

added vanadate (10 mg, V), molybdate (20 mg, Mo) and tungstate (5 mg, W) solutions. Then, 0.1 g each of hydroxylamine hydrochloride or ascorbic acid, oxalic acid and tartaric acid were mixed for reduction and masking, respectively, and the solution was slightly warmed and cooled. pH of the mixture was adjusted to 2.7. A 0.1% reagent (5 ml) was then added, cooled and transferred quantitatively into a 25 ml volumetric flask. The volume was made up with 50% alcohol at room temperature. Similarly, a solution was prepared without adding copper and used as the blank for absorbance measurement at 550 nm.

**Determination of copper in presence of  $As^{V}$ ,  $Sb^{III}$ ,  $Bi^{III}$  and  $Pb^{II}$ :** To a  $Cu^{II}$  (0.1 mg) solution was added arsenic (50 mg, As), antimony (50 mg, Sb), bismuth (50 mg, Bi) and lead (50 mg, Pb) nitrate solutions. Then, a 20% aqueous solution (5 ml) of triethanolamine hydrochloride and/or acetic acid were mixed for complexation and masking, and pH was adjusted to 2.7 with acetic acid. The solution (5 ml) was transferred and a 0.1% reagent solution added to it. The volume was made up to the mark with ethanol. Similarly, a solution blank was prepared for the absorbance measurement at 550 nm.

**Determination of copper in alloy steel in presence of  $Fe^{III}$ ,  $Co^{II}$ ,  $Ni^{II}$ ,  $Mn^{II}$  and  $Cr^{III}$ :** Steel sample (0.5 g) was dissolved in 3 M sulphuric acid (50 ml) and the solution was digested on a hot-plate with repeated addition of the acid. The solution was then treated with a few drops of concentrated nitric acid for complete digestion. The clear solution obtained was evaporated to a thick mass and then cooled, diluted with water (50 ml), filtered and washed with dilute acid. The filtrate and washings were cooled and transferred quantitatively into a 100 ml volumetric flask and the volume made up to the mark. Aliquots (5–10 ml) were taken, ascorbic acid solution (5 ml) added to it and pH adjusted to 2.7. The solution was transferred into a 25 ml volumetric flask, the volume made up to the mark with ethanol. A blank was prepared for the absorbance measurement at 550 nm.

## Results and Discussion

The reagent (TQA) reacts with the metal to give a violet chelate at pH 0.5–6.5 in 1 : 1 alcohol–water or 1 : 1 acetone–water. The violet complex is non-extractable in solvents such as chloroform, benzene, carbon tetrachloride, isoamyl alcohol, methyl isobutyl ketone, dichloromethane and ether.

The composition of the  $Cu^{II}$  complex was found to be 1 : 3 (Cu–TQA) by continuous variation method and mole-ratio method. The complex was not extractable in non-polar phases and absorbed maximum at 550 nm.

The copper content was determined in presence of a typical class of refractory metals, base and toxic metals. The average of several determinations (Table 1) were almost same in 50% acetone medium.

TABLE 1—ANALYSIS OF SYNTHETIC MIXTURES AND STANDARD SAMPLES

Sample type	Cu present	Cu found
Refractory (V, Mo, W)	0.1 mg	0.099 ± 0.001 mg
Base and Toxic (As, Sb, Bi, Pb)	0.1 mg	0.099 ± 0.001 mg
Alloy Steel (BAS)	0.32, 0.10, 0.08 (%)	0.32, 0.10, 0.08 (%)

For the determination of alloy steels (Table 1) analysis in 50% acetone gave a better result, but required longer time for the development of a clear violet colour. The present method is a very fast, simple, accurate and direct for trace analysis of copper in mild steel and low alloys. Both the reagent and the method was found very sensitive for detection and estimation of Cu in presence of many metal ions.

