophenyltriazene as an indicator for the simultaneous complexometric determination of Cr (III) with Fe (III), Cu(II) and Ni (II) in binary and ternary metal ion mixtures. The presence of 20-fold excess of eleven diverse cations and anions did not interfere with the determination of 5.2 mg of Cr (III). The amount of metal ions was found to be in good agreement with the amount of metal ions actually present; so the determinations are quite accurate. Thus a useful complexometric method for Cr(III) determination in binary as well as ternary metal ion mixture has been developed.

Maroo *et al.* /9/ have reported a spectrophotometric method for determination of lead(II) using 3-hydroxy-3-m-totyl-1-o-chlorophenyl-triazene. The reagent forms yellow lead complex having a composition of 1:2 (Pb:R::1:2) between pH 6.9-7.3 at 404 nm. The molar absorbptivity and Sandell's sensitivity have been reported to be 14,500L mol^{-1} cm^{-1}, 14.3 ng/cm^2 respectively and Log K and β values have been found to be 9.65 and 13.247 kcal/mol respectively. The Beer's law validity is reported to be between $1.0x10^{-5}$ M to $6.0x10^{-5}$M i.e. the entire concentration range studied. Interference of 20 cations and anions also has been studied.

Sharma *et al.* /10/ have used 3-hydroxy-3-phenyl-1-m-hydroxyphenyl triazene for the spectrophotometric determination of Co(II). The composition of yellow coloured complex has been found to be 1:2 (Co:R) with absorption maximum at 404 nm in the pH range 6.80-7.45. Absorbance measurements were made at 412 nm. It is reported that Beer's law was followed in the studied concentration range 5.0x10-6 M to 3.0x10-5 M. The value of molar absorptivity, Sandell's sensitivity, stability constant (log β) and free energy of formation were found to be 20,000 L/mole cm, 2.94 ng/cm^2, 10.18 and – 13.88 kcal/mole respectively. Interference of twenty five diverse ions has also been examined.

Yadav *et al.* /11/ have reported the use of 3-hydroxy-3-phenyl-1-o-carboxyphenyltriazene at 20-40°C in hexamine buffer (pH 7.1-7.6) in the formation of a stable dark green yellow complex. The [Lead(II):R] reagent ratio in this complex is 1:1 with absorption maximum at 401 nm. The molar absorptivity and Sandell's sensitivity values of the complex are 9000 L/mole

cm and 23.021 ng/cm^2 respectively at the working wavelength 407 nm. Beer's law is valid over the concentration range $0.2x10^{-4}$ M – $1.2x10^{-4}$M of lead (II). The standard deviation of the method for the determination of 8.28 ppm of lead (II)±0.047 ppm (0.57%). Interference studies with 22 cations and anions have also been performed.

Sharma *et al.* /12/ have reported the use of 3-hydroxy-3-m-totyl-1-p-sulphonato(Na-salt)phenyltriazene for the spectrophotometric determination of Cu(II). The reagent forms 1:2 yellow complex with copper at pH 6.4 to 6.9 with λ_{max} at 402 nm. At working wavelength 418 nm, values of molar absorptivity, Sandell's sensitivity, stability constant (log β) and free energy of formation were found to be 7,037 L/mole cm, 9.02 ng/cm^2, 9.02. (from Harvey and Manning's method) and –12.30 K. Cal/mol respectively. Beer's law is obeyed in the entire concentration range studied i.e. $2.0x10^{-5}$ M to $1.2x10^{-4}$ M. It was possible to determine copper (6.35 mg) in the presence of equimolar amounts of eighteen cations and anions, as has been reported.

Maroo *et al.* /13/ have reported the use of 3-hydroxy-3-o-totyl-1-o-choloro-phenyltriazene for spectrophotometric estimation of lead(II). The reagent forms a 1:2 yellow complex with lead at pH 6.8-7.2 at a working wavelength of 394 nm. Values of molar absortivity, Sandell's sensitivity, stability constant (log β) and free energy of formation were found to be $11.7x10^3$ L/mol^{-1} cm^{-1}, 17.8 ng/cm^2, 9.36 and -12.85 k.cal/mol respectively. Beer's law is valid in the concentration range $1.0x10^{-5}$ M to $6.0x10^{-5}$ M. It was possible to determine lead (12.4 mg) in the presence of twofold molar excess of twenty and anions, as reported.

Yadav *et al.* /14/ have reported the use of 3-hydroxy-3-phenyl-1-o-cholorophenyltriazene for the spectrophotometric determination of lead (II) at 20-40°C. The complex is stable and does not change thereafter. The composition of the complex (Lead:R) is 1:1 with absorption maximum at 394 nm and optimum pH 7.0-7.5. The molar absorptivity and Sandell's sensitivity values are 7750 L/mole cm and 26.73 ng/cm^2 respectively at the working wavelength 406 nm. Beer's law is obeyed in the concentration range $0.2x10^{-4}$ M $-12x10^{-4}$ of lead. The standard deviation (10 measurements) for 8.28 ppm of lead was found to be 0.002 ppm (0.60%). It has been reported that interference studies of 22 diverse cations and anions have also been performed.

Maroo *et al.* /15/ have reported the use of 3-hydroxy-3-m-totyl-1-p-cholorophenyltriazene for the spectrophotometric determination of lead (II). It forms a 1:2 [Lead(II):R] acetone soluble yellow complex with maximum

absorbance at 400 nm. It is reported that the working wavelength was chosen as 430 nm (ε=11,900). For spectrophotometric determination the optimum Lead:R ratio was 1:6 and pH range for maximum constant absorbance was 6.8-7.2. Values of molar absorptivity, Sandell's sensitivity, stability constant (log β) and free energy of formation were 11,900 L.mole^{-1}cm^{-1}, 17.4 ng/cm^2, 9.53 and –13.082 k.cal/mole respectively. Beer's law is obeyed in the entire concentration range studied i.e., 1.0x10^{-5} M to 6.0x10^{-5} M. It was possible to determine lead (6.26 ppm) in the presence of two fold molar excess of twenty cations and anions.

