The determination of thiourea, particularly by redox methods, has been a subject of vast study. Almost all the known oxidants have been used for the purpose. Szebelledy and Madis\textsuperscript{1} determined thiourea by oxidising it to urea and sulphate with potassium bromate in hydrochloric acid medium at 40--50\textdegree{} in presence of potassium bromide and a little of gold chloride. Mahr\textsuperscript{2} titrated thiourea with standard bromate-bromide solution in sulphuric acid medium at 35\textdegree{} in presence of potassium iodide and starch. The end-point was marked by the appearance of blue colour when thiourea was oxidised to formamidine disulphide. Grover and Mehrotra\textsuperscript{3} reported that thiourea is oxidised to urea and sulphate by hypoiodite and to sulphate, carbonate and nitrogen by hypobromite in alkaline solutions. Joshi\textsuperscript{4} determined thiourea by treating it with an excess of selenious acid and determining the unreacted excess of the reagent iodometrically. Thiourea was reported to be oxidised to urea, sulphuric acid and formamidine sulphonic acid. Werner\textsuperscript{5} developed an indirect method representing the oxidation of thiourea to formamidine disulphide in sulphuric acid medium by selenious acid. Reynolds and Werner\textsuperscript{6} estimated thiourea by oxidising it quantitatively to formamidine disulphide by iodine in aqueous solutions. Cuthill and Atkins\textsuperscript{7}, and Joshi\textsuperscript{8}, however, reported that thiourea is oxidised to urea and sulphate by iodine in alkaline medium. Quite different oxidation products of thiourea have been reported with different oxidants or with the same oxidant under different conditions. This

Thiourea as Reductimetric Standard: Standardisation of Iodine Containing Oxidants

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aspect has hampered the use of thiourea as a reductant in quantitative analysis. Among the few attempts made to use it as a titrimetric reagent, Mahr and Ohle carried out the determination of manganese dioxide, lead dioxide, and hydrogen peroxide. The excess of thiourea left after reaction with each compound was titrated with standard bromate-bromide solution. These workers also titrated chromate with thiourea solution in the presence of potassium iodide and starch; the end-point was detected by the disappearance of starch iodide colour. Aggarwal and Ghosh titrated Ce(IV) and iodate against thiourea solution in sulphuric acid medium using diphenylamine and starch respectively as indicators.

Prior to the work of Singh and Verma, no systematic study regarding the oxidimetric determination of thiourea or its derivatives was made. These authors, on the basis of their extensive study covering the determination of thioureas with potassium iodate, iodine halides (monochloride, trichloride and monobromide), potassium dichromate, Ce(IV), potassium bromate, chloramine-T, potassium ferricyanide and sodium vanadate found that thiourea and its derivatives can be rapidly quantitatively oxidised to the corresponding disulphides under specific conditions. Therefore,

\[
2 \text{RHN} \xrightarrow{C-SH} \text{RHN} \xrightarrow{C-S-S-C} \text{NHR} + 2H^+ + 2e
\]

(R = Hydrogen atom, alkyl or aryl group) the properties of thiourea were investigated for the purpose of testing it as a reductimetric standard. Preisler and Berger reported the oxidation-reduction potential of thiourea-formamidine disulphide system to be 0.42 volts in 0.05 to 1.00 N hydrochloric acid. Thiourea (m. p. 180) is available in pure crystalline form. Less pure material may be crystallised from ethanol and dried at 100°C. The compound does not show any tendency to undergo decomposition or deliquescence. It is extremely soluble in water (solubility: 17.12 g per 100 g of water at 25°C) and gives colourless solution. As its oxidation involves a single-electron change, its equivalent weight is the same as molecular weight (76.12). Its standard solution can be prepared by dissolving the calculated amount of pure compound in water. A 0.1 N solution of thiourea does not show any change in titre, as checked by its titration with potassium iodate, for about 10 weeks and the fall in titre for the next 18 weeks is only 3%.

Iodine containing oxidants such as potassium iodate, potassium periodate, iodine monochloride, iodine monobromide, iodine trichloride, etc. are extensively employed as redox reagents for the