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## *N*-Bromophthalimide as an Oxidimetric Titrant. Some Direct Visual Titrations in Aqueous Acetic Acid Medium

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RECENTLY, *N*-bromophthalimide (NBP) has been developed as a typical oxidimetric titrant in aqueous acetic acid medium<sup>1</sup>. In view of the facts that NBP is much stabler than NBS and is a better oxidant than the earlier developed oxidants of similar type we have considered it would be

worthwhile to explore the possibility for employing NBP as a titrant for direct visual titrations of some typical reductants. Hence, simple direct visual titrations using NBP as the titrant have been developed for the determination of a total of 30 reductants of diverse types and the results are reported in this paper.

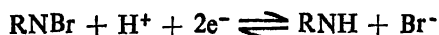
### Experimental

*N*-Bromophthalimide (NBP) was prepared by the bromination of phthalimide as reported in literature<sup>2</sup>. A decinormal solution (~0.05 M) of NBP was prepared in anhydrous acetic acid, stored in an amber coloured bottle and standardised iodometrically as described earlier<sup>1</sup>. Standard solutions of all the reductants listed in Table 1 were prepared in appropriate solvents and their strengths were checked by standard methods<sup>1,3,4</sup>. The metal oxinates and anthranilates were prepared by the conventional methods<sup>4,5</sup>. Quinoline yellow (0.5%), amaranth (0.1%), methyl orange (0.1%), methyl red (0.1%) and starch (0.2%) indicators were prepared by dissolving the respective substances in water as described in literature<sup>4</sup>. These five indicators were tried for the titrations. The suitable indicator for a particular titration was selected by noting the colour change during the slow addition of the oxidant using a titration potentiometer with necessary fittings as described earlier<sup>1</sup>.

**Procedure:** Once the suitable indicator had been selected, the following procedure was used for the titration of all the reductants. To a measured aliquot (10–25 ml) of the reductant solution, other reagents such as potassium bromide, sodium acetate, perchloric acid, etc., if required, were added. Then after adding 2–3 drops of the selected indicator, the solution was diluted to 100 ml with 50% (v/v) aqueous acetic acid. The resulting solution was titrated with standard NBP solution taken in a burette. A blank titration was carried out in each case, and no blank corrections were found necessary for all the systems studied.

### Results and Discussion

Results of the titrations are given in Table 1. During the reaction with any of the reductants, NBP undergoes reduction to form phthalimide,



where,  $\text{R} = \text{C}_6\text{H}_4\text{O}$ , part of phthalimide excluding NH. The formal potential of the redox couple involved in the above half-cell reaction in 50% (v/v) aqueous acetic acid has been reported to be +1.09 V at 32° indicating that NBP is a moderately strong oxidant<sup>1</sup>.

Among the six indicators tried, quinoline yellow is found most suitable for all reductants except