Maroo *et al.* /16/ have reported the use of 3-hydroxy-3-o-totyl-1-p-cholorophenyltriazene for the spectrophotometric determination of Lead (II). Lead forms a 1:2 (Lead:R) yellow complex with the reagent. The complex shows maximum absorbance at 395 nm. (ε = 7,000) in the pH range 7.0-7.5. Absorbance measurements were made at 400 nm. Values of molar absorptivity, Sandell's sensitivity, stability constant (log β) and free energy of formation were found to be 7,000 L.mole^{-1}cm^{-1}, 29.6 ng/cm^2, 9.08 and 12.465 k.cal/mole respectively. Beer's law is obeyed in the entire concentration range studied i.e., 1.0x10^{-5} M to 7.0x10^{-5} M. It was possible to determine lead (10.36 mg) in the presence of two fold molar excess of twenty cations and anions.

Sharma *et al.* /17/ have reported the use of 3-hydroxy-3-m-tolyl-1-o-chlorophenyltriazene for the spectrophotometric determination of Cu(II). The composition of yellow coloured complex has been found to be 1:2 (Cu:R) with absorption maximum at 390 nm in the pH range 6.6-7.2. Absorbance measurements were made at 400 nm. Beer's law was followed in the concentration range 2.0x10^{-5} to 1.0xl10^{-4} M. The value of molar absorptivity, Sandell's sensitivity, stability constant (log β) and free energy of formation were found to be 4107 L/mole cm, 15.47 ng/cm^2, 10.10 and -13.77 kcal/mole respectively. Interference of twenty-five diverse ions has been examined.

Maroo *et al.* /18/ have reported the use of 3-hydroxy-3-m-tolyl-l-p-nitrophenyltriazene for the spectrophotometric determination of Mg(II). Magnesium forms a 1:2 (Mg:R) acetone soluble, cherry colour, complex with the reagent. The complex shows maximum absorbance at 530 nm. At working wavelength 560 nm, ε = 11,500 L mole^{-1} cm^{-1}. For constant maximum colour development Mg:R was 1:6 and pH was between 10.4-10.8. Values of molar absorptivity, Sandell's sensitivity, stability constant (log β) and free energy of formation were found to be 11,500 L mole^{-1} cm^{-1}, 0.21 ng/cm^2, 11.00 and -15.101 kcal/mole respectively. Beer's law is obeyed in

the entire concentration range studied, i.e., $1.0x10^{-6}$ M to $6.0x10^{-6}$ M. It was possible to determine magnesium (0.12 ppm) in the presence of two-fold molar excess of nineteen cations and anions as reported.

Jain *et al.* /19/ have reported the complexometric determination of Fe(III) using two hydroxytriazenes as metallochromic indicators in two medicines Rubraplex (Sarabhai, India) and Fesovit (SKF, India) respectively. The hydroxytriazenes used are 3-hydroxy-3-methyl-1-m-nitrophenyltriazene and 3-hydroxy-3-ethyl-1-p-nitrophenyltriazene

Yadav *et al.* /20/ have reported the use of 3-hydroxy-3-p-tolyl-l-p-nilrophenyltriazene for the simultaneous complexometric determination of Cr(lll) from binary and ternary metal ion mixtures by kinetic masking. The method is simple and efficient for the complexometric determination of trace amount of Cr(III) as reported.

Yadav *et al.* /21/ have reported the use of 3-hydroxy-3-phenyl-l-p-formylphenyltriazene for the simultaneous complexometric determination of Cr(lll) from binary and ternary metal ion mixtures by kinetic masking. It is reported that the method is simple and efficient for the complexometric determination of trace amount of Cr(III).

Paliwal *et al.* /22/ have reported the use of 3-hydroxy-3-phenyl-l-m-nitrophenyltriazene as metallochromic indicator for the complexometric determination of chromium (III) and for the complexometric determination of Cr(III) by kinetic masking in the presence of other metal ions viz. Fe(III), Cu(II) and Ni(Il) in binary mixtures containing ion pairs Cr(III)-Fe(Ill)-Cr(III)-Cu(Il) and Cr(III)-Ni(II). The study has been further extended to determine Cr(III) in ternary mixtures containing any of the three ions, *viz.*, Cr(lll)-Fe(II)-Cu(II), Cr(III)-Fe(III)-Ni(II) and Cr(III)-Cu(II)-Ni(II). It is reported that the amount of metal ions found was in good agreement with the amount of metal ions actually present; so the determinations are quite accurate. For the sake of comparison parallel titrations were carried out using xylenol orange as indicator.

Shekhawat *et al.* /23/ have reported the use of 3-hydroxy-3-n-propyl-1-p-carboxyphenyltriazene for spectrophotometric determination of Ni(II). It forms a light green ethanol soluble complex with Ni(II) in the ratio 1:2 (NiR_2), with absorption maximum at 380 nm and optimum pH 6.8 to 8.0. The molar absorptivity and Sandell's sensitivity values are 7000 dm^3 mol^{-1} cm^{-1} and 8.3 ng/cm^2 respectively. Beer's law is obeyed over the concentration range of 0.3 ppm to 1.7 ppm of Ni(II). The stability constant has been worked out to be $\log \beta = 9.0$. Standard deviation (10 determinations) for 4.69 ppm of

Ni(II) has been found to be ±0.007 ppm. Interference studies have also been done.

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