

line width  $\Delta_{ms}$  (the width between the points of maximum slope taken from the first derivative of the e.s.r. spectrum) is 13.1 gauss. The electron spin concentrations were found to increase at first with an increase in absorbed dose but became almost constant at higher doses. The maximum value observed was  $6.8 \times 10^{17}$  spins per gram of the irradiated salt for an absorbed dose of  $5.7 \times 10^{20}$  ev per gram.

The above results alone are not sufficient to make a positive identification of the radical (or radicals) responsible for the e.s.r. spectrum. By their observations on liquid sulphur and other sulphur compounds, Gardner and Fraenkel<sup>6</sup> have made the tentative suggestion that polyatomic free radicals in which the odd electron is primarily associated with a sulphur atom would be expected to have a  $g$  value of about 2.02. However, if the odd electron is in a sulphur containing compound and is not primarily localized on a sulphur atom, the  $g$  value would be closer to the free spin value of 2.0023. The  $g$  value of 2.009 obtained for sodium tetrathionate has a considerable  $g$  shift from the free spin value. This could indicate that the unpaired electron is considerably involved with a sulphur atom in the free radical responsible for the spectrum. Further, the value is significantly higher than the  $g$  values reported for sodium dithionate<sup>7</sup> and sodium dithionite,<sup>8</sup> which could mean that the central line in the spectrum may not be due to  $SO_3$  or  $SO_2^-$  radical ions.

The  $g$  factor calculated for the low field shoulder of the low field structure is 2.024. Spectroscopic splitting factors about 1% larger than the free electron spin  $g$  factor of 2.0023 have been reported in the e.s.r. spectra of sulphur dissolved in oleum<sup>9</sup> and of chilled sulphur vapour.<sup>10</sup> This is ascribed to spin orbit interactions and hence free radicals in which the odd electron is primarily involved with the sulphur atom could be responsible for this structure. Such a conclusion is supported by the observation that colloidal sulphur is produced when gamma irradiated tetrathionate is dissolved in water.<sup>2</sup>

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1. Eager, R. L. and Mahadevappa, D. S., *Canad. J. Chem.*, 1963, **41**, 2106.
2. — and — (to be published).
3. Alegg's *Handbuch der Anorganischen Chemie IV*, Verlag Von S. Hirzel, Leipzig, 1927, p. 554.
4. Buijs, K., *J. Inorg. and Nucl. Chem.*, 1962, **24**, 229.
5. Goehring, H., Feldmann, U. and Helbing, W., *Chem. Abstr.*, 1950, **44**, 1851.
6. Gardner, D. M. and Fraenkel, G. K., *J. Amer. Chem. Soc.*, 1956, **78**, 3279.
7. Chantry, G. W., Horsfield, A., Morton, J. R., Rowlands, J. R. and Whiffen, D. H., *Mol. Phys.*, 1962, **5**, 232.
8. Clark, H. C., Horsfield, A. and Symons, M. C. R., *J. Chem. Soc.*, 1961, **7**.
9. Ingram, D. J. E. and Symons, M. C. R., *Ibid.*, 1957, p. 2437.
10. Radford, H. E. and Rice, F. O., *J. Chem. Phys.*, 1960, **33**, 774.

#### STUDIES ON THE USE OF 8-HYDROXY QUINOLINE AND SOME OF ITS DERIVATIVES AS REDOX INDICATORS

It has been observed that 8-hydroxy-quinoline and its derivatives, oxine-5-sulphonic acid and 7-iodo-oxine-5-sulphonic acid (ferron) undergo oxidation on adding cerium (IV) sulphate, to an almost colourless state through intermediate unstable red brown and red products respectively. If iron (II) is added to the solution of these oxidized substances while still the brown or red product is present, it is reduced back to the original oxine or its corresponding derivative, whereas if they are oxidized beyond the red stage, they cannot be reduced at all by adding iron (II). Thus the oxidation-reduction is reversible only up to the red stage. In this communication, the results of the studies on the use of these substances as redox indicators, based on the reversible nature of their oxidation, are recorded.

#### EXPERIMENTAL

*Indicator Solutions.*—0.005 M solutions of the oxine, oxine-5-sulphonic acid and ferron are prepared respectively by dissolving (1) 0.0725 gm. of oxine in 100 ml. 0.1 N sulphuric acid, (2) 0.1126 gm. of oxine-5-sulphonic acid in 100 ml. of warm distilled water and (3) 0.1756 gm. of ferron in 100 ml. of distilled water. 0.5 ml. of any of these indicator solutions is found adequate in titrations.