TABLE 1—VISUAL TITRATIONS\* OF SOME COMMON REDUCTANTS, METAL OXINATES AND METAL ANTHRANILATES USING *N*-BROMOPHTHALIMIDE

Reductant	Range studied mmol	Coefficient of variance %	Maximum error %
As <sup>III</sup>	0.29–0.57	0.23	0.32
Sb <sup>III</sup>	0.24–0.47	0.20	0.37
Ascorbic acid	0.47–0.63	0.14	0.42
Hydroquinone	0.43–0.82	0.23	0.40
Hydrazine	0.37–0.72	0.21	0.38
Benzhydrazide	0.31–0.63	0.23	0.38
Isoniazid	0.14–0.28	0.26	0.50
Semicarbazide	0.24–0.47	0.13	0.21
Thiosemicarbazide	0.12–0.25	0.27	0.44
Thiourea	0.13–0.26	0.24	0.54
Aniline	0.18–0.34	0.08	0.16
Phenol	0.15–0.30	0.12	0.23
Oxine	0.25–0.50	0.20	0.40
Anthranilic acid	0.14–0.28	0.26	0.49
Mg <sup>II</sup> -oxinate	0.18–0.31	0.25	0.55
Mn <sup>II</sup> -oxinate	0.13–0.26	0.42	0.74
Co <sup>II</sup> -oxinate	0.11–0.23	0.30	0.47
Ni <sup>II</sup> -oxinate	0.11–0.22	0.28	0.59
Cu <sup>II</sup> oxinate	0.11–0.23	0.25	0.49
Zn <sup>II</sup> -oxinate	0.11–0.23	0.34	0.79
Cd <sup>II</sup> -oxinate	0.12–0.24	0.22	0.46
Al <sup>III</sup> -oxinate	0.24–0.35	0.20	0.43
La <sup>III</sup> -oxinate	0.08–0.14	0.25	0.50
Mn <sup>II</sup> -anthranilate	0.08–0.16	0.37	0.34
Ni <sup>II</sup> -anthranilate	0.07–0.15	0.14	0.30
Cu <sup>II</sup> -anthranilate	0.07–0.14	0.15	0.39
Zn <sup>II</sup> -anthranilate	0.08–0.16	0.16	0.28
Co <sup>II</sup> -anthranilate	0.07–0.14	0.16	0.28
Cd <sup>II</sup> -anthranilate	0.08–0.16	0.25	0.32
Pb <sup>II</sup> -anthranilate	0.08–0.17	0.13	0.39

\*Ten replicates.

hydroquinone, oxine and metal oxinates, in which oxidised or brominated products are coloured. In the cases of hydroquinone, oxine and metal oxinates, either amaranth or methyl red is found most suitable. The end-points are very sharp and clear when the suitable indicator as specified above is used for a given titration. The results indicate that direct visual titrations for all the reductants studied are accurate and precise.

Simple titrations without adding any auxiliary agents are successful only for As<sup>III</sup>, Sb<sup>III</sup>, ascorbic acid, hydroquinone, benzhydrazide and semicarbazide. All the remaining 24 reductants studied require auxiliary agents as mentioned below. Thus, for hydrazine 5 ml of perchloric acid (60% v/w); for isoniazid 1 g of sodium acetate and 0.5 g of potassium bromide; for thiosemicarbazide and thiourea 1 g of sodium acetate; for aniline, phenol, oxine and metal oxinates 0.5 g of potassium bromide; and for anthranilic acid and metal anthranilates 1 g of sodium acetate and 0.5 g of potassium bromide must be added for the success of the titrations. The function of perchloric acid is to make the potential of the oxidant higher, which will give a distinct colour change at the end-point.

Sodium acetate may act as a catalyst for making direct titrations possible. The function of potassium bromide is to produce bromine *in situ* by its reaction with the oxidant, and the bromine so produced acts as a reaction intermediate.

All the 30 reductants studied undergo their usual oxidation schemes reported elsewhere. In conformity with the usual oxidation schemes,  $As^{III}$ ,  $Sb^{III}$ , ascorbic acid and hydroquinone consume 2 equivalents of NBP; hydrazine, benzhydrazide, isoniazid, semicarbazide and oxine consume 4 equivalents of NBP; aniline, phenol and anthranilic acid consume 6 equivalents of NBP; thiourea and oxinates of divalent cations consume 8 equivalents of NBP; thiosemicarbazide consumes 10 equivalents of NBP (it is converted into sulphate and cyanide as in the cases of other *N*-bromo oxidants); and oxinates of trivalent cations and all the metal anthranilates consume 12 equivalents of NBP.

NBP has some definite advantages over the earlier developed *N*-halogeno oxidants. The present reagent is extremely stable in solid state when kept out of light and moisture. Its standard solution has better keeping qualities than most of the earlier

developed oxidants of similar type. Therefore, it is possible to prepare fresh solutions from a ready stock of the solid substance and these solutions can be used within a couple of days. These are some of the advantages of the present reagent.

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