

## Some Analytical Applications of N-Chlorosuccinimide: Direct Potentiometric & Visual Titrations in Aqueous Acetic Acid Medium

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N-Chlorosuccinimide (NCS) has been used as an oxidimetric titrant in aqueous acetic acid medium. Both direct potentiometric and visual titrations of reductants such as As(III), Sb(III), Fe(II), hexacyanoferrate(II), iodide, sulphide, ascorbic acid, hydroquinone, hydrazine and its derivatives, aniline, phenol, sulphanilic acid, *p*-aminobenzoic acid, oxine and its metal derivatives, and anthranilic acid and its metal derivatives have been developed.

In contrast to N-bromosuccinimide (NBS) the potential of its chlorine analogue, viz., N-chlorosuccinimide (NCS) has not been much exploited as an oxidimetric titrant; though it has been used for the determination of certain hydrazines and pharmaceuticals<sup>1,2</sup>. It is, therefore, considered of interest to explore the possibility of employing NCS as a potential oxidimetric titrant. In the present investigation both direct potentiometric and visual titrations have been developed using NCS as the titrant for a total of 40 reductants of diverse types.

### Materials and Methods

A Toshniwal titration potentiometer type CL06A with a "null meter" detector, and a platinum-SCE electrode assembly was used for potentiometric titrations.

N-Chlorosuccinimide (NCS) was prepared by chlorinating commercial sample of succinimide (Hopkin & Williams), filtered, dried and kept in a dark coloured bottle, m.p. 148° (Found: Cl, 26.5%. Required: Cl, 26.6%). NCS is insoluble in water, but fairly soluble in acetic acid and other common organic solvents. Approximately 0.1 N (0.05 M) solution of NCS was prepared by dissolving the dry sample (6.6 g) in a litre of anhydrous acetic acid and standardized iodometrically<sup>3</sup>. Since the solution of NCS is decomposed by light, heat and moisture, it was kept in amber-coloured bottles at room temperature with guard tubes. Such a stock solution of NCS is found fairly stable to meet the requirement of a typical oxidant in partially nonaqueous medium. However, daily standardization is recommended for accurate work.

Standard solutions (~0.1 N) of all the reductants listed in Table 1 were prepared in water unless otherwise specified. Standard solution of As(III) was prepared by dissolving a known weight of pure As<sub>2</sub>O<sub>3</sub>

in 1 N sodium hydroxide, neutralising it with 1 N sulphuric acid and making up to definite volume with water. Iron(II) solution was prepared in 2 N sulphuric acid and oxine solution in 50% (v/v) of aq. acetic acid. Standard solution of sulphanilic acid was prepared in 2 N hydrochloric acid.

The metal oxinates and anthranilates listed in Table 2 were prepared by standard methods<sup>4,5</sup>. Standard solutions of all the metal oxinates (except that of MoO<sub>2</sub><sup>2+</sup>) and anthranilates were prepared in 2 N hydrochloric acid. Solution of the MoO<sub>2</sub><sup>2+</sup> oxinate was prepared in 2 N sulphuric acid. The strengths of all these reductant solutions were checked by standard methods<sup>5,6</sup>.

### Potentiometric method

To a measured aliquot (3-7 ml) of the reductant solution taken in a titration cell, potassium bromide (0.5 g) and other reagents such as sodium acetate (0.5 g), 2 N hydrochloric acid (2-5 ml) etc. if required, were added. The solution was diluted to 50 ml with water and acetic acid to get 50% (v/v) in aq acetic acid and titrated with standard NCS solution from a microburette. Near the equivalence point addition of NCS was restricted to 0.1 ml portions and the reaction mixture was stirred for 30 sec before noting the steady potential. The titration was continued until there was no significant change in potential on further addition of NCS.

### Visual method

To a measured aliquot (10-20 ml) of the reductant solution, potassium bromide (0.5 g) and 2 drops of the suitable indicator were added. Other reagents such as 2 N hydrochloric acid (2-5 ml), sodium acetate (0.5 g) etc., if required, were added. After diluting the solution to 50 ml with water and acetic acid to get 50% (v/v) in aq acetic acid, the solution was titrated with standard

Table 1—Direct Potentiometric and Visual Titrations of Some Common Reductants Using N-Chlorosuccinimide