Cerium (IV) sulphate solution is prepared from a sample of (G.R., E. Merck) ceric ammonium sulphate by dissolving it in sulphuric acid and the solution is made up to the desired

volume, keeping the overall acidity 1 N with respect to sulphuric acid. This solution is standardised by potentiometric titration with standard oxalate solution.<sup>1</sup>

Iron (II) solution is prepared by dissolving the requisite amount of (G.R, E. Merck) ferrous ammonium sulphate in 1 N sulphuric acid solution and is standardized by titration with the above ceric sulphate, using ferroin as indicator.

All other chemicals used are of reagent grade quality.

Of the three substances, we find that ferron and oxine-5-sulphonic acid are preferable in view of their water solubility and easily discernible colour change at the end-point to oxine which is soluble in acids only.

In titration of iron (II) sulphate in sulphuric acid medium with cerium (IV) sulphate, these indicators give sharp end-points. The acidity can be varied from 0.5 to 6 N without any effect on the end-point. In hydrochloric acid medium, the intense yellow colour of ferric chloride complex masks the colour change at the end-point, but this difficulty can be overcome by adding about 5 ml. of syrupy phosphoric acid to the titration mixture. In perchloric and nitric acid media, using cerium (IV) perchlorate or cerium (IV) nitrate for the titration of iron (II) perchlorate, up to 2% higher titres are obtained because of simultaneous oxidation of the indicator to the irreversible stage. It is obvious from these observations that sulphate ion has some retarding effect on the irreversible oxidation of these substances. With permanganate as oxidant, the oxidation of the indicators to the irreversible stage occurs so rapidly that the red product is hardly perceived. Dichromate and vanadate require 15 and 20 N acidity respectively to oxidise the indicators. However, in actual titrations of iron (II) sulphate, the detection of the colour change of the indicators at the end-point is made difficult by the green chromium (III) and the blue vanadium (IV) that are generated in the titration mixture. Thus, these substances are not suitable as indicators in permanganometry, dichrometry and vanadometry.

**Transition Potential of the Indicators.**—By adopting the procedure of Belcher, Nutten and Stephen,<sup>2</sup> we found that the colour change of these indicators occurs at  $950 \pm 10$  (mV) vs. N.H.E. in the titration of iron (II) sulphate with cerium (IV) sulphate in 1 N sulphuric acid medium. The potential at which the colour changes in the reverse titrations could not be

determined due to the fact that it is irreversibly oxidised in presence of excess oxidant.

**Indicator Correction.**—The indicator correction is determined by noting the difference in the titres obtained potentiometrically and with the indicator using 0.5 ml. of 0.005 M solution. It is observed that if a titration is carried out potentiometrically with the indicator present in the mixture, the break is obtained only after all the indicator is oxidised. The correction thus determined amounts to 0.22 ml. of 0.01 N cerium (IV) sulphate.

**Recommended Procedure for the Determination of Iron (II).**—An aliquot of iron (II) sulphate is taken in a conical flask and acidified with sulphuric acid such that the overall acidity is 1 N on dilution to 50 ml. 0.5 ml. of 0.005 M solution of either of the indicators is added and the solution is titrated with cerium (IV) sulphate with vigorous stirring till the colour changes to red.

Some typical results of such titrations are given in Table I.

TABLE I

Amount of iron (II) taken millimoles	Amount of iron (II) found millimoles
0.2354	0.2364
0.3356	0.3366
0.5359	0.5359
0.5509	0.5509
0.7161	0.7176
0.9716	0.9726
1.118	1.119
1.275	1.277

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1. Willard, H. H. and Young, P., *J. Am. Chem. Soc.*, 1928, 50, 1322.
2. Belcher, R., Nutten, A. J. and Stephen, W. I., *J. Chem. Soc. (London)*, 1952, p. 3857.

### OCCURRENCE OF MANGANESE ORES IN ADILABAD DISTRICT, ANDHRA PRADESH

King (1881), Heron (1948) and Pascoe (after Hughes, 1948) who worked on geology of parts of Adilabad District, Andhra Pradesh, have not made any reference to the manganese ores now under report. Geological Survey of India