Reductant	Potentiometric			Visual		
	Range studied (mmol)	St.* dev. ( $\mu\text{mol}$ )	Av. error (%)	Range studied (mmol)	St.* dev. ( $\mu\text{mol}$ )	Av. error (%)
As(III)	0.09-0.30	2.4	$\pm 0.18$	0.48-0.93	1.7	$\pm 0.13$
Sb(III)	0.10-0.31	3.8	$\pm 0.41$	0.49-0.95	2.4	$\pm 0.19$
Fe(II)	0.30-0.70	2.6	$\pm 0.25$	1.00-1.90	2.1	$\pm 0.17$
Hexacyanoferrate(II)	0.27-0.64	2.3	$\pm 0.18$	0.88-1.68	1.6	$\pm 0.19$
Iodide	0.19-0.60	2.2	$\pm 0.20$	Unsuccessful		
Sulphite	0.09-0.23	2.2	$\pm 0.22$	0.32-0.62	1.9	$\pm 0.15$
Ascorbic acid	0.09-0.30	2.3	$\pm 0.23$	0.49-0.95	1.0	$\pm 0.80$
Hydroquinone	0.06-0.19	1.4	$\pm 0.25$	0.30-0.59	1.8	$\pm 0.17$
Hydrazine	0.04-0.15	3.9	$\pm 0.38$	0.24-0.48	2.5	$\pm 0.20$
Benzhydrazide	0.04-0.13	3.2	$\pm 0.38$	0.20-0.39	1.2	$\pm 0.11$
Isoniazide	0.04-0.15	2.5	$\pm 0.23$	0.17-0.34	1.4	$\pm 0.12$
Semicarbazide	0.04-0.14	2.1	$\pm 0.17$	0.25-0.49	2.8	$\pm 0.26$
Aniline	0.03-0.10	3.4	$\pm 0.36$	0.17-0.33	2.5	$\pm 0.19$
Phenol	0.03-0.11	3.5	$\pm 0.34$	0.16-0.33	2.2	$\pm 0.21$
Oxine	0.05-0.16	3.6	$\pm 0.40$	0.25-0.49	2.9	$\pm 0.24$
Sulphanilic acid	0.04-0.11	3.0	$\pm 0.28$	Unsuccessful		
Anthranilic acid	0.04-0.10	2.6	$\pm 0.28$	0.14-0.27	1.1	$\pm 0.20$
<i>p</i> -Aminobenzoic acid	0.06-0.16	2.2	$\pm 0.17$	0.21-0.42	0.7	$\pm 0.06$

\*Ten replicates

Table 2—Direct Potentiometric and Visual Titrations of Some Metal Oxinates and Anthranilates Using N-Chlorosuccinimide

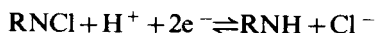
Reductant	Potentiometric			Visual		
	Range studied (mmol)	St.* dev. ( $\mu\text{mol}$ )	Av. error (%)	Range studied (mmol)	St.* dev. ( $\mu\text{mol}$ )	Av. error (%)
Hg(C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub> ·2H <sub>2</sub> O	0.03-0.08	2.5	$\pm 0.25$	0.10-0.20	1.5	$\pm 0.13$
Al(C <sub>9</sub> H <sub>6</sub> ON) <sub>3</sub>	0.01-0.04	2.6	$\pm 0.16$	0.05-0.10	2.3	$\pm 0.22$
Ca(C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub>	0.03-0.09	1.7	$\pm 0.24$	0.11-0.23	1.2	$\pm 0.11$
Mn(C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub> ·2H <sub>2</sub> O	0.02-0.06	2.6	$\pm 0.22$	0.07-0.15	2.1	$\pm 0.17$
Fe(C <sub>9</sub> H <sub>6</sub> ON) <sub>3</sub>	0.01-0.05	2.5	$\pm 0.21$	Unsuccessful		
Ni(C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub> ·2H <sub>2</sub> O	0.02-0.06	2.4	$\pm 0.16$	0.08-0.17	1.9	$\pm 0.18$
Co(C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub> ·2H <sub>2</sub> O	0.03-0.09	2.2	$\pm 0.26$	0.12-0.23	1.7	$\pm 0.14$
Cu(C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub> ·2H <sub>2</sub> O	0.03-0.08	2.0	$\pm 0.16$	0.11-0.22	2.1	$\pm 0.20$
Zn(C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub> ·2H <sub>2</sub> O	0.03-0.08	2.4	$\pm 0.27$	0.10-0.20	0.9	$\pm 0.70$
MoO <sub>2</sub> (C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub>	0.02-0.06	2.3	$\pm 0.16$	Unsuccessful		
Cd(C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub> ·2H <sub>2</sub> O	0.03-0.08	1.4	$\pm 0.09$	0.10-0.20	2.2	$\pm 0.22$
La(C <sub>9</sub> H <sub>6</sub> ON) <sub>3</sub>	0.02-0.06	2.3	$\pm 0.16$	0.08-0.16	1.0	$\pm 0.07$
Th(C <sub>9</sub> H <sub>6</sub> ON) <sub>4</sub> ·C <sub>9</sub> H <sub>7</sub> ON	0.01-0.04	2.3	$\pm 0.16$	Unsuccessful		
UO <sub>2</sub> (C <sub>9</sub> H <sub>6</sub> ON) <sub>2</sub> ·C <sub>9</sub> H <sub>7</sub> ON	0.02-0.05	3.1	$\pm 0.25$	0.05-0.12	1.6	$\pm 0.19$
Mn(C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> N) <sub>2</sub>	0.02-0.06	3.2	$\pm 0.34$	0.08-0.16	1.1	$\pm 0.88$
Ni(C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> N) <sub>2</sub>	0.02-0.06	2.8	$\pm 0.26$	0.08-0.17	1.7	$\pm 0.13$
Co(C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> N) <sub>2</sub>	0.02-0.06	2.3	$\pm 0.23$	0.07-0.15	1.7	$\pm 0.14$
Cu(C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> N) <sub>2</sub>	0.02-0.06	3.1	$\pm 0.26$	0.07-0.15	1.5	$\pm 0.12$
Zn(C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> N) <sub>2</sub>	0.02-0.06	2.6	$\pm 0.17$	0.08-0.16	1.7	$\pm 0.14$
Ag(C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> N) <sub>2</sub>	0.01-0.05	2.8	$\pm 0.23$	0.05-0.12	1.9	$\pm 0.16$
Cd(C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> N) <sub>2</sub>	0.02-0.05	2.1	$\pm 0.18$	0.07-0.14	1.8	$\pm 0.14$
Pb(C <sub>7</sub> H <sub>6</sub> O <sub>2</sub> N) <sub>2</sub>	0.02-0.05	2.1	$\pm 0.22$	0.06-0.13	2.5	$\pm 0.20$

\*Ten replicates

NCS solution from a macroburette. A blank titration was also carried out in each case.

### Results and Discussion

The results of potentiometric and visual titrations of all the 40 reductants are presented in Tables 1 and 2. In the potentiometric method, end points are calculated by the graphical method and the results are checked by the Hostetter-Roberts method<sup>7</sup> or the Yan method<sup>8</sup>. During the reaction NCS undergoes reduction to give succinimide as per the reaction



where R stands for succinimide part excluding NH. The formal potential of the redox couple involved in the above reaction in 50% (v/v) aq acetic acid has been determined to be +1.24 V indicating that NCS is a moderately strong oxidant. The results confirm this and sharp potential breaks are obtained in all the potentiometric titrations.

In the visual method of titration, quinoline yellow indicator is found to be the most suitable for all the systems except Fe(II), hexacyanoferrate(II), hydroquinone and metal oxinates, for which amaranth is the most suitable. Of the 40 reductants studied, iodide, sulphanilic acid and oxinates of Fe<sup>3+</sup>, MoO<sub>2</sub><sup>+</sup> and Th<sup>4+</sup> could not be determined by the visual method. Indicators such as methyl orange, methyl red and *p*-ethoxychrysoidine have also been found suitable for most of the systems. In all the visual titrations the end points are very clear and distinct and no indicator correction is found necessary.

Addition of potassium bromide (0.5 g) is required in both the methods. For the Fe(II) titration addition of orthophosphoric acid (2 ml) is essential to remove the Fe(III) formed via complexation. For Sb(III) and hydrazine addition of 2 N hydrochloric acid (2 ml) is necessary. In the case of anthranilic acid and metal anthranilates sodium acetate (0.5 g) is added, which acts as a catalyst in these systems.

All the reductants undergo their usual oxidation schemes reported elsewhere. Thus As(III) and Sb(III) are oxidised to +5 state, Fe(II) and hexacyanoferrate(II) to +3 state, iodide to iodine, sulphite to sulphate, ascorbic acid to dehydroascorbic acid, hydroquinone to quinone, hydrazine part to molecular nitrogen; aniline, phenol, oxine, sulphanilic acid, anthranilic acid and *p*-amino benzoic acid are brominated. In conformity with these oxidation schemes one equivalent of oxidant is consumed by Fe(II), hexacyanoferrate(II) and iodide; 2 equivalents by As(III), Sb(III), sulphite, ascorbic acid and hydroquinone; 4 equivalents by hydrazine, benzhydrazide, isoniazid, semicarbazide and oxine; 6 equivalents by aniline, phenol, sulphanilic acid, anthranilic acid and *p*-aminobenzoic acid; 8 equivalents by oxinates of Mg<sup>2+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, MoO<sub>2</sub><sup>+</sup> and Cd<sup>2+</sup>; 12 equivalents by oxinates of Al<sup>3+</sup>, Fe<sup>3+</sup>, La<sup>3+</sup> and UO<sub>2</sub><sup>+</sup> and anthranilates of Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>; and 20 equivalents by Th<sup>4+</sup> oxinate.

The present studies show that NCS is superior to NBS as an analytical reagent and therefore, it can be substituted for the latter in quite a number of determinations. The reagent is suitable for the determination of several reductants by direct titrations.

### References